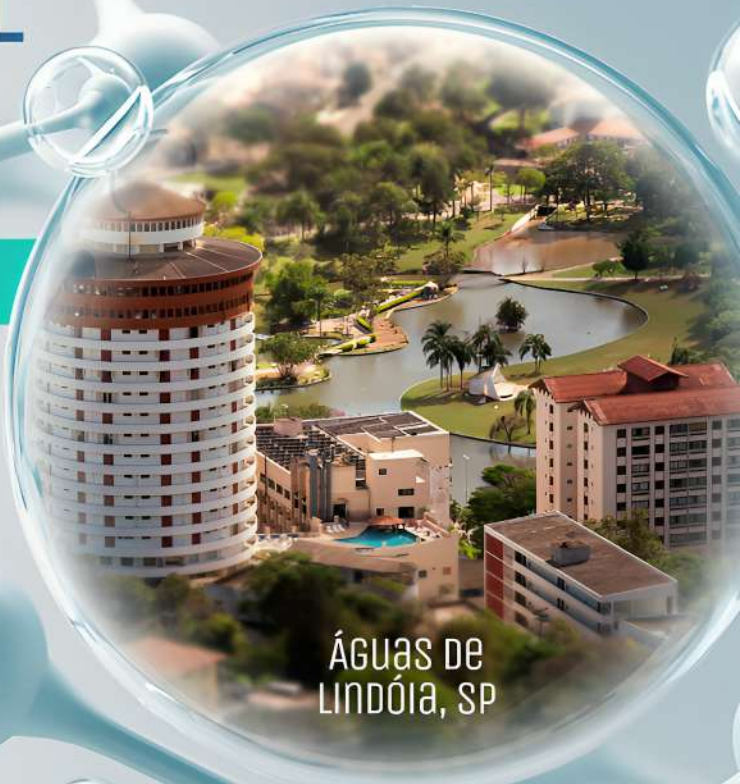
47ª

SBQ.COM.BR

Reunião anual da SBQ

22 a 25 de maio de 2024

A centralidade da química na educação do cidadão e na inovação científica e tecnológica



Sociedade Brasileira de Química

ANAIS

Anais da 47ª Reunião Anual da SBQ

Águas de Lindóia-SP
2024

Copyright © 2024 para os autores

Revisão textual e gramatical: Resposanbilidade dos respectivos autores.

Todos os direitos reservados 2024
A reprodução não autorizada desta publicação, no todo ou em parte,
constitui violação de direitos autorais (Lei 9.610/98).

Dados Internacionais de Catalogação na Publicação (CIP)
(Câmara Brasileira do Livro, SP, Brasil)

Reunião Anual da SBQ (47. : 2024 : Águas de Lindóia, SP)
Anais da 47ª Reunião Anual da SBQ [livro eletrônico] : a centralidade da química na educação do cidadão e na inovação científica e tecnológica. -- 1. ed. -- Águas de Lindóia, SP : Aptor Software, 2024.
PDF

Vários autores.
Bibliografia.
ISBN 978-85-63273-58-1

1. Química - Estudo e ensino I. Título.

24-216704 CDD-540.7

Índices para catálogo sistemático:

1. Química : Estudo e ensino 540.7

Aline Graziele Benitez - Bibliotecária - CRB-1/3129

PREFÁCIO

No período de 22 a 28 de maio de 2024, a comunidade Química brasileira esteve reunida em Águas de Lindóia/SP na 47ª Reunião Anual da Sociedade Brasileira de Química (47RASBQ). As Reuniões Anuais da SBQ constituem um dos eventos mais importantes e tradicionais da ciência brasileira e reúnem um grande número de estudantes participantes, entre alunos de graduação e pós-graduação, professores e pesquisadores (jovens e sêniores) de Química e áreas afins. Nos últimos dez anos as reuniões atraíram, anualmente, entre 1200 e 2000 participantes, inscritos e convidados, nacionais e internacionais. As características mais importantes das reuniões anuais da SBQ são o forte caráter científico e a interdisciplinaridade da programação, sempre voltada para temas na fronteira do conhecimento. Em 2024 não foi diferente, foram mais de 1300 participantes, representantes de 25 estados do Brasil, subdivididos principalmente em 39% de pesquisadores, 26% de estudantes de pós-graduação e 24% de alunos de iniciação cientifica das mais diversas áreas de Química e afins de todo Brasil e do exterior. Este ano, o tema da reunião foi "A centralidade da Química na educação do cidadão e na inovação científica e tecnológica". A 47ª Reunião Anual contou com uma programação rica e bastante diversificada, envolvendo os mais diversos e atuais aspectos da Química. Nos três dias de evento, tivemos as seguintes atividades: 9 workshops, uma conferência de abertura, 10 minicursos, 15 conferências convidadas, 2 simpósios, 5 sessões temáticas, 12 sessões coordenadas, 2 sessões de *flash poster presetation*, e 2 sessões de painéis. Nestas atividades pesquisadores, alunos de pós-graduação e alunos de iniciação científica fizeram apresentações orais de seus trabalhos, e um total de 883 trabalhos apresentados na forma de painéis. Desta forma, a 47RASBQ contribuiu para um dos seus principais objetivos que é a formação de recursos humanos qualificados na área de Química e afins.
Neste livro de anais constam todos os resumos dos trabalhos apresentados no evento.

Luiz Gonzaga de França Lopes
Secretário Geral da SBQ (2022-2024)
Presidente do Comitê Organizador

SUMÁRIO

1	AMB - Química Ambiental
52	ANA - Química Analítica
121	BEA - Alimentos e Bebidas
135	BIO - Química Biológica
146	CAT - Catálise
188	EDU - Ensino de Química
242	ELE - Eletroquímica e Eletroanalítica
299	FIS - Físico-Química
329	FOT - Fotoquímica
338	INO - Química Inorgânica
439	MAT - Química de Materiais
561	MED - Química Medicinal
599	ORG - Química Orgânica
700	QPN - Produtos Naturais
795	QVE - Química Verde
805	TEC - Química Tecnológica
820	TEO - Química Teórica

AMB

Química Ambiental

Sociedade Brasileira de Química

Área: AMB
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Activated palm fiber waste remove 100% of methylene blue from contaminated water.

Jobson Larrubia de Almeida Júnior* **(PG),[1] Wilma de Araujo Gonzalez (PQ),[1] Kátia Regina de Souza (PQ).[1]**

jobsonlarrubia@ime.eb.br; d5wilma@ime.eb.br; katia.souza@ime.eb.br;

[1]*Departamento de Química, IME.*

Palavras Chave: Sustainable chemistry, Palm fiber waste, Adsorption, Wastewater, Water treatment, Environment.

Highlights

The aim was the application of a sustainable and Amazon resource, palm fiber waste, as an adsorbent of the Methylene Blue. The outcome proved the efficiency of 100%.

Resumo/Abstract

Water treatment is a topic widely investigated by Global Environment Outlook, representing also some ODS and Brazilian constitution articles. Especially contaminated water by organic pollutant which is a common outcome from industries waste most of the times. This project was created to apply a sustainable and Amazon resource (Palm fiber waste - FD) as a solution. In that way, palm fiber waste can receive more market value by the reuse of the waste, the Brazilian economic may enhance, and the contaminant might be removed.

It was prepared 0,1 mol/L of NaOH to activate this biomass. 500mL of this solution was added in a becker containing approximately 0,375g of FD (diameter until 0,149 mm) and it was shaken for 24h. After this, the FD was washed in distillated water until the filtered obtain neutral pH. The activated biomass was dried in environment temperature. Subsequently, 0,25g of FD was put in Erlenmeyer with 100ppm of methylene blue which had pH=4. The test was made in triplicates and the adsorption was simulated: 125 rpm in 30 min an 40ºC. The commercial activated carbon (CA - CC8X30) was chosen as adsorbent reference and submitted to the same process. Afterwards, the filtered were assessed by UV-Vis spectrophotometer in 665 nm. The calibration curve was created and the R^2 is 0,99955 for the equation $y = 0{,}00853723x - 0{,}00611267$ considering the points 0, 25, 50, 75 and 100. The outcomes proved 100% of efficiency of FD to remove methylene blue. This result contrast with 69% of CA removal capacity in the conditions of the test.

To use FD demonstrade a better option when it compared also with the species of its taxonomic family called *Arecaceae*. For instance, Buriti fiber in the conditions detailed in Lima's study (2017), presented 94% of effience. The açaí seed and tucumã endocarp which represent efficieny percentages of 42% and 41,9% respectivetly, both according Bentes' investigation (2017). Even in the proper specie one difference can be highlighted. According to Rosales' study (2021), palm oil waste pyrolysised and then activated with $ZnCl_2$ resulted 36% of methylene blue removal capacity.

This outcome obtained from this project represents an important advance in sustainable chemistry as a starting point to investigate FD as a biomass that may remove another organic pollutants wasted in water. For example, fuels and medicines.

Agradecimentos/Acknowledgments

Our best thanks for CAPES and FAPERJ for all financial support and Instituto Militar de Engenharia (IME) for all knowledge and infrastructures support for this research.

Referências/References

BENTES, V. I. Preparação e caracterização de compósitos a base de fosfatos de ferro suportados em carvões ativados de resíduos de caroços de açaí e do endocarpo de tucumã para aplicação ambiental. 137 p. Tese (Doutorado) — Universidade Federal do Amazonas, Manaus, 2017.
LIMA, S. N. P. Caracterização das fibras de buriti e sua aplicabilidade como adsorvente de metais e corantes. 97 p. Dissertação (mestrado) — Universidade Federal do Tocantins, Gurupi, 2017.
ROSALES, D. H., "Obtención de carbon activado a partir de la cáscara del fruto de la higuerilla para la remoción de azul de metileno. 87 p. Tese (Doutorado) — Facultad de ingeniería química, Puebla, 2021.

Área: AMB
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

ADVANCED COMPOSITE MEMBRANES FOR THE PURIFICATION OF WATER CONTAMINATED WITH POTENTIALLY TOXIC METALS

Ana Maria Tischer (PG)[1], Rafaela Reis Ferreira (PG)[2], João Gabriel Ribeiro (PG)[2], Derval dos Santos Rosa (PQ)[2], Alexandre Tadeu Paulino (PQ)[3*]
E-mail: alexandre.paulino@udesc.br

[1]Politecnico di Milano, Piazza Leonardo da Vinci, 32, 20133, Milano/MI, Italy; [2]Engineering, Modeling and Applied Social Sciences Center (CECS), Federal University of ABC, Av dos Estados, 5001, Bairro Bangu, 09210-580, Santo André/SP, Brazil; [3]Department of Chemistry, Santa Catarina State University, Rua Paulo Malschitzki, 200, Zona Industrial Norte, 89219-710, Joinville/SC, Brazil.

Palavras-Chave: *Polysaccharide; Pectin; Membrane; Composite; Water Purification; PTEs.*

Highlights

- Pectin/pine sawdust/magnetite membrane as potential support for PTE sorption
- Polysaccharide-based membrane for water purification
- Efficient removal of PTEs from water using pectin-based membrane

Abstract

Anthropogenic activities can lead to high contents of potentially toxic elements (PTEs) in soil and water. Thus, there is a worldwide need to find effective, environmentally friendly sorbents for remediating sites polluted with metals. In this study, we investigated how pectin/magnetite/pine sawdust (PE/Fe_3O_4/P) membranes serve as sorbents for the removal of Cd(II), Cr(VI), Cu(II), Mn(II), Ni(II), and Zn(II) from aqueous media containing multiple metals. The tested membranes were prepared with PE, 1.0 wt-% Fe_3O_4 (w/w) and different amounts of P (1, 3, 5, or 10 wt-%). $CaCl_2$ was used as the crosslinking agent and glycerol was used as the plasticizer. Briefly, a mass of esterified PE was dissolved in distilled water. After PE dissolution, glycerol and different amounts of P were added. The mixture was heated to 70ºC and pre-crosslinked by adding $CaCl_2$ solution at a flow rate of 1 mL min^{-1} under magnetic stirring for 90 min. Subsequently, Fe_3O_4 was added to the still hot pre-crosslinked solution under magnetic stirring to improve the mechanical and thermal resistance of the final material. Lastly, the solution was poured into Petri dishes, which were placed in a Famem® Orion 515 forced-air circulation oven at 40 ºC for 20 h. The formed membranes were immersed in glycerol solution containing $CaCl_2$ for 30 min to complete the crosslinking process. The final membranes were washed with distilled water and dried in a forced-air circulation oven at 25ºC for 5 h. All membranes were then stored in a vacuum desiccator at 25ºC and low relative humidity for 72 h before being applied in the sorption and removal of PTEs from aqueous solutions. The metal/membrane interaction was confirmed by Fourier-transform infrared (FTIR) spectroscopy, thermogravimetry (TG), derivative thermogravimetry (DTG), scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDS) after the sorption assays. Among the six PTEs tested, the PE/Fe_3O_4/P5% membrane had the highest sorption capacity for Cu(II) (~43 mg g^{-1}). The following selectivity sequence was found for the PE-based membranes: Cu(II) > Zn(II) > Ni(II) > Cd(II) > Cr(VI) > Mn(II). Cu(II) was always favorably sorbed in/on the membranes over Zn(II), Ni(II), Cd(II), Cr(VI), and Mn(II), with removal efficiencies higher than 80 %. Moreover, Cr(IV) and Mn(II) had the lowest affinities. When the PTEs co-existed at higher concentrations, Cu(II) competed with Cr(IV) and Mn(II) for the active sorption sites of the PE-based membranes, resulting in the decreased sorption of Cr(IV) and Mn(II). The addition of P and Fe_3O_4 generally improved the affinity of the membrane for less selective metals. Sometimes, however, the sorption of Cd(II) and Cr(VI) decreased with the increase in P content. The addition of 1% P increased the affinity for Cd(II), but decreased the affinity for Ni(II) and Zn(II). This decrease is related to the affinity of Ni(II) and Zn(II) for partially esterified polygalacturonic acid (PGA). The findings of this work indicate that green sorbents as the PE/Fe_3O_4/P membranes constitute a promising strategy for the remediation of aquatic environments contaminated with PTEs. These types of biomaterials demonstrated to be efficient, eco-friendly sorbents for the removal of PTEs from water and wastewaters in either membrane-filtration processes or sorption filters.

Acknowledgments

ATP thanks FAPESC, Brazil for financial support (Grant number: 2023/TR331) and CNPq, Brazil for the research productivity fellowship (Grant number: 313064/2022-9). DSR thanks CNPq (Grant number: 308053/2021-4 and 403934/2021-4) and FAPESP, Brazil for research support (Grant numbers: 2023/04147-8 (JGR), 2022/01382-3 (RRF), 2021/14714-1, and 2020/13703-3). This study was also funded in part by CAPES, Brazil – Finance Code 001 and Multiuser Central Facilities (CEM - UFABC).

Área: AMB

Analysis of coffee grounds' adsorptive capacity for Aldrin and Dieldrin removal from water

Diego R. Silva (IC),[1] Geisyellen O. Martins (IC),[1] Karen B. Souza (IC),[1] Mirian G. Costa (IC),[1] Rodrigo L. Silva (IC),[1] Marcos C. Machado (PQ).[1]*

marcos.machado@fiec.edu.br

[1]*Centro de Educação Tecnológica da Fundação Indaiatubana de Educação e Cultura, CETEF/FIEC.*

Palavras Chave: Adsorption; Pesticides; Contaminant removal; Environmental impacts.

Highlights

Coffee grounds adsorb of Aldrin and Dieldrin in distilled water;
Thermal treatment enhances adsorbent capacity;
Sustainable and efficient removal of organochlorine pesticides

Abstract

Organochlorine pesticides, such as Aldrin and Dieldrin, pose a significant environmental concern due to their persistence and adverse effects on human health and aquatic ecosystems (CETESB, 2022). These highly toxic substances have been detected in alarming concentrations in water bodies (PANIS et al., 2022), necessitating the search for effective removal methods. Accordingly, the adsorptive capacity of thermally treated coffee grounds was investigated for the removal of these substances. Initially, coffee grounds underwent a thermal treatment process: washing with distilled water, filtration, drying in an oven at 105°C, and calcination in a muffle furnace at 400°C for carbonization. Characterization revealed a reduction in particle diameter from 439.044 µm (original coffee grounds) to 175.579 µm (calcined coffee grounds), along with increased surface area (60.020 m²/g) and pore volume (0.02808 cm³/g), enhancing the material's adsorptive capacity. Adsorption tests were carried out using a factorial design (2^3 = 8 treatments) with different masses of calcined coffee grounds (7.5 g or 15.0 g) under different stirring times (60 min or 120 min) and levels of pH (4.0 or 7.5) using initial pesticide concentrations of 0.01 mg/L in 125 mL of distilled water. Liquid-liquid extraction of the different treatments was performed and the solutions were analyzed by UV-VIS and GC-FID after calibration ($r^2 > 0.99$) using standard solutions ranging from 0.0025 to 0.1 mg/L. The best results were obtained at pH 7.5 and using the highest values of time and adsorbent mass and indicated 81.7 to 92.0% adsorption of the Aldrin and 73,4 to 96% adsorption of Dieldrin. These differences can be attributed to different properties of the compounds such as their solubility in water and competition for adsorption sites (BANDALA et al., 2006). Langmuir isotherms showed favorable adsorption behavior with maximum adsorption capacities of 0.0015 mg/g for Aldrin and 0.0013 mg/g for Dieldrin. Overall, the study demonstrates the promising adsorptive capacity of calcined coffee grounds for removing organochlorine pesticides from water, with over 90% removal efficiency under specific experimental conditions, suggesting its viability for contaminated water remediation. However, further research is needed to evaluate its effectiveness in real-world water matrices.

CETESB. (2022). Aldrin e dieldrin: Ficha de informação toxicológica. São Paulo: CETESB.
Bandala, E. R., Andrés-Octaviano, J., Pastrana, P., & Torres, L. G. (2006). Removal of Aldrin, Dieldrin, Heptachlor, and Heptachlor Epoxide Using Activated Carbon and/or Pseudomonas fluorescens Free Cell Cultures. Journal of Environmental Science and Health Part B, 41(6), 553–569.
Panis, C., Candiotto, L. Z. P., Gaboardi, S. C., Gurzenda, S., Cruz, J., Castro, M., & Lemos, B. (2022). Widespread pesticide contamination of drinking water and impact on cancer risk in Brazil. Environment International, 165.

Acknowledgments

The authors would like to thank the Indaiatubana Foundation of Education and Culture for the financial support provided for the analyses conducted.

Area: AMB

Analysis of Triclosan Sorption in Polyethylene Therephthalate Microplastics

Giovanna P. Carril (IC),[1] Mariana A. Dias (PG),[1] Cassiana C. Montagner (PQ).[1]

g236445@dac.unicamp.br; giovannapcarril@gmail.com

[1] *University of Campinas (UNICAMP), Institute of Chemistry, Department of Analytical Chemistry*

Key words: PET, water quality, emerging contaminants, MPs.

Highlights

An initial assessment of the sorption of Triclosan in virgin and degraded PET microplastics was carried out in controlled laboratory tests with ultrapure, river and sea waters, resulting in a sorption capacity between 8 – 32% with a tendency to be stronger in virgin MPs.

Abstract

Microplastics (MPs) are particles of synthetic organic polymers less than 5 mm in size, which have become ubiquitous contaminants in the environment. Triclosan (TCS) acts as a preservative and fungicide in industry and is widely used in personal care and household products, despite its acute and chronic toxicity in aquatic environments. Due to sorption, microplastics can behave as Triclosan vectors and modify the environmental behavior of this contaminant. It is known that this sorption depends on various factors ranging from the type and shape of the polymer, the degree of degradation, the physical-chemical characteristics of the compound, and the complexity of the aquatic matrix (such as the presence of organic matter, high ionic strength, etc.). Therefore, the aim of this research was to analyze the differences in Triclosan sorption in virgin and degraded (by UV-C light) PET microplastics in controlled laboratory tests, using different aquatic matrices (ultrapure, river and sea waters). The sorption capacity was measured by indirect method, tracking the concentration of triclosan in the water using high-performance liquid chromatography coupled to diode array detector (HPLC-DAD, Shimadzu SCL10AVP). The instrumental method was developed using a C18 reverse stationary phase (Agilent Eclipse XDB-C18, with an internal diameter of 4.6 mm, a length of 150 mm and a particle size of 5 µm), and isocratic mobile phase of 85% MeOH in 7 min. The limit of quantification was 10 µg L^{-1}, referring to the lowest concentration point analyzed in the calibration curve. The sorption tests were made with 20 mg of microplastics and 4 mL of a 1 mg L^{-1} solution of TCS in a glass tube with a PTFE cap. All samples were centrifuged in a Marconi Roto Torque MA 161 shaker, operating at 40 rpm, for different contact time intervals (10 min, 20 min, 30 min, 40 min, 50 min, 1 h and 2 h) and filtered before HPLC-DAD analysis. Through the tests, it was concluded that there was significant retention of Triclosan in all the filters used: the PTFE filter showed the least interaction with TCS (50%), followed by the Nylon filter (73%) and, finally, PVDF (98%). It was also noted that sorption of TCS occurred in the Eppendorf bottle (made of polypropylene), which was used to dilute the samples before analysis. This issue was resolved by previous PTFE filter saturation and replacing the Eppendorf flask with an amber vial, where there was no sorption of the compound. The results shows that the sorption efficiency of triclosan in virgin PET microplastics after 40 min (equilibrium time) was highest in ultrapure water (32.4%), followed by seawater (29.6%), while river water showed the lowest sorption efficiency (26.1%). This latter scenario, associated with a matrix considered to be more complex with high organic matter content, made the sorption process more difficult, as well as the presence of salt ions in solution in seawater. For degraded MPs, the trend was the same, however with lowest rate: highest sorption efficiency in ultrapure water (25.25%), the least complex matrix, followed by seawater (17.21%) and river water (7.97%). Analysis of variance showed that the mean qt values between virgin and degraded MPs in ultrapure water, river water and seawater at equilibrium time were statistically different, with P values less than 0.05 in all tests. After analyzing the virgin and degraded PET polymers by ATR-FTIR spectroscopy, no notable structural changes were observed. However, due to the change in color, it can be seen that the MP has been degraded, which can affect the hydrophobicity and sorption capacity of organics, justifying the difference in sorption.

Acknowledgments

The authors are thankful for the scholarships provided by CNPq and CAPES, and the financial support provided by the National Institute of Advanced Analytical Science and Technology (INCTAA), grants CNPq 465768/2014-8 and FAPESP 2014/50951-4.

Área: AMB

Assessing the origin and fate of tarballs on the coast of Brazil in late 2023 by forensic environmental geochemistry: disclosing international oil dumping

Laercio L. Martins (PQ),[1,2*] Vinícius B. Pereira (PG),[3] Adriana P. Nascimento (PG),[2] Rufino Neto A. Azevedo (PG),[4] André H.B. Oliveira (PQ),[2,4] Carlos Eduardo P. Teixeira (PQ),[2] Débora de A. Azevedo (PQ),[3] Georgiana F. da Cruz (PQ),[1] Rivelino M. Cavalcante (PQ),[2] Tommaso Giarrizzo (PQ)[2]

laercio@lenep.uenf.br

[1]Laboratory of Petroleum Engineering and Exploration, UENF; [2]Institute of Marine Sciences, UFC; [3]Institute of Chemistry, UFRJ; [4]Analytical Chemistry and Physical Chemistry Department, UFC

Keywords: *Oil Spill, International Waste, Marine Pollution, Northeastern Brazil, Organic Geochemistry*.

Highlights

Mysterious oily materials have frequently contaminated the Brazilian coast. This study discloses a new event related to dumping Middle Eastern crude oil from tankers on the South Atlantic routes.

Resumo/Abstract

Oil spills have become a chronic problem on the coast of Brazil, with countless social, economic, and ecological impacts. In September 2023, spilled oils like tarballs from an unknown source reached the coast of the state of Bahia, contaminating many beaches and coastal areas over 120 km of coastline. Tarballs are toxic and persistent spherical oily residues that can remain for a long time, drifting on the sea until stranded in seashore areas. In this context, we applied concepts of forensic environmental geochemistry to investigate the source and fate of four tarball samples collected at the beaches of Bahia in 2023, in addition to possible similarities with two oily residue samples from each of three previous oil spills on the Brazilian coast (2019, early 2022, and late 2022). Accordingly, saturated (e.g., *n*-alkanes, isoprenoids, terpanes, steranes, and tetracyclic polyprenoids) and aromatic (e.g., triaromatic steroids, anthracene, methylanthracene, methylphenanthrene, dibenzothiophenes) compounds were assessed by gas chromatography. The geochemical fingerprint (i.e., their specific chemical composition) based on the resistant biomarkers, such as the steranes and terpanes, of the 2023 spilled oil did not correlate with those of previous events, indicating a novel oil spill event off the Brazilian coast. However, their fingerprint point to oil with carbonate marine origin from early mature source rocks, which correlates with oils produced by Middle Eastern countries, most likely Kuwait, when comparing our results with data available in the literature. In addition, the distribution of aromatic compounds indicates a crude oil (not fuel) with a moderate level of weathering. These results imply that the oil was dumped close to the shore of Brazil, probably by an oil tanker on an international route in the South Atlantic transporting Middle Eastern oil.

Agradecimentos/Acknowledgments

This work was supported by the universities UFC, UENF, and UFRJ. We thank CNPq, FAPERJ, CAPES, and FUNCAP for researcher funding and student grants.

Área: AMB

Assessment of NOx levels emitted by trucks using real-time sensors and Internet-of-things (IoT).

Luis Fhernando Mendonça da Silva (PG),[1*] André H. M. Nunes (PQ),[2] Adrien Deroubaix (PQ),[3,4] Guy Brasseur (PQ),[3,5] Adriana Gioda (PQ)[1]

luisfhernando2903@gmail.com; agioda@puc-rio.br

[1] Departamento de Química, Pontifícia Universidade Católica do Rio de Janeiro (PUC-Rio),22451-900 Rio de Janeiro-RJ, Brazil; [2] ZANE-Tecnologia da Informação LTDA, 22451-900 Rio de Janeiro-RJ, Brazil, [3] Max Planck Institute for Meteorology, 20146 Hamburg, Germany; [4] Institute of Environmental Physics, University of Bremen, Bremen, Germany; [5] National Center for Atmospheric Research Atmospheric Chemistry Observations and Modeling Laboratory, 80307, Colorado, USA.

Keywords: *NOx, Emission factor, Sensor, PROCONVE, Atmospheric chemistry, Internet-of-things.*

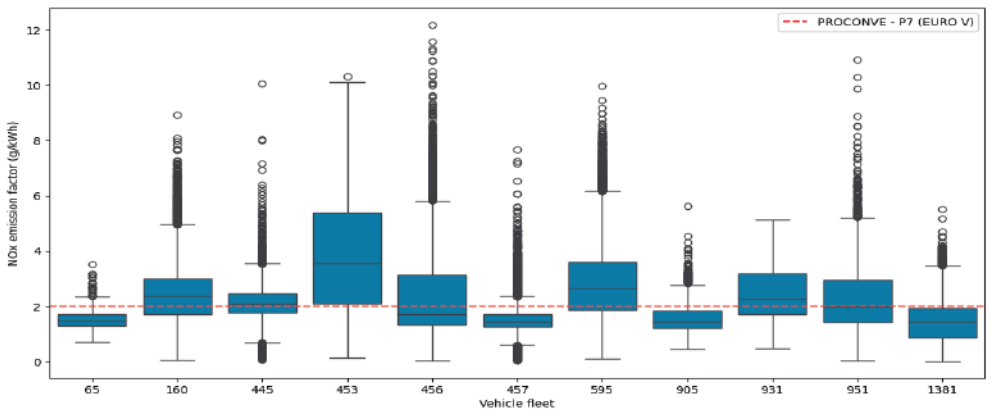
Highlights

Five of the 11 monitored vehicles (45%) surpassed the NOx emission factor limits set by Brazilian legislation. In comparison to the prior study, a notable decrease in pollutant emissions was observed following maintenance.

Resumo/Abstract

The Metropolitan Region of Rio de Janeiro is one of the most densely populated areas in Brazil and serves as a crucial transportation route for heavy vehicles carrying goods. These vehicles are the primary contributors to nitrogen oxide (NOx) emissions in the atmosphere. To assess NOx emission factors, this study utilized sensors, based on the Internet-of-Things (IoT), for monitoring of exhaust gases in real driving conditions from 11 trucks between January and April 2023. The obtained data were compared with previously published data by the author. Despite existing regulations aimed at reducing pollutant emissions from the vehicle fleet, the results indicated that only 5 out of the 11 trucks exceeded the limit of 2 g kWh^{-1} (P-7), as stipulated by the Program for the Control of Air Pollution from Motor Vehicles (PROCONVE), reaching 7 g kWh^{-1} (Fig. 1). When compared to the study conducted by SILVA et al. (2023), we observe a reduction in vehicle emissions after maintenance. Thus, real-time measurement of NOx emission factors using a low-cost sensor presents an alternative. The use of sensors can help mitigate vehicle issues related to NOx emissions and ensure compliance with PROCONVE legislation. Additionally, an atmospheric modeling study will be conducted to assess the dispersion of these pollutants in the atmosphere of the Metropolitan Region of Rio de Janeiro.

Figure 1. NOx emission factors in eleven trucks monitored with sensor (January - April of 2023).



Agradecimentos/Acknowledgments

This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) - Brazil (finance code 001). The authors thanks to CNPq, and FAPERJ for financial support.

SILVA, L. F. M.; DE LA CRUZ, A. H.; NUNES, A. H. M.; GIODA, A. (2024). Real-Time Monitoring of Nitrogen Oxides Emission Factors Using Sensors in the Exhaust Pipes of Heavy Vehicles in the Metropolitan Region of Rio de Janeiro. *Journal of the Brazilian Chemical Society*. 10.21577/0103-5053.20230170.

Área: AMB

Assessment of oxidative stability and antioxidant efficiency in extract of *Rosmarinus officinalis,* after additivation in soy methyl ester

Tayná de S. V. Moura (PG),[1*] Bruno A. S. dos Santos (PG),[2] Rayanne C. S. dos Santos,[1] Renato de O. Soares (PQ),[3] Márcio Mattos (PQ),[4] Pedro L. M. Penedo (PQ), [4] Vânia Mori (PQ),[3] Vera L. D. Resende (PQ),[3] Eduardo H. S. Cavalcanti (PQ),[3] Kátia R. de Souza (PQ).[1] Email: tayna@ime.eb.br

[1]Seção de ensino de engenharia química, IME; [2]Departamento de Química, UFF; [3]LACOR, INT; [4]CESBRA.

Palavras-chave: *Rosmarinus officinalis;soy methyl ester; antioxidant activity; oxidative stability;*

Highlights

The present work evaluated the antioxidant activity and oxidative stability in different extracts of *Rosmarinus officinalis*. A known methodology for extraction was used, but the extracts differ in terms of particle size, the smallest showed better results. A commercialized extract was also evaluated. From there, it was added soy methyl ester. The results found were promising.

Resumo/Abstract

Biodiesel é um combustível pouco poluente, proveniente de óleos vegetais ou gordura animal, que possui alta reatividade com o oxigênio, sofrendo oxidação, resultando em seu envelhecimento e prejuízos severos aos sistemas de injeção, filtragem e ao motor dos automóveis. Devido à baixa estabilidade deste, frente a processos oxidativos, torna-se necessária a adição de antioxidantes a fim de preservar o limite mínimo de 12 h para estabilidade oxidativa (EO), conforme exigido pela resolução ANP nº 45 de 2014. Dessa forma, este trabalho tem como objetivo avaliar e analisar diferentes extratos do *Rosmarinus officinalis* (alecrim), que serão aditivados no biodiesel puro (B100) como antioxidante. Foram testados três extratos para este trabalho, em que o extrato mesh 100 apresentou melhor índice de estabilidade oxidativa e por isso, foi escolhido para a aditivação do biodiesel e avaliação dos parâmetros exigidos pela ANP. O alecrim desidratado foi submetido à trituração, maceração, peneiração e pesagem (36 g), com adição de 200 mL de etanol, seguido de agitação manual por 15 dias consecutivos e agitado em mesa agitadora no último dia, por 2h. Após, foi filtrado a vácuo e levado ao rotaevaporador. Foram analisadas as amostras de B100 (éster metílico de soja), éster metílico de soja aditivado com 1500 mg.L^{-1} de TBHQ, éster metílico de soja aditivado com 500 mg.L^{-1} de TBHQ e 1000 mg.L^{-1} de extrato etanólico de alecrim, para determinação da EO, índice de acidez (IA), massa específica (ME), metais, viscosidade cinemática (VC), dienos e trienos, teor de água e teor de éster. Parte dos resultados obtidos estão apresentados na Tabela 1.

Tabela 1. Características quantitativas das amostras de éster metílico de soja puro e aditivadas, nos tempos 0, 15 e 30 (dias):

CARACTERÍSTICAS	B100			B100 + TBHQ 1500			B100 + TBHQ + EEA (500:1000 ppm)			Óleo de soja
	t_0	t_{15}	t_{30}	t_0	t_{15}	t_{30}	t_0	t_{15}	t_{30}	
ME a 20°C (Kg/m^3)	883,2	-	-	883,2	883,2	883,2	883,2	883,2	883,2	914,0
Teor de água (mg.Kg^{-1})	216,1	-	-	406,0	996,1	1007,1	490,0	993,0	935,9	-
VC a 40°C (mm².s^{-1}) - media/tanque	4,78	-	-	-	3,91	4,18	-	3,86	4,77	-
					4,09	4,28		4,26	4,74	-
					4,31	4,57		4,33	4,16	-
Estabilidade oxidativa (h)	3,74	-	-	9,47	19,50	18,60	12,39	2,0	4,87	-
IA (mg KOH.g^{-1}) - média/tanque	0,29	0,29	0,30	0,13	0,14	0,29	0,22	0,28	0,28	0,9
					0,23	0,25		0,23	0,26	
					0,23	0,24		0,24	0,26	

As análises para metais apontaram alto teor destes no extrato, o que era esperado, uma vez que este é um produto natural. Com o passar do tempo, a viscosidade e a acidez aumentaram, o que se justifica pela degradação do combustível. Percebe-se que o extrato obtido pode ser empregado como antioxidante natural em substituição aos antioxidantes sintéticos TBHQ e BHT, por estar em conformidade com as exigências da ANP. Vale destacar que os antioxidantes sintéticos são prejudiciais ao meio ambiente e, consequentemente, ao ser humano.

Agradecimentos/Acknowledgments

Este estudo foi financiado em parte pela Coordenação de Pessoal de Nível Superior -(CAPES)- Código Financeiro 001, FAPERJ (edital nº05/2020), IME (Instituto Militar de Engenharia) e CESBRA Química.

Área: AMB

Assessment of the chemical composition of precipitation in the regions of Gávea and Serra dos Órgãos National Park (PARNASO), RJ

Marcos Felipe S. Pedreira (PG),[1]* Adriana Gioda (PQ).[1]

mfspedreira@gmail.com; mfspedreira@gmail.com

[1]*Chemistry Department, PUC-Rio*

Key words: *Rainwater, íons, Metals, Air Pollution*

Highlights

Gávea suffers a direct impact from anthropogenic emissions, unlike the Serra dos Órgãos National Park (PARNASO).

The chemical composition of the samples confirmed the proximity to local sources.

Rainwater was an excellent tool for assessing air quality

Resumo/Abstract

Total precipitation samples were collected monthly in two different locations (Gávea and Serra dos Órgãos National Park - PARNASO) in the state of Rio de Janeiro, from April 2022 to April 2023, totaling 12 samples in each location. The samples were analyzed for ionic constituents by ion chromatography (IC) and to trace elements by ICP-MS to determine their concentrations and identify potential sources. The ion concentration (μeq L^{-1}) of the Gávea samples was $C_2O_4^{-2}<F^-<CH_2(COO)_2^{2-}<Br^-<CH_3COO^-<SO_4^{2-}<K^+<Mg^{2+}<NH_4^+<Ca^{2+}<NO_3^-<Na^+<Cl^-$, while in PARNASO it was $Br^-<C_2O_4^{2-}<CH_3COO^-<Ca^{2+}<Mg^{2+}<SO_4^{2-}<NO_3^-<PO_4^{3-}<K^+<Na^+<Cl^-$. The concentration (mg L^{-1}) of the trace elements in Gávea was Cr = Ni = Sn < Mn < Cu < Fe < Pb < Zn, while in PARNASO it was Cr < Mn < Ni < Fe < Sn < Pb < Cu < Zn. The samples from Gávea had an average pH of 5.73 and an average conductivity of 21.9 μS cm^{-1}, while those from PARNASO had a pH of 6.05 and a conductivity of 21.4 μS cm^{-1}. Na^+ e Cl^- were the most abundant ions in precipitation in both locations, having their origin strongly associated with sea spray. Significant correlations, enrichment factors, non-marine fractions and source fractionation were performed to suggest the origin of the determined ionic species. The urban region of Gávea suffered a greater impact from anthropogenic sources (52 %), while the preserved region of PARNASO from natural sources (62 %). The main trace elements were evaluated based on comparison with previous studies in the literature. Sn and Pb have been linked to wear on vehicle components, fuel additives, and traffic. The increases in Fe, Ni and Zn in PARNASO suggested the contribution, respectively, of soil, liquid fuels/coal and geological plant materials/micronutrients. Thus, the effectiveness of rainwater as another tool for assessing air quality in a region was confirmed. Furthermore, it was proven, as expected, that pollution in Gávea was greater than in PARNASO.

Agradecimentos/Acknowledgments

SBQ, CAPES, CNPq and FAPERJ

Área: AMB

Atmospheric micro(nano)plastics in a Brazilian elementary school: concentrations and cell viability using an air-lung model

Gabriel M. Ferraz (PG), Aline S. de Moraes (IC), Gustavo B. dos Santos (IC), Ingrid T. de Miranda (IC), Roberta C. Urban (PQ)

gabriel.ferraz@estudante.ufscar.br

Chemistry Department, Federal University of São Carlos (UFSCar – São Carlos)

Keywords: Atmospheric microplastics; Emission sources; Indoor and outdoor environments; μ-Raman; Cell viability tests

Highlights

The atmospheric microplastic concentrations ranged from LOD to 168.03 items m^{-2} day^{-1}.

Seasonal variations were observed in indoor fiber concentrations, but no seasonal differences were identified in the outdoor environment for both fragments and fibers.

Polyester was the most abundant polymer, followed by ethylene vinyl acetate, polyethylene, and polyethylene terephthalate.

Concentration and size-dependencies were observed in the cell viability.

Resumo/Abstract

The widespread production and use of plastics revolutionized the modern world but resulted in environmental pollution. However, while microplastics and nanoplastics (MNPs) pollution in aquatic environments have been well documented, knowledge of air pollution by MNPs and airborne MNPs-induced adverse health outcomes is still limited.[1] This study focused on atmospheric MNP concentrations at Alvaro Guião School (São Carlos - Brazil) from November 2021 to July 2022. Sample collection took place in the school's service area, an open space near a street with heavy pedestrian and vehicular traffic, positioned approximately 170 cm above the ground. The indoor passive sampler was placed in the school's coordination office, which measures 12 m², has two doors, and one window, and is in use for about 14 hours a day. The sampler was positioned on top of a cabinet, approximately 160 cm above the ground, and the sampling points are approximately 100 meters apart from each other. The microplastic concentrations (>25 μm) ranged from LOD to 168.03 items m^{-2} day^{-1} outdoors and LOD to 60.16 items m^{-2} day^{-1} indoor (**Figure 1**). These MNPs were predominately composed of fragments (mainly <60 μm) instead of fibers (ranging from <60 μm to 3000-5000 μm), indicating sources like vehicular traffic and resuspension. Seasonal variations were observed in indoor fiber concentrations, with higher levels during the dry season attributed to the colder temperatures that led to increased clothing use and reduced ventilation, promoting particle accumulation in indoor spaces. The main components of the MNPs, identified employing μ-Raman spectroscopy, were polyester (outdoor: 83-100%; indoor: 29-100%) and ethylene vinyl acetate (outdoor: 0-17%; indoor: 0-57%). Polyester is a significant material in synthetic clothing, widely used in the textile industry, and ethylene vinyl acetate is extensively used in school supplies, toys, and shoe soles. Therefore, the school's activities, with over 1,400 students, also contributed to the presence of MNPs in the atmosphere. Additionally, common plastics found in packaging and bottles, such as polyethylene (0-14%) and polyethylene terephthalate (0-6%), were also identified in the room samples. These similar compositions may also indicate that there is an exchange of suspended particles between the indoor and outdoor environments., with residence time in the atmosphere, air circulation, and proximity to potential primary emission sources being some of the important factors to explain the compositions and concentrations founded.

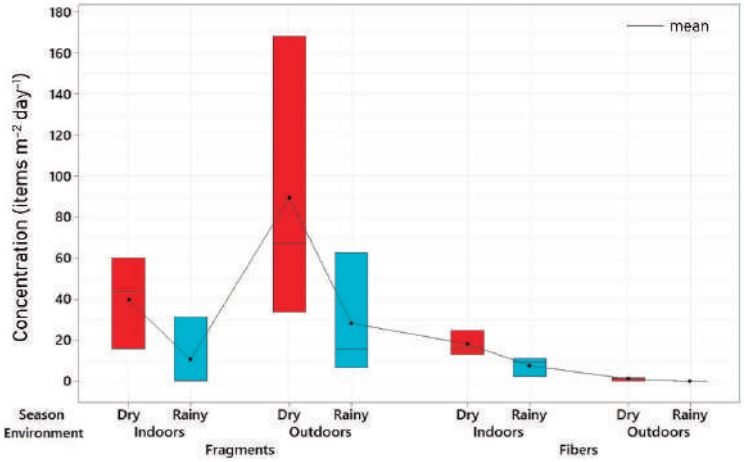


Figure 1. Mean concentrations of atmospheric MPs in samples collected in the dry and rainy seasons in indoor and outdoor environments

Exposure of A549 cells to polystyrene MNPs using an air-lung interface system (ALI) indicated that reductions in cell viability (MTT assay) were dose-dependent (20 μg and 100 μg) and size-dependent (0.05 μm, 0.1 μm, and 0.5 μm). Moreover, differences were observed in cell viabilities using the ALI and submerged cell culture models, although the same trends were observed. However, more studies need to be carried out to analyze the significance of the results. In conclusion, this study sheds light on the relatively unexplored field of atmospheric MNPs, emphasizing their presence and possible sources in a school environment in São Carlos, Brazil, and their impacts on human health.

1. Zhang, Y.; Kang, S.; Allen, S.; Allen, D.; Gao, T.; Sillanpää, M.; Earth Sci Rev 2020.

Agradecimentos/Acknowledgments

Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES, Finance Code 001), São Paulo State Research Foundation (FAPESP, grant #2018/04820-6; #2021/10187-7; #2022/03087-9; #2023/06768-0), INCTAA (CNPq, grant #465768/2018-8; FAPESP, grant #2014/50951-4)

Área: AMB

Atmospheric microplastics and nanoplastics: optimization of the sample pretreatment by digestion

Débora M. da Silva (IC), Gabriel M. Ferraz (PG), Roberta C. Urban (PQ)*
debora.martins@estudante.ufscar.br
Chemistry Department, Federal University of São Carlos (UFSCar – São Carlos)
Keywords: oxidation process, microplastics, nanoplastics

Highlights

Surprisingly, higher WSOC concentrations were observed during the digestion process using agitation and longer degradation times, suggesting potential improvements in the extraction process.

The concentrations in mg L^{-1} of TC and IC in the sampled filters increased considering the parameters of longer agitation time and a greater volume of the oxidizing reagent.

Resumo/Abstract

Plastics contribute to modernizing the world and are widely used by humans, for example, to improve health through personal protective equipment, food packaging, product packaging, among others (PRATA et al., 2020). However, the disposal of plastics results in the release of microplastics and nanoplastics (MNPs) into the environment (ZANG et., 2020). Although these are ubiquitous environmental contaminants, the analysis of atmospheric MNPs is highly challenging due to the complex environmental background, size constraints, and the lack of standardized methods for sample preparation that have not been established (MITRANO; WICK; NOWACK, 2021). In this context, the objective of the present study was to study the digestion of organic matter during the pretreatment of atmospheric samples. For this, punches (diameter = 47 mm) of glass fiber filters containing atmospheric particulate matter (PM_{10}) were treated with H_2O_2 (concentrations of 10 and 50% v/v). They were kept at 23ºC for different periods (7 or 14 days) with and without agitation. It should be mentioned that these samples were collected in the Praça dos Voluntários, a central square located in Sao Carlos, a city in the north-central region of the State of Sao Paulo – Brazil, using a high-volume sampler, and that each condition was analyzed in triplicates. Moreover, treatments using water instead of H_2O_2 were also performed to compare the results. After the digestion processes, the solutions were filtered using mixed filters composed of esters and cellulose acetate (MCE; pore size of 0.45 µm), and the water-soluble organic carbon (WSOC) concentrations were determined by high-temperature catalytic oxidation, using a Total Organic Carbon Analyzer. The linearity of the method was established by analyzing 3 to 5 repetitions of 5 different standard solutions at concentrations ranging from 0.100 to 3.000 mg L^{-1} of a mixture of sodium bicarbonate and sodium carbonate for inorganic carbon analysis and another 5 standard solutions of potassium hydrogen phthalate with concentrations ranging from 20.00 to 1,000.00 mg L^{-1}. The method was linear within these ranges. The limit of detection (LOD) was 0.12 ng mL^{-1} for TC and was sufficient to satisfactorily describe the data behavior. Higher WSOC concentrations were quantified after the process with agitation and a longer degradation time. This behavior was not expected, and the possible explanation for this could be the improvement in the extraction process. Moreover, it was possible to observe that the concentrations of WSOC in the sampled filters increased with the concentration of H_2O_2. The analyses of WSOC in the MCE filters are currently being carried out and could confirm this hypothesis. The results will be presented during the conference, as well as the results of studies with different textile materials, which are ongoing.

1. MITRANO, D. M.; WICK, P.; NOWACK, **Nature Nanotechnology**, v. 16, n. 5, p. 491–500, 29 maio 2021.
2. PRATA, J. C. et al. **Environmental Science & Technology**, v. 54, n. 13, p. 7760–7765, 7 jul. 2020.
3. ZHANG, Y. et al. **Earth-Science Reviews**, v. 203, n. September 2019, p. 103118, abr. 2020.

Agradecimentos/Acknowledgments

São Paulo State Research Foundation (FAPESP, grant #2018/04820-6; #2021/10187-7; #2022/03087-9), INCTAA (CNPq, grant #465768/2018-8; FAPESP, grant #2014/50951-4)

Área: AMB

Bioaerosol from a Midsized Tropical City of Brazil: Sao Carlos - SP

Gustavo B. dos Santos (IC)*, Jonatas S. Carvalho (PQ), Roberta C. Urban (PQ)

*gustavobitencort@estudante.ufscar.br

Chemistry Department, Federal University of São Carlos (UFSCar – São Carlos)

Keywords: Atmospheric particulate matter; Saccharides; Fungi; qPCR

Highlights

The sugar concentrations ranged from 4.70 to 358 ng m^{-3} of air.

Arabitol, glucose, levoglucosan, mannitol, sucrose, and fructose were the most abundant sugars.

During the dry season, the median saccharides concentration was higher compared to the rainy season.

The fungi markers had a maximum concentration during the rainy season.

Resumo/Abstract

Air pollution is one of the main environmental risks to human health, with particulate matter (PM) standing out as one of the most studied due to its harmful potential to human health.[1] Although the presence of bioaerosols, PM of biological origin, in the atmosphere has been known for centuries, there is a lack of studies in Brazil on this topic.[2] Fungal spores constitute a sizeable fraction of bioaerosols, and tracers for quantifying the spore in atmospheric aerosol are sought. Arabitol and mannitol have been used as such tracers.[3] In this context, the main goal of this study was to determine the concentrations of sugars and fungal cells in PM_{10} samples from an agro-industrial region (São Carlos – SP). Sugars were extracted using dichloromethane and methanol (3:1; 3 x 5 mL) and analyzed by gas chromatography-mass spectrometry,[4] while fungal cells were extracted from the filters under shaking for 24h in a sterile saline solution (NaCl 9 g L^{-1}, 15 mL), genomic DNA was extracted from the saline solution using a Blood-Animal-Plant DNA Preparation Kit and then quantified by qPCR using the SYBR Green Master Mix.[5] Analytical curves for sugars were constructed in the range from 50 to 5,000 ng mL^{-1}, resulting in a linear correlation coefficient higher than 0.99 and the limits of quantifications (LOQ) for all analytes were 50 ng mL^{-1}. The abundance of fungal cells was estimated by the quantification of the number of copies of the 18S rRNA, the forward primer used was: 5´-CGGCTACCACATCCAAGGAA-3´, and the reverse primer: 5´-GCTGGAATTACCGCGGCT-3. Analytical curves were developed using solutions with known concentrations of genomic DNA. The concentrations of the 21 saccharides analyzed in the PM_{10} collected from 2015 to 2018 ranged from 4.70 to 358 ng m^{-3} (n = 95), with the annual mean concentrations ranging from 83.3 ± 44.7 to 142 ± 85.9 ng m^{-3}, these values are similar to those observed in other cities in the state. As expected, the saccharides concentrations were higher during dry seasons (median = 130 ± 77.2 ng m^{-3}; n = 48; April to September) compared to the rainy periods (median = 95.4 ± 47.6 ng m^{-3}; n = 47; October to March). The most abundant saccharides in the samples were arabitol, glucose, levoglucosan, mannitol, sucrose, and fructose. The concentrations of the fungi markers: arabitol and mannitol, in the PM_{10} samples ranged from below the LOQ to 60.4 and 113 ng m^{-3}; respectively, and for these sugars the concentrations were higher during the rainy seasons. qPCR analysis is being carried out, and the results will be presented at the conference. The concentrations of fungi markers and fungi will be correlated to understand the impact of fungi on emissions in the region, especially mannitol and arabitol.

1. World Health Organization. https://www.who.int/en/news-room/fact-sheets/detail/ambient-(outdoor)-air-quality-and-health (2022).

2. Can-Güven, E. International Journal of Environmental Science and Technology 19, 7857–7868 (2022).

3. Bauer, H. et al. Atmospheric Environment 42, 588–593 (2008).

4. Carvalho, J. S. et al. Chemosphere 326, 138450 (2023).

5. Rodríguez, A. et al. Environment Research 191, (2020).

Agradecimentos/Acknowledgments

São Paulo State Research Foundation (FAPESP, grant #2018/04820-6; #2021/10187-7; #2022/03087-9; #2023/07601-1), INCTAA (CNPq, grant #465768/2018-8; FAPESP, grant #2014/50951-4).

Área: AMB
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Biomaterial for removing organic compounds from hospital wastewater

Lucas Felipe de Lima (PG) [1]*, Luciana Camargo de Oliveira (PQ),[2] Luana Maria Tavares Rosa (PG),[2] Elisabete Alves Pereira (PQ),[2]

ealves@ufscar.br; lucasflima14@gmail.com ou l264620@unicamp.br

[1] Universidade Estadual de Campinas (UNICAMP), Instituto de Química, Laboratório de Sensores Químicos Portáteis (LSPQ), Campinas; [2] Universidade Federal de São Carlos (UFSCar-So), Departamento de Física, Química e Matemática (DFQM), CCTS, Sorocaba

Palavras Chave: hospital wastewater, glutaraldehyde, biomaterial adsorbent, and capillary electrophoresis

Highlights

Hospital waste represents a significant source of pollutants for the environment;

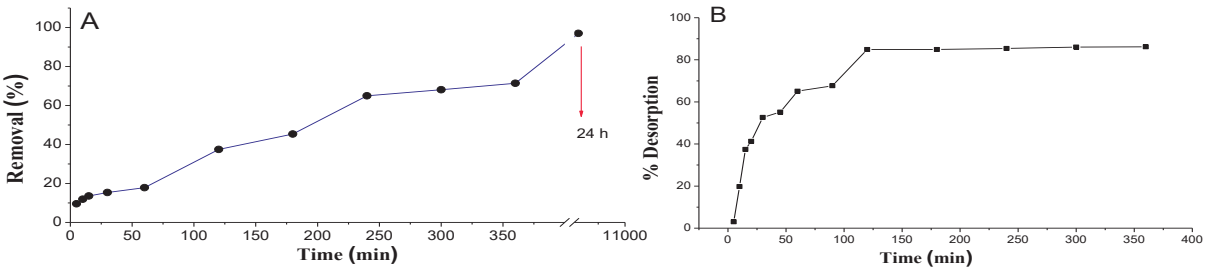
Biomaterial for glutaraldehyde removing;

Glutaraldehyde from hospital wastewater.

Resumo/Abstract

Glutaraldehyde is a chemical substance widely used in hospital settings for the disinfection and sterilization of various types of equipment such as catheters, endoscopes, dialysis instruments, bronchoscopes and nose, ear and throat instruments. The inappropriate disposal of glutaraldehyde in the wastewater network may cause contamination of water resources and be toxic to aquatic organisms. Therefore, the study of materials that can promote the removal of glutaraldehyde is important for the environment. The aim of the present work was to determine the optimum conditions for the adsorption and desorption of glutaraldehyde in solution using Natural Organic Residues (NOR) as a biosorbent. The NOR used in this work is the residue obtained in the alkaline extraction of humic substances. The alkaline extraction was performed using a proportion of soil/extractor (1:10), under 4-h stirring. The residues were separated from the supernatant, washed thoroughly with distilled water, and dried at room temperature to a constant mass. NOR was characterized by different techniques that included infrared spectroscopy, ultraviolet spectroscopy, x-ray, fluorescence, and, dispersive electronics spectroscopy. Batch experiments included the mass of NOR, glutaraldehyde concentration, time contact, pH, and, temperature. Capillary electrophoresis (CE) was performed as analytical technique for determining glutaraldehyde concentration before and after adsorption experiments. The adsorption process was described by a pseudo-second order kinetic model (R^2 = 0,99752) and equilibrium was reached in 45 min described by Freundlich model (R^2 = 0,98736). Batch experiments showed adsorption efficiency of 71.4 % at 360 min (Q_t= 2.86 mg g^{-1}) and more than 95% at 24h (Figure 1A) and desorption efficiencies of 86.2% at 360 min (pH=11) (Figure 1B) by heating at 55^{0}C.

Figure 1 A. Glutaraldehyde removal by NOR; **1B**. Thermal desorption of glutaraldehyde



Legend. 1A: 500 mg of NOR, pH 6, glutaraldehyde concentration = 40 mg L^{-1}. 1B: 500 mg of NOR complexed with glutaraldehyde 100 mg L^{-1} at pH 11; 55 ± 3°C and stirring time: 6 hours x180 rpm

The NOR presented excellent potential for the removal of glutaraldehyde in solutions. Furthermore, showing the applicability to waste that is generally discarded without specific function is in line with the current concept of waste recovery.

Agradecimentos/Acknowledgments

Elisabete Alves Pereira wishes to acknowledge FAPESP for financial support (2019/03582-7). Lucas Felipe Lima wishes to acknowledge CNPQ (PIBIC) for the fellowship granted.

Área: ____AMB_____
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Branched-polyethyleneimine (b-PEI) modified with Biguanide Groups for Efficient Removal of Phosphate Ion from Aqueous Solution

Mateus H. Keller (PG), Douglas Kviatkowsky J. (IC), Bruno S. Souza (PQ)*.

bruno.souza@ufsc.br

Departamento de Química, Universidade Federal de Santa Catarina (UFSC), Florianópolis-SC

Phosphate, adsorption, biguanide, polymer, polyethyleneimine, fertilizer.

Highlights

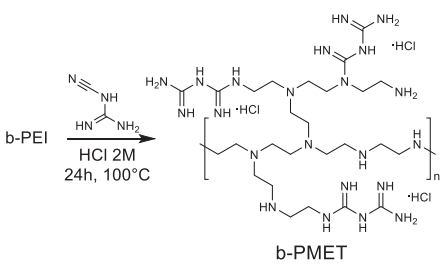
Biguanidinium groups were easily inserted in b-PEI for phosphate ion (Pi) removal from aqueous solution. The adsorption follows a Langmuir isotherm, with q_{max} of 85 mg g^{-1}. Interference by added ions and reuse were investigated.

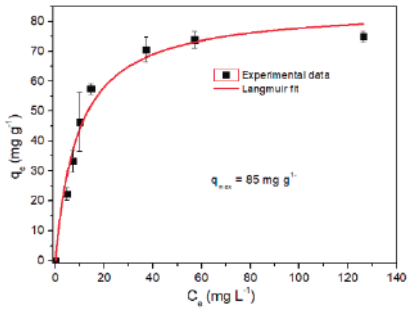
Resumo/Abstract

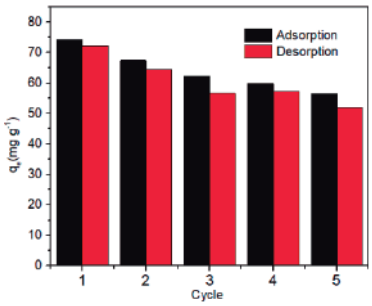
The global demand of food induced the high production of fertilizers in such a way that the biogeochemical cycles of nitrogen and phosphorus are being strongly perturbed. A substantial amount of fertilizer added to soil is not absorbed by plants, leading to eutrophication. On the other hand, the known reserves of phosphate rock may be completely depleted in about 300 years. Thus, processes capable of recovering the Pi dissolved in aqueous solutions, like phosphorous rich water bodies or wastewater, can be applied to mitigate both above-mentioned problems.

Selectivity is crucial due to the presence of other anions in aqueous systems. In biological systems, the guanidium cation plays a significant role due to its strong and selective interaction with phosphate group, serving as inspiration to the development of Pi adsorbents. However, functionalizing materials with guanidine groups is not straightforward. Conversely, insertion of biguanidine, a closely related structure, can be accomplished in a single step using 2-cyanoguanidine (DCD), a safe and affordable reactant.

Herein we studied a novel material, labeled b-PMET, for the removal of Pi from aqueous solutions. b-PMET was obtained by reacting b-PEI and excess of DCD (10 equiv) (see scheme). The material was characterized by FT-IR, TGA, ^{1}H-NMR and CHN. In batch experiments adsorption of Pi occurs in about 10 min. The adsorption follows a typical Langmuir isotherm, in agreement with a monolayer adsorption process (see middle figure). The material showed selectivity of Pi adsorption over chloride and nitrate, whereas sulfate interferes negatively in the process. The Pi adsorption was also carried out in a flow reactor. In this system, Pi was first loaded on the material and subsequently desorbed by using a highly concentrated saline solution, allowing the desorption and recovery of Pi. In total, five adsorption-desorption cycles could be performed with very little loss in activity (see right figure).







Agradecimentos/Acknowledgments

The authors are grateful to CNPq/INCT-Catalise (grant 444061/2018-5) and FAPESC (grant 2019TR0847) for financial support. BSS thanks the CNPq for research productivity fellowship.

Área: AMB

Colorimetric analyzer based on mobile phone camera for determination NO_2 in the atmosphere

Expedito de Sousa Morais (PG),[1]* Arnaldo Alves Cardoso (PQ)[2]

expedito.morais@unesp.br; arnaldo.cardoso@unesp.br

[1]*Departamento de Química analítica, IQ-UNESP;*

Palavras-Chave: *Nitrogen dioxide, Digital images, RGB, ImageJ.JS.*

Highlights

Legislation exists, but few cities in Brazil know the NO_2 concentration in their atmosphere. We propose an analysis method that can help expand Brazilian environmental data.

Resumo/Abstract

NO_2 is recognized as the most critical gas pollutant in urban atmospheres. In Brazil, CONAMA has established limit values based on the National Air Quality Control Program (PRONAR). However, few studies have been conducted on NO_2 in Brazil, potentially due to the absence of low-cost analytical methods for air quality monitoring. This study adapted the Griess Saltzman chemical method for determination of NO_2 on atmosphere, Sampling was conducted using a C-18 column, and colorimetric determination was achieved via digital image processing. The study comprised three stages: a) digitization of the image obtained in the colored solution; b) preparation of the analytical curve and determination of its limits; c) method validation by evaluating parameters such as standard deviation and confidence limits. To determine the concentration of NO_2, a calibration curve was prepared using calibration gas standards with varying concentrations, and analyses were carried out using UV-Vis spectroscopy at 550 nm. Image processing was performed using the RGB green (G) channel on a 12 megapixel cell phone camera (4000x3000 resolution) a 2x capture zoom. The outdoor NO_2 data obtained from the UV-Vis spectrophotometer was 0.50 ppb, whereas the digital images yielded a concentration of 0.49 ppb, indicating that the two methods, in terms of concentration and minimum signal, showed significant agreement. For UV-Vis spectroscopy, the minimum signal = 0.028274 and minimum concentration 0.028273 ppb, whereas for the RGB technique the values were minimum signal = 0.025763, minimum concentration = 0.025763 ppb, confirming the reliability of RGB digital images for determining NO_2 in the atmosphere.

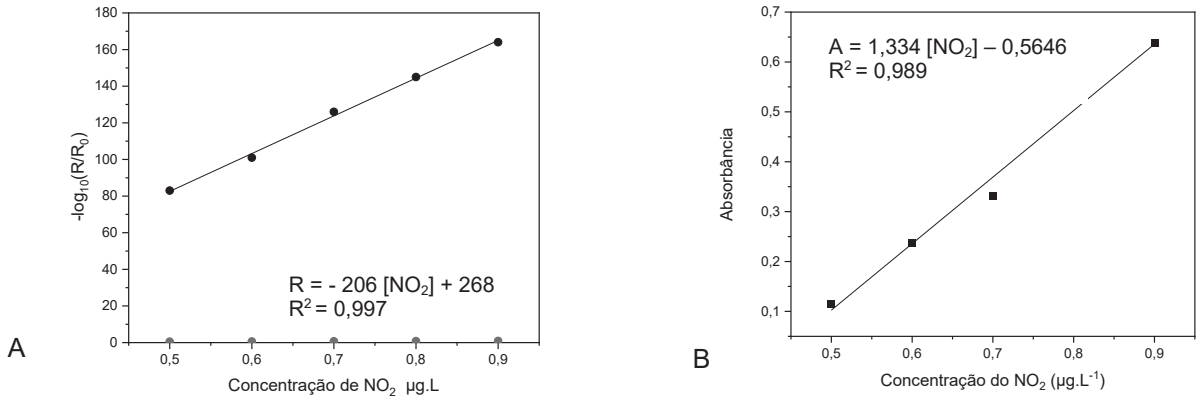


Figure 1A and B: NO_2 Calibration curve obtained by digital imaging; B) Calibration curve obtainedby UV-VIS spectroscopy.

Agradecimentos/Acknowledgments

Funding agency CAPES, project (88887.839180/2023-00).

Área: __AMB_____
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Determinação de Hidrocarbonetos Policíclicos Aromáticos (HPAs) em amostras de poeira de rua em Belém/PA e avaliação do risco de câncer: Comparação de resultados na pandemia de COVID-19 e pós pandemia

Thalita de Moura Negrão (PG)[1,2], Michelle Costa da Silva (PQ)[3], Annibal D. Pereira Netto (PQ)[1,2]

thalitanegrao26@gmail.com; michelle.silva@ifrj.edu.br; annibalnetto@id.uff.br

[1]Laboratório de Química Analítica Fundamental e Aplicada, *Departamento de Química Analítica, Instituto de Química, UFF*
[2]*Programa de Pós Graduação em Química, Instituto de Química, UFF*
[3]*Instituto Federal do Rio de Janeiro, Campus Nilópolis, IFRJ*

Palavras Chave: HPAs, CG-EM, benzo[a]pireno, COVID-19.

Highlights

Importância da emissão de HPA pelo transporte hidroviário na capital paraense

Aumento expressivo das concentrações de HPAs no período pós pandemia

Resumo/Abstract

A ocorrência de HPAs em poeira de rua decorre de diferentes tipos de fontes. A região norte do Brasil faz uso rotineiro de meio de transporte fluvial além dos transportes terrestres, que contribui como outra fonte de emissão destas substâncias ao meio ambiente. O presente trabalho tem o objetivo de avaliar as concentrações de 18 HPAs em amostras de poeira de rua coletadas em 8 pontos na cidade de Belém/PA no período da pandemia de COVID 19 (BEL1: agosto/2020) e no período pós pandemia (BEL2: janeiro/2023). Os pontos escolhidos são relativos a importantes avenidas da cidade, rodoviária da capital, terminal hidroviário, e ruas de alto trânsito, e representam diferentes cenários. O tratamento de amostras teve algumas etapas: 1) coleta e acondicionamento de amostras; 2) secagem; 3) fracionamento por tamanho em 4 frações (F1, F2, F3 e F4); 4) extração em banho de ultrassom com diclorometano, 5) reconcentração dos extratos; 6) filtração (Franco *et al.*, 2017). A determinação dos 16 HPAs prioritários da EPA, além de benzo[e]pireno e perileno, foi realizada por cromatografia a gás acoplada a espectrometria de massas (CG-EM) em condições otimizadas em coluna Agilent J&W select PAH (30 m; 0.25 mm; 0.15 µm) e a quantificação empregou padrões internos perdeuterados. As condições cromatográficas foram: temperatura inicial do forno de 60 ˚C, mantida por 1 min, aquecimento a 40 ˚C min^{-1} até 230 ˚C, mantido por 1 min, de 230 a 260 ˚C 4,5 ˚C min^{-1} mantido por 1 min e de 260 a 310˚C com 4 ˚C min^{-1} mantido por 6 min, totalizando 28 min de análise. A a interface e injetor foram mantidos a 310 e 350˚C, respectivamente. He foi usado como gás de arraste (1 mL min^{-1}) como gás de arraste e o volume de injeção foi 1 µL em modo *splitless*. Os limites de detecção e quantificação foram obtidos a partir de curva analítica obtida com soluções padrão de 0,5 a 100 ng mL^{-1}, injetados em triplicata. As frações, F3 (850 a 63 µm) e F4 (< 63 µm) apresentam resultados mais expressivos em termos de concentrações de HPAs. Os pontos A1, A7 e A8 que correspondem respectivamente à rodoviária e a 2 avenidas importantes da cidade, apresentaram praticamente o dobro das concentrações de certos HPAs no período pós-pandemia (BEL2) que no período da pandemia de COVID-19, como por exemplo benzo[a]pireno (A1: 0,904 e 2,02 ug g^{-1}; A7: 0,768 e 1,48 ug g^{-1}; A8: 5,43 e 8,12 ug g^{-1}) e perileno (A1: 0,750 e 1,53 ug g^{-1}; A7: 0,696 e 2,85 ug g^{-1}; A8: 0,738 e 3,29 ug g^{-1}). Além disso, o ponto A4 localizado em frente a um terminal hidroviário apresentou concentração mais elevadas de 14 HPAs dos 18 monitorados nas amostras do período pós pandemia. Cálculos de exposição humana e risco de câncer para a população da cidade de Belém/PA, decorrentes da exposição a HPAs estão sendo realizados (Franco *et al.*, 2017*).* O aumento de concentrações de HPAs em poeira de rua no período pós pandemia pode ser pelo menos parcialmente creditado à retomada das atividades da cidade e ao aumento de tráfego na região.

Franco *et al.* (2017). Science of the Total Environment 599–600, 305–313

Agradecimentos/Acknowledgments

CNPq, CAPES, IFRJ, UFF

Área: AMB

Determinação de hidrocarbonetos policíclicos aromáticos (HPAs) por CG-DIC em solução aquosa após processo de remoção com carvão ativado

Vitória A. P. dos Santos*(IC)[1,2], Ana C. A. da Silva (TM)[1], Camila C. Lopes (PG)[1], Natália G. Figueiredo (PQ)[1]

vitoria@int.gov.br; natalia.figueiredo@int.gov.br

[1]Laboratório de Ensaios e Desenvolvimento em Química Analítica (LADEQ), Instituto Nacional de Tecnologia (INT); [2] Instituto de Química, Universidade Federal Fluminense (UFF)

Palavras Chave: Hidrocarbonetos Policíclicos Aromáticos, Adsorção, Cromatografia a gás

Highlights

Analysis of polycyclic aromatic hydrocarbons (PAHs) by GC-FID in aqueous solution after activated carbon treatment. Analytical methods development. Analysis of PAHs by GC-FID. Evaluation of PAHs removal from water.

Resumo/Abstract

HPAs são poluentes persistentes em praticamente todas as esferas ambientais e compreendem um grupo de mais de 100 moléculas orgânicas comuns ao petróleo, carvão e xisto, sendo também produzidos através da queima incompleta de matéria orgânica[1]. O monitoramento desses compostos é fundamental devido à características prejudiciais como toxicidade aguda (HPAs de baixa massa molecular), carcinogenicidade e mutagenicidade (HPAs de alta massa molecular)[1]. Devido aos impactos que podem causar à saúde humana e ao meio ambiente, mesmo quando presentes em baixas concentrações, a *US EPA* classifica 16 HPAs como prioritários para monitoramento em matrizes aquosas. Já no Brasil, a Resolução CONAMA 357/05 inclui 7 desses 16 HPAs prioritários como parâmetros de monitoramento para águas superficiais de Classe 1: são eles benzo[a]antraceno, criseno, benzo[b]fluoranteno, benzo[k]fluoranteno, benzo[a]pireno, indeno[1,2,3-cd]pireno e dibenzo[a,h]antraceno[1]. O objetivo deste trabalho foi determinar a concentração dos HPAs em soluções aquosas antes e após contato com carvão ativado comercial. Dessa forma, pode-se avaliar a aplicação dessa metodologia em estudos que buscam minimizar os impactos da presença de HPAs no ambiente aquático através de sua remoção utilizando processos de adsorção[2,3]. As análises foram realizadas em Cromatógrafo a gás 7890A (Agilent®) com DIC, coluna HP-5 30 m x 0,320 mm x 0,25 µm, hélio 1,32 mL.min^{-1}, volume de injeção de 1,2 µL, temperatura do injetor e detector 260 e 300 °C, respectivamente. A programação de temperatura do forno foi de 40°C (1 min); 25°C/min até 160°C; 5°C/min até 270°C (11 min), totalizando 38,8 minutos de análise. Soluções individuais dos 16 HPAs prioritários, em DCM/acetona (1:1, v/v) como solvente, foram analisadas para determinação do tempo de retenção de cada um deles. Curvas de calibração (6 pontos) foram preparadas a partir de um mix contendo os 16 HPAs na faixa entre 0,10 a 38,58 µg.mL^{-1} em uma mistura DCM/Acetona (1:1,v/v) como solvente. Todas as análises foram realizadas em triplicata e obtidos coeficientes de determinação (R^2) > 0,99 e DPR < 10% (n=3). Os valores de LD e LQ calculados ficaram entre 0,16 a 5,31 µg.mL^{-1} e 0,05 a 1,75 µg.mL^{-1}. Os experimentos de adsorção foram realizados utilizando carvão ativado comercial e soluções de três diferentes HPAs. A escolha dos HPAs para os experimentos (acenafteno, pireno e criseno) foi realizada de forma que estes fossem representativos de diferentes faixas de pesos moleculares dentre os 16 HPAs prioritários. O procedimento para remoção foi iniciado com a ativação de 2 g de carvão, lavados com 3 mL de metanol e 3 mL de água ultrapura, que em seguida foram levados à estufa a 120ºC por 24 horas. Foram preparadas, em triplicata 100 mL de solução aquosa contendo 20 µg.mL^{-1} de acenafteno, 2 µg.mL^{-1} de pireno e 2 µg.mL^{-1} de criseno, além de metanol como como solvente na proporção máxima de 30% (v/v). Durante os testes realizados, os melhores resultados foram obtidos adicionando 15 mg de carvão ativado à solução contendo HPAs, sendo mantidas sob agitação a 360 rpm e temperatura ambiente por 120 minutos. Ao fim da agitação, as alíquotas foram analisadas em CG-DIC, conforme o método descrito anteriormente. Os resultados obtidos nos testes mostraram porcentagens de remoção 33% e 43% (n=3, DPR<10%), para acenafteno e pireno, respectivamente. Para o criseno, HPA de maior peso molecular analisado, foi obtido um rendimento máximo de 4% (n=3 DPR<10%), mostrando uma relação negativa entre a adsorção e o tamanho da molécula. Os resultados obtidos demonstram que o método proposto pode ser utilizado para avaliação da eficiência de processos de adsorção para remoção de HPAs em matrizes aquosas e podem embasar futuros estudos relacionados ao monitoramento de sítios contaminados e à exposição humana.

Referências: [1]De Sousa, L. C. Estudo de hidrocarbonetos policíclicos aromáticos (HPAs) em amostras de água e material particulado em suspensão no rio Aurá, Belém-PA, 2019. [2]Brito e Silva. *REEC*, v. 1, n. 3, p. 36-47, 2012. [3] Kong et al. J. *Environ. Qual.* v. 40, n.6, p.1737-1744, 2011.

Agradecimentos/Acknowledgments

Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) pela bolsa PIBIC-INT concedida

Área: AMB

Environmental diagnosis of the presence of perfluorinated compounds in the Cantareira System, São Paulo - SP

Roberta O. Servilha (PG),[1*] Ricardo S. Silva (PG),[1] Lúcia H.G Coelho (PQ),[1] Joanne Roberts (PQ).[2]

roberta.servilha@ufabc.edu.br

[1]Programa de Pós Graduação em Ciência e Tecnologia em Química, UFABC; [2]Department of Applied Science – Glasgow Caledonian University – GCU.

Palavras Chave:*(Diagnostic, PFAS, Sulfluramide).*

Highlights

EtFOSA breaks down into PFOS, a compound that is part of the polyfluoroalkyl substances (PFAS);

Combating leafcutter ants, pest of reforestation;

The use of sulfluramid can compromise the quality of the water offered to the population.

Abstract

The compound N-ethyl – perfluor – octanosulfonamide (EtFOSA), popularly known as Sulfluramide is a synthetic chemical, classified in many countries in the toxicological category IV. The main environmental concern is that it decomposes into perfluoro-octanosulfonic acid (PFOS), a compound that is part of the polyfluoroalkyl substances (PFAS) and that meets the criteria of the Stockholm Convention for persistence, bioaccumulation, adverse effects and long-distance transport. One acceptable use is the use of sulfluramide in spears to control leafcutter ants of the *genus Atta spp* and *Acromyrmex spp*. Despite abundant use, studies on Sulfluramide behavior, distribution and ecosystem impacts are incipient and restricted to some agricultural areas in the southern and southeastern regions of the country. In the reform of re-forested areas with eucalyptus are carried out several fights to the leafcutter ants, the main plagues of reforestation in Brazil. In view of this scenario, it is expected that areas with forest production may be contaminated with Sulfluramide due to its intense use. This process can be especially critical in areas of springs for public supply such as the Cantareira System region, which supplies about 7.5 million people in the São Paulo metropolitan region and has 15% of its area (~35,000 ha) occupied by eucalyptus planting. Thus, the present study aimed to show that the application of Sulfluramide in land management and use can compromise the quality of the water offered to the population as well as impact the ecosystems. Subsurface water samples from 24 basins of the Cantareira system were collected (triplicated) using stainless steel coils. The samples were characterized (pH, electrical conductivity, turbidity, organic, inorganic and total carbon and elementary analysis by ICP-OES), and the diagnosis on the presence of PFAS after solid phase extraction (SPE) was performed using Oasis WAX cartridges (Waters). The samples were then analyzed by ultra-efficient liquid chromatography (UPLC) coupled with mass spectrometry (QTof) using an electrospray ionization interface (ESI) operated in negative mode for the determination of these contaminants. The method was validated with the aquous matrices showing good linearity (R2>0.99), recoveries (60-110%, for most compounds), detection/quantification limits (on the ng L-1 scale), SPE process efficiency (43% –119%), expanded measurement uncertainty (<32%) and accuracy (<20%). It was possible to identify the presence of ten species of PFAS in surface waters, with the predominant being perfluorooctanoic acid (PFOA), PFOS and perfluorheptanoic acids (PFHpA) with detection frequency of 50%, 62%, 87%, respectively. Thus, the results of this study aim to fill an existing gap on the relationship between the intense use of this formicide and the economic, environmental and social relevance that these areas of forest plantations have in the Brazilian scene.

Acknowledgments

The authors thank the support of CAPES, FAPESP (Case No. 21/12427-5) and the (UFABC).

BERAJANO, F. et al. NO TO SULFLURAMID. REASONS FOR BANNING THIS PESTICIDE WORLDWIDE.IPEN. Available at: https://ipen.org/sites/default/files/documents/ipen-sulfuramide_portugues-factsheet-v1_10a-pt

GILLJAM, J. L. et al. Is Ongoing Sulfluramid Use in South America a Significant Source of Perfluorooctanesulfonate (PFOS)? Production Inventories, Environmental Fate, and Local Occurrence. Environmental Science and Technology, 50 (2), 653–659, 2016. Available at: https://doi.org/10.1021/acs.est.5b04544.

Área: AMB

Environmentally critical element determination in Antarctic seaweed after ultrasound-assisted extraction

Alessandra S. Henn (PG)[1], Gustavo Gohlke (PG)[1], Vitoria H. Cauduro (PG)[1], Emanuele Frozi (IC)[1], Luana F. Rocha (PG)[1], Giancarlo R. Machado (IC)[1], Marcia F. Mesko (PQ)[2], Erico M. M. Flores (PQ)[1]*

alessandrahenn@gmail.com; *ericommf@gmail.com

[1]Departamento de Química, UFSM; [2]Centro de Ciências Químicas, Farmacêuticas e de Alimentos, UFPel

Palavras Chave: *Ultrasound-assisted extraction; Seaweed analysis; Environmentally critical elements; ICP-MS; Sample preparation*

Highlights

- The extraction of environmentally critical elements from seaweed was performed by UAE
- The optimized UAE method was simple, employed diluted reagents and short times
- Potentially toxic elements were determined in seaweed from the Antarctic region

Resumo/Abstract

The presence of environmentally critical elements (such as As, Cd, Pb, Mn, Sr, and V) in the marine environment can be derived from natural sources, as well as contamination from industrial, agriculture and municipal waste. Bioaccumulation of these elements can occur in animals and aquatic plants, potentially causing environmental damage.[1] Moreover, the presence of As, Cd, Pb and V in the marine environment may cause the contamination of other food sources (such as seafood).[2] Thus, in order to monitor these elements in marine environment, seaweed can be used as bioindicator.[3] In this study, ultrasound (US) was evaluated for As, Cd, Pb, Mn, Sr and V extraction from seaweed from the Antarctic region. The following parameters of ultrasound-assisted extraction (UAE) using an US bath were evaluated: frequency (25 to 130 kHz), amplitude (30 to 100%), temperature (30 to 80 °C), sample mass (50 to 200 mg), extractant concentration (1 to 3 mol L^{-1} of HNO_3) and extraction time (5 to 30 min). The optimized UAE conditions were 200 mg of sample, 10 mL of 2 mol L^{-1} HNO_3 and 30 min of sonication in a 25 kHz US bath at 70% of amplitude and 70 °C. Analytes were quantified using inductively coupled plasma mass spectrometry (ICP-MS) and results were compared with values obtained using “silent” conditions (magnetic or mechanical stirring at 500 rpm, and without stirring), and a reference method based on microwave-assisted wet digestion (MAWD). The UAE method demonstrated the best extraction efficiency (higher than 95%) for all analytes, especially for As, Cd and V, with lower standard deviations (up to 5%) and lower blank values in comparison with the silent conditions. The proposed UAE method was more advantageous than the reference method, being faster, simpler, safer, more environmentally friendly, and with higher detectability (lower limits of quantification, from 0.0033 to 1.34 µg g^{-1}). In addition, negligible blank values were obtained for UAE and no interference was observed in the determination step. Furthermore, the optimized UAE method was applied for Antarctic seaweed samples and analyte concentrations varied greatly among different seaweed species (15.8 to 55.4 µg g^{-1} of As; 0.5 to 11.2 µg g^{-1} of Cd; <0.13 to 0.4 µg g^{-1} of Pb; 2.25 to 44.5 µg g^{-1} of Mn; 0.5 to 1.46 µg g^{-1} of V; 9.58 to 1192 µg g^{-1} of Sr). The combination of UAE and ICP-MS was demonstrated to be a suitable approach for the determination of environmentally critical elements in seaweed.

1. Souza *et al*., Revista Brasileira de Farmacognosia, 22 (2012) 825-837.
2. Topcuoğlu *et al*., Chemosphere, 52 (2003) 1683-1688.
3. Farías *et al*., Spectrochimica Acta Part B 57 (2002) 2133-2140.

Agradecimentos/Acknowledgments

The authors are grateful to CAPES, CNPq and FAPERGS for the financial support.

Área: AMB

Evaluate the occurrence of fires in the municipalities of Vale do Pindaré - MA

Angela M. C. M Santos (FM),[1*] Flávio E. Silva (IC),[1] Paulo H. A. Martins (IC),[1] Eva D. F. Carneiro (PQ),[1] Ronilson L. Brito (PG).[2]

angela.mouzinho@ifma.edu.br; flavio.e@acad.ifmaeu.br; amorimm@acad.ifma.edu.br; eva.carneiro@ifma.edu.br; ronilson.brito@ifma.edu.br

[1]Departamento de Ensino, IFMA-Campus Santa Inês; [2]Departamento de Química, IFMA-Campus Monte Castelo

Palavras Chave:*Queimadas, Análise, Vale do Pindaré.*

Highlights

The number of fires in the state of Maranhão has increased considerably in recent years. The aim of the study was therefore to map the occurrence of fires, particularly in the municipalities of the Pindaré Valley, and to examine the possible causes of fires in this region.

Resumo/Abstract

Maranhão is the third most fire-prone state in Brazil, according to the National Institute for Space Research. More than 3,500 outbreaks have already been recorded in 2022. The number of fires in the state increased by more than 10% in July 2022 compared to the same period in 2021 (INPE, 2022). And the Vale do Pindaré micro-region is one of the 32 administrative regions of the State of Maranhão, the largest in terms of municipalities, with a total of 22 (IBGE, 2021). The aim of this study is to map the occurrence of fires in the municipalities of the Pindaré Valley, which are part of the Legal Amazon. A survey of the databases of the National Institute of Meteorology (INMET), the Brazilian Institute of Geography and Statistics (IBGE) and the National Institute of Space Research (INPE) was carried out to map the occurrence of fires in this region over a five-year period. Based on a survey of INPE's BDQueimadas and IBGE's database and information, it was found that among the municipalities in the Pindaré Valley that are part of the Legal Amazon, Santa Luzia, Buriticupu and Bom Jardim had the highest number of fire outbreaks. This is due to the phytoecological characteristics that predominate in these ombrophilous dense forest regions. This type of dense, closed forest has a milder microclimate and a higher and more stable fuel content than a sparse, open forest (MENDONÇA FILHO, 2008). It is a complex biome that is extremely threatened by the pressure to convert its areas for logging, agriculture and real estate activities. When fires break out in these forests, certain conditions prevent them from being detected, such as when the fire is only on the ground, because in this type of dense vegetation it can occur without affecting the tops of the trees. The municipalities of Tufilândia and Pindaré Mirim, on the other hand, had fewer outbreaks, with a predominantly open ombrophilous forest area. It was observed that the existing vegetation cover in these municipalities is mostly used for livestock (pasture) and has secondary vegetation on most of its territory. According to data from the INMET database, a study was carried out of the maps of average monthly temperature anomalies in Brazil, and it was found that the months of June to October have a significantly higher average temperature than the other seven months of the year, and this pattern was repeated over the five years analysed. During these months, Maranhão is in summer, the hottest period of the year, with little rain and strong winds, which contribute to the transformation of fire outbreaks into wildfires. It was also observed that because of the dry grass and the amount of wind that occurs during this period, the flames can reach up to four meters high and advance rapidly, bringing destruction to the fauna, flora and inhabitants of these places who suffer from the smoke that enters their homes, causing respiratory problems. In addition, in Maranhão it is still quite common to use burning to prepare land for small plantations, which contributes to the increase in particulate matter released into the atmosphere. The effects of this particulate matter emitted by burning on human health mainly affect the elderly and children. Therefore, the variables of average temperature and phyto-ecological regions can significantly influence the increase of fire outbreaks in the same period. Regions with a predominance of dense ombrophilous forest tend to have higher fire outbreaks. For this reason, implementing environmental control actions on fire outbreaks is a way of contributing to the sustainable development and ecological balance of this region.

Agradecimentos/Acknowledgments

To FAPEMA for the grant, to IFMA, to INPE for providing the images.

Área: AMB

Evaluating solid-phase extraction of drugs of abuse and metabolites in wastewater via full factorial design

Antonio Pedro Guimarães (PG), Nickolas V. da Silva (PG), Fábio M. S. Nascimento (PG), Rafael F. Silva (PG), Hadassa S. R. P. Moura (PQ), Luiz T. Gomes (PQ), Jez W. B. Braga (PQ), Fernando F. Sodré (PQ)*

ffsodre@unb.br

Universidade de Brasília, Instituto de Química, Grupo AQQUA, Brasília, DF, 70910-900, Brasil

Palavras Chave: *Wastewater-based epidemiology, Illicit drugs, Factorial design, Solid-phase extraction, LC-MS/MS.*

Highlights

Wastewater analysis estimates drug use effectively. Factors like pH and solvent-type impact recovery rates during solid-phase extraction. Future research aims to refine methodology for better accuracy.

Resumo/Abstract

Wastewater-based epidemiology (WBE) has proven to be an effective tool for estimating the consumption of drugs of abuse for a given population. Drugs such as cocaine, amphetamine-like substances, cannabinoids, opioids, new psychoactive substances, antibiotics and adulterants are frequently investigated during wastewater surveillance. The complexity of the matrix demands a careful analytical sequence, which includes composite sampling, transport, preservation, pH adjustment, analyte extraction and analysis, usually employing liquid chromatography coupled to in tandem mass spectrometry (LC-MS/MS). This study aimed to evaluate recovery rates during solid-phase extraction of different substances, including cocaine and its metabolites (benzoylecgonine, anhydroecgonine, anhydroecgonine methyl ester), amphetamine-type stimulants (amphetamine, methamphetamine, MDA, and MDMA), antibiotics (trimethoprim and sulfamethoxazole), and the cocaine adulterant levamisole in wastewater. To achieve this goal, a full factorial design with two levels and three factors (2^3) was explored. After extraction, analysis was performed using a matrix-matched calibration approach with LC-MS/MS and multiple reaction monitoring, in order to achieve high selectivity in identification and quantification. The factors used in the design and their codifications were: pH (F1, pH 2 (-1) and pH 6 (+1)); the order of wastewater filtration (F2, prior pH adjustment (+1) and after pH adjustment (-1)); and sampling co-solvency with methanol (F3, addition of 10 mL MeOH to 100 mL of wastewater (+1) and without methanol addition (-1)). The response variables of the design were obtained in two steps. Analytes were added before solid-phase extraction (SPE), and the recoveries were then assessed (%R1). Additionally, to evaluate possible matrix effects, the same analytes were added after SPE, and recovery results were obtained (%R2). The design responses of the overall process were calculated as weighted averages of the ratio %R1/%R2 for each analyte [1]. Overall recovery varied between 61% and 108%, with combined uncertainty below 15%. Cocainics present better overall recoveries, followed by amphetamine-type substances. All main effects and their interactions were deemed significant: F1 +11.6%, F2 +4.5%, F3 -2.7%. Results indicate that, on average, there was an 11.6% increase in overall recovery when transitioning from pH 2 to pH 6; choosing pH adjustment before filtration contributed to a 4.5% recovery increase; and, finally, it is preferable not add methanol as a co-solvent in the process. It is possible that, since methanol is a polar solvent, it favors the solubilization of polar interferents present in wastewater that may suppress the signal of the analytes. As a future perspective, we intend to investigate a narrower pH range, with higher values than those used in the present study.

[1] Matuszewski BK et al. Anal Chem 75(13), 3019-3030, 2003. doi:10.1021/ac020361s

Agradecimentos/Acknowledgments

This work was supported by INCTAA and the Ministry of Justice and Public Security (TED 04/2020)

Área: AMB

Evaluation of the anthropogenic contaminants in Imboassica lagoon with the analysis of geochemical biomarkers with the application of GC×GC-TOFMS.

Manoel Mendes Alves Junior (IC), Vitor Hugo Santos Goes (IC), Vinicius Barreto Pereira (PG), Alexander Andrey Lopes (PG), Ananda da Silva Antonio (PQ), Raquel Vieira Santana da Silva (PQ), Débora de Almeida Azevedo (PQ) *.

manoelmaj@gradu.iq.ufrj.br; debora@iq.ufrj.br

Universidade Federal do Rio de Janeiro, Instituto de Química, Ilha do Fundão, Rio de Janeiro, RJ 21941-598, Brazil

Keywords: *GC×GC-TOFMS, mass spectrometry, environmental chemistry, geochemical biomarkers.*

Highlights

The lagoon faces challenges from unplanned urban settlements lacking essential infrastructure and proper planning. The absence of sewage treatment systems in these urban areas contributes to water pollution, impacting the lagoon's ecosystem.

Abstract

The Imboassica Lagoon is located in the city of Macaé in the state of Rio de Janeiro, Brazil, and has an area of 5 km^2. Currently, the lagoon has areas impacted by urban settlements developed without planning or infrastructure such as sewage treatment systems and part of the lagoon basin is used for industrial activities, reflecting changes in the local ecosystem[1]. Due to its high sensitivity and resolution, the application of two-dimensional gas chromatography coupled with time-of-flight mass spectrometry (GC×GC-TOFMS) analysis is widely used to evaluate differences in the chemical composition of geochemical works[2].Thus, this work aimed to evaluate the extent of the anthropogenic contribution to this ecosystem to assess the presence of geochemical biomarkers such as steroids, aromatic compounds, and aliphatic hydrocarbons, evaluating an anthropogenic action in this surface sediments. A set of four sediment samples were collected from different locations in the Imboassica lagoon such as close to the freshwater inlet and closer to companies, in the middle of the lagoon, close to the sewer outlet, and close to the sea exit. The sediment was lyophilized, weighted, and extracted using ultrasonic agitation with 3 × 50 mL of dichloromethane/methanol solution (9:1) in an ultrasonic bath for 30 min. The extract was concentrated by rotoevaporation. These were fractionated into aliphatic hydrocarbons, aromatic hydrocarbons, and polar compounds using activated silica liquid chromatography[3]. The analyses were performed on a GC×GC–TOFMS system (Pegasus 4D, Leco, St. Joseph, MI, USA). The GC column set consisted of a RTX-5 column (10.0 m × 0.18 mm i.d., 0.20 µm df) as the first dimension (^{1}D) and a DB-17 (1.0 m × 0.25 mm d.i., 0.15 µm df) as the second-dimension column (^{2}D). The analyses in the method fast GC×GC–TOFMS had a time of performance of 22 minutes. The four sediments showed signs of anthropogenic contamination at different levels. The GC×GC–TOFMS sediment analyses allow the separation and identification of major components of the sample collected close to the sewer outlet presenting the highest concentrations, such as *n*-alkanes (*n*-C_{16} to *n*-C_{38}). The αβ and ββ-hopane C_{30} ratio varied between 0.5 and 1.5 for the samples showing the different levels of contamination by petroleum products in the lagoon, and the evaluation of hopanoids showed the prevalence of αβ-hopane stereoisomers, by αβ/(ββ) ratio, commonly associates petroleum input. Thus sterols with configuration ααα and αββ with 27, 28, and 29 carbon atoms were identified. In addition, polycyclic aromatic hydrocarbons (PAHs) were identified, such as phenanthrene, fluoranthene, pyrene, chrysene, benzopirenes, and dibenzopyrenes, probably related to petroleum deriveted compounds. The ratio coprostanol / cholestanol, which indicates the presence of raw sewage discharge, varied between 0.2 and 2.5, with maximum value in the sample collected close to the sewer outlet. The evaluation of these results shows that the sample collected close to the sewer outlet was probably the most anthropogenic contribution, indicating that the Imboassica lagoon is not homogeneous, as contamination is accentuated in regions with greater urban density.

[1] Santos *et al.*, *Acta Limnologica Brasiliensia* v. 25, n. 3, p. 352-360, 2013.
[2] Skoog et al., *Fundamentos de química analítica. 8. ed. São Paulo: Thomson, 2006. cap. 31, p. 899-923.*
[3]Lopes et al., *Organic Geochemistry* (159) 104287, 2021.

Acknowledgments

The authors thank CAPES, FAPERJ, and CNPq (Brazilian research councils) for fellowships and financial support.

Área: AMB

Exploring the Catalytic Potential of UOW-6/Pt Metal-Organic Framework in $NaBH_4$ Hydrogen Evolution

Renata Pereira Lopes Moreira (PQ),[1] Gessica do Carmo Dias (PG),[1*] Noemí Cristina S. de Souza (PG)[1], Geraldo Magela de Lima (PQ)[2], Satarupa Das (PG)[3], Richard I. Walton (PQ)[3]

renata.plopes@ufv.br; gessica.dias@ufv.br

[1]Department of Chemistry, (UFV); [2]Department of Chemistry, (UFMG); [3]Department of Chemistry, University of Warwick.

Keywords:*(Hydrogen storage, Hydrides, Catalyst; Heterogeneous Catalysis)*

Highlights

The MOF UOW-6/Pt demonstrates remarkable efficacy as a catalyst for $NaBH_4$ hydrolysis, ensuring a hydrogen generation rate of 31,217.32 mL min^{-1} g^{-1} at 299.65 K.

Abstract

Hydrogen emerges as a promising clean and renewable fuel option. However, storage and transportation present significant challenges for widespread use [1]. $NaBH_4$ has been highlighted as a solid-state hydrogen storage agent due to its high storage density, approximately 10.8% m/m, and chemical stability [1]. Nevertheless, dehydrogenation occurs slowly, necessitating interventions. Metal-organic frameworks (MOFs) have been extensively explored, offering a highly accessible catalytic surface [2]. This study evaluates a MOF as a support for platinum (Pt) nanoparticles to catalyze hydrogen evolution from $NaBH_4$. The MOF UOW-6 is constructed from Ni^{2+} and 1,5-furan-dicarboxylate, produced from renewable biomass.

Pt nanoparticles (Pt NPs) were immobilized onto MOF UOW-6 via chemical reduction, employing $NaBH_4$. The experiments were conducted using aqueous solutions of $NaBH_4$ with varying Pt NPs loadings. The results are shown in Figure 1. It is evident that the utilization of MOF without Pt NPs, yielded promising results. However, the introduction of Pt NPs significantly enhanced performance, both in terms of yield and reaction kinetics. It is noteworthy that the MOF contains nickel, and it is possible that during the deposition of Pt NPs, reduction of nickel occurred. To verify this, a control experiment was conducted using MOF without Pt NPs but pretreated with $NaBH_4$. While the reduced MOF exhibited good performance, it was notably lower than original MOF. The hydrogen evolution rate (HGR) was determined, as showed in Table 1. Notably, the composition of 20 mg of MOF UOW-6, with 0.1000 mmol of Pt, exhibited the most favorable performance, achieving a promising HGR of 31,2117.32 mL min^{-1} g^{-1}.

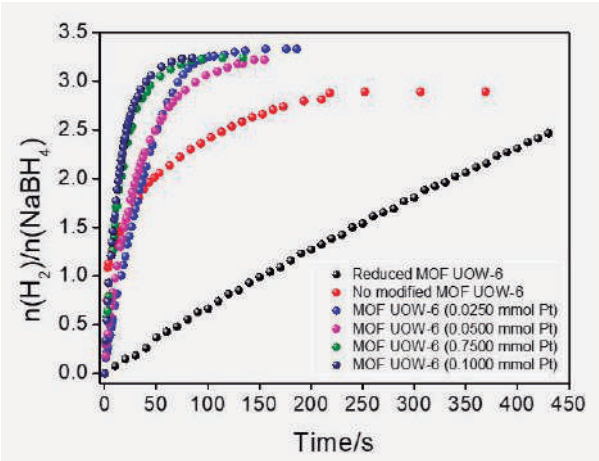


Fig. 1. H_2 evolution from $NaBH_4$ using MOF(UOW-6). Conditions: 1.0 mL de $NaBH_4$ (0.50 mmol L^{-1}); 25 mg of MOF(UOW-6); T= 299.65 K.

Table 1. Hydrogen generation rate (HGR)

MOF (mg)	Pt NPs (mmol)	HGR (mL $min^{-1}g^{-1}$)
25	0.1000	5,184.43
20	**0.1000**	**31,217.32**
15	0.1000	18,453.59

The findings suggest that the new material yielded highly promising results in hydrogen evolution.

References

[1] Q. Yao, X. Zhang, Z.-H. Lu, and Q. Xu, Coord Chem Rev, vol. 493, p. 215302, Oct. 2023.
[2] L. Zhang et al. Small, vol. 17, no. 52, Dec. 2021.

Acknowledgments

The authors acknowledge the support from Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brazil (CAPES); Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) [grant number 312400/2021-7 and 405828/2022-5]; and Fundação de Amparo à Pesquisa do Estado de Minas Gerais (FAPEMIG) [FAPEMIG RED-00144-22 and FAPEMIG APQ-01275-18].

Área: AMB

Identification of residue from electric fryer and airfrying pan using peroxide index and infrared spectroscopy

Mauro Cesar Dias (PQ),[1] Sara Oliveira de Souza (IC),[1] Maria Eduarda da Silva Alexandre (IC),[1] Victor Davi Ferreira (IC),[1] Ícaro Marques Vasconcelos (IC),[1] Samira Gomes Brandão (TM),[2] Fabiana Kauark (PQ).[1]

maurocesar@ifes.edu.br; maurocesar@ifes.edu.br

[1]Coordenação de Licenciatura em Química, IFES-Vila Velha; [2]Coordenação de Metalurgia de Química IFES-Vitória

Palavras Chave: Frying, Airfrying, Aldehyde compounds, Peroxide index, Infrared spectroscopy.

Highlights

The use of an airfryer in chicken preparation indicated changes in the fat, as evidenced by the pronounced violet coloration in the Kreis test, a high peroxide value (72.3 ± 5.7 meq kg^{-1}), and bands in the IR spectrum (1746 cm^{-1} and 1727 cm^{-1}).

Resumo/Abstract

The per capita consumption of virgin soybean oil (VSO) in Brazil was 46 L-VSO/capita in 2023. It is possible to project the formation of 10.8 million L frying oil residue (FOR) for Vila Velha-ES city. However, the use of oil is being replaced by the use of air fryers, oil-free fryers, and other variables may occur due to the degradation of fats in foods. This study aims to evaluate the oxidation degree of oil and fat was evaluated by preparing chicken in an electric fryer and air fryer using the Kreis test, peroxide index (Ip / meq kg^{-1}), and infrared spectroscopy (IV) region. The Ip values of the fryer chicken fat (GF-F) and airfryer chicken fat (GF-airfryer) samples were compared with the reference sample of crude chicken fat (GF-cru), with an increase of 2.3 and 43 times, respectively (Table 1). The oxidation process can be observed in the spectrum IR of the GF-airfryer sample in which there is an increase in the intensity of the band at 1746 cm^{-1} and the appearance of a shoulder at 1727 cm^{-1} (Figure 1-B), indicating the formation of product secondary with an aldehyde functional group (LIANG et al., 2013), which corroborates the interpretation of the Kreis test and the high peroxide index (WANG et al., 2019).

Table 1 – Peroxide index of analyzed samples from VSO, FOR-IVV1, FOR, GF-cru, GF-F e GF- airfryer

Samples	Ip / meq kg^{-1}
VSO	0,44 ± 0,19
FOR-IVV1	29,5 ± 0,40
FOR	3,53 ± 0,37
GF-cru	1,66 ± 0,33
GF-F	3,81 ± 0,80
GF-airfryer	72,3 ± 5,74
VR	10

Reference Value for virgin soybean oil (VR).

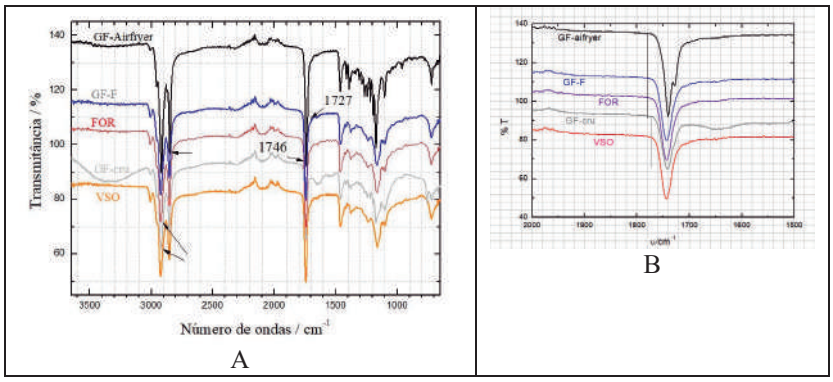


Figure 1 - Espectros comparativos na região do IV das amostras VSO, GF-cru, FOR, GF-F, GF-Airfryer.

LIANG, P. et al. Application of Fourier Transform Infrared Spectroscopy for the Oxidation and Peroxide Value Evaluation in Virgin Walnut Oil. Journal of Spectroscopy, v. 2013, p. 1-5, 2013. http://dx.doi.org/10.1155/2013/138728

WANG, Y. et al. Comparison of Furans Formation and Volatile Aldehydes Profiles of Four Different Vegetable Oils During Thermal Oxidation Journal of Food Science: Toxicology & Chemical Food Safety, v. 84, p. 1966-1978, 2019. https://doi.org/10.1111/1750-3841.14659

Agradecimentos/Acknowledgments

CNPq, FAPES, Instituto Verde Vida (IVV)

Área: AMB
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Immobilization of laccase on green coconut husk biochar for the simultaneous adsorption and degradation of 2,4-dichlorophenol in water

Larissa S. de O. Mota (PG),[1,2] Alyne A. G. Leal (IC),[2] Bruno S. Peixoto (PQ),[1,2] and Marcela C. de Moraes (PQ).[1,2*]

larissa_mota@id.uff.br; * mcmoraes@id.uff.br

[1]*Programa de Pós-Graduação em Química, UFF;* [2]*BioCrom, Departamento de Química Orgânica, UFF.*

Keywords: *Biochar, Laccase, Adsorption, Degradation, Water treatment*

Highlights

The immobilized laccase is more stable than the free laccase and can be reused for 10 cycles.
The biochar with laccase is more efficient in removing 2,4-dichlorophenol compared to biochar alone.

Abstract

Water quality has been increasingly affected by the presence of emerging contaminants. The use of laccase enzymes (LAC) for contaminant degradation is a highly efficient and environmentally friendly technology, as they only require oxygen to catalyze oxidation reactions, producing water as a byproduct. Immobilizing LAC on a solid support enhances its stability under adverse conditions and allows for reuse. Biochar stands out as a support due to its low cost and environmentally friendly synthesis. Additionally, its use enables the creation of dual-functional materials capable of adsorbing and degrading contaminants simultaneously, enhancing process efficiency. Therefore, this study aims to immobilize LAC on biochar from green coconut husk for adsorption and degradation of 2,4-dichlorophenol (2,4-DCP).

Biochar (ACP) was obtained through the pyrolysis of green coconut husks impregnated with H_3PO_4 (at a 1:3 mass ratio) at 500 °C. For LAC immobilization, ACP was stirred with an enzyme solution in citrate-phosphate buffer (100 mM) in a thermostatic bath at 180 rpm, and the efficiency of the process was assessed by centrifuging the suspensions and measuring LAC activity in the supernatant before and after the immobilization using 2,2-azino-bis (3-ethylbenzothiazoline-6-sulfonic acid) (ABTS) as substrate. The best immobilization conditions were 1 hour of agitation, pH 4, 45 °C, and 500 ppm of LAC, resulting in an immobilization efficiency of 81%. ACP-LAC FTIR revealed bands at 3288 cm^{-1} and 1005 cm^{-1} not present in the ACP FTIR, indicating the success of the immobilization process. TGA of ACP-LAC exhibited an 11% mass loss at 230 °C, linked to protein degradation. N_2 adsorption showed that the reduction in surface area (1213 to 841 $m^2.g^{-1}$), due to enzyme occupation of biochar pores, did not render ACP-LAC unsuitable as a concurrent adsorbent in water contaminant removal. Zeta potential values became less negative after laccase insertion into the biochar, suggesting interaction between the surface oxygenated functional groups of ACP (quantified by Boehm titration) and LAC during immobilization, possibly through hydrogen bonding. The free and immobilized LAC were characterized for stability against variations in pH and temperature, as well as storage stability at room temperature and refrigeration. The results evidenced that the immobilization process extended LAC stability range to pH and temperature variations, especially in more acidic pH levels and higher temperatures. Storage stability testing revealed that after 2 months, the immobilized LAC at room temperature maintained 84%, while under refrigeration increased to 144% of the original activity, respectively. In contrast, free LAC completely lost stability at room temperature and retained 78% activity under refrigeration. The reusability of the immobilized enzyme was evaluated through successive cycles of activity reactions, and demonstrated that the enzyme can be reused for up to 10 cycles before reaching 43% of its initial activity. For application purposes, ACP and ACP-LAC were compared for the removal of a 500 ppm solution of 2,4-DCP (citrate-phosphate buffer, 100 mM, pH 4) evaluating the influence of agitation mode and medium aeration on the catalytic efficiency of the immobilized enzyme. In these experiments, magnetic stirring with an open flask showed enhanced removal efficiency by ACP-LAC, improving oxygen supply for the enzyme to catalyze the oxidation of the contaminant. After 24 hours of stirring, the removal efficiency for ACP and ACP-LAC was 52% and 98%, respectively. The introduction of air pumping into the medium further enhanced catalysis by ACP-LAC. 2,4-DCP removal after 3 h was 40%, but with additional air supply increased to 80%. Therefore, it is concluded that LAC was efficiently immobilized in ACP, increasing its stability and allowing its reuse. Furthermore, the developed material proved to be more efficient in removing 2,4-DCP compared to the biochar alone, becoming even more efficient with greater aeration of the medium.

[1] Pandey D, Daverey A, Arunachalam K. Journal of Cleaner Production. 2020;255:120267.

Acknowlegments

CAPES, CNPQ, FAPERJ, and LAMATE-UFF

Área: AMB

Incorporação de resíduos vítreos às tecnologias socioambientais.

Wladmir Teodoro da Silva (PG),[1*] Patterson P. Souza (PQ),[3] Patrícia S.O. Patrício (PQ),[3] Thaís F. Ramos (IC),[3] Kauã G.M.B. Martins (IC),[3] Janaína P. Silva (PG),[1] Bernardo R.B. Ladeira (TC),[1] Fernando S. Lameira (PQ),[2] Rochel M. Lago (PQ),[1] Rita C. O. Sebastião (PQ),[1*]

wladmirt@ufmg.br; ritacos@ufmg.br;

[1]Departamento de Química, UFMG; [2]CDTN, [3]CEFET-MG

Palavras-Chave: *Resíduo Vítreo, Vidro, Sustentabilidade, Desenvolvimento Socioambiental, Desenvolvimento Tecnológico*

Highlights

Socio-environmental technologies associated with vitreous residues incorporation

Technologies associated with vitreous waste

Development of products and services associated with vitreous waste processing

Resumo/Abstract

O Brasil gera cerca de 3 milhões de toneladas/ano de resíduo de vidro que não retornam ao ciclo produtivo, sendo descartados em aterros sanitários e/ou controlados e lixões. Este quantitativo representa uma perda da ordem de R$ 840 milhões/ano em matéria prima não reprocessada, além dos custos relativos a ações de mitigação socioambiental. Artigos publicados entre 2002 e 2020, com mais de 100 citações nas bases de dados Web of Science e Scopus, foram analisados com o intuito de compreender quais são as principais tecnologias que incorporam resíduo (RV) vítreo como aditivo ou agregado, para utilização além da indústria de transformação do vidro. Dentre os 35 artigos principais foi observada a incorporação de resíduos de vidro principalmente à concreto, cimento e materiais poliméricos de alta compressão. Algumas dessas tecnologias já são consolidadas em processos de P&D, porém, outras são emergentes e carecem de maior investimento em pesquisas e negócios. Esse trabalho apresenta a incorporação de RV ao desenvolvimento de tecnologias socioambientais, como uma alternativa sustentável para a redução dos impactos gerados pelo não reprocessamento desses resíduos e pela extração não controlada de matérias primas como SiO_2 e CaO. A tecnologia proposta pode ser associada a startups brasileiras, que desenvolvem produtos/serviços que conectam o resíduo vítreo a negócios de impacto socioambiental. Foram identificadas 16 startups com ações que contemplam Tecnologia *Blockchain*, logística reversa e economia circular. Neste trabalho, optou-se pelo desenvolvimento de tecnologias socioambientais emergentes, que incorporam o resíduo vítreo como matéria prima e são associadas ao desenvolvimento de novos produtos e negócios que estimulam a redução de impactos socioambientais nas comunidades vinculadas ao manejo desse resíduo. Estão em desenvolvimento duas tecnologias; tijolo ecológico de base solo-cimento-vidro, com cura a temperatura ambiente e compósito polimérico à base de resina de poliéster e resíduo vítreo. Em ambos os compostos foram aplicadas técnicas de caracterização como testes de resistência mecânica, microscopia eletrônica de varredura (MEV), medidas de ângulo de contato, análise termogravimétrica (TG) e fluorescência de Raio X. Os resultados iniciais apresentam melhora significativa de resistência mecânica à compressão e isolamento termoelétrico. Ambas as tecnologias passam por estudo de viabilidade técnica e econômica e se caracterizam como tecnologias sociais a serem desenvolvidas em parceria com estudantes da Educação Básica e comunidade de catadores/associações de reciclagem, em interface com o Programa de Extensão 1000 Futuros Cientistas (UFMG), INCT Midas, Unidade de Escalonamento (Escalab), Laboratório InTechLab (CEFET-MG) e CDTN. Referências: SILVA, W.T.; FILGUEIRAS, C. A. O vidro e sua importância na vida e na química. Química Nova, v. 46, p. 491-501, 2023.

Agradecimentos/Acknowledgments

The authors would like to thank INCT Midas, CEFET-MG, CDTN, CNPq, FAPEMIG and UFMG/PRPq/Proex for financial support.

Área: AMB

Insights from Wastewater Surveillance for Drugs and Metabolites in the Brazilian Federal District by means of the Cloacina Project

Fernando F. Sodré (PQ)*, Hadassa S. R. P. Moura (PQ), Luiz Eduardo T. Gomes (PQ), Cristiane A. M. Caldenhof (TC), Antonio Pedro N. Guimarães (PG), Fábio M. S. Nascimento (PG), Pedro Judah M. Messias (PG), Rafael F. da Silva (PG).

ffsodre@unb.br

Universidade de Brasília, Instituto de Química, Grupo AQQUA, Brasília, DF, 70910-900, Brasil

Palavras Chave: *Wastewater-based epidemiology, Illicit drugs, Cocaine, Amphetamine-type substances, LC-MS/MS.*

Highlights

The project extends wastewater-based epidemiology for drugs in Brazil. Analysis using SPE and LC-MS/MS. Cocaine, amphetamine, and MDMA peaks in weekends. Significant drug use in Brasília's Pilot Plan.

Resumo/Abstract

Estimates of drug use have been accessed through wastewater analysis. In Brazil, the CLOACINA Project extends wastewater-based epidemiology (WBE) to complement drug use data, aiding policy improvements. This study presents recent findings of the CLOACINA Project for the Federal District (DF), which has been extensively studied through WBE since 2010. Composite samples (24 h) from eight wastewater treatment plants (WWTPs) were collected over seven consecutive days in early August 2023. Samples underwent solid-phase extraction (Strata-X, Phenomenex, pH 2) and analysis by liquid chromatography (Agilent 1290 Infinity II) coupled with a triple quadrupole mass spectrometer (Agilent 6470B) using an electrospray ionization source. Separation utilized a Zorbax SB-C18 column (30x2.1mm,3.5µm, Agilent), with quantification via matrix-matched calibration with surrogate deuterated internal standards. Population normalized mass loads (PNML) of three cocaine metabolites were notably higher in areas served by Brasília North (BN) and Riacho Fundo (RF) WWTPs. In such areas, benzoylecgonine, the predominant and more stable cocaine metabolite, showed average loads of 952 and 758 mg/1000inhab/day, respectively, while in areas served by other WWTPs values were around 600 mg/1000inhab/day. For anhydroecgonine methyl ester, PNML in the areas served by BN- and RF-WWTP were 215±21 and 233±13 mg/1000inhab/day, respectively, whereas for cocaethylene, PNML were 9.6±0.4 and 11.1±0.4 mg/1000inhab/day, respectively. Ethyl sulfate, a biomarker of alcohol consumption, was higher in both WWTPs serving Brasília's Pilot Plan (BN WWTP [74±6 mg/1000inhab/day] and Brasilia South – BS WWTP [76±6 mg/1000inhab/day]), regions with high Municipal Human Development Index (IDHM). Weekly cocaine consumption peaked on weekends for all regions except for Planaltina WWTP, indicating a more stable cocaine consumption. Average amphetamine loads were also higher in Brasília's Pilot Plan (49±2 mg/1000inhab/day for BN WWTP and 26±2 mg/1000inhab/day for BS WWTP). The region served by BN WWTP, with the largest young population, also showed elevated MDMA loads (9,0±0,7 mg/1000inhab/day), an indicative of recreational use of ecstasy. Peaks in ecstasy consumption between Sunday and Monday were observed, especially in areas served by BN and BS WWTPs. Despite concerns, amphetamine and MDMA loads were lower than those in many European cities [1]. Cocaine consumption, however, as estimated using benzoylecgonine, was higher than in the majority of European cities, except for Antwerp and Amsterdam [1].

[1] EMCDDA, 2023. Wastewater analysis and drugs: a European multi-city study. Lisbon. https://www.emcdda.europa.eu/publications/pods/waste-water-analysis_en

Agradecimentos/Acknowledgments

This work was supported by the Ministry of Justice and Public Security (TED 04/2020)

Lithium extraction from spodumene for CO_2 capture

Maria Clara Sewaybricker Leite (IC) [1], **Ana Paula de Carvalho Teixeira (PQ)**[1]

mariasewaybricker@ufmg.br

[1]*Departamento de Química, UFMG*

Keywords: CO_2 capture, Lithium extraction, Spodumene, Hydrothermal alkaline extraction

Highlights

The project assesses CO_2 capture and Li_2CO_3 synthesis potentials through the optimization of two alkaline hydrothermal routes for lithium extraction – NaOH and $Mg(OH)_2$ – from spodumene, $Li_2OAl_2.4SiO_2$.

Resumo/Abstract

According to NASA's close monitoring of CO_2's concentration levels in the atmosphere, the amount of carbon dioxide has increased 13% in the last 20 years. With this, CO_2 capture, storage and usage has become a relevant field of research, which can also be applied in the search for alternative energy sources. Amongst the different alternatives found, electric car batteries demand a high amount of lithium carbonate, rapidly increasing its commercial value. The project meets demands of a new sustainable world, by searching for lithium extraction routes to synthesize materials capable of capturing carbon dioxide and producing lithium carbonate. For this, two different routes are hydrothermally tested: using sodium[1] and magnesium hydroxides[2], to synthesize zeolites and magnesium silicates through spodumene.

The spodumene – alpha or beta -, is added to the reactor, along with the alkaline source – sodium or magnesium hydroxides – and it is submitted to high temperatures, in an electric kiln. Materials were characterized through XRD (X-Ray diffraction) and TGA (thermogravimetry analysis in CO_2 atmosphere), and in the diffractograms – Figures 2A and 2B - it was observed that zeolites (hydroxycancrinite) and magnesium silicates were synthesized. The solid materials showed good CO_2 capture results – indicated in Figure 1 -, with its peak at 12.1%, and the lithium-rich solutions are still in a methodology development stage so to increase the precipitation rate.

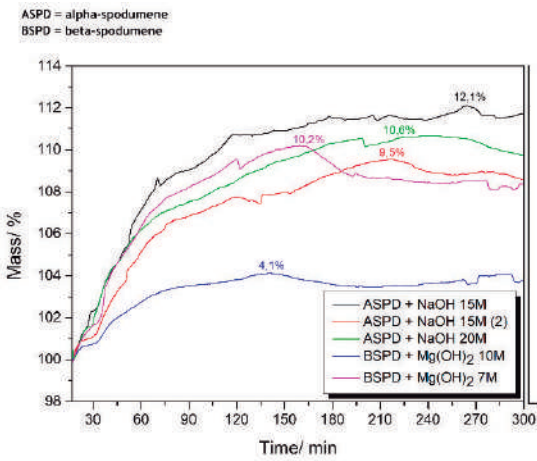


Fig. 1 - CO_2 capture curves of the solid phases obtained in different extractions

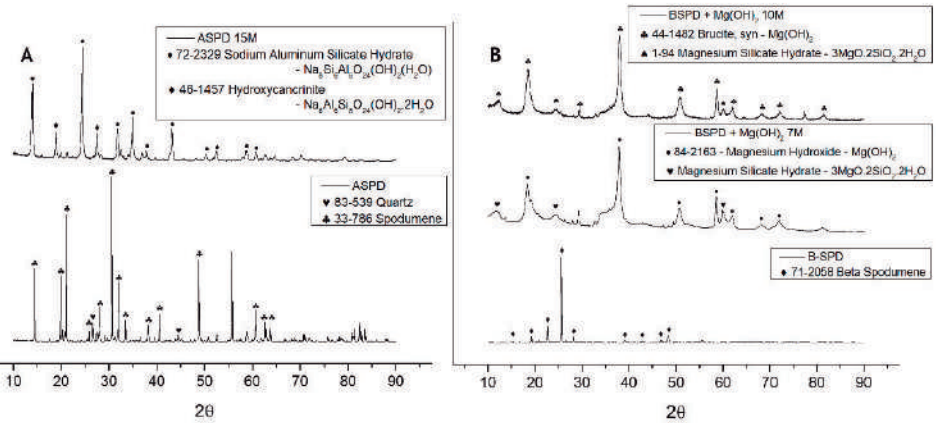


Fig. 2 - XRD diffractograms of the reactants and solid phases obtained from NaOH and alpha-spodumene (A), and with $Mg(OH)_2$ and beta-spodumene(B)

Even though there are still parameters to be defined and conditions to be optimized, it is noted that the project has shown good results in CO_2 capture with the formation of high added value products.

References:

1 P. Xing, C. Wang, L. Zeng, B. Ma, L. Wang, Y. Chen and C. Yang, *ACS Sustain Chem Eng*, 2019, **7**, 9498–9505.

2 Nicholson Clifford Mcintosh

Agradecimentos/Acknowledgments

escalab FAPEMIG GRUTAM Tecnologias Ambientais CNPq INCT MIDAS

Área:____AMB_____

Innovation and Green Certification in the Chemical Industry: A Case Study

Emiliane Gerbasi Ricci* **(PQ)[1], Liziane Marçal (PQ)[2], Liliane Martins (PG) [2], Eduardo José Nassar (PQ)[2], Ygor Metidieri (PQ) [3].**

emiliane@ricciambiental.com.br

[1]*Ricci Soluções Ambientais – Empresa de Consultoria Ambiental – Franca-SP*
[2]*Universidade de Franca – Grupo de Pesquisa em Materiais pelo Método Sol-Gel – Franca- SP*
[3]*Empresa Amazonas - Indústria e Comércio – Divisão Quimicam*
Keywords: *Green Certification, Chemical Innovation, Cleaner Production (P+L), Sustainability,*

Highlights

- ✓ Presentation of a case study from a company located in Franca-SP, demonstrating the positive impact of green certification on Sustainability promotion;
- ✓ Successful implementation of Cleaner Production (CP) principles through innovation and the development of a new line of sustainable products;
- ✓ The acquisition of the Green Seal not only highlighted the reduction of environmental impacts but also contributed to the enhancement of corporate image the strengthening of marketing strategies.

Resumo/Abstract

In recent years, there has been a significant increase in awareness of environmental issues, including climate change, pollution, biodiversity loss, and natural resource depletion. Faced with this competitive landscape, characterized by stricter environmental regulations and a growing global environmental consciousness, companies are challenged to invest in sustainable practices to meet the expectations of stakeholders and environmental demands. Particularly, chemical sector companies have a variety of options for incorporating innovative sustainable practices into their operations, whether through green product innovation or sustainable process innovation. This study presents a proposal suggested by *Ricci Soluções Ambientais* to *Amazonas* Company, which aimed at adapting a new line of sustainable products developed by the R&D team. For this adaptation, it was suggested to obtain a Green Certification, also known as Green Label or Seal, as companies are increasingly seeking these certifications to demonstrate their commitment to sustainability. The proposed strategy emphasizes the integration of sustainable raw materials and the adoption of innovative processes, aligned with the principles of Cleaner Production (CP). This approach includes replacing hazardous inputs with safer and less harmful alternatives, a crucial measure to mitigate the environmental impacts of production and strengthen the company's market image. To achieve the proposed objective in this project, research focused on identifying and evaluating nationally recognized green seals was conducted, considering their criteria and the benefits associated with certification. It is widely recognized that environmental certifications not only demonstrate a commitment to sustainability but also bring tangible benefits, such as improved stakeholder perception and reduced environmental impacts of their activities. In conclusion, this study highlights the importance of innovation and green certification as competitive differentials for companies seeking to stand out in a challenging market. The new product line, named "*Linha Eco Amazonas Sustentável*", is the first line of sustainable adhesives certified with the "*Selo Verde Ecolmeia Série Ouro"*. The partnership between *Amazonas* and *Ricci Soluções Ambientais* reflects a commitment to sustainability that not only meets regulatory requirements and stakeholder expectations but also paves the way for sustainable success in the chemical sector. This study shares insights and practices that can inspire other companies to follow a similar path towards sustainability.

Agradecimentos/Acknowledgments

Empresas: Amazonas, Ricci Soluções Ambientais e Ecolmeia. Universidade de Franca.

Área: AMB
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

In vitro potential of the strain *Cupriavidus* sp. 395/10 for biosorption-bioaccumulation of cadmium, chromium, and nickel

Michelle de Souza Santos (PG),* Daiane Silva Bonaldi (PQ), Lúcia Maria Carareto Alves (PQ), Luciana Maria Saran (PQ).

lm.saran@unesp.br; *mii.souza95@gmail.com

São Paulo State University (UNESP), School of Agricultural and Veterinarian Sciences, Department of Agricultural, Livestock and Environmental Biotechnology, Jaboticabal, São Paulo, Brazil.

Keywords: Bacteria; Resistance; Heavy metals; Bioremediation.

Highlights

- Bacteria isolated from polluted environments develop resistance mechanisms to pollutants.
- *Cupriavidus* sp. 395/10, isolated from soil contaminated with Cd, Cr, and Ni, can remove them from the environment.

Abstract

Industrial wastewater is among the main anthropogenic sources of cadmium ions (Cd^{2+}), chromium (Cr^{3+}), and nickel (Ni^{2+}).[1] Bioremediation, employing live or inactive microorganisms capable of bioaccumulating and/or adsorbing such chemical species is a sustainable alternative to remove them.[2] In a research previously conducted by our group, 592 bacteria were isolated from tropical soil contaminated with Cd^{2+}, Cr^{3+}, and Ni^{2+}.[3] The isolate 395/10, identified as *Cupriavidus* sp., removed 60% of Cr(VI) from the culture medium and produced indole acetic acid.[4] Thus, aiming to expand the understanding of the potential of this bacterium for bioremediation, it was studied the capacity of the bacterium for the removal of Cd^{2+}, Cr^{3+}, and Ni^{2+}, considering its future application for the treatment of wastewater. The minimum inhibitory concentrations (MIC) of Cd^{2+}, Cr^{3+}, and Ni^{2+} for the isolate *Cupriavidus* sp. 395/10 in nutrient broth (NB) medium, were 3, 4, and 225 mmol L^{-1}, respectively. In NB medium containing Cd^{2+}, Cr^{3+}, and Ni^{2+} simultaneously, the MIC was 1 mmol L^{-1}. The optimal range for cell multiplication occurred between 12 and 24 h of incubation, both in the absence and presence of the three metal ions. There was an increase in the pH of the NB medium over time, culminating in a pH between approximately 8.25 and 8.75 after 96 h. Scanning electron microscopy (SEM) showed changes in the morphology and quantity of bacterial cells after its incubation in NB medium containing Cd^{2+}, Cr^{3+}, and Ni^{2+}. In the transmission electron microscopy (TEM) micrographs were observed discrete aggregates of electroconductive nature inside and on the wall of some cells of the isolate, signaling possible biosorption-bioaccumulation of Cd^{2+}, Cr^{3+}, and/or Ni^{2+}. The results of *Cupriavidus* sp. 395/10 cells analysis by molecular spectroscopy in the infrared region (FTIR) showed the presence of functional groups, such hydroxyl and carbonyl groups, on the cell wall, which can act as adsorption sites for metal ions. It was concluded that the strain *Cupriavidus* sp. 395/10 possesses mechanisms that can be exploited for the removal of Cd^{2+}, Cr^{3+}, and Ni^{2+} from wastewater.

Acknowledgments

This work was carried out with the support of the Coordination of Superior Level Staff Improvement Coordination - Brazil (CAPES foundation) - Financing Code 001. Therefore, we would like to thank the master's scholarship granted by CAPES.

References

1. Renu, Agarwal, M., Singh, K., 2017. Methodologies for removal of heavy metal ions from wastewater: an overview. *Interdisciplinary Environmental Review*, ***18***(2), 124-142.
2. Liu, S., Zeng, G., Niu, Q., Liu, Y., Zhou, L., Jiang, L., Tan, X., Zhang, C., Cheng, M., 2017. Bioremediation mechanisms of combined pollution of PAHs and heavy metals by bacteria and fungi: A mini review. *Bioresource Technology*, ***224***, 25-33.
3. Minari, G.D., Rosalen, D.L., Cruz, M. C. P., Melo, W.J., Alves, L.M.C., Saran, L.M., 2017, Agricultural management of an Oxisol affects accumulation of heavy metals. *Chemosphere*, ***185***, 344–350.
4. Minari, G.D., Saran, L.M., Constancio, M.T.L., Silva, R.C., Rosalen, D.L.C., Melo, W.J., Alves, L.M.C., 2020. Bioremediation potential of new cadmium, chromium, and nickel-resistant bacteria isolated from tropical agricultural soil. *Ecotoxicology and Environmental Safety*, ***204***, 111038.

Área: _____AMB_____

Medidas de CO_2, COS e CO em perfil vertical para determinar o balanço de CO_2 da Amazônia utilizando aviões de pequeno porte

Luciana V. Gatti (PQ),[1*] Camilla L. Cunha (PQ),[1] Luciano Marani (PQ),[1] Caio S. C. Correia (PQ),[1] Lucas G. Domingues (PQ),[2] Raiane A. L. Neves (PG),[1] Ricardo Santana (TC),[1] Stephane P. Crispim (TC),[1] Guilherme B.M. Machado (TC),[1] Francine M. Silva (TC),[1] Felipe L. Lopes (TC),[1] Elliott Campbell (PQ),[3] Joseph A. Berry (PQ),[4] Jennifer E. Johnson (PQ),[4] John B. Miller (PQ)[5].

luciana.gatti@inpe.br; lvgatti@gmail.com

[1]Coordenação Geral de Ciências da Terra, INPE; [2]Instituto de Astronomia, Geofisica e Ciencias Atmosféricas – USP-SP, [3]Environmental Studies Department, UC Santa Cruz, CA, USA, [4]Carnegie Institution for Science, Dept. of Global Ecology, Stanford, CA, USA, [5]Global Monitoring Laboratory, National Oceanic and Atmospheric Administration -NOAA, CO, USA

Palavras Chave:*(CO2, COS, Amazonia, Balanço de carbono, CO, GEE).*

Highlights

Aircraft vertical profiles of CO_2, COS and CO to evaluate the Amazon carbon balance
Vertical profiles CO_2 sampling from surface to 4.5km with light aircraft at 4 sites over the Amazon, since 2010 to 2022 to evaluate Amazon Carbon Balance and understand the drivers of Amazon Change

Resumo/Abstract

Amazon represents around 50% of tropical forest and an important ecosystem in the global carbon balance. Deforestation, biomass burning and land use change are modifying the climate conditions in Amazon Forest. To determinate the Amazon carbon flux and balance, we have been using CO_2 concentration from surface to 4.5 km with light aircraft at 4 sites over the Amazon Rainforest, representing northeast region (SAN 2.9° S 55.0° W), southeast ALF (8.8° S 56.8° W), southwest RBA (9.4° S 67.6° W) and northwest TAB (2010-12, 6.0° S 70.1° W) and TEF (2013-21, 3.4° S 65.6° W). Our results indicate that carbon up-take is declining, and that some areas are becoming a source. We report here the methods to determine CO_2, COS and CO in air samples collected in vertical profiles since 2010 to 2021[1,2,3] and how to calculate flux and Amazon Balance. We use the CO to calculate biomass burning and COS to estimate photosynthesis. We use climate variables to understand the drivers that are producing changes in forest function. There is correlation between deforestation, carbon emission, losses in precipitation, increase in temperature and increase in forest flammability. The regions more deforested showed climate stress and losses in carbon sink.

Reference

1. Gatti, L. V. *et al.* Drought sensitivity of Amazonian carbon balance revealed by atmospheric measurements. *Nature* **506**, 76–80 (2014).
2. Gatti, L. V. *et al.* Amazonia as a carbon source linked to deforestation and climate change. *Nature* **595**, 388–393 (2021).
3. Gatti, L. V. *et al.* Increased Amazon carbon emissions mainly from decline in law enforcement. *Nature* **621**, 318–323 (2023).

Agradecimentos/Acknowledgments

FAPESP *(16/02018-2, 11/51841-0, 08/58120-3, 21/09020-0, 20/05108-8), (NERC) AMAZONICA (NE/F005806/1), NASA (11-CMS11-0025, NRMJ1000-17-00431), 7FP-EU (283080), MCTI/CNPq (2013), CNPq (134878/2009-4, 444418/2018-0), ERC/Horizon 2020 (649087), PPGCST/INPE and PROEX/CAPES.*

Área: __AMB_____
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Microplastics in water bodies: Quantification and Characterization of MPs in surface water and sediments samples.

Natalí da Silva Schio (PG),[*1] Guilherme Martins Grosseli (TC),[1] Pedro Sergio Fadini (PQ)[1]

natalischio@estudante.ufscar.br

[1] *Chemistry Department, Federal University of São Carlos (UFSCar – São Carlos)*

Key words: *Microplastic Pollution, Urban Water Bodies, FTIR-ATR, Optical Microscopy.*

Highlights

Microplastics in waters and sediments of urban water bodies.
Identification of the composition of 917 plastic particles.
Polypropylene, Polyethylene, and Polyethylene terephthalate were the most found polymers.

Resumo/Abstract

The potential of microplastics (MPs) to cause deleterious effects on aquatic biota and human health has raised concerns regarding the presence of these compounds in water bodies. This study conducted a pioneering assessment of the presence of MPs in surface waters of the Jundiaí, Monjolinho, Tietê, and Barnabé Creek rivers, as well as in sediments of the Jundiaí River, during the rainy season (February 2023). The concentration of particles in water samples ranged from 0.22 items L-1 in the Jundiaí River to 2.51 items L-1 in the Monjolinho River. In sediment samples from the Jundiaí River, the particle concentration varied across sampling points, ranging from 88.02 to 380.01 items Kg-1. In total, 4759 items were physically characterized using optical microscopy. Fibers and fragments were the most frequently found morphologies, and the predominant colors of the items were black (18.87%) and blue (18.00%) (Figure 1). The size of the items found in the water samples ranged from 68 µm to 4949 µm (Figure 2), and in the sediment samples it ranged from 81 µm to 4905 µm (Figure 3). Of the 4759 items physically characterized, 1191 were chemically characterized by FTIR-ATR, with 917 items identified as plastic. The predominant compositions were PE (36.86%), PP (25.41%) and PET (11.67%) (Figure 4).

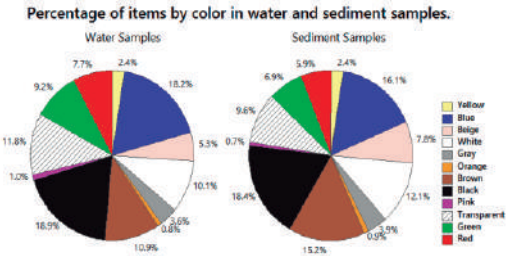


Figure 1 - Percentage of colors of particles found in water and sediment samples.

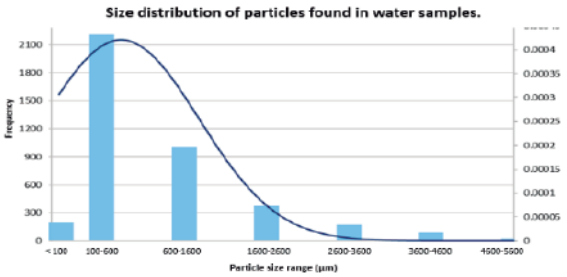
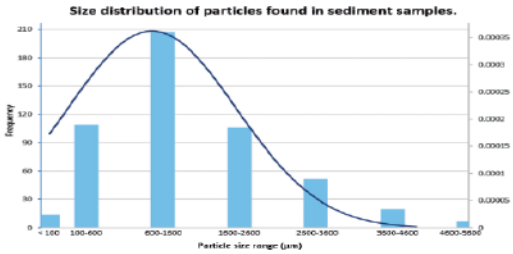


Figure 2 - Particle size distribution found in water samples.



"Figure 3 - Particle size distribution found in sediment samples.

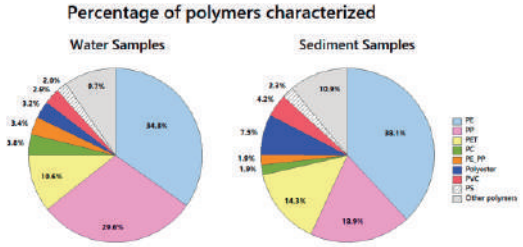


Figure 4 - Proportion of polymer types found in water and sediment samples.

Agradecimentos/Acknowledgments

Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES, Finance Code 001), INCTAA (CNPq, grant #465768/2018-8; FAPESP, grant #2014/50951-4).

Área: AMB

Modelling the Phosphorus adsorption dynamics in sanitary wastewater using a SiO_2@FeOOH composite obtained from wastes: a chemometric approach

Renan S. Nunes (PG),[1] Gabriela T. M. Xavier (PQ),[1] Alessandro L. Urzedo (PG),[1] Marcio Romeiro (PQ),[2] Pedro S. Fadini (PQ),[3] Wagner A. Carvalho (PQ) [1]

renannunes.bm@gmail.com

[1] Center for Natural and Human Sciences, Federal University of ABC (UFABC), Santo André, Brazil; [2] Invict Pró Água, Campinas, Brazil; [3] Department of Chemistry, Federal University of São Carlos (UFSCar), São Carlos, Brazil

Palavras-chave: *Phosphorus, Adsorption, Goethite, Chemometrics, Wastewater Treatment, Circular Economy.*

Highlights

Chemometrics was used to investigate and optimize the adsorption dynamics of P in sanitary wastewater, revealing an efficient and robust performance, crucial for sustainable water treatment practices.

Resumo/Abstract

Clean water, sanitation, and zero hunger are important goals set by the United Nations (UN) that need collaboration across different areas to be achieved. In this context, the removal and recovery of Phosphorus (P) from sanitary wastewater have emerged as a promising strategy to contribute toward achieving these goals. This approach not only contributes to the production of sustainable fertilizers for food cultivation but also addresses the issue of eutrophication resulting from nutrient discharge into water streams. Therefore, with appropriate technology, P can be efficiently recovered from sanitary wastewater, improving the quality of the final effluent, while the wastewater can serve as an alternative source of this nutrient for fertilizer production. In this study, a SiO_2@FeOOH composite previously developed, characterized, and optimized by our research group was employed for efficient P removal from simulated treated sanitary wastewater (SW). The adsorbent was produced using a simple precipitation method that required the use of quartz sand waste obtained from the glass industry, Fe^{3+} obtained from the acid dissolution of scrap iron, and inexpensive reagents as raw materials. The production process generates no waste and results in the SiO_2@FeOOH composite in aqueous suspension form, consisting mainly of quartz sand particles covered with an amorphous goethite layer. Advanced chemometric techniques were applied to model and optimize the adsorbent's performance. Additionally, chemometrics was used to investigate interactions of the adsorbent with various organic and inorganic species typically found in Wastewater Treatment Plants (WWTPs). Demonstrating a remarkable P adsorption capacity of up to 40 mg P/g and the simultaneous removal of organic matter, our tests revealed that the adsorbent can eliminate at least 95% of inorganic P in SW in less than 1 minute of contact time. The material's efficiency remained unaffected in an extended pH range (4-9) and in varied initial P concentrations (1-15 mg P/L). Moreover, its performance remained unaltered in the presence of typical inorganic and organic species found in WWTPs. Extensive characterization using XRD, SEM/EDS, and FTIR techniques revealed significant interactions of the adsorbent with Ca^{2+} species. While Ca^{2+} enhanced P capture during adsorption, its presence during alkaline desorption led to the formation of insoluble Ca/P deposits. Recent literature and experimental evidence obtained in this work support the potential future application of the spent adsorbent as an alternative fertilizer, contributing to Circular Economy metrics. In conclusion, the results demonstrated substantial potential for P uptake in WWTPs, marking a significant advancement toward achieving UN's sustainable development goals. The SiO_2@FeOOH composite proved to be an efficient and versatile potential solution, contributing to sustainable water and natural resource management practices and addressing critical environmental concerns.

Agradecimentos/Acknowledgments

This research was supported by the Industrial Academic Doctoral Program of Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq – Brasil) [grant numbers 140277/2020-0 and 142536/2020-2]. The authors also acknowledge the experimental support of the Multi-User Central Facilities (CEM/UFABC) and BRTech Soluções Tecnológicas Ltda. This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) - Finance Code 001.

Área: AMB

MORPHOLOGICAL AND CHEMICAL CHANGES IN L. ESCULENTUM (TOMATO) CAUSED BY SOIL CONTAMINATION WITH FLUORESCENT LAMP

Gabriela do N. Camargo (PG)*, Rodolfo S. Barboza (PQ)[1], Débora F. de Andrade (PQ)[1], Camila V. de Farias (PG)[2], Lívia G. L. Soares (PQ)[3], Manuel C. Carneiro (PQ)[3] Fernanda V. M. Pontes (PQ)[1], Jéssica F. Paulino (PQ)[1].

camargogabi.97@gmail.com; rodolfosb@iq.ufrj.br

[1]Departamento de Química Analítica, Instituto de Química, UFRJ; [2]SENAI, Centro de Tecnologia da Indústria Química e Têxtil; [3]CETEM, Centro de Tecnologia Mineral.

Keywords: Lycopersicon esculentum, Tomato, Phenolic profile, Fluorescent lamp, Metal accumulation.

Highlights

Morphological and chemical changes in *L. esculentum* (Tomato) caused by soil contamination with fluorescent lamp; determination of potentially toxic elements assimilated and characterization of the overexpressed substance.

Resumo/Abstract

Among the various emerging pollutants caused by anthropogenic actions, fluorescent lamps (FL) stand out due to their high consumption and the presence of Potentially Toxic Elements (PTEs) (Mn, Ni, Cu, Zn, and Pb) in their composition. The FL waste is considered "class I" (hazardous) not only because of mercury but also because of PTEs[1]. Improper disposal of this waste can result in soil, water, and air contamination. Human Health Risk Assessment determined that vegetables grown in soil contaminated with Cd are classified as a potential hazard for both children and adults, and residual Hg is classified as a high risk for children[2]. The mobility of PTEs present in FL powder in the soil can promote bioaccumulation in plants, influencing their development and metabolism. Phenolic compounds are one of the main classes of secondary metabolites produced by the species *Lycopersicon esculentum* Miller (tomato – Solenacea)[3]. The present study investigates the cultivation of tomato under FL powder stress, with soil contamination with 10 g and 20 g of FL powder per 300 g of soil (level I and II, respectively), for 60, 90 and 120 days, in triplicate and using control samples (samples cultivated without FL powder). The assessment of the influence of soil contamination on plant development was conducted through morphological modifications, assimilation and translocation of PTEs, and changes in the production of phenolic substances. After the cultivation period, the specimens were harvested, cleaned, separated (roots, stems, and leaves), dried, ground, and stored. The masses per surviving specimen of roots, stems, and leaves of contaminated plants were statistically similar to the control, except for plants harvested at 120 days, where observed masses of leaves and stems were lower compared to control plants. Regarding the assimilation and translocation of metals present in FL powder in plants cultivated for 120 days, samples were solubilized in HNO_3 and analyzed by ICP-MS. Mn, Zn, and Cd were assimilated throughout the extent of plants grown in contaminated soil. The assimilation of these metals could lead to oxidative stress in the studied specimens, thus allowing the modification of the polyphenolic profile. To evaluate the polyphenolic content, leaves (10 mg) were extracted with $MeOH/H_2O$ 3:1 (v/v) (1 mL) and subsequently partitioned with hexane (3 × 1 mL). Dried degreased extracts were solubilized in 100 µL of MeOH and analyzed by Thin-Layer Chromatography (TLC) under monitoring conditions for polyphenolic substances (flavonoids, phenolic acids, among others)[4]. TLC chromatographic profiles suggested the selective production of a polyphenol from specimens grown under contamination conditions at levels I and II at cultivation times of 90 and 120 days. Additionally, the polyphenolic substance and other substances exhibited prominent antioxidant activity through the DPPH• reaction. Due to the limited amount of leaf mass, a second planting under the same cultivation conditions was necessary, harvested after 90 days of seeding. The TLC chromatographic profile presented the same pattern as the first cultivation, demonstrating the reproducibility of the method. Thus, a solid-phase extraction (SPE) method was developed for isolating the phenolic substance and others. Through the enriched fraction obtained by SPE, it was possible to characterize the polyphenolic substance as 5-*O*-feruloylquinic acid using NMR and MS techniques. Additionally, a second substance was isolated and identified as quercetin-3-*O*-α-L-rhamnopyranosyl(1'''→6'')-β-glucopyranoside (rutin).

[1] ABNT. NBR 10.004 (2004): Resíduos sólidos – Classificação. Rio de Janeiro: ABNT,p.71

[2] DE FARIAS, C. V. et al. Chemosphere, v. 261, 2020.

[3] KISA, D. Russian Journal of Plant Physiology, v. 64, n. 6, p. 876–882, 2017.

[4] WAGNER, H., BLADT S., 1996. Plant Drug Analysis: A Thin Layer Chromatography Atlas.

Área: AMB

O extrativismo do calcário: impactos ambientais e socioeconômicos gerados na comunidade de Palheiros III, Município de Upanema/RN

Mônica R. Oliveira (PQ),[1] Aldefran A. da Silva (IC),[2*] Késia K. V. Castro (PQ),[3] Izabelly Larissa Lucena (PQ),[4]

monica@ufersa.edu.br; silva.aldefran@gmail.com; kesia.castro@ufersa.edu.br;izabellylucena@ufersa.edu.br

[1]Departamento de Engenharia e Tecnologia, UFERSA; [2]Departamento de Ciências Humanas; [3]Departamento de Ciências Naturais, Matemática e Estatística,UFERSA; [4]Departamento de Engenharia e Tecnologia, UFERSA

Palavras Chave: *Extrativismo, Impactos, Socioeconômico, Ambiental, Palheiros III.*

Highlights

Limestone extrativism: environmental and socioeconomic impacts generated in the Palheiros III community, municipality of Upanema/RN. This study is relevant for undderstanding the challenges faced by extraction workers and local residentes regarding education and the socioeconomic problems associated with extraction activities.

Resumo/Abstract

Com o aumento da produção industrial, a demanda por matérias-primas tem crescido exponencialmente. Isso levou a uma intensificação da atividade extrativista no mundo, cujo aumento não vem sem consequências. A exploração excessiva dos recursos naturais pode levar à degradação ambiental, à perda de biodiversidade, entre outros impactos negativos. Além disso, as comunidades locais sofrem efeitos negativos da extração, como o deslocamento forçado e baixo índice de desenvolvimento humano. Portanto, o presente trabalho avaliou a prática do extrativismo de calcário na comunidade de Palheiros III, município de Upanema/RN. No estudo foi aplicado um questionário de 8 perguntas, realizado com participação de 20 trabalhadores extrativistas de calcário da comunidade citada. Pela análise dos dados, constatou-se que a maioria dos entrevistados está na faixa etária entre 16 e 35 anos. Observou-se que 75 % dos pesquisados não estão matriculados na escola, 50 % dos trabalhadores não concluíram o ensino fundamental, 15 % concluíram o ensino médio e, apenas 10% concluíram o ensino fundamental, o que pode indicar uma falta de acesso à educação devido as condições socioeconômicas da população. Quanto ao entendimento se a prática de extração do calcário apresenta impactos ambientais, 80 % dos entrevistados acreditam que a atividade tem impactos significativos e 50 % deles apontam que a extração causa destruição ambiental. Porém, 35 % veem benefícios na prática de extração, devido ao uso do calcário na construção civil. Essas observações indicam uma preocupação com os impactos desta atividade, especialmente entre os jovens entrevistados, e que a conscientização sobre esses impactos podem ser temas importantes para políticas públicas ou iniciativas de conscientização ambiental e socioeconômica. Dessa forma, verificou-se que esse estudo é relevante para compreender os desafios dos moradores locais, especialmente no que diz respeito à educação e aos problemas socioeconômicos associados à atividade de extração. Ao compreender as inter-relações entre o baixo nível de formação escolar, a precariedade das condições de vida e a falta de educação ambiental na comunidade de Palheiros III, será possível identificar áreas de intervenção e desenvolver estratégias para promover o desenvolvimento sustentável e melhorar a qualidade de vida dos moradores. Isso pode incluir iniciativas para melhorar o acesso à educação, capacitação profissional, criação de programas de conscientização ambiental adaptados realidades locais.

Agradecimentos/Acknowledgments

Departamento de Engenharia e Tecnologia, UFERSA; Departamento de Ciências Humanas, UFERSA; Departamento de Ciências Naturais, Matemática e Estatística, UFERSA.

Área: AMB

Performance evaluation of free software for predicting benzimidazole pesticides DL_{50} and its application in environmental risk analysis.

Paulo H. Peruquetti (PG),[1]* Aline T. Bruni (PQ),[1]

paulo.peruquetti@usp.br

[1]*Departamento de Química, FFCLRP (USP)*

Palavras Chave: *Benzimidazole pesticides, In silico* toxicology*, Environmental risk analysis, QSAR, Chemometrics*

Highlights

- Analysis of whether free software could predict DL_{50} values for benzimidazole pesticides.
- Based on the results, we discussed if the data could be used for environmental risk analysis.

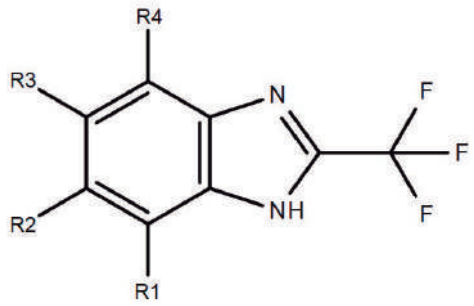


Figure 1 General structure of the benzimidazoles pesticides.

Resumo/Abstract

The group of benzimidazole pesticide molecules was composed of 123 different substances and their general form, according to Figure 1.

All the structural changes were at R1, R2, R3, and R4 sites; the experimental values of acute lethal dose for 50% (DL_{50}) of a population of rats with the toxicant being administered via oral pathways were obtained from two different sources: a reference paper[1] and PubChem[2], a data bank.

To calculate the *in silico* values of DL50 for all 123 molecules, we used four online software that were free of charge. These software were T.E.S.T., Pro-Tox II, Gusar, and Cactus. We used SMILES structures to represent all the studied molecules and selected the same endpoint so the software could predict a value for that specific toxicological property.

With the experimental and *in silico* values in hands, we analyzed the data's accuracy. We evaluated the correlation between the experimental values available in both sources and those calculated by the different software. This analysis showed that the predicted data had a meaningful correlation to the experimental data and could be applied to a preliminary study regarding environmental risk assessment. The correlation was expressed by the value of Pearson's r, as shown in Table 1.

Table 1 Pearson's correlation values for the toxicological data analyzed

	Artigo	*PubChem*	*T.E.S.T.*	*Pro-Tox II*	*Gusar*	*Cactus*
Artigo	1,0000					
PubChem	0,8923	1,0000				
T.E.S.T.	0,8096	0,7384	1,0000			
Pro-Tox II	0,7352	0,8663	0,6255	1,0000		
Gusar	0,7671	0,8394	0,8264	0,7649	1,0000	
Cactus	0,7504	0,7815	0,8191	0,6804	0,8436	1,0000

Furthermore, the different software can rank most compounds according to their toxicological classification.

In conclusion, the analysis showed that theoretical toxicological data can help predict possible toxic effects in preventive environmental risk studies. Silico data could also provide insights into substance classification, allowing the development of mitigation strategies.

References

1. Adamson, G. W., Bawden, D., & Saggers, D. T. (1984). Quantitative structure-activity relationship studies of acute toxicity (LD_{50}) in a large series of herbicidal benzimidazoles. Pesticide Science, 15(1), 31–39. https://doi.org/10.1002/ps.2780150106
2. Kim, S., Chen, J., Cheng, T., Gindulyte, A., He, J., He, S., Li, Q., Shoemaker, B. A., Thiessen, P. A., Yu, B., Zaslavsky, L., Zhang, J., & Bolton, E. E. (2023). PubChem 2023 update. Nucleic Acids Res., 51(D1), D1373–D1380. https://doi.org/10.1093/nar/gkac956

Agradecimentos/Acknowledgments

We would like to thank CAPES for the scholarship and the Department of Chemistry of FFCLRP/USP.

Área: AMB

Phytochemical prospecting of compounds present in mucilaginous plants for use in flotation of ferrous minerals in alluvial gold ores

Camila Alves Arcanjo (IC)[1], Matheus Dias dos Passos (IC)[1], Daiana Rocha do Espírito Santo (PG)[1], Rute Cunha Figueiredo (PQ)[1], Roberta E. S. Froes (PQ)[1]*
robertafroes@ufop.edu.br ; Camila.arcanjo@aluno.ufop.edu.br

[1]Department of Chemistry, Federal University of Ouro Preto - UFOP;
Key Words:(Ora-pro-nobis, mining, mercury, gold, phytochemistry)

Highlights

Mercury-free gold extraction

Phytochemical study of ora-pro-nobis extract

Identification of possible flotation agents present in ora-pro-nobis leaf extracts

Iron ore flotation using ora-pro-nobis

Optimization of the iron ore flotation process

Abstract

Recent studies, have shown promising results in the utilization of mucilage from certain plants in artisanal gold extraction. A methodology for artisanal gold extraction from the leaves of Pereskia aculeata Miller (known as "ora-pro-nobis" - OPN) is being developed and utilized in the district of Antônio Pereira in Ouro Preto, MG, Brazil. The alluvial ore found in the gold pan concentrate in this region is composed of a significant amount of iron minerals. A phytochemical study on OPN leaves is underway with the aim of identifying the main agents that promote iron ore flotation and optimizing the separation of gold in the gold pan concentrate, thus promoting clean artisanal mining. A mass of previously dried and crushed OPN leaves was weighed and exposed for 14 days to a sequence of solvents, starting with hexane followed by dichloromethane, ethyl acetate, and ethyl alcohol. After the contact time, the residue was filtered, and the extract, after solvent recovery, was stored for further analysis. Thin-layer chromatography tests on hexane extracts indicated the absence of groups such as aldehydes, ketones, unsaturated compounds, olefins, and easily oxidizable groups. Gas Chromatography-Mass Spectrometry (GC-MS) is being employed to identify compounds that promote an iron ore flotation. Linoleic and oleic acids was identified in aqueous extract. These compounds are already used industrially in iron ore flotation processes. Others compounds with this type of interaction investigated.Therefore, mucilage derived from Pereskia aculeata Miller has shown promise as an agent for artisanal gold extraction without the need for mercury.

Acknowledgments

PPGQUIM-UFOP, PROPPI-UFOP, FAPEMIG, CNPq, CAPES

Área: AMB
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

$PM_{2.5}$, La-Niña, and El-Niño: Are there differences in the composition of the particles collected under these phenomena?

Karenn S. Fernandes (PQ),[1*] Fabiany P. Honorato (IC),[1] Eduarda T. Moraes (IC),[2] Marcos D. de O. Monteiro (PG),[1] Elaine C. da S. Pereira (PG),[1] Danielle C. de Alencar (TC),[1] Maria C. Solci (PQ),[2] Leticia G. Manzato (PG),[2] Cristine de M. D. Machado (PQ).[1]

karennsilveira@ufam.edu.br

[1]Departamento de Química, UFAM; [2]Departamento de Química, UEL.

Keywords*: Fine particles, soluble ions, BC, Manaus, PCA.*

Highlights

$PM_{2.5}$ collected during La-Niña and El-Niño were separated in two groups by PCA analysis. During El-Niño there was an 82% increase in $PM_{2.5}$ mass and 105% in NH_4^+ concentration.

Resumo/Abstract

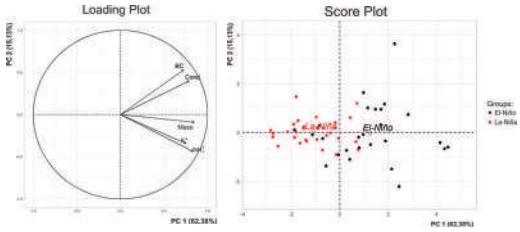
Knowledge about the composition of particulate matter (PM) of the Amazon is of fundamental importance, as it has a significant effect on air quality, and on local and national climatology. Are there differences in the PM collected under the influence of La-Niña and El-niño phenomena? If so, what would they be? These and other questions guide this research. The $PM_{2.5}$ was collected in the urban area of Manaus, during the 2022 dry season (occurrence of La-Ninã) (n = 30) and 2023 (occurrence of El-Niño) (n = 27), using a high volume sampler (1.14 m^3 min^{-1}) and quartz filters. It was determined: the mass of the particles by gravimetry; soluble cations concentrations (K^+, Na^+, Ca^{2+}, $Mg^{2+}$and NH_4^+) by ionic chromatography, aqueous solution conductivity with a bench conductivimeter and black carbon (BC) by reflectance analysis. All equipment was properly calibrated with certified standards, the values of the blank filters were subtracted and deionized water (18 Ω) was used for aqueous solutions. Calibration curves were obtained with good regression values. Table 1 shows the descriptive statistics. All concentrations during El-niño were larger than the year of La-Niña influence. Mass and BC were 82% and 16% higher in 2023, respectively, showing that there was a mass contribution during El-Niño, but possibly fuel burning sources were not the majority for this increase. Conductivity in 2023 was 37% higher and NH_4^+ stands out with an increase of 105%. Treating conductivity as an indirect measure of the amount of ions in solution, it is noted that the El-Niño phenomenon contributed significantly to these analytics, probably due to the difference in the rainfall during the phenomena leading to the accumulation of these compounds. The increase in NH_4^+ points to an aerosol, probably with greater inclination for the formation of secondary particulate matter. Loading and Scores plots for the PCA analysis are showed in Figure 1. Cations Na^+, Ca^+ and Mg^{2+} were removed from the analysis because they have high collinearity. There was statistical separation between the samples of the two periods. 87% of the samples collected during La-Niña grouped (red points), and 77% of the 2023 samples form the group to the right (influence of El-Niño - black points). The scattering of the El-Niño group demonstrating multiple influences on samples, and the important contribution of K^+ for PC1 shows biomass burning as a likely significant source for the PM. Thus, it is concluded that there were sufficient chemical differences in the PM so that there was separation of the groups El-Niño and La-Niña in the PCA analysis, as well as p-value <<1% for T test performed between the averages (2022 and 2023) for each parameter. Thus, discussions about PM can't be restricted to concentrations and chemical influences but should consider atmospheric and oceanic phenomena such as El-Niño and La-Niña for a more assertive discussion about the real meaning of values obtained.

Tabel 1 – Average (Av.) ± standard deviation (DP), minimum (Min.) and maximum (Max.) concentrations (μg m^{-3}) determined in $MP_{2.5}$ collected in Manaus.

	La-Niña (2022)			El-Niño (2023)		
	Av. ± SD	Min.	Max.	Av. ± SD	Min.	Max.
Massa	26.99 ± 4.52	18.07	35.87	49.02 ± 17.72	20.48	97.00
Ca^{2+}	0.07 ± 0.04	0.02	0.17	0.12 ± 0.06	0.05	0.28
Mg^{2+}	0.01 ± 0.01	0.00	0.03	0.02 ± 0.01	0.01	0.03
K^+	0.27 ± 0.11	0.08	0.51	0.36 ± 0.13	0.13	0.67
Na^+	0.11 ± 0.06	0.03	0.29	0.12 ± 0.06	0.01	0.23
NH_4^+	0.45 ± 0.18	0.13	0.82	0.92 ± 0.43	0.27	1.96
BC	1.79 ± 0.58	0.87	3.38	2.34 ± 0.75	1.32	3.66
Cond.*	43.33 ± 15.39	10.00	70.00	73.50 ± 29.33	30.00	168.00

Cond. = conductivity

Figure 1 - Loading and score plot of PCA analysis.



Agradecimentos/Acknowledgments

The authors thank CNPq, UFAM, UEA, UEL, FINEP, FAPEAM and CAPES.

Área: AMB

Polyamide microplastics and their interaction capacities with environmental contaminants

Mariana A. Dias (PG)[1]*, Cassiana C. Montagner (PQ)[1]

marimari.dias@gmail.com

[1]*Environmental Chemistry Laboratory, Institute of Chemistry, University of Campinas, Build I-155, Brazil*

Keywords: *Virgin microplastics, Photodegraded microplastics, Pesticide, Hormone.*

Highlights

Both pristine and degraded PA MPs have more affinity with hydrophobic compounds. The inclusion of polar groups on the structure of degraded PA increases the interaction of more hydrophilic compounds.

Abstract

Microplastics (MPs) are polymeric particles with sizes smaller than 5 mm. These particles have been a concern in the environment due to their interactions with biota and capacity to act as vectors of numerous chemicals, especially in aquatic systems. Our main goal was to study the interaction capacity of pristine and photodegraded polyamide (PA) MPs with pesticides (atrazine-ATZ and tebuconazole-TEB) and hormones (progesterone-PGT and testosterone-TTR). In the sorption experiments, 20 mg of PA MPs and 2.0 mL of contaminant solution containing the mixture of ATZ, TEB, PGT, and TTR were added to glass tubes (10 mL) capped with polytetrafluoroethylene (PTFE) caps and placed on a roto torque shaker at room temperature (~ 20 °C) and 80 rpm. Kinetic experiments were conducted with a fixed initial contaminant concentration of 1.0 mg L^{-1}. The equilibrium time was defined as 48 h. The sorbed amount was obtained indirectly, measuring the contaminant concentration in aqueous media. The supernatant was filtered through 0.22 µm PTFE syringe filters and diluted for liquid chromatography coupled to mass spectrometry in tandem (LC-MS/MS) analysis. The contaminant-sorbed MPs from the equilibrium point of the sorption experiments were used in the desorption assessment. For this, 1.5 mL of the contaminant solution were replaced by 1.5 mL of ultrapure water in the same tubes used in the sorption kinetics experiment. Then, these tubes were kept for 48 h (equilibrium time) on a roto torque shaker at 20 °C. The sample preparation and chemical analysis were performed using the same method to evaluate the sorption. Significant differences were observed between sorption efficiencies with pristine and degraded PA for all contaminants. In general, the degraded PA was able to sorb a higher ATZ amount than pristine PA, an increase of approximately 17% (**Fig. 1**). This variation could be directly related to the inclusion of polar groups in the structure of degraded PA, making it more hydrophilic and increasing its ability to sorption. Thus, interactions with more hydrophilic compounds, such as ATZ, can be favored. This result brings an environmental concern, as the MPs found in the environment, weathered, can transport more significant amounts of ATZ than those found in the controlled experiments carried out in the laboratory. However, for the other contaminants, degraded PA decreased the sorption capacity by approximately 8% for TEB, 6% for TTR, and 9% for PGT. As they are more hydrophobic compounds, the change in hydrophobicity of PA can affect its ability to interact with these molecules, decreasing the sorption capacity. Only for ATZ, desorption efficiency using pristine PA (~ 66%) was more significant than the sorption efficiency (~ 16%), showing its preference to remain solubilized in water. The opposite was observed for the contaminants PGT, TTR, and TEB, which presented desorption efficiencies of approximately 12%, 26%, and 36%, respectively. Lower desorption efficiencies than sorption efficiencies were observed for all contaminants with degraded PA. The average desorption values statistically differed between the two PAs for ATZ and TEB. No significant difference was noted in the efficiency of desorption for hormones.

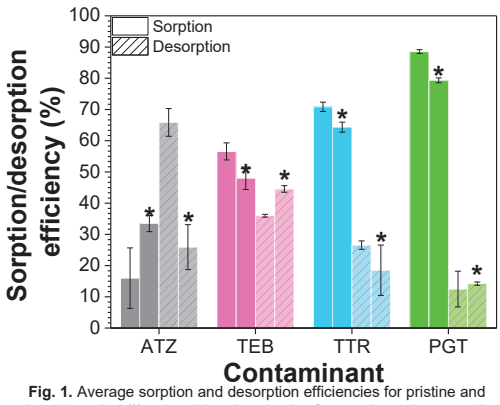


Fig. 1. Average sorption and desorption efficiencies for pristine and photodegraded (*) polyamide microplastics for atrazine, tebuconazole, testosterone and progesterone.

Acknowledgments

This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – Brasil (CAPES) #2015/18790-3 – Finance Code 001 | FAPESP | INCTAA | UNICAMP

Área: AMB
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Preparation and Characterization of Titanosilicate Matrices for Removal of Organic Pollutants in Industrial Effluents: An Approach to Environmental Contamination Reduction

Marcos D. Metidieri (IC)*, Vinicius F. Lima (IC), Eduardo J. Nassar (PQ), Katia J. Ciuffi (PQ), Emerson H. de Faria (PQ), Liziane Marçal (PQ).

damascenomarcos00@gmail.com; liziane.silva@unifran.edu.br

Universidade de Franca (UNIFRAN). Av. Dr. Armando Salles Oliveira, 201. Pq. Universitário. CEP: 14404-600 - Franca/SP, Brasil.
Keywords: Organic pollutants, titanosilicate, adsorption, photodegradation, sol-gel.

Highlights

- Description of the method for preparing titanosilicate matrices using the sol-gel process, emphasizing the use of different catalysts and complexing agents.
- Presentation of the characterization techniques used, including X-ray diffraction, Fourier-transform infrared spectroscopy, thermal analysis, and scanning electron microscopy.
- Observation that only samples treated at higher temperatures exhibited relative crystallinity due to the presence of peaks corresponding to the anatase and rutile phases.

Abstract

Currently, the presence of large volumes of liquid waste represents one of the main problems of environmental contamination. Domestic and industrial discharges generally discarded in rivers and seas, without any treatment or even with inefficient treatment, cause great damage to the ecosystem. In Brazil, an example of this problem is effluents from textile companies, which are characterized by the variety of their residual components. Textile dyes and aromatic organic compounds are one of the main sources of surface water contamination. Inorganic matrices are widely used to remove pollutants present in the aquatic environment by various methods, such as adsorption and photodegradation. In this work, the titanosilicate matrices were prepared using the sol-gel process, by the reaction of tetraethylorthosilicate (TEOS) with titanium isopropoxide (IPTi) in a molar ratio of 1:1, in ethanolic solution. The mixture was carried out using 0,25 mL of HCl or NH_4OH as catalysts, and 1,3 mL of 2.4 pentanedione (ACAC) as a complexing agent for Titanium. The synthesis mixtures were then placed in an oven and dried for 24h at 50 °C. They were subsequently macerated using an agate mortar. The powders were calcined at 500°C or 900°C for 6 hours in a muffle furnace and the samples were characterized by X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), thermal analysis (TG/DTA) and scanning electron microscopy (SEM). The results showed that the characterization techniques confirmed the formation of the titanossilicate matrix, but only the sample treated at 900°C exhibited relative crystallinity due to the presence of peaks corresponding to the anatase and rutile phases. The particles have dimensions of the order of 1 to 100 µm, and rough surfaces, similar characteristics for basic and acid catalysis. These systems have the potential to serve as effective adsorbents or function as metal catalysts, particularly in catalytic photodegradation processes. The objective is to harness the capabilities of these matrices to significantly enhance the adsorption and/or degradation of organic compounds. This outcome not only confirms but also suggests that the sol-gel methodology is a viable technique for generating novel adsorption sites capable of adsorbing hydrophobic compounds such as dyes, pharmaceuticals, pesticides, and others.

Acknowledgments

FAPESP, CAPES, CNPq

Área: _____
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Proof of concept for plasma electrolytic oxidation process as an alternative for microplastic remediation: first results

Lorena Alves Rodrigues (IC),[1] Francisco T. Strixino (PQ),[1] Walter R. Waldman (PQ)[1]*

walter@ufscar.br

[1]*Departamento de Física, Química e Matemática, UFSCar*

Keywords: *Remediation, PEO, microplastics, pollution.*

Highlights

Plasma Electrolytic Oxidation has the potential to remediate microplastics.

The mechanism encompasses the formation of degradation products and inorganic carbon on the surface of the electrode.

Abstract

Plastic pollution is a contemporary and global problem. The most pervasive face of it are the microplastics, ubiquitous in all the biomes. Several measures are being planned and taken to tackle the problem, including a UN initiative to lead the discussions around a Global treaty to regulates several aspects of the polymer production and trade. Despite the effects and progress to understand the microplastic impacts and the actions to stop the leakage into the environment, remediation of such contaminant is still a challenge. In this work we started to test the potential of the Plasma Electrolytic Oxidation process to remediate microplastics in water. Aluminum electrodes (98,7%) immersed in an electrolytic solution of 0.1 mol/L Sodium Silicate containing approximately 0.15 g of microplastics were used in a process under stirring for 90 minutes with a current density set at 20 mA/cm^2. Microplastics and electrodes were studied using a Scanning Electron Microscope, Optical Microscope, and a Fourier Transform Infrared Spectroscopy. Microscopies showed the formation of crackings in the microplastics surface morphology, decrease of the mean size of microplastics and fragmentation, whereas formation of inorganic carbon was observed on the electrodes surface (Figure 1a and 1c). Additionally, fluorine was also found, probably linked to the usage of a Teflon tape used in the system assembling. Fourier Transform Infrared Spectroscopy showed no significant changes in the microplastics. The overall result of this work pointed to a process encompassing the degradation of the microplastics with potential migration of the degradation products to the aqueous media and to the electrode.

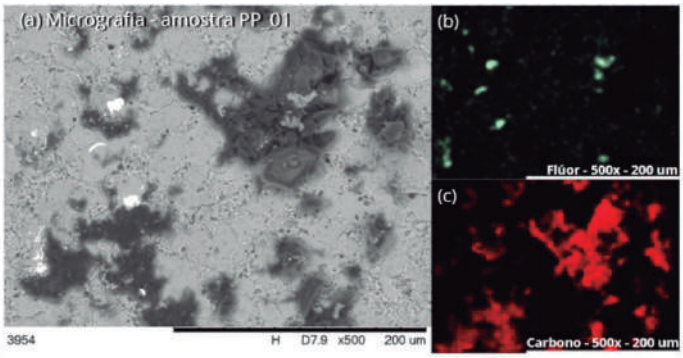


Figure 1: SEM images of the electrode: a) conventional SEM image; b) EDS results for fluorine; c) EDS results for carbon

Acknowledgments

We acknowledge the São Paulo Research Foundation (FAPESP) for the grants 2016/24936-3 and 2022/12104-4, the National Council for Scientific and Technological Development (CNPq) for the grant 406391/2021-1, and the Financial Agency for Studies and Projects (FINEP) for the grant 01.22.0179.00.

Área: _____
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Química atmosférica em remanescentes de mata Atlântica na região metropolitana de São Paulo

Adalgiza Fornaro (PQ)[1], Amauri P. Oliveira (PQ)[1], Lucas Silveira (PQ)[1], Lucas Chiari (PG)[1], Maciel Pinero (PQ)[1], Samara Carbone (PQ)[2], Pauline Fombelle (PG)[3], Agnes Borbon (PQ)[3]Georgia Codato (TC)[1], Olatunde Muran (PG)[4], Marina Jamar (PQ)[4], Joel Brito (PQ)[4], Victória Peli (PG)[1], Ávila Benaya (PG)[1], Jacques Florêncio (PG)[1], Jean Eudes Petit (PQ), Pamela Dominutti (PQ)[6], Jean Luc Jafrezzo (PQ)[6].

Adalgiza.fornaro@iag.usp.br

[1]Departamento de Ciências Atmosféricas (IAG-USP); [2]Instituto de Ciências Agrárias (UFU); [3]Université Clermont Auvergne, Laboratoire de Météorologie Physique, OPGC/CNRS, France; [4]Centre for Energy and Environment, IMT Nord Europe, Université de Lille, France; [5]Department of Particulate Matter, National Research Centre, France, [6]Institut des Géosciences de l'Environnement (IGE), France.

Palavras Chave: *Poluição do ar, Material Particulado, Compostos orgânicos voláteis*

Highlights

Atmospheric chemistry in remnants of the Atlantic forest in the metropolitan region of São Paulo.

- Importance of the Atlantic forest for negative CO_2 fluxes.
- Anthropogenic versus biogenic emissions.

Resumo/Abstract

A poluição atmosférica é o resultado de uma mistura complexa de emissões naturais e antropogênicas, tais como compostos orgânicos voláteis (COV) e dióxidos de nitrogênio (NOx), pois dependendo da condição atmosférica, como presença de radiação solar, podem produzir ozônio e aerossóis secundários. A região metropolitana de São Paulo (RMSP) possui sérios problemas de qualidade do ar afetando seus mais de 22 milhões de habitantes. A complexidade das emissões envolve mais de 7 milhões de veículos e industrias, somado à região ser rodeada pela Mata Atlântica (serras do Mar e Cantareira), além de ter importantes remanescentes representativo desse bioma, por exemplo fora (Reserva do Morro Grande, RMG) e dentro (Matão-IAG) da mancha densamente urbanizada (1). O objetivo desse trabalho é apresentar resultados preliminares envolvendo campanha intensiva de abril a julho de 2023 com medidas simultâneas na RMG e Matão-IAG, com duas torres de fluxo (sistema LICOR - CO_2, H_2O e energia) e uma variedade de instrumentos de última geração para estudar a dinâmica e as propriedades físico-químicas de gases e aerossóis no contexto meteorológico regional. Entre os instrumentos destacam-se PTR-TofMS-Charon (proton-transfer-reaction-mass spectrometer) e ACSM (Aerosol Chemical Speciation Monitor) para medidas da composição de gases e aerossol em tempo real, além de amostradores de alto volume para análises diversas de MP_{10}, amostrando e medindo simultaneamente em ambos os sites. Em relação ao CO_2, na RMG observou-se fluxo negativo de –15 μmol m^{-2} s^{-1}, entre 10 e 15h, enquanto no mesmo horário no Matão-IAG o fluxo foi positivo +5 μmol m^{-2} s^{-1}, indicando a importância da fotossíntese da vegetação da RMG em relação às emissões devido queima de combustíveis na área densamente urbanizada. As concentrações do MP_1 foram 3 vezes maiores no Matão-IAG do que na RMG (15,2 e 5,2 µg.m^{-3}, respectivamente), contendo mais de 60% de compostos orgânicos em ambos os sítios. Isopreno e monoterpenos atingiram 0,51 ppb e 0,26 ppb, respectivamente. Enquanto que o tolueno, marcador antropogênico, atingiu 1,52 ppb.

(1) Santos et al., Science of The Total Environment, vol. 824, p. 153728, 2022.

Agradecimentos/Acknowledgments

FAPESP 2020/07141-2 e ANR n° CE01-0019-20.

Área: AMB

Rare Earth Elements: An Overview of Primary Sources, Applications, Investing Companies, and Characterization Techniques.

Lílian Lefol Nani Guarieiro* (PQ),[1,2] Alexandre Pereira Wentz (PQ),[1] Fabiano Ferreira de Medeiros(PQ),[1] Fabricio Dias Rodrigues (PG),[1] Sara Silva Alves (PG), [1] Jefferson Bettini (PQ),[3] Jeancarlo Pereira dos Anjos (PG)[4], Maria das Graças Andrade Korn (PQ)[5]

[1] Centro Universitário SENAI CIMATEC, 41650-010, Salvador - BA, Brazil.
[2] National Institute of Science and Technology in Energy and Environment - INCT, Federal University of Bahia, 40170-115 Salvador, BA, Brazil.
[3] Brazilian National Nanotechnology Laboratory LNNano, BR-13083970 Campinas, SP – Brazil
[4] Centro de Ciências Naturais e Humanas (CCNH), Universidade Federal do ABC, 09210-580 Santo André-SP, Brazil
5 Universidade Federal da Bahia, 40110-905 Salvador-BA, Brazil
***liliaguarieiro@gmail.com**

Palavras Chave: *Elementos Terras Raras, Aplicações, Empresas Mineradoras, Técnicas Analíticas.*

Highlights

Brazil has reserves, but production is small; Rare earths are essential for the energy transition. Sustainable mining is a priority and a challenge; Advances in new characterization techniques.

Resumo/Abstract

Rare earth elements (REEs) are a group of 15 transition metals belonging to the lanthanide series, including the elements yttrium and scandium. These elements share similar chemical and physical characteristics due to their lanthanide contraction that keeps these ions in the series with, approximately, the same size and the same oxidation state and, because they occur in the same ore deposits such as monazite, bastnasite, xenotime and adsorption clays. ionic REEs have intrinsic properties, such as optical, magnetic, thermal stability, luminescence and electrical conductivity, which guarantee their use in several modern technologies. Thus, this review aims to present an overview of primary sources, applications, investing companies and characterization techniques. Through an extensive literature review using indexed databases and patents, it was possible to map the state of the art about REEs, supporting the development of a sampling campaign to prospect for these elements. As a result of this study, it was possible to observe that, commercially, 75% of REEs produced are applied in the synthesis of chemical catalysts, 10% are used as additives to improve mechanical and thermal properties and polishing of optical components in the production of ceramics and special glasses, another 10% act as activators in phosphors for production of light, in the manufacture of lasers, fiber optics for telecommunications, spectroscopy, medicine for diagnosis and treatment. In Metallurgy and Alloys, they contribute to the production of magnets with strong and light magnetic fields, used in motors, electrical generators, speakers, and special metallic alloys for manipulating material properties. Although global reserves of these elements are considerable, mineable concentrations are less common than for other minerals. Estimation of reserves and commercial extraction is often based on rare earth oxide equivalents (OTR) due to the electrodeficient nature of REE ions in forming stable oxides. Globally, estimated OTR equivalent reserves are around 130 million tones, with China leading with 34% of the world's reserves. Brazil has 21 million tons. Despite Chinese dominance in this market, countries such as the United States, Australia and Myanmar are reinforcing their rare earth element (REE) exploration and processing chains. China Northern Rare Earth (Group) operates the world's largest, rare earth mine in Bayan Obo, while MP Materials Corp operates the Mountain Pass mine in California, supplying approximately 15% of the rare earths consumed globally. Energy Fuels: acquired a project in Brazil and Aclara Resources operates in Chile and Brazil, exploring heavy rare earth deposits, developing innovative and sustainable extraction methods. Currently, the criteria for choosing the analytical technique include detection limits and working range. Inductively Coupled Plasma Mass Spectrometry (ICP-MS) is widely used due to its multi-element capacity, sensitivity, and precision. Recent studies bring different approaches, such as the use of ICP-MS/MS for effective quantification, evaluation of sample opening methods, and method development, in marine sediments. Additionally, micro- and nanoscale geochemical analyses, including Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) and High-Resolution Transmission Electron Microscope (HRTEM), are discussed. LA-ICP-MS stands out for avoiding acid digestion, while HRTEM allows detailed morphological analyzes at the nanoscale.

Agradecimentos/Acknowledgments

CNPq405664/2022-2, PRH 27.1 ANP/FINEP, SENAI CIMATEC, Mineradora TABULEIRO, EMBRAPII.

Área: AMB

Recognition of kaolinite in soil samples for forensic purposes: the potential use of FTIR in Baixada Fluminense, RJ

Aline de Almeida Pinto*[1] (IC), Julia Baltar Augusto [1] (IC), Janaina de Assis Matos [1] (PQ), Paloma de Queiroz Rosa [1] (IC), Glaucio Braga Ferreira[2] (PQ), Carla Semiramis Silveira [1] (PQ)

alinealmeidapinto@id.uff.br

[1]Geochemistry Department, Chemistry Institute Universidade Federal Fluminense; [2]Inorganic Department, Chemistry Institute Universidade Federal Fluminense

Keywords: Spectroscopy, Kaolinite, Infrared, Mineralogy, XRD

Highlights

FTIR-ATR absorbance peak ratios (907 cm^{-1}/517 cm^{-1} and 998 cm^{-1}/907 cm^{-1}) seem promising for kaolinite identification and quantification as a forensic tool in real soil samples from RJ.

Abstract

The Baixada Fluminense (BF), in the state of Rio de Janeiro (RJ), has a high rate of intentional homicides but a low solution rate (an average of 10%, while in other countries this rate reaches 90%). In this sense, soil is a good forensic tool as it helps to solve crimes due to its high transferability, great variability, and persistence. So, the development of forensic methods and techniques associated with soil is critical. FTIR-ATR stands for Fourier Transform Infrared Spectroscopy using the Attenuated Total Reflectance sampling technique. It is a widely used technique and the equipment is simple to operate. Furthermore, the technique is non-destructive, which means that the sample can be reused or saved for future analysis. This work aims to test the use of ratios between absorbance peaks in the IR spectrum of kaolinite to recognize similarities between soil samples for forensic purposes. 23 topsoil samples were collected in 4 municipalities of the BF in RJ. The organic matter was removed using H_2O_2 and the fraction below 63 um was separated (sieved). In addition to the soil samples, a standard pattern $Al_2Si_2O_5(OH)_4$ (here called kaolinite) from Sigma Aldrich was used for individual analysis and in a mixture (50%-50%) with grounded quartz (SiO_2). Kaolinite was chosen because it is the main mineral in the < 63um fraction of these soils. All the samples were analyzed using FTIR-ATR (Thermo iS-50 - LAME-UFF, 4cm^{-1} resolution). The basic principle of the technique is to hit the sample with a beam radiation in the mid-infrared spectrum (4000-150 cm^{-1}). The result of this interaction is a function of the vibration of the molecular bonds, which ultimately reflects the chemical composition, crystal structure and the types of chemical bonds, i.e. the mineral composition. Adimensional ratios between the absorbance peaks were calculated on the normalized spectra. To confirm the mineral results, all the samples were analyzed by X-ray diffraction (XRD) (Bruker D2 Phaser at Laminx - UFF) and quantified by Rietveld Method. According to the XRD analyses the pattern has 71% of kaolinite. The peaks 998 cm^{-1}, 907 cm^{-1} and 517 cm^{-1} were recognized, which correspond to stretching of the Si-O bond, deformation of the O-H bond, and in-plane Si-O bond, respectively. The calculated ratio between peaks 998 cm^{-1} and 907 cm^{-1} (ratio 1) was 1.48, between 907 cm^{-1} and 517 cm^{-1} (ratio 2) was 0.74 and between 998 cm^{-1} and 517 cm^{-1} (ratio 3) was 1.10. In the quartz kaolinite mixture, these ratios remained the same. In the soil samples, ratio 2 (907 cm^{-1}/517 cm^{-1}) is the best for identifying kaolinite. This is because several silicates, especially feldspars ($KAlSi_3O_8$ and $Na(AlSi_3O_8)$-$Ca(Al_2Si_2O_8)$) have absorption features in the 998 region that causes interferences. However, this interference can be a good tool to quantify kaolinite. There is an inverse correlation between kaolinite amount and a shift in ratio 1 values. Amorphous and crystalline iron compounds seem to disturb ratio 2. Ratio 3 was found to be very poor in discriminating samples. Therefore, to recognize soil sites in the BF, the use of ratios 2 (907 cm^{-1} /517 cm^{-1}) and ratio 1 (998 cm^{-1} /907 cm^{-1}) seems promising for kaolinite identification and quantification as a forensic tool.

Acknowledgments

Faperj for funding the research (Process number: E-26/290.039/2021) and Proppi- UFF for the Technological Initiation scholarship for the 1st author

Área: AMB

Síntese de dióxido de silício (SiO_2) obtido a partir da calcinação do bagaço de cana-de-açúcar

Maria E. S. Reis (TM),[1]* Bianca G. Rodrigues (PG)[2] Jocélia P. C. Oliveira (PQ),[2] Marccus V. A. Martins (FM),[1]

maria.seixas@estudante.ifgoiano.edu.br

[1]*Instituto Federal Goiano – Campus Catalão;* [2]*Instituto de Química, Universidade Federal de Catalão.*

Palavras-Chave: Cana-de-açúcar, Mercerização, SiO_2.

Highlights

Synthesis of silicon dioxide obtained from the calcination of sugarcane bagasse

The work refers to the sintese and spectroscopic characterization of silica (SiO_2) from sugarcane bagasse.

Chemical treatment was used in a basic medium with the use of NaOH to reduce the organic character of the fibers and subsequent calcination at 800 °C to obtain SiO_2.Spectroscopy indicated the disappearance of organic compounds after treatment with NaOH and the presence of silicate groups in the ash. The synthesis of crystalline silica was confirmed by X-ray diffractometry.

Resumo/Abstract

A demanda pela utilização de materiais de origem renovável passou a ser amplamente disseminada como alternativa à minimização dos impactos ambientais. Diante disso, as cinzas provenientes do bagaço da cana-de-açúcar tornam-se uma alternativa viável a uma gama de aplicações. Nesse contexto, o presente trabalho abordou a obtenção e caracterização espectroscópica da sílica (SiO_2) a partir da biomassa do bagaço da cana-de-açúcar. Inicialmente, empregou-se o tratamento químico em meio básico com uso de NaOH para a diminuição do caráter orgânico das fibras. Após essa etapa, essas foram calcinadas a 800 °C para obtenção de SiO_2. Os espectros de infravermelho (FTIR) revelaram a conversão do perfil orgânico para inorgânico, devido ao aparecimento do estiramento da ligação Si-O-Si na região de 1030 cm^{-1}(Fig. 1a).

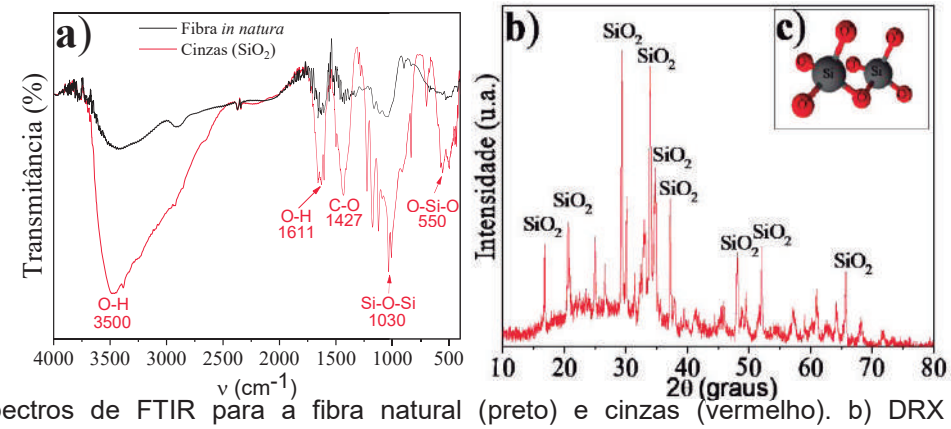


Figura 1. a) Espectros de FTIR para a fibra natural (preto) e cinzas (vermelho). b) DRX das cinzas e c) representação esquemática do SiO_2 cristalino.

A Figura 1 (b) apresenta o difratograma de raio-X com a predominância de picos estreitos em regiões de 2θ típicos e característicos de sílica cristalina na fase de quartzo, conforme esquematizado na Figura 1 (c). Tanto o processo de tratamento em solução básica como a calcinação revelaram-se eficientes para a produção de sílica cristalina com elevado potencial para aplicações biotecnológicas, como reações de adsorção e de fotodegradação.

Agradecimentos/Acknowledgments

Os autores agradecem ao CNPq pela bolsa concedida, a Universidade Federal de Catalão, (UFCAT), ao Instituto de Química da UFCAT e ao IFGoiano – Campus Catalão.

Área: AMB

Surface water quality assessment of the Lagoa do Mato, in São Raimundo Nonato - PI

Ilany S. P. Landim (IC),[1*] Fernando C. Damasceno (PQ),[1] Aparecida M.S. Mimura (PQ).[1]

fernando.damasceno@univasf.edu.br; ilanylandim@gmail.com

[1]Colegiado de Licenciatura em Química, Universidade Federal do Vale do São Francisco - UNIVASF

Keywords: Water, Lagoa do Mato, domestic sewage.

Highlights

In urban areas, water pollution is a cause of concern.

Physical-chemical and microbiological parameters were evaluated.

The degradation of water quality was related to the release of domestic sewage.

Abstract

In urban areas, the water pollution can affect negatively the environment and cause risks to human health. One of the main difficulties faced in Brazil is the preservation of water resources as their degradation is common and primarily caused due to the discharge of untreated domestic sewage and industrial effluents. In regions with a semi-arid climate, ponds play a crucial role as water reserves for daily activities. In the city of São Raimundo Nonato (PI) there are few natural water reserves, such as Lagoa do Mato, which in the past was considered a source of good quality water for the population. The aim of this study was to evaluate and discuss the water quality of the Lagoa do Mato, located in São Raimundo Nonato. To this end, studies were conducted with samples collected in September 2023 from three points in the surroundings of the pond. Physical-chemical and microbiological parameters were assessed, including color, temperature, conductivity, total dissolved solids, pH, chlorides, dissolved oxygen (DO), Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD), thermotolerant coliforms and *Escherichia coli*. The parameters temperature, pH and DO remained within the limits established by CONAMA Resolution No. 357/2005 for fresh waters.[1] However, the water samples showed a yellowish color, with suspended particles. The electrical conductivity results ranged from 6,690 to 6,900 µS cm^{-1}, above the limit (1000 µS cm^{-1}) established by the Water Quality Surveillance Program for Human Consumption.[2] The levels of total dissolved solids found ranged from 5,825 to 7,228 mg L^{-1}, exceeding the maximum limit (500 mg L^{-1}) established by the CONAMA resolution. Likewise, chloride values (2351 to 2430 mg L^{-1}) significantly exceeded those established by this resolution (up to 250 mg L^{-1}). Regarding the COD and BOD parameters, the results ranged from 1633 to 2209 mg L^{-1} and 14.6 to 50.7 mg L^{-1}, respectively, indicating a high load of organic matter in the medium. In addition, substantial amounts of thermotolerant coliforms (5,600 to 11,000 CFU/100 mL) and *Escherichia coli* (5,600 to 9,400 CFU/100 mL) were found, which should be absent in the water, according to *Portaria* n° 888 of the Brazilian Ministry of Health. The results indicated that the degradation of water quality of the Lagoa do Mato is related mainly to the release of domestic sewage, a fact supported by on-site visits. This type of pollution can cause dire consequences for the wildlife that inhabits this ecosystem, such as fish, alligators, ducks, and other animals, which are directly affected, as well as for the population that lives nearby. It is up to public agencies to promote remediation and control strategies.

[1]CONAMA. Resolução nº 357, de 17 de março de 2005. Available in: <http://pnqa.ana.gov.br/Publicacao/RESOLUCAO_CONAMA_n_357.pdf.> Access at: 12 jun. 2023.

[2]BRASIL. Ministério da Saúde. Secretária em Vigilância em Saúde. Vigilância e Controle da Qualidade da Água Para O Consumo Humano. Brasília: Ministério da Saúde, 2006.

Acknowledgments

UNIVASF and Prefeitura de São Raimundo Nonato.

Área: AMB

Traceability of water quality using the Arduino platform as a low-cost instrument.

Kauan D. P. Pereira (TC); Heron D. T. da Silva (PQ);

heron.silva@unifesp.br; kauanpaz1309@gmail.com

[1]*Instituto De Ciências Ambientais, Químicas e Farmacêuticas, UNIFESP;*

Key-words: water monitoring, Arduino, quality testing.

Highlights

The main points of the research work are the development of a reliable and low-cost equipment (about 30 dollars), and its testing and feasibility in the monitoring of water resources. Bringing together 2 areas, electronics, and chemistry, bringing great confidence and accessibility to the equipment.

Resumo/Abstract

In the vast territory of Brazil, the presence of incredibly diverse landscapes is evident, especially in metropolitan ar eas, where social segregation becomes manifest. A notable example of this disparity can be found in the v icinity of the Guarapiranga Reservoir, located in the city of São Paulo. In this context, we observe a high-end neighborhood on one side and, on the opposite side, an area densely populated by communities. In the metr opolitan region of São Paulo, the responsibility for water supply and treatment falls upon a basic sanitation com pany. This institution plays a fundamental role in supervising water quality, employing various methods of phy sicochemical analysis. Three specific parameters, namely pH, conductivity, and total dissolved solids, provide crucial information about water quality, including the detection of impurities that can render it unsuitable for hum an consumption. However, a significant challenge lies in the fact that traditional analytical methods are not always readily accessible. In this context, the use of Arduino presents a viable solution to simplify the water monitorin g process, enabling field measurements. The scope of this project aimed to characterize water quality in two dist inct localities supplied by the system that extends from the Guarapiranga Reservoir to residential areas, with the purpose of assessing physicochemical parameters. As a result, it was found that the zone displaying the highest nu mber of sampling points and the greatest variation in physicochemical parameters predominantly exhibits character istics of a community, with approximately 16% of points falling outside the established specifications.

Figura 9 – Classificações dos pontos de análise. **Fonte:** Adaptado do Software Qgis, 2023.

Agradecimentos/Acknowledgments

Lab*In*Sciences - Laboratory of Integrated Sciences – Univeersidade Federal de São Paulo - UNIFESP

Área: __AMB_____

TRANSFORMAÇÃO DE UM RESÍDUO DA SIDERURGIA EM UM FERTILIZANTE NITROGENADO: DA BANCADA À ESCALA PILOTO

Julia Braga Marques Pereira (IC)* [1], Thamires Luciana Braz Alves (PG) [1], Breno Germano de Freitas Oliveira (PG) [1] Rochel Lago Monteiro (PQ) [1], , Arnaldo Terra Gontijo (PG) [2], Henrique Hélcio Eleto dos Santos (PG) [2], João Paulo Freitas Kohler (PG)[2], Carlos Murillo Leandro Ferreira (PG) [2].

juliabraga@escalab.com.br;

[1]Departamento de Química, UFMG; [2]Bioesfera Soluções Sustentáveis,

Palavras Chave:*Fertilizante; Resíduo Nitrogenado; Siderurgia.*

Highlights

TRANSFORMATION OF STEEL WASTE INTO NITROGEN FERTILIZER: FROM BENCH TO PILOT SCALE

Resumo/Abstract

As siderúrgicas brasileiras produzem aproximadamente 36 milhões de toneladas/ano de aço. Durante a produção desse material, é gerado o gás de coqueria (COQ) cujo de tratamento que produz um efluente nitrogenado, com uma taxa de produção de aproximadamente 150 milhões de litros por mês. Entre os contaminantes presentes nesse resíduo, destaca-se os compostos nitrogenados, dos quais aproximadamente 5-15% são de amônia.

Diante desse cenário, o Escalab, em conjunto com a empresa Biosfera, e com recursos obtidos a partir do CNPq, está executando um projeto para a produção de fertilizantes nitrogenados a partir do resíduo amoniacal produzido nas siderúrgicas. Esse projeto está estruturado em etapas principais, as quais tem o intuito de desenvolvimento da tecnologia, escalonamento da tecnologia e testes com clientes reais do mercado. As principais etapas são: 1) Pesquisa e Desenvolvimento (P&D) no laboratório do ESCALAB/DQ para otimização da reação; 2) Escalamento no CIT-SENAI com a construção de um protótipo de reator com capacidade de 10L-80L; 3) Operação da planta piloto a ser testada na siderurgia.

Na primeira etapa de otimização da tecnologia, foram realizados experimentos preliminares, até construção de protótipo de reator com capacidade de 5L. Obtendo como resultado médio 500g de fertilizante nitrogenado, utilizando 3 L do resíduo nitrogenado industrial. Em relação a rendimentos na reação para produção do fertilizante observou-se que o rendimento em temperatura ambiente (35ºC) era de 2% e em sistemas refrigerados (8°) era aproximadamente 70%. Desse modo, observa-se que a reação em estudo possui um rendimento maior quanto o sistema é refrigerado (<10ºC), uma informação muito importante para o escalonamento da tecnologia. Além da temperatura, outros parâmetros importantes para a reação foram otimizados como a velocidade de agitação, forma de dispersão do gás (utilizado para a precipitação) e tamanho do reator (proporção líquido contato com o gás).

A partir dos resultados obtidos na etapa de P&D, a tecnologia para produção do fertilizante nitrogenado com resíduo industrial, foi validada. Esse projeto é viável e necessário para os objetivos de desenvolvimento sustentável da ONU. Assim, as próximas etapas envolvem escalonamento da tecnologia a partir de testes em reatores maiores (protótipos de 10-80 litros) no CIT-SENAI e a instalação da planta piloto (100-200L) em siderurgia parceira.

Agradecimentos/Acknowledgments

Ao CNPQ, UFMG, Escalab e Bioesfera.

Área: AMB

Uso de Nanoestruturas Zeolíticas para a Remoção de Íons Amônio a partir de Efluentes Reais

Matiara S. C. Amaral (PG),[1] Marcella A. da Silva (IC),[2] Fabiana S. dos Santos (PQ),[1] André M. dos Santos (PQ),[1,3] Mendelssolm K. Pietre (PQ).[1,2*]

mkpietre@yahoo.com.br

[1]Programa de Pós-graduação em Tecnologia Ambiental (PGTA-UFF); [2]Departamento de Química-ICEx-UFF, [3]Departamento de Bioquímica-IQ-UFRRJ

Palavras-Chave:*(Zeólita Beta, Faujasita, Adsorção, Íons Amônio, Cinética, Efluentes Reais).*

Highlights

- Use of zeolitic nanostructures for the removal of ammonium ions from real wastewater.
- Faujasite and beta zeolites were produced.
- Synthetic zeolites showed superior performances compared to commercial beta zeolite.
- The better performance of the faujasite sample is due to both higher Al content and elevated specific surface area.

Resumo/Abstract

O presente trabalho utilizou as zeólitas sintéticas faujasita (Fau) e a zeólita beta (BEA_sintética) além da zeólita beta comercial (BEA_comercial) para a remoção de íons amônio a partir de efluentes reais, proveniente de uma estação de tratamento de esgoto (ETE) do município de Volta Redonda. Os resultados de DRX (Fig. 1A) revelam que as amostras apresentam pureza de fase, enquanto a razão molar Si/Al (Fig. 1A), medidos por FRX, apresentou menor valor para a amostra faujasita. Isso significa que mais sítios de troca iônica estão disponíveis para remoção dos íons amônio. Aliado a isso, a amostra faujasita apresentou maior área superficial (não mostrado) o que permite maior acesso e difusão dos íons amônio aos sítios de adsorção. Espectros de ^{29}Si-RMN (Fig. 1B) revelam que a amostra faujasita apresenta perfil típico de sólidos com alto teor de Al, devido à presença de sinais na região entre -80 a -95 ppm [1]. Por outro lado, as amostras BEA sintética e comercial são essencialmente silícicas, em concordância com os resultados de FRX. Espectros de ^{27}Al-RMN (Fig. 1C) mostram que as amostras sintéticas apresentam somente um sinal em torno de 60 ppm, responsáveis pela geração de cargas negativas, fundamentais na troca iônica. Por outro lado, um sinal em 0 ppm é observado para a amostra BEA_comercial sugerindo a presença de Al extra-rede, que não contribui para a geração de sítios de adsorção [1]. Estudos cinéticos e isotermas de adsorção revelaram a seguinte ordem na performance dos adsorventes: Fau > BEA_sintética > BEA_comercial. Essa ordem pode estar relacionada à dois efeitos principais; i) maior teor de Al e ii) elevada área superficial, o que pode promover maior disponibilidade dos sítios de adsorção e fácil acesso dos íons amônio ao interior dos poros da zeólita faujasita.

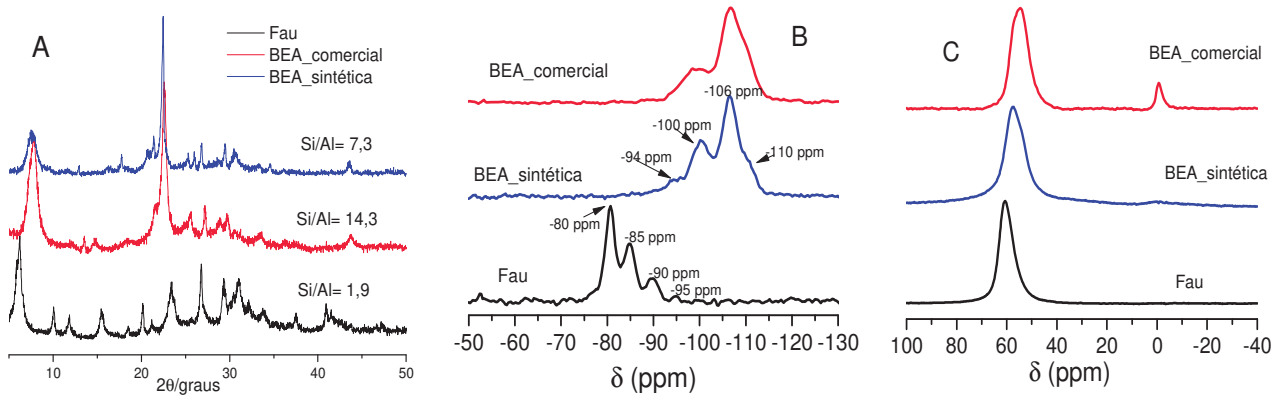


Figura 1: Espectros de DRX (A), espectros de ^{29}Si-RMN (B) e ^{27}Al-RMN (C) das zeólitas utilizadas nesse trabalho.

Agradecimentos/Acknowledgments

Os autores agradecem à FAPERJ pelo suporte financeiro e à UFES pelas caracterizações das amostras.

[1] Goncalves MB, Schmidt DVC, dos Santos FS, et al (2021) Nanostructured faujasite zeolite as metal ion adsorbent: kinetics, equilibrium adsorption and metal recovery studies. *Water Science and Technology* 83:358–371.

Área: AMB

Utilização do fruto da amendoeira-da-praia como fonte de matéria-prima para a obtenção de triacilglicerídeos e biocarvão visando a produção de biodiesel

Gustavo Taveira Albuquerque (IC),[1] Carolina Guimarães de Souza Lima (PQ),[1] Isakelly Pereira Marques (PQ) [1]

isakellymarques@id.uff.br; gtaveira@id.uff.br

[1]*Departamento de Química Orgânica, UFF*

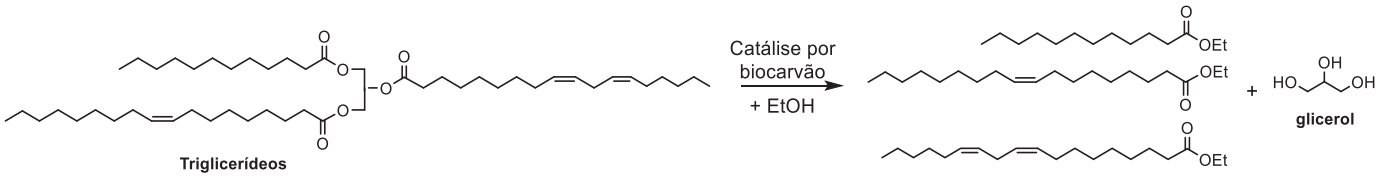
Palavras Chave: *amendoeira da praia, co-pirólise, biomassa, biocarvão; biodiesel, sustentabilidade.*

Highlights

The fruit of the almond tree (*Terminalia catappa Linn)* was used as a source of raw materials - triacylglycerides and biochar - for biodiesel production.
The extraction of oil was accomplished via the Soxhlet method, and the cake residue of the extraction was used to produce biochar catalysts through co-pyrolysis.

Resumo/Abstract

A *Terminalia catappa Linn*., popularmente conhecida como amendoeira-da-praia, tem uma grande produção de frutos que pode ocasionar problemas urbanos como o entupimento de bueiros, e, portanto, este resíduo deve ser coletado e encaminhado frequentemente para lixões e aterros sanitários. Desta forma, o desenvolvimento de novas estratégias para o aproveitamento dos resíduos da amendoeira-da-praia é altamente desejável. Estudos recentes revelaram que o fruto da amendoeira-da-praia possui alta quantidade de óleo vegetal, o que abre a possibilidade do seu emprego como oleaginosa para produção de biodiesel. Além disso, a torta gerada como resíduo após a extração do óleo vegetal pode ser empregada no processo de co-pirólise para a produção de biocarvão que pode ser utilizado como catalisador heterogêneo e reutilizável na síntese do próprio biodiesel. Neste sentido, o presente trabalho teve como objetivo a extração do óleo dos frutos da amendoeira-da-praia, a produção de biocarvão a partir da co-pirólise da torta obtida e testar o potencial deste biocarvão como catalisador heterogêneo em reações de transesterificação do óleo visando a obtenção de biodiesel.
O óleo vegetal foi obtido através da extração por Soxhlet da amêndoa previamente seca e triturada, utilizando o hexano como solvente. A torta residual foi seca em estufa e impregnada com ácido fosfórico, para realização da co-pirólise, visando a aplicação como suporte catalítico. O processo de co-pirólise foi realizado alterando-se a temperatura, para verificar se haveria alguma mudança na estrutura do carvão obtido. Os carvões obtidos foram triturados, peneirados e utilizados como catalisador na reação de transesterificação do óleo vegetal com etanol, sob refluxo, levando a obtenção do biodiesel com rendimento de 57%. Os produtos obtidos foram caracterizados por Espectroscopia na região do infravermelho e por Ressonância Magnética Nuclear de ^{1}H. Estudos de otimização das condições relacionais encontram-se em andamento.



Esquema 1: Esquema reacional para obtenção do biodiesel.

Agradecimentos/Acknowledgments

UFF, CAPES - Código de Financiamento 001, CNPq e Faperj

ANA

Química Analítica

Sociedade Brasileira de Química

Área: ANA

3D printed device used to perform gas-diffusion microextraction and applied in the formaldehyde determination in milk samples

Juliana C. Pinho (IC)[1*], Natália dos S. Trindade (IC)[1], Gabriel B. Piassalonga (PG)[1], Karen C. Ferreira (PG)[1], Paulo C.F. de Lima Gomes (PQ)[1].

juliana.pinho@unesp.br;

[1] *Department of Analytical Chemistry, Physical Chemistry and Inorganic Chemistry, National Institute for Alternative Technologies of Detection, Toxicological Evaluation and Removal of Micropollutants and Radioactives (INCT-DATREM), Institute of Chemistry, São Paulo State University (UNESP), Araraquara, São Paulo, Brazil*

Keywords: *Formaldehyde, Extraction, GDME*.

Highlights

Development of 3D printed device to perform gas diffusion microextraction to be applied in the formaldehyde determination through colorimetric reactions.

Resumo/Abstract

Formaldehyde, a colorless compound and carcinogenic agent, was prohibited by the Ministério da Agricultura, Pecuária e Abastecimento (MAPA) in 1997[1] in the food sector, as an adulterant or preservative. Gas diffusion microextraction (GDME) is a rapid extraction method that repairs the disadvantage of the traditional method (method B of the AOAC 931.08 standard)[2], providing quantitative results from colorimetric reactions. The commercial GDME uses a closed polypropylene cylinder and PTFE filter, both of which are expensive (approximately R$200.00). With the advent of 3D printing, in particular the fusion and deposit modeling (FDM) technique, it makes it possible to develop a lower-cost device manufactured according to the user's specifications and the extraction technique. Therefore, the objective of this study is to develop a 3D-printed device for determining formaldehyde in milk samples. The first stage of this project was the design and optimization of a GDME prototype for 3D printing. PTFE sealing tape was used in place of PTFE filter. The GDME was optimized by a fractional factorial design 2^{5-1} evaluating the parameters: pH, salting out, sample volume, temperature and extraction time. These experiments were carried out using formaldehyde fortification at 25 mg L^{-1} in formaldehyde-free UHT skimmed milk samples, using 500 µL of the acetylacetone derivative of concentration 0.0196 mol L^{-1} deposited on the PTFE tape. The reaction product was analyzed by spectrophotometry at a wavelength of 412 nm. GDME was printed with polylactic acid (PLA) and acrylonitrile butadiene styrene (ABS). However, the device received a polymer coating of polydimethylsiloxane (PDMS) to ensure that there was no loss of formaldehyde through the walls of the printed device. PDMS was applied to the device and heated in an oven at 70°C. PLA was not suitable, as it could not withstand the applied temperature. The optimized GDME conditions for formaldehyde extraction were: 10.00 mL of milk sample, temperature of 70°C, extraction time of 50 minutes using ultrasound, pH equal to 3.0, addition of NaCl (salting-out) 0.5% (m/v). From the optimized extraction conditions, the analytical curve was made in milk with concentrations of 5.00 to 25.0 mg L-1, in triplicate. The equation A = 0.043[Formaldehyde] - 0.048 and R^2 = 0.99 was obtained. The limit of detection and quantification were 1.50 and 5.00 mg L-1, respectively. The method presented precision that varied from 2 to 9% at the 6 different levels of the analytical curve. As a result, the 3D-printed device proved to be accurate in determining formaldehyde in UHT milk samples. The estimated cost of the 3D device was R$2.00, making it possible to determine formaldehyde using GDME at a lower cost compared to the commercial one. The current GDME device will be evaluated to determine formaldehyde using digital images obtained by smartphones. Furthermore, a comparison will be made using MBTH (2-methyl-3-benzothiazolinone hydrazone) as a derivatizing reagent.

[1] Brasil. Ministério da Agricultura, Pecuária e Abastecimento. Mapa. Instrução. Normativa Mapa nº 68, de 12 de dezembro de 2006, sobre a regulamentação e outras.
[2] Determinação Qualitativa de Formaldeído. AOAC Official Methods of. Analysis. 931.08 21th.ed.

Agradecimentos/Acknowledgments

To the following research agencies: FAPESP (#2022/02991-3) e INCT-DATREM #2014/50945-4.

Área: ANA

Acid-base titration on wax-printed paper-based microzones for determination of acetylsalicilyc acid: a laboratory experiment for chemical education

Monise C.R. Casanova (FM) ,[1]**Jordanna E.A. dos Santos (IC-EM),**[1*] **Thiago M.G. Cardoso (PQ),**[2] **Lucas C. Duarte (PQ),**[2] **Wendell K.T. Coltro (PQ).**[2]

monise.coltro@ifg.edu.br

[1]*Departamento de áreas acadêmicas, IFG;* [2] *Instituto de Química, UFG*

Palavras Chave: analytical chemistry, chemical reactions, miniaturization, visual detection, portable instrumentation.

Highlights

- Low-cost, disposable, global affordable and equipment free device for chemical education;
- An innovative teaching method for visually monitoring acetylsalicylic acid titration.

Resumo/Abstract

Paper-based titration can be considered an innovative teaching method due to its shorter analysis time, smaller volumes of reagents and faster analysis. In this study, a methodology was developed to perform volumetric acid-base titrations on paper microzones. The microzones (5 mm in diameter) were drawn in Corel Draw graphics software and printed on chromatographic paper with a wax printer. The devices were placed in an oven at 120ºC for 1 min to obtain the hydrophobic barriers. Then, the zones were thermally laminated against a thermosensitive film at 150ºC. Acetylsalicylic acid was titrated with a NaOH solution in the presence of phenolphthalein. The titration end point was detected visually. As a proof of concept, initially, two adult AAS tablets from different brands were dissolved in the presence of ethyl alcohol and transferred to a 500 mL flask. Then, a 5 µL aliquot of the AAS solution was added to different microzones, in the presence of phenolphthalein, where they were kept at room temperature for 5 min. Next, aliquots of 0.75 to 6 µL of 0.01 mol/L NaOH solution were added to the different microzones. As the NaOH reacted with the AAS with phenolphthalein, a color change from colorless to pink was observed. The titration turning point occurs when the microzone is completely filled and pink in color, which can be observed visually (Figure 1). From the visual perception of the titration end point, the corresponding volume of NaOH spent in the microzone was used to quantitatively calculate the mass of the adult AAS tablet of the two brands. The masses of AAS found in the two samples were 630 ± 64 mg (brand 1) and 585 ± 64 mg (brand 2). Considering the theoretical value of 500 mg, the errors obtained were 26 and 17% for brands 1 and 2, respectively. Although errors are high, it is a visual technique that can replace conventional volumetric titration in high school chemistry laboratory classes.

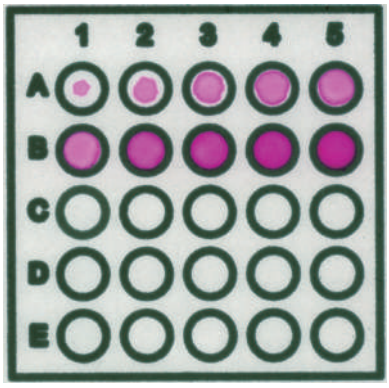


Figure 1. Optical image showing the acid-based titration on wax-printed paper-based microzones varying the volume of NaOH solution added inside zones. In line A, the volume varied from 0.75 (column 1) to 3.75 µL (column 5). In line B, the volume varied from 4.50 (column 1) to 6.00 µL (column 5).

Agradecimentos/Acknowledgments

UFG, IFG, CNPq, FAPEG and INCTBio.

Área: ANA

A green liquid chromatography method for simultaneous quantification of caffeine and its three major metabolites in urine, drinks, and herbal products

Débora M. B. Goldner (PG),[1*] **Fernando H. do Nascimento (PQ),[1] Jorge C. Masini (PQ)[1]**

debora.goldner@usp.br

[1] *Departamento de Química Fundamental, Instituto de Química, Universidade de São Paulo*

Palavras Chave: *Ethanol, Monolithic chromatography, Environmental friendless, Food samples, Biological samples, Caffeine.*

Highlights

Green separations of caffeine and main metabolites with ethanol/water solvents; Backpressure issues circumvented by monolithic columns; Urine, drinks and infusions were analyzed in less than 10 min

Resumo/Abstract

A new green reversed-phase liquid chromatography method was developed to determine caffeine (CF) and its three major metabolites – theobromine (TB), theophylline (TP), and paraxanthine (PX). The stationary phase was a C18 monolithic (100 × 3.0 mm i.d.) thermostated at 35°C, and eluted with a gradient from 6 to 10% (v v^{-1}) of ethanol in water, at a flow rate of 0.75 mL min^{-1}. UV detection was performed at 272 nm. The compounds were separated in less than 6 minutes, with a total run time of 10 minutes for column reconditioning, and the injection volume was 2 µL. The effect of gradient composition, flow rate, injection volume, and column temperature was evaluated in the separation efficiency, especially regarding the critical pair paraxanthine/theophylline, for which the best resolution was 1.37 (Fig. 1A). The linear range was between 0.5 and 100 µg mL^{-1}. The LODs were 0.065, 0.057, 0.040, and 0.044 µg mL^{-1}; and the LOQs were 0.12, 0.13, 0.11, and 0.30 µg mL^{-1} for theobromine, theophylline, paraxanthine, and caffeine, respectively. The method was applied to samples of green tea and yerba mate infusions, soft drinks, energy drinks, and soluble coffee (Fig. 2). Urine samples were also analyzed before and after solid-phase extraction cleanup. The accuracy of the proposed method was evaluated by the spiking/recovery strategy standing in the 79.6 to 116.4 % range. The separation performance and the mobile phase consumption were similar to those of another method using a linear gradient from 14 to 18% of methanol in water in 6 min, with a total run time of 11 min (Fig. 1B). In comparison with common HPLC organic modifiers such as acetonitrile and tetrahydrofuran, both ethanol (0.495 mL/analysis) and methanol (0.831 mL/analysis) are preferred eluents according to Green Analytical Chemistry concept because of their lower toxicity and simpler waste treatment

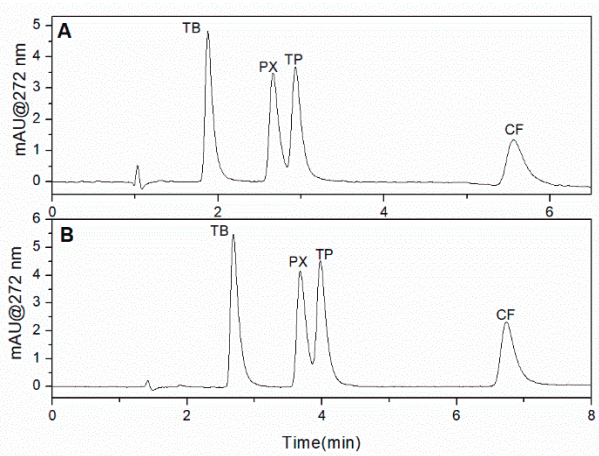


Fig 1. Representative chromatograms of 5 µg/mL standard using: (A) ethanol/water mixtures, and (B) methanol/water mixtures

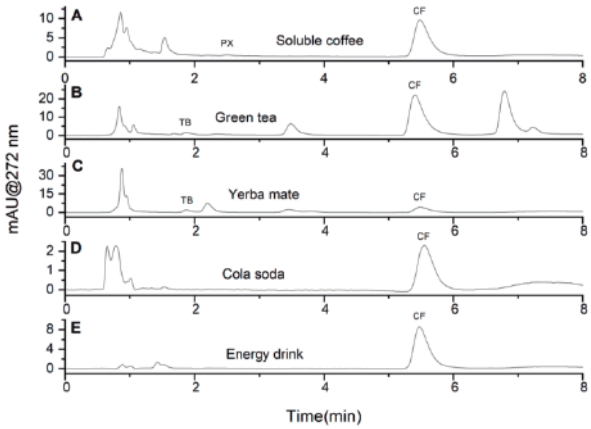


Fig. 2. Chromatograms of (A) soluble coffee; (B) green tea; (C) yerba mate; (D) cola soda and (E) energy drink.

Agradecimentos/Acknowledgments

CNPq - Processes 306674/2021-1 and 131226/2022-3; CAPES - Contract 88882.315696/2019–01

Área: ANA

Analysis of counterfeit washing powder by differential scanning calorimetry allied with chemometric tools

Hélio M. M. A. Neto (PG)[1*], Ana C. C. Fulgêncio (PQ)[1], Enrico M. P. Zago (IC)[1], Rogério A. Lordeiro (PQ)[2], Marcelo M. Sena (PQ)[1], Elionai C. L. Gomes (PQ)[1]

heliomilito@gmail.com

[1]*Chemistry Department, Institute of Exact Sciences (DQ-ICEX) – Universidade Federal de Minas Gerias (UFMG), Belo Horizonte*
[2] *Instituto de Criminalística da Polícia Civil de Minas Gerais, Belo Horizonte*

Keywords: *Laundry powder, Forensic analysis, Thermal Analysis, Discriminant analysis, PLS-DA*

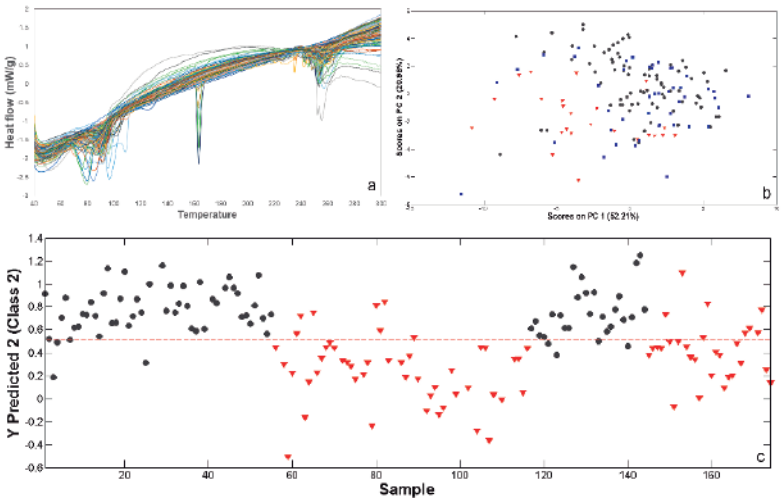
Highlights

Analysis of counterfeit washing powder seized by the Civil Police of Minas Gerais using differential scanning calorimetry allied with chemometric tools.

Resumo/Abstract

In this work, samples of washing powder seized in the Imperfect Washing ("Lavagem Imperfeita") Operation by the Civil Police of Minas Gerais[1] were analyzed and compared with authentic samples of the target brand acquired in local markets (and low-cost authentic brands). For this aim, 174 samples were analyzed by differential scanning calorimetry (DSC) with a heating rate of 10 ºC min^{-1} from temperatures between 40 ºC and 300 ºC and under nitrogen atmosphere with gas flow of 50 mL min^{-1}. DSC curves were normalized by the sample's mass and pre-processed with Savitzky-Golay filter, standard normal variate (SNV, for correcting drifts) and mean center (Fig. 1a). Chemometric models used were principal component analysis (PCA) and partial least squares discriminant analysis (PLS-DA). PCA results showed a reasonable discrimination between counterfeit (triangles) and authentic target (circles) samples on PC2 (21%), with authentic low-cost samples (squares) in an intermediate position (Fig. 1b). Samples were split in 116 (training set) and 58 (test set) for PLS-DA model (Fig. 1c). Authentic samples of the target brand were classified with sensitivities of 92.9 and 85.2%, and specificities of 86.5 and 73.3%, for training and test samples, respectively. These results suggest that lower cost laundry powders were repackaged to emulate the market leader one, configurating a sophistication fraud.

Figure 1. Pre-processed DSC curves (a), PCA scores (b) and PLS-DA predictions (c).



1. G1 Centro-Oeste de Minas (Brasil), Empresas envolvidas no esquema de falsificação de sabão em pó no Centro-Oeste de MG são identificadas. http://bit.ly/3HzSCXi, 2022 (acessed February 26th 2024).

Agradecimentos/Acknowledgments

CNPQ, CAPES, PROCAD SPCF (CAPES), Rede Mineira de Ciências Forenses (FAPEMIG).

Área: ANA

A new contactless electrical sensor based on resonance frequency for monitoring water quality control

Andressa D. W. V. Martinez, Kelly A. Wink (IC),[1] Marianna J. Rodrigues (IC),[1] Camila A. André (IC)[1], Adriano M. Jaime (PG),[2] Charles A. Haab (PG)[2], Fábio A. Duarte (PQ),[1] Jussiane S. Silva (PQ)[1]*

jussiane.silva@ufsm.br

[1] Departamento de Química, Universidade Federal de Santa Maria, Santa Maria, RS, Brasil, 97105-900;
[2] Auftek Serviços de Tecnologia LTDA, Universidade Federal de Santa Maria, Santa Maria, RS, Brasil, 97105-900.

Keywords: *Contactless sensor, Water, Quality control, Conductivity.*

Highlights

A new contactless electrical sensor based on resonance frequency, aligned with green chemistry and IoT, offers a practical and efficient solution for water analysis in the laboratory and the field.

Abstract

Ensuring the quality of drinking water is essential for public health. Conventional water quality control methods involve collection, preservation, sample preparation, and laboratory analyses, which are time-consuming and costly, compromising feasibility for end-users and field testing. In response, seeking out more accessible technologies capable of performing in-situ monitoring and integrating with Internet of Things (IoT) solutions becomes necessary. Electrical conductivity is a parameter widely used to assess water purity across various sectors, including the pharmaceutical industry. It is typically measured using contact sensors (electrodes) or inductive (toroidal) sensors. The first is highly sensitive but prone to polarization and corrosion damage; the latter avoids direct contact with the sample, minimizing corrosion, but interference and signal losses can occur. In this context, a new electrical device based on a capacitively coupled contactless resonance frequency detector (C^3 RFD) was developed to monitor the electrical conductivity. This device uses electrodes coupled to a glass tube, detecting variations in resonance frequency due to changes in the electrical properties of the medium without physical contact with the sample [1, 2]. The sensor was evaluated by correlating the resonance frequency measured by the device C^3 RFD with the conductivity results obtained by the standard method (Physical Test Method 645) [3], using regression models based on a derivative of a 4-parameter logistic curve and a free knot spline. These models were constructed from the analysis of 300 samples (n=3) of ultrapure water and KCl and NaCl solutions (0.0001 to 0.05 mol L^{-1}), with all measurements performed at 25 ºC. Applying the Newton-Raphson numerical method to compensate for the impossibility of defining the inverse function of the resulting non-injective curve. Comparative tests with the conventional method and standard conductivity solution confirmed the accuracy and precision (< 10%) of the C^3 RFD method in the range between 1 and 7000 µS cm^{-1}. Thus, the device aligns with the principles of green chemistry and IoT integration, representing an effective alternative for monitoring water conductivity, standing out for its accessibility, sensitivity, specificity, and ease of use.

[1] Haab, C. A. et al., Brazilian Patent 10 2021 025 274 0, jul. 27, 2021.
[2] Haab, C. A. et al., **IEEE Sensors Journal**, 2024. doi: 10.1109/JSEN.2024.3361311.
[3] United States Pharmacopeia, 40th Edition. Physical Test Method 645 Water Conductivity.

Agradecimentos/Acknowledgments

The authors are grateful to CNPq, CAPES, UFSM, Cepetro, LAQIA, and Auftek.

Área:Ana

(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

A Preformulation study using Thermal Analysis to check Bisoprolol Hemifumarate and Pseudoephedrine Hydrochloride compatibility with some excipients

Lucas Y. Sato (IC)*, Maria Inês G. Leles (PQ).

yugosato@discente.ufg.br; yugosato@discente.ufg.br

Laboratório de Métodos de Extração e Separação, Universidade Federal de Goiás (UFG), Goiânia, Brasil

Palavras-Chave: *Bisoprolol Hemifumarate, Pseudoephedrine Hydrochloride, Excipients, Compatibility, TGA, DSC.*

Highlights

Bisoprolol Hemifumarate and Pseudoephedrine Hydrochloride were analyzed by TGA and DSC in the presence of some excipientes to check for drug-excipient compatibilities between them.

Resumo/Abstract

Thermal analysis (TA), more specifically, Thermogravimetric analysis (TGA) and Differential Scanning Calorimetry (DSC) have proven themselves to be quite useful in preformulation studies by being simple and fast analysis while also requiring small amounts of samples to give reliable information about some physical chemical properties of the Active Pharmaceutical Ingredients (API) and excipients. One use of TA in preformulation studies and the focus of this work, is the investigation of drug-excipient compatibility. So, in the present work, two APIs, Bisoprolol Hemifumarate (BH) and Pseudoephedrine Hydrochloride (PSE) and four physical mixtures 1:1 (w/w), BH + pre-gelatinized corn starch (CS), BH + Silicon Dioxide (SD), BH + Microcrystalline cellulose 102 (MC) and PSE + Magnesium Stearate (MS), were analyzed by TGA and DSC and compared to their respective isolated components DSC data to assess their compatibility. The physical mixtures were prepared by grinding equal parts of the API and excipient in a mortar and pestle. The TG curves of the API and excipients were obtained using a model TG/SDTA/851^e Mettler Toledo by heating approximately 7.000 mg of sample from 25 to 1000 ºC in a α-Al_2O_3 pan. The DSC curves of the APIs, the excipients and the binary mixtures were obtained using a model DSC 822^e Mettler Toledo by heating approximately 5.000 mg of sample in a perforated Aluminum pan from 25 to 300 ºC. In both analysis a N_2 atmosphere was used with a flow rate of 50 mL min^{-1} and a heating rate of 20 ºC min^{-1}. The DSC curve of BH showed three endothermic events at 60-90 ºC, 100 ºC and 180-260 ºC corresponding to dehydration, melting and thermal decomposition, respectively [1]. The DSC curve of PSE showed two endothermic events at 180 and 270 ºC, relative to the melting and decomposition of the drug, respectively [2]. When checking for drug-excipient compatibility, the DSC curve of the binary mixture should be the superimposition of that of the single components, meaning that all the thermal events observed in the DSC curves of the isolated components must also be observed in the DSC curve of the mixture at the same temperature interval but at lower intensity (due to lower concentrations). For all mixtures containing BH this superimposition is observed meaning that there were no interactions between BH and the three excipients. PSE + MS showed an endothermic event at 240 ºC, speculated to be the anticipation of PSE's thermal decomposition. A limitation in DSC analysis is that it's not able to give information about the nature of these supposed interactions. In conclusion, formulations between BH and CS, SD and MC are possible given that there were no interactions between them, but more tests (IF, XRD, DSC analysis with different mixture ratios) should be done regarding PSE and MS to properly identify and characterize the possible interaction that was observed in this work.

[1] Bakheit, A. H., Ali, R., Alshahrani, A. D., & El-Azab, A. S. (2020). Bisoprolol: A comprehensive profile. Profiles of Drug Substances, Excipients and Related Methodology. doi:10.1016/bs.podrm.2020.07.006

[2] Sohn, J. S., & Choi, J.-S. (2021). Development and evaluation of pseudoephedrine hydrochloride abuse-deterrent formulations using thermal modified rice starch. International Journal of Biological Macromolecules, 182, 1248–1258. doi:10.1016/j.ijbiomac.2021.05.055

Agradecimentos/Acknowledgments

The authors would like to thank FUNAPE for managing the project.

Área: ANA

Assessment of metabolic differences between humans and bovines via HS/GC-MS analysis of volatile organic compounds in cerumen

Rhyan César S. Dias* **(IC),[1] Ana Luiza R. R. da Cunha (PG),[1] João Marcos G. Barbosa (PG),[1] Nelson Roberto Antoniosi Filho (PQ)[1]**

rhyancesarb2018@outlook.com;

[1] *Laboratório de Métodos de Extração E Separação (LAMES), Instituto de Química (IQ), Universidade Federal de Goiás (UFG), Campus II – Samambaia, Goiânia, GO 74690-900, Brasil*

Palavras-Chave: *Metabolômica, Cera de Ouvido, Headspace, Cromatografia Gasosa, Espectrometria de Massas*

Highlights

Demonstrating the potential of earwax metabolomics in accessing specific biochemical routes of humans and bovines that can be used for clinical and evolutionary purposes.

Resumo/Abstract

A metabolômica é uma ciência ômica que tem por objetivo entender o funcionamento e as alterações metabólicas dos organismos a partir da análise de compostos obtidos em uma amostra biológica[1]. O cerúmem é um exemplo desse tipo de amostra, que pode ser coletado de forma não invasiva, e que possui grande potencial como biomatriz em estudos de diagnósticos dentro da medicina tanto humana quanto veterinária[2]. O presente trabalho teve como objetivo demonstrar que a partir da análise de compostos orgânicos voláteis (VOC) do cerúmen é possível avaliar as diferenças no perfil metabólico de dois organismos distintos (bovinos e humanos), assim como identificar as principais assinaturas voláteis que os distinguem. Para isso, foi coletado cerúmen de 10 bovinos e 10 humanos, e realizada a análise via *Headspace/Gas Chromatography-Mass Spectrometry* (HS/GC-MS) em uma abordagem de metabolômica global. Os cromatogramas gerados (Figura 1) foram deconvoluídos no software MZmine (*v2.53*, mzmine.github.io/), e os dados processados utilizando a plataforma *MetaboAnalyst (v6.0*, *metaboanalyst.ca/)*, que apontou 9 VOC com maior diferença estatisticamente significativa ($p < 0,05$) entre humanos e bovinos.

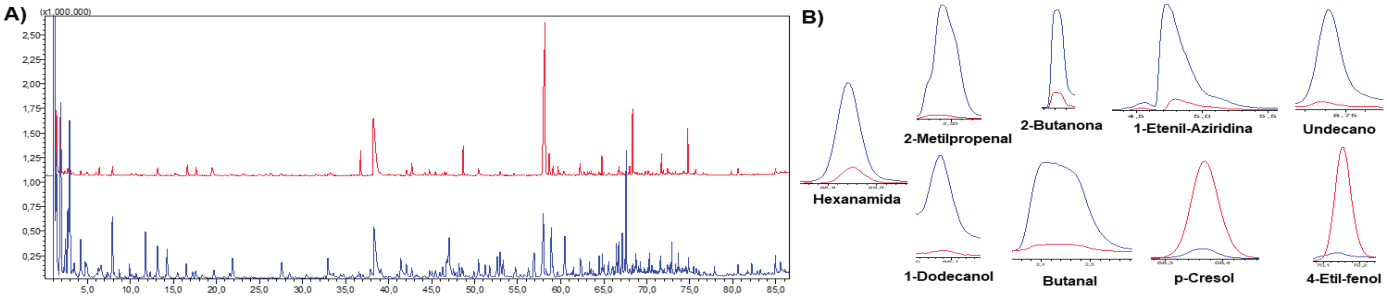


Fig.1. A) Cromatogramas de VOC em cerúmen humano (azul) e bovino (vermelho). **B)** Picos dos 9 principais VOC.

Os compostos voláteis apresentando maiores intensidades no organismo humano (2-metil-2-proprenal, butanal, 2-butanona, undecano, 1-etenil-aziridina, 1-dodecanol, e hexanamina) são majoritariamente associados às rotas de oxidação de ácidos graxos no estresse oxidativo mitocondrial, o que implica uma provável maior atividade dessas rotas em humanos quando comparadas com bovinos. Por outro lado, os compostos com maior intensidade em bovinos (*p*-cresol e 4-etil-fenol) são majoritariamente oriundos do metabolismo mamífero-microbiano, representando um perfil bioquímico característico em animais ruminantes. Assim, a partir da análise do perfil volátil do cerúmen é possível acessar assinaturas bioquímicas que mostram vias metabólicas específicas que podem ser exploradas para investigações clínicas e na compreensão dos processos evolutivos pelos quais humanos e bovinos passaram.

[1]Gisele A. B. Canuto et al. Metabolômica: definições, estado-da-arte e aplicações representativas, Quim. Nova, Vol. 41, No. 1, 75-91, 2018. https://doi.org/10.21577/0100-4042.20170134

[2]Engy Shokry, Nelson Roberto Antoniosi Filho. Insights into cerumen and application in diagnostics: past, present and future prospective. Biochem Med (Zagreb) 2017;27(3):030503. https://doi.org/10.11613/BM.2017.030503

Agradecimentos/Acknowledgments

UFG, FUNAPE, FUNADAÇÃO RTVE, MCTI, FINEP, ANP, LAMES.

Área: ANA

A straightforward approach for copper determination in fish samples by direct solid sample analysis and graphite furnace atomic absorption spectrometry

Matheus F. Filgueiras (PG),[1]* Jefferson S. de Gois (PQ).[1]

matheus.filgueiras@ppgeq.uerj.br

[1]*Programa de Pós-graduação em Engenharia Química, Instituto de Química, UERJ – Campus Maracanã.*

Palavras Chave: Environmental samples, Sample preparation, Atomic spectrometry.

Highlights

A new method was developed for the determination of Cu in fish samples through direct solid sample analysis and graphite furnace atomic absorption spectrometry. The method was applied for monitoring Cu in fish samples collected in the state of Rio de Janeiro.

Resumo/Abstract

Fish tissues can be used to monitor the presence of potentially toxic elements in aquatic systems. Among the toxic elements, Cu has an important role in biological systems, however, it can be dangerous in high concentrations. Copper contamination can occur from different sources such as antifouling coating of boat shell, domestic and industrial effluents and residues of coal combustion. Therefore, monitoring Cu in fish samples may be an important task that can be accomplished by the use of graphite furnace atomic absorption spectrometry (GFAAS). In this work, glass capillary tubes were used as a lab-made solid sampling device to directly quantify Cu in powdered fish samples by a line source GFAAS, with high sensitivity and selectivity. The accuracy of the method was assessed by the analysis of two different certified reference materials: one of fish muscle (ERM-BB422, certified Cu concentration value 1.67 ± 0.16 mg kg^{-1}) and a fish protein certified reference material (DORM-5, certified Cu concentration value 3.3 ± 0.07 mg kg^{-1}). Finally, seven fish samples (*corvina, viola, atum, cação, congro rosa, sardinha and pescada*) were collected in Rio de Janeiro, Brazil, and analyzed by the proposed method. The fish samples were dried at 95 °C up to 72h and pulverized using an electric mill. Mass aliquots from 0.1 to 1.1 mg were weighted into glass capillary tubes, subsequently the hook line was used to push samples and inject in graphite furnace, manually. All determinations were performed at 324.8 nm. Pyrolysis and atomization temperatures were optimized without the use of chemical modifiers, the optimal conditions were achieved at 1100 °C (pyrolysis) and 2400 °C (atomization). External calibration using an aqueous solution showed similar sensitivity as the solid calibration using certified reference materials. The limits of detection and quantification obtained were 0.11 ng g^{-1} and 0.03 ng g^{-1}, respectively. The analysis of fish samples collected in Rio de Janeiro presented the following results: 0.95 ng g^{-1} for *viola* (RSD = 12%), 0.56 ng g^{-1} for *atum* (RSD = 32%), 0.99 ng g^{-1} for *cação* (RSD = 11%), 0.98 ng g^{-1} for *congro rosa* (RSD = 10%), 1.12 ng g^{-1} for *pescada* (RSD = 10%) and 2.01 ng g^{-1} for *sardinha* (RSD = 4%). The proposed solid sampling method demonstrated to be very sensitive, straightforward, simple, reliable, and has a low risk of contamination.

Agradecimentos/Acknowledgments

UERJ, FAPERJ, CAPES and CNPq.

Área: ANA

A Synergystic Approach for Small-Molecule Detection: Molecularly Imprinted Polymers, Electrolytic Transistors, and Machine Learning Integration

Gabrielle Coelho Lelis (IC),[1] Wilson Tiago Fonseca (PQ),[1] Alessandro Henrique de Lima (PG),[1] Anderson Kenji Okazaki (PQ),[1] Eduardo Costa Figueiredo (PQ),[2] Antonio Riul Junior (PQ),[3] Gabriel Ravanhani Schleder (PQ),[1,4] Paolo Samorì (PQ),[5] Rafael Furlan de Oliveira (PQ)*.[1,3]

Gabrielle.lelis@lnnano.cnpem.br ; Rafael.furlan@lnnano.cnpem.br

[1]*Brazilian Nanotechnology National Laboratory (LNNano), Brazilian Center for Research in Energy and Materials (CNPEM), Campinas, SP*

[2]*Faculty of Pharmaceutical Sciences, Federal University of Alfenas, Alfenas, MG, 37130-001, Brazil*

[3]*Universidade Estadual de Campinas, Instituto de Física Gleb Wataghin, Campinas, SP, 13083-859, Brazil*

[4]*John A. Paulson School of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts 02138, United States*

[5]*université de Strasbourg, CNRS, ISIS, Strasbourg 67000, France*

Palavras Chave: *Point-of-Care Sensors, Diagnostics, Molecularly Imprinted Polymers, Hippuric Acid, Electrolyte-Gated Transistors, Machine Learning.*

Highlights

Molecularly Imprinted Polymers and Electrolyte-Gated Transistors on Reduced Graphene Oxide for hippuric acid detection. Stable, sensitive, and selective platform.

Resumo/Abstract

Small molecules play a crucial role as biomarkers in various diseases and are present in physiological fluids like urine, blood, and saliva [1]. However, detecting and quantifying these molecules become challenging in complex media, especially physiological fluids, particularly at low concentrations in the micro- and nanomolar range [2]. The objective of this research was to create a platform that synergistically combines molecularly imprinted polymers (MIPs) and electrolyte-gated transistors (EGTs) based on reduced graphene oxide (rGO) to ensure reproducibility and selectivity in detecting small molecules in complex environments. The target analyte was hippuric acid (HA), a disease biomarker [3]. This approach can potentially advance healthcare technologies by enabling precise and highly sensitive point-of-care (PoC) diagnostics for small-molecule biomarkers in challenging contexts. In this study, we assessed the characteristics of the rGO film on the device channel before conducting sensing experiments, confirming operational stability through consistent retracing of transfer curves during consecutive scans in KCl 1mM. The device demonstrated stability, especially in the channel current, making it suitable for sensing experiments. It also showcased sensitivity and selectivity to hippuric acid (HA), as indicated by linear responses in standard HA solutions. Remarkably, the device maintained excellent performance against a wider range of HA concentrations even after two months of storage. Machine learning (ML) analysis of the sensor response using principal component analysis provided accurate predictions of HA concentrations. The produced device displayed low operating voltages (<0.5V), rapid response times (≤10s), and effective operation across a broad range of HA concentrations (from 0.05 to 200 nmolL^{-1}). Additionally, it demonstrated a low limit of detection (LoD) of 39 pmol L^{-1}. ML multivariate analysis showed a 2.5-fold improvement in device sensitivity (1.007 μA/nmolL–1) compared to human data analysis (0.388 μA/nmolL^{-1}). This comprehensive assessment highlights the robustness and efficacy of the device, showcasing its potential for precise and highly sensitive point-of-care diagnostics for small-molecule biomarkers in challenging contexts.

[1]Sim, D.; Brothers, M. C.; Slocik, J. M.; Islam, A. E.; Maruyama, B.; Grigsby, C. C.; Naik, R. R.; Kim, S. S. Biomarkers and Detection Platforms for Human Health and Performance Monitoring: A Review. Adv. Sci. 2022, 9, 2104426.

[2] Magdalena Pisoschi, A.; Iordache, F.; Stanca, L.; Ionescu Petcu, A.; Purdoiu, L.; Ionut Geicu, O.; Bilteanu, L.; Iren Serban, A. Comprehensive Overview and Critical Perspective on the Analytical Techniques Applied to Aflatoxin Determination- A Review Paper. Microchem. J. 2023, 191, 108770.

[3] Pelletti, G. Toluene Abuse: A Medicolegal Perspective. Handbook of Substance Misuse and Addictions: From Biology to Public Health 2022, 2591−2609.

Agradecimentos/Acknowledgments

Financial support from the Sao Paulo Research Foundation FAPESP, CNPq, and SisNANO Programme.

Área: ANA
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Biodiesel como solvente verde em microextração líquido-líquído dispersiva

Samara Soares (PQ), Fábio R.P. Rocha (PQ)

soaressamara@usp.br

Centro de Energia Nuclear na Agricultura, Universidade de São Paulo, Laboratório de Química Analítica "Henrique Bergamin Filho", Av. Centenário, 303, 13416-000, Piracicaba, SP

Palavras-Chave: *Digital image photometry; smartphone; green chemistry*

Highlights

- Biodiesel as a solvent for liquid-liquid microextraction
- Environmentally friendly solvent suitable for dispersive liquid-liquid microextraction
- Analytical alternative exploiting digital-image photometry

Resumo

O biodiesel é um combustível proveniente de fontes renováveis, como óleos vegetais (principalmente óleos de soja e de algodão) e gordura animal, composto por ésteres alquílicos de ácidos carboxílicos de cadeia longa (e.g. $C_{20}H_{38}O_3$), o que o caracteriza como um líquido apolar. Devido à produção em larga escala e à baixa toxicidade, o biodiesel pode ser uma alternativa aos solventes tóxicos geralmente usados em extrações líquido-líquido e sólido-líquido (e.g. clorofórmio, metanol, hexano, acetona e acetato de etila). Neste contexto, o biodiesel foi explorado como um solvente extrator verde na microextração líquido-líquido dispersiva de analitos modelo com diferentes polaridades: cristal violeta < verde de bromocresol < 1-(2-piridilazo)-2-naftol (PAN). Biodiesel também foi avaliado na extração de potenciais contaminantes de alimentos, como Cu(II) e Al(III), que foram extraídos na forma de complexos com PAN e quercetina, respectivamente. As medidas analíticas (intensidade de radiação refletida) foram baseadas em fotometria por imagens digitais, utilizando o *smartphone* Samsung S22 equipado com câmera de 10 megapixels (abertura da lente f/2.4). Fatores de enriquecimento (FE), coeficiente de partição (log *P,* determinado em biodiesel/água a 25º C), e eficiência de extração foram estimados para avaliar a aplicabilidade do biodiesel como solvente extrator. Os valores de log *P* foram de –0,45 (pH 2,0) para cristal violeta, –1,3 (pH ,.0) para verde de bromocresol, 1,05 para PAN 3,48 para o complexo Cu(II)-PAN e 2,14 para o complexo Al(III)-quercetina. O biodiesel não foi eficiente para extrair espécies mais polares, com FE e eficiência de extração de (1,04 e 26% para cristal violeta, 1,01 e 5% para verde de bromocresol), mas foi adequado para as espécies apolares (2,21 e 90% para o PAN, 4,66 e 99%, e 5,73 e 99% para os complexo Cu(II)-PAN e Al(III)-quercetina). Foram construídas curvas de calibração e avaliadas as recuperações, utilizando o complexo Cu(II)-PAN como produto modelo, e o biodiesel, clorofórmio e acetato de etila como solventes extratores. Os coeficientes angulares (CAs) obtidos para as curvas de calibração construídas com diferentes tipos de biodiesel, produzidos com 100% de óleo de soja (S = **48,7**C + 6,4; r = 0,999), 90% de óleo de soja e 10% de óleo de algodão (S = **42,2**C + 7, 9; r = 0,997) e 70% de óleo de soja e 30% de gordura animal (S = **42,2**C + 12,0; r = 0,997) foram semelhantes ao CA da curva construída com acetato de etila (S = **45,0**C + 19,6; r = 0,999) e *ca.* 50% superior ao CA obtido com o clorofórmio (S = **32,9**C + 11,2; r = 0,999). Foram estimadas recuperações de 95 a 114% (biodiesel), 96 a 114% (acetato de etila) e 65 a 114% (clorofórmio). O procedimento requer apenas 300 µL de biodiesel, 300 µL de etanol, 5 mL de solução de referência ou amostra e gera apenas 5,6 mL de resíduo (composto majoritariamente por água) por determinação. Os resultados indicam a potencialidade do biodiesel como alternativa verde para substituir solventes orgânicos tóxicos utilizados nas análises de alimentos e ambientais.

Agradecimentos

INCTAA, FEALQ, FAPESP, CNPq e CAPES

Can firearms be identified through the analysis of residue? Exploring the forensic microtraces combining techniques SEM/EDS and chemometrics.

Milena D. da C. Sousa (PG),[*1,3] Caio H. P. Rodrigues(PQ),[2,3] Jesus A. Velho(PQ),[1,2,3,4] Michele A. dos Santos(PQ)[4], Luciana L. Schimidt(PQ)[4], Aline T. Bruni (PQ)[1,2,3]

milenadantasc@usp.br

[1] *Programa de Cooperação Acadêmica – Segurança Pública e Ciências Forenses (PROCAD-SPCF)*
[2] *Instituto Nacional de Ciência e Tecnologia Ciências Forenses (INCT-Forense),*
[3] *Departamento de Química, Faculdade de Filosofia, Ciências e Letras de Ribeirão Preto- Universidade de São Paulo.*
[4] *Instituto Nacional de Criminalística (INC), Polícia Federal.*

Keywords: *Gunshot Residuals, MEV/EDS, Statistical evaluation*

Highlights

The research focuses on the analysis of gunshot residues in fabrics as a means of identifying weapons used in incidents. SEM/EDS analised the residues to identify elements deposited after the gunshot.
The study demonstrated that it was possible to differentiate between weapons using descriptive statistics and chemometric analyses.

Resumo/Abstract

According to the 2023 Brazilian Public Security Yearbook, in 2022, Brazil recorded 47,452 intentional violent deaths, and 76.5% of these cases occurred through firearms. Violence and death through guns represent a significant challenge for many societies around the world, deeply impacting communities, families, and individuals. When a gun is fired, a considerable amount of gaseous or solid phase material is produced and expelled along with the projectile. These are called gunshot residue (GSR). The present study aims to identify the elements deposited on the cotton fabric after the shot, intending to identify the weapon that originated them. We used three gun models (9mm, 357, 38) to obtain spectra and fired three shots for each. Eight fields were randomly selected from each shot, and three points were analyzed for each field. The average concentration of the elements was used. One hundred twenty samples were obtained, of which 24 were obtained by specialist A, 24 by specialist B with the 9mm gun, and 72 by specialist C with the three study weapons. The work is still under development, and we intend to increase the number of firearms. As variables, we have the five majority elements identified (Pb, Cu, O, C, Sb) at each point. This made it possible to create a matrix that included 120 samples and five variables. Figure 1 illustrates the design of the experiment. After constructing this initial matrix, several statistical analyses were carried out using the Pirouette software for exploratory analyses without pre-processing the samples.Two exploratory approaches were carried out using the average obtained in each field: Pearson correlation coefficient with heatmap analysis (univariate) and principal components analysis (PCA) (multivariate). The Pearson correlation results indicated that the strongest correlation is between .357 and .38 caliber firearms, with a coefficient of 0.80, followed by the relationship between 9mm pistols and .357 caliber revolvers, with a coefficient of 0.73. The correlation between 9mm pistols and .38 caliber revolvers is the weakest, at 0.38. The results of the multivariate analysis show a cluster related to .38 caliber firearms, although a clear separation between 9mm pistols and .357 caliber revolvers were not achieved. Furthermore, a multivariate classification technique, Soft Independent Modeling of Class Analogy (SIMCA), was applied. We concluded that the model demonstrated an accuracy of approximately 79%. In conclusion, we showed that the research design used to distinguish firearms through GSR analysis presented a reasonable development. However, further improvements can be applied to overcome sources of uncertainty and achieve better accuracy.

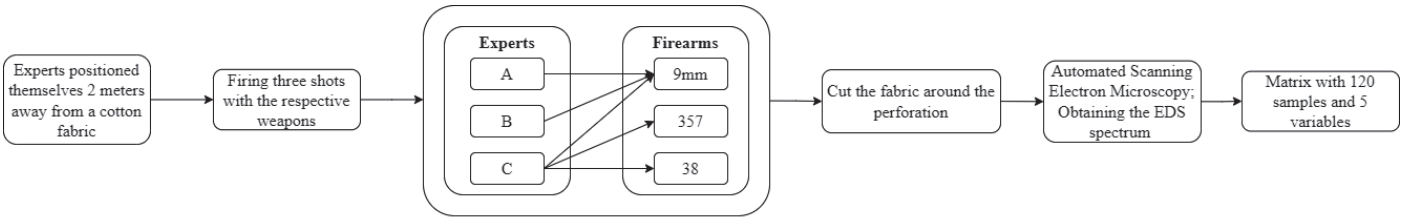


Figure 1. Flowchart representing the data collection steps

Acknowledgments

Conselho Nacional de Desenvolvimento Científico e Tecnológico: Grants: 465450/2014-8, 104496/2023-1. Coordenação para o Aperfeiçoamento de Pessoal de Nível Superior PROCAD-SPCF/CAPES 16/2020 - process 88887.613955/2021-00. Instituto Nacional de Criminalística (INC), Polícia Federal.

Área: ANA

Carbon quantum dots obtained from p-phenylenediamine as a chemical sensor: evaluation of chromium in commercial dietary supplements

Thyago Marques Monteiro (TM),[1] Gilvan Pozzobon Pires (PQ),[2] Kátia Messias Bichinho (PQ) [2*]

katia@quimica.ufpb.br; **thyago_mm@hotmail.com**

[1]*Departamento de Engenharia Química, UFPB;* [2]*Departamento de Química UFPB*

Palavras-chave: *Pontos de Carbono Luminescentes, Picolinato de cromo(III), Suplementos Alimentares, Fluorimetria, Fluorescência de raios-X.*

Highlights

- Red emission of carbon quantum dots with a quantum yield of 11.3%
- Carbon quantum dots for analytical quantification of chromium in food supplement
- X-ray fluorescence spectrometry as a potencial reference method supplements

Abstract

In the present work, we developed luminescent carbon quantum dots (CQD) for the analytical determination of chromium in commercial food supplements. For this purpose, CQD were synthesized by the solvothermic method using ethanol from p-phenylenediamine as a precursor. The CQD obtained was purified in a chromatographic column and characterized by transmission electron microscopy, Fourier Transform Infrared Absorption Spectroscopy, X-ray Excited Photoelectron Spectroscopy, UV-Visible Spectroscopy as well as luminescence spectroscopy. The CQD obtained showed intense emission in red color, presenting a quantum yield equal to 11.3%. The characterizations carried out allowed to relate the observed emission to the carbon point surface characteristics, such as the content of chemical species containing oxygen and the presence of carboxylic groups. The qualitative Energy Dispersive X-ray Fluorescence Spectroscopy (EDS) revealed a similar chemical composition of the samples with lower amounts of Cr, Si, S, traces of K, Fe, Cu in all three samples, Ti in samples 2 and 3, and Br in sample 1. The pH study of nanoparticles dispersed in water showed strong suppression of fluorescence between 1.5 to 3.0 and signal stability between 3.5 and 10.0, decreasing again at pH 11.0. Thus, the fluorimetric measurements were performed in a pH 7.0 medium for the quantification of chromium content. A linear response between 4,0 and 20 mg L^{-1} of chromium ions was obtained by suppressing the fluorescence of the CQD, probably related to the internal filter effect, being I = 0.0134 (±0.0072) + 0.0019 (±0.0005) × [chromium content], where I is the signal intensity obtained, r^2 = 0.9975 (n=3), with detection and quantification limits equal to 0.05 mg L^{-1} and 0,179 mg L^{-1}, respectively. The samples were prepared by acid digestion with aqua regia, under heating, at a ratio of 1 mL of the acid solution for every 100 mg of sample. After digestion, the pH of the solution was adjusted to 7.0. For the quantification of chromium, an aliquot of 250 µL of the CQD solution (17.5 mg L^{-1}) was added to 250 µL of each sample solution, ensuring a contact time of the mixture equal to 5 minutes. Subsequently, fluorimetric analyses were conducted. The chromium content in the three samples analyzed ranges from 0.197 to 0.387 mg L^{-1}, with the values determined being higher than the nominal value described on the product label for sample 1, and lower for samples 2 and 3. The statistical analysis comparing the mean values of chromium in the samples, for a confidence level of 95%, indicates that there is no significant difference between the proposed method when compared to the EDS method, for the determination of chromium ions in chromium(III) picolinate supplement samples. These results enhance the importance of more effective control of the quality of dietary supplements commercialized in Brazil by Brazilian Health Regulatory Agency.

Acknowledgments

The authors would also like to thank the Brazilian agencies Capes and CNPq for research fellowships and scholarships. We also thank to the Physics Institute of UFRGS for conducting the XPS analyses, and to the Laboratory of Automation and Instrumentation in Analytical Chemistry/UFPB where this study conducted.

Área: ANA

Characterization of the FAMEs profile by GC-MS for biodiesel production from *Carthamus tinctorius L.* seed oil

Lilian F. de Oliveira (IC),[1]* Aline M. Aguiar (IC),[1] Dayane C. da Costa (PD),[1] Juliana E. Lichston (PQ),[2] Nelson R. A. Filho (PQ)[1]

lilianfernandesoliver@gmail.com

[1]Instituto de Química – Laboratório de Métodos de Extração e Separação, UFG; [2]Departamento de Botânica, Ecologia e Zoologia – Centro de Biociências, UFRN

Palavras-Chave: *Óleo de cártamo, Ésteres metílicos de ácidos graxos, Transesterificação, Biodiesel, Cromatografia gasosa.*

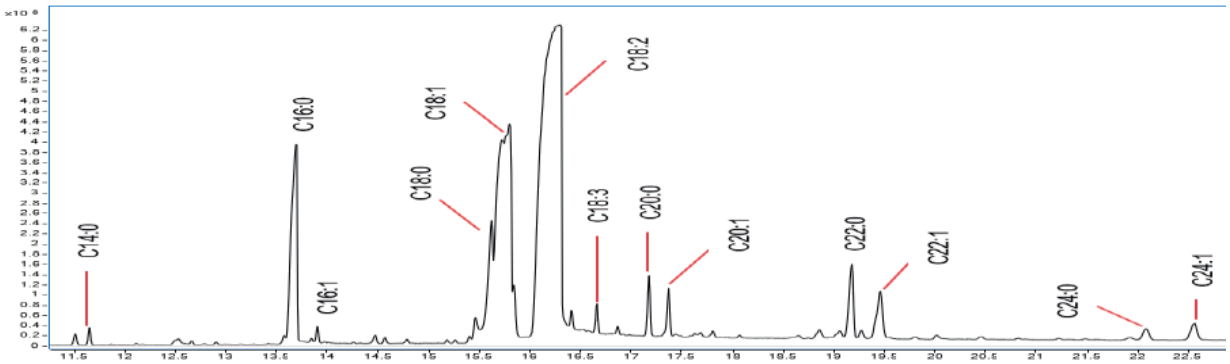
Highlights

Safflower is a species of oilseed adapted to the semi-arid northeastern region of Brazil. This work evaluates whether the fatty acids in Safflower seed oil are suitable for biodiesel production.

Resumo/Abstract

Os diversos impactos socioambientais resultantes do uso de combustíveis fósseis têm levado a busca pelo uso de biocombustíveis, em especial etanol e biodiesel. Nesse contexto, visando atender a enorme demanda de combustíveis de motores do ciclo diesel, combustíveis provenientes de biomassa, como o biodiesel, se tornaram parte da política energética de vários países em ordem de amenizar problemas no setor energético.[1] Visando impulsionar a produção de biodiesel no semiárido nordestino, diversas espécies oleaginosas estão sendo avaliadas naquela região, sendo que o *Carthamus tinctorius* L se mostrou uma das mais promissoras. Dessa forma, o objetivo desse trabalho é analisar a aplicabilidade dessa matriz oleaginosa como fonte de biodiesel ao empregar a caracterização do óleo extraído via sistema Soxhlet das sementes da espécie *Carthamus tinctorius L.,* a partir da identificação dos ésteres metílicos de ácidos graxos (FAMEs) obtidos por processo de transesterificação direta pelo método de Hartman e Lago adaptado para microescala, com separação e identificação via cromatografia gasosa (GC) e espectrometria de massas (MS). O cromatograma obtido para a análise de FAMES do óleo de semente de Cártamo é apresentado na Figura 1. Obteve-se teores de ácidos graxos saturados (19,2%), monoinsaturados (26,5%) e somatória de di- e tri-insaturados (54,3%) similares aos apresentados pelo óleo de Soja (respectivamente, de 15,9%, 25,9% e 58,4%),[2] sendo esse último a base para a produção brasileira de biodiesel. Dessa forma, esse trabalho demonstra que o Cártamo, uma das poucas oleaginosas comprovadamente adaptáveis à região semiárida nordestina do Brasil, pode ser utilizado como matéria-prima graxa para a produção de biodiesel, o qual deverá receber, tal como o biodiesel de soja, a adição de ácidos graxos saturados oriundos de outras fontes graxas como gorduras vegetais (palmáceas) ou animais (sebo bovino), e/ou antioxidantes, visando melhorar a estabilidade oxidativa do biocombustível baseado em óleo de Cártamo.

Figura 1. Cromatograma (GC-MS) dos FAMEs do óleo de semente de Cártamo.



1. Vieira, M. G., Batista, L. R., Muniz, A. S., Lichston, J. E., Oliveira, A. R. S., César-Oliveira, M. A. F., & Filho, N. R. A. (2021). Synthesis of antioxidant additive from safflower seed oil. *Journal of the Brazilian Chemical Society*, *32*(1), 40–46. https://doi.org/10.21577/0103-5053.20200151.
2. Howard, K. A., Forsyth, D. M., Cline, T. R. The effect of an adaptation period to soybean oil additions in the diets of young pigs. *Journal of Animal Science,* 68(3):678-83. DOI: http://dx.doi.org/10.2527/1990.683678x.

Agradecimentos/Acknowledgments

IQ-UFG, LAMES, FUNAPE, UFRN.

Área: ANA

CHEMICAL ANALYSIS OF CERAMIC FRAGMENTS: an archaeometric study using X-ray fluorescence (XRF)

Larissa S. Vieira (IC),[1*] Morgana Cavalcante Ribeiro (PG)[2], Alencar de Miranda Amaral (PQ),[2,3] Benedito B. F. Filho (PQ)[4], Éverton L. F. Ferreira (PQ)[1]

larissa.silvavieira@discente.univasf.edu.br

[1]Colegiado de Licenciatura em Química, UNIVASF; [2]Departamento de Arqueologia, UFPE, [3]Colegiado de Arqueologia e Preservação Patrimonial, UNIVASF; [4]Departamento de Química, UFPI

Keywords: *Archaeometry, Ceramic, X-ray fluorescence, Elemental analysis.*

Highlights

Rescue archaeology in Bahia protects Canaã artifacts from dam flooding, unveiling ancient manufacturing insights. Elemental analysis reveals - Al, Si, Cl, Fe - connecting raw materials to ancient ceramics at Canaã site.

Resumo/Abstract

The use of analytical techniques to study traditional archaeological artifacts, such as ceramic fragments, human remains, lithic materials, and cave paintings, constitutes the primary focus of archaeometry. Notably, X-ray fluorescence (XRF) and Raman spectroscopy stand out for being non-destructive techniques. In this study, ceramic fragments were collected at the Canaã site in Bahia through a rescue operation, prompted by the imminent threat of destruction with the closure of the gates of the Rio Colônia Dam causing the flooding of the hydraulic basin. The selected ceramic fragments, **c-69-31**, **c-87-08**, and **c-113-9** in this study, belong to the same classificatory unit. The first two were extracted from the same layer (10 cm), while the latter was retrieved from the 40 cm layer. Initially, the fragments underwent in situ analysis using a handheld portable optical microscope (Handheld ProScope CSI) to identify interferents such as antiplastics. Following the analysis, points deemed more homogenous, devoid of interferents, were chosen for X-ray fluorescence analysis (Thermo Fisher Scientific, model Nilton XL3t Ultra portable) to determine the elemental chemical composition. All fragments underwent analysis at three points (internal, external, and core). The results of semi-quantitative measurements obtained by portable XRF pertain solely to the major chemical elements detected in the analyzed samples. As depicted in **Figure 1**, the predominantly identified elements were Al, Si, Cl, Fe, Ar, K, Ca, and Ti. Additionally, traces of P, S, and Mn were identified. The chemical analysis results support the hypothesis that the presence of these elements may be attributed to the type of raw material used in their fabrication, such as antiplastics, clays, spices, pigments, and resins, as well as the firing technique and duration. In a previously conducted analysis, it was suggested that the ceramic fragments found at the Canaã site were employed in food preparation. Consequently, the presence of graphite was identified in some fragments. The graphite presence may be associated with the technique used in the preparation of ceramic vessels. Therefore, an analysis utilizing Raman spectroscopy and X-ray diffraction (XRD) of the pieces mentioned in this study will be conducted to verify the presence of graphite in their composition.

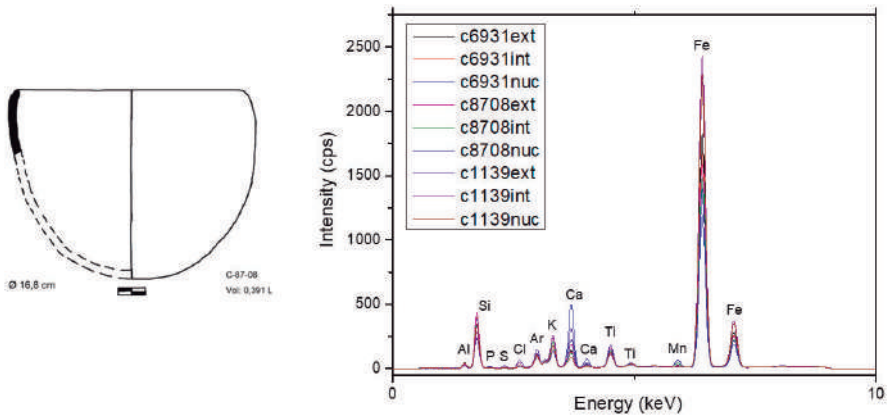


Figure 1. Representation of ceramic fragment **c-87-08** and X-ray fluorescence analysis.

Acknowledgments

The authors would like to express their gratitude to EMBASA and IPHAN for authorizing the analysis of the ceramics.

Área: ANA

Chemometric evaluation using pixel-based approach in Brazilian crude oils from the Santos Basin by GC×GC-TOFMS

Mônica C. Santos (PD),[1] Manoel M. Alves Junior (IC),[1] Dayane M. Coutinho (PQ),[1] Clarisse L. Torres (PQ),[1] Michele F. de Resende (PD),[1] Vinícius B. Pereira (PG),[1] Daniel S. Dubois (PQ),[2] Joelma P. Lopes (PQ),[2] Francisco R. Aquino Neto (PQ),[1] Débora A. Azevedo (PQ).[1*]

mcs@iq.ufrj.br; debora@iq.ufrj.br*

[1]*Universidade Federal do Rio de Janeiro, Instituto de Química, LADETEC, Ilha do Fundão, Rio de Janeiro, RJ 21941-598, Brazil*
[2]*Petrobras, CENPES/PDIEP/GEOQ, Cidade Universitária, Ilha do Fundão, Rio de Janeiro, RJ 21941-915, Brazil*

Keywords: *crude oils, GC×GC-TOFMS, pixel-based, chemometrics.*

Highlights

The pixel-based approach provides a chemical evaluation of 800 compounds between 13 crude oil GC×GC fingerprints, ranging from *n*-C_5 to *n*-C_{12}.

Abstract

Target petroleum analysis using comprehensive two-dimensional gas chromatography (GC×GC) has been widely used for individual identification and group-type analysis. However, in some cases, the non-target analysis is more favorable and less time-consuming, especially when dealing with GC×GC data.[1] Among the approaches to treat GC×GC data, the pixel approach makes it easier for the analyst to explore regions or compounds in the two-dimensional chromatogram that are important for comparing several sets of complex mixtures using chemometrics tools.[2] This study employed the pixel-based approach to discriminate hydrocarbon compounds in Brazilian crude oils from the same field and different wells. Principal component analysis (PCA) was applied to discover class-distinguishing analytes in the structured chromatograms that could show subtle discriminations between wells from the same field but from different geographic positions. The analyses were performed on a GC×GC–TOFMS system (Pegasus 4D, Leco, St. Joseph, MI, USA). All data analysis was performed under MATLAB (R2023b, The Mathworks, MA, USA, 2023) numerical computing, visualization, and programming environment. PLS Toolbox 9.2 (Eigenvector Research Ltd., Manson, WA, USA) was used for chemometric data analysis. In this study, a set of 13 pre-salt crude oils were evaluated. Total ion chromatograms (TIC) were used to construct concatenated matrices. The aligned TIC was normalized before applying the exploratory analysis step. PCA results for 13 samples showed differentiation of the wells by geographic positioning (North, Center, and South) in PC1 (Figure 1A). The loading coefficients of C6, C7 and C8 hydrocarbons are positive and important to differentiate crude oils of North region (Figure 1B). The samples that present the lowest concentration of these target hydrocarbons are in the southern region of the oil field. The compounds that differentiated the samples are used in studies of light hydrocarbon ratios in reservoir geochemistry and are associated with the level of thermal maturation and type of source rock (Figure 1C). This approach streamlined data processing and the PCA methodology proved to be an interesting alternative for classifying crude oils.

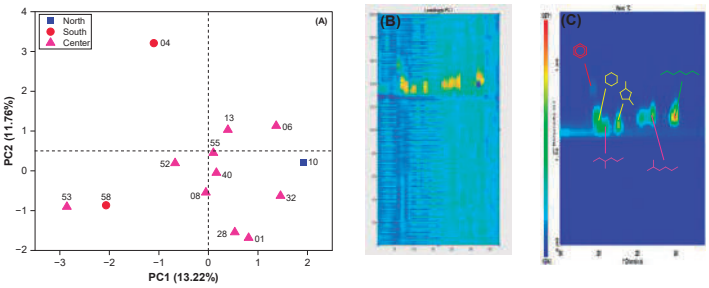


Figure 1. (A) Scores on PCA, (B) Loadings on PCA and (C) Expanded two-dimensional chromatogram showing the identified substances: benzene, cyclohexane, dimethylcyclopentanes.

[1]Vial, J., *et al.*, Talanta, 83 (4), 1295-1301, 2011.
[2]Castiblanco, J. E. B., *et al.*, Talanta, 268, 125343, 2024.

Acknowledgments

The authors thank CENPES-Petrobras for authorizing this study and providing the crude oil samples. We thank the financial support of Petrobras (no. 0050.0121394.22.9), CNPq, FAPERJ, and Capes (Finance Code 001).

Área: ANA_____
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Data analyis tools for e-tongues used to detect estrogen in tap water

Tiago Reis (PG)[1], Maria H. Fino (PQ)[2], Paulo A. Ribeiro (PQ)[1], Débora Gonçalves (PQ)[3], Maria Raposo (PQ)[1,*]

gdebora@ifsc.usp.br; mfr@fct.unl.pt

[1]Department of Physics, School of Science and Technology, Universidade Nova de Lisboa, Caparica, Portugal; [2]Department of Electrotechnical and Computer Eng, School of Science and Technology, Universidade Nova de Lisboa, Caparica, Portugal; [3]Institut of Physics of Sao Carlos, University of Sao Paulo, Sao Carlos-SP, Brazil;

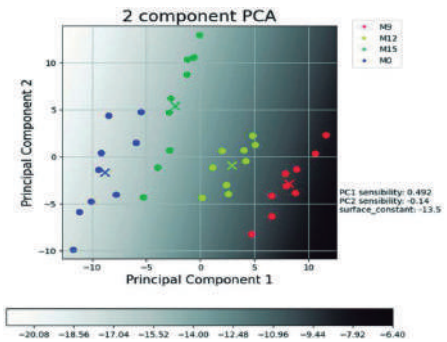
Palavras Chave: Electronic tongue, Sensors, Principal components analysis, Natural hormones, Estrogen.

Highlights

Development of e-tongue prototypes to detect natural estrogens in tap water. Preparation of interdigitated electrodes using graphene oxide, nanotube, and polyelectrolytes to obtain sensor arrays. Use of impedance spectroscopy to analyze electrical responses of sensors in estrogen solutions at different concentrations. Extract data of e-tongues for detection of estrogen via principal components analysis (PCA) method in a 3D plane. Electronic Tongues Data Analytics (ETDA) tool developed in Python to data evaluation and calibration using PCA for sensors of estrogen.

Resumo/Abstract

Effect-based screening methods are alternatives to detect low concentrations of estrogen; however, these protocols have their drawbacks- long incubation periods, cost and no real-time monitoring. Estrogen can be detected by sensing, and efficent e-tongues have shown portability, selectivity, sensitivity, fast response and recovery time. Sensorial arrays were developed using polyethyleneimine (PEI) or poly(allylamine hydrochloride) (PAH)/functionalized carbon multiwall nanotubes (mwcnt) or graphene oxide (GO) via layer-by-layer (LbL) with 5 bilayers on Au interdigitated electrodes (Metrohm DropSens) (Fig. 1). Under concentrations varying from 10^{-10}, 10^{-13}, 10^{-16}, and 0 mol/L, it was obtained calibration curves and detection limit of 10^{-16} mol L^{-1} of estradiol-17β. The impedance spectra were obtained using a Solartron 1260/1296A Dielectric Interface 1Hz to 1MHz. PCA analysis was applied to amplitude/phase or real/imaginary parts of impedance and loss tangent. The dataset obtained was condensed with PCA to obtain 3D plane vs. concentration, and heatmap with optimal calibration curve. A heatmap loss tangent was obtained for PAH/mwcnt and PEI/GO films with each concentration as 9 points, allowing to separate concentrations/regions, with calibration matching concentrations. A new procedure named ETDA tool was developed in Python in orde to data extraction, evaluation, and calibration. PCA was initially used to condense features into a 2D plane and visualize dataset from impedance spectra. All impedance values for each sensor were converted into variable data sets that were calibrated to predict concentration. This protocol allows one to assess most efficient sensors and obtain calibration plane based on different concentrations of estradiol-17β in tap water. ETDA tool proved to be a way of facilitating extraction of relevant features, generating and calibrating PCA for sensor arrays, minimizing effects of external variables on experimental data. In addtion, it helped to optimize performance of the sensor arrays with a significative number of data, in particular when it was necessary to calibrate the PCA after several experiments and by using different samples. The interdigitated electrodes proved to be capable of being achieved inexpensive real-time analysis, detecting low concentrations of estrogen with good reproducibility. Impedance spectra were obtained using arrays, named electronic tongues (e-tongues), when immersed in tap water containing different concentrations of estrogen: 10^{-15}, 10^{-12}, 10^{-9} and 0 mol L^{-1}. ETDA is a tool capable to assist with the development of any e-tongue system.



Agradecimentos/Acknowledgments

FCT-MCTES, PTDC/FIS-NAN/0909/2014, UIDB/04559/2020, UIDP/04559/2020 , Bilateral Project - *Deteção de Estrogénio um Contaminante Emergente em Corpos Hídricos* - Cooperação Transnacional_FCT (Portugal)-CAPES (Brazil), CAPES (Finance code 001) (88887.837887/2023-00), CNPq (402816/2020-0), FAPESP (2018/22214-6).

Área: ANA

Determination *in situ* of available phosphate in soils with digital imaging techniques

Stella Sales Macedo (IC)*[1] ; Expedito de Sousa Morais (PG)[1], Arnaldo Alves Cardoso (PQ)[1].

stella.macedo@unesp.br

[1]*Departamento de Química Analítica, Físco-Química e Inorgânica IQ-UNESP.*

Palavras-Chave: Spot analysis, *RGB, phosphate in soil, phosphomolybdenum blue, soil analysis.*

Highlights

A field colorimetric analyzer based on a digital image was developed to determine available phosphorus content in soil. The method involved a reaction of phosphorus with ammonium molybdate to produce the molybdenum blue.

Resumo/Abstract

The in situ determination of the macronutrient phosphorus is essential for agriculture, whether on a large scale or for family agricultural production. The method was developed to provide rapid, in situ data on phosphate levels in soil. Knowledge about the availability of macronutrients in the soil is crucial for farmers to manage the use of fertilizers efficiently. Excessive application of these inputs can cause economic losses and significant environmental impacts.

Initially, the reaction of phosphate with the formation of molybdenum blue was studied, aiming to find the best conditions for using digital images to analyze chemical signals. The intensity of the molybdenum blue color is directly related to the phosphate concentration. It is quantified through the RGB color space using a smartphone 12-megapixel camera with 4000x3000 pixel resolution and a 2x capture zoom IOS system (iPhone 13) to capture the images, which are subsequently processed by MATLAB software.

A titration microplate containing 24 wells of 3 milliliters each was attached to a photographic box. Having established the ideal conditions, the next step was to prepare an analytical calibration curve with concentration range of 0.15 to 1.00 mgP/L. It was found that channel R presented the best correlation between color intensity and standard phosphorus concentration in the solutions (Signal R = 0.34456*[$P_{(mg/L)}$] - 0.02034, R^2= 0.9634). The limits of quantification (LOQ) and detection (LOD) of the method were determined as 0.60 mgP/L and 0.18 mgP/L, respectively.

Three certified soil samples were used to establish the analytical parameters for analysis. The standard method used as a reference is a Shimadzu UV-1800 spectrophotometer. According to the student's t-test with a 95% confidence level, the results of the soil samples showed no significant difference between the standard method and the one proposed. The experimental results indicate that the proposed method has the potential to determine the concentration of available phosphorus in soils quickly.

Agradecimentos/Acknowledgments

S.S. Macedo would like to acknowledge FAPESP proc 2023/08034-3 and CNPq for the research grant PIBIC 9029.

Área: ANA

Determination of cadmium in makeup products using functionalized magnetic nanoparticles and FAAS

Milena Secco de Souza (IC) [1*], Ítalo Agnis Da Silva Gomes (IC) [1], Cristiane Dos Reis Feliciano (PG)[1*], Mariane Gonçalves Santos (PQ)[1].

Ítalo.gomes@sou.unifal-mg.edu.br; milena.souza@sou.unifal-mg.edu.br*

[1]*Institute of Chemistry, UNIFAL;*

Palavras Chave: *Makeup, Magnetic nanoparticles, FAAS, Cádmium.*

Highlights.

- This study proposed a new analytical method using dispersive magnetic solid phase extraction (DMSPE) with Fe_3O_4 nanoparticles functionalized with tetraethyl orthosilicate (TEOS) and Flame Atomic Absorption Spectrometry (FAAS) to determine cadmium in solid makeup samples.

Resumo/Abstract

The use of beauty products has increased over the years due to the search for a better appearance. Therefore, quality control and inspection policies are extremely important to ensure the safety of the final products. In the manufacturing process of solid makeup such as eyeshadows or blushes, to obtain the color, inorganic pigments such as iron oxide, titanium dioxide, copper, and chromium oxide are used. Heavy metals such as Cd may be unintentionally incorporated into the product during the production process because they can be present as contaminants in the used pigments[1]. Cadmium, an element of high toxicity for the human body, has a slow excretion (biological life of decades in the body) and can cause kidney damage and calcium absorption disorders[2]. In this sense, the proposition of new analytical methods, useful, cheap, and efficient, is necessary to monitor the levels of Cd in many products. The use of magnetic nanoparticles has great potential related to the sample preparation for analysis in complex matrices, such as makeup products, since this material has an extensive surface area, the possibility of surface functionalization, and its magnetic properties allow its recovery at the end of the processes. Thus, this work proposes the development of a new method for the determination of Cd in solid makeup, through the use of magnetite nanoparticles functionalized with tetraethyl orthosilicate (TEOS) and flame atomic absorption spectrometry (FAAs). The synthesis of nanoparticles will be performed by the co-precipitation method[3]. Sample pH, sample volume, mass of adsorbent, adsorption time, desorption time, and elution solvent, were assessed and optimized using a fractional factorial design. The method was validated and demonstrated linearity in the range of 0.025 to 1.0 mg L^{-1}, with a correlation coefficient exceeding 0.99 and a quantification limit of 0.020 mg L^{-1}. Furthermore, the method exhibited good intra- and inter-day precision (RSD ranging from 7.95 to 12.64%) and accuracy (relative error ranging from -10.23 to 8.94%). The method was employed to analyze real solid makeup samples; however, no residues of cadmium were detected. Overall, this innovative method significantly improves the monitoring of cadmium levels in makeup products.

Referências/ References

1- Borowska, S.; Brozóska, M. M. **Journal of Applied Toxicology**. V. 35 p. 551-572, 2015
2- Oyetade et al. **Desalination and water treatment.** p. 253-267, 2018.
3- Cavalcanti, et al. Chemical Engineering Journal. V. 431 p. 134128, 2022.

Agradecimentos/Acknowledgments

CAPES, FAPEMIG, CNPQ.

Área: ANA

Determination of drug of abuse residues in breast milk by GC/MS for prevalence studies in human milk banks

Bruno Bernacchi[1,2] (PG), Maria C. de S. Paranhos[1] (IC), Livia A. P. Ferreira[1] (IC), Rafaella S. Aredes[1] (PG), Eliani Spinelli[2] (PQ), Flávia F. de C. Marques[1] (PQ)

bbernacchi@id.uff.br; flaviamarques@id.uff.br

[1]Laboratório de Química Analítica Fundamental e Aplicada,IQ/UFF; [2]Laboratório Toxfree, Faculdade de Farmácia/UFF

Key words: *Cocaine, Breast milk, Gas chromatography, Human milk bank*

Highlights

Chromatographic determination of cocaine residues in breast milk to contribute to the monitoring of the quality of milk donated to milk banks in Brazil, which is already a world reference.

Abstract

Breast milk is the best food for newborns because it has important nutrients, as well as anti-inflammatory components, agents that modulate immune function and hormones that are essential for their growth and development. However, disease-causing pathogens and drugs of abuse are transferred into breast milk and can be harmful to babies. Cocaine (COC), for example, due to its nonpolar and alkaline characteristics (pKa = 8.6), is easily transported and stored in breast milk, and can expose infants to its harmful effects. [1] Milk banks in Brazil do not perform chemical analysis to detect drug residues in samples, as during the donors' anamnesis the use of drugs of abuse is accessed through self-declaration. Thus, this work aims to develop/implement an analytical method, based on gas chromatography with mass spectrometry detection (GC/MS), which will allow: **(i)** the determination of COC residues and derivatives (cocaethylene - EC, and anhydroecgonine methyl ester - AEME) in breast milk; **(ii)** application of the method in the evaluation of samples obtained from human milk banks, preserving the anonymity of the mothers, **(iii)** to estimate the prevalence of these substances in donated milk. From this analysis, it will be possible to consider whether or not there is a need to implement a screening of drugs of abuse in these banks. All donors will fill out a Free and Informed Consent Form, already approved by the Research Ethics Council of UFF. Using a CG-Agilent Technologies 789 A gas chromatography, coupled to the MS-Agilent Technologies 5975 C mass spectrometer, equipped with an HP – 5MS IU column (0.25 mm x 0.25 µm x 30 m), the following instrumental parameters were applied: helium as a transport gas with a flow rate of 1 mL/min, 2.0 µL of sample injection with 3 pumps, syringe cleaning performed 10 times in dichloromethane and then in ethyl acetate, liner with silanized glass wool, injector temperature at 280 ºC, with oven heating ramp (starting at 70 ºC and ending at 300ºC). [2] The running time of 12.5 min allowed the separation and detection of ions with the following m/z ratios: COC (303, 198.2 and 182.2), COC-D3 (306.1, 201.2 and 185), CE (317.2, 272.1 and 196.2), CE-D8 (325.2, 274.8 and 204.2) and AEME (181.1, 165.9 and 152.2). Among the sample treatments studied, the one that showed the best recovery values (80-120%) used the following liquid-liquid extraction: **(a)** 0.5 mL of breast milk were transferred into an 2 mL-microtube; **(b)** addition or not (sample blank) of COC, COC-D3, EC, EC-D8 and AEME analytical standards; **(c)** acidification was performed with 50 µL of 1.0 mol/L HCl; **(d)** after centrifugation for 15 min at 13000 rpm, the aqueous phase was transferred to a new eppendorf tube; **(e)** 1.0 mL of 1:1 ethyl acetate:hexane mixture was added for sample cleaning; **(f)** after vortexing for 5 minutes, the samples were left torest for 5 minutes to reduce emulsion formation, and then the organic phase was discarded; **(g)** 100 µL of 1.0 mol/L NaOH, 100 mg of NaCl (salting-out) and 1.0 mL of ethyl acetate (extraction solvent) were added to aqueous phase; **(h)** after vortexing the tubes for 5 min, they were left to rest for 5 min; **(i)** the organic phase was transferred to a glass tube and evaporated to dryness under nitrogen at 45 ºC; **(j)** the dry residue was redissolved in 50 µL of ethyl acetate and an aliquot of 1 µL was injected in the GC-MS system. Using breast milk samples free from the drugs studied (donated by nursing mothers close to those responsible for the work), validation studies are being carried out contemplating linearity, limits of detection and quantitation, precision, accuracy and robustness.

[1] Cressman, A. M. et al. Maternal cocaine use during breastfeeding. Canadian Family Physician, v. 58, 2012.

[2] Winecker, R. E. et al. Detection of Cocaine and Its Metabolites in Breast Milk. Journal of Forensic Sciences, v. 46(5), 2001.

Acknowledgments

FAPERJ (E-26/200.523/2023), PIBIC-UFF, CNPQ, Hospital Universitário Antônio Pedro (HUAP)

Determination of formaldehyde in milk samples using gas-diffusion microextraction and lab-made 3D-printed photometer

Gabriel B. Piassalonga (PG)[1], Juliana C. Pinho (IC)[1], Karen C. Ferreira (PG)[1], Paulo C. F. de Lima Gomes (PQ)[1].

gabriel.baroffaldi@unesp.br

[1]*Department of Analytical Chemistry, Physical Chemistry and Inorganic Chemistry, National Institute for Alternative Technologies of Detection, Toxicological Evaluation and Removal of Micropollutants and Radioactives (INCT-DATREM), Institute of Chemistry, São Paulo State University (UNESP), Araraquara, São Paulo, Brazil*

Keywords: Formaldehyde, Extraction, Milk, GDME.

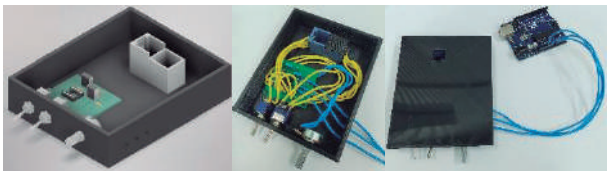
Highlights

GDMEs are devices that capture the volatilized analyte and react with a separate derivatizing agent in a gas-permeable membrane in an easy and inexpensive way. The filter used in this work, PTFE tape, further reduces the cost per analysis.

Resumo/Abstract

Formaldehyde is a carcinogenic substance present in various everyday products [1]. The method used by MAPA in milk analysis is time-consuming and high-cost, using a reagent in a medium with 72% sulfuric acid. 3D printing is a manufacturing technique that allows for rapid and low-cost prototyping of parts, and the use of LED as an emission source makes it possible to construct simple and small-sized photometers. To solve these problems, it is proposed to use gas-diffusion microextraction (GDME) for the extraction of the analyte and the use of a micro volume of derivatizing agent for colorimetric analysis in a low-cost photometer produced in a 3D printer. The first part of the work consists of optimizing the GDME using a fractional factorial design 2^{5-1} to identify the best extraction conditions of the analyte evaluating the following factors: extraction time, temperature, milk volume, pH, and salting-out. The chosen derivatizing agent was acetylacetone, using 500 µL of a 0.0196 mol L^{-1} solution in a buffered medium 2 mol L^{-1} sodium acetate pH = 10. The GDME was made in a 50 mL Falcon tube, formaldehyde concentration 25 mg L^{-1} in 25 mL of milk. The tested filter was PTFE tape (pipe tape) because it is easily accessible and low cost. The solutions were analyzed in a Shimadzu UV-1800 spectrophotometer. An analytical curve between 0.25 to 15 mg L^{-1} was produced, in triplicate, using optimized extraction conditions and analyzed in the spectrophotometer. And finally, an analytical curve was produced in an aqueous medium between 0.25 to 5.0 mg L^{-1} to demonstrate the operation of the printed photometer and compared with the commercial spectrophotometer. The photometer was produced using ABS filament, violet LED, photodiode, signal amplifier circuit, and Arduino Uno for the acquisition of the analytical signal. The best extraction conditions presented by the planning were: 55 minutes, 70 °C, 10 mL of milk, pH 3, and 0.5% NaCl. An analytical curve was made in milk using the GDME under these conditions, the data obtained in the commercial spectrophotometer, and presented the following equation: A = 0.0551[Formaldehyde] + 0.1764 and R^2 = 0.9964. Already using the printed spectrophotometer, the analytical curve obtained in water in the concentration range of 0.25 to 5.0 mg L^{-1} presented the following equation: A = 0.2084[Formaldehyde] + 7,500 x 10^{-3} and R^2 = 0.9996. The same analytical curve made in a commercial spectrophotometer had the following equation: A = 0.2472[Formaldehyde] - 3,200 x 10^{-3} and R^2 = 0.9999. The slope of the curves indicates the method sensitivity which for the printed spectrophotometer was less only 16 % lower than the commercial spectrophotometer. Therefore, the results show that it is possible to extract and quantize formaldehyde in milk with a low-cost photometer (estimated USD 25) which has performance similar to a commercial spectrophotometer and it is expected to increase sensitivity using a derivatizing agent that results in a reaction product with a color close to red.

Figure 1: Comparison between the CAD project and the built photometer



[1] Formaldehyde | NIOSH | CDC. (n.d.). Retrieved January 28, 2024, from https://www.cdc.gov/niosh/topics/formaldehyde/default.htm

Agradecimentos/Acknowledgments

This work has been supported by the following Brazilian research agencies: FAPESP(#2022/02991-3), INCT-DATREM #2014/50945-4, CNPq and CAPES.

Área: ANA

Determination of Polybrominated Flame Retardants in Sludge by Gas Chromatography with Electron Capture Detection using Magnetic Ionic Liquid

Letícia Maciel de Souza (IC)[1*], Iara Graciele da Silva[1] (IC), Thais Rodrigues (PG)[1], Paulo Clairmont Feitosa de Lima Gomes (PQ)[1]

leticia.maciel@unesp.br

[1]*Department of Analytical Chemistry, Physical Chemistry and Inorganic Chemistry, National Institute for Alternative Technologies of Detection, Toxicological Evaluation and Removal of Micropollutants and Radioactives (INCT-DATREM), Institute of Chemistry, São Paulo State University (UNESP), Araraquara, São Paulo, Brazil*

Palavras Chave: *Preparo de amostra, Solvente extrator, GC-ECD, PBDEs.*

Highlights

Preparation and use of magnetic ionic liquid as an extractor phase in sample preparation; Determination of polybrominated flame retardants in sludge samples.

Resumo/Abstract

The polybrominated diphenyl ethers (PBDEs), widely used as flame retardants, are identified as emerging contaminants in various environmental matrices, posing potential risks to human health and the environment. The growing awareness of the threats posed by these contaminants has driven the search for advanced analytical methods for their monitoring. Chromatographic techniques are essential for such analyses, require efficient sample preparation to minimize damage to equipment, eliminate interfering compounds, and enable the precise determination of analytes at levels ranging from µg L^{-1} to ng L^{-1} through sample preparation. Thus, this study aims to evaluate an innovative sample preparation approach, integrating dispersive liquid-liquid microextraction (DLLME) with magnetic ionic liquid (MIL), for the simultaneous determination of PBDE 28, PBDE 47, PBDE 99, PBDE 100, and PBDE 153 in sludge and sewage samples. The MIL used ($[P_{66614}^{+}]_2[MnCl_4^{2-}]$) was prepared following the procedure described by Merib et al. (2018), trihexyltetradecylphosphonium chloride ($[P_{66614}^{+}][Cl^{-}]$) (2:1) and tetrahydrated manganese (II) chloride salt ($MnCl_2.4H_2O$) (1:2) were dissolved in dichloromethane. A small amount of deionized water was added for complete solubilization of the salt. The mixture was stirred for 24 hours without heating. Subsequently, the aqueous phase was discarded, and the organic phase was removed and placed in a rotary evaporator. Purification was performed by removing the excess remaining salt ($MnCl_2.4H_2O$) in the organic phase through successive washes with deionized water. Finally, the resulting mixture was taken to the oven at 70°C for 24 hours. A gas chromatograph with electron capture detector (GC-ECD – Varian 450) using a ZB-5 column (dimension: L= 30m, ID = 0.25 mm, FT = 0.50 µm + 5 m Guardian TM) was utilized under nitrogen flow rate of 1.0 mL min^{-1}. The oven temperature programming used was 80°C (1 min), ramp 70°C/min to 320 °C (11 min), totaling an analysis time of 15.43 minutes. The MIL was characterized by UV-Vis and FTIR spectroscopy. The magnetic susceptibility of the MIL was validated by applying an external magnetic field (neodymium magnet). Thermal behavior was studied through thermogravimetric analysis (TG) and differential thermal analysis (DTA). UV-Vis and FTIR spectroscopies confirmed the successful incorporation of the manganese ion, with UV-Vis analysis showing a characteristic absorption in the range of 425 nm to 465 nm, and FTIR revealing a symmetric stretching $^{\upsilon}{}_{S}$(Mn-Cl) at 1643 cm^{-1}. The prepared MIL showed favorable thermal stability, corroborated by TG and DTA analyses, in addition to exhibiting excellent magnetism, ensuring the elimination of centrifugation step. The GC-ECD method provided reliable retention times, 8.01, 9.32, 11.2, 10.5, and 13.5 min for PBDE 28, PBDE 47, PBDE 99, PBDE 100, and PBDE 153, respectively. The obtained LOD and LOQ values varied from 1.00 to 30.0 µg L^{-1} and from 5.00 to 30.0 µg L^{-1}, respectively. A analytical curve of the extraction performed in a fortified sludge and sewage sample with PBDE 28 was represented by y = 73454 x + (-21038), with an R^2 = 0.9760 in the concentration range of 600.0 to 1600 µg L^{-1}, highlighting the sensitivity of the proposed method. According to the mentioned facts, it is noted that the MIL presented a promising strategy in DLLME for the simultaneous determination of PBDEs in complex environmental matrices. The method efficiently determined PBDE 28, providing secure results for contaminant analysis. Future research should explore the use of MIL in other sample preparation techniques, based on RDSE, to obtain a better extraction efficiency.

References: MERIB, J. et al.. Magnetic ionic liquids as versatile extraction phases for the rapid determination of estrogens in human urine by dispersive liquid-liquid microextraction coupled with high-performance liquid chromatography-diode array detection. Analytical and Bioanalytical Chemistry, 2018.

Agradecimentos/Acknowledgments

IQ-UNESP, CAPES, FAPESP (#2022/02991-3), INCT-DATREM (#2014/50945-4), CNPq and PROPe (09/2023)

Área: ANA

Determination of sulfur dioxide in ambient air using microsampler and ion chromatography.

Augusto Sciamana de Moraes (PG),[1]* Arnaldo Alves Cardoso (PQ)[1]

augusto.moraes@unesp.br

[1]*Department of Analytical Chemistry, IQ-UNESP.*

Keywords: *Sulfur Dioxide, Ambient Air, Microsampler, Ion Chromatography.*

Highlights

This work aims to determine SO_2 in ambient air using a short time sampling device in hydrogen peroxide collector solution and its determination by ion chromatography.

Abstract

Due to its high reactivity, sulfur dioxide is considered a polluting gas, having a significant impact on the environment and public health because of the formation of acid rain and fine aerosols.[1,2] Analytical methods for quantifying sulfur dioxide present difficulties due to its reactivity and volatility, transportation, preservation, and quantity of samples.[2]

This work used hydrogen peroxide as a sulfur dioxide collection solution. Sulfuric acid is formed as a product reaction, which is quite stable for a short period. A µ-impinger device was built with a 1,5 mL Ion Chromatography vial bottle to reduce sampling time sample handling. The results showed that it is possible to determine 0,4 – 200 µg of SO_2 with samplings of 5 - 25 minutes, with a 64,6% efficiency collection of SO_2 (Fig 2).

Fig. 1

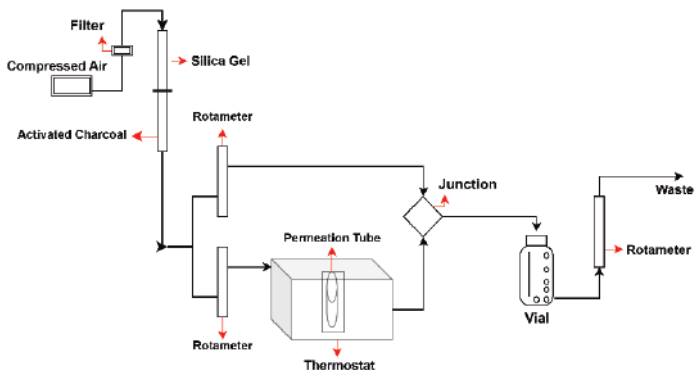


Fig. 2

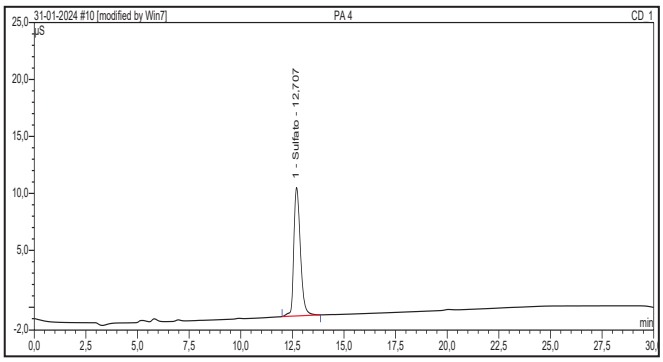


Figure 1: Microsampler system device and standard sulfur dioxide gas generation system. **Source:** Author.

Figure 2: Chromatogram of standard sulfur dioxide solution of 4 ppm. **Source:** Author.

[1] Khalaf, Eman M et al. "Effects of sulfur dioxide inhalation on human health: a review." Reviews on environmental health, 10.1515/reveh-2022-0237. 22 Dec. 2022, doi:10.1515/reveh-2022-0237

[2] Rall, David P. "Review of the Health Effects of Sulfur Oxides." Environmental Health Perspectives 8 (1974): 97–121. https://doi.org/10.2307/3428194.

Acknowledgments

This work was supported by FAPESP proc 2023/08034-3 and ASM for CAPES (scholarship).

Área: ANA

Development and validation of a method for quantifying H_2O_2 in milk using iron nanoenzymes synthesized through a green process

Luísa Faria Monteiro Mazzini (PG),[1*] Ana Clara Martins (IC),[2] Kleryton Luiz Alves de Oliveira (TC),[2] Renata Pereira Lopes Moreira (PQ),[1]

luisafmazzini@gmail.com

[1]*Departamento de Química, UFV*
Keywords:*(Eucalyptus grandis, green chemistry, nanoparticles, o-phenylenediamine, UV-Vis spectroscopy).*

Highlights

In this work, iron nanoenzymes were synthesized from *Eucalyptus grandis*. They were used for the detection of H_2O_2 in milk with low limits. The method is ideal for the dairy industry and laboratories.

Resumo/Abstract

Hydrogen peroxide is a chemical compound widely used in the food industry as a disinfectant and bactericide, and it is also utilized as an adulterant in milk. It poses a threat to living organisms and has the potential to harm cells. Due to its harmful potential, it is crucial to actively monitor and detect the presence of this compound [1]. In the present work, iron nanoparticles (FeNPs) were synthesized by a green method using *Eucalyptus grandis* leaf extract as a reducing and stabilizing agent. The FeNPs were used as nanoenzymes in the oxidation of *o*-phenylenediamine (OPD), a colorless compound, which is oxidized in the presence of hydrogen peroxide to form yellowish 2,3-diaminophenazine. Then, H_2O_2 monitoring can be accomplished through UV-Vis spectroscopy in the visible region.

The synthesis of FeNPs was confirmed by FTIR, EDS and XRD analysis. The material showed a spherical morphology with an average size of 97.8 nm, as observed in the Fig. 1.

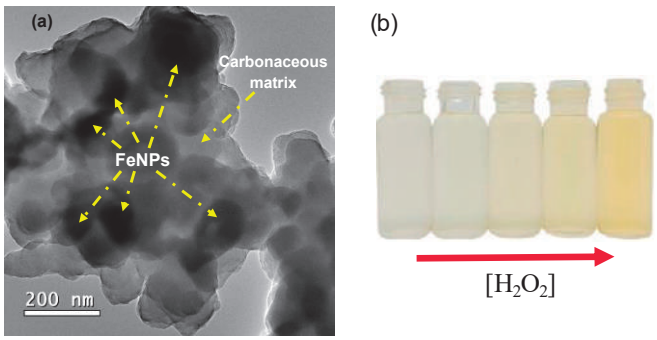


Figure 1. (a) TEM images and (b) Images of color enhancement with increasing H_2O_2 concentration.

First, the catalytic activity of FeNPs in the presence of the OPD substrate was evaluated by a kinetic study. The data was fitted to the Michaelis-Menten model, yielding a maximum velocity (V_{max}) of 2.0 μmol L^{-1} s-1 and a Michaelis-Menten constant (K_m) of 307 μmol L^{-1}. These results closely resemble those obtained for horseradish peroxidase. Thus, a simple method based on green chemistry principles was developed for the detection and quantification of hydrogen peroxide in milk. The method was validated according to the validation protocols. The analytical curve (8.97 to 112.16 μmol L^{-1}) for UHT (ultra-high temperature) whole milk showed a good linear fit, with detection and quantification limits of 2.96 μmol L^{-1} and 9.89 μmol L^{-1}, respectively. The change in color of the system with increasing of H_2O_2 concentration can be observed in Fig. 1. Accuracy, repeatability, and intermediate precision were evaluated at levels 44.86, 78.51 and 112.16 μmol L^{-1}. The method presented accuracy between 85.1 and 102.8%, repeatability ≤ of 3.9% and intermediate precision ≤ of 7.5%. Furthermore, it was applied to different types of milk, demonstrating its effectiveness, including semi-skimmed UHT milk, skimmed UHT milk and pasteurized whole milk type A. Finally, the method was compared with conventional methods used in the dairy industry and with others reported in the literature.

Therefore, it can be concluded that a simple and economical method for the detection and quantification of peroxide in milk has been developed.

References

[1] Mazzini, L. F. M. et al. **J. Braz. Chem. Soc**., vol. 1 (2023) 1-11.

Agradecimentos/Acknowledgments

CAPES, FAPEMIG (APQ-00083-21 e RED-00144- 22), CNPq (Processos 312400/2021-7 e 405828/2022-5).

Área: ANA

Development of a core@shell Moleculary Imprinted Polymer (MIP) selective to xylose for application in dispersive solid phase extraction (DSPE)

Diogo Hideki Moriya (IC),[1*] Maria Del Pilar Taboada Sotomayor (PQ)[1]

[*] **diogo.h.moriya@unesp.br ; m.sotomayor@unesp.br**

[1]*Departamento de Química Analítica, Físico-Química e Inorgânica (DAFQI), IQ-UNESP.*

Keywords: xylose, MIP, NIP, functionalized nanoparticles, dispersive solid phase extraction (DSPE), Molecular Absorption Spectroscopy in the Ultraviolet and Visible Regions (UV-Vis).

Highlights

- Core@shell polymer for extracting xylose from fruit growing waste.
- Method to achieve products with high added value.
- Less solvent and reagents used compared to solid phase extraction (SPE).

Resumo/Abstract

Fruit growing is one of the most economically important sectors in Brazil and, because it is highly valued, its production generates large quantities of residues. Among these residues, it is possible to obtain xylose, a sugar that can be used to obtain high value-added products. In this work, a SiO2-C=C@MIP is presented for the extraction of xylose from this organic waste using DSPE and its efficiency and selectivity analyzed by UV-Vis and its comparison with SiO2-C=C@NIP which is formed without the presence of the analyte. The SiO2-C=C@MIP was characterized using electron microscopy (SEM) (Figure 1,a,b) and Fourier transform infrared spectroscopy (FTIR) . For the adsorption analyses, 5 mg of the material was dispersed in 5 ml of xylose solution of known concentration and left to interact for 1h. As a result, MIP and NIP showed a retention % of 43.48% and 34.78%, respectively, from the spectrogram obtained (Figure 1,c). In conclusion, further tests will be carried out such as adsorption isotherms, adsorption kinetic studies, evaluation of interferents and application to real samples of orange pomace.

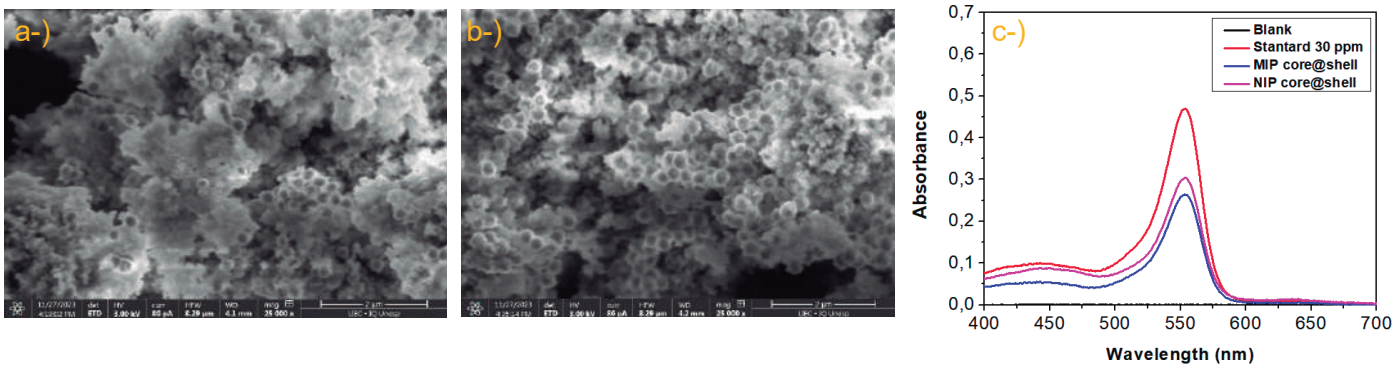


Figure 1: Representation SEM of SiO2-C=C@MIP (a) and SiO2-C=C@NIP (b) at 25.000x scale and the spectrogram obtained from the analysis (c).

Agradecimentos/Acknowledgments

The authors are grateful for the collaboration of FAPESP (process nº 2023/06494-7 and 2017/22401-8), NanoBiomimetic Sensors and IQ-UNESP for all the infrastructure and resources provided for the research of the project.

Área: ANA

Development of an analytical method for quantifying illicit drugs in wastewater samples during Brazilian Carnival in Recife/Olinda, Brazil

Jandyson M. Santos (PQ),[1] Ana Flávia B. de Oliveira (PG),[1]* Aline de M. Vieira (PG),[1] Pedro Gabriel C. de Lucena (PG),[1] Bruna R. de S. Gomes (PG),[1] Thayane Cristina da S. Moreira (PG)[1], Ignes Regina dos Santos (PG),[1] Kauê de O. Chinaglia (PG),[2,3] José Luiz da Costa (PQ),[2,3]

jandyson.machado@ufrpe.com; flaviabo.quimica@gmail.com*

[1]Chemistry Department, UFRPE; [2]Campinas Poison Control Center, UNICAMP; [3]Faculty of Pharmaceutical Sciences, UNICAMP.

Keywords: Wastewater-Based Epidemiology, Drug Consumption, Illicit Drugs, Solid-Phase Extraction, Gas Chromatography-Mass Spectrometry.

Highlights

- SPE and GC-MS was validated to quantify illicit drugs in wastewater;
- Drug concentration significantly increased during the event;
- Festive events exhibited a direct impact on drug consumption.

Resumo/Abstract

In recent years, global concerns have risen due to a significant increase in illicit drug (ID) consumption, posing substantial implications in social, health, and environmental domains.[1] To address this, innovative approaches are crucial for obtaining accurate and rapid data on drug consumption. Wastewater-based epidemiology (WBE) has emerged as a method focusing on measuring biological or chemical markers, such as ID and their metabolites, in sewage excreted by population. This approach enables a faster, non-invasive, and more cost-effective estimation of drug consumption through retrocalculation.[2] Recognizing the limited extent of WBE studies in Brazil, especially in the northeastern region, we have developed an analytical method for quantifying IDs and their metabolites in wastewater samples collected in the main treatment plants of Recife and Olinda, Pernambuco state – Brazil, focusing in the Carnival event. The samples were collected through grab sampling over two periods, as following: seven days during Carnival festivities (Feb 17-23, 2023) and seven days during a typical week (Mar 17-23, 2023), in a total of fourteen samples. A full factorial design 2^3 was employed to found the optimal conditions for solid-phase extraction (SPE) of IDs focusing on cocaine (COC), benzoylecgonine (BE), cocaethylene (COE), and carboxy-THC. The extracts underwet derivatization and subsequent analysis by gas chromatography-mass spectrometry (GC-MS), with minor adjustments of conditions to a previously validated method.[3] The best SPE condition was found using 100 mL of wastewater sample, washing step with 6 mL of ultrapure-water, and conditioning/elution of cartridges with 6 mL of MeOH, which exhibited recoveries between 70 - 120% for all IDs. The developed method was successfully validated following the Standard Practices for Method Validation in Forensic Toxicology through six parameters: recovery, matrix effect, precision linearity, limit of detection (LD) and limit of quantification (LQ)[4]. The quantification of COC, BE and carboxy-THC was achieved for all samples, whereas COE was just quantified in 28% of them. Preliminary assessments of individual concentrations revealed the highest values of all IDs occurring during the Carnival, which decrease during the weekend of a typical week. For instance, the concentration of COC detected on Carnival Saturday was 752.6 ng L^{-1}, whereas in a typical week, this value was equivalent to 448.2 ng L^{-1}. The findings emphasize the notable influence of Carnival events and leisure days on the heightened drug consumption in the state of Pernambuco, providing preliminary insights into the consumption dynamics.

References:

[1]Sulej-Suchomska et al. **Scientific Reports**, v. 10, n. 1, p. 81–87, 2020.
[2]De Oliveira et al. **Analytical and Bioanalytical Chemistry.** n. 18, v. 415, p. 3749-3758, 2023.
[3]Gonzalez-Marino et al. **Journal of Chromatography A**. n. 11, v. 1217, p. 1748–1760, 2010.
[4]ANSI/ASB Standard 036. **Standard Practices for Method Validation in Forensic Toxicology.** v. 1, 2019.

Agradecimentos/Acknowledgments

CAPES, FACEPE, COMPESA, BRK AMBIENTAL, LPNBio/UFRPE.

Área: ANA

Development of a new PSI-MS substrate for Cypermethrin determination in Tomato Samples

Yuri Arrates Rocha (IC)[1]*, Camila C.S.M. Brito (PQ)[1], Jean C.P. Sousa (PG)[2], Pedro A. B. Ferreira (PG) [1], Lívia F. Sgobbi (PQ) [1], Andréa R. Chaves (PQ) [1]

yuriarrates@hotmail.com;

[1]Instituto de Química, Universidade Federal de Goiás-UFG; [2]Faculdade de Farmácia, Universidade Federal de Goiás-UFG

Keywords: Paper Spray Ionization, Mass Spectrometry, Functionalized Polymer, Pesticides

Highlights

- A novel analytical approach for detecting cypermethrin in tomatoes employing an ambient ionization mass spectrometry technique.
- Utilization of a functionalized polymer as a substrate for PSI-MS improves the quantification of the cypermethin.

Abstract

The use of insecticides has been widely employed in agriculture in the past few decades to ensure high crop yields, acting as combatants against insects in farmlands. In this aim, pyrethroids are a class of insecticides commonly used for agricultural purposes.to controlling insects. Among them, cypermethrin, a synthetic pyrethroid, was developed to present lesser toxicity to humans, while contributing to crop productivities. However, the use of insecticides raises serious concerns regarding environmental, health, and safety issues for both aquatic and terrestrial ecosystems, humans, animals, and plants. ANVISA reported the Maximum Limit Residue for cypermethrin in tomatoes is 0,9 mg/kg. Typically, the analysis of pesticide residues in tomatoes involves chromatographic methods coupled to mass spectrometry systems such as GC-MS or LC-MS methodologies, which usually demanding multiple sample preparation steps. Paper spray ionization-mass spectrometry (PSI-MS) is an ambient mass spectrometry method, that uses a minimal sample volume and has been successfully reported in the literature to food pesticides residues analysis [1]. The PSI-MS methods employ a triangular piece of chromatographic paper as a substrate for sample ionization, which is not selective for the analytes, Aiming improve the analytical responses for PSI-MS method to cypermethrin determination in tomatoes sample, a new substrate was developed. To achieve this objective, a chromatographic paper was coated with polyhydroxamicalkanoate (PHA), a polymer that mimetic an artificial enzyme functionalized with hydroxamic acid and carboxylic acid groups . This coating aimed to enhance the selectivity of the analytical method for pesticides during PSI-MS analysis [2]. The PHA was synthetised followed the Melo et al. (2011) protocol, and subsequently, dissolved in a water solution at a concentration of 10 $mg.mL^{-1}$ for immobilization into equilateral triangle-shaped pieces (1 cm sides) of chromatographic paper. The immersion time from 30 to 60 min was evaluated for better paper modification and dried at 50°C. For sample analysis, 20 µl of tomato extract in methanol was deposited onto the coated paper and allowed to dry for 30 s. After that, a solution of methanolic acid containing 0.1% formic acid (35 µL) was used as the spray solvent, and a voltage of 4.0 kV was applied in positive ionization mode. The PSI-MS analysis was conducted using a Thermo -Scientific LTQ XL instrument. The results showed that cypermethrin detection and quantification were improved using the PHA coated paper when compared to the non-coated chromatographic paper. The PSI-MS methodology presented good linearity with r^2=0.98 with adequate precision and accuracy for cypermethrin determination in tomato samples.

[1] Santos, A.M.S.;et al. Paper Spray Ionization Mass Spectrometry Applied for Quantification of Pesticides and Discrimination from Tomato Varieties. *Journal of Food Composition and Analysis* 2022, *109*, 104467
[2] Sgobbi, L.F; et al. Polyhydroxamicalkanoate as a bioinspired acetylcholinesterase-based catalyst for acetylthiocholine hydrolysis and organophosphorus dephosphorylation: experimental studies and theoretical insights. Catalysis Science & Technology, v. 7, n. 15, p. 3388–3398, 2017.
[3] Melo, R. S. et al. Polymers containing hydroxamate groups: nanoreactors for hydrolysis of phosphoryl esters. Langmuir. v. 27, p. 15112-15119, 2011.

Acknowledgments

LaCEM IQ/UFG, CNPq and FAPEG.

Development of new analytical tools for comparison and procedure assurance of cigarette brands sold in Brazil

Lucas Soares Rodrigues (PG),[1] Carlos German Massone (PQ),[1] José Marcus de Oliveira Godoy (PQ)[1]

lucassrodrigues31.12.2014@gmail.com

[1]*Departamento de Química, Pontifícia Universidade Católica do Rio de Janeiro (PUC-Rio)*

Palavras Chave: : Cigarettes, extraction, smuggling, falsification, analytical methods and Linear Discriminant Analysis

Highlights

This work aims to develop chemometric methods for predicting the origin of cigarette brands sold in Brazil using linear discriminant analysis associated with the GCalignR package.

Resumo/Abstract

The Nicotiana tabacum plant is known for its main use as raw material for the production of various types of cigarettes. As smuggling, counterfeiting and the sale of brands without health records represent infractions related to the sale of this product, it is necessary to develop new tools that can distinguish legal products from irregular products. Therefore, this work proposes the application of a new analytical method to compare 33 brands of cigarettes sold in Brazil. The brands studied were subdivided into five groups: cigarette brands smuggled from Paraguay, national **counterfeits of Paraguayan cigarette brands, cigarette brands belonging to small national companies, cigarette brands without health registration and legal cigarette brands belonging to multinational companies**. The method consists of verifying the effectiveness of two analytical techniques for extracting organic compounds for separating these five groups. The first technique is accelerated solvent extraction (ASE) of organic substances (Fig.1) using n-hexane as the extracting solvent. The second technique is ultrasound-assisted extraction (UAE), at room temperature, using dichloromethane as the extracting solvent. The crude extracts resulting from both procedures were injected into the GC-FID. The GCalignR package, belonging to the R software, was used to perform the alignment procedure for the retention times obtained (Fig. 2) Using this package, associated with the Linear Discriminant Analysis (LDA) chemometric technique (Fig 3) and it was found that both methods were effective in differentiating the cigarette brands studied, in addition to the proposed prediction model having a high accuracy rate (Fig.4). Furthermore, the results confirmed a similarity between smuggled cigarette brands and multinational brands, indicating that the preparation procedure and/or raw materials are the same. An approximation between counterfeit cigarette brands and cigarette brands from small national companies was also detected, serving as a possible indication of involvement between these groups.

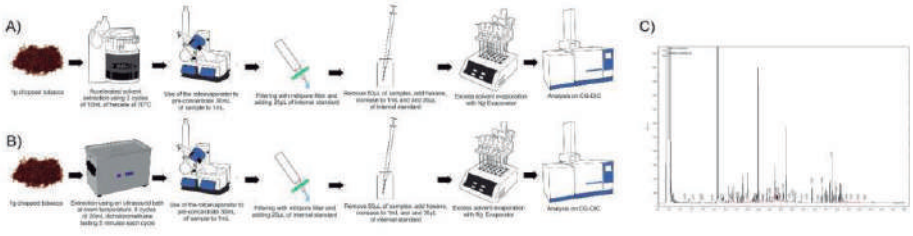
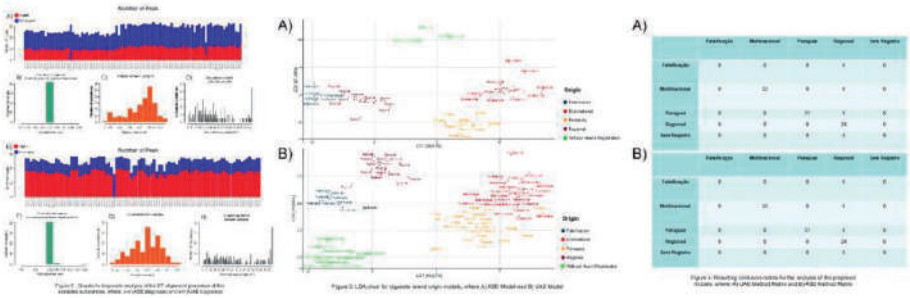


Figure 1 - Schematic representations of the methodologies used, where A) Solvent Accelerated Extraction, B) Ultrasound Assisted Extraction and C) Example of chromatogram obtained



Agradecimentos/Acknowledgments

À CNPq pelo fomento e à PUC-Rio pela infraestrutura

Área: ANA

Direct Magnetic Sorbent Sampling in Flame Atomic Absorption Spectrometry (DMSS-FAAS) for determination of cadmium and lead in foods

Thainá Alves Rocha Rosa (PG)[1*], Eduardo Costa de Figueiredo (PQ)[1]

Thaina.rosa@sou.unifal-mg.edu.br;
Thaina.rosa@sou.unifal-mg.edu.br *

[1]*Laboratory of Toxicant and Drug Analyses, Faculty of Pharmaceutical Sciences UNIFAL-MG*

Keywords: Direct sampling of magnetic solid sorbent, Magnetic biosorbent, Cadmium, Lead, Coffee, Tea

Highlights

- DMSS-FAAS, utilizing a magnetic biosorbent derived from orange peel, offers a rapid, cost-effective and environmentally friendly approach for determining potentially toxic metals in food at minimal concentrations. It overcomes the limitations of conventional methodologies, thereby contributing to food safety and public health.

Resumo/Abstract

A técnica DMSS-FAAS[1] foi desenvolvida pelo nosso grupo de pesquisa com o objetivo de melhorar a detecção de metais tóxicos e simplificar análises utilizando Espectrometria de Absorção Atômica com Chama (FAAS). DMSS-FAAS envolve a extração magnética dispersiva em fase sólida de analitos de uma amostra líquida, seguida da captura do sorvente na ponta de uma sonda magnética inoxidável e, posteriormente, inserção direta da sonda na chama do Espectrômetro de Absorção Atômica com Chama para atomização. Neste estudo, a técnica foi aplicada para determinação de cádmio (Cd) e chumbo (Pb) em amostras de café e chá de camomila, duas bebidas amplamente consumidas em todo o mundo. Estes metais, mesmo em pequenas quantidades, são prejudiciais à saúde devido aos seus efeitos mutagênicos e cancerígenos. O biossorvente magnético foi sintetizado conforme metodologia descrita por Borges et al. (2023)[2], utilizando casca de laranja seca e triturada, e incorporando nanopartículas de magnetita. A caracterização do composto foi realizada por Análise Termogravimétrica, Infravermelho, Potencial Zeta, Dispersão Dinâmica de Luz, Microscopia Eletrônica de Transmissão e BET. Primeiramente foi realizada otimização univariada do pH das amostras, seguida de um planejamento fatorial completo 2^3 dos parâmetros de extração: tempo de adsorção, massa do sorvente e volume da amostra. Os resultados indicaram os melhores pHs para Cd e Pb como 7,0 e 4,0, respectivamente. A quantidade otimizada de massa de material foi de 3 mg, com volume de amostra de 30 mL e tempo de adsorção de 25 minutos. Com os parâmetros otimizadas e a confirmação da obtenção de um composto com as características desejáveis, foram construídas curvas analíticas em amostras de chá de camomila e café para Cd e Pb, abrangendo as faixas analíticas de 2 a 70 µg L^{-1} e 20 a 750 µg L^{-1}, respectivamente. Os resultados das curvas revelaram coeficientes de correlação (R^2) superiores a 0,97, e desvio padrão relativo (DPR%) na faixa de 1,5 a 25,9%, proporcionando precisão e baixa variação entre as réplicas. Em trabalhos anteriores foi apresentado um ganho significativo de sensibilidade na determinação de metais em alimentos, aproximadamente 71 vezes para chumbo em amostras de água e suco[2,3], em comparação às análises convencionais. Os resultados obtidos demonstram que o método DMSS-FAAS é sensível, rápido, fácil e reprodutível para determinação de baixas concentrações de cádmio e chumbo em amostras de chá de camomila e café.

Referências/References

1 FIGUEIREDO, E.C.; et al. BR1020210184361. Depósito: 16 set. 2021
2 BORGES, F. A.; et al. **FOOD CHEMISTRY**, v. 413, 2023
3 COSTA, L. M.; et al. **ANALYTICA CHIMICA ACTA**, Minas Gerais, v. 1251, 2023

Agradecimentos/Acknowledgments

A CAPES, FAPEMIG e CNPQ.

Área: ANA

Effective, wide range application and low-cost approach for IoT implementation on laboratory benchtop spectrophotometric devices

Diogo Morais de Jesus* **(PG),[1] Felippe Delaqua (IC),[2] Sidnei Gonçalves da Silva (PQ),[1]**

diogomorais203@gmail.com

[1]Chemistry Institute, Federal University of Uberlândia — UFU; [2]Electrical Enginering Department — UFU

Key-words: *Analytical instrumentation, Light sensors, Urea determination, Internet of Things*

Highlights

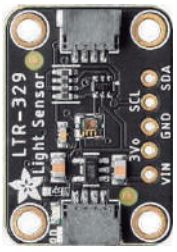
A low-cost approach for laboratory devices upgrade is presented. Sensors response results are useful for works on easy access photometers. Urea could be successfully determined on obtained samples.

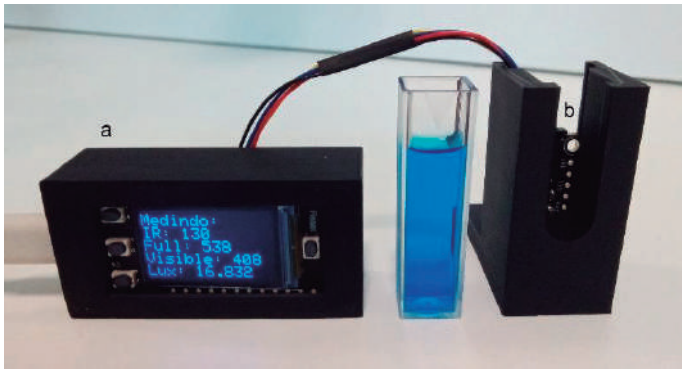
Abstract

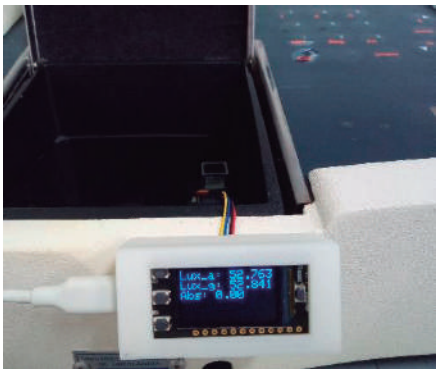
Since 1999, the freshly created term at the time, Internet of things (IoT), refers to the connection between devices and integrated operation with computing units using the internet infrastructure. In recent years, the term “Internet of Analytical Things” (IoAT) has gained space in scientific papers, by introducing the junction between the IoT concept and analytical chemistry methods. IoAT devices can employ a variety of simple components for determinations using different methods and connectivity features. For colorimetric analysis, these devices can use light sensors, LEDs, microcontroller boards, and 3D-printed structures to accommodate the components. Such systems can often be considered low-cost and a “do it yourself” approach for instrumentation, since they have accessible technical requirements for development and implementation. In this work, three photodiodes (BH1750, TSL2591, and LTR329) were tested as light sensors on the determination of dyes with absorbance at different wavelengths. The results could then be analyzed to confirm the LTR best applicability. The light source used was the spectrophotometer (Femto 600-s model) monochromatic output, and the absorbance measurements could be showed immediately on the microcontroller integrated display. The device parts (**Fig. 1**) include the LTR329 light sensor (a), the Esp32 microcontroller (b) 3D-printed structures, and cost about US$ 30. Most photodiodes have low or no-response for wavelengths below 430 nm, and the analytical sensitivity will be sharply reduced for measures on this range. To prove the sensor’s wide application, the photodiode was tested for urea determination on samples of Urea-SCR products (selective catalytic reduction) obtained commercially at Uberlandia (MG, Brazil), in which the chromogenic reaction forms a Schiff base with absorption measured at 420 nm. The fully integrated device (**Fig. 2**) presented accurate determinations (CV = 3,34) and linearity for 0,25 – 3 % urea and detection limit of 0,08%. Calibration curves obtained (0,066 + 0,305C; 0,061 + 0,297C) for femto and LTR respectively shows very similar sensitivity. For sample 1, the system obtained 33,0% ± 0,7 to 33,6% ± 1,01 for Femto 600-s spectrophotometer and 33,9 ± 0,7 to 35,3 ± 1,1 for LTR and Femto respectively on sample 2.

Fig. 1. Separated components. A cuvette is shown for size comparison. **Fig. 2.** Device coupled with Femto-600s light source.

LTR329 sensor







Acknowledgments

(CAPES) - Finance Code 001. CNPq - process number 403929/2021-0 and FAPEMIG - process number APQ-01395-22.

Área: ANA_____
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Electronic tongue based on stanniocalcin-1 (STC1) protein antibodies applied in prostate cancer studies via STC1 antigen detection

Renato S. Ferreira (PG)[1], Paulo A. Ribeiro (PQ)[1], Adelino V.M. Canário (PQ)[2], Débora Gonçalves (PQ)[3], Maria Raposo (PQ)[1,*]

gdebora@ifsc.usp.br; mfr@fct.unl.pt

[1]Department of Physics, Universidade Nova de Lisboa, Caparica, Portugal; [2]Faculdade de Ciências e Tecnologia, Universidade de Algarve, Portugal; [3]Institut of Physics of Sao Carlos, University of Sao Paulo, Sao Carlos-SP, Brazil;

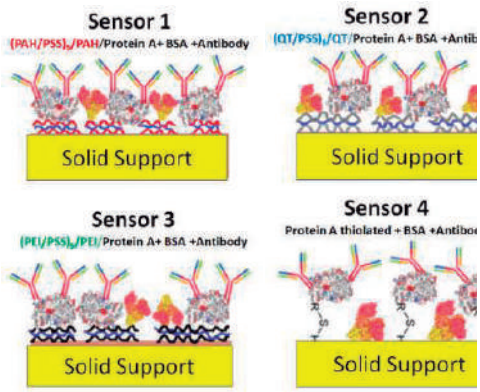
Palavras Chave: Sensors; Electronic tongue; principal component analysis; prostate-specific antigen.

Highlights

Electronic tongue with stanniocalcin 1 (STC1) antibodies. Sensors used to avoid initiation and progression of tumors prepared by layer-by-layer via antigen concentration by impedance spectroscopy.

Resumo/Abstract

Rectal examination, tissue biopsy, and analysis of prostate-specific antigen (PSA) have been used to diagnose prostate cancer, but with drawbacks such as low sensitivity and specificity; also, ageing, benign prostatic hyperplasia and prostatitis can increase production of PSA and false positives. Secretion of glycoprotein stanniocalcin-1 (STC1) has been related to different malignant tumors, and can be used as a tumor marker for detection of STC1 and, consequently, prostate cancer. Here, we fabricated electronic tongue (e-tongue) based on sensor arrays from layer-by-layer films on Au interdigitated electrodes, which detected low concentrations of STC1 antigen. Detection was performed by impedance spectroscopy in solutions with different antigen concentrations for 4 different sensor (Figure) with 5 layers. The electrical properties were studied by principal component analysis (PCA). Sensors: polyallylamine hydrochloride (PAH), polysodium polystyrene sulfonate (PSS), and polyethyleneimine (PEI), chitosan (CT). Antibody layer: protein A and bovine serum albumin (BSA) and protein A thiolated. Sensors detected antigen concentration of 5×10^{-4} mol L^{-1} and mean saturation of 20 min, and data were statistically analyzed using PCA. E-tongues showed a sensitivity of 5371±820 and sensors (1-3) of 4863±634, with small error rate at concentrations of 5×10^{-11}-5×10^{-4} (v/v) and linear dependence with logarithm of concentration. These result were compared with the best of the sensors, with e-tongues producing robust and stable data. Our prototype allows one to obtain impedance and loss tangent spectra for sensors immersed in antigen solutions at different concentrations, with perspectives of advance to calibration phase with real samples.



Agradecimentos/Acknowledgments

CAPES (Finance code 001) (88887.837887/2023-00), CNPq (402816/2020-0), FAPESP (2018/22214-6), FCT/Portugal (PTDC/FIS-NAN/0909/2014), FCT/MCTES/Portugal (UIDB/FIS/04559/2020 and UIDP/FIS/04559/2020 LIBPhys).

Área: **ANA**

Encapsulation of Hydrophobic Deep Eutectic Solvent (HDES) in Alginate Beads: A Green Sorbent for Preconcentration of Inorganic Analytes

Mateus O. Müller (PG),[1]* Floriatan S. Costa (PQ),[1] Mario H. Gonzalez (PQ),[2] Clarice D. B. Amaral (PQ)[1]

* mateusmuller@ufpr.br.

[1] *Department of Chemistry, Federal University of Paraná, Curitiba, PR, Brazil;* [2] *São Paulo State University (UNESP), INCT-DATREM, Department of Chemistry and Environmental Science, São José do Rio Preto, SP, 15054-000, Brazil*

Keywords: *SPME, Lead, Alternative solvents, Sample preparation, Green Chemistry, Chemometrics.*

Highlights

- HDES encapsulated in alginate beads for the SPME of trace elements.
- The study of extraction time and adsorbent mass was evaluated using a full-factorial design 2^3.
- A novel green application for sample preparation.

Abstract

Hydrophobic deep eutectic solvents (HDES) are a new class of sustainable, biodegradable, and customizable solvents with potential chemical properties for application in microextraction methods for trace elements extraction. Methods based on HDES in chemical analyses can provide promising results, especially in the development of new application in harmony with the principles of Green Analytical Chemistry (GAC). However, measurements in HDES medium pose a challenge for most plasma-based techniques that require sample nebulization due to high viscosity/surface tension, and matrix interference, in addition to evaluating extraction efficiency. This study evaluated the application of HDES encapsulated in alginate beads for the solid-phase microextraction (SPME) of Lead (Pb) in aqueous samples before determination by inductively-coupled plasma optical emission spectroscopy (ICP-OES). The HDES was encapsulated in alginate beads that were used as a green sorbent phase for Pb extraction in test samples. The samples will consist of aqueous solutions, including water or beverages; however, their specific composition has not yet been fully determined. After extraction, the analyte was eluted in nitric acid (5% v v^{-1}) in a low-volume solution before measurement. In the multivariate study of sorbent mass (100 and 300 mg), extraction time (1 and 5 min), and Pb analyte concentration (100 and 10,000 µg L^{-1}), using a full-factorial design (2^3) with the execution of 8 experiments. The extraction time (Effect = 33) and sorbent mass (Effect = 28) positively affected the extraction recovery, indicating high-levels as adequate experimental conditions. The high recovery rates, 96%, were obtained with the optimum condition. Furthermore, the limit of detection (LOD) 0,968 µg L^{-1} and the limit of quantification (LOQ) was 2,935 µg L^{-1} for lead analysis, while the maximum enrichment factor achieved was 10-fold times. These results provide relevant insights and demonstrate the potential for this application in sample preparation with high efficiency of pre-concentration, improving sensitivity and overcoming challenges of measurements in HDES medium. Other analytes, as Cd, Cu, Ni and others will be assessed throughout the study, as well as additional variables will be optimized. In addition to high extraction efficiency and high sample throughput, the SPME method will meet miniaturization requirements and use of HDES improve the GAC criteria, guiding the development of more sustainable methods.

Acknowledgments

CAPES [Finance code 001], CNPq/MCTI [Grant numbers: 465571/2014-0 and 403839/2023-8], FAPESP [Grant numbers: 2014/50945-4 and 2021/14759-5], and FUNPAR-PRPPG-UFPR

Área: ANA

Estudo dos efeitos de óleos de Cannabis *full-spectrum* em modelo *in vitro* de doenças neurodegenerativas

Bruna B. Soldera (PG),[1] Marcelo B. Jesus (PQ),[2] Alessandra Sussulini (PQ)[1*]

b145458@dac.unicamp.br; dejesus@unicamp.br; sussulini@unicamp.br

[1]Departamento de Química Analítica, IQ-Unicamp; [2] Departamento de Bioquímica e Biologia Tecidual, IB-Unicamp

Palavras Chave: *cannabis, modelo celular, canabidiol, perfil molecular, GC-MS*

Highlights

- Study of the effect of *Cannabis sativa* full-spectrum oils in an *in vitro* neurodegenerative disease model.
- Cell viability assays using different oils resulted in IC50 values of 3.9 and 5.5 µg/mL of CBD.
- Molecular profile analysis of the oils by GC-MS identified cannabinoids, terpenes, and fatty acids.

Resumo/Abstract

Nos últimos anos, a planta *Cannabis sativa* vem sendo estudada no campo das neurociências, em especial considerando seu potencial no tratamento de doenças neurodegenerativas. Majoritariamente, seu consumo se dá na forma de produtos oleosos com substâncias isoladas ou *full-spectrum*, sendo este o óleo que possui todo o espectro de substâncias da planta, promovendo um efeito sinérgico. Desta forma, o presente trabalho se propõe a estudar de maneira interdisciplinar o efeito do óleo de cannabis *full-spectrum* (OC) em modelo *in vitro*. Dois tipos diferentes de óleo de cannabis *full-spectrum* (OC1 e OC2) foram analisados e seus efeitos foram estudados em uma linhagem celular usada como modelo de doenças neurodegenerativas, a SH-SY5Y (neuroblastoma humano). As análises de toxicidade foram realizadas com o objetivo de otimizar a concentração de trabalho que será aplicada às células visando as análises de metabolômica e lipidômica, que consistem nos próximos passos deste trabalho. Realizou-se, também, uma análise global para o mapeamento das substâncias presentes na composição dos OCs por cromatografia gasosa acoplada à espectrometria de massas (GC-MS), empregando um método adaptado da literatura. Para os ensaios *in vitro*, o óleo base dos OCs – triglicerídeos de cadeia média (TCM), que são moléculas altamente lipofílicas, contendo de 6 a 12 carbonos – foi usado como controle. Em experimentos de viabilidade celular por MTT, o TCM não apresentou toxicidade nas mesmas quantidades que os OCs, resultando nos valores de IC50 de 3,9 e 5,5 µg/mL de canabidiol (CBD) para OC1 e OC2, respectivamente. É importante mencionar que os OCs estudados são produtos oriundos de diferentes processos de extração, sendo o OC1 um produto de extração caseira e o OC2 obtido por processo industrial, e possuem diferentes concentrações de canabinoides, conforme descritas na Tabela 1.

Tabela 1. Concentrações de CBD e THC nos óleos de cannabis *full-spectrum* (OC) usados nos estudos de viabilidade celular fornecidas pelo fabricante

OC	CBD (mg/mL)	THC (mg/mL)
OC1	5,4	2,9
OC2	47,5	1,8

Os valores encontrados de IC50 vão de encontro a dados previamente reportados na literatura. Apesar dos valores serem descritos em função da concentração de CBD, a presença de outras substâncias na composição do óleo altera o efeito sinérgico, e também, como consequência, a resposta biológica celular. Nas análises do perfil molecular dos OCs por GC-MS, foram identificados canabinoides majoritários como CBD, tetrahidrocanabinol (THC) e outros (canabicromeno), terpenos como cariofileno, humuleno, ácidos graxos (ácido caprílico), além de outros compostos naturais como xilitol e ácido oleico.

Agradecimentos/Acknowledgments

FAPESP, CAPES, CNPq, INCTBio, FAEPEX-UNICAMP, IQ-UNICAMP, IB-UNICAMP e ao grupo de pesquisa LaBIOmics.

Área: ANA

Evaluation of different types of paper as solid substrate for detection of Cu and Mn by Laser-Induced Breakdown Spectroscopy (LIBS)

Adriana L. Sales (PG)*, Nilvan A. Silva (PQ) and Ivo M. Raimundo Jr. (PQ).

a234900@dac.unicamp.br.

Instituto de Química, Unicamp.

Key words: *Laser-induced breakdown spectroscopy (LIBS), Paper substrate, Copper, Manganese.*

Highlights

Paper type can significantly affect the emission intensity of metallic species, such as Cu and Mn, due to its impurities. A proper choice of paper substrate can improve the sensitivity of LIBS method.

Abstract

Laser-Induced Breakdown Spectroscopy (LIBS) has low analytical sensitivity for analysis of liquid samples. The strategy of transferring the liquid sample to a solid substrate has been employed to improve the spectral emission intensity. Among the solid substrates, the cellulosic support enables to improve the emission intensity for trace elements. One of the main characteristics of paper is its low-cost and easy handling, as well as its porous surface.[1,2] In the present work, different types of paper were used as solid substrates for the detection of Cu(II) and Mn(II) in aqueous solution. A Q-switched Nd:YAG laser (Brilliant Quantel B) operating at 1064 nm, with a repetition rate of 20 Hz, pulse duration of 5 ns and laser energy of 90 mJ was employed. A volume of analyte solution was chosen in order to form a thin film of liquid on the paper, ensuring a homogenous distribution of Cu(II) and Mn(II) on the substrate. For this, the transference was performed by adding of 600 µL of solution onto the papers, followed by drying in an oven at 60ºC for 120 min before being analyzed by LIBS. The differences in the signal intensities for Cu and Mn (Figure 1) are due the presence of small amounts of metal ions that remain in the papers after their production, such as Na, Ca, Fe, Ba, Cl and S. The office paper provided the higher enhancement in the emission intensity among 17 different types of substrates (Figure 1) due to the presence of metal ions from the raw material itself, which come from the equipment parts in contact with the cellulose pulp or present in other compounds. Detection limits of 0.1 and 0.7 mg L^{-1} for Cu(II) and Mn(II), respectively, were obtained when calibration curves were prepared with office paper, results that demonstrate the usefulness of common papers for detection of metal ions in environmental monitoring.

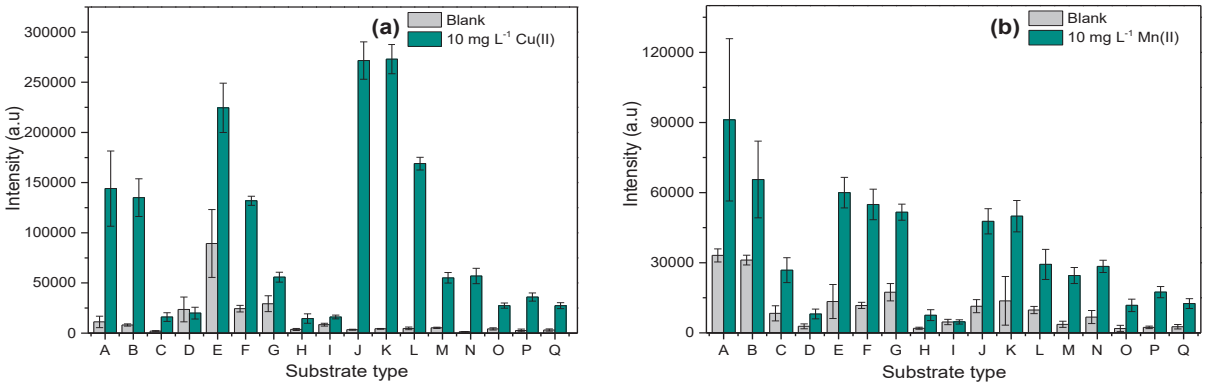


Figure 1 – Effect of the paper substrate on the emission intensity of (a) Cu I 324.74 nm and (b) Mn I 403.23 nm. (A) thermal paper, (B) recycled, (C) photographic, (D) tracing paper I, (E) color set, (F) craft, (G) wood, (H) tracing paper II, (I) laid I, (J) office, (K) egshell, (L) linen, (M) coffee filter, (N) laid II, (O) quantitative, (P) chromatographic, (Q) qualitative.

[1] K. Keerthi, Sajan D. George, Suresh D. Kulkarni, Santhosh Chidangil and V. K. Unnikrishnan, *Opt. & Laser Technol.,* 2022, **147**, 1-14.
[2] T. Stockinger, M. Steiner, F. Egger, F. Padinger, R. Schwödiauer, D. Wilmer, A.R. Mahendran, M. Kaltenbrunner and U. Müller, *Sensors and Actuators A: Phys.*, 2023, **350**, 114098.

Acknowledgments

INCTAA: CNPq #465768/2014-8 and FAPESP #2014/50951-4, INCT NanoVida: CNPq # 406079/2022-6.

Área: ANA

EVALUATION OF INTERFERENCES IN METAL DETERMINATION BY MIP-OES IN FOOD SUPPLEMENT EXTRACTS FROM *IN VITRO* BIOACESSIBILITY PROTOCOLS

Thaís dos S. Berón (PG)[1], Gustavo R. Bitencourt (PG)[1], Érico M. M. Flores (PQ)[1], Fábio A. Duarte (PQ)[1], Paola de A. Mello (PQ)[1]*

thaisufsm1993@gmail.com; paola.mello@ufsm.br

[1]*Universidade Federal de Santa Maria, Departamento de Química, Santa Maria, RS, Brazil.*

Keywords: *Bioacessibility, Dietary supplements, Interferences*, *MIP-OES*

Highlights

Interferences in metals determination by MIP OES in extracts from bioaccessibility protocols.
Suppression and intensification of signals were observed the presence of high concentrations of EIEs.

Abstract

Food supplements have been largely consumed due to their aesthetic and health benefits, which turns important to know the bioaccessibility of the elements that are common constituents or contaminants. For this, microwave-induced plasma optical emission spectrometry (MIP OES) can be an alternative. However, studies have reported that MIP-OES is prone to matrix interferences.[1] Given this, considering the complexity of the food supplement matrices, as well as the large quantity of reagents used in bioaccessibility protocols, an evaluation of the interferences in the determination of metals (Al, As, Ba, Be, Bi, Cd, Co, Cr, Cu, Fe, La, Mg, Mn, Mo, Ni, Pb, Sr and Zn) by MIP-OES was performed after obtaining extracts by two *in-vitro* bioaccessibility protocols (COST INFOGEST and UBM BARGE). For this, one botanical-based dietary supplement sample was used. The COST INFOGEST protocol comprises the gastric and the gastrointestinal phases in a single stage (saliva + gastric fluid + intestinal fluid).[2] On the other hand, the UBM BARGE procedure consists in one stage simulating the gastric phase (saliva + gastric fluid) and a second stage simulating the gastrointestinal phase (duodenal fluid + bile).[3] All extractions were performed at 37 ºC. For the study of interferences, 100 µg L^{-1} of all analytes were added in sequential dilutions of a extract obtained from both the COST INFOGEST and UBM BARGE protocols (1000, 500, 200, 100, 50, 20, 10, 5, 2 times, and without dilutions). The results were evaluated according to their relative intensities, comparing the values for the digest dilutions with those obtained for the digest dilutions with those obtained for a solution containing the analytes in 5% v v^{-1} HNO_3. Considering the study of interferences, both suppression and intensification effects were observed. The results obtained from the COST INFOGEST protocol showed that Cu, Cr, and Sr (200-fold dilution), Mo and Al (100-fold), and La (5-fold) presented intensified signals. On the other hand, signal suppression was observed for Zn (20-fold), Ag, Ba, Pb, and V (5-fold), and As, Be, Cd, Fe, Mn, and Ni (2-fold). Regarding the results obtained from the UBM BARGE protocol, As, Ba, Be, Cu, Cd, Cr, Fe, La, Mn, Ni, Pb and V had no effects on any of the phases, regardless the sample dilution. In the gastric phase, the elements that had their signals intensified were: Al and Mo (2-fold), and Sr (20-fold). On the other hand, signal suppression was observed only for Ag and Zn 50-fold dilution. Considering the gastrointestinal phase, signal intensification occurred for Al (10-fold), Cu and Mo (2-fold), and Sr (50-fold), while Zn (50-fold) had its signal suppressed. High concentration of C, Ca, Na, and K (maximum concentration of 20, 25, 0.7, and 10 g L^{-1}, respectively) was found in the extracts of both protocols, which probably induced the effects observed. Therefore, in order to guarantee the accuracy of the results obtained after extraction by COST INFOGEST procedure, a minimum dilution factor of the extracts was defined, ranging from 500 (Cr and Al) to 2 times (Fe and Mn). In the same way, but less expressive, minimum dilution factor was defined for the extracts from the BARGE procedure, ranging from 50 (Sr and Zn) to 2 times (Al, Co, and Mo) for both phases. Therefore, MIP-OES can be considered a suitable alternative for the determination of the bioaccessibility of essential and non-essential elements in food supplements, but special attention might be devoted to the matrix interferences promoted by the matrix from bioaccessibility protocols.

1. Serrano, R., *et al.* (2021). Acta Part B: Atomic Spectroscopy, 177, 106070
2. Silva EN, *et al*. (2018). Journal of Food And Analysis 68, 65-72.
3. Wragg J, *et al.* (2011). Science of the Total Environment, 409, 4016-4030.

Acknowledgments

CNPq, CAPES, ACS, and UFSM.

Área: ANA

Evaluation of iron content in wheat, corn, coconut and eggplant flour samples after acid digestion on a hot plate

Anderson da S. Pereira (IC),[1*] Kaio H.S. da Silva (IC),[1] Fernando C. Damasceno (PQ),[1] Aparecida M.S. Mimura (PQ).[1]

aparecida.mimura@univasf.edu.br; anderson.silvapereira@discente.univasf.edu.br

[1]Colegiado de Licenciatura em Química, Universidade Federal do Vale do São Francisco - UNIVASF

Keywords: Anemia, Acid digestion, Flour, Iron.

Highlights

Anemia is often related to a diet with low iron content.
Samples flours were prepared using acid digestion.
Iron was determined by FAAS.
The intake of flours can contribute to the prevention of anemia.

Abstract

Among the diverse types of anemia that exist in the world, iron-deficiency anemia is the most common and is often related to an inadequate diet with low nutrient content, such as iron. To minimize anemia in Brazil public policies have been implemented, making it mandatory to fortify wheat and corn flours with iron.[1,2] Although there are many types of research involving wheat flour, few studies have been reported on other types of flour. Recently, coconut and eggplant flours have been gaining prominence in the market, being widely used by people who are intolerant or allergic to gluten. Thus, this work aimed to determine the Fe content in different types of flour. The studied wheat, corn, coconut, and eggplant flour samples were obtained from commerce in São Raimundo Nonato-PI. Initially, several tests were made with different mineral acids to verify the best digestion conditions. Among these, the method that proved most suitable for flour samples is described below. The acid digestion procedure was conducted on a hotplate at 100 °C for 40 min. The mass used was 0.500 g of sample, over which were added 5.0 mL of H_2O, 5.0 mL of concentrated HNO_3, and 2.0 mL of H_2O_2 (35% v/v). After digestion, the volume was made up to 15.0 mL with distilled water in volumetric flasks. All procedures were done in triplicate. Blanks were also prepared. Fe was determined by flame atomic absorption spectrometry (F AAS) at 248.3 nm and with an air-acetylene flame. To check the accuracy, spike tests were performed at one concentration level (1.0 mg L^{-1} of Fe). The Fe content found was: 6.81 ± 0.58, 6.01 ± 0.11, 6.12 ± 0.52 and 6.61 ± 0.20 mg/100g for wheat, corn, coconut, and eggplant flour samples, respectively. The method used showed good precision, evaluated from the relative standard deviation, with results lower than 9.0%, and good accuracy, with recoveries around 98%. Thus, this sample preparation method was adequate for flour analysis. The iron content found was accordingly to the data in the literature for wheat and corn flour and also accordingly to the values recommended by ANVISA and Ministério da Saúde (between 4.0 and 9.0 mg/100g)[3]. Therefore, eggplant and coconut flours can contribute to the prevention of anemia as well as commercially available fortified wheat and corn flours. The next steps of this work include analyzing other brands and evaluating the application of ultrasound-assisted extraction for this type of sample.

[1] Buzzo ML, Carvalho MFH, Tiglea P, Arauz LJ, Arakaki EEK, Matsuzaki R, Rev Inst Adolfo Lutz, 71, 2012, 645.
[2] Martins CA, Cerveira C, Scheffler GL, Pozebon D, Food Anal Methods, 8, 2014, 1652.
[3] ANVISA. Agência Nacional de Vigilância Sanitária. Resolução – RDC n° 344, de 2002; Resolução – RDC n° 269, de 2005; Resolução – RDC n° 150, de 2017. Disponível em: <http://www.portal.anvisa.gov.br >. Acesso em: 25 de julho de 2022.

Acknowledgments

PRPPGI - UNIVASF and CNPq.

Área: ANA

Evaluation of linear models for the prediction of important fuel properties using GC×GC-HRMS and chemometrics

Amilton M. Oliveira (PG), Carlos A. Teixeira (PQ), Leandro W. Hantao (PQ)*.

wang@unicamp.br

Instituto de Química, Universidade Estadual de Campinas (UNICAMP).

Palavras Chave: cromatografia a gás, espectrometria de massas de alta resolução, modulação térmica, mínimos quadrados parciais, regressão.

Highlights

GC×GC-HRMS revealed significant differences in the relative amounts of hydrocarbons (saturates, resins, aromatics). Such valuable compositional data was used to predict important fuel properties.

Abstract

The chemical composition of fuels determines their properties and, ultimately, their engine-performance characteristics. Middle distillates, such as diesel, exhibit C_9 to C_{20} hydrocarbons with a boiling point interval of 150 to 370 °C. Due to the overwhelming occurrence of constitutional isomers and diastereomers, a high-resolution technique is required to obtain pure and meaningful compositional measurements of such compounds. In this context, comprehensive two-dimensional gas chromatography coupled to high-resolution mass spectrometry (GC×GC-HRMS) was used to profile diesel fuels. It can be readily observed that diesel from different oils exhibits unique profiles, ranging from more paraffinic fractions to more aromatics, as shown in Figure 1. Likewise, such molecular composition strongly influences the fuel properties. A linear model was calibrated using partial least squares (PLS) regression, correlating the raw pixels of the chromatographic data with the properties of interest. These models allowed the prediction of important properties such as cetane number (R^2 of 0.991), cloud point (R^2 of 0.947), cold filter plugging point (R^2 of 0.987), and fluidity point (R^2 of 0.811). This proof-of-concept highlights the potential of GC×GC-based chemometrics for multi-parameter modeling as an efficient alternative to time-consuming standard methods used in the petroleum industry. Perspectives include conducting additional experiments to ensure a broader coverage of the heterogeneous compositional data present in our samples.

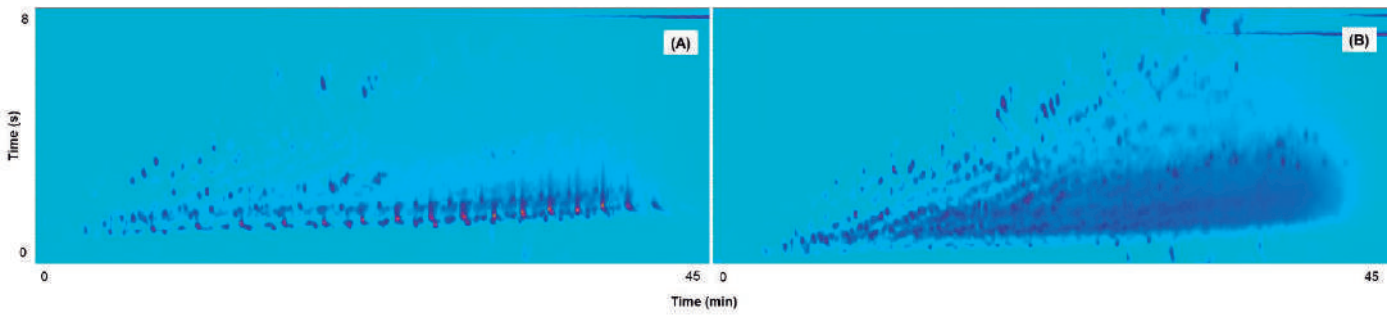


Figure 1. Total ion GC×GC-HRMS obtained for two distinct diesel samples, illustrating the broad compositional data available for chemometrics using partial least squares (PLS) regression. Column setting: non-polar × mid-polar. Modulation period: 8 s. Thermal modulation with ZX-2 interface (Zoex Corp.). Measurements were made on a TRACE1310 gas chromatograph coupled to a Q Exactive GC high-resolution mass spectrometer (Orbitrap®).

Acknowledgments

This study was financed by ANP/PETROBRAS (2019/00209-3, 2019/00210-1), CNPq (302748/2018-0, 316202/2021-5), FAPESP (14/50867-3, 20/01064-6), CAPES (001).

Área: ANA
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Evaluation of short-chain fatty acids from dog microbiota by GC-MS

Alissandra R. Gaudencio (PG)[1] *, Márcio V. da S. Gomes (PG)[1], Débora C. D. Estevam (IC)[1], Rafael P. C. Queiroz (PQ)[2], Henrique M. G. Pereira (PQ)[1], Marina A. Alves (PQ)[3], Monica C. Padilha (PQ)[1] *

monicapadilha@iq.ufrj.br; ar.gaudencio@hotmail.com

[1]Laboratório Brasileiro de Controle de Dopagem, LBCD/LADETEC/IQ/ UFRJ; [2]Clínica Veterinária Campello Queiroz, Rio de Janeiro; [3] Laboratório de Metabolômica Aplicada à Medicina de Sistemas, IPPN/UFRJ, UFRJ

Palavras Chave: *GC-MS, microbiota intestinal, short-chain fatty acids*

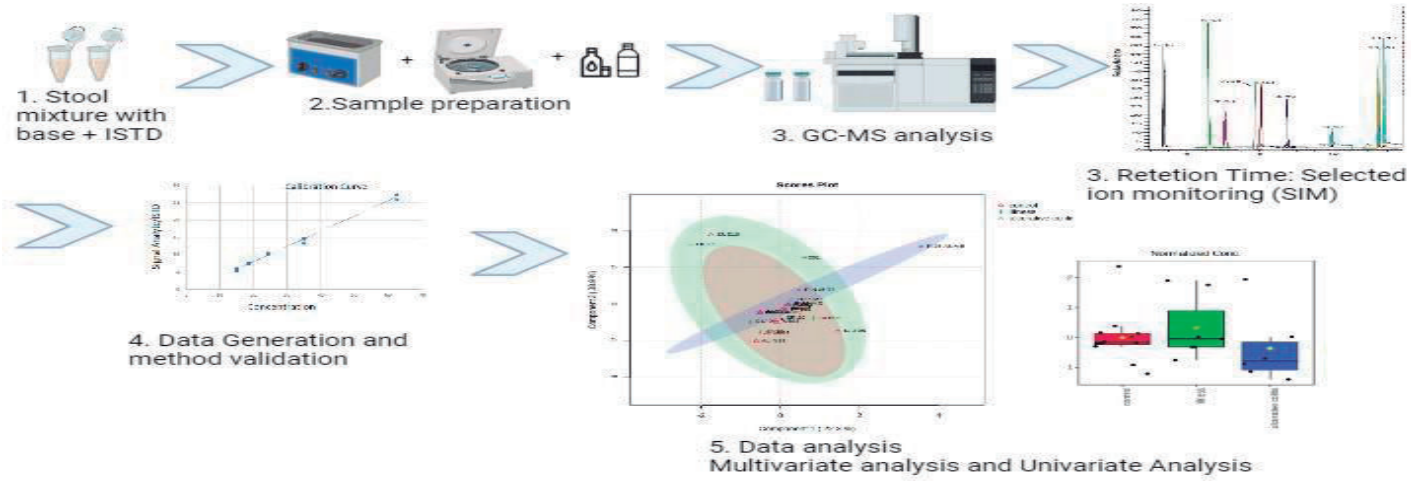
Highlights

Method developed was validated, showing recovery between 60% and 98% and linear range values of R^2 above 0.99. Dog with ulcerative colitis presented a low amount of fatty acids (p value < 0.05).

Resumo/Abstract

Inflammatory bowel disease is a chronic inflammatory disease of the gastrointestinal tract, mainly including Crohn's disease and ulcerative colitis, and is one of the most frequent causes of chronic vomiting, anorexia and diarrhea in dogs. There are studies that speculate that the intestinal microbiota is an important component for the pathogenesis of these diseases, however, the majority of studies are focused on investigating diseases in humans. Short-chain fatty acids are metabolites that represent a potential biomarker for studying the pathophysiology of inflammatory bowel diseases and are found in great abundance in feces, being an appropriate biological material for their determination. GC-MS is the analytical technique used for the determination of short-chain fatty acids because of its high sensitivity to detect small amounts of these metabolites. RESULTS: The method was developed and validated, following ANVISA RDC resolution nº 166, and applied to evaluate fatty acids in dogs that do not have diseases, dogs with disease conditions, and dog with ulcerative colitis. The validated method showed good recovery, between 60% and 98%, and linearity with regression coefficients (R) higher than 0.99. The dog with ulcerative colitis prior to meropenem treatment was separated from the other groups by PLS-DA. The Box Plot showed that fatty acids are in lower quantity in the dog with ulcerative colitis and is statistically significant, presenting a p value < 0.05 ($p = 0.04$).

Figure 1: General scheme for evaluating short-chain fatty acids



REFERENCES: COLLIER, A. J. et al. Investigating fecal microbial transplant as a novel therapy in dogs with inflammatory bowel disease: A preliminary study. PloS One, v. 17, n. 10, p. e0276295, 2022.

Agradecimentos/Acknowledgments

FAPERJ PGQu/IQ/UFRJ

Área: ANA

Evaluation of the Marin-5 nebulization system in the determination of trace elements in craft beers by MIP-OES

Alexsandro S. Martins (PG),[1,*] Heronides A. Dantas Filho (PQ),[1] Kelly G. Fernandes Dantas (PQ),[1]

kdgfernandes@ufpa.br; alexmartim@yahoo.com.br

[1]*Faculdade de Química de Química, UFPA*

Palavras Chave: *Experimental design, Inorganic elements, nebulizers, Beer, MIP-OES.*

Highlights

An experimental design was carried out to obtain the best analysis condition. Figures of merit were obtained using standard nebulization and the Marin-5 nebulization system. The Marin-5 nebulization system provided an increased sensitivity of the MIP-OES.

Resumo/Abstract

In this study, the performance of the Marin-5 nebulization system coupled to MIP-OES was evaluated. An experimental design was carried out in order to obtain the best conditions using the Marin-5 nebulization system for the determination of Al, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni and Pb in samples of amazonian craft beers by MIP-OES. The fourteen samples of craft beers of six different brands and flavors were purchased in supermarkets. The samples were placed in an ultrasonic bath for 90 min. After sonication, a volume of each sample (n = 3) was transferred to the digestion flask and HNO_3 14 mol L^{-1}, H_2O_2 (30%; m/m) and ultrapure water were added. The mixture was digested in a microwave oven with a cavity. After cooling, the solutions obtained were transferred to volumetric flasks and measured to a final volume of 10 mL with ultrapure water. The final acidity of the samples was 4.0 %. A central composite design (2^4) with five central points and two axial points was carried out to establish the best condition for quantifying the elements in the samples. Optimization of the experimental conditions was carried out in a multivariate manner using sensitivity as the response, which was measured in the form of the limit of detection (LOD) for the elements Fe 259.9 nm and Mn 403.0 nm. Standard solutions containing 1, 2, 3, 4 and 5 µg L^{-1} in HNO_3 medium (4%; v/v) of Fe and Mn were used. The variables evaluated were nebulizer pressure (80, 120, 160, 200 and 240 kPa), viewing position (-120, -60, 0, 60, 120), nebulizer chamber temperature (60, 80, 100, 120 and 140 ºC) and condenser temperature (-1, 1, 3, 5 and 7 ºC). The analyte addition and recovery method was used to evaluate the MIP-OES analysis procedure. The recoveries obtained ranged from 83.2 to 119.6 % for MIP-OES with standard nebulization and from 86.2 to 114.5 % for MIP-OES with the Marin-5 nebulization system. After optimizing the operating conditions, lower detection limits were obtained for all the elements. Among the elements studied, the best increases in sensitivity were observed for Fe, Pb, Ni and Co. The sensitivity of Fe, Pb, Ni and Co increased 27, 21, 17 and 13 times, respectively. Some elements such as Fe, Mo and Pb in the samples were below the detection limit when using MIP-OES with standard nebulization. However, by increasing the sensitivity caused by coupling the Marin-5 nebulization system to MIP-OES, all the elements studied were quantified in the samples. The proposed procedure proved to be a potential low-cost analysis procedure for the elements studied in craft beers and could be extended to other matrices.

Agradecimentos/Acknowledgments

CNPq, CAPES

Área:___ANA_____

Evaluation of the new Simplify digester and use of dilute acid in the preparation of animal food samples for elemental determinations by ICP-OES.

Rayane C. Vieira Costa (PG)[1 *], Edilene C. Ferreira (PQ)[1], Alex Virgilio (PQ)[2] and José A. Gomes Neto (PQ)[1].

rayane.cristina@unesp.br

[1]São Paulo State University (UNESP), Institute of Chemistry; [2]University of São Paulo (USP), Center for Nuclear Energy in Agriculture.

Keywords: *Sample preparation, animal food and ICP-OES.*

Highlights

The new convective heated digestion system with closed vessels (Simplify digester) was evaluated for the preparation of animal food samples and with the use of dilute acid, for subsequent elemental determinations by ICP-OES.

Resumo/Abstract

The food animals market has expanded significantly and its growth is a reflection of the appropriate nutritional requirements according to the animal's needs. In view of this, determining the mineral composition of food is of great importance, consequently, the study of new decomposition methods for these samples is promising[1]. Considering the simplicity and efficiency of digestion, the new convective heated digestion system with closed vessels (Simplify Digester) was evaluated for the preparation of food samples (for cats, dogs, rodents, birds, fish and horses) using hydrogen peroxide and diluted nitric acid, for the later determinations of Ca, Cu, Fe, K, Mg, Mn, P and Zn by ICP-OES[2]. The 6 food samples were obtained from the market in Araraquara-SP, and digested with 1 mL of H_2O_2 and HNO_3 3.5, 7 and 14 mol.L^{-1}. The accuracy of the method was evaluated using certified reference materials (CRM) bovine liver (*NIST 1577b*), fish food (*Embrapa MR-E1002A*) and corn bran (*NRC BRAN-1 8433*). The results showed accuracy between 88 and 107% (3.5 mol.L^{-1}), 89 and 118% (7.0 mol.L^{-1}) and 92 and 110% (14 mol.L^{-1}). Digestion efficiency was also evaluated by determination residual carbon content (RCC) and showed RCC concentrations between 852 and 1398 mg.L^{-1} (3.5 mol.L^{-1}), 597 and 1385 mg.L^{-1} (7.0 mol.L^{-1}), and 738 and 1521 mg.L^{-1} (3.5 mol.L^{-1}). The RCC results were lower than 2000 mg.L^{-1}, which is adequate for determinations using ICP OES and ICP-MS techniques[3]. Based on the results, the Simplify Digester showed promise for preparing animals food samples for the determination of macronutrients and micronutrients. In addition, digestions with dilute acid (3.5 mol.L^{-1}) were efficient, permitting lower reagent consumption and the generation of less acid residue, in accordance with green chemistry recommendations.

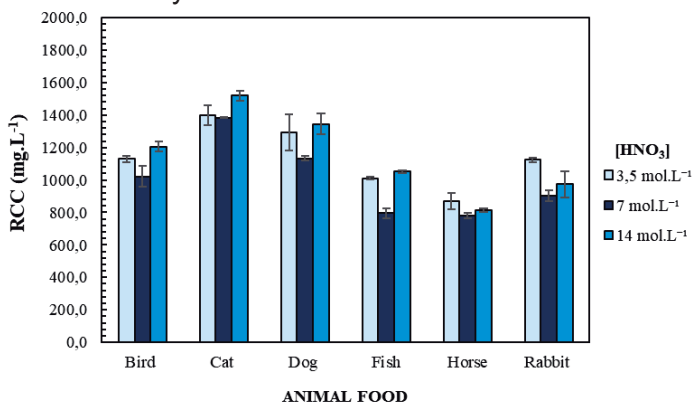


Figure 1: Determination residual carbon content.

[1]R. C. V. Costa, J. V. B. Santiago, E. C. Ferreira, A. Virgilio and J. A. Gomes Neto, *Braz. J. Anal. Chem.*, 2024, 11, 41-54.
[2]A. L. Vieira, G. G. A. Carvalho, J. A. Gomes Neto, P. V. Oliveira, M. Y. Kamogawa, *J. Anal. At. Spectrom.*, 2023, 20, 1-8.
[3]C. A. Bizzi, J. S. Barin, E. E. Garcia, J. A. Nóbrega, V. L. Dressler and E. M. M. Flores, *Spectrochim. Acta, Part B*, 2011, 66, 394-398.

Acknowledgments

[FAPESP (2019/07537-6); CNPq (303607/2021-1 and 304026/2021-2); CAPES (88887.649792/2021-00)]

Área: ANA
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Exploiting digital videos in catalytic methods: determination of saccharose in sugarcane spirits

Gabriel M. Fernandes* (PG), Fábio R.P. Rocha (PQ)

***gmartins3510@gmail.com**

Centro de Energia Nuclear na Agricultura, Universidade de São Paulo, 13416-000, Piracicaba, SP, Brasil,
Palavras-Chave: *Copper, kinetic methods, Digital-image photometry, Smartphone, Beverages.*

Highlights

Pioneering exploitation of smartphone-based digital videos in catalytic analytical methods; A novel catalytic method for saccharose determination; Simple alternative for quality control of sugarcane spirits.

Abstract

Catalytic analytical methods are a class of kinetic methods typically characterized by high sensitivity, sometimes yielding limits of detection (LOD) in the order of nmol L^{-1} [1]. These methods encompass a variety of reactions, such as redox reactions, ligand-substitution reactions, and metalloporphyrin formation, as well as a diversity of analytical applications [1]. However, as a kinetic method, proper application requires strict time control, which hinders the widespread application, and most procedures rely on flow-based systems [2]. In the present work, digital videos obtained with a smartphone were pioneering exploited in a catalytic method. It was exploited the catalytic effect of Cu(II) on the oxidation of 1,5-diphenylcarbazide (DPC) to 1,5 diphenylcarbazone (DPCO, orange) and further to 1,5-diphenylcarbadiazone (DPDO, colorless) in alkaline medium (pH > 12.4) [2]. Saccharose in alkaline medium (pH > 9) form a Cu(II) complex and inhibit its catalytic effect, so with strict time control it is possible to quantify the sugar based on the diminution of the reaction rate. Digital videos were recorded for 10 min and analytical information (channel B, RGB color system) was extracted with the software ImageJ from frames taken each 10 s, using the software VLC media player. Data treatment was based on the ($t - t_0$), where t and t_0 are the time to achieve the reaction plateau and initial reaction time, respectively [4]. Saccharose was quantified in sugarcane spirits as it is an important factor in evaluating the quality of the final product, as the sugar can be added to adjust sensory characteristics of the beverage. The Ministry of Agriculture and Livestock (MAPA) established threshold limits of 6 g L^{-1} and 30 g L^{-1} in sugarcane spirits and for the product labelled as “cachaça adoçada” the threshold is 30 g L^{-1}. To ensure an excess of Cu (II) a concentration 15 μmol L^{-1} was used, and under the optimized conditions a linear response was observed from 0.1 to 5 g L^{-1} ($r^2 > 0.99$) with LOD of 0.03 g L^{-1} and a coefficient of variation of 4.2% (n = 10). To evaluate the applicatility of the proposed method, sugarcane samples were spiked with 1.0 and 2.5 g L^{-1}, and recovery values ranged from 95 to 116%. The proposed catalytic method is a cost-effective and green alternative to quantify saccharose in sugarcane spirits since it only requires 60 µg DPC, 2 mg NaOH, and generates 1000 µL of waste per determination.

1. T. Kawashima, S. Nakano, M. Tabata, M. Tanaka, Catalytic reactions as applied to trace analysis, TrAC - Trends Anal. Chem. 16 (1997) 132–139. https://doi.org/10.1016/S0165-9936(97)00012-5

2. V. Cerdà, A. González, K. Danchana, From thermometric to spectrophotometric kinetic-catalytic methods of analysis . A review, Talanta. 167 (2017) 733–746. https://doi.org/10.1016/j.talanta.2017.02.004.

3. G.A. Crespo, F.J. Andrade, F.A. Iñón, M.B. Tudino, Kinetic method for the determination of trace amounts of copper(II) in water matrices by its catalytic effect on the oxidation of 1,5-diphenylcarbazide, Anal. Chim. Acta. 539 (2005) 317–325. https://doi.org/10.1016/j.aca.2005.03.013.

4. G.M. Fernandes, D.N. Barreto, A.D. Batista, J.F. da Silveira Petruci, A fully integrated 3D printed platform for sulfite determination in beverages via gas diffusion membrane extraction and digital video treatment, Food Chem. 406 (2023) 135094. https://doi.org/10.1016/j.foodchem.2022.135094.

5. H. Müller, Catalytic Methods of Analysis: Characterization, Classification and Methodology, Iupac Stand. Online. 67 (1995) 597–600. https://doi.org/doi.org/10.1515/iupac.67.0129.

6. B.E. Kim, T. Nevitt, D.J. Thiele, Mechanisms for copper acquisition, distribution and regulation, Nat. Chem. Biol. 4 (2008) 176–185. https://doi.org/10.1038/nchembio.72.

Acknowledgments

The authors are grateful to the Brazilian agencies: Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP, proc. 2022/05785-5), Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), and Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES). This is a contribution of National Institute of Advanced Analytical Sciences and Technology.

Área: ANA

Explorando a eficiência dos solventes eutéticos profundos naturais (NADES) no preparo de amostras de sedimento para análise elementar por ICP-OES

Lívia Davel Gomes (IC),[1,2*] Bruna Silva Correa (TC),[2] Poliana Borges de Oliveira (PG),[1,2] Larissa Dias Roriz (TC),[2] Rômulo Silveira Rodrigues (IC),[1,2] Geisamanda P. Brandão (PQ),[1,2] Luana Santos Moreira (PQ),[1,2] Maria Tereza W. D. Carneiro (PQ).[1,2]

livia.d.gomes@edu.ufes.br

[1]Departamento de Química, UFES; [2]Núcleo de Competências em Química do Petróleo – NCQP, Laboratório de Espectrometria Atômica – LEA, UFES.

Palavras Chave: *Solventes Eutéticos Profundos Naturais, Sedimento, Elementos traço, Planejamentos experimentais.*

Highlights

Exploring the efficiency of Natural Deep Eutectic Solvents (NADES) in the preparation of sediment samples for elemental analysis by ICP-OES

- NADES was efficiently applied as a solvent in the ultrasonic-assisted extraction of inorganic species in sediment samples
- Choline chloride-oxalic acid NADES presented the best results for the extraction of Ba, Cr, Cu, Mn, Ni, Sn e Zn

Resumo/Abstract

O uso dos solventes eutéticos profundos naturais (NADES) é uma alternativa para o preparo de amostras devido ao seu fácil preparo, custo comercial e baixo potencial tóxico, o que acarreta menor impacto ao meio ambiente e ao operador.[1] O preparo dos NADES é feito pela mistura de um receptor de ligação de hidrogênio (HBA), como o cloreto de colina (ChCl), e um doador de ligação de hidrogênio (HBD), como, por exemplo, a ureia (Ur) e o ácido oxálico (Ox).[2] Desse modo, o objetivo desse trabalho foi desenvolver um método rápido, simples e ecologicamente correto para o preparo de amostra assistido por ultrassom utilizando NADES para a extração e posterior determinação de Ba, Cr, Cu, Mn, Ni, Sn e Zn em amostra de sedimento de rio. A determinação dos elementos-traço foi realizada utilizando a Espectrometria de Emissão Óptica com Plasma Indutivamente Acoplado (modelo Optima 7300 DV – Perkin Elmer, Califórnia, USA). A decomposição ácida assistida por radiação micro-ondas (MW-AD), método US EPA 3051A, foi utilizada como método de referência. Inicialmente, foi realizada a otimização univariada para a escolha do solvente, proporção molar, massa de amostra e volume de solvente mais eficiente para a extração dos analitos. A extração foi realizada em banho ultrassônico (modelo Elmasonic Select 100 – Elma Schmidbauer GmbH, Singen, Alemanha) durante 15 minutos a 60 ºC. Para formação dos NADES foram avaliados ChCl, como HBA, Ur e Ox, como HBD, na presença e ausência de água (Wa). Os NADES foram avaliados em três diferentes proporções: 1:2:0, 1:1:2 e 1:1:4 para ChCl:Ox:Wa e ChCl:Ur:Wa. O solvente ChCl:Ur:Wa, em todas as razões molares, apresentou-se ineficiente para a extração, ficando todos os elementos abaixo do limite de quantificação. A extração com ChCl:Ox:Wa na proporção 1:2:0 alcançou recuperações na faixa de 7,49% (Zn) a 91,84% (Mn) quando utilizados uma massa de 150 mg e 3,00 mL de solvente. Embora, para alguns elementos baixas recuperações foram obtidas, ChCl:Ox foi o solvente mais adequado. Ao comparar os resultados obtidos na extração, nas condições estabelecidas, com MW-AD os valores foram concordantes quando o teste *t* a 95% de confiança foi realizado para Ba, Cu e Mn. Estudos futuros, visando a otimização do tempo e temperatura da sonicação serão realizados visando melhorar os resultados para os demais elementos. Com os resultados obtidos, o uso do NADES ChCl:Ox:Wa 1:2:0 demonstrou ter potencial para ser uma alternativa ao convencional MW-AD. Sendo assim, o método desenvolvido pode ser caracterizado como seguro, simples e eficaz e está alinhado aos princípios da Química Analítica Verde.

1 Matong, J. M.; Nyaba, L.; Nomngongo, P. N.; Ecotoxicol. Environ. Saf.135,152, 2017
2 El Achkar, T; Fourmentin, S.; Greige-Gerges, H. J. Mol. Liquids, 288, 111028, 2019

Agradecimentos/Acknowledgments

CNPq, FAPES, UFES/NCQP/LEA

Área: ANA

Frontal Chromatography as a tool for evaluation of new adsorbent materials

Bruno S. Peixoto (PQ),[1] Eduardo C. Pinto (PQ),[1,2] Stefhany L.S. Krugel (IC),[1] Larissa S.O. Mota (PG),[1] Marcela C. Moraes (PQ).[1*]

brunosalarini@id.uff.br; mcmoraes@id.uff.br

[1]BioCrom, Instituto de Química, Universidade Federal Fluminense, Niterói, RJ, Brasil; [2]Centro de Ciências Biológicas e da Saúde, Universidade Estácio de Sá, Rio de Janeiro, RJ, Brasil.

Keywords: *Adsorption, Frontal chromatography, Biochar, Green coconut, Salicylic acid, HPLC.*

Highlights

Frontal chromatography with biochar columns in HPLC-DAD system allowed the study adsorption behavior.
Results were coherent with batch studies.
The complete study used less than 10 mg of the adsorbent.

Abstract

The use of liquid chromatography instruments can be a reliable tool for investigating the adsorption phenomena between liquid solutions and solids, but its use for direct investigation of adsorbents in environmental applications is still scarce. Frontal chromatography has been used with great efficiency to study the adsorption behavior of materials used as stationary phases or for studying the affinity of biomaterials. there is still a predominance of batch tests in the study of new adsorbents intended for water and wastewater treatments, even though most environmental applications operate with fixed-bed columns. While most works study the fixed-bed adsorption process by collecting discrete samples within constant time intervals, with the sample analysis as a separate step, the use HPLC system allows for continuous online detection, with compatible hardware and software ready to use.[1] This work investigates the feasibility of using frontal chromatography in studies of drug removal from aqueous solutions using a H_3PO_4 activated biochar from green coconut husk, as the adsorbent, and salicylic acid (SA) aqueous solutions, as a model pollutant.[2] The study was performed by filling an empty stainless steel HPLC column (1.0 cm x 0.46 cm) with a dry mixture (≈200 mg) of activated biochar (45-150 µm) and sand (210-297 µm) in a weight ratio of 1:100. Another column was packed using only sand to act as the control. A Shimadzu NexeraXR (LC-20ADXR) HPLC-DAD system was used to collect data and set the parameters, allowing real-time study of the fixed-bed adsorption system. In the adsorption studies, direct infusion, through the instrument's solvent delivery system, of the selected SA concentrations (10; 50; 100; 150; 250; 350 µmol/L) into the columns produced a series of breakthrough curves resulting in a staircase chromatogram (Figure 1). The differences between the area of the control and that of the adsorbent result in the adsorption uptake (q), with each SA solution concentration resulting in the adsorption capacity for each thermodynamic condition, which could be used to plot an adsorption isotherm graph. The results obtained were compared to batch adsorption data of SA in ACP previously published.[2] The adsorption capacity of the biochar column for SA was 392 µmol/g, at the temperature of 303 K, and a 2 mL/min flow of 350 µmol/L SA solution. This value is next to 120% of the uptake obtained in batch studies, which are adequate preliminary results. Even though some parameter adjustments are still underway, the presented study shows the potential of frontal analysis to be a fast and reliable method to evaluate fixed-bed adsorption systems with the advantages of using minimal adsorbent quantities. On top of that, this approach also facilitates studies of the reuse and regeneration of adsorbents, that are currently in progress.

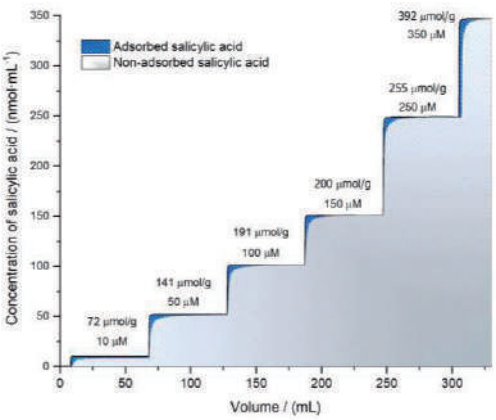


Fig. 1: Staircase frontal analysis of SA at 10-350 µM

(1) Lu, Z.; MacFarlane, J. K.; Gschwend, P. M. *Environ. Sci. Technol.* **2016**, *50* (1), 285–293.
(2) Peixoto, B. S. et al. *J. Environ. Chem. Eng.* **2023**, *11* (5), 110835.

Acknowledgments

This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – Brasil (CAPES) – Finance Code 001, FAPERJ, and CNPq (317724/2023-1).

Área: ____ANA_____

HS/GC-MS analysis of VOCs in flowers of *Couroupita guianensis* aiming at its preservation through the prospecting of fragrances for the cosmetic industry

Aline M. Aguiar (IC)[1*], Lilian F. de Oliveira (IC)[1], Dayane C. da Costa (PD)[1], Nelson R. A. Filho (PQ)[1]

aguiarninha4@gmail

[1] *Instituto de Química, UFG*

Keywords: Abricó-de-macaco, *Volatile Organic Compounds, GC, Cosmetics, Environmental Chemistry*

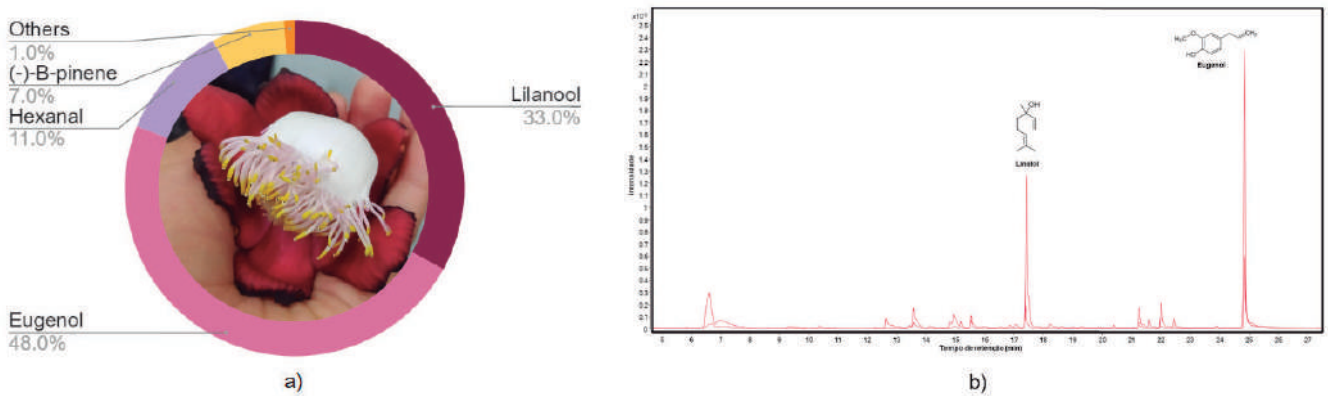
Highlights

Prospection of compounds of interest for cosmetic industry through the analysis of VOCs in flowers of *Couroupita guianensis* taking into account principles of green chemistry by using HS/GC-MS.

Abstract

Essential oils, a natural and complex mixture of secondary metabolites called terpenes found in some plant extracts, are of major importance in flavor and fragrance industries due to its high applicability in this sector. However, small amounts of these oils require a high volume of feedstock which can be the starting point for predatory extractivism, illegal activity that may endanger vegetal species. Worried about this situation, companies inserted in the global industry 4.0 market are constantly searching for innovative, eco-friendly, efficient and low-cost products which calls for sustainable research to prospect new aromatic species that are made up of molecules already consolidated for use in personal hygiene products and cosmetics.[1] With that in mind, aiming at finding options for supplying the market of perfumery, praising local biodiversity and giving preference for extraction and analysis methods inherent to the principles of environmental chemistry, the present work applies an extraction technique of volatile organic compounds (VOCs) of *Couroupita guianensis* (Abricó-de-macaco) flowers via headspace (HS) coupled to gas chromatography (GC) and mass spectrometry (MS) in order to minimize the amount of raw material used in this screening, providing reliable results of essential oil profile. The major VOCs present in these flowers, as well as its chromatogram, are shown in figure 1, respectively.

Figura 1. Level of major compounds in flower of *Couroupita guinenis* (a) and its chromatogram (b)



Considering the high portion of linalool and eugenol, important ingredients in cosmetic industry, presented in flowers of *Couroupita guianensis*, this species has the potential to become an alternative matrix for obtaining these ingredients for use in the perfumery sector.

1. COSTA,D.C. **Controle de qualidade e classificação de essências e perfumes comerciais e prospecção de fragrâncias de plantas do Cerrado**, TESE. IQ-UFG, Goiânia, 2021.

Acknowledgments

LAMES, IQ-UFG, FUNAPE

Área: _ANA_

Inoculation of *Leishmania amazonensis* and *Leishmania braziliensis* in wild-type and *fabp4* knockout macrophages for untargeted metabolomic analyses.

Júlia M.S. Rossi (IC),[1*] Mariana B.C. Brioschi (PG),[2] André L.M. Camelo (PG),[1] Danilo C. Miguel (PQ),[2] Ana V. C. Simionato (PQ).[1,3]

j204522@dac.unicamp.br

[1]*State University of Campinas, Department of Analytical Chemistry/Institute of Chemistry, Campinas, São Paulo, Brazil, 13083-970;*
[2]State University of Campinas, Department of Animal Biology / Institute of Biology, Campinas, São Paulo, Brazil, 13083-862;
[3]*National Institute of Science and Technology in Bioanalytics (INCTBio), Brazil.*

Palavras Chave: *Leishmania, Metabolomics, GC-MS*

Highlights

Application of untargeted metabolomics in the study of WT and KO mice cells infected with *L. braziliensis* and *L. amazonensis*, to comprehend the metabolism in different biological systems by GC-MS.

Abstract

Leishmaniasis, caused by protozoa of the genus *Leishmania*, is one of the world's most neglected diseases, which can manifest in three different forms: cutaneous leishmaniasis, visceral leishmaniasis, and mucocutaneous leishmaniasis. Despite being an epidemic and potentially lethal disease, there are no vaccines or safe medications for controlling this pathology, since most of them do not completely cure the disease and are highly toxic.(1) Recent findings indicate that amastigotes efficiently incorporate fatty acids to aid amino acid biosynthesis. Besides, it has been reported that fatty acid-binding proteins (FABPs), abundant in the cytoplasm of adipocytes and macrophages, transport fatty acids to different cellular compartments.(2) In this context, the purpose of this work is the untargeted metabolomics analyses of mammalian cells upon macrophage infections with *L. braziliensis* and *L. amazonensis* to assess the interference of FABP4 activity. Differentiated bone marrow macrophages from Wild-type-C57BL/6 (WT) and Knockout *fabp4*-C57BL/6 (KO) mice were cultured and divided into three groups: *i)* control group (not subjected to infection); *ii)* test group 1 (infected with *L. braziliensis*); *iii)* test group 2 (infected with *L. amazonensis*) (Figure 1). The KO mice were genetically modified by silencing the *fabp4* gene, since increased levels of the FABP4 protein in macrophages infected by *Leishmania* have been observed.(3). Metabolites have been extracted from mice's tibia and femur and derivatized (methoxymation and silylation reactions), following the procedures described in the literature for the analysis of *Leishmania* promastigotes, and analyzed by GC-MS according to the Fiehn´s library conditions.(4,5) The obtained data are being evaluated using software and algorithms dedicated to metabolomics, such as MS-Dial, MZMine, Excel and MetaboAnalyst, in order to identify potential biomarkers for leishmaniasis, and comprehend the metabolism related to fatty acids presence involved in the course of the infection.

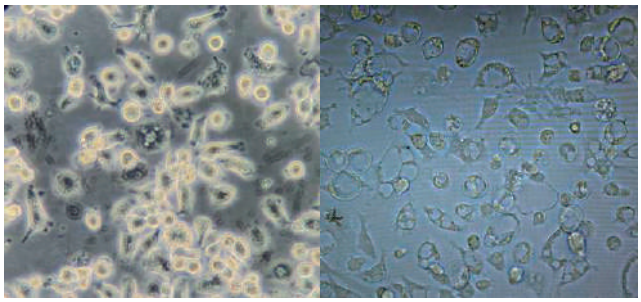


Figure 1- Macrophages after 1 hour of infection by *L. braziliensis* (left) and *L. amazonensis* (right).

References: [1] NAFARI, A. *et al. Parasite Epidemiol. Control*, 10, e00156, 2020.
[2] COSTA, M. B. 2020. Dissertação (mestrado) - Universidade Estadual de Campinas, Instituto de Biologia, Campinas, SP.
[3] FORTÉA, J. O. *et al. BMC Genômica* **10**, 119 (2009).
[4] REY-STOLLE, F. *et al. Anal. Chim. Acta*, 1210, 339043, 2022.
[5] FIEHN, O. *Curr. Protoc. Mol. Biol.* 2016.

Acknowledgments

CAPES, CNPq and IFSP.

Área: ANA

IRON NANOPARTICLES FUNCTIONALIZED WITH CYSTINE AS SOLID PHASE FOR TRACE ELEMENTAL ANALYSIS BY ICP-OES

Débora R. O. Silva* (PG)[1], William M. X. Silva (IC)[1], Fernando L. Menezes (PG)[1], Pierre B. A. Fechine (PQ)[1], Francisco L. F. Silva (PQ)[2], Wladiana O. Matos (PQ)[1]

wladianamatos@ufc.br; debora_fos@hotmail.com

[1]Departamento de Química Analítica e Físico-química, UFC; [2]Faculdade de Educação e Ciências Integradas de Crateús, UECE

Palavras-chaves/Keywords: *Nanomaterial, Magnetic solid phase extraction, Preconcentration, Trace elements*

Highlights

A MSPE method was studied to evaluate magnetite nanoparticles functionalized with cystine as solid phase to analyze inorganic trace elements in complex samples.

Resumo/Abstract

The analysis of trace elements in samples with complex composition might be a challenge. For these cases, separating the analyte(s) from the matrix may be a convenient sample preparation strategy. In this context, nanomaterials emerge as an attractive option as solid phase mainly due to their unique magnetic properties, high surface-to-volume ratio, and the possibility of functionalization. This last feature can promote a selective extraction of trace elements, while their magnetic properties provide an effective separation of analytes from the matrix sample under a magnetic field. In this work, magnetite nanoparticles functionalized with cystine (Fe_3O_4@cyst) were synthesized and characterized to be used as a solid phase in an extraction/preconcentration procedure for Cr, Mo, Pb, and V quantification by ICP-OES. For the synthesis of nanoparticles, about 1.1618 g of $FeCl_3 \cdot 6H_2O$ with 1.8518 g of $FeSO_4 \cdot 7H_2O$ was dissolved in 15 mL of distilled water. This mixture was subjected to ultrasonic agitation for 4 min until it reached a temperature of 60° C, and then 7 mL of NH_4OH was added dropwise. After the solution turned black, it was stirred for another 4 min. Finally, 4.0 mL of 0.2 mol L^{-1} cysteine was added and the solution was stirred for more 4 min. The nanomaterial was characterized using DRX and FTIR (fig.1). The optimization of the extraction method was performed using a full factorial design with 2 levels. The variables pH, extraction time and nanomaterial mass were studied. The desirability function was used in response to analyte recovery (fig.2). The desirable conditions were for 40 mL of sample: pH = 8.0, 30 mg of Fe_3O_4@cyst mass and 10 min of extraction time. For desorption, 1 mL of 10 % v v^{-1} HNO_3 was added and mixed for 5 min. The solution was magnetically separated to the nanomaterial, and the supernatant was carried out to ICP-OES analysis. In this experimental condition, the Cr, Mo, Pb and V showed recovery above 85%. As a perspective, the best experimental condition will be applied to real samples of seawater and seaweed.

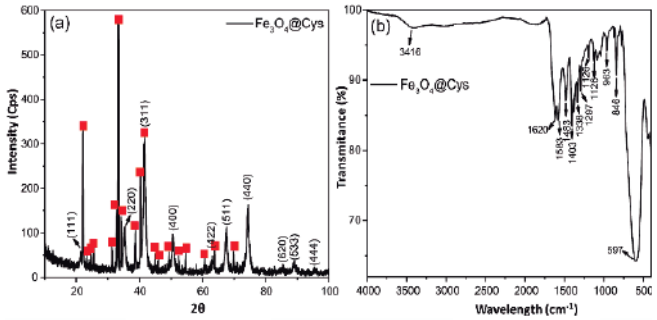


Figure 1: DRX diffractogram and FT-IR Spectra for Fe_3O_4@cyst

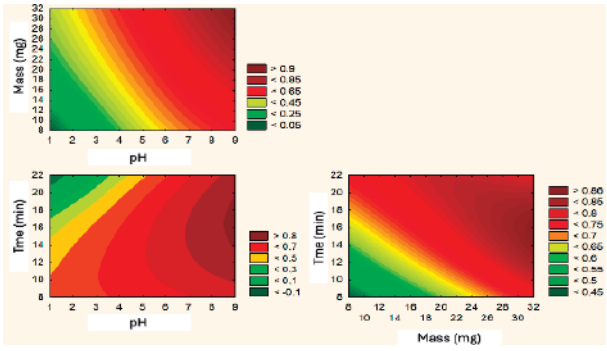


Figure 2: Desirability graph for full factorial design

Acknowledgments

UFC, PGQUIM, NUTEC, CAPES, CNPq

Área: ANA
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Is it possible to predict the classification of illicit drugs? Combined use of analytical, computational chemistry, and chemometrics methods.

Caio Henrique Pinke Rodrigues (PQ)[1], Lívia Salviano Mariotto (PG)[1], Aline T. Bruni (PQ)[1]

caio.pinke.rodrigues@usp.br; aline.bruni@usp.br

[1] *Instituto Nacional de Ciência e Tecnologia Forense (INCT Forense) e Departamento de Química, Faculdade de Filosofia, Ciências e Letras de Ribeirão Preto, Universidade de São Paulo. Ribeirão Preto, SP, Brasil, 14040-900.*

Palavras Chave: . *New Psychoactive Substances, Infrared Spectroscopy, Chemometrics, Computational Simulation*

Highlights

We observed that it is possible to classify the drug classes studied.
We demonstrated that the methodology was suitable for evaluating definitive tests and databases.

Resumo/Abstract

New psychoactive substances (NPS) have been known for at least a decade but still pose a significant challenge for identification. This is due to the constant emergence of a variety of new structures. Several forensic centers follow the recommendations of the Scientific Working Group for the Analysis of Seized Drugs (SWGDRUG). This group outlines minimum requirements for the identification of seized drugs. Infrared spectroscopy (IR) is one of the techniques used for identification. Considered a Category A technique, it indicates the potential for structural information and a high level of selectivity. The main objective of this work was to use infrared spectra of NPS obtained through density functional theory (DFT) to classify structures available in virtual libraries. Data were simulated for five groups of drugs: a) Amphetamines (21 molecules), b) Cathinones (21 molecules), NBOHs (4 molecules), NBOMes (16 molecules), and 2C (11 molecules). All were simulated using the B3LYP functional with the TZVP basis with the ORCA software. All values showed positive frequencies, indicating a minimum energy conformation. These 73 molecules were used to generate the prediction model. Infrared experimental data were collected from the SWGDRUG and the European Network of Forensic Science Institutes (ENFSI) libraries. We collected data for prediction, including a) Amphetamines (39 molecules), b) Cathinones (40 molecules); NBOHs (26 molecules), NBOMes (5 molecules), and 2C (19 molecules). All data were adjusted for transmittance with a resolution of 4 cm^{-1} from 400 to 4000 cm^{-1}. Two exploratory approaches were used: two univariates, including the Pearson correlation coefficient with a heat map, and one multivariate, Principal Component Analysis. A multivariate classification technique, Soft Independent Modeling of Class Analogy (SIMCA), was applied to verify the substance classes. Exploratory results with theoretical data indicated clear information with a strong positive correlation within each class but weak between different classes. SIMCA results indicated that classes required three components to model each. The model successfully predicted 74.4% of molecules in the correct classes. Specifically, the model made accurate predictions for amphetamines (97.4%), cathinones (97.5%), and 2C (100.0%). NBOHs and NBOMes were not predicted in any class. We conclude that theoretical infrared spectra libraries can be used to predict experimental data correctly. In the case of unpredicted molecules, there is a need to expand the library for this data. Thus, using this data to feed training sets can be an essential ally in predicting molecules of unknown drugs.

Agradecimentos/Acknowledgments

The authors are thankful agencies for their financial support: Instituto Nacional de Ciência e Tecnologia Ciências Forenses (INCT Forense/CNPq, project 465450/2014-8; process 104496/2023-1), Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES, Financial Code 001), the Programa Nacional de Cooperação Acadêmica - Segurança Pública e Ciências Forenses (PROCAD-SPCF/CAPES Notice 16/2020 - process 88887.613955/2021-00).

Área: ANA

Low-cost fluorometer using Arduino microcontroller and TSL2561 light sensor.

Eduarda Garcia Santana (PG),[1] James Michael Silva (PG),[1*] Vanessa Nunes Alves (PQ),[1].

eduardagarciasantana212@gmail.com; james.silva19@discente.ufcat.edu.br.

[1]*Instituto de Química, Universidade Federal de Catalão.*

Palavras Chave: *Analytical instrumentation, Internet of Analytical Things, TSL2561 sensor, Fluorescein, Arduino.*

Highlights

A system for the detection and quantification of the Fluorescein dye was built using low-cost materials and 3D printing. This was achieved through an Arduino microcontroller and a light sensor (TSL2561).

Resumo/Abstract

The production and use of dyes are undeniably important for society as a whole. Their use is present from the textile industry to the pharmaceutical industry and food manufacturing. However, their incorrect disposal in rivers and lakes represents a growing environmental concern, as it not only harms the environment but also human health. Due to this reason, monitoring of these pollutants is of paramount importance. Currently, there are various techniques capable of detecting a variety of dyes, whether of organic origin or inorganic compounds. These are often considered extremely robust techniques, such as mass spectrometry, magnetic resonance imaging, chromatography, fluorescence, spectrophotometric techniques, and others. However, such techniques require a certain cost of operation and maintenance. Due to these factors, there is a constant search for equally efficient and accessible methods for monitoring dyes and other pollutants. In this context, this work aims to construct a fluorimeter, using low-cost components for detection and quantification of the dye Sodium Fluorescein (FS) in aqueous medium. For the construction of the fluorimeter, an Arduino nano microcontroller, together with a TSL2561 light sensor model and an LED as a radiation source, were used. The assembly scheme can be seen in Figure 1. The LED used was the blue one with a wavelength of 464 nm, this close to the excitation wavelength of FS (436 nm). The parameters of the sensor channel (infrared, UV, and UV-vis) were evaluated together with the current applied to the LED, whose control was carried out through resistors. It was observed that the UV-vis channel had the best sensor performance, while the ideal current for the LED was 22 mA, which was regulated by a 150 ohm resistor. Another important aspect evaluated was the influence of the LED radiation on the sensor reading. Ideally, the radiation reaching the sensor/detector should be only that coming from the sample, but the blue radiation from the LED can undergo scattering in solution, directly influencing the signal obtained by the sensor. To try to minimize this problem, a yellow gelatin filter (commonly used in photographic cameras) was used, which in turn was positioned in front of the sensor. After system optimization, an analytical curve was obtained, and it presented good sensitivity and R2 values, respectively 61.1513 and 0.9985. This can be observed in Figure 2.

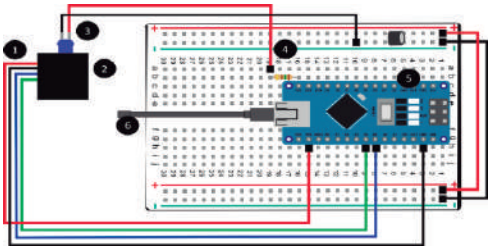


Figure 1: Assembly diagram of the system: 1-TSL2561 Sensor, 2-Cuvette sampler, 3-LED, 4-Resistor, 5-Arduino Nano, and 6-USB cable for computer connection.

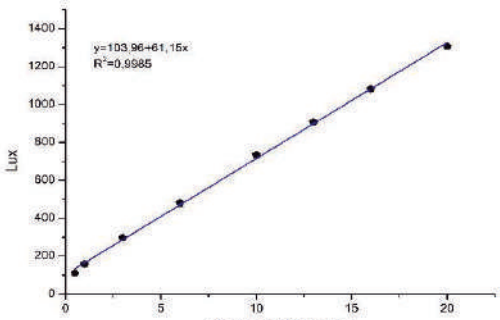


Figure 2: Calibration curve after system optimization.

Agradecimentos/Acknowledgments

The authors express their gratitude for the financial support provided by FAPEG and CAPES.

Área: ANA

Lubricity improvement evaluation of a ternary mixture of diesel-biodiesel-ethyl levulinate

Caio M. Ferreira* (IC),[1] Felipe M. Cairo (PQ),[1] Natália G. de Figueiredo (PQ),[1] Marco A. Fraga (PQ),[1,2] Camila C. Lopes (PG)[1,2]

camila.lopes@int.gov.br; caio.maia@int.gov.br

[1]Instituto Nacional de Tecnologia (INT); [2]Instituto Militar de Engenharia (IME)

Palavras Chave: *Fuel bio-additive, Lubricity, Biodiesel, Ethyl levulinate, Lignocellulosic biomass.*

Highlights

Ethyl levulinate (EL) was evaluated as an alternative bio-additive in a ternary diesel-biodiesel-EL blend. EL appears to be acceptable as a diluent for biodiesel, helping improving blend´s lubricity.

Resumo/Abstract

As time goes by, society became increasingly dependent on fossil fuels. The combustion of this type of fuel is directly related to environmental problems such as the intensification of the greenhouse effect. In order to overcome such problems, the scientific community has been studying alternative renewable energy sources. Alkyl levulinates, esters of levulinic acid obtained from waste biomass, have been investigated as fuel aditives and biolubricants.[1] According to the literature, the addition of levulinates improve diesel´s characteristics such as kinematic viscosity, specific gravity and lubricity. These parameters are directly linked to fuel efficiency in the engine.[2]

Fuels with high viscosity present low particle dispersion, reducing engine efficiency, while specific gravity is related to the fuel combustion efficiency. Lubricity is an important parameter that provides less friction to engine parts, providing longer service life for these parts.[2] For this study, pure diesel (A S10) and pure biodiesel (B100) samples were tested as received. A sample prepared with the biodiesel content in pure diesel oil predicted by Brazilian legislation (15% v/v) was also tested (B15). Additionally, a ternary blend was also tested with volumetric fractions of 85% of diesel A + 10% of B100 + 5% of EL (A85B10EL5). All samples were evaluated with respect to kinematic viscosity at 40 °C (ASTM D445), specific gravity at 20 °C (ASTM D4052) and lubricity (ASTM D6079), according to standard methods.

For the blended samples, both kinematic viscosity and specific gravity were in line with Brazilian´s legislation requirements for biodiesel blend fuel (2,0-4,5 $mm^2\ s^{-1}$ and 0,815-0,850 g/cm^3, respectively). As regarding to lubricity, it´s well known that biodiesel addition improves this property in petrodiesel. However, only few information is available with respect to the addition of EL. In this contribution, it was possible to see that a ternary mixture, meeting the Brazilian´s legislation requirement of 15 % v/v of biofuel, improves significantly petrodiesel lubricity, reducing in almost 50% the scar produced in the test specimen (Table 1). These results opens an interesting opportunity to introduce biomass-derived alkyl levulinates into energy sector boosting its sustainability.

Sample	Kinematic viscosity (mm^2/s)	Specific gravity (g/cm^3)	Lubricity (µm)
A S10	2,965	0,8320	526
B100	4,090	0,8814	189
B15	3,143	0,8393	197
A85B10EL5	2,883	0,8443	260

Table 1. Physicochemical properties of all samples.

Agradecimentos/Acknowledgments

Authors acknowledge financial support from CNPq. CMF thanks PIBITI/CNPq/INT for his scholarship. Authors also thanks Iconic Lubricants for providing pure diesel and biodiesel samples.

[1] Tingzhou Lei, Zhiwei Wang, Xia Chang, Lu Lin, Xiaoyu Yan, Yincong Sun, Xinguang Shi, Xiaofeng He, Jinling Zhu; Energy 95 (2016), 29-40.
[2] Derya Unlu, Nezahat Boz, Oguzhan Ilgen, Nilufer Hilmioglu; Open Chem., 2018; 16: 647–652

Área: ANA

Mass spectrometry imaging as a potential technique to evaluate non-targeted analysis of biological markers of cadmium toxicity in basil tissues

Vânia de Lourdes das Graças Teles (PQ),[1] Matheus Henrique Monteiro Silva (IC),[1] Frede de Oliveira Carvalho (PQ),[1] Rodinei Augusti (PQ),[2] Letícia Malta Costa (PQ).[3*]

vania.teles@ctec.ufal.br; leticia@qui.ufmg.br

[1]Centro de Tecnologia, Universidade Federal de Alagoas; [2]Laboratório de Espectrometria de Massas-LEMS, Departamento de Química, Instituto de Ciências Exatas, Universidade Federal de Minas Gerais; [3]Laboratório de Espectrometria Atômica e Química Analítica e Ambiental - LEAQUAA, Departamento de Química, Instituto de Ciências Exatas, Universidade Federal de Minas Gerais.

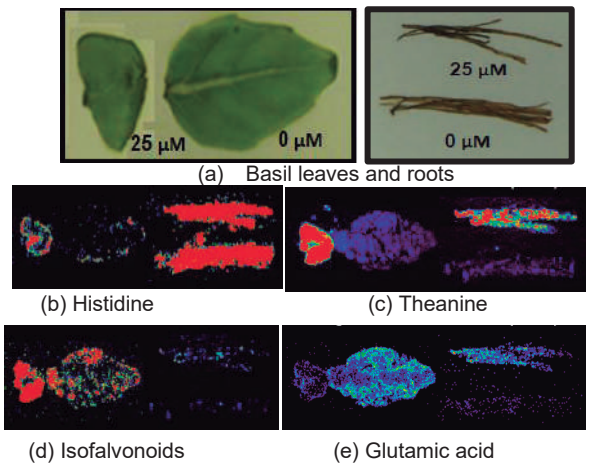
keywords: *mass-spectrometry, imaging, metabolomics, toxic metals*

Highlights

- Non-targeted screening analysis to identify metabolites in basil exposed to Cd
- The root is the key plant organ for Cd biomarker studies in plants

Abstract

Imprinting basil leaves and roots (*Ocimum basilicum* L.) intoxicated with Cd^{2+} (0 and 25 µM) were analyzed on TLC plate substrate for the non-targeted analysis by Desorption Electrospray Ionization Mass Spectrometry Imaging (DESI-MSI). These analyses showed 207 images of ions putatively identified with high accuracy (mass deviation -2.715 to 5.374 ppm) in contaminated and uncontaminated leaves and roots (Fig. 1a). The images showed that 35% of the compounds are present in both samples, characterizing them as naturally present in the basil samples. In addition, approximately 10% of the compounds were identified only in the basil leaf and were inhibited by Cd. Approximately 80% of the metabolites showed no differences in accumulation in the two plant tissues studied, i.e., Cd did not disturb their assimilation through the plant. Some of these metabolites appeared as possible biomarkers to the root and/or leaf, or they were possibly inhibited in the leaf by the presence of the toxic element (Fig. 1b, c e d). It is worth noting that glutamic acid (*m/z* 192.02) was inhibited in the leaf and accumulated in the root, suggesting a possible ability of defense response to Cd intoxication (Figure 1e). Therefore, the images obtained in this study clearly demonstrated the spatial distribution and an integrated view of the plant metabolome. The root is the key plant organ to investigate Cd absorption and translocation through the plant (Fig. 2).



(a) Basil leaves and roots

(b) Histidine (c) Theanine

(d) Isofalvonoids (e) Glutamic acid

Figure 1: (a) Basil leaves and roots at Cd concentration (0 and 25.0 µM) and their images by DESI-MSI such as (b) Histidine (m/z 156,07675), (c) Theanine (Na^+ adduct, m/z 197.0896), (d) isoflavonoids (Na^+ adduct, m/z 383,07374), (e) glutamic acid (K^+ adduct, m/z 192,02438)

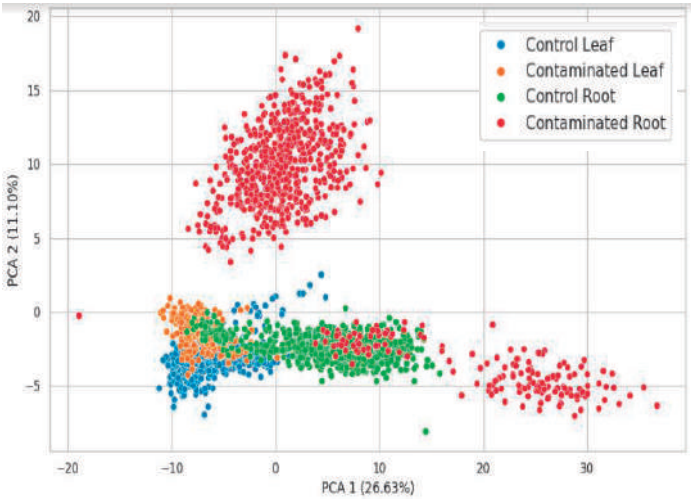


Figure 2: Scores plot generated from PCA for leaves and roots with Cd concentrations of 0 and 25.0 µM

Acknowledgments

CAPES, CNPq, FAPEMIG, PPGQ-UFMG, UFAL and UERR

Área: ANA

METABOLOMICS APPROACH IN BOVINE FECES FOR IDENTIFYING BIOMARKERS ASSOCIATED WITH EXTREMES OF FEED EFFICIENCY AND PERFORMANCE IN NELORE CATTLE

Lívia C. S. Epifanio (IC), Aline T. B. Morais (PQ), Daniel Rodrigues Cardoso (PQ), Luciana C. A. Regitano (PQ)

cicilinilivia@usp.br; drcardoso@iqsc.usp.br

Instituto de Química de São Carlos, USP - Av. Trabalhador São Carlense, 400 – 13566-590 – São Carlos- SP, Brasil

Embrapa Pecuária Sudeste - Rod. Washington Luiz, Km 234 - Fazenda Canchim, -13560-970- São Carlos - SP,, Brasil

Key-words: *Functional genome, Metabolomics, Multi-omics, Metagenome.*

Highlights

Feed efficiency and performance in bovines. Metabolomics. Polar compound profile in Nelore cattle feces. Extremes of feed efficiency and performance in Nelore cattle.

Resumo/Abstract

For the sustainable production of quality meat, it is necessary for the animal to have feed efficiency, since the most expensive and damaging part for the environment is the extensive strip of land needed. Using a controlled diet it is possible to reduce the environmental impact and cost of meat production, increasing its efficiency. The intestine is the organ responsible for the absorption and metabolization of food, serving as a general metabolic source of nutrients, which are produced by the rumen microbiota and are destined by the organism to absorption and excretion. Therefore, metabolites and lipids in the feces of Nelore cattle can assist in the determination of important characteristics for feed efficiency analysis, for example, certain metabolites may be associated with metabolic processes that influence muscular weight gain (loin eye area) or subcutaneous fat deposition. The comprehensive study of metabolome components is called metabolomics, which determines the profile of metabolites generated during metabolism and identification of potential biomarkers. Thus, the present project aims to evaluate the polar metabolites in the feces of Nelore cattle (*Bos indicus*), castrated males, kept in confinement during a performance test conducted in 2019 in the PNAT program, to understand how the metabolites can contribute to the feed efficiency and performance of the animals using metabolomic analysis at the extremes of loin eye area (LEA), subcutaneous fat thickness (SFT), and residual feed intake (RFI) phenotypes. The proposal was to investigate the profile of metabolites in extremes of efficiency of LEA, SFT, and RFI using NMR (Nuclear Magnetic Resonance) as a powerful tool for untargeted quantitative metabolomics. Principal component analysis (PCA) and partial least squares discriminant analysis (PLS-DA) were applied to the NMR spectra data to visualize differences in the two groups of extremes: efficient (E) and non efficient (NE) animals. To define which compounds contributed for extremes of efficiency in the PLS-DA model, a feature selection based on VIP (variable importance in the projection) scores, which is useful to guide the selection of relevant attributes, was performed, and glucose and maltose presented VIP > 1.5 in RFI and LEA, while aspartate and carnitine were the only present metabolites in the SFT group, with a VIP > 0,5. By conducting these initial analyses, it was possible to observe that metabolites are associated with the ingested diet, reflecting in the phenotype of the animal and its feed efficiency.

Agradecimentos/Acknowledgments

Área: ANA
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Method of sample preparation using microwave-assisted mineralization and HG-AAS for selenium quantification

Eduardo A. Orlando (TC),[1*] Augusto C. Costa-Santos (PG),[1] Gisele M. Luz (PG),[1] Juliana A. L. Pallone (PQ)[1]

eduardo9@unicamp.br

[1]*Faculty of Food Engineering, UNICAMP*

Keywords: *selenium, cashew nuts, antioxidant element, food control, rapid method*

Highlights

Sample preparation assisted by microwave without use of muffle furnace incineration. A novel option for determination of selenium in foods. 50% reduction in time spent for sample preparation.

Abstract

The hydride generation atomic absorption spectrometry (HG-AAS) technique is a highly sensitive and low-cost alternative for determining Selenium (Se) in foods. Cashew nuts can be a source of this mineral, considered an antioxidant. Therefore, alternative analytical approaches that allow evaluating the element more quickly are necessary.

The aim of this work was to develop a method for preparing cashew nut samples for Se quantification by HG-AAS using microwave-assisted mineralization (MO), to eliminate the muffle incineration step, which requires a lot of time, frequent supervision and action by the analyst, which may add errors to the determination of the mineral

In this context, the performance evaluation of the proposal was carried out using two alternative options, named method 1 (reference) and methods 2 and 3, which used initial mineralization by MO, followed by drying by heating (to eliminate nitric acid residue), Se reduction and quantification by HG-AAS. Method 2 consisted of direct drying an aliquot of the solution mineralized in MO on a heating plate. Method 3 consisted of adding Magnesium nitrate hexahydrate with the mineralized aliquot in MO, followed by drying and calcining on a heating plate at 450 ºC to form Magnesium Oxide. Four different commercial samples of cashew nuts (A, B, C and D) were analyzed by the three methods, in triplicate.

The results obtained are showed in Figure 1. The use of method 2 presented, on average, Se concentration values 53% lower, when compared to the reference method, indicating that there was a loss of the element during the drying stage.

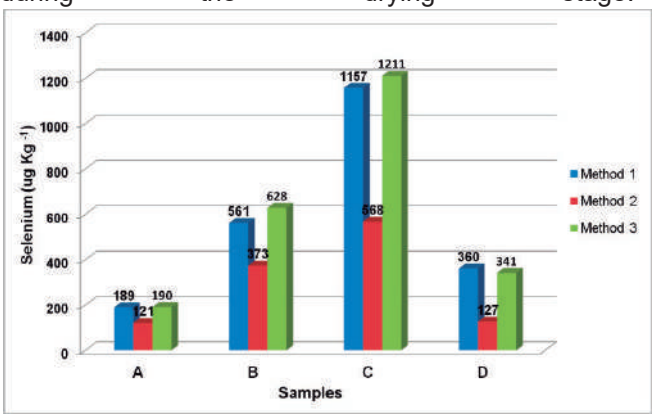


Figure 1: Quantification of Se in cashew nuts with the application of different sample preparation procedures.

In contrast, the results obtained when applying method 3 did not show a significant difference to the reference method (paired t test, α=0.05), indicating that the use of $MgNO_3$ during the drying stage, followed by calcination, was efficient in avoiding losses of Se. In addition, with this new sample preparation method, total duration of the analysis was around 50% shorter compared to the reference method.

Among the evaluated samples, Se content varied between 189-1157 µg Kg^{-1}, indicating a wide variation in the element's concentration and the relevance for the control of its amounts in food. On average, one serving size of cashew nuts (15 g) can provide 5-31% of the Recommended Daily Intake of Se.

Acknowledgment

The authors acknowledge the São Paulo Research Foundation (FAPESP) and the Coordination for the Improvement of Higher Education Personnel (CAPES) for their support in the progress of the study.

Área: ANA

MODIFIED NUCLEOSIDES AS PUTATIVE BIOMARKERS OF PROSTATE CANCER: TARGET METABOLOMICS OF *IN VITRO* SAMPLES BY CE-UV

Isabela Rocha (IC)[1]*, Ingridi Rafaela de Brito (PG)[2], Aline Mara dos Santos (PQ)[2], Ana Valéria Colnaghi Simionato (PQ)[1]

rocha-isabela@outlook.com

[1]*Institute of Chemistry, UNICAMP*
[2]*Institute of Biology, UNICAMP*

Palavras Chave: *Cancer, nucleosides, in vitro samples, metabolomics, capillary electrophoresis*.

Highlights

Evaluation of some conditions of analyses and method validation. Metabolomics analyses by capillary electrophoresis with detection via ultraviolet radiation absorption are underway.

Resumo/Abstract

Prostate cancer is the fourth most diagnosed tumor in the world, and the second most common among men.[1] The incidence of prostate cancer has raised, as there is a trend towards an increase in life expectancy, that is, population aging.[2] In this work, targeted metabolomics analysis of extracellular medium from both healthy and cancerous prostate cells using capillary electrophoresis with UV absorption detection (CE-UV) are underway.

The CE-UV method had already been optimized in previous work.[3] Even though, some parameters were evaluated, and validation step was entirely performed again according to National Health Surveillance Agency Guide (Resolution of the Collegiate Board – RDC nº166, of December 24th, 2017).

The condition that provided the best resolution and peak shape was selected as follows (Figure 1): background electrolyte (BGE) composed of 30 mmol/L sodium tetraborate at pH 9.90, 50 mmol/L cetyltrimethylammonium bromide , 10% MeOH (v/v); V = -10 kV; T = 20 °C; λ = 260 nm; hydrodynamic introduction at 50 mbar for 120 s, followed by the application of 25 kV for 15 s between BGE vials. The nucleoside standards for method development and validation were: Cytidine (C), Adenosine (A), Thymidine (T), Guanosine (G), Xanthosine (X), Inosine (I), and 8- Bromoguanosine (8BrG) (internal standard). Some of the validation parameters are described in Table 1.

Healthy and cancer prostate cells were cultivated, the extracellular media were collected, and are under analyses for metabolomics evaluation.

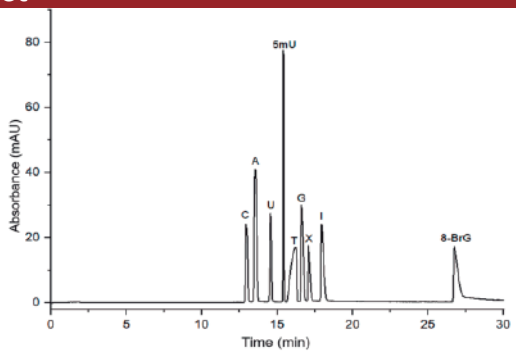


Figure 1. Electropherogram obtained after optimization.

Table 1. Limits of quantification, Analytical curve equation, correlation coefficient (r), intra-day precision, and accuracy for each standard using internal standardization.

Standards	LOQ (μmol L^{-1})	Analytical Curve Equation	r	Precision (%) *	Accuracy (%) **
C	55	$y = 4{,}45x10^{-4}x + 0{,}001$	0,9968	2,33	
A	37	y = 0,00132x + 0,0085	0,9959	4,17	5,21
G	2,5	y =0,01226x + 0,0204	0,9963	1,90	12,79
T	10	y =0,00456x + 0,004	0,9997	0,24	8,92
X	2	y =0,00456x + 0,004	0,9967	3,24	4,74
I	1,5	y =0,03191x + 0,02755	0,9971	1,90	4,91
8-BrG	3	-	-	-	-

*Relative standard deviation of the medium concentration.
**Relative standard deviation of the medium concentration.

REFERENCES

[1] The Global Cancer Observatory. Prostate Cancer incidence and mortality statistics worldwide and by region. Disponível em: <https://gco.iarc.fr/today/data/factsheets/cancers/27-Prostate-fact-sheet.pdf>. Acesso em: 11 jul. 2023

[2] TEOH, Jeremy Y. C.; HIRAI, Hoyee W.; HO, Jason M. W.; et al. Global incidence of prostate cancer in developing and developed countries with changing age structures. Plos One, v. 14, n. 10, p. e0221775, 2019.

[3] BUZATTO, A. Z. et al. Assessment of nucleosides as putative tumor biomarkers in prostate cancer screening by CE–UV. Analytical and Bioanalytical Chemistry, v. 409, n. 13, p. 3289–3297, 25 mar. 2017.

Agradecimentos/Acknowledgments

We gratefully acknowledge financial support from FAPESP 2022/14825-0.

Área: ANA
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Molecular fingerprint of oil spills in Brazil for the investigation of environmental crimes and forensic studies

Flavia R. Alvares (PG)[1]*, Vinícius B. Pereira (PG)[2], Ana Luiza B. S. Silva (IC)[1], Luiz Augusto de O. Costa (PQ)[3], Débora de A. Azevedo (PQ)[2], Francisco R. de Aquino Neto (PQ)[1], Gabriela V. Costa (PQ)[1]*

flaviarodrigues@pos.iq.ufrj.br; gabrielavanini@iq.ufrj.br

1 Núcleo de Análises Forenses (NAF), Instituto de Química, UFRJ; 2 Laboratório de Geoquímica Orgânica, Molecular e Ambiental (LAGOA), Instituto de Química, UFRJ; 3 Instituto Brasileiro do Meio Ambiente e dos Recursos Naturais Renováveis (IBAMA)

Palavras-Chave: *Biomarcadores, Geoquímica Forense, Petróleo, GC×GC-TOFMS, Orbitrap-HRMS*

Highlights

Analysis of oil spills occurring in Brazil. Application of Orbitrap-HRMS and GC×GC-TOFMS in forensic geochemistry. Organic geochemistry applied to forensic studies aiming at environmental crimes.

Resumo/Abstract

Petroleum is the world's main energy source. Recently, its large production chain increased the occurrence of oil spills, which can cause major environmental and economic impacts. The geochemistry characterization of spilled oils is an important tool to study their origin, and helps in the investigations of environmental crimes.[1] In this study, the molecular analyses of seven spilled oils from different sites in Brazil (four in Fernando de Noronha and three in Ceará States) were performed using comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometry (GC×GC-TOFMS) and high-resolution mass spectrometry (Orbitrap-HRMS) to investigate geochemical biomarkers and polar compounds. Oil samples were extracted using Soxhlet, followed by the asphaltenes precipitation procedure. Thereafter, maltenes were fractionated by liquid chromatography, which separated them into saturated, aromatic, and polar compounds. Cyclic and branched hydrocarbons were separated in the saturated fraction using the urea adduct procedure and analyzed by GC×GC-TOFMS. The biodegradation level of the oils can be estimated according to the presence of 25-nor-hopane (25-NH), 25,28-bis-nor-hopane (25,28-BNH), 25,30-bis-norhopane (25,30-BNH), and 25,28,30-tris-nor-hopane (25,28,30-TNH), and their geochemical ratios with 17α(H),21β(H)-29-hopane (H29), and 17α(H),21β(H)-30-hopane (H30). The biodegradation of Fernando de Noronha samples had average values of: 25NH/H30= 0.12; 25,28BNH/H30= 0.02; 25,30BNH/H29= 0.02; 25,28,30TNH/H29= 0.01; 25,28,30TNH/H30= 0.01. These parameters indicate that these oils are severely degraded or constitute a mixture of oils.[2] Oils from Ceará present a low concentration of these compounds, indicating a lower biodegradation. Unusual biomarkers, such as demethylated hopanes (D30-31), can corroborate with the biodegraded characteristic of the Fernando de Noronha samples (**Figure 1**).[3] The ratio of C27ααα S/(R+S) steranes varied between 0.39 and 0.48 and C27[αββ/(ααα+αββ)] was between 0.30 and 0.47 in oils from Fernando de Noronha. In oils from Ceará, C27αααS/(R+S) varied between 0.52 and 0.74 and C27[αββ/(ααα+αββ)] was between 0.44 and 0.70. These results indicate that oils from Ceará have greater thermal maturity than those from Fernando de Noronha. In addition, the most abundant chemical species detected in Fernando de Noronha sample were from the classes N [H], NO [H] and NO2 [H]. Meanwhile, Ceará samples presented the classes N [H], N2 [H] and NO [H] in greater abundance. These geochemical characteristics enable to correlate the spill oils, as they were not significantly affected by degradation processes.[1] Based on these results, the spills in Ceará and Fernando de Noronha are inconsistent with each other, indicating different spills'sources on the Brazilian coast.

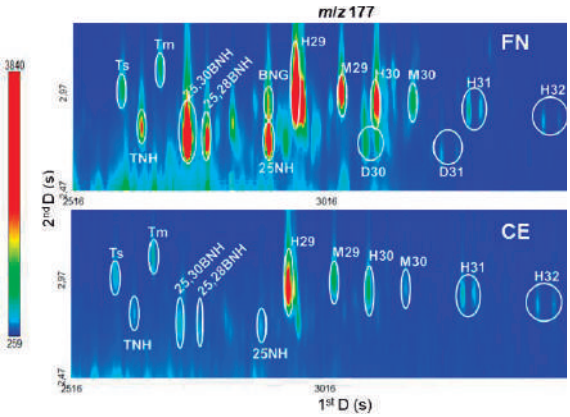


Figure 1. EIC (m/z = 177) of oil spill samples.

1. LIMA, B. D. *et al.* Marine Pollution Bulletin **2023**, 189, 114744
2. SOARES, R. F. *et al.* J. Braz. Chem. Soc. **2013**, 24, 1570-1581
3. VOLKMAN, J. K. *et al.* Geoch. Et Cosmo. Acta **1983**, 47, 785-794

Agradecimentos/Acknowledgments

The authors gratefully acknowledge the financial support from the IBAMA, PRH-ANP, Finep, CNPq and CAPES

Área: ANA

Multielement analysis, cannabinoid profile determination and their correlation in medicinal *Cannabis* herbal extracts (CHE) from Rio de Janeiro

João Victor Meirelles Leite (PG)[1,2], Monica Costa Padilha (PQ)[2], Tatiana Dillenburg Saint Pierre (PQ)[1]

jvmeirelles18@seuemail.com;

[1]*Pontifical Catholic University of Rio de Janeiro, Department of Chemistry, Rio de Janeiro, RJ, Brazil, 22451-900;*
[2]*Federal University of Rio de Janeiro, Institute of Chemistry, Rio de Janeiro, RJ, Brazil, 21941-909*

Keywords: Cannabis, ICP-MS, LC-MS, Orbitrap*, multiement analysis, cannabinoid content.*

Highlights

Optimized and validated methods by ICP-MS and LC-Orbitrap were applied to 6 *Cannabis* herbal extracts. Higher Pb and Al and lower Sn and Sb contents were found compared to vegetable oils. Heterogenous cannabinoid profiles were observed, suggesting no standardized quality and integrity. K and Mg demonstrated strong negative correlations with therapeutic cannabinoids, while Ni and Sn provided strong positive correlations with degradation products.

Resumo/Abstract

Cannabis is a highly diverse and polymorphic plant genre with an extensive capacity for metabolite biosynthesis. The psychoactive potential of Cannabis has been known for more than 5 millennia, and the search for its use, both medicinal and recreational, is currently expanding. Medicinal *Cannabis* herbal extracts (CHE) stand out among therapeutical *Cannabis*-derived products. As judicial and social advancements are made the need to standardize risk assessments and quality monitoring approaches is emphasized. In this work, analytical methods for multielement analysis by ICP-MS and CBD, THC, and CBN quantification by HPLC-Orbitrap, both previously optimized by Design of Experiments and validated by ANVISA RDC 166/2017, were applied to 6 Cannabis herbal extracts, kindly donated by a *Cannabis*-supporting association from Rio de Janeiro. Compared to a traditional vegetable oil analyzed, all samples demonstrated statistically higher concentrations of Pb and Al and lower concentrations of Sn and Sb, while 4 of 6 samples provided higher content of Mg and Mn. Regarding cannabinoid profile, heterogenous THC:CBD ratios were reported in a single production batch, ranging from 1218 to 0.25, and diversified concentrations of CBN (a THC-degradation product and a CHE-degradation marker) were observed, reiterating a non-standardized integrity. Both K and Mg demonstrated strong negative correlations ($\rho > -0.5$) with CBD and THC – therapeutic cannabinoids and active ingredients of CHE – while CBN provided strong positive correlations ($\rho > 0.5$) with Ni and Sn, suggesting partaking of these elements in the matrix oxidative mechanisms. Notably Ni provided a perfect negative correlation with THC ($\rho = -1$) while a moderate positive correlation with CBN ($\rho = 0.5$) suggesting a highlighted contribution. On the other hand, Mn demonstrated a strong negative correlation ($\rho = -0.800$) with CBN, suggesting a protective effect. Further investigations of cannabinoid degradation in the presence of strategic elements with considerable oxidative potential, such as Ni, will be conducted.

Agradecimentos/Acknowledgments

The authors gratefully acknowledge the financial support from Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Fundação de Amparo à Pesquisa do Estado do Rio de Janeiro (FAPERJ), and Laboratório Brasileiro de Controle de Dopagem (LBCD).

Área: ANA
Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Nickel and cobalt separation from iron in laterite sulfuric leachate by selective precipitation of hydroxides.

Samuel Cursino Faria (TM),[1*] Marisa Nascimento (PQ),[2] Flávio de Almeida Lemos (PQ),[2] Andrey Linhares Bezerra de Oliveira (PQ),[3] Caroline Diniz Valente Corrêa (TM),[1]

samuel_cursino@hotmail.com

[1]Técnico em Química, IFRJ; Bolsista PCI-DE, CETEM; [2]Coordenação de Processos Metalúrgicos e Ambientais, CETEM; [3]Coordenação de Análises Minerais, CETEM.

Palavras Chave: *Nickel, Laterite, Sulfuric leaching, Selective precipitation.*

Highlights

Laterites are rich in iron, requiring purification of the leachate. The solubility of $Fe(OH)_3$ is lower than that of $Ni(OH)_2$ and $Co(OH)_2$, thus, it may be possible to separate the iron with pH control.

Resumo/Abstract

1 INTRODUCTION

Zhao et al. (2013) reported separation efficiencies of 77.29% and 65.87% for nickel and cobalt in laterite leachate when using sodium hydroxide as a precipitating agent. Efficiencies of 95.36% for iron were also indicated.

2 RESULTS AND DISCUSSION

To construct the theoretical diagram of the separation of metallic species in solution, the initial concentration values in the leachate and the Kps of the respective hydroxides of the metallic species were considered.

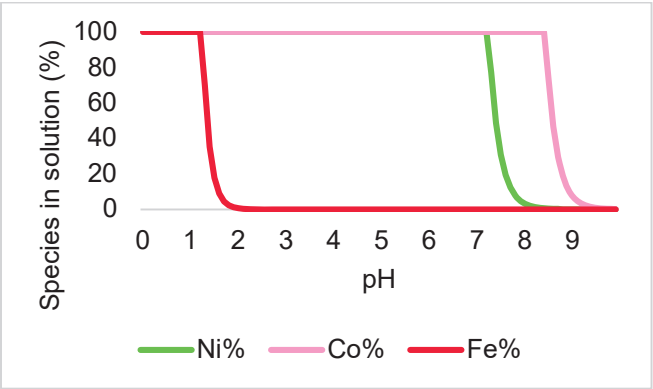


Figure 1. Theoretical diagram of species separation in the leachate.

According to the graph, it would be possible to carry out the separation of iron. However, the separation between nickel and cobalt would not be effective.

Figure 2 shows the separation diagram of the metals. When performing the tests, the separation did not occur as expected according to the theoretical diagram.

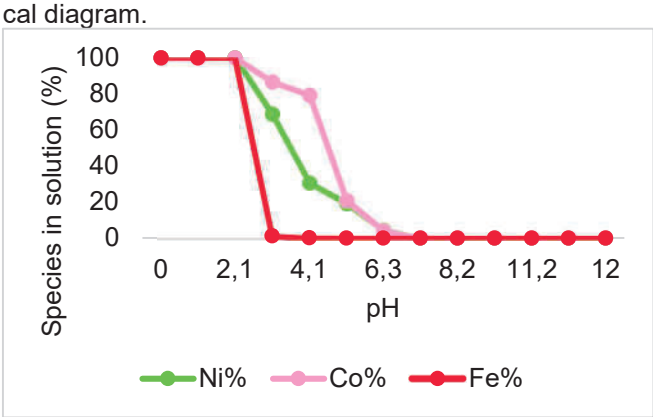


Figure 2. Experimental diagram of species in the leachate.

The separation was not considered satisfactory because at pH 4, when 99.9% of the iron had precipitated, there was co-precipitation of 69.2% of nickel and 20.5% of cobalt. Iron(III) hydroxide is a colloidal precipitate that is capable of adsorbing other ions (Skoog, 2005). Thus, the observed phenomenon is explained where, despite the being possible in theory, it was not carried out in practice.

3 REFERÊNCIAS

SKOOG, D. A. et al. **Fundamentos de química analítica**. 8ª edição. Thompson. Mexico DF, 2005.

ZHAO, Yan et al. Extraction and of nickel and cobalt fr om saprolite laterite ore by microwave assisted hydrot hermal leaching and chemical deposition. **Internationa l Journal of Minerals, Metallurgy, and Materials**, v. 20, p. 612-619, 2013.

Área: ANA

Preparation and application of hydrophobic deep eutectic solvents in the extraction of polybrominated flame retardants present in slugde samples

[1*] **Iara Graciele da Silva (IC), [1] Karen Chibana Ferreira (PG), [2] Thais Rodrigues (PG), [3] Letícia Maciel de Souza (IC), [1] Paulo Clairmont Feitosa de Lima Gomes (PQ)**

ig.silva@unesp.br

[1]Instituto de Química Unesp – Araraquara

Keywords: Sample preparation, HDES, DLLME

Highlights

Use of hydrophobic deep eutectic solvents as extraction solvent of PBDE through dispersive liquid-liquid microextraction (DLLME)

Abstract

Emerging contaminants, such as polybrominated diphenyl ethers (PBDEs), may be present in environmental samples, posing risks to human health and the aquatic ecosystem due to their use as flame retardants. Monitoring PBDEs in environmental samples is essential, and hydrophobic deep eutectic solvents (HDES) are proposed due to their low toxicity. HDES constitutes a subgroup of deep eutectic solvents (DES) produced by mixing two or three precursors, forming intermolecular hydrogen bonds involving a hydrogen bond donor (HBD) and an acceptor species (HBA). Gas chromatography requires a sample preparation step to minimize potential damage to the system. The use of miniaturized techniques, such as dispersive liquid-liquid extraction (DLLME) presents advantages since, it is based on the partitioning of analytes using small volumes of a solvent mixture (disperser and extractor), offering benefits such as miniaturization, low cost, speed, high extraction efficiency, and pre-concentration. The research aims to prepare HDES and use it as an extractor solvent in DLLME to determine PBDE-28, PBDE-47, PBDE-99, PBDE-100, and PBDE-153 in sludge samples by GC-ECD. Initially, 1µL injections of each PBDEs standard [1] were made. .The column used was ZB-5MS (dimension: L= 30m, ID = 0.25 mm, FT = 0.50 µm + 5 m Guardian TM) using temperature programming starting at 80ºC finishing at 320ºC with rate of 30 ºC min^{-1} with N_2 as carrier gas at 1.0 mL min^{-1} . To prepare HDES, DL-menthol was used as the HBA, and organic acids (acetic, decanoic, and dodecanoic) as the HBDs. The precursor mixture was heated to 50ºC with stirring for 20 minutes and then cooled to room temperature. HDES characterization was performed using Fourier-transform infrared spectroscopy (FTIR), thermogravimetry (TG), differential scanning calorimetry (DSC), and differential thermal analysis (DTA) to confirm HDES formation. Subsequently, DLLME was performed on water and sludge samples fortified with PBDE-28, PBDE-47, PBDE-99, PBDE-100 e PBDE-153 As optimal conditions for DLLME in these samples were 300 µL of HDES, 350 µL of hexane as solvent dispersor, and sample pH = 10. Retention times for PBDE 28, PBDE 47, PBDE 99, PBDE 100, and PBDE 153 were 8.01, 9.32, 11.2, 10.5, and 13.5 min, respectively. All HDES appeared clear, except for the mixture containing dodecanoic acid, which exhibited a yellowish color due to its precursor.The density of DL-Menthol + Acetic acid was 0.94 g/cm^3, DL-menthol + dodecanoic acid was 0.90 g/cm^3, and DL-Menthol + decanoic acid was 0.91 g/cm^3. All HDES had lower densities compared to water, indicating that the upper phase containing HDES should be collected for subsequent analyses. The detection and quantification limits were ranged from 1 to 30 µg L^{-1} and 5 to 30 µg L^{-1}, respectively. The analytical curve of PBDE-28, PBDE-47, PBDE-99, and PBDE 100 was determined and represented as follows: y= 60.8x - 2.23 with an R^2 = 0.99 in the concentration range of 5.00 to 800 µg L^{-1}; y = 50.7x - 14.9 with an R^2 = 0.99 in the concentration range of 5.00 to 600 µg L^{-1}, y = 44.4x - 112 with an R^2 = 0.99 in the concentration range of 10.0 to 1200 µg L^{-1}, y = 65.5x - 20.5 with an R^2 = 0.99 in the concentration range of 5.00 to 600 µg L^{-1} and y = 35.2x - 531 with an R^2 = 0.98 in the concentration range of 30.0 to 2400 µg L^{-1}. Furthermore, the three HDES were effective as extracting solvents, proving to be a promising strategy in the liquid-liquid microextraction technique with dispersive droplets (DLLME) for the simultaneous determination of PBDEs in environmental samples.

References:

CALDEIRÃO, L. et al. A novel dispersive liquid-liquid microextraction using a low density deep eutectic solvent-gas chromatography tandem mass spectrometry for the determination of polycyclic aromatic hydrocarbons in soft drinks. Journal of Chromatography A, 2020.

Acknowledgments

Instituto de Química FAPESP 2022/02991-3 CNPQ CAPES DATREM INCT 2014/50945-4 PROPe 09/2023

Área: ANA
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Procedimento automático para determinação fotométrica de etanol em cerveja sem desgaseificação prévia

Rafael A. Alexandre*(PG), Boaventura F. Reis (PQ)

rafaelalcarde@usp.br; reis@cena.usp.br.

Centro de Energia Nuclear na Agricultura, Laboratório de Química Analítica "Profº Henrique Bergamin Filho" Universidade de São Paulo, Piracicaba, SP, Brasil

Palavras Chave: *Etanol em cerveja,* F*otômetro de LED, Determinação fotométrica de etanol, Separação por arraste com fluxo de ar, Automação com Arduino Due; Método ambientalmente sustentável.*

Highlights

Automatic procedure for photometric determination of ethanol in beer without prior degassing step.

-Integrategration of reaction unit and detecting devices to achieve a compact and downsized setup.
-Instrumental setup with facilities to control all step of the analytical procedure and data acquisition.
-Analytical procedure designed to meet the “Green Analytical Chemistry” guidelines..

Resumo/Abstract

Etanol é um parâmetro de qualificação de cerveja, portanto sua determinação é essencial, principalmente na etapa de preparação, e tem sido realizada empregando métodos analíticos baseados em cromatografia em fase gasosos, eletroforese capilar, reação enzimática com detecção por amperometria ou espectrofotometria. A cerveja é uma matriz complexa, constituída por várias substâncias, tais como sacarídios, proteínas, alcóis, vitaminas, polifenóis, e outros mais. Essas espécies químicas podem dificultar a determinação. Para contornar essa dificuldade tem sido empregada uma etapa de separação, usando membrana de hidrofóbica (Teflon). A determinação fotométrica baseada na reação de oxidação do etanol com dicromato de potássio ($Cr_2O_7^{-2}$) em meio de ácido sulfúrico, também tem sido usada. O espectro de absorção de radiação eletromagnética do íon cromo (III) em meio aquoso, é em torno de 590 nm, então permite usar um LED como fonte de radiação e um fotodiodo como sensor fotométrico, o que reduz o custo da instrumentação, entretanto requer uma etapa de separação do etanol da amostra, pois outros composto presentes na cerveja podem ser oxidados.

Neste trabalho, foram desenvolvidos um equipamento e um procedimento analítico para a determinação de etanol em cerveja, baseado na reação de oxidação do etanol com dicromato de potássio. O equipamento foi constituído pelo dispositivo de separação do analito por arraste com fluxo de ar, usando um mini compressor de ar; e cela de reação integrada ao dispositivos de detecção fotométrica. O etanol transportado pelo fluxo de ar, foi borbulhado na cela de deteção, onde previamente foi colocada uma alíquota da solução de $Cr_2O_7^{-2}$. Todas as etapas do procedimento analítico foram controladas com uma plataforma Arduino Due.

Após a seleção das variáveis de controle, os seguintes dados foram obtidos: volume de amostra 10 mL; concentração de reagente ($Cr_2O_7^{-2}$) 0,08 molL^{-1}, volume da alíquota usada 1,0 mL; tempo para separação do analito 60 s; resposta linear na faixa de 2 – 10% (v/v) etanol, absorbância = 0,107[x] + 0,047 (r^2 = 0,999); [x] = concentração de etanol. O reagente foi preparado em solução de ácido sulfúrico 5 mol L^{-1}.

Os resultados obtidos para amostras de diferentes tipos de cerveja foram semelhantes aos valores de rótulo, indicando que o método proposto é viável, e apresenta como vantagem aos método existentes, não ser necessário uma etapa de desgaseificação das amostra de cerveja.

Agradecimentos/Acknowledgments

Os autores agradecem ao CNPq e a CEPES pelo apoio financeiro, incluindo as bolsas de mestrado de Rafael A. Alexandrino e pesquisador de Boaventura F. Reis.

Área: ANA

Restricted double access ionic imprinted polymer for online extraction and determination of copper from milk samples via FIA-FAAS system

Daysla Fernanda Moreira Naves (PG)[1*], Cristiane dos Reis Feliciano (PG)[1], Saulo Alves de Souza (PG)[1], Mariane Gonçalves Santos (PQ)[1].

saulo.souza@sou.unifal-mg.edu.br; dayslamoreira@gmail.com*

[1]*Institute of Chemistry, UNIFAL;*

Palavras Chave: *Restricted access materials, cooper, ionic imprinted polymers, FIA-FAAS, milk.*

Highlights

- Restricted Access Ionic Imprinted Polymers (RAIIPs) are a good strategy for solid-phase extraction (SPE) of metals from complex samples rich in proteins.
- RAIIPs are capable of, simultaneously, selectively retaining the analyte and excluding proteins from the milk samples.
- So, a new double restricted access ionic imprinted polymer (RAIIP-BSA), was synthesized and utilized for determining Cu2+ in untreated milk samples using flow injection analysis and flame atomic absorption spectrometry (FIA-FAAS).

Resumo/Abstract

Conventional methods for determining metals in milk samples typically involve dry or wet digestion processes. However, these techniques often face limitations such as low selectivity, the potential risk of contamination, and the consumption of large volumes of reagents[1]. To address these challenges, solid phase extraction (SPE) employing multifunctional sorbents has been extensively investigated. In this context, our study proposed the synthesis of a new restricted double access ionic imprinted polymer (RAIIP-BSA) for determining Cu^{2+} in untreated milk samples, using flow injection analysis and flame atomic absorption spectrometry (FIA-FAAS). The polymer was synthesized via bulk polymerization, using Cu^{2+} as template, 4-vinylpyridine as functional monomer, and glycidyl methacrylate as hydrophilic comonomer. Subsequently, the epoxide ring was opened and the polymer was coated with bovine serum albumin (BSA), creating a double barrier with restricted access[2]. The synthesized material demonstrated an ability to exclude 97% of proteins from milk samples. Fourier transform infrared spectroscopy and thermogravimetric analysis were used to characterize the sorbent. The adsorption kinetics study revealed that adsorption equilibrium was reached within 10 minutes, with the pseudo-first order model providing the best fit to the experimental data. Furthermore, the adsorption isotherm was more accurately represented by the Sips model. Then, the primary extraction variables were optimized using multivariate optimization techniques. Through interfering ion test, it was determined that RAIIP-BSA exhibits superior selectivity for the analyte compared to the non-imprinted polymer. The developed method presented linearity in the range of 0.05 to 1.0 mg L^{-1}, with limits of detection (LoD) and quantification (LoQ) of 0.03 and 0.05 mg L- 1, respectively. Intra- and inter-day accuracy ranged from 0.73% to 4.14% and 0.16% to 3.68%, respectively, while intra- and inter-day accuracy ranged from 97.0% to 115.0% and 103.0 % to 119.0%, respectively. In conclusion, this developed method has significant potential to replace traditional metal analysis methods in complex matrices.

Referências/ References

1- Silvestre, et al. **Chemistry**, v. 68, n.1, p. 95–99, 1999.
2- De Faria, et al. **Analytica Chimica Acta**, v. 959, p. 43–65, 2017.
3- Borges, et al. **Preparo de amostras para análise de compostos orgânicos**. Rio de Janeiro: LTC, 2015. p. 88-96.

Agradecimentos/Acknowledgments

CAPES, FAPEMIG, CNPQ.

Área: ANA

Síntese e aplicação de resina ZIF-8 para remoção de íons bário de amostras de água de produção

Maria Silvaneide Anjos dos Santos (IC),[1] Nathaly Almeida de Oliveira (PG),[1, 2] Rodrigo da Silva Viana (PQ),[1] Cintya D'Angeles do Espirito Santo Barbosa (PQ),[1] Daniela Santos Anunciação (PQ),[1]

daniela.anunciacao@iqb.ufal.br

[1] *Instituto de Química e Biotecnologia (IQB), Universidade Federal de Alagoas (UFAL).*
[2] *Origem Energia*

Palavras Chave*:* ZIF-8, adsorção, bário, DRX, água produzida, incrustação.

Highlights

Synthesis and application of ZIF-8 resin for removing barium ions from production water samples.

Resumo/Abstract

A ZIF-8 (zeolitic imidazolate framework-8) tem sido um material promissor de grande interesse científico e tecnológico devido às suas características e propriedades estruturais, capaz de formar ligações fortes entre aglomerados metálicos de íons Zn^{2+} e do ligante orgânico 2-metilimidazol dando origem a um complexo. Por apresentar espaçamentos que resultam em sólidos cristalinos com elevada área superficial porosa, a ZIF-8 tem sido amplamente aplicada nas áreas de catálise, separação de gases e na adsorção de íons metálicos em águas residuais. Tendo em vista esses aspectos, o objetivo desse trabalho foi sintetizar e caracterizar a ZIF-8 para atuar como adsorvente de íons Ba^{2+} em água de produção. Inicialmente, a ZIF-8 foi obtida por precipitação sob agitação magnética (2 horas), seguida de uma única etapa de purificação com metanol, sendo recolhida por centrifugação (14500 RPM, 20 min), seca à 25 ºC, e, por fim, macerada para utilização como material adsorvente de bário. Na etapa de caracterização, foi feita a difratometria de raios X (DRX) cujos dados evidenciaram a formação da ZIF-8 com picos característicos condizentes com os do simulado (Figura 1). No teste de adsorção 4 fatores foram avaliados em diferentes condições (pH, tempo, massa de ZIF-8, concentração de $BaCl_2$) a partir de um planejamento fatorial fracionário (2^{4-1}) com 8 experimentos e 4 pontos centrais. Após adsorção, foi feito o DRX da ZIF-8 retida na membrana impregnada com bário e o padrão de difração do material adsorvido não sofreu alterações significativas (o material adsorvido não alterou a estrutura da ZIF-8). A análise das amostras exploradas na adsorção foi feita por espectrometria de absorção atômica com atomização em chama (FAAS), e de acordo com os resultados obtidos, a condição de ponto central (pH 5,5, 35 min, 30 mg de ZIF-8 e concentração de Ba^{2+} de 150 mg/L) apresentou melhor eficiência, com uma média de 69,42% de adsorção(Figura 2). Testes subsequentes estão em andamento para avaliação do uso da ZIF-8 em amostras reais de forma a evitar incrustações de $BaSO_4$ comprometendo assim a produção industrial em empresas de origem petrolífera.

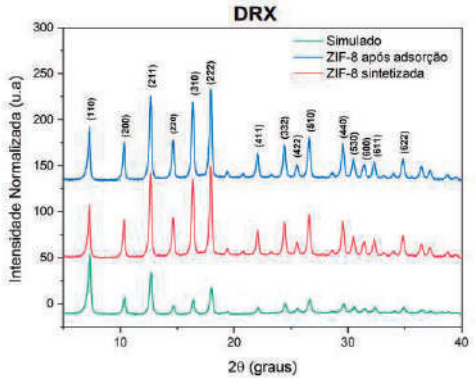


Figura 1: Difratogramas de raios-x (DRX) do padrão simulado obtido da literatura e dos compostos ZIF-8 antes e após adsorção do Ba^{2+}

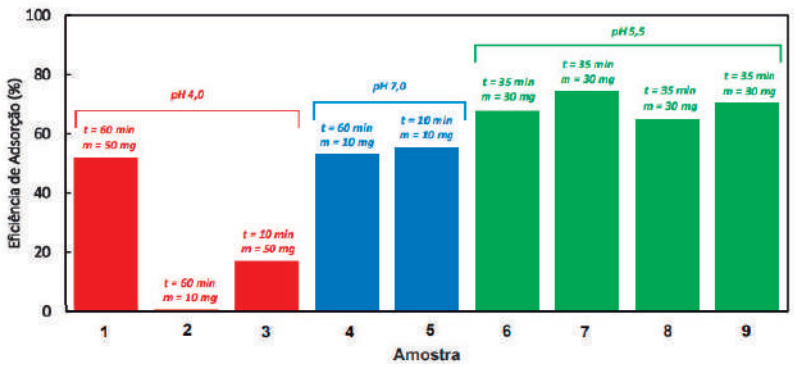


Figura 2: Resultados do estudo de eficiência de adsorção da ZIF-8.

Agradecimentos/Acknowledgments

UFAL, IQB – PPGQB, Caps (Procad), CNPq, FAPEAL e Origem Energia.

Área: ANA

Sample preparation for subsequent metals determination by MIP-OES in biodiesel

Ana Caroline V. Rubin (PG),[1] Alice P. Holkem (PG),[1] Ana Luiza B. Nunes (PG),[2] Fernanda de Castilhos (R),[2] Rochele S. Picoloto (R)[1], Paola A. Mello (R).[1]*

anacvrubin@gmail.com; paola.mello@ufsm.br

[1]Departamento de Química, [2]Departamento de Engenharia Química; Universidade Federal de Santa Maria, Brazil.

Keywords: *sample preparation, MIP-OES, biodiesel.*

Highlights

A protocol for metals determination in biodiesel was proposed; sample preparation of 750 mg was feasible in a closed system with microwave radiation and diluted HNO_3; suitable limits of quantification were obtained using MIP-OES.

Abstract

Biodiesel has been investigated as an alternative for fossil fuels and has been added to diesel oil, reducing polluting gases and promoting the use of renewable resources. It is produced through the process of transesterification of vegetable oil or animal fat with a short-chain alcohol, preferably methanol, through catalysis.[1] The diversified constitution of raw materials and the process itself can contaminate the final product by chemical elements.[1] The determination of contaminants in biodiesel have great importance, as their presence, even at lower concentrations, can change some characteristics, such as, reduced oxidation stability, kinematic viscosity, specific density and cold filter plugging point.[1] In Brazil, the Resolution 920/2023 of the National Agency of Petroleum, Natural Gas and Biofuels (ANP) stipulates the concentration limits for S (10 mg kg^{-1}), Na+K (2.5 mg kg^{-1}), Ca+Mg (2.5 mg kg^{-1}) and P (3.0 mg kg^{-1}). Through NBR 15553:2019, biodiesel samples can be diluted five times with xylene or kerosene for further direct determination of Na, K, Ca, Mg, and P by inductively coupled plasma optical emission spectrometry (ICP-OES). In spite of its simplicity, this approach can impair some problems in the measurement step, due to the formation of carbon deposits in the equipment spare parts as well as interferences, and poor precision, among other problems. Despite acid digestion be an easy approach in routine laboratories to convert samples into aqueous solutions compatible with spectrometric techniques, the decomposition of biodiesel is not a simple task. In this work a protocol was developed for the determination of Na, K, Ca, and Mg by microwave-induced plasma optical emission spectrometry (MIP-OES) in biodiesel. This technique has been used for several matrices, however, it can present worse limits of quantification (LOQs) for some analytes when compared to ICP-OES. The challenge was to obtain a suitable condition for the digestion of sample masses higher than 500 mg, to allow the achievement of the LOQs required by RANP 920/2023, using MIP-OES. An acid digestion method was optimized using a microwave oven with single reaction chamber technology (model UltraWave, Milestone, Italy), equipped five quartz vessels (40 mL of maximum internal volume). The system operates with maximum temperature, pressure, and power of 300 °C, 199 bar, and 1500 W, respectively. After optimization, up to 750 mg of biodiesel were digested using 6 mL of diluted nitric acid (50% v v^{-1} HNO_3) with the following heating program: *i*) 20 min ramp at 80 °C with 10 min hold; *ii*) 20 min ramp at 120 °C with 5 min hold; *iii*) 20 min ramp at 220 °C with 5 min hold; and *iv*) 15 min at 0 W for cooling. Suitable digests were obtained (about 10 g L^{-1} of carbon content and 27% of residual acidity). Using this protocol, the LOQs were: 0.3 mg kg^{-1} for Na, 0.5 mg kg^{-1} for K, 0.7 mg kg^{-1} for Ca, , and 0.1 mg kg^{-1} for Mg by MIP-OES; and 0.4 mg kg^{-1} for Na, 0.2 mg kg^{-1} for K, 1.9 mg kg^{-1} for Ca, and 0.1 mg kg^{-1} for Mg by ICP-OES, which are in agreement with RANP 920/2024. Finally, recoveries higher than 87% were achieved for spiked samples.

1. Ferreira C.C. *et al*. Talanta 138 (2015) 8-14.

Acknowledgments

CNPq, CAPES, and FAPERGS

Área: ANA

An easy access to USB/RS-232 signal in web page: a low-cost alternative for potentiometric titrations as example

Ana Carolina Sebastião Lisboa (IC),[1] Sérgio L. Olivo (PG),[2] Astréa F. de Souza Silva (PQ),[1] André Fernando de Oliveira (PQ),[1*]

andref.oliveira@ufv.br

[1]Departamento de Química, UFV; [2]Departamento de Elétrica e Computação, UNICAMP

Palavras Chave: *potentiometric titration, Web Page, serial port communication, alkalinity, redox titration.*

Highlights

A webpage for interface instruments via RS-232 or USB

A potentiometric titration made with micropipette and using a web page for collecting data from RS232 or USB and construction of a titration curve in real-time.

Resumo/Abstract

The interface of simple instruments is not a trivial task, even nowadays, once it needs a programming step, construction of GUI (Graphical User Interfaces), etc. A web page with tools to collect data from RS232 or USB will be very interesting for several researchers. Actually, it is possible due to the Serial API. In this work, a web page was developed to access a serial port (RS-232 or USB) of pH meters and show the results. All data sent by pHmeter are collected and the analyst selects the stable point after the addition of titrant solution pressing a button. A graphic of pH (or electrical potential difference) vs time and the titration curve are shown in real time. The web page was written with JavaScript using Bootstrap plugin and Web Serial API. In the page is possible to select different kinds of structure of data sent by serial port. Gradually, more patterns of data structure will feed onto the page. Besides, the system allows receive other instruments data, such as conductivity meters or instruments based in Arduino-like prototypes. The web page implementation permits easy access by everyone allied to the fact that pHmeters with RS232 are usual. To show the facilities of this system, we resolve a great problem in the potentiometric titrations. Still the potentiometric titration, mainly the Bronsted Acid-Base, is very important for the characterization of solutions, however, the use of the technique is limited due the fact that commercial instruments are expensive, and homemade titrators are not commercialized. The simplest alternative has been the use of a burette and the titrand solutions with a pH sensor. An expensive time is consumed by written manually the data of volume and pH allied for the difficult of the addition of the right volume and the slow step in the annotation. The two sets of data can be saved to import by other software, such as MS Excel or OriginLab Origin. The results of redox and alkalinity titrations were compared with a commercial titrator (Metrohm Titrando 942) and with a titration simulator software (TiGer). The equivalent point was obtained with Lorentz non-linear model for first derivative graph. The coefficient of variation was less the 3% in the pH values and the time of titration was less than half of time for totally manual titration. The smoothing and other treatment of the input data are possible via Python. By this way, the potentiometric titration will be more applied in research and learning. Advantages are also the web page interface is compared with a version of software written with Python using the Tkinter GUI library; No need of software installation; the GUI is more friendly and easier to upgrade.

Agradecimentos/Acknowledgments

FAPEMIG RED-00144-22 e CNPq: Process: 405828/2022-5

Área: ANA

Sondas colorimétricas para detecção de ácidos nucleicos (DNA e RNA) em amostras biológicas

Carlos Arthur B. Araujo (IC)*, Verônica D. Silva (PQ), Dimas José P. Lima (PQ), Josué C. Caldas Santos (PQ).

carlos.araujo@iqb.ufal.br; josue@iqb.ufal.br

Universidade Federal de Alagoas, Campus A. C. Simões, Maceió - AL, Brasil.

Palavras-chave: Sondas, detecção colorimétrica, aplicações forenses, crimes sexuais.

Highlights

Colorimetric probes for detecting nucleic acids in biological samples. Innovative technology for investigating sexual crimes exploring low-cost, non-destructive probes for qualitative and quantitative analysis.

Resumo/Abstract

Evidências biológicas com interesse forense podem ser encontradas em vários casos de agressão, sendo particularmente relevantes nos crimes de natureza sexual.[1] Os fluidos corporais mais comuns encontrados em cenas de crime são sangue, sêmen e saliva, mas outros, como fluido vaginal, urina e suor, também podem contribuir como evidências valiosas para obtenção de perfil genético.[2] A detecção colorimétrica de ácidos nucleicos (DNA/RNA) empregando tecnologias de baixo custo, não destrutivas, rápidas e práticas é desejável. Neste trabalho foram sintetizadas sondas (**Fig. 1a**) que se ligam não covalentemente ao DNA/RNA, com alteração de cor, sendo, de forma geral, com maior sensibilidade para o DNA comparada ao RNA. Inicialmente, avaliaram-se as sondas frente a DNA/RNA quanto à resposta em função do pH (5, 7 e 9), sendo a maior sensibilidade (coeficiente angular da curva analítica) em pH 7 (**Fig. 1b**). Diferentes sistemas tampões (PIPES, MES, HEPES, TRIS, Britton–Robinson e MOPS), foram avaliados, sendo a maior sensibilidade na detecção de DNA obtida em HEPES (sonda 6B), e MES (sonda 6A) (**Fig. 1c**) a 10 mM. A faixa linear para detecção de ácidos nucleicos foi de 5 – 20 µg mL^{-1} (λ_{max} = 555 nm). De forma geral, a presença de ácidos nucleicos é indicada pela coloração rosa na amostra, que tem sua intensidade relacionada à concentração de DNA/RNA no meio (**Fig.1d**). Alterando-se as concentrações das sondas de 5 – 12,5 µM, a condição de maior sensibilidade na detecção de DNA/RNA foi a concentração de 10 µM. A influência da força iônica foi avaliada, variando-se as concentrações de NaCl, sendo observada redução da sensibilidade, indicando que ocorre interação eletrostática dentre sondas e ácidos nucleicos nas amostras (**Fig. 1e**). Ademais, a sonda 6B (LOD = 0,8 µg mL^{-1}) foi 3× mais sensível que a sonda 6A (LOD = 2.5 µg mL^{-1}) na detecção de RNA (**Fig. 1f**). O método permitiu a detecção/quantificação de ácidos nucléicos totais em amostras complexas (DNA + RNA), conduto, pode ser usado para determinar DNA ou RNA separadamente, desde que, as macromoléculas sejam previamente separadas. Por fim, as sondas desenvolvidas apresentam amplo potencial de aplicação em diferentes áreas, incluindo ciências forenses.

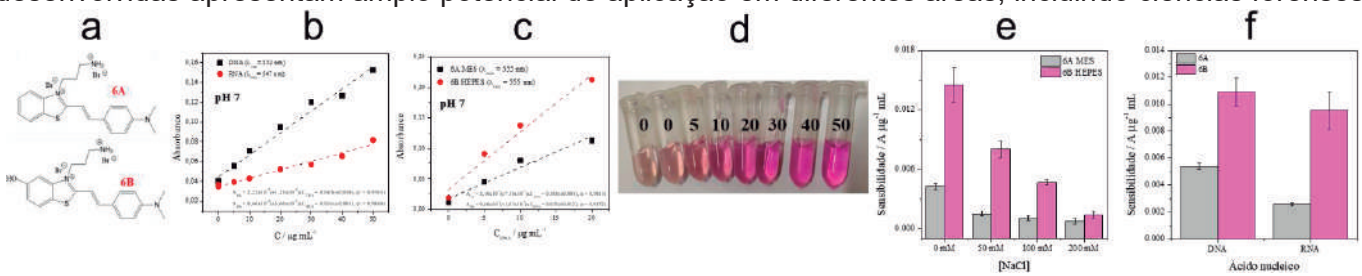


Fig. 1. (a) Estruturas químicas das duas sondas colorimétricas utilizadas (6A e 6B). **(b)** Curvas analíticas empregando DNA e RNA frente à sonda 6A em tampão Britton-Robinson (pH 7). **(c)** Curvas analíticas empregando DNA utilizando as sondas 6A e 6B, tampões MES e HEPES, ambos em pH 7. **(d)** Ensaio qualitativo de amostras contendo a sonda 6B com DNA a 0, 5, 10, 20, 30, 40 e 50 µg mL^{-1}. **(e)** Gráfico de sensibilidade na detecção de DNA na presença de NaCl (0, 50, 100 e 200 mM) para as sondas 6A e 6B. **(f)** Gráfico comparativo de sensibilidade na detecção de DNA e RNA utilizando-se ambas as sondas nas condições otimizadas.

References

[1]Magalhães et al. The Scientific World Journal. 2015, 365674 // [2]Virkler et al. Forensic Science International. 2009, 188, 1-17.

Agradecimentos/Acknowledgments

UFAL, IQB – PPGQB, CAPES, CNPq, FAPEAL e FINEP.

Área: ANA

Statistical comparison between theoretical and experimental infrared spectra of Novel Designer Benzodiazepines.

Valter D.D. Abdo (PG),[1*] Lívia Salviano Mariotto (PG),[1,2] Caio Henrique Pinke Rodrigues (PQ),[1,2] Christiano dos Santos(PG),[1] Aline Thais Bruni (PQ),[1,2]

vddabdo@usp.br; aline.bruni@usp.br

[1]*Departamento de Química Faculdade de Filosofia, Ciências e Letras de Ribeirão Preto. Universidade de São Paulo;*
[2]*Instituto Nacional de Ciência e Tecnologia Ciências Forenses (INCT-Forense)*

Keywords: *Novel Designer Benzodiazepines, Infrared spectroscopy, Statistical Analysis, Forensic evaluation.*

Highlights

Theoretical IR spectra for 20 Novel Designer Benzodiazepines were obtained by means of DFT.
Statistical analysis assessed the theoretical spectra's quality against experimental data.

Abstract

Novel Designer Benzodiazepines (NDBz) pose a significant threat to public health when they are not adequately regulated. The abuse of these compounds has increased in recent years. Despite their prevalence, spectroscopic data on these substances are lacking, posing a significant challenge for forensic identification due to the variety of new structures. The Scientific Working Group for the Analysis of Seized Drugs (SWGDRUG) recommends minimum requirements for the forensic identification of seized drugs. Techniques are classified into three categories based on the level of selectivity. Category A techniques provide selectivity through structural information. Category B techniques offer selectivity through physical/chemical characteristics, and Category C provides general or class information. Infrared (IR) spectroscopy is considered a Category A technique because it allows for structural information and a high level of selectivity. Twenty NDBz compounds were studied, with nine classified as halo-benzodiazepines (black samples), five as nitro-benzodiazepines (red), and six as triazole-benzodiazepines (blue). The main goal of this work was to gather infrared spectra for these substances using DFT calculations and to use statistics to compare these data with experimental ones found in different databases. The theoretical infrared spectra of 20 NDBz compounds were simulated using quantum calculations applying Density Functional Theory (DFT), employing the B3LYP functional with the TZVP basis. We collected experimental infrared spectra for the same molecules from different spectra libraries (SWGDRUG, European Network of Forensic Science Institutes (ENFSI), National Institute of Standards and Technology (NIST), and SpectraBase). All data were set to transmittance with a 1 cm-1 resolution from 400 to 4000 wavenumbers, resulting in 3600 wavenumbers. Principal Component Analysis (PCA) and Hierarchical Cluster Analysis (HCA) were employed to explore the data. HCA used the Euclidean distance and the incremental cluster method. Soft Independent Modelling of Class Analogy (SIMCA) was applied to verify the classification of the substances into the three different classes. PCA and HCA results for theoretical and experimental data showed similar results, indicating that the other classes can be observed. SIMCA reproduced these results, and no misclassification was observed. For experimental data, this separation was not observed for the classes. However, there is a correspondence between each molecule in the principal components space. SIMCA results revealed some overlap among the classes once misclassifications were observed. Correlation heat maps showed significant variation in experimental infrared spectra even for the same molecule. We concluded that theoretical data showed a best separation into the classes, and the experimental data from libraries showed significant variation. Finally, using these data to classify diverse molecules requires careful management and interpretation.

Acknowledgments

1.Conselho Nacional de Desenvolvimento Científico e Tecnológico CNPq. Grants: 465450/2014-8, 104496/2023-1.
2. Coordenação para o Aperfeiçoamento de Pessoal de Nível Superior, CAPES. Financial Code 001.

Área: ANA

Surfactant-free microemulsions for *Citrus* essential oils analysis by spectrofluorimetry

Rosana C. Macedo (PG),[1,2] Beatriz S. M. Bastos (PG),[2] Alessandra L. M. C. da Cunha (PQ),[2] Ricardo Q. Aucelio (PQ)[1]

rosana.macedo@ifrj.edu.br

[1]*Departamento de Química, PUC-Rio;* [2]*Departamento de Química, IFRJ*

Palavras Chave: *Surfactant-free microemulsions, Citrus essential oils, Spectrofluorimetry.*

Highlights

Surfactant-free microemulsions containing *Citrus* essential oils were obtained. An improvement in fluorescence signal intensity was observed. The systems have proven to be efficient for fluorescence spectroscopy analysis.

Resumo/Abstract

Surfactant-free microemulsions (SFME) are homogeneous and thermodynamically stable systems, formed by two immiscible phases (oil and water), stabilized by the addition of short-chain alcohols. Recently, this research group reported that surfactant-free pseudoternary systems of essential oil (EO) in octan-1-ol (as the oily phase), water, and propan-1-ol are useful for obtaining fingerprint patterns of sweet orange EO by 3D fluorescence spectro-analysis. The micelle-like aggregates formed by SFME systems can improve fluorescence by decreasing non-radiative decay of fluorophores in excited state, resulting in enhanced signal intensity. Additionally, the high dilution contributes to reducing the internal filter effect, minimizing the need for spectral correction. In this work, these systems were replicated for different *Citrus* EOs, including sweet and sour orange, tangerine, lemon, and grapefruit. New SFME component proportions were established after optimization experiments through monitoring fluorescence. As a result, it was observed that, for all *Citrus* EOs, conditions requiring low sample content displayed a significant increase in fluorescence intensity at 336/436 nm ($\lambda_{ex}/\lambda_{em}$). Complementary analyses by high-performance liquid chromatography coupled with a fluorescence detector revealed a clear association between the fluorophores and the coumarin derivatives, which are characteristic compounds of cold-pressed *Citrus* EOs. To demonstrate the potential of this approach in discriminating *Citrus* EO samples, the data from 3D spectrofluorimetric analysis, obtained for each evaluated species (in 10 replicates), were subjected to chemometric treatment using unfolded principal component analysis (UPCA). A cumulative variance of 99.5% was achieved for the first three principal components. For this evaluation, 15 µL of EO in octan-1-ol (1:2, v/v), 19 mL of ultrapure water, and propan-1-ol up to 25 mL was used. Leveraging the fact that there is a characteristic wavelength, the application of SFME systems in quantifying *Citrus* EO in mixtures was also tested. Analysis of blends of sweet orange and lavender EOs (common commercial mixture used in aromatherapy) were also performed using synchronous fluorescence first derivative. In this case, to adapt the system in function of the analytical response, 50 µL of EO in octan-1-ol (1:5, v/v), 2.0 mL of ultrapure water, and propanol up to 5 mL was used. Limit of quantification of 7.97 µg mL^{-1} was obtained, indicating the possibility to quantify 0.46% of sweet orange EO in mixtures with lavender EO. Recoveries of 88.9 to 115.5% (coefficient variation of 3.1% to 9.2%) were achieved for simulated blends containing 25%, 50%, and 75% of sweet orange EO. Currently, spectrofluorimetry is a technique that is underexplored for EOs. The high viscosity and low transparency of these products can lead to analytical implications, such as difficulty in cleaning materials and the risk of cross-contamination. The minimal sample requirement, tolerance to high water content, and enhancement of fluorescence render these systems highly beneficial for their application as complementary analysis.

Agradecimentos/Acknowledgments

PUC-Rio, IFRJ, CAPES, CNPq, FAPERJ

Área: ANA

Synthesis and characterization of M-RACNTs for the extraction of secondary metabolites from Lasiodiplodia sp. fermentation broth

Cristiane Dos Reis Feliciano (PG)[1*], Heloisa Sales de Souza (IC)[1], Vinicius Câmara Costa (PQ)[2], Omar Cabezas Gómez (PQ)[1], Jaine Honorata Hortolan Luiz (PQ)[1], Luiz Fernando Gorup (PQ)[1,3,4,5], Mariane Gonçalves Santos (PQ)[1].

crisfeliciano2018@gmail.com; crisfeliciano2018@gmail.com*

[1]Institute of Chemistry, UNIFAL; [2]Embrapa Instrumentation, São Carlos; [3] Department of Chemistry, UFSCar; [4]School of Chemistry and Food Science, FURG; [5]Materials Engineering, UFPEL.

Palavras Chave: *Restricted access materials, Nanocomposite, Endophytic fungi, Lasioplodia sp., Dispersive solid-phase extraction, Magnetic carbon nanotubes.*

Highlights

- Sorbents as the restricted access magnetic carbon nanotubes (M-RACNTs) offer great potential for pre-concentration and separation of bioactive compounds from the fermentation broth.

Resumo/Abstract

Examining organic compounds in complex matrices is a time-consuming and costly process, often leading to numerous errors. So, analytical chemistry has developed innovative solutions, enhancing the efficiency and reliability of this process. In this sense, this work proposed the synthesis and characterization of bovine serum albumin-covered restricted access magnetic nanotubes (M-RACNTs) to be used as sorbent in the magnetic dispersive solid-phase extraction (MDSPE) of organic compounds from the fermentation broth of the endophyte *Lasiodiplodia sp.* Synthesis was performed by functionalizing commercial multiple-walled carbon nanotubes with magnetic nanoparticles[1] (M-CNTs) and by coating the M-CNTs with a layer of bovine serum albumin. The materials were characterized by infrared spectroscopy with Fourier Transform, thermogravimetry, zeta potential, and scanning electron microscopy. Then, the M-RACNTs were used in MDSPE to extract secondary metabolites from the fermentation broth of the endophyte *Lasiodiplodia sp.* GC-MS and LC-MS/MS investigated the crude extract constitution. The material proved to be capable of extracting many different organic substances, including some with bacteriostatic and bactericidal activity against gram-positive bacteria and preventing the adsorption of macromolecules, such as lysozyme, confirmed by SDS-PAGE analysis. A multivariate optimization, through fractional factorial planning, for four independent variables (mass of sorbent, adsorption time, elution solvent volume, and desorption time), was performed for a hydrocarbon (hexadecane) and one possible jasmonic acid derivative, both with antimicrobial activity related in the literature[2,3]. After optimization, the analytical signal increased 3.7 times for hexadecane and 1.4 times for the potential jasmonic acid derivative. Finally, it should be emphasized that the purpose of this study was not to isolate or separate a specific secondary metabolite originating from the fermentation of Lasiodiplodia sp., but rather to evaluate the potential of MDSPE in preparing this sample as a substitute for other conventional extraction techniques. This was confirmed by the obtained results.

Referências/ References

1- Qu, et al. **Electroch Commun.** V.9 p. 2812–2816, 2007.
2- Gomez, et al. **Brazil. J. Dev.** V.7 p. 3795–3816, 2021.
3- Eng, et al. **PloS One.** V. 11 p. 1–18, 2016.

Agradecimentos/Acknowledgments

CAPES, FAPEMIG, CNPQ

Área: ANA

The spectrophotometric determination of the 1,1-Diphenyl-2-Picrylhydrazyl Radical (DPPH•)

Bryan B. de Menezes (PG),[1] Lucas M. Frescura (PG),[1] Paulo R. S. Salbego (PQ),[1] Ronaldo A. Funari Junior (PG),[1] Rafael Duarte (PG),[1] Marcos A. Villetti (PQ),[2] Marcelo B. da Rosa (PQ).[1]*

bryan.menezes@ufsm.br; marcelo.b.rosa@ufsm.br

[1]Departamento de Química, UFSM; [2]Departamento de Física, UFSM

Keywords: *DPPH, IC_{50} Correction, Stoichiometry, Mathematical Model.*

Highlights

Misconceptions in DPPH analysis arise from inconsistent IC_{50} unit choices in literature; Both molecular and radical DPPH absorbs in 515 nm region; A new equation discounts the molecular contribution.

Abstract

The DPPH method has been reported with misconceptions in a large number of studies, precluding the direct comparison of results. The use of IC_{50} to represent the antioxidant potential aims to standardize comparisons between studies. The most appropriate way to report IC_{50} is the ratio of antioxidant moles per mole of DPPH. However, studies still report their results using IC_{50} in absolute form without specifying 50% of what. To avoid confusion, we propose using AIC_{50} and RIC_{50} for absolute and relative IC_{50} values, respectively. We suggest renormalizing AIC_{50} data from the literature based on the initial DPPH concentration reported in each study. Only two out of 25 reviewed studies correctly reported the RIC_{50}. Data from 25 studies with widely varying IC_{50} values were renormalized according to reaction stoichiometry, making values coherent and closer to the ideal one of 0.25 for at least 15 of them. Now that major misconceptions in reporting DPPH analysis results are addressed, let's focus on a minor, but important, correction. The equation commonly used to calculate the percentage of scavenged DPPH• ($\%DPPH_{Sca} = [(Abs_{NC} - Abs_{samp}) / (Abs_{NC})] \times 100$) (eq. 1) shows a difference between expected and calculated values. In eq. 1, $\%DPPH_{Sca}$ is the percentage of inhibited DPPH•, and Abs_{NC} and Abs_{samp} are the Negative Control (NC) and sample absorbance, respectively. Equation. 1 calculates the percentage of scavenged DPPH• based on discoloration, comparing NC and sample absorbance. However, this approach oversimplifies by not considering absorbance from reaction products. As a result, the apparent discoloration percentage at 515 nm region does not reflect the true scavenged DPPH•, as the reaction product, DPPH-H, also absorbs in this region. This means DPPH• never reaches zero, even with an excess of antioxidant. Other studies highlight the importance of considering DPPH-H absorbance for accurate analysis (Szabo *et al.*, 2007). Thus, we can use a positive control (PC) along with the NC to consider the effect of reaction products. The PC has the same DPPH• concentration as the NC but with an excess of antioxidant, so only DPPH-H molecules contribute to the spectrum. This helps us measure the impact of reaction products on sample absorbance, achieving a new equation: ($\%DPPH_{Sca} = [(Abs_{NC} - Abs_{samp}) / (Abs_{NC} - Abs_{PC})] \times 100$) (eq. 2). Equation 2 efficiently transposes the problem of the inaccurate determination of inhibition, based on the apparent discoloration of the sample (de Menezes *et al.*, 2021).

REFERENCES:

DE MENEZES, B. B. *et al.* A critical examination of the DPPH method: Mistakes and inconsistencies in stoichiometry and IC_{50} determination by UV–Vis spectroscopy. **Analytica Chimica Acta**, [*s. l.*], v. 1157, p. 338398, 2021. Disponível em: https://doi.org/10.1016/j.aca.2021.338398.

SZABO, M. *et al.* Improved DPPH determination for antioxidant activity spectrophotometric assay. **Chemical Papers**, [*s. l.*], v. 61, n. 3, p. 214–216, 2007. Disponível em: http://www.degruyter.com/view/j/chempap.2007.61.issue-3/s11696-007-0022-7/s11696-007-0022-7.xml.

Acknowledgments

CNPq CAPES PPGQ UFSM

Área: _____ANA_____

Volatilome study of the Jabuticaba pells (*Plinia cauliflora*) using a hydrophilic microporous cartridge with direct immersion solid-phase microextraction and GCxGC/Q-TOFMS

Jhonatan B. de Oliveira (PG)[1], Patterson P. de Souza (PQ)[2], Samantha C. Rodrigues (PG)[1], Helvécio C. Menezes (PQ)[1], Zenilda de L. Cardeal (PQ)[1]

jhonatanbo@hotmail.com.

[1]Departamento de Química, UFMG; [2]Departamento de Química, CEFET-MG.

Keywords: *Volatilome; Jabuticaba; hydrophilic microporous cartridge; direct immersion solid-phase microextraction; comprehensive two-dimensional gas chromatography*

Highlights

Development of a hydrophilic microporous cartridge to protect the fiber using DISPME; Optimized method for the extraction of natural products from the jabuticaba peels; New method for extracting organic compounds from fruit and GCxGC/QTOFMS.

Abstract

Volatile organic compounds (VOCs) represent an essential part of the plant metabolome and attract agronomic and biological interest due to their contribution to fruit properties, aroma, and flavor [1]. Furthermore, VOCs are very informative regarding the interactions of plants with their environment, from attracting pollinators and seed dispersers to protecting against pathogens, parasites, and herbivores, being considered a kind of “odorous imprint” of vegetation. When analyzed comprehensively, odorous imprint compounds can reveal details about the state of specific plants and entire ecosystems. Plants present a diversity of metabolites in different concentrations. The qualitative and quantitative study of the complex mixture of VOCs present in plants comprises volatilomics. It is necessary to implement appropriate analytical methodologies to detect variations in the composition of volatiles emitted from vegetation [2].

This pioneer study focusses on the analysis of the volatile components of jaboticaba peels using the solid-phase microextraction method (SPME) in combination with a new device, the hydrophilic microporous cartridge (HMCart), which allows analysis by direct immersion. The jabuticabas harvested from the rural region of Minas Gerais, were selected for the study of volatile and semivolatile components This cartridge was developed with the aim of protecting the polymer phase fiber in the aqueous phase containing the plant material, avoiding breakage and impregnation. The developed method is simple using few steps in the preparation of jabuticaba pells samples. The fibre selected for analysis was a divinylbenzene/carboxyene/polydimethylsiloxane (DVB/CAR/PDMS) of 30/50 µm. A comprehensive gas chromatography time-of-flight mass spectrometry (GCxGC/Q-TOFMS) system was used to separate and identify natural products in jabuticaba peels.

The method was optimised on the basis of a factorial design and was able to detect 217 organic compounds. Of particular note is the detection of terpenes, fatty acids and ethyl esters, which are mainly responsible for the nutritional properties and odor of the fruit. This developed methodology enabled an understanding of the phytochemical composition, aroma, flavour and bioactivity of jabuticaba, which will allow future work on the quality of the fruit, the products and the by-products obtained from the peel.

[1] H. Zhang, H. Yan, Q. Li, H. Lin, X. Wen, *Scientific Reports*, 11 (2021) 1–13.

[2] T. Majchrzak, W. Wojnowski, M. Rutkowska, A. Wasik. *Trends in Plant Science*, 25 (2020) 302–312.

Agradecimentos/Acknowledgments

CAPES · química pós-graduação UFMG · INTECHLAB · RMCA Rede Mineira de Cromatografia Avançada · UFMG

BEA

Alimentos e Bebidas

Sociedade Brasileira de Química

Área: BEA

A green method for microwave-assisted extraction of bioactive compounds from berries

Luís C. Martins (PG),* **Fábio R. P. Rocha (PQ)**

***luis.claudio.martins@usp.br;**

Center for Nuclear Energy in Agriculture, University of São Paulo, Piracicaba, SP, Brazil.

Keywords: *Green extraction, Phenolic compounds, Acerola, Food analysis, Sample preparation.*

Highlights

- Improved hydroalcoholic extraction of phenolic and flavonoid compounds;
- Greener and fast microwave-assisted extraction;
- Multivariate optimization using Doehlert experimental design.

Abstract

Microwave-assisted extraction (MAE) is an attractive alternative to increase extraction efficiency with less toxic solvents (usually aqueous solutions). It usually requires short extraction times, minimal reagent consumption and, because of the mild extraction conditions, is attractive for extraction of thermolabile species, such as bioactive compounds. Microwave irradiation provided a fast and uniform heating, mainly when water, dielectric constant (ε′) = 80, and its mixtures with polar solvents (e.g. ethanol, ε′ = 24) are used for extraction of polar and moderately polar compounds. Non thermal effects also contribute to increase the extraction efficiency. Berries are small fruits rich in ascorbic acid (AA), phenolic and flavonoid compounds with biological and antioxidant activities and promising applications in agro-food and pharmaceutical industries. Nonetheless some hindrances for the industrial application of bioactive compounds are the lack of standardization of the extraction process and the use of harmful solvents. In this sense, this work aimed at the development of a greener and faster approach for the extraction of bioactive compounds (phenolic acids and flavonoids) from berries (blackberry, blueberry, and acerola), exploiting MAE and multivariate optimization. Extraction was performed using 500 mg of lyophilized samples in 30 mL of solvent, and a microwave equipment (Ethos 1600, Milestone, Italy). Optimization was performed by using Doehlert multivariate design, evaluating the effects of time (3 levels, 10 to 50 min), temperature (5 levels, 30 to 60 °C) and extractor solvent (7 levels, 0 to 99% v/v ethanol) on the total phenolic content (TPC) from each sample. The analysis of variance (ANOVA) was exploited to assess the effects of the variables on prediction models. Under the optimized conditions (66% ethanol, 38 °C, and 50 min for blackberry; 50% ethanol, 30 °C, and 30 min for blueberry; 75% ethanol, 32 °C, and 10 min for acerola), the MAE procedure was compared with different extraction procedures/extractor solvents based on convective heating with water (CHE)[1], sequential extraction with methanol and acetone (SQE)[2], and sequential ultrasound-assisted extraction (UAE) with methanol/acetic acid[3]. This comparison included the extraction efficiency, TPC and total flavonoid content (TFC), free radical scavenging capacity (ABTS method), as well as the AA, chlorogenic acid (CGA), and quercetin (QUE) contents determined by HPLC. The optimized MAE conditions demonstrated results up to 136% and 46% higher (versus CHE and SQE, respectively) for TPC, 182%, 14%, and 18% higher (versus CHE, SQE, and UAE) for TFC, and 62% higher (versus CHE) for ABTS. The extraction rates for MAE were from 1.4 to 15.8 g min^{-1} phenolic compounds and from 13.3 to 24.8 mg min^{-1} flavonoids, which were significantly higher than those achieved by CHE (0.6 to 2.1 g min^{-1} and 1.3 to 9.0 mg min^{-1}), SQE (1.1 to 1.7 g min^{-1} and 1.0 to 9.1 mg min^{-1}), and UAE (0.5 to 1.5 g min^{-1} and 0.6 to 5.4 mg min^{-1}) for phenolic and flavonoid compounds, respectively. The proposed method extracted ca. 8, 5, and 4-fold more QUE (from blackberry), AA (from acerola), and CGA (from blueberry) than CHE, SQE, and UAE methods, respectively. The extraction time for acerola was reduced from 200 to 10 min compared to UAE. The optimized MAE method provided high extraction efficiency in a short time with environmentally friendly solvents (water and ethanol) at low temperatures. This procedure offers an alternative for producing extracts with high bioactive compounds contents contributing to industrial applications in accordance with the requirements of green chemistry.

[1] Food Chem., v. 277, p. 698-705, 2019; [2] Food Chem., v. 156, p. 362-368, 2014; [3] Int. J. Mol. Sci., v. 16, p. 14540-14553, 2015.

Acknowledgments

CAPES, CNPq, FAPESP, INCTAA, and FEALQ.

Área: BEA

Assessment of risk to human health resulting from cadmium and lead in chicken liver samples sold in Salvador, Bahia

Joselânio J. Coutinho (PG),[1,2*] Luana B. Santos (PQ),[2] Márcio J. S. Santos (PQ),[2] Anderson S. Melo (PQ),[2] Valfredo A. Lemos (PQ),[2] Sérgio Luís. C. Ferreira (PQ).[1]

lanio_coutinho@outlook.com

[1]*Instituto de Química,UFBA, Programa de Pós-Graduação em Química, Campus Ondina, Salvador, Bahia 40170-280, Brasil.*
[2]*Departamento de Química, UESB, Programa de Pós-Graduação em Química, Campus Jequié, Jequié, Bahia 45208-091, Brasil.*

Palavras Chave:*(health risk assessment, cadmium, lead, chicken liver, ETAAS).*

Highlights

Cadmium and lead were determined in 21 samples of chicken liver from different locations.

Three non-carcinogenic and one carcinogenic indices were used in the toxicological evaluation.

The indices showed that the ingestion is safe, considering the Cd and Pb levels found in the investigated samples.

Introduction

Chicken and beef livers are essential proteins in human nutrition due to their high iron content, recommended even in anemia treatments, as well as being sources of vitamins and essential chemical elements. However, these matrices may contain toxic metals and metalloids due to the feed used in animal management. In this work, lead and cadmium were determined in twenty-one chicken liver samples acquired in different Salvador, Bahia locations.

Results and Discussion

Chicken liver samples were washed and subsequently freeze-dried. They were then digested using microwave radiation in a closed system. Then, cadmium and lead were determined using atomic absorption spectrometry with electrothermal atomization using palladium as a chemical modifier. The analytical method was fully validated by IUPAC recommendations, with accuracy confirmed by analyzing two liver reference materials. The results found on a wet basis ranged from 0.026 to 0.053 µg g^{-1} for cadmium and from 0.103 to 0.186 µg g^{-1} for lead. The estimated weekly intake (EWI), target hazard quotient (THQ), maximum safe consuming quantity (MSCQ), and target carcinogenic risk (TCR) indices were used in the toxicological assessment. The consumption rate used in calculating the indexes was 15 grams per day. The moisture content of the samples was determined in a homemade infrared oven developed in our laboratory.

Conclusion

This study demonstrated that the cadmium and lead levels in the chicken liver samples analyzed do not cause carcinogenic or non-carcinogenic adverse effects on resident consumers.

References

[1] Ferreira, S.L.C. et al. Talanta, 2022, 247, 123557.
[2]Ferreira, S.L.C. et al, TrAC Trends in Analytical Chemistry, 2023, 167,117281

Acknowledgments

Área: BEA
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Contents of bitter acids, xanthohumol and trace elements in *Humulus lupulus L*: Potential fingerprint for regional traceability

William M.X. Silva (IC),[1] Samile K.O. Sousa (IC),[1] Samuel P. D. Marques (PQ),[2,3] Maria T.S. Trevisan (PQ),[2] Wladiana O. Matos (PQ),[2] Francisco L. F. Silva (PQ).[4]*

luan.fonseca@uece.br*

[1]Departamento de Química Analítica e Físico-Química, UFC; [2]Departamento de Química Orgânica e Inorgânica, UFC, [3]Departamento de Ensino, IFCE; [4]Faculdade de Educação e Ciências Integradas de Crateús, UECE

Keywords: *Bitter Acids; Trace Elements; Hops; Chemometrics; PCA.*

Highlights

The contents of bitter acids, xanthohumol, and trace elements could be used as fingerprints for the regional origin of hop plants using multivariate exploring analysis.

Resumo/Abstract

Hops (*Humulus lupulus* L.) is a climbing plant belonging to the Canabiaceae family, originating from the Southeast Asian and cultivated in cold regions such as the USA and Europe. Recently, some experimental plantations have been carried out in the Northeast of Brazil[1]. This work will attempt to associate the levels of bitter acids and 14 trace elements for a possible fingerprint of different hop cultivars in Brazil. For this, 21 samples of different hop cultivars produced in Teresópolis (RJ), Lages (SC) and Rio Grande do Norte (RN) were studied. To extract bitter acids and xanthohumol, about 0.5 g of crushed flowers was weighed into centrifuge tubes, then 7.5 mL of ultrapure water, and 10 mL of acetonitrile were added. This mixture was homogenized and inserted into tubes of salts containing: 6 g of $MgSO_4$; 1.5 g of NaCl; 1.5g of $C_6H_5Na_3O_7.2H_2O$ and 0.75 g of $C_6H_6Na_2O_7{\cdot}1.5H_2O$. The supernatant was separated, centrifuged, and analyzed by HPLC-UV following the method of Marques et al., 2024. For trace element analysis, about 0.250 mg of the samples was weighed into Teflon® tubes with lids and 5 mL of aqua regia was added, then samples were heated in a block digester for 3 h at 120ºC after this it was diluted for 20 mL and the analytes (Al, B, Ba, Ca, Cr, Cu, Fe, K, Mn, Mg, Na, P, Sr, Zn) were quantified by ICP-OES. Three replicates of each sample were analyzed. International hop calibration extract (ICE-4) and SRM NIST 1515 (Apple Leaves) analysis were performed to verify the trueness of bitter acids/xanthohumol and trace elements analysis, respectively. The contents of bitter acids, xanthohumol and trace elements were autoscaled and a principal component analysis was carried out (Figure 1). There is a tendency to discriminate between samples from different hop cultivars by PC1 versus PC2, since PC1 explains 32% of the sample variability and PC2 is responsible for explaining 17% of the data variation. It is important to observe that the commercial pellets of hops are closer to the sample from RJ with higher concentrations of bitter acids and they are completely separated of the samples from SC and RN. Besides that, samples from the same state (RN) are differentiated for periods of plantation (January/2020 (□) and April/2020 (●)). It occurs mainly for the concentration of K, Mn, and Zn. More experiments must be done, but these preliminary results show that the trace elements and bitter acids have potential to be used as fingerprints for the regional origin of Brazilian hops, mainly through the trace elements content.

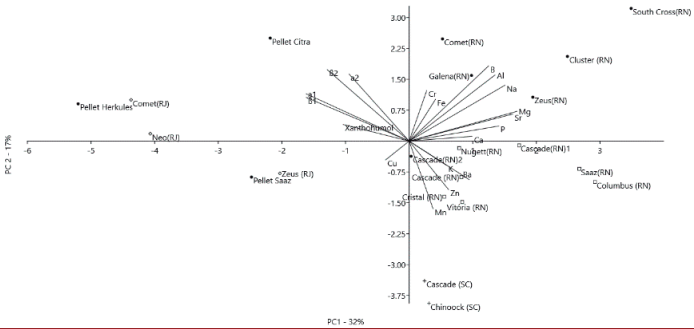


Fig 1: Biplot PC1 x PC2 graph (49 % of the total variation) for hops plant.

α1: Cohumulone; α2: n - Humulone + Adhumulone; β1: Colupulone; β2: n - Lupulone + Adlupulone

[1]Marques et al., Quim. Nova (2024), 1-19.

Agradecimentos/Acknowledgment

CNPq, CAPES, UFC, PGQUIM, UECE, NUTEC

Área: BEA

Desenvolvimento de método para quantificação de carboidratos totais em amostras comerciais de feijões por espectrofotometria na região UV-Vis

Ryan Guilherme Maurício França da Silva (IC),[1,2*] Micherlane Maria da Silva (IC),[1,2] Iago José Santos da Silva (TC),[2] Elvis Joacir de França (PQ),[3] Maria José de Filgueiras Gomes (PQ),[1] Mario Takayuki Kato (PQ).[2]

jose.filgueiras@ufrpe.br; ryan.guilherme@ufrpe.br

[1]Departamento de Química, UFRPE; [2]Laboratório de Saneamento Ambiental – LSA, Departamento de Engenharia Civil e Ambiental, UFPE; [3]Centro Regional de Ciências Nucleares do Nordeste, PE.

Palavras Chave: *Dispersão, Espectrofotometria, Grãos, IDRs, Macronutrientes*

Highlights

Total carbohydrates in beans by UV-Vis: Development of new methodology for quantification in commercial samples in suspension and the concentrations were compared with the value of total carbohydrate on the label

Resumo/Abstract

O feijão é um dos alimentos básicos mais presentes na dieta brasileira. As preferências dos consumidores variam regionalmente, especialmente em relação à cor e ao tipo de grão. Devido a versatilidade, torna-se um destaque quanto aos preparos culinários e por seus benefícios nutricionais (fonte de proteínas, fibras e vitaminas). Quanto a prática agrícola, desempenha um papel significativo para as culturas de subsistência em comunidades das regiões Sul, Sudeste e Nordeste do Brasil. Nesse cenário, a determinação de carboidratos, é crucial para estudos nutricionais confiáveis. Este estudo visou implementar um novo método para quantificação de carboidratos em feijões por espectrofotometria na região UV-Vis (490 nm), sendo avaliada as figuras de mérito linearidade, limite de quantificação e detecção, precisão e exatidão. Trinta e seis amostras de grão de feijão obtidas na região metropolitana do Recife (PE) foram pré-tratadas por moagem e peneiramento (250 µm). Foram feitos testes preliminares com padrões de glicose para identificar possíveis interferentes na matriz de feijão, empregando o método de Dubois que foi modificado para amostras sólidas em suspensão (reação colorimétrica com 0,5 mL de fenol 5% e 2,5 mL de H_2SO_4 concentrado). Os resultados demonstraram-se satisfatórios com uma faixa de trabalho de 10 a 300 mg L^{-1} e, adicionalmente, realizou-se testes com as amostras trituradas. Como nos rótulos a alta concentração média de carboidratos nas amostras de feijão (50% m m^{-1}), condicionaria a pesagem de uma massa pequena (0,25 mg) para a faixa de trabalho do método proposto.Tais aspectos provocariam a ocorrência de erros significativos na precisão e exatidão do método. Entretanto, o aumento da escala demandaria mais reagentes tóxicos e corrosivos. Assim, considerou-se a análise das amostras em suspensão e para otimização foram realizados cálculos estimativos e obteve-se uma massa de 50 mg e pipetagem de 0,5 mL da suspensão (Figura 1) e os resultados apresentaram viabilidade ambiental e analítica. O método apresentou um coeficiente de determinação (r^2) de 0,9995 e limites de quantificação e detecção 5,3% m m^{-1} e 1,63% m m^{-1} respectivamente. A exatidão foi comprovada utilizando quatro materiais de referência (Amido de milho RM NIST 8432; Farelo de milho RM NIST 8433; Farinha de trigo duro RM NIST 8436; Glúten de trigo RM NIST 8418), evidenciando concordância entre os valores determinados e os certificados. Na Tabela 1 os dados representam as amostras em que as concentrações obtidas estavam ou não de acordo com os valores informados nos rótulos. Um estudo posterior avaliou como o consumo de feijão pode ajudar a atender à Recomendação de Ingestão Dietética (RDA) de carboidratos, Levou-se em conta o consumo médio de feijão no Brasil (142,2 g dia^{-1}) fornecido pelo IBGE[1], a RDA de carboidratos. para indivíduos de 1 a 70 anos (130 g dia^{-1})[2], e a concentração média de carboidratos no grão. As contribuições percentuais para a RDA de carboidratos foram calculadas para os três tipos de feijão mais consumidos no Brasil, apresentados na Tabela 2. Assim, mostra-se que dentre os mais consumidos, o carioca lidera ao atender expressivos 58% da RDA para carboidratos, que são fontes essenciais de energia para o corpo humano.

Figura 1. Procedimento experimental de amostragem por suspensão.

Tabela 1. Comparação do percentual de carboidratos nas amostras reais e informadas no rótulo do produto.

Amostra	Média dos valores rotulados (%)	Média dos valores encontrados nos ensaios (%)[a]	Desvio (%)
Feijão caupi	56	49,2	12,4 (inferior ao declarado)
Feijão preto	53	51,3	3,2 (inferior ao declarado)
Feijão carioca	41	53,2	29,75 (inferior ao declarado)

[a] (Média) n=7 (caupi); n=13 (preto); n=9 (carioca).

Tabela 2. Contribuição de diferentes tipos de feijão com a Recomendação de Ingestão Dietética de carboidratos por indivíduos brasileiros.

Amostra	Concentração média de carboidratos totais (% m m^{-1})	RDA (g dia^{-1})[b]	% RDA em relação a 100 g de feijão
Feijão caupi	49,2 ± 2,9	130	54
Feijão preto	51,3 ± 3,8		56
Feijão carioca	53,2 ± 2,9		58

[a] (Média ± Desvio padrão) n=7 (caupi) n=13 (preto); n=9 (carioca).
[b] O grupo de indivíduos corresponde à faixa etária média dos 1 a 70 anos.

[1] IBGE. Instituto Brasileiro de Geografia e Estatística. POF – Pesquisa de Orçamentos Familiares: microdados: 2017-2018. [Rio de Janeiro, 2010c]
[2] Institute of Medicine. 2006. Dietary Reference Intakes: The Essential Guide to Nutrient Requirements. Washington, DC: The National Academies.

Agradecimentos/Acknowledgments

PROPESQI-UFPE, LSA-UFPE, UFRPE e CRCN-PE.

Área: BEA

Determination of minerals by MIP OES and evaluation of the phenolic andantioxidant profile of cocoa honey from different varieties of cocoa (*Theobroma Cacao* L.) produced in the state of Bahia

Manuela B. do Nascimento (PG),[1,2*] Thaís L. Souza (PG),[2] Lívia R. Amorim (IC),[1] Leonardo F. Maciel (PQ),[1] Anibal F. S. Junior (PQ),[3] Paulo R. R. Mesquita(PQ),[2] Sergio E. Soares(PQ).[1]

manuelabarreto_n@hotmail.com

[1]Faculty of Pharmacy, UFBA; [2]Agricultural Technological Center of the State of Bahia, CETAB.; [3]University of the State of Bahia, Department of Life Sciences, UNEB

Keywords:Validation; Micronutrients; Macronutrients; Phenolic compounds.

Highlights

A method for determining minerals using MIP OES was developed and validated. The work proved the high quality of cocoa honey and its potential application as a nutritional supplement.

Abstract

Cocoa honey, obtained from cocoa pulp after pressing the beans, is a translucent liquid with chemical and sensorial characteristics like those of the original pulp (Figure 1). The present work aims to determine the mineral composition, phenolic profile, and antioxidants of honey from different cocoa varieties (CCN51, PS1319, SJ02, and Parazinho). The results showed that the validation parameters of the minerals by microwave plasma atomic emission spectrometry (MIP OES) were considered acceptable. All analyzed elements had a correlation coefficient greater than 0.9949. The method was considered to have good precision with deviation <10%. Element recovery values ranging from 78% to 128% were obtained, indicating good agreement, and confirming the efficiency of the method. The limit of detection (LOD) values ranged from 0.12 to 12.71 mg Kg^{-1} and the limit of quantification (LOQ) were from 0.57 to 42.35 mg Kg^{-1}.Therefore, the LOD and LOQ values show that the proposed method presented adequate sensitivity for the detection and quantification of the investigated elements. Figure 2 shows that the variety influences the concentration of minerals in cocoa honey. The presence of Al, Fe and Ni characterizes the PS1319 variety, while the other parameters (Zn, Sr, Na, K, Mg, and Ca) characterize the CCN51 and SJ02 varieties. Total phenolic content differed significantly between varieties and SJ02 presented the highest concentration (50.44 mg/100mL). The CCN51 and PS1319 varieties presented statistically equal results for total flavonoids (19.49 and 16.49 µg/mL, respectively), while no concentrations were detected in the SJ02 and Parazinho varieties. Therefore, the data obtained in this work indicate that polyphenols may be present in the entire structure of cocoa, including its by-products. DPPH values between varieties ranged from 134.92 to 179.46 µg mL^{-1} Trolox equivalent, thus demonstrating the importance of consuming cocoa honey and its antioxidant capacity.Therefore, the consumption of cocoa honey or its incorporation into food products can contribute to better health outcomes or improve the nutritional aspects of foods, having the potential to be a healthy option for people with heart disease, hypertension and those who practice physical activity.

Figure 1. Cocoa honey extracted from cocoa (*Theobroma cocoa* L.)

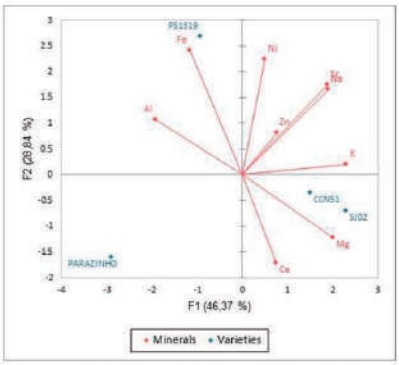


Figure 2. PCA relating the mineral profile of different varieties of cocoa honey.

Acknowledgments

Ministry of Science, Technology, and Innovation (+Brasil Platform no. 904399/2020); CAPES (Processes number 88887.504355/2020-00)

Área: BEA **Nº de Inscrição: _____**

Exploiting fluorescence enhancement of ionic liquid-modified carbon nanoparticles: determination of biogenic amines in beverages

Camila Gonçalves R. N. Barbosa (PG)[1], Nattany T. G. de Paula (PQ)[2], Ana Paula S. Paim (PQ)[1]. ana.paim@ufpe.br

[1] Fundamental Chemistry Department, CCEN, UFPE; [2] Chemical Engineering Department, CTG, UFPE.

Keywords: Histamine. Citrate. Hexafluorophosphate.

Highlights

Use of carbon dot conjugated with ionic liquid (CDs@IL) to determine biogenic amines in beverages
The conjugation improves the stability and sensitivity of the CD.
The procedure is linear from 1.0 to 10.0 mg L^{-1} biogenic amines

Abstract

In this work, an analytical procedure for the determination of biogenic amines is proposed based on the increase of the fluorescence intensity of carbon dots (CDs). The CDs synthesized from citrate were conjugated with ionic liquid (1-methyl-3-octyl-imidazolium hexafluorophosphate) (CDs@IL) by electrostatic interactions to improve stability and sensitivity of the synthesized fluorescent probe[1,2]. CDs@IL showed strong fluorescence emission at 450 nm when excited at 385 nm with high solubility and stability in water, Fig. 1. The biogenic amines determination employed 250 µL of CDs@IL, along with varying volumes of standard solution of 100 mg L^{-1} histamine and its analogues (tyramine, spermidine, and phenylethylamine) and distilled water to make the volume up to 2.0 mL. The linear response was obtained for a concentration range between 1.0 and 10.0 mg L^{-1} of biogenic amines (F/F_0 = (0.02339 ± 0.00093) *[C] + (1.01967 ± 0.00565), R^2 = 0.9970, n = 3), (Fig. 2) at room temperature. The estimated detection limit of 0.29 mg L^{-1} biogenic amines and a relative standard deviation (RSD) of 0.64% (n = 10, 4 mg L^{-1}) were obtained. The concentration of biogenic amines in beer and white wine samples were respectively from 1.4 to 2.7 mg L^{-1} and 2.6 to 3.3 mg L^{-1}. Recovery tests were carried out on beer and white wine samples, resulting in recoveries in the range of 85.0% to 98.3%. Additional recovery studies are being carried out for other beverage samples at the moment.

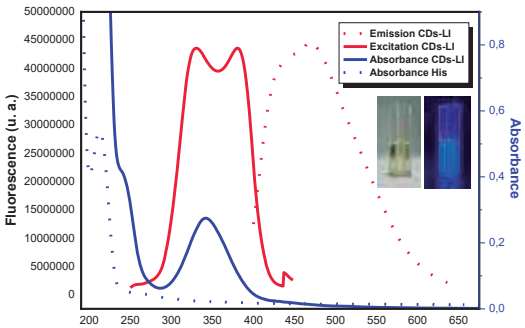


Fig. 1. Fluorescence and absorbance of CDs@IL and histamine absorbance.

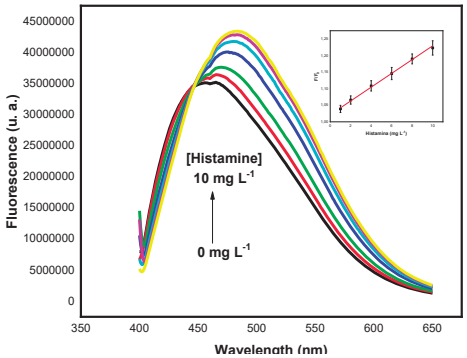


Fig. 2. Emission spectra obtained for different histamine concentrations.

1. WANG, Q. H. et al. Fluorescent Sensing Probe for the Sensitive Detection of Histamine Based on Molecular Imprinting Ionic Liquid-Modified Quantum Dots. **Food Anal. Methods,** 2017.
2. WANG, Y. et al. Synthesis and modification of biomass derived carbon dots in ionic liquids and their application: A mini review. **Green Chemical Engineering**, v. 1, p. 94-108, 2020.

Acknowledgments

The authors are grateful to INCTAA (CNPq grant 465768/2014-8, and FAPESP grant 2014/50951-4), CAPES finance code 001 and CNPq (grant 309539/2021-8) for financial support.

Área: BEA

Fatty acids profile of monovarietal Arbosana Brazilian extra virgin olive oils

Julianna dos S. Viana (PG),[1] Jean M. P. Lourinho (PG),[1] Nathalia S. Brilhante (PG),[1] Rosemar Antoniassi (PQ),[2] Adelia F. Faria-Machado (PQ),[2] Allan E. Wilhem (TC),[2] Humberto R. Bizzo (PQ).[1,2*]

juxsviana@gmail.com; humberto.bizzo@embrapa.br

[1]Programa de Pós Graduação em Ciência de Alimentos, UFRJ; [2]Embrapa Agroindústria de Alimentos

Palavras-chave: *Brazilian olive oils, FAME, Arbosana, identity standard for olive oils.*

Highlights

The profile of fatty acids is an important marker for the identity of olive oils. Eleven samples of monovarietal Arbosana Brazilian olive oils were analyzed. Three did not pass the regulation limits, but experimental evidence from other regions points out this may be due to edaphoclimatic variations in plant metabolism, rather than adulteration.

Abstract

Arbosana is an olive variety originary from Spain. It has been cultivated in Chile, USA, Uruguay, Australia, and Argentina. In Brazil, Arbosana has been grown in the Serra da Mantiqueira, both in Minas Gerais (MG) and São Paulo (SP) states, as well as in Rio Grande do Sul (RS). The profile of fatty acids, expressed as a percentage of their methyl esters (FAME), is an important parameter for the identity standard of olive oils. Contents outside of specific ranges are indicative of adulteration with other oils. In Brazil, the contents for the different fatty acids are established by official normative,[1] which mirrors that of *Codex Alimentarius*. The FAME for 11 samples of olive oils from Arbosana cultivars were prepared and analyzed by gas chromatography.[2] The fatty acids contents for all samples were within the legal limits, except for a single fatty acid, (*Z*)-10-heptadecenoic (C17:1), in 3 samples from RS (Table 1: RS1, RS2 and RS3). Similar out-of-limit figures have been reported for Arbosana and other varieties cultivated in several areas in the Americas.[3] Based on these experimental data, the International Olive Council (IOC) has raised the limit of C17:1 to 0.6 % in 2016. This change, however, was not followed, so far, by the *Codex Alimentarius*, neither by the Brazilian authorities.[1] Collect experimental evidence of national olive oils from certified precedence is useful to establish more adjustable limits to food composition, which reflect the effects of the edaphoclimatic conditions on the plant metabolism and, therefore, in the oil composition. The analyses and gathering of data shall support changes in the legislation for olive oils in Brazil.

Table 1. Fatty acids in Brazilian olive oils from Arbosana variety (in %).

Fatty acid	Samples and States											Official Limits
	MG1	RS1	RS2	RS3	RS4	RS5	SP1	MG2	RS6	RS7	RS8	
C16:0	12.09	15.77	15.55	15.62	13.85	16.80	14.56	11.13	14.67	16.37	12.09	7.5-20.0
C16:1	1.42	1.85	1.93	1.81	1.54	2.72	1.69	1.07	1.94	2.38	1.42	0.3 - 3.5
C17:0	0.09	0.13	0.14	0.13	0.12	0.10	0.12	0.09	0.08	0.09	0.09	≤0.3
C17:1	0.24	0.32	0.33	0.31	0.30	0.25	0.29	0.24	0.20	0.23	0.24	≤0.3
C18:0	1.76	2.20	2.08	2.08	2.00	1.86	2.04	1.86	1.91	1.94	1.76	0.5 - 5.0
C18:1	75.98	68.78	69.51	69.04	72.70	65.22	71.05	78.92	70.68	66.36	75.98	55.0 - 83.0
C18:2	5.72	8.34	7.67	8.35	6.67	10.76	7.62	4.12	7.96	10.10	5.72	3.5 - 21.0
C18:3	0.74	0.86	0.88	0.84	0.92	0.82	0.82	0.72	0.86	0.80	0.74	≤0 1.0
C20:0	0.39	0.42	0.44	0.42	0.43	0.39	0.42	0.38	0.42	0.40	0.39	≤0.6
C20:1	0.39	0.30	0.31	0.30	0.37	0.30	0.33	0.38	0.35	0.29	0.39	≤0.4
C22:0	0.16	0.16	0.17	0.15	0.18	0.16	0.16	0.16	0.17	0.15	0.16	≤0.2

Acknowledgments

This study was by supported by CNPq (INCT 406921/2022-9; GM 146829/2019-0; PQ 311021/2021-2) and FAPERJ (E-26/201.047/2022).

[1] Brazil. Ministry of Agriculture and Livestock. Normative Instruction n° 01/2012. Available at: https://sistemasweb.agricultura.gov.br/sislegis/action/detalhaAto.do?method=visualizarAtoPortalMapa&chave=629707739. Accessed: 02 feb 2024.

[2] Antoniassi et al. Boletim de Pesquisa e Desenvolvimento, 26, 2018, Embrapa Agroindústria de Alimentos. Available at: https://ainfo.cnptia.embrapa.br/digital/bitstream/item/198136/1/Boletim-PD-26-metodo-Hartman-e-Lago.pdf)

[3] Li, X.; Flynn, J.D.; Wang, S.C. Journal of the American Oil Chemist's Society, v. 96, 215-230, 2019.

Área: BEA

Feasibility of real-time monitoring of bacterial growth in raw milk using a new contactless electrical sensor based on resonance frequency

Jussiane S. Silva (PQ)[1]*, Charles A. Haab (PG)[2]*, Adriano M. Jaime (PG) [2], Vanessa R. Nascimento (PG)[1], Vandré S. Pinto (PG)[3], Juliano S. Barin (PQ)[3], Leandro Michels (PQ)[2]

jussiane.silva@ufsm.br, auftek@auftek.com

[1] Departamento de Química, Universidade Federal de Santa Maria (UFSM), Santa Maria, RS, Brazil, 97105-900; [2] Departamento de Processamento de Energia Elétrica, UFSM, Santa Maria, RS, Brazil, 97105-900; [3] Departamento de Tecnologia e Ciência dos Alimentos, UFSM, Santa Maria, RS, Brazil, 97105-900.

Keywords: *Contactless sensor, Bacterial growth, Real-time microbiological analysis, Impedance microbiology.*

Highlights

An electrical sensor based on a capacitively coupled contactless resonance frequency detector was developed for real-time monitoring of bacterial growth. The sensor is suitable for determining the TBC at various contamination levels in raw milk in only 8 hours.

Abstract

Bacterial count analysis is essential to ensure safety in healthcare and the food industry, serving as a quality control criterion. The total bacterial count (TBC) allows you to identify contaminated food and establish the shelf life of products. The conventional method used for TBC is the standard plate count (SPC), which is laborious and challenging to automate. In this context, a new electrical bacterial growth sensor (EBGS) based on a capacitively coupled contactless resonance frequency detector (RFD) was developed. This device involves electrodes attached to a glass tube containing the sample, capable of detecting changes in resonance frequency due to bacterial growth based on contactless impedance microbiology. The measurement chamber of the EBGS-RFD was designed to use 10 mL glass test tubes, aiming for cost-effectiveness and ease of acquisition. Stainless steel conductive rings (16 x 16 x 1 mm) are positioned axially in the sample tube and separated by 5 mm [1]. The efficacy of the EBGS-RFD method was proven by analyzing 56 raw milk samples using the proposed sensor and the conventional method, the SPC, according to the Food and Drug Administration [3]. The inflection point (β) was obtained from the bacterial growth curves, indicating when the average rate change reaches its maximum value [2]. The β value from the bacterial growth curves by EBGS-RFD was correlated with the TBC obtained by the SPC method, resulting in an equation $CFU(\beta) = 9.502 \times 10^6 \times \beta^{-2.426} + 2.403$, with a correlation coefficient of 0.74 and a root mean square error of 0.59. Results with low levels of contamination (< 4 log CFU mL^{-1}) showed high RSD values (10-25%). This can be attributed to the uncertainties associated with the conventional SPC method, as the procedure involves several steps of sample dilution and manipulation. Consequently, for samples with higher bacterial contamination (4-7 log CFU mL^{-1}), a lower RSD (5-15%) was observed. This study demonstrates that the EBGS-RFD can effectively determine the TBC, offering an economical and rapid solution, with analyses completed in just 8 hours. Moreover, the sensor presents a wide operational range (25 to 10,000,000 CFU mL^{-1}), compatible with the legal limits of raw milk contamination, highlighting its potential for bacterial growth monitoring and applications in various areas of microbiology.

[1] Haab, C. A. et al., Brazilian Patent 10 2021 025 274 0, jul. 27, 2021.
[2] Haab, C. A. et al., **IEEE Sensors Journal**, 2024. doi: 10.1109/JSEN.2024.3361311.
[3] Bacteriological Analytical Manual, U.S. Food and Drug Administration, 2023.

Agradecimentos/Acknowledgments

The authors are grateful to CNPq, CAPES, FAPERGS and FINEP.

Área: BEA

Food fraud analysis of green banana flour using chemometric models and portable analytical instruments

Alessandro de M. B. Martins (PG) [1], **Licarion Pinto (PQ).** [1]

alessandromagalhaesmartins@gmail.com; licarion@gmail.com

[1] *Analytical Chemistry Department, Rio de Janeiro State University, Chemical Engineering Graduate Program, Rua São Francisco Xavier, 524 – Maracanã – Rio de Janeiro, RJ, Brazil, 20550-013*

Keywords: Pattern recognition, machine learning, banana flour, adulterations, portable instruments.

Highlights

Food fraud analysis of green banana flour using chemometric models and portable analytical instruments

- Use of portable digital image instrument for food fraud
- Machine learning models to identify green banana flour adulteration
- Advantages of class modeling and discriminant analysis model were evaluated

Abstract

Food adulteration, whether intentional or unintentional, poses substantial threats to public health and the credibility of the food industry. This study focuses on intentional adulteration, termed food fraud, involving deliberate manipulation for economic gain. Portable instruments, such as digital imaging (DI), prove invaluable for food fraud monitoring due to their non-destructive nature and on-site applicability, optimizing analysis time for fraud detection. However, DI datasets often lack direct and univariate information on fraud, underscoring the fundamental role of chemometrics in food quality analysis. This research aims to identify adulteration in green banana flours using portable instruments and cloud-based chemometrics modeling. To ensure the authenticity of samples, the project encompasses initial steps of sample staging, including the preparation of pure banana flour and variants adulterated with wheat, oat, corn, and cornstarch. Thirty green banana flours were produced from bananas obtained from various local markets. The samples were dried at 65 ºC over a day, ground, and sieved through a 50-mesh sieve. Adulterants were similarly sieved, and adulteration levels ranged from 1% to 100%. The dataset, generated using a Canon LiDE 300 flatbed scanner, consisted of colored 600dpi resolution images in png format. Chemometric analysis involved a near-zero variance filter to eliminate variables with mostly zero values, followed by robust principal component analysis (RobPCA) for exploratory insights. RobPCA scores revealed a separation trend, suggesting that DI data holds valuable information for building an efficient pattern recognition model. Data-Driven Soft Independent Modelling by Class Analogy (DD-SIMCA) and Partial Least Squares-Discriminant Analysis (PLS-DA) models were developed to assess the effectiveness of class modeling and discriminant analysis in identifying food fraud using DI data. Initial results indicate that model accuracies were 85% for PLS-DA and 65% for the DD-SIMCA model. However, the accuracy significantly increases with adulterants above 10%, where it was achieved 93% accuracy for PLS-DA and 81% for the DD-SIMCA model. These results are promisor once food fraud occurs with concentrations of adulterants at levels equal to or greater than 10%. The present work indicate that DI analysis can be used efficiently to identify fraud in green banana flour. Subsequent analyses will refine models to identify specific adulterants and their concentrations.

Acknowledgments

FAPERJ, LTAP, PPGEQ/UERJ, UERJ.

Área: BEA

Green and fast analytical method for iron determination in olive oil in a single flask using RP-DLLME and digital image

Roseleia da Silva Rodrigues (PG),[1*] Murilo Oliveira Beato (PG),[1] Marcos André Bechlin (PQ),[2] Oldair Donizeti Leite (PQ),[2] Poliana Macedo dos Santos (PQ),[1] Eder Lisandro de Moraes Flores (PQ)[1,2].

eder.utfpr@gmail.com; rose17rdg@gmail.com

[1]Programa de Pós-graduação em Química, UTFPR-CT; [2]Departamento de Química UTFPR-MD

Palavras Chave: *Iron, Digital image, Olive oil, microextraction, Green sample preparation*

Highlights

Green and fast sample preparation method for further iron determination in olive oil.

New method combining RP-DLLME with digital image detection in a single-flask analysis.

Simple and low cost sample preparation procedure using RP-DLLME.

Resumo/Abstract

In this work, a method was developed based on single-flask analysis conception to determine iron (Fe) in olive oil samples. The sample preparation, using reversed-phase dispersive liquid-liquid microextraction (RP-DLLME), and the detection by digital imaging, was carried out using the single-flask analysis concept. The colorimetric reaction of Fe and thiocyanate ion (SCN^-) in acidic medium was used in the studies to optimize the procedure and to determine Fe in olive oil samples. The following parameters of the procedure, involving the preparation and detection steps, were evaluated univariately: type of dispersant, pH of the solution, proportion between the dispersant/extractant mixture, theconcentration of the SCN^- ion, agitation time and centrifugation time.

A graphical user interface software (SisGARQ) was programmed in Python language, and implemented in a web environment, using the Flask framework tool. The software permits the management of a webcam for the acquisition of digital images. OpenCV Contrib-Python, which allows the use of the Open Source Computer Vision Library's features, was used to obtain and process the images. The obtained analytical response is based on the calculation of the vector norma, employing the mean RGB values derived from image processing and equation 1

$$\text{Eq. 1: Signal} = \sqrt{(dr - cr)^2 + (dg - cg)^2 + (db - cb)^2}$$

Due to the influence of the oil matrix on the analyte detection step, calibration by standard addition method was necessary. The optimized RP-DLLME conditions were 5 g of sample, addition of 1000 µL of a dispersant:extractant solution consisting of ethanol and SCN^- (3.0 mol L^{-1}) in the proportion of 50:50 (v v^{-1}) at pH 1.0 and 1.0 min of shaking prior to centrifugation. The limit of quantification for Fe was 0.1 mg kg^{-1} and accuracy was higher than 95% based on recovery tests. The proposed method was tested on various brands of commercial olive oil, and all samples analyzed presented Fe concentrations below 3.0 mg kg^{-1}, which is the maximum limit allowed, established by Brazilian legislation. The integration of RP-DLLME procedure and digital detection in a single-flask was suitable for the determination of iron in commercial olive oil samples, and can be characterized by low-cost, low consumption of diluted reagents, and using of a single-flask for the sample preparation and determination step, with focus on the principles of green analytical chemistry.

Agradecimentos/Acknowledgments

We thank the financial support of UTFPR, CAPES, Fundação Araucária, and CEANMED - Central Analítica Mulltiusuário/UTFPR.

Área: BEA

Incorporation of *Humulus lupulus* L. byproducts into food evaluated by Box-Behnken design

Rita de C. M. Alves* **(PG)[1], Winston P. C. Gomes (PG)[1], Wanessa R. Melchert (PQ)[2]**

rita.malho@usp.br

[1]Center for Nuclear Energy in Agriculture, University of São Paulo, Piracicaba, SP, Brazil; [2]College of Agriculture "Luiz de Queiroz", University of São Paulo, Piracicaba, SP, Brazil.

Keywords: *Circular economy, Hop, Residue, Reuse, Texture profile analysis*

Highlights

The use of Box-Behnken design to obtain hardness and resilience values.
The analytical parameters are strongly influenced by the amount of residue used to replace wheat flour.

Abstract

Hops (*Humulus lupulus* L.) is a plant used to make pallets and incorporated into beer[1]. Its production has been growing in Brazil, due to its antimicrobial effects and antioxidant potential[2, 3]. According to the Food and Agriculture Organization (FAO), around 1.3 billion tons of agricultural waste are lost or wasted[4]. Byproducts such as stems, roots, and peels provide adequate nutritional sources for human consumption, providing an opportunity to improve the circular economy as global hop production continues to grow[5]. This work evaluated the incorporation of hop residue (stem and leaf) as an enrichment of conventional wheat flour using the Box-Behnken design. This planning increases the precision of the analysis, as it can capture non-linear relationships within the planning, guaranteeing the reliability of the results[6]. The byproducts were previously dried in an oven with air circulation at 60 °C and then ground and standardized on 20 mesh., Box-Behnken design formulated the cakes into which the waste was added. The cakes were prepared using egg (21 g), oil (22 g), sugar (50 g), milk (33 g), wheat flour (25 to 45 g), flour leaf flour (0 to 10 g), stem flour (0 to 10 g), mixed flour (0 to 10 g). The response variables used were hardness (stiffness) and resilience (deformation) parameters. For this, concentrations of leaf flour (residue A), stem flour (residue B), and a mixture of both flours (residue C) were used in a proportion of 50:50 each, according to the proposed design. Texture characteristics were obtained using a texturometer with a 5 kg load cellule (TA.XTplus Texture Analyzer). For texture profile analysis (TPA) conditions were used compression of 50%, a pre-test speed of 2.0 mm s^{-1}, and a test speed of 1.0 mm s^{-1}[7]. The Box-Behnken experimental design was carried out in the Statistica software (v. 14), which was recorded by the Exponent software (v. 6). The hardness and resilience value for the control sample (sample made without adding any of the residues, as a comparison parameter) was 1956 g and 0.211. For the formulations, these parameters ranged from 3097 to 5833 g and 0.082 to 0.209 for hardness and resilience, respectively. The hardness was highly influenced by the amount of residue used to replace wheat flour, and the predicted response for the hardness of the cakes could be evaluated using the equation: Hardness = 4693+585.8*"A"-315.8*"A²"+198.8*"B"-70.64*"B²"+269.0*"C"-109.5*"C²"-195.0*"A"*"B"-320.1*"A"*"C"-48.76*"B"*"C". Resilience presents the opposite behavior, as can be predicted using the equation: Resilience = 1332-50.61*"A"-23.10*"A²"-261.5*"B"-83.91*"B²"-251.8*"C"-68.02*"C²"-142.0*"A"*"B"-201.0*"A"*"C"-90.97*"B"*"C". In both equations A, B and C were the coded values of the independent variables, residue A, B, and C. The highest hardness value was obtained with the highest level of substitution, regardless of the composition of the residue. As for resilience, the highest value was observed with the lowest concentration of waste, regardless of the composition of the waste. This is probably linked to the amount of total dietary fiber (that provides structural resistance to food products) present in Hop by-products, as it can vary from 36 to 69% (w/w), regardless of the residue. Looking for a product with low hardness and high resilience, formulations 11 (replacement only with stem residue at 10%, w/w) and 14 (replacement only with leaf residue at 10%, w/w) are the best options. Therefore, the next step of this study will be to evaluate the use of these residues individually and evaluate the appropriate replacement concentration, taking as a starting point a concentration of 10% (w/w) in both residues.

[1]Limousin, R. et al. Industrial Crops & Products. 2023.
[2]Duarte, L. M. et al. Food Chemistry. 2022.
[3]Alfeo, V. et al. LWT. 2023.
[4]Çağındı, Ö. et al. Food Chemistry. 2023.
[5]Jastrombek, J. M. et al. Horticulture, 2022.
[6]Al-Ahmed, Z. A. et al. International Journal of Biological Macromolecules. 2024.
[7]Salehi F, Kashaninejad M. Journal of Food Measurement and Characterization, 12, 2018.

Acknowledgments

The authors acknowledge the financial support from the Coordination for the Improvement of Higher Education Personnel - Brazil (CAPES), São Paulo Research Foundation (FAPESP), and Study Foundation Agrarians Luiz de Queiroz (FEALQ).

Área:
BEA_____
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Initial studies on heme iron nanoencapsulation with milk proteins for dairy applications.

Edmilson Arruda Santos (PG)[2], João Victor S. de Araújo (IC)[3], Thiago Silva Santos (IC)[3], Christiane Duyck (PQ)[1] *Rafaella Regina A. Peixoto (PQ)[1] edmilson_arruda@id.uff.br; rafaellapeixoto@id.uff.br.

[1] Department of Analytical Chemistry, UFF; [2]Postgraduate Program in Chemistry, UFF [3]Industrial Chemistry Course

Key words: H*eme iron, Milk, Nutritional Deficiency, Hemin*

Highlights

Development of a method of nanoencapsulation of heme iron, using milk proteins, to enhance its stability in dairy products. Initial results indicated efficient nanoencapsulation to be applied in future promising applications.

Resumo/Abstract

One of the most important metallic elements in the diet is iron (Fe). Its deficiency is the most critical nutritional deficiency in the world and causes anemia, characterized by insufficient levels of hemoglobin in the blood. One of the main strategies to combat its deficiency is the consumption of fortified food products. However, the fortification of foods with iron generally involves the use of salts, which has led to limitations, including the short-term instability of the fortifier in ready-to-eat dairy foods, such as milk and their derivatives, making the fortification only suitable for solid food, such as wheat flour. In addition, iron in ionic form presents low absorption by the human organism, as it can compete with Ca^{2+} ions and interact with other milk components, causing an alteration in the sensory quality. In a scenario of high prevalence of iron-deficiency anemia, this study aimed to develop a nanoemulsion (NE) as a source of heme Fe (hemin, ferriprotoporphyrin IX chloride), which is the most bioavailable form of iron in the human diet, for application in dairy food. The NEs were prepared with WPI (Whey Protein Isolate) as an emulsifier, forming the aqueous phase, whereas Hemin performed as the organic phase. Initial tests were carried out on the aqueous phase with WPI, in proportions of 1% (m m^{-1}) to 10% (m m^{-1}). The mixture was homogenized using a mechanical rod stirrer with a maximum rotation of 1500 rpm for 90 min. The organic phase was prepared in a 4.76 g L^{-1} Hemin solution. Both phases were then mixed under low-speed magnetic stirring for 10 minutes and then taken to a sonicator for 4 cycles of 6 minutes at a 120W power. The NE's were characterized and the best iron nanoencapsulation results were obtained for the nanoemulsions with WPI of 4 % and 5 % with encapsulation efficiency greater than 83 %, whereas the droplet size was between 179.3 nm and 210.8 nm, with Zeta potential ranging from -29.12 to -16.57 mV and polydispersity index (PDI) with a maximum value of 0.327. Table 1 shows the characterization results of the NEs. It was also observed that there were no physicochemical changes within 60 days. The morphological analysis was carried out via scanning electron microscopy and corroborated the results found via DLS, suggesting success in the development of the heme Fe-NE. Subsequently, studies will be conducted to evaluate the bioaccessibility and bioavailability of the iron in the NE developed.

Table 1: Measurement and characterization of hem Fe-nanoemulsions

NANO	Diameter (nm)	Zeta potential (mV)	Polydispersion Index	pH	ORP(mV)
NANO 1%	*194 ± 4*	*-25 ± 3*	*0.28 ± 0.01*	*7.05 ± 0.06*	*-2.5 ± 0.3*
NANO 2%	189 ± *4*	-16.6 ± *0.2*	0.33 ± *0.05*	6.87 ± *0.07*	9.4 ± *0.4*
NANO 4%	179 ± *3*	-18 ± *4*	0.233 ± *0.003*	6.73 ± *0.07*	18.1 ± *0.8*
NANO 5%	190 ± *2*	-25 ± *2*	0.23 ± *0.02*	6.9 ± *0.1*	55 ± *0.4*
NANO 10%	211 ± *6*	-29 ± *3*	0.21 ± *0.09*	7.12 ±*0.09*	6.2 ± *0.9*

Agradecimentos/Acknowledgments

Projects FAPERJ nº 201.363/2022 and nº E-26/210.125/2023 and project CNPq nº407080/2021-0. The authors would also like to thank FAPERJ, FAPEMA e CNPq student grants and laboratories LAEGA e LESPA.

Área: BEA

Phenols and tocopherols content in Brazilian extra virgin olive oils from six different cultivars

Jean M. P. Lourinho (PG),[1] Julianna S. Viana (PG),[1] Nathalia S. Brilhante (PG),[1] Rosemar Antoniassi (PQ),[2] Adelia F. Faria-Machado (PQ),[2] Allan E. Wilhem (TC),[2] Humberto R. Bizzo (PQ).[1,2*]

jeanlourinho@gmail.com; humberto.bizzo@embrapa.br

[1]Programa de Pós-Graduação em Ciências de Alimentos, UFRJ; [2]Embrapa Agroindústria de Alimentos.

Palavras-chave: *Extra virgin olive oil, phenolic compounds, tocopherols, UPLC-UV-MS.*

Highlights

The content of biophenols and tocopherols in 18 Brazilian extra virgin olive oils from six cultivars was analyzed by UPLC-UV-MS. Secoiridoids were the main phenolics found. Alpha-tocopherol corresponded to *c.a.* 80 % of total tocopherols.

Abstract

Commercial production of olive oil in Brazil has started recently and is concentrated especially in the states of Rio Grande do Sul and Minas Gerais States. It has experienced a constant growing, although it corresponds to only 1% of internal market. Phenolic compounds and tocopherols are important for the oxidative stability of olive oils. As any product from plant origin, chemical composition is dependent on the plant genetics (cultivars, in this case), as well as on the edaphoclimatic conditions where cultivation took place. Herein, we report the results of biophenolics and tocopherols from olive oils of the cultivars Coratina, Frantoio, Galega, Grappolo, Manzanilla and Picual produced in Minas Gerais (MG) and Rio Grande do Sul (RS) states. Phenolic compounds were extracted with MeOH:$H_2O$and analyzed by UPLC-UV-MS [1]. For tocopherols, samples were diluted in isopropanol and injected, with detection by fluorescence (HPLC-FLR). The concentration of total phenolic compounds ranged from 96 to 330 mg/kg for the samples from MG, and 175 to 615 mg/kg for those from RS. Secoiridoids, hydroxytyrosol and luteolin were the main compounds found: (435 mg/kg for a Picual and 366 mg/kg for a Coratina sample, both from RS. Regarding tocopherols, figures varied from 152 to 235 mg/kg (MG samples), and from 212 to 419 mg/kg for the RS ones. Alpha-tocopherol was the main component (*c.a.* 80 % of the total), with up to 342 mg/kg in a Coratina from RS. No significant difference ($p>0.05$) was observed among samples from RS and MG, but there is a trend of higher amounts of tocopherols and phenolics RS samples (Figure 1). The amount of both phenolics and tocopherols are in the range observed for the same varieties cultivated in Europe [2].

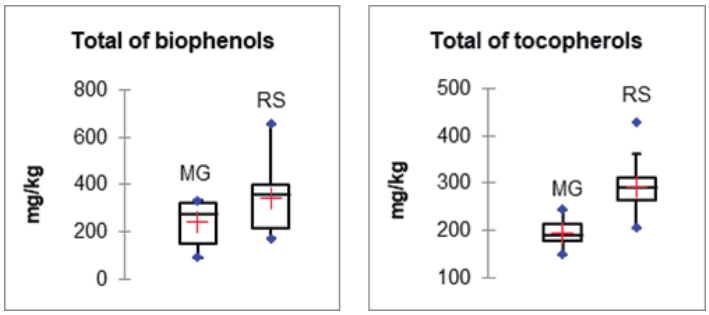


Figure 1. Total concentrations of biophenols and tocopherols by geographic origin.

[1] International Olive Council (IOC). Method COI/T.20/Doc. 29, rev.2. Madrid: IOC, June 2022.
[2] Boskou, D. (ed.). Olive and Olive Oil Bioactive Constituents. Urbana (IL): AOCS Press, cap. 1, p. 1-23, 2015.

Acknowledgments

This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – Brasil (CAPES) – Finance Code 001; by CNPq (INCT 406921/2022-9; PQ 311021/2021-2); and by FAPERJ (E-26/201.047/2022).

BIO

Química Biológica

Sociedade Brasileira de Química

Área: BIO

Analyzing the Complex Relationship between Scorpions and Health: Toxicity Study, and Incidents in Alagoas. A Biochemical Approach.

Alice V. R. Barreto (PG) [1] , Maria T. P. de Farias (PG)[1] , Evanny L. dos Santos (PG)[1] .
alice.barreto@arapiraca.ufal.br
[1]*Programa de Pós-graduação em Agricultura e Ambiente, Universidade Federal de Alagoas – Campus Arapiraca.*

Keywords: Scorpion accidents, Toxicity, Biochemistry.

Highlights

The cases of accidents with venomous animals reached 61,860, 84.7% of which were caused by scorpions between the years 2018 and 2022. In terms of biochemical interest, studies have shown that from the venom of scorpions one can develop favorable anti-tumor results.

Abstract

Scorpions are responsible for a large proportion of accidents with venomous animals, reaching up to 58% of cases. Nationally, cases of accidents involving venomous animals reached around 155 thousand. As a result, the reported number of scorpion accidents, covering the entire Brazilian territory, is of high importance with regard to public health, being considered by the World Health Organization (WHO) a neglected public health problem. Furthermore, the National Toxic-Pharmacological Information System (Sinitox) shows that accidents caused by scorpions are the second biggest cause of human poisoning, surpassing snakebite, and are predominant in tropical and subtropical areas of the world, with a higher incidence in months in which there is an increase in temperature and humidity. Scorpions are of great scientific interest, mainly due to studies in the medical field and scorpionism, in addition to studies on the biochemistry of the venom and drug development. In Brazil, there are five families of scorpions, with the genus Tityus being the species with the highest prevalence in accidents involving humans in the country. Thus, there are four species in the country that are of great importance in public health: Tityus serrulatus, Tityus bahiensis, Tityus stigmurus and Tityus obscurus. Due to the high toxicity of its venom, the yellow scorpion is currently considered the most venomous in all of South America. Its venom has a variety of biochemical activities and pharmacological functions, it is a substance with a milky and opalescent appearance, containing insoluble mucus, mucopolysaccharides, natriuretic peptides, kallikrein inhibitors, amines, lipids, high molecular weight proteins, hyaluronidases, metalloproteases, serine proteases, inorganic salts, peptides and low molar mass proteins with neurotoxic activities. Therefore, this work aims to present the accidents caused by scorpions in Alagoas between 2018 and 2022, in addition to highlighting their biochemical importance. To obtain data, an analysis was carried out in the bibliography on digital platforms, such as Scielo, Google Scholar and PUbmed, regarding the biochemical importance, and there was a search in the official SINAN Net database. It was possible to verify in the literature that there are studies with scorpions, examples of biochemical use can be confirmed through the high rate of development of drugs to treat pain, as well as the development of drugs to control arrhythmia and heart pressure, anticonvulsants and antibiotics , in addition to insecticidal agents, marking and targeting of tumors. Regarding the number of accidents, between 2018 and 2022, 61,860 accidents due to venomous animals were recorded, 84.7% of which were due to scorpions. Most of them are female, aged between 40 and 64 years old. Sometimes, accidents occur in the foot area followed by the fingers. In this way, it is possible to conclude that there is a universe to be studied in relation to scorpions, since there are still few biochemical studies and many accidents, even though they pose a risk to public health.

Acknowledgments

FAPEAL and CNPq.

References

1. Ministério da Saúde**. Guia de Vigilância Epidemiológica**. Brasília: Ministério da Saúde: Secretaria de Vigilância Epidemiológica, 2022. Ministério da Saúde.

Área: BIO

A novel screening assay for identifying SmMTAP inhibitors in natural products

Renato C.S. Lessa (PG),[1] Miguel F.S. Abreu (IC),[1] Lucas G. Amaral (IC),[1] Pamella C.O. Oliveira (PQ),[1] Thiago M. Lima (PQ),[2] Vanessa G.P. Severino (PQ),[3] Marcela C. Moraes (PQ)[1*]

pamella_ortega@id.uff.br; mcmoraes@id.uff.br

[1]Departamento de Química Orgânica, UFF; [2]Departamento de Química Inorgânica, UFF; [3]Instituto de Química, UFG

Palavras Chave: *HPLC, Natural libraries, Immobilized enzymes, Screening assay, Affinity selection.*

Highlights

SmMTAP was immobilized on a silica support. The composite was used to screen eighteen plant extracts. The most promising natural library underwent AS-MS assay, that highlighted a new ligand.

Resumo/Abstract

Enzyme immobilization on solid supports is a process that provides increased mechanical, thermic, and pH stability. Moreover, simple separation methods allow enzyme recovery and reuse, significantly reducing the cost of screening assays.[1] This approach is particularly interesting for medicinal chemistry in the development of new screening assays aimed at identifying novel enzyme inhibitors. In this work, the enzyme SmMTAP (5'-deoxy-5'-metyltioadenosine phosphorylase from *Schistosoma mansoni*) was covalently immobilized on dendritic silica, a mesoporous support with large surface areas and pore channels that favor mass transfer.[2,3] SmMTAP plays a crucial role in the purine salvage pathway of the causative agent of schistosomiasis, a neglected tropical disease that lacks efficient drugs for adequate control and treatment.[4] A previously optimized HPLC-DAD method for separating and quantifying the catalytic product adenine from the substrate adenosine[5] was employed for direct SmMTAP activity monitoring. The bioreactor consisted of 50 µg of composite in a final volume of 200 µL in K_2HPO_4 100 mM pH 7.4 medium. The reaction time was 20 minutes under rotative mixing (21ºC). For the kinetic study, crescent adenosine concentrations (2 to 896 µM) were used in duplicity. The obtained data yielded a hyperbolic graph that fitted the Michaelis Menten enzymatic behavior (R^2 of 0.9944) and Michaelis Menten constant value of 64.7 ± 6.7 µM. The stability assays demonstrated that at 4ºC in TRIS HCl 100 mM pH 7.4 buffer, the bioreactor retained the maximum level of its activity over the first three days. Reusability assays indicated over 70% retention of initial activity after seven consecutive reaction cycles. An initial screening assay with eighteen different natural extracts at 200 µg/mL allowed easy identification of those with the most promising bioactivity (SmMTAP inhibition between 67.5 and 81.6%). IC_{50} assay highlighted HS-EEC (0.88 ± 0.22 µg/mL) as the most promising extract. Using an affinity selection-mass spectrometry (AS-MS) assay, the ligands present in this extract were fished out and their structures are being inferred using feature-based molecular networking. Therefore, the immobilization of SmMTAP on dendritic silica provided a bioreactor with high stability as a novel tool for the identification of new ligands in complex libraries.

References: 1) De Oliveria, P. C. O.; Lessa, R. C.; Ceroullo, M. S.; Wegermann, C. A.; De Moraes, M. C. *Front. Anal. Sci.* **2022**, 2:1004113; 2) Jorge, E. Y. C.; Lima, C. G. S.; Lima, T. M.; Marchini, L.; Gawande, M. B.; Tomanec, O.; Varma, R. S.; Paixão, M. W. *Green Chem.* **2020**, 22, 1754; 3) Zhang, S.; Bai, J.; Kong, W.; Song, H.; Liu, Y.; Liu, G.; Ma, L.; Zhou, L.; Jiang, Y. *GreenChE* **2023**, *In Press*. 4) Wang, J.; Paz, C.; Padalino, G.; Coghlan, A.; Lu, Z.; Gradinaru, I.; Collins, J. N. R.; Berriman, M.; Hoffmann, K. F.; Collins III, J. *J. Science* **2020**, 369, 1649; 5) Kiebling, P.; Scriba. G. K. E.; Sub, F.; Werner, G.; Knoth, H.; Hartmann, H. *J. Pharm. Biomed. Anal.* **2004**, 36, 535.

Agradecimentos/Acknowledgment

FAPERJ and CNPq. This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – Brasil (CAPES) – Finance Code 001.

Área: BIO

Evaluation of the *in vitro* stability of [^{68}Ga]gallium radiolabeled peptides in biological tissue homogenates and serum

Giovana O.A. Santos (IC),[1,2] Marcio Ferrarini (PQ),[3] Ulisses L.F. Sa (PQ),[3] Koiti Araki (PQ),[2] Fabio L.N. Marques (PQ),[1*]

giovanaoliveiraalves@usp.br; fabio.marques@fm.usp.br

[1]Departamento de Radiologia e Oncologia (LIM 43), Faculdade de Medicina, USP; [3]Departamento de Química Fundamental, Instituto de Química, USP; [3]Cinrad-Instituto de Radiologia, HCFMUSP.

Keywords: *Radioisotope, Gallium-68; Radiolabeled peptide, In vitro stability, Tissue homogenate.*

Highlights

This work describes the study of the stability of the radiolabeled peptides [^{68}Ga]Ga-PSMA-11 and [^{68}Ga]Ga-DOTATATE in the liver and kidneys homogenates and in the serum.

Abstract

Introduction: Drug stability is a fundamental parameter for developing pharmaceuticals and radiopharmaceuticals. Usually, it is done by evaluating the *in vivo* concentration of the integre drug in blood or urine samples or, *in vitro*, by incubation in the serum. An alternative method is incubating the drug in homogenates of biological tissues such as the liver and kidney[1]. In this work, we evaluated the stability of radiolabeled peptides [^{68}Ga]Ga-PSMA-11 and [^{68}Ga]Ga-DOTATATE, clinically used for imaging diagnostic of prostate and neuroendocrine tumors, respectively. **Material and methods:** [^{68}Ga]Ga^{3+} was produced in the cyclotron by nuclear reaction ^{68}Zn(p,n)^{68}Ga and reacted with peptides containing chelators; radiochemical purity > 99 % was assessed in HPLC. Animal experimentation was approved by the Ethical Committee for Animal Use of the University of Sao Paulo Medical School (# 1974/23). Mice were deeply anesthetized (5% isoflurane in 100% oxygen) and euthanized by heart excision. The liver and kidney were removed, sectioned, and frozen at -80 °C. Serum was obtained from human volunteers. Homogenates were prepared at 100 mg/mL in HEPES 20 mM pH 7.4. Radiolabeled peptides were added to tissue homogenates and in 0.25 mL of serum, then incubated for 1, 15, 30, and 60 minutes at 37 °C. Samples were centrifuged at 5,000 rpm, and the supernatant was removed and mixed with acetonitrile, followed by a new centrifugation step to separate any protein content. Samples were analyzed by HPLC, using an RP-C18 column and gradient mode for H_2O/TFA 0.1 % and acetonitrile/TFA 0.1 % mobile phases at 1 mL/min. Signals were measured in a radiation detector.

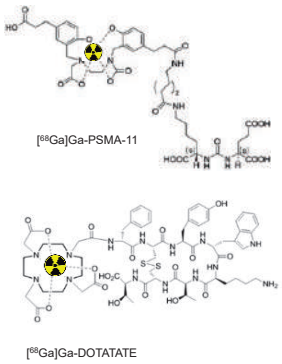


Figure 1- [^{68}Ga]Gallium radiolabeled peptides

Table 1. Percentage of the peak area at specific retention time for radiolabeled peptides after incubation with tissue homogenates

Compound	Tissue	Incubation time (min)			
		1	15	30	60
[^{68}Ga]Ga-PSMA-11	Liver	100 %	100 %	100 %	100 %
	Kidney	100 %	100 %	100 %	100 %
	Serum	100 %	100 %	100 %	100 %
[^{68}Ga]Ga-DOTATATE	Liver	100 %	100 %	100 %	100 %
	Kidney	100 %	100 %	100 %	100 %
	Serum	100 %	100 %	100 %	100 %

Results: The HPLC retention time for [^{68}Ga]Ga^{3+}, [^{68}Ga]Ga-PSMA-11, and [^{68}Ga]Ga-DOTATATE were 3.5 min, 8 min, and 8.8 min, respectively. As shown in Table 1, both radiolabeled peptides were stable for 1 h in tissue homogenates and serum, since no changes were observed in their concentration at retention time or were not observed any other signal in the chromatogram. These data agree with literature related to serum stability, close to 4 h[2,3]. **Conclusion:** The protocol is a practice tool to study the drug's *in vitro* stability, complementary to the serum test, since the drugs will be in contact with liver and kidney tissue and their enzymes and proteins, giving data comparable to *in vivo* assay. Furthermore, this allows to save animals since the organs of one animal can be used to test drug stability in several times or for different compounds.

1- Ocak, M.; et al. Eur J Nucl Med Mol Imaging (2011) 38:1426–1435; 2- MukherjeeJ, A.; et al. Radioanal Nucl Chem (2014) 302:889–894
3- Urbanova, K.; et al. Appl Radiat Isot (2021) 172:109692

Acknowledgments

To CNPq - Grant 182312/2023-2

Área: BIO

LIGAND FISHING OF NATURAL PRODUCTS AS POTENTIAL INHIBITORS FOR NUCLEOSIDE HYDROLASE

Pedro R.C. Medeiros (IC),[1*] Pamella C.O. Oliveira (PQ),[1] Martin Albino (PQ),[2] Claudio Sangregorio (PQ),[2] Jorge L.S. Simão (PG),[3] Luzineide W. Tinoco (PQ),[3] Vanessa G.P. Severino (PQ), [4] Marcela C. Moraes (PQ).[1]

pedrorcm@id.uff.br; mcmoraes@id.uff.br

[1]BioCrom, UFF, Niterói, Brazil; [2]LAMM, UNIFI, Firenze, Italy; [3]IPPN, UFRJ, Rio de Janeiro, Brazil; [4]LabPN, UFG, Goiânia, Brazil.

Keywords: *Iron oxide nanoparticle, Leishmania donovani, Natural products, Nucleoside Hydrolase, Ligand fishing.*

Highlights

Nanosized magnetic particles as a support to immobilize *Ld*NH. Within a natural product library, *Banisteriopsis laevifolia* leaves and flower extracts were selected as a promising source of *Ld*NH inhibitors in screening assays.

Abstract

BACKGROUND: The enzyme nucleoside hydrolase (NH) is essential for RNA and DNA biosynthesis in *Leishmania donovani* (*Ld*) and can be considered a promising target for developing potential new drugs against visceral leishmaniasis.[1] Magnetic particles (MPs) are widely used for immobilizing macromolecules due to their versatility.[2] Coating MPs with the biological target presents an interesting approach for developing screening assays.[3] Herein, *Ld*NH-coated magnetic nanoparticles (MNPs) were employed in screening potential inhibitors in *Banisteriopsis laevifolia* extracts.

METHODS: *Ld*NH was covalently immobilized onto MNPs' surface, functionalized with $-NH_2$ groups, using glutaraldehyde for the formation of Schiff bases. *Ld*NH catalytic activity was monitored by quantifying the product (hypoxanthine) generated from substrate (inosine, INO) hydrolysis via HPLC-DAD. *Ld*NH-MNPs were used in screening assays with natural libraries, employing INO at 500 µmol L^{-1}, *Ld*NH-MNPs at 0.8 µg mL^{-1}, and extracts at 200 µg mL^{-1}. *B. laevifolia* leaves and flower extracts were selected to determine their IC_{50} values. Ligand fishing assays were conducted on *B.laevifolia* leaves extract to identify binders present in this natural library. For this, 500 µL of *B. laevifolia* leaves extract (4.0 mg mL^{-1} in ammonium acetate) was added to 2.5 mg of *Ld*NH-MNPs and incubated for 15 min. After magnetic extraction, the supernatant was removed, generating S_0. The *Ld*NH-MNP were washed (2 x 500 µL) with ammonium acetate buffer producing S_1 and S_2. Then, the *Ld*NH-MNPs were incubated with MeOH (500 µL) for 25 min for ligand elution. After magnetic extraction, the supernatant was removed (S_3). This procedure was carried out for both active and inactive *Ld*NH, used as a control assay. Additionally, a chromatography method was developed to profile *B. laevifolia* leave extract and supernatants (S_0 and S_3) by HPLC-DAD-HRMS analysis. The method employs an INERTSUSTAIN C18 column (250 X 4.6 mm, 5 µm), with a mobile phase consisting of acetonitrile and ultrapure H_2O, both acidified with 0.1% formic acid, in gradient elution mode at 0.8 mL min^{-1}. With the acquired HPLC-DAD-HRMS supernatants data, the affinity ratio (AR) of the ligands were calculated according to the equation:

$$AR = \frac{S_3 \text{ Ligand area}_{Ld\text{NH-Active}}}{S_3 \text{ Ligand area}_{Ld\text{NH-Inactive}}}$$

. The considered threshold to identify ligands were AR ≥ 1.2.

RESULTS: Both *B. laevifolia* leaves and flower extracts exhibited inhibition percentages above 99% in the initial screening, with IC_{50} values determined as 0.76 ± 0.03 and 1.59 ± 0.09 µg mL^{-1}, respectively. The ligand fishing assay showed selective retention of more than 10 *Ld*NH ligands, with 1.2 ≤ AR ≤ 3.5, as potential enzyme inhibitors. Currently, the structures are undergoing annotation using virtual libraries such as GNPS, Sirius, PubChem, and MassBank.

CONCLUSIONS: The screening assay identified a potential natural source for *Ld*NH inhibitors. Further studies are required to determine the specific components within the extracts related to the inhibitory activity.

[1]Figueroa-Villar, J.D.; Sales, E.M. Chem.-Biol. Interact **2017**, 263, 18; [2]Ximenes, I. A. T. *et al*. Pharm. Biomed. Anal. **2021**, 204, 114286; [3]Lima, J. M. *et al*. Anal. Methods, **2020**, 12, 4116.

Acknowledgments

CNPq, FAPERJ, CAPES – Finance Code 001, and CAPES PrInt.

Área: BIO
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Metabolomics analysis of cardiac tissue by RPLC-MS to understand the metabolic changes caused by Chagas Disease

Hanna Carvalho de Sá (PG),[1] Breno Cardim Barreto (PQ),[2] Milena Botelho Pereira Soares (PQ),[2] Gisele André Baptista Canuto (PQ),[1]*

***gisele.canuto@ufba.br**

[1]Departamento de Química Analítica, Instituto de Química, UFBA; [2]Instituto Gonçalo Moniz, FIOCRUZ (BA).

Palavras Chave: untargeted metabolomics, LC-MS, Chagas disease, T. cruzi, metabolism.

Highlights

Untargeted metabolomics demonstrated multi-target infection mechanism in chagasic cardiac tissue of mice.
Changes in lipid metabolism may be associated with the presence of *T. cruzi* in biological organisms.

Resumo/Abstract

Chagas Disease (CD) is a neglected tropical disease, and despite being known for more than 100 years, there is still little knowledge about the pathological mechanisms underlying this infection. Additionally, there are no efficient drugs or vaccines available for the prevention and treatment of the disease, especially at advanced stage. Thus, there is a need to elucidate the metabolism involved in this disorder, in order to search alternative and more effective treatments[1]. Metabolomics is an efficient and important tool for elucidating altered metabolic pathways by parasitic and other infections[2]. In this work, the metabolic changes caused by Chagas Disease were determined using an untargeted metabolomic approach in heart tissue samples from mice 60 days post-infection with *Trypanosoma cruzi*.
The metabolites were extracted using a tissue disruption instrument (tissuelyzer) by adding 50% methanol, followed by a mixture of dichloromethane/methanol (3:1 v/v). Metabolomics analyses were performed by reverse-phase liquid chromatography coupled with mass spectrometry (RPLC-MS), in positive and negative ionization modes. Raw data were processed in XCMS[3] software package running at R platform to extract molecular features (MF). Statistical analysis using multivariate and univariate methods were performed to find discriminants. The results showed 969 and 709 significant MF for ESI+ and ESI-, respectively, in which 228 metabolites (146 for ESI+ and 82 for ESI-) were annotated based on the *m/z* in public databases.
The main metabolic changes observed were related to lipid metabolism, which is associated with the progression of heart disease and Chagas Disease. Among the altered classes of metabolites, acyl carnitines and eicosanoids were notable, as they are implicated in the development of cardiac dysfunctions and disease progression. Particularly acyl carnitines are involved in energy metabolism and may be associated with cardiac dysfunction caused by CD[4]. The eicosanoids belonging to the arachidonic acid pathway (increased in the infected group) has been correlated with an increase in inflammatory activity. Our results indicate the involvement of different metabolic pathways, highlighting the complexity of this disease. The metabolic information obtained in this work serves as a starting point for better understanding the disease to search for specialized treatments and accurate diagnosis.

References

[1]WHO. Chagas disease (American trypanosomiasis). < https://www.who.int/health-topics/chagas-disease#tab=tab_1> Acesso em Fevereiro 2024.
[2]CANUTO, G. A. B. et al. Quimica Nova, 41; 2018:75-91.
[3]SMITH, C. A. et al. Analytical Chemistry,78; 2006:779-87.
[4]LIZARDO, K. et al. Disease Markers, 2019; 2019:4956016.

Agradecimentos/Acknowledgments

H.C.S. is grateful to the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) for the fellowship, and the Laboratório de Análises Cromatográficas e Espectrométricas (LACE – IQ-UFBA).

Área: BIO

Optimized recombinant protein expression and purification of Ornithine Decarboxylase (ODC) from *Leishmania donovani* (*L. donovani*)

Douglas G. dos Santos (PG),[1] Vanessa de P. Borges (IC)[1], Luzineide W. Tinoco (PQ)[1].

dgaldino@ufrj.br; luzitinoco@gmail.com

[1]*Centro de Ciências da Saúde (CCS), Instituto de Pesquisa em Produtos Naturais (IPPN), UFRJ;*

Keywords: *Ornithine Decarboxylase, Leishmania donovani, expression, purification.*

Highlights

L. donovani is a leishmaniasis-causing protozoan. ODC is a key enzyme in the biosynthesis of polyamines.
The study aimed to modify parameters in the expression and purification process of ODC to improve enzyme recovery.

Resumo/Abstract

Leishmania donovani is a trypanosome protozoan of the genus Leishmania that causes leishmaniasis, and this species is one of the causes of visceral leishmaniasis, the severe form of the disease. ODC, a key enzyme and limiting step in the biosynthesis of polyamines, is involved in the control of cell proliferation.[1] Due to its importance in the parasite's life cycle, its expression and purification are significant steps in the search for new inhibitors. There are protocols already described in the literature for recombinant expression and purification, however a common problem is that most of the enzyme remains trapped in the cell pellet. [2],[3]
In this work, parameters used in the expression and purification process were modified and the impact on enzyme recovery was evaluated using normalized SDS-PAGE gel electrophoresis. The first parameter changed was the sonication time in the lysis stage. Using an ultrasonic cell disruptor (sonicator) with 20 kHz frequency and 350 W power, configured for 65% power, a time of 900s was evaluated, with 3s on and 3s off, commonly used in protocols, compared to times of 1200s, 1500s and 1800s. In the next test, the sonicator power was changed from 65% to 100% using a time of 900s. No substantial changes were noted in the electrophoresis gel for either test. In the expression stage, the first factor changed was the concentration of Isopropyl β-d-1-thiogalactopyranoside (IPTG), used to induce protein expression. Solutions with final concentrations of 0.4mM, 0.6mM, 0.8mM and 1mM were used. At a concentration of 0.4mM, expression is very slow and the amount of enzyme obtained is not satisfactory. However, from a concentration of 0.6mM the expression is efficient, with 1mM producing overexpression, which can lead to the formation of inclusion bodies. Still in the expression stage, the expression time after induction was also evaluated, with variations of 10 hours and 22 hours. The 10-hour test proved to be more appropriate in terms of the amount of enzyme produced that was not trapped in the cell pellet. The next test, carried out in the purification stage using a nickel affinity chromatography column, analyzed the change from Tris-HCl buffer to phosphate buffer, which is used to store the enzyme after purification. It was possible to notice that the Tris-HCl buffer performed better in purification. The last modification verified was the use of a buffer gradient containing different concentrations of imidazole, a competitive agent for eluting histidine-tagged proteins. In the first test, 5 buffers containing imidazole concentrations of 10mM, 50mM, 100mM, 300mM and 500mM were used. In the second test, 4 buffers were used with imidazole concentrations of 10mM, 50mM, 300mM and 500mM. After analyzing the electrophoresis gel, it was possible to notice that the 100mM buffer was not necessary, since almost no contaminating proteins bound to it. Thus, the optimized parameters found for recombinant expression and purification of *L. donovani* ODC were final concentration of 0.6mM IPTG, 10 hours of expression after induction, sonication of 900s (3s on, 3s off) at 65% power and and nickel affinity purification with 4 Tris-HCl buffers containing imidazole concentrations of 10mM, 50mM, 300mM and 500mM with the enzyme being eluted in the 300mM buffer.

[1] Pérez-Pertejo, Y. et. al. Polyamine Metabolism for Drug Intervention in Trypanosomatids. **Pathogens**, *2024*, 13, 79.
[2] Das M., Singh S., Dubey V. K. Novel Inhibitors of Ornithine Decarboxylase of Leishmania Parasite (LdODC): The Parasite Resists LdODC Inhibition by Overexpression of Spermidine Synthase. **Chem Biol Drug Des**. *2016*, 87(3), 352-60.
[3] Yadav A. et. al. Leishmania donovani: impairment of the cellular immune response against recombinant ornithine decarboxylase protein as a possible evasion strategy of Leishmania in visceral leishmaniasis. **Int J Parasitol**. *2015*, 45(1), 33-42.

Agradecimentos/Acknowledgments

CAPES, CnPQ, FAPERJ

Área: BIO

Production of a recombinant L-asparaginase for developing a heterogeneous biocatalyst to mitigate acrylamide production in French fries.

Lucas A. Freitas (PG),[1,3*] Gilvan P. Furtado (PQ),[1,3] Luciana R.B. Gonçalves (PQ),[2] Marcos R. Lourenzoni (PQ).[1,3]

lucas.freitas@fiocruz.br

[1]Departamento de Engenharia de Pesca, UFC; [2]Departamento de Engenharia Química, UFC; [3]Fundação Oswaldo Cruz - Ceará

Keywords: *L-asparaginase, Acrylamide, Fermentation, Immobilization.*

Highlights

L-ASNase use in food industry reduces acrylamide content. Recombinant production of L-ASNase allowed high yields. L-ASNase immobilization produced suitable biocatalysts for industrial application.

Abstract

Heat treatments, such as baking, frying, and roasting, of some foods, in the food industry, may induce the production of acrylamide, a genotoxic, neurotoxic, and probably carcinogenic compound to humans. Acrylamide is formed through the Maillard reaction when foods rich in short-chain reducing sugars and L-asparagine (Asn) are heated to temperatures above 120 °C. The abundance of these precursors in some plants, such as potatoes, wheat, and coffee, makes for derivatives rich in acrylamide, such as French fries, potato chips, crackers, bread, and roasted coffee. Since these are largely consumed products, the World Health Organization (WHO) recommends the development of acrylamide mitigation strategies to reduce the overall dietary exposure to acrylamide. One of these strategies is to treat these foods with an enzyme, L-asparaginase (L-ASNase), before the heat procedure. The L-ASNase hydrolyzes Asn to ammonia and L-aspartate (Asp), which is not a precursor to acrylamide, reducing its content on the product. This work aims to stablish a recombinant microbial system to produce L-ASNase and to develop a biocatalyst through immobilization of this enzyme that is applicable for acrylamide mitigation in French fries' production. The production of L-ASNase was conducted through the insertion of *ansB*, the gene encoding for *Escherichia coli* L-ASNase II (EcAII), in a constitutive expression vector containing a signal sequence for periplasmatic expression, and its transformation on *E. coli* cells. The enzyme was then obtained in the fermented broth, which could be precipitated with ammonium sulfate to obtain a protein extract. The recombinant enzyme production was successful, reaching 14810 $U \cdot L^{-1}$ in the fermented broth. The EcAII extract was used for the covalent immobilization on *Santa Barbara Amorphous-15* (SBA-15), a mesoporous silica. The SBA-15 was functionalized with (3-aminopropyl)triethoxysilane to add amino groups to the support and activated with glutaraldehyde to insert reactive aldehyde groups. After optimizing the immobilization conditions, a biocatalyst with 97% global yield relative to the free enzyme was obtained. The biocatalyst's Michaelis-Menten constant (K_M) was reduced compared to the free enzyme, from 3,72 mM to 2,69 mM, indicating an increase in substrate affinity. Still, the maximum catalysis velocity was also reduced from 13,42 $\mu M \cdot min^{-1}$ to 7,04 $\mu M \cdot min^{-1}$. The biocatalyst was also coated with polyethyleneimine (PEI) to obtain a more thermally stable product. The biocatalysts were more stable at 50 °C than the free enzyme, raising the half-life time from 2,5 min on the free enzyme to 5,0 and 8,5 min on the original and the PEI-coated biocatalysts, respectively. The biocatalysts were also used on subsequent operation cycles on Asn 100 mM at 55 °C, for 1 h each cycle. Both original and PEI-coated biocatalysts were able to retain more than 50% of their initial activities after 10 cycles of reuse. The results of operational stability prove that the biocatalysts are suitable for reuse. At the same time, the free soluble enzyme can't be used in more than 1 cycle due to its recuperation difficulty. The results point to the applicability of the biocatalysts on French fries' production to reduce the acrylamide content in this product, which should be acknowledged on future works.

Acknowledgments

Fundação Cearense de Apoio ao Desenvolvimento Tecnológico (Funcap), Fundação Oswaldo Cruz - Ceará (Fiocruz-CE), Universidade Federal do Ceará (UFC).

Área: BIO

Protein kinase AP2 (AAK1): Expression, purification and activity assay

Hortência A.S. Monteiro (PG)*, **Kézia S. Bispo (IC), Luzineide W. Tinoco (PQ)**

hortencia.a.s.monteiro@gmail.com; lwtinoco@ippn.ufrj.br

Instituto de Pesquisa de Produtos Naturais, Universidade Federal do Rio de Janeiro - UFRJ

Keywords: SARS-CoV2, Hepatitis C, Dengue, Zika, Neuropathic pain, Alzheimer's, Parkinson's.

Highlights

AAK1 kinase plays a crucial role in clathrin-mediated viral endocytosis. Purified AAK1 was quantified and used in enzymatic assays to determine optimal ATP and substrate concentrations (SQITSQVTGQIGWRREG).

Abstract

Several viruses invade host cells through receptor-mediated endocytosis. This process is essential for viral replication in intracellular compartments, avoiding detection by the immune system. Adapter-associated protein kinase AP2 (AAK1) is crucial in viral internalization, notably in infections with positive single-stranded RNA viruses such as dengue, Zika, Sars-CoV-2, and hepatitis C (Strazic Geljic, et al, 2021, 5274). Furthermore, AAK1 is ubiquitous in the central nervous system (CNS) and plays an important role in neuropathic pain and a variety of other human diseases such as Alzheimer's disease, Parkinson's syndrome, etc. (X. Xin et al, 2023, 115102). Therefore, AAK1 is considered an important target for the development of drugs for the treatment of various diseases. The objectives of this work were to express, purify, and establish a protocol to evaluate the activity of the AAK1 kinase. These results will be used in the next step to evaluate potential inhibitors of this enzyme. The plasmid containing the genetic sequence of the AAK1 protein (AAK1-T27A365) cloned in the pNIC-CTH0 vector was obtained from the company Addgene (#73244) supplied in Escherichia coli DH5α cells. This plasmid allows the expression of the AAK1 protein with a tail of six histidine residues at the C-terminus, with a cleavage site by the TEV enzyme. After purification with the Sigma-Aldrich GenElut mini-prep kit, the plasmid was extracted and transformed by heat shock into competent E. coli BL21(DE3) cells. Protein expression and purification were successfully carried out following the protocol described by Sorrel et al. (2016). After purification, AAK1 was quantified with a 3.7 mg/mL concentration. AAK1 activity assays are being carried out using the ADP-Glo kit (Promega), through luminescence analysis. AKK1, in the presence of ATP and substrate (SQITSQVTGQIGWRREG), consumes ATP and phosphorylates the substrate to produce ADP. Initially, it was necessary to determine the ideal concentrations of ATP and substrate for assays to evaluate AAK1 activity. The assay was carried out by varying the ATP concentrations from (1uM to 1mM), with 1 mM as the ideal concentration for the enzymatic reaction. The substrate concentrations from 250μM to 1mM were evaluated, with 250 μM determined as the optimal concentration for the enzymatic assay. Concentrations determined for ATP and substrate will be used for the kinetic characterization of AAK1 and enzyme inhibition assays. The enzymatic activity of AAK1 will also be evaluated by ^{1}H and ^{31}P NMR based on the analysis of its substrate and ATP in the absence and presence of known inhibitors (Baricitinib and SGC). Such results will serve as a basis for establishing protocols for enzyme inhibition assays to search for new AAK1 inhibitors.

Acknowledgments

FAPERJ, CAPES and CNPq.

Área: BIO

Studies of the antiglycation potential of piceatannol using human hemoglobin (Hb) as target.

Tauane S. Rocha (PG),[1] Rosylene P. C. Lopes (IC),[1] Wallison S. Dias (PG),[1] Iara B. Valentim,[2] Júlio C. S. Da Silva (PQ),[1] Josué C. C. Santos (PQ),[1] Marília O. F. Goulart (PQ),[1] Jadriane A. Xavier (PQ)[1*]

tauane.rocha@iqb.ufal.br; jadrianexavier@iqb.ufal.br

[1]*Instituto de Química e Biotecnologia, UFAL.* [2]*Instituto Federal de Alagoas, IFAL*

Palavras Chave: *Hemoglobin, Antiglycation, Piceatannol, molecular docking.*

Highlights

Hb glycation was evaluated by analyzing the production of AGEs from reducing sugars (glu and fru). PIC was used to evaluate the inhibition of AGEs formation and interaction process with Hb at different temp, and molecular docking.

Abstract

Advanced glycation end products (AGEs) can induce diverse effects on human health, such as neurodegenerative diseases and other metabolic disorders such as diabetes, heart disease and cancer[1]. As such, the objective of this study was to obtain the progression or decrease of Hb's glycation, through the measurement of fluorescent advanced glycation end-products (AGEs), using glucose (glu) and fructose (fru) as reducing sugars and PIC (10 – 300 μM) as inhibitor of AGE formation, performed over a period of 5 weeks. The interaction of Hb with PIC was performed experimentally using fluorimetry at different temperatures (23, 30 and 37 ºC), as well as molecular docking simulations. PIC showed a great ability to inhibit glycation at 89, 78 and 73%, respectively, at the concentration of 300 μM (Figure 1). Figure 2 displays the most stable protein-substrate complex generated in the molecular docking simulations for the interaction of PIC and hemoglobin. These findings suggest that the PIC molecule preferentially binds to chain B of the protein, engaging critically with the terminal portion of the HEME group and forming essential hydrogen bonds with Arg40, Glu43, and Ser44 residues. Additionally, docking studies reveal that the attachment of PIC to hemoglobin represents a thermodynamically favorable process characterized by a binding free energy of -6.50 kcal/mol, which correlates to an equilibrium binding constant of approximately 5.81×10^4.

Figure 1. Monitoring of fluorescence intensity at concentrations (10 – 300 μM) of PIC and at different incubation times for the Hb (75 μM) + glucose (0.5 M) system (A), Hb (75 μM) + glucose/fructose (0.5 M) system (B) and Hb (75 μM) + fructose (0.5 M) system (C).

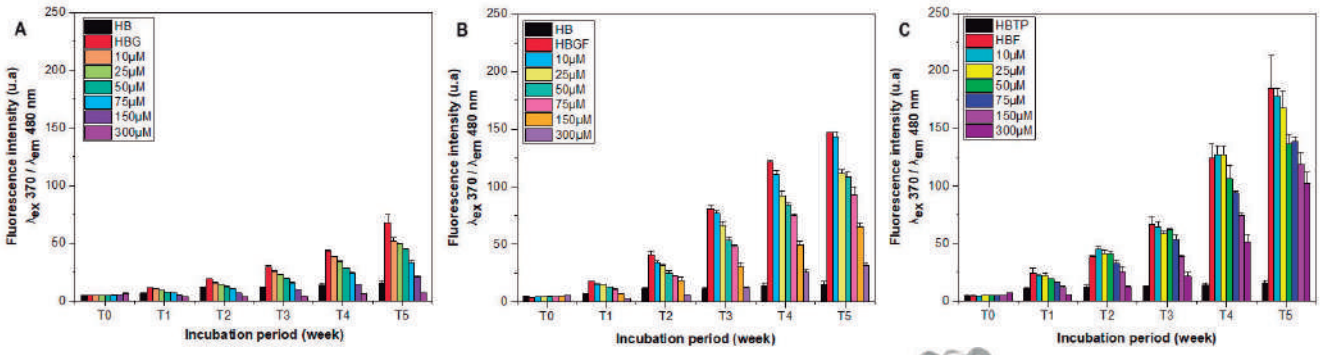
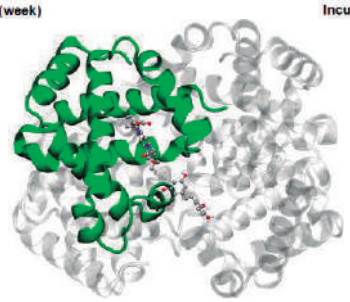


Figure 2. Most stable protein-substrate complex generated from molecular docking simulations for the binding process of PIC molecule to Hb.



[1]FEROZ et al. **Int J Biol Macro**, p.1844-1858, 2020.

Acknowledgments

CAPES, CNPq, FAPEAL and LEEO.

Área: BIO

Vibrational spectroscopy of cell membrane models by Sum-Frequency Generation (SFG spectroscopy)

Bruna Borges Freri (PG),[1*] Paulo Barbeitas Miranda (PQ)[2]

bruna_borges@usp.br; miranda@ifsc.br

[1]São Carlos School of Engineering, University of São Paulo; [2]São Carlos Physics Institute, University of São Paulo

Keywords: *Langmuir film, SFG spectroscopy, BAM microscopy, Biological membrane.*

Highlights

SFG spectra related to lipid density for saturated, unsaturated, and branched chain lipids.

Study enables SFG spectroscopy to probe changes in model membrane conformation with drugs and biomolecules.

Abstract

Several cellular processes depend on the interaction of the membrane with molecules in the cytoplasm or the extracellular environment. Therefore, the study of the structure of cell membranes and their interaction with other molecules is fundamental for the advancement of cell biology. For performing these in vitro studies, mimetic membrane models are often used, such as lipid vesicles, lipid bilayers on solid supports, and Langmuir films. Langmuir films are highly versatile, and various techniques can be employed to study them, with Sum-Frequency Generation (SFG) vibrational spectroscopy being a powerful technique [1]. SFG spectroscopy yields the vibrational spectra of lipid monolayers for probing of the average conformation of the hydrophobic chains, which is directly related to the degree of molecular packing. It has been shown that the amplitude ratio (d^+/r^+) of stretch vibrations of CH_2 and CH_3 groups are a quantitative indicator of the average chain conformation [2]. Nevertheless, the majority of SFG spectroscopy investigations have concentrated on Langmuir films of lipids with saturated chains [3,4]. Our study extends these previous investigations to lipid monolayers featuring more complex chains, such as branched (DPhPC) and unsaturated lipids (DOPC and POPC) [5]. A comparison with a saturated lipid that forms an expanded and homogeneous monolayer (DLPC) is also presented. Our findings reveal a direct correlation between the SFG spectrum of CH stretching vibrations and the degree of packing within these more complex lipid monolayers, yielding a valuable "calibration curve" for the amplitude ratio (d^+/r^+) as a function of monolayer density, for each type of lipid. This study will extend the utility of SFG spectroscopy to investigating more realistic membrane models and their interaction with drugs or other biological compounds.

References

[1] Lambert AG, Davies PB, Neivandt DJ. Implementing the Theory of Sum Frequency Generation Vibrational Spectroscopy: A Tutorial Review. :44.

[2] Volpati D, Aoki PHB, Alessio P, Pavinatto FJ, Miranda PB, Constantino CJL, et al. Vibrational spectroscopy for probing molecular-level interactions in organic films mimicking biointerfaces. Advances in Colloid and Interface Science. 2014;207:199–215.

[3] Guyot-Sionnest P, Hunt JH, Shen YR. Sum-frequency vibrational spectroscopy of a Langmuir film: Study of molecular orientation of a two-dimensional system. Phys Rev Lett. 1987;59:1597–600.

[4] Miranda PB, Pflumio V, Saijo H, Shen YR. Surfactant monolayers at solid–liquid interfaces: conformation and interaction. Thin Solid Films. 1998;327–329:161–5.

[5] Harayama T, Riezman H. Understanding the diversity of membrane lipid composition. Nat Rev Mol Cell Biol. 2018;19:281–96.

Acknowledgments

The authors thank FAPESP (grant 2022/14488-4), CAPES (grant 88887.803925/2023-00) and CNPq (grants 315772/2020-4 and 442239/2017-3) for financial support.

CAT

Catálise

Sociedade Brasileira de Química

Área: CAT

Avaliação de nanocatalisadores de cobre e níquel na desidrogenação do 2-hexanol para produção de precursores de combustível de aviação

Karina M. Lima (PG),[1,2*] Leon F. Feitosa (PQ),[2] Welington L.S. Soares (PG),[1,2] Carla R. Moreira (PQ),[2] Andréa M.D. Farias (PQ),[2] Marco A. Fraga (PQ).[1,2*]

karina.lima@int.gov.br; marco.fraga@int.gov.br

[1]*Instituto Militar de Engenharia, IME;* [2]*Instituto Nacional de Tecnologia, INT.*

Palavras Chave*: 2-hexanona, Desidrogenação, Nanopartículas, Cobre, Níquel.*

Highlights

Evaluation of copper and nickel nanostructured catalysts in the dehydrogenation of 2-hexanol to production of precursors fuel aviation. Core-shell catalysts present higher selectivity for 2-hexanone than conventional ones. The more protected the nucleus, the higher the selectivity, but the lower the conversion due to the accessing.

Resumo/Abstract

Em meio à necessidade do uso consciente dos recursos naturais, as biorrefinarias vêm se destacando mundialmente. Para a questão de combustíveis a partir de fontes renováveis, considerar a obtenção do 2-hexanol a partir da hidrólise da biomassa lignocelulósica é interessante, pois este álcool pode ser usado como molécula plataforma na obtenção da 2-hexanona, sendo esta usada como intermediária na produção de hidrocarbonetos renováveis, por exemplo, para o setor de aviação[1]. O desenvolvimento de nanocatalisadores heterogêneos que sejam estáveis em reações em fase líquida e que cessem problemas de sinterização e lixiviação dos sítios ativos é essencial para garantir processos eficientes. Sendo assim, neste trabalho, catalisadores com estrutura *core-shell* foram sintetizados empregando metais não nobres, tal como o cobre que vêm sendo utilizado na desidrogenação de álcoois em substituição a metais nobres[2]. Além do cobre, avaliou-se o poder desidrogenante também do níquel em catalisadores impregnados (Cu/SiO_2 e Ni/SiO_2) e, os já citados, *core-shell* ($Cu@SiO_2$ e $Ni@SiO_2$).

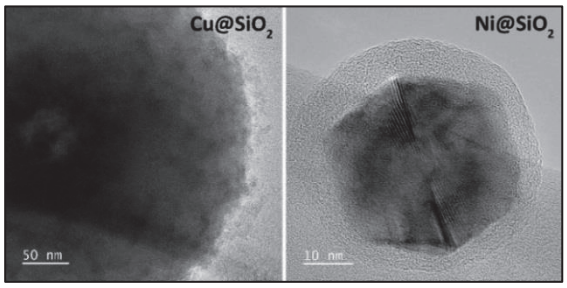


Figura 1 – Nanocatalisadores *core-shell* de cobre, níquel e sílica.

Nestes dois últimos, observam-se cascas amorfas e porosas de sílica, porém, para o $Ni@SiO_2$, observou-se um poliedro de Ni^0 na faixa de 50 nm e a casca com espessura de 5-10 nm. Enquanto que para o $Cu@SiO_2$ o núcleo é menor que 10 nm com uma camada de sílica maior que 100 nm (Figura 1).

Os catalisadores foram avaliados em um reator batelada do tipo Parr, usando uma solução 0,1 mol/L de 2-hexanol e γ-valerolactona como solvente, sob agitação constante, 10 bar de hidrogênio, durante 4 h. e a 200 °C. Todos os catalisadores apresentaram atividade, entretanto, a estrutura pode ter influenciado na seletividade. Os catalisadores impregnados apresentaram maior atividade, onde o catalisador de Ni/SiO_2 mostrou seletividade para 2-hexanona e o catalisador Cu/SiO_2 apresentou seletividade para o álcool isopropílico (produto esse obtido a partir da reação paralela de hidrogenólise do 2-hexanol). Por outro lado, os *core-shell* apresentaram seletividade para 2-hexanona maiores do que os catalisadores impregnados, possivelmente devido à preservação dos sítios ativos para desidrogenação dentro da casca de SiO_2, sendo a desidrogenação favorecida quando se utiliza catalisadores com essa arquitetura. Ressalta-se, portanto, que o catalisador $Cu@SiO_2$ apresentou seletividade para 2-hexanona, diferentemente do catalisador impregnado. Porém, a atividade deste catalisador foi a mais baixa de todas, recaindo sobre a dificuldade do reagente em acessar as nanopartículas de Cu envoltas na grande camada de sílica.

[1] Doi: 10.1016/j.fuel.2016/j.fuel.2016.02.084 / [2] Doi: 10.1016/j.catcom.2020.106179

Agradecimentos/Acknowledgments

Os autores agradecem ao LABNANO-CBPF e ao MCTI/SISNANO/INT-CENANO-CNPq (Proc. 442604/2019) pelas análises de microscopia eletrônica. CNPq e CAPES pelas bolsas de estudo.

Área: CAT

Bifunctionalized cellulosic biocatalysts for chemical neutralization of organophosphates

Mariana Helena Nazareno (IC),[1*] **Willian H. Takarada (PG),[1] Rilton A. de Freitas (PQ)[2] and Elisa S. Orth (PQ).[1]**

mariana.helena@ufpr.br

[1]*Department of Chemistry, UFPR;* [2]*Department of Pharmacy, UFPR.*

Palavras Chave: *Carboxymethyl cellulose, hydroxamic acid, imidazole, dephosphorylation, biopolymer, pesticide.*

Highlights

Bifunctionalization of carboxymethylcellulose with imidazole and hydroxamic acid, for the development of biocatalysts able to degrade organophosphates, highly toxic chemical compounds.

Resumo/Abstract

Phosphate triesters, highly toxic synthetic compounds, are used for the development of pesticides and chemical weapons, due to the high stability of their P-O bonds, which reach the target without being chemically altered, causing serious damage to living beings. Therefore, the study of neutralization reactions of these compounds is very important, one of which is studied here, the development of biocatalysts with anchored nucleophilic groups. The bifunctionalization of carboxymethylcellulose (CMC) was carried out through its carboxylic acid sites using API imidazole and hydroxylamine hydrochloride (FIGURE 1A), molecules with already known catalytic potential in dephosphorylation reactions. The effect of varying the synthesis conditions was evaluated, such as the order of addition of the nucleophilic groups and synthesis time. The material was then characterized by several techniques, such as FTIR, complexation with iron (III) and potentiometric titration, confirming chemical functionalization. To investigate their catalytic activity, the samples were analyzed in reactions with the model organophosphate diethyl 2,4-dinitrophenyl phosphate (DEDNPP) (FIGURE 1B). The bifunctionalized samples showed catalytic activity up to 10^4 times greater in relation to the spontaneous hydrolysis of DEDNPP (FIGURE 1C), indicating the success of the proposed work, in addition to presenting greater catalytic increments than their analogous monofunctionalized biocatalysts. Catalyst recycling studies show that the biocatalyst can perform up to 5 organophosphate neutralization cycles, a very promising result that allows the design of sustainable biocatalysts that can be used effectively in chemical detoxification.

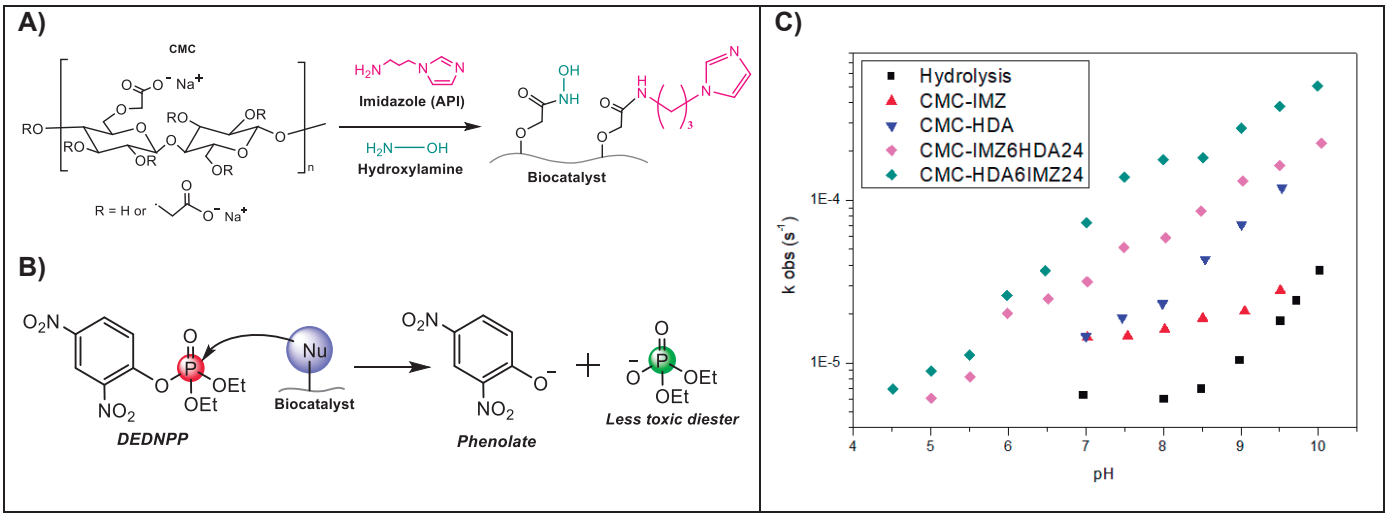


Figure 1. A) Dephosphorylation reaction of DEDNPP; **B)** Functionalization route scheme for CMC-IMZandHDA; **C)** K_{obs} profile at 21ºC of samples degrading the organophosphate model DEDNPP.

Agradecimentos/Acknowledgments

UFPR, CAPES, CNPq, L'Oréal UNESCO-ABC, PhosAgro/UNESCO/IUPAC, INCT NanoVida, INCT Nanocarbono

Área: CAT

Catalisadores de Sn dispersos sobre g-C_3N_4 para conversão de Di-hidroxiacetona a compostos de valor agregado

Ruan S. A. Ribeiro (PG),[1] Roberto de Oliveira Fernandes (IC),[1] Daniel G. S. Quattrociocchi (PQ),[1] Vinicius Rossa (PQ),[1] Sancler C. Vasconcelos (PG),[1] Ernesto A. Urquieta-González (PQ),[2] André V. H. Soares (PQ),[3] Fabio B. Passos (PQ)[3], Thiago M. Lima (PQ)[1]

tmlima@id.uff.br

[1]Departamento de Química Inorgânica, UFF; [2]Departamento de Engenharia Química UFSCar; Escola de Engenharia, UFF[3]

Palavras Chave: *Biomass, Carbon Nitride, dihydroxyacetone, alkyl lactate, tin oxide*

Highlights

Sn catalysts dispersed over g-C_3N_4 for the conversion of dihydroxyacetone to value-added compounds. Small SnO_2 nanoparticles dispersed over graphitic carbon nitride catalysts were produced using remarkably low Sn loadings, yielding a high conversion of dihydroxyacetone to ethyl lactate.

Resumo/Abstract

Currently, through technological advances applied to lignocellulosic biomass, it is being used as an alternative or complementary source to petroleum. It can be applied, for example, to producing biofuels, solvents, and building blocks for various value-added chemical products. In this study, small SnO_2 nanoparticles and clusters (< 4.5 nm) were made by the dispersion of ultralow Sn loadings (1 and 2 wt.%) over bulk g-C_3N_4 and applied in the conversion of dihydroxyacetone (DHA) to ethyl lactate (EL) and other value-added compounds. Ethyl lactate can be used as a food additive, in perfumery, as a flavoring agent, plasticizer, and in cosmetic formulations. However, the application of this compound as a solvent is the most targeted, mainly by the paint industry, due to its high solvency power, boiling point, vapor pressure, and surface tension. From TEM images (Figure 1), it is possible to observe a good dispersion of the SnO2 for the catalyst Sn 1%, while the Sn 2% presented a more agglomerated system. The nanoparticle size highly influenced the catalytic activity and acidity, in which the Sn 1% presented the highest value. In this way, the catalyst with the lowest Sn loading showed a higher DHA conversion and selectivity to the desired product EL.

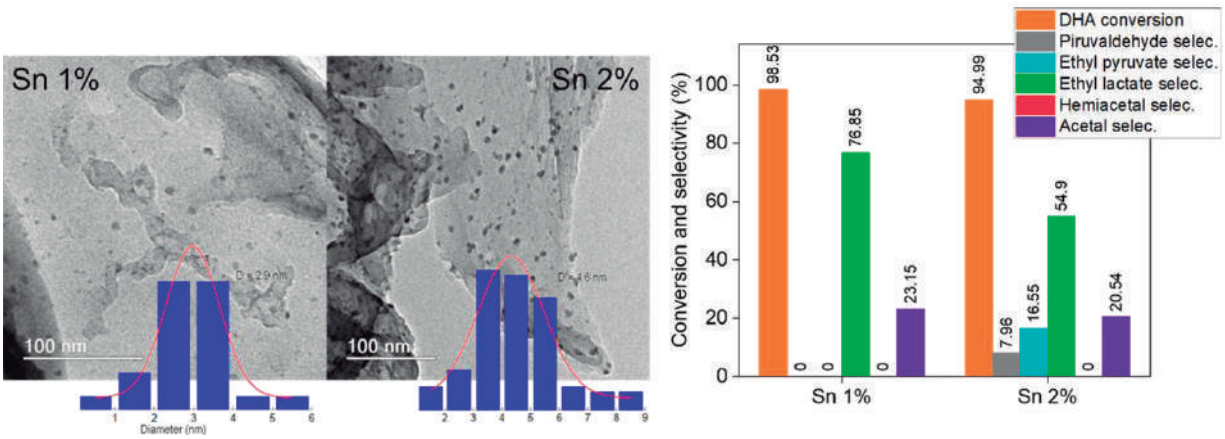


Figure 1. TEM images and catalytic evaluation of the Sn1% and Sn2% catalysts.

Agradecimentos/Acknowledgments

The authors acknowledge FAPERJ (E-26/201.358/2022), CNPq, and CAPES for the funding and the fellowships granted.

Catalytic activity of benzimidazolium halides ionic liquids in the cycloaddition of CO_2 to epoxides

Pedro H.G.P.A. Oliverio (IC)[1], Rafael P. Chagas (PQ)[2], Jorge L.S. Milani (PQ)[1*]

pedrooliverio15@gmail.com

[1]Departamento de Química, Instituto de Ciências Exatas, UFJF; [2]Instituto de Química, UFG.

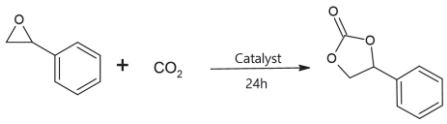
Keywords: *Benzimidazole, Ionic Liquids, Carbon Dioxide, Cyclic carbonates.*

Highlights

A series of simple benzimidazolium halides ionic liquids were synthesized and applied as bifunctional, metal-free catalysts for CO_2 cycloaddition to epoxides.

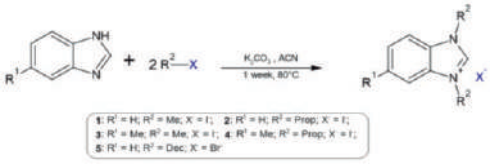
Resumo/Abstract

The high levels of CO_2 in the atmosphere, concerns about climate change and public pressure for benign and greener processes have prompted scientists to study the development of methodologies to use and prevent the release of CO_2. In this sense, routes to produce value-added products from CO_2 and mitigate its emissions have been extensively investigated. In in this work, we present a series of simple organocatalysts for CO_2 cycloaddition to epoxides (scheme1).



Scheme 1: cycloaddition of CO_2.

First, the benzimidazoles derivatives were synthesized according literature procedure; then the alkylation of respective benzimidazole using excess of R-X was carried out to produce the ionic liquids (**1-5**) quantitatively (Scheme 2). All compounds were characterized using ^{1}H NMR.



Scheme 2: Synthesis of the ionic liquids.

The catalytic reactions were performed using 5 mol% of catalyst, 6.25 mmol of styrene oxide, under 1 bar o CO_2 at 90°C. The catalytic activity was estimated using ^{1}H NMR (Table 1).

Despite the usual hydrogen bond donors (HBD) O-H or N-H groups are largely studied in literature as organocatalysts, we hypothesized the unusual C-H imidazole bond is also able to act as active site, activating the epoxide oxygen. It favors the nucleophilic attack by the X^- from ionic liquid opening the ring. The alkoxide intermediate can easily interact with CO_2 and the carbonate is obtained. The data obtained support the hypothesis of C-H bond act as active catalytic center and, conversions up to 98% at 8 hours was obtained. In order to make the system greener, a reaction at room temperature was carried out, however, almost no conversion was detected.

The conversions correlates well with the solubility, the more soluble the catalyst in epoxide the highest conversion.

Table 1: Catalytic activity of the benzimidazolium ionic liquids in the cycloaddition of CO_2[1]

Entry	Catalyst	T (°C)	t (h)	Conversion (%)	TOF (h^{-1})	Selectivity (%)
1	**1**	90	8	76	1.9	100
2	**1**	90	24	96	0.82	100
3	**2**	90	8	84	2.1	100
4	**2**	90	24	99	0.83	100
5	**3**	90	8	98	2.4	100
6	**3**	90	24	99	0.83	100
7	**4**	90	8	84	2.1	100
8	**4**	90	24	99	0.83	100
9	**5**	90	8	65	1.6	100
10	**5**	90	24	90	0.83	100
11	**3**	35	24	0.7	0.005	22

[1] Reaction conditions: 6,25 mmol of Styrene Oxide, 5 mol% of catalyst, [2]TOF = mol carbonate/mol cat. T.

In summary, a series of ionic liquids were synthesized and presented excellent conversions of styrene oxide in the respective cyclic carbonate under 1 bar of CO_2.

As perspectives, ion exchange will be promoted to dive deep into how the counter ion affects the reaction, including, acetate and lactate anions to obtain a metal- and halogen-free organocatalysts. Also, kinetic study will be done in order to better understand the reaction mechanisms.

Agradecimentos/Acknowledgments

FAPEMIG and CNPq.

Área: CAT

Chemical fixation of CO_2 catalyzed by an aluminophosphate containing ionic liquid

Francine Bertella* **(PQ),[1,2] Thainá N. Alves (IC),[1] Maria de Fátima F. Rodrigues (IC),[1] Michèle O. de Souza (PQ)[1].**

francinebertella@gmail.com

[1]Instituto de Química, UFRGS; [2]Departamento de Química, UFPR.

Keywords: Chemical fixation of CO_2, Ionic liquids, Aluminophosphates.

Highlights

An ATO aluminophosphate was synthesized using 1-butyl-3-methylimidazolium chloride as a structure-directing agent. The solid was successfully applied as a catalyst in the CO_2 cycloaddition reaction.

Resumo/Abstract

The utilization of CO_2 as a carbon feedstock in the cycloaddition reaction with epoxides to produce cyclic carbonates has gathered attention owing to the varied industrial uses of these compounds (as polar aprotic solvents, intermediates in pharmaceutical and fine chemical synthesis, polycarbonate precursors, etc.). This reaction exhibits green and sustainable characteristics due to the use of a non-toxic and readily accessible reagent (CO_2) and its 100% atomic efficiency (incorporation of all reactants into the product). Ionic liquids, classically defined as organic salts formed by ions and liquid below 100 ºC, are well-known catalysts for the cycloaddition reaction and also great candidates to be used as organic structure-directing agents in the synthesis of molecular sieves, such as zeolites and aluminophosphates. Given this, the objective of this work was to use the 1-butyl-3-methylimidazolium chloride (BMIm·Cl) ionic liquid (IL) as an organic structure-directing agent (OSDE) and as a solvent in the synthesis of aluminophosphates (AlPOs). In addition, the resulting material (IL@AlPO) was tested as a catalyst in the cycloaddition reaction with propylene oxide to generate propylene carbonate. The synthesis gel was prepared using the following molar ratio: 7.5 BMIm·Cl: 1 Al: 1.12 P: 0.75 HF: 2.32 H_2O. Next, the prepared gel was transferred to a Teflon-lined autoclave, which was placed in an oven at 160 ºC for crystallization through 24 h under static or agitation mode. The prepared AlPOs were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), thermogravimetric analysis (TGA), ^{13}C, ^{27}Al, and ^{31}P solid-state nuclear magnetic resonance (NMR), and elemental analysis. Under static conditions, a mixture of AEL and AFI crystalline phases was detected, along with the presence of a dense phase. On the other hand, the synthesis under agitation resulted in a pure ATO framework featuring a unidimensional pore system composed of 12-membered rings. The sample showed a uniform rod-like morphology, with crystals sizing approximately 1 µm. The ATO sample (containing the IL from synthesis) was used as a catalyst in the CO_2 cycloaddition reaction with propylene oxide to produce propylene carbonate. The reaction was performed in a Parr reactor employing 71.4 mmol of epoxide, 20 bar of CO_2, mechanical stirring at 100 ºC for 24 h, with 1 mol % of catalyst (on an epoxide basis) and 0.5 mol % of $ZnBr_2$ as a co-catalyst. Under these reaction conditions, a high selectivity (86 %) and a moderate yield (41 %) to propylene carbonate were achieved. The use of IL@AlPO enables the easy recovery of the catalyst (by a simple filtration), which allows its reuse.

Agradecimentos/Acknowledgments

Financial support by CAPES and CNPq is acknowledged for the fellowships. The authors also thank the National Center for Research in Materials (CNPEM) for granting beamtime (20222244) for SEM analysis at the LNNano.

Área: CAT_____
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Cobalt-Catalyzed Deoxygenation of Benzaldehyde Derivatives under Hydroformylation Conditions

Fábio G. Delolo (PQ),[1*] Helfried Neumann (PQ),[2] Eduardo N. dos Santos (PQ),[1] Matthias Beller (PQ),[2] Elena V. Gusevskaya (PG),[1*]

fabiodelolo@ufmg.br; matthias.beller@catalysis.de; elena@ufmg.br

[1]Departamento de Química, Universidade Federal de Minas Gerais, Belo Horizonte, MG 31270-901, Brazil; [2]Leibniz-Institut für Katalyse e.V., Albert-Einstein-Straße 29a, Rostock 18059, Germany

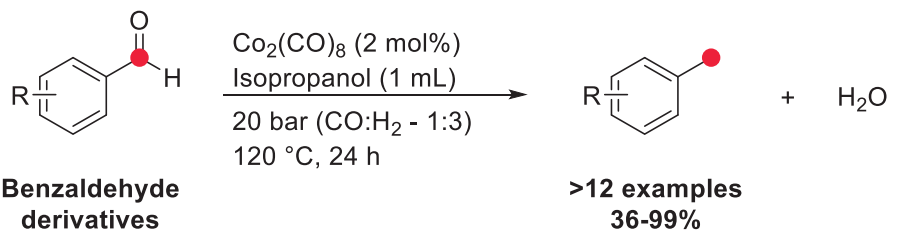
Palavras Chave:*(green solvents, base-metal catalysis, reduction reaction, synthetic organic chemistry, syngas, carbonyls).*

Highlights

Green deoxygenation process using non-noble metal catalyst that operates under mild conditions. High functional group tolerance. Control experiments confirmed the crucial role of syngas.

Resumo/Abstract

The reductive deoxygenation of aldehydes stands as a crucial transformation in industry and synthetic organic chemistry. This approach has been used to produce sustainable fuels and chemicals from bio-oil (product from the fast pyrolysis of lignocellulosic biomass). Wolff-Kishner, Clemmensen, and Mozingo reductions are classic methods for deoxygenation of carbonyl compounds, each approach carries its own set of disadvantages (e.g. harsh reaction conditions, incompatibility with sensitive functional groups, environmental and safety concerns). Therefore, these limitations underscore the need for alternative methods that offer milder conditions, improved selectivity, and functional group tolerance. Herein, we presented an alternative method using cobalt, a non-noble metal catalyst, for the deoxygenation of benzaldehyde derivatives that operates under mild conditions. The reaction parameters such as ligands, promoters, solvents, temperature, and syngas pressure were investigated using vanillin as model substrate. After the optimization, the versatility and generality of this methodology was investigated including substrates with electron-donating and electron-withdrawing groups. Several benzaldehyde derivatives were converted to their respective deoxygenated products with moderate to high yields (36-99%). To get a clearer picture of the reaction mechanism as well as the role of CO, control experiments confirmed the crucial role of syngas in the generation and stabilization of catalytically active cobalt species. This process was successfully applied on a gram scale obtaining satisfactory results.



- Mild conditions;
- Functional group tolerance;
- Non-noble metals;
- Water as byprduct;

Agradecimentos/Acknowledgments

CNPq, CAPES, FAPEMIG, and INCT-Catálise (Brazil) are gratefully thanked for the financial support and fellowships. We thank LAREMAR - Laboratório de Ressonância Magnética for the NMR measurements.

Área: CAT

Complexes containing N-Heterocyclic arene 9,10-phenanthroimidazole /Ruthenium (II) as catalysts in the dehydrogenation of formic acid to generate hydrogen.

José Antonio Fernandes Silva* **(PG),[1] Douglas Poleto de Oliveira (PG), [1] Gustavo Henrique Cicero Masson (PG), [1] André Luiz Bogado (PQ),[2] Beatriz E. Goi (PQ)[1] Valdemiro Pereira de Carvalho Júnior (PQ).[1]**

ja.silva@unesp.br

[1]Departamento de Química e Bioquímica, Faculdade de Ciências e Tecnologia – FCT/UNESP – Presidente Prudente, São Paulo
[2]Instituto de Ciências exatas e Naturais do Pontal – ICENP/UFU – Ituiutaba, Minas Gerais

Keywords: *symmetric ligands; Organic synthesis; NHC's; dehydrogenation*

Highlights

This work reports the synthesis of aromatic Ru-NHC complexes for dehydrogenation of formic acid. The new complexes can be potentially active in photo-dehydrogenation.

Resumo/Abstract

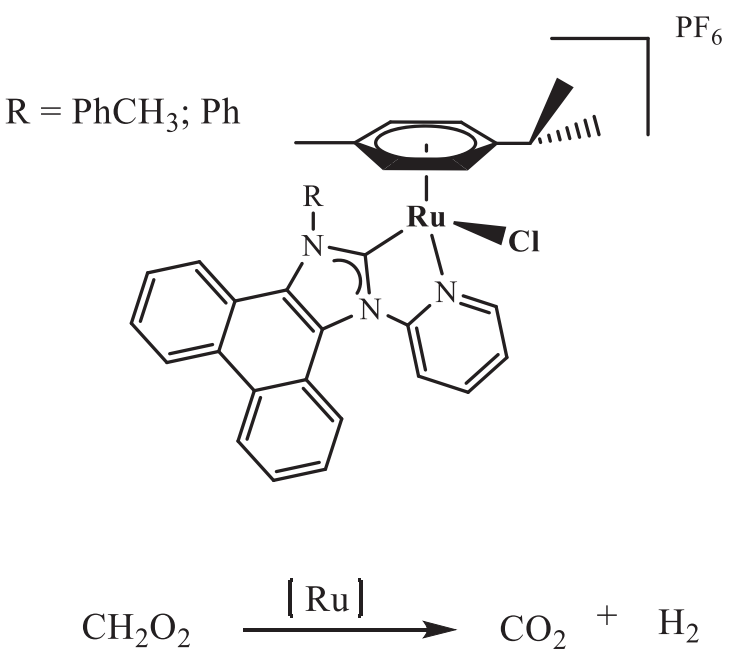


Figure 1. Ru complexes for dehydrogenation of formic acid.

Molecular hydrogen can represent a risk, to be highly flammable, both in its storage and in its transportation. several industrial processes, however, its application can be explored in aspects that have more impact on society, if such risks are minimized. Formic acid (FA) represents a non-hazardous source of hydrogen from the dehydrogenation process using complexes of transition metals. Ru complexes has been described in the literature as a promising path for this reaction. In this sense, the exploration of neutral and cationic complexes is important in the investigation of new routes and the effect ligand/metal synergy in the hydrogenation of FA. In this work, we report the synthesis of complexes of the type [Ru(*p*-cym)(9,10-phenanthoimidazole)Cl]PF_6, potentially active for dehydrogenation and photo-dehydrogenation reactions of formic acid. The complexes were synthetized by reactin a solution of 2-bromopyridine (3.80g, 24 mmol) and 9,10-phenanthroimidazole (24 mmol) neat at 160°C for 20 hours. Precipitate with pentane to obtain the ligand precursor. Silver (I) oxide (26 mg, 0.11 mmol) and ligand precursor (62 mg, 0.2 mmol) were mixed in degassed acetonitrile (8 mL) in a Schlenk tube. The reaction mixture was stirred for 6 h at room temperature under dark conditions. $[Ru(p\text{-cym})Cl_2]_2$ (62 mg, 0.1 mmol) was added to the reaction mixture. This reaction was again stirred overnight under dark conditions. The solution was filtered through a Celite plug. The solution was concentrated and precipitate. The complexes were characterized by FTIR, UV-Vis, ^1H and $^{31}P\{^1H\}$ NMR, FTIR, and cyclic voltammetry techniques.

Agradecimentos/Acknowledgments

Proc: 2021/11873-1 and 2021/13128-1

Área: CAT
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Dehydrogenation of formic acid catalyzed by bidentate N-heterocyclic carbene/arene-ruthenium(II) complexes.

Douglas. P. Oliveira (PG),[1*] André Luiz Bogado (PQ),[2] Valdemiro P. C. Júnior (PQ).[1]

douglas.poleto@unesp.br; valdemiro.carvalo@unesp.br; albogado@pontal.ufu.br ;

[1]*Departamento de Química e Bioquímica, UNESP;*

[2] *Química da Universidade Federal de Uberlândia, UFU;*

Keywords: Ruthenium; NHC's; Dehydrogenation; Formic acid.

Highlights

New Ru(II)-based catalysts with NHC-type ligands (N-heterocyclic carbenes), which are resistant to oxidation and humidity, were developed to improve reactivity in formic acid dehydrogenation reactions.

Resumo/Abstract

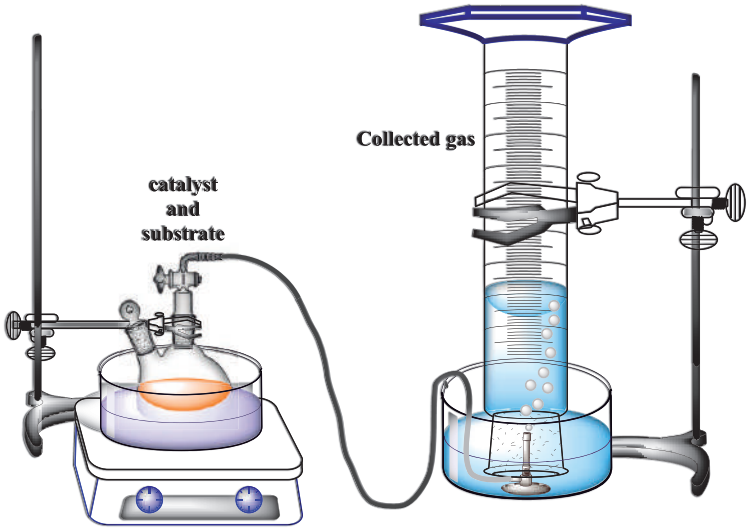


Figure 1. Gas collection system.
Source: The author.

Formic acid (FA) has recently been proposed as a chemical hydrogen (H_2) carrier because of its favorable properties. FA contains 4.4 wt % of hydrogen, and it is liquid under ambient conditions, allowing it to be handled, stored, and transported easily and safely.[1] Therefore, new Ru(II) catalysts with NHC-type ligands were synthesized for the selective decomposition of formic acid into H_2 and CO_2 in the absence of any organic additives. The new catalysts were characterized by FTIR, Cyclic Voltammetry, ^{1}H and ^{32}P NMR. The formic acid decomposition reaction was carried out using an adapted method described by TREIGERMAN and SASSON. [2] The general method consists of adding 2 mL (0.014 mol) of triethylamine and a known amount of pre-catalyst. The system is kept heated at 80 °C where, subsequently, 0.75 mL (0.02 mol) of formic acid will be added to the reaction system. Initially a turnover frequency of 1740 h^{-1} at 80°C was obtained using a ratio of 1/5000 of catalyst and substrate.

1. Mellmann, D.; Sponholz, P.; Junge, H.; Beller, M. Formic acid as a hydrogen storage material - development of homogeneous catalysts for selective hydrogen release. Chem. Soc. Rev. 2016, 45, 3954−3988.
2. Treigerman, Z., & Sasson, Y. (2017). Further Observations on the Mechanism of Formic Acid Decomposition by Homogeneous Ruthenium Catalyst. ChemistrySelect, 2(21), 5816–5823.

Agradecimentos/Acknowledgments

CAPES FAPESP CNPq Pós-Graduação Química Programa de Pós-Graduação em Química IBILCE/Unesp - São José do Rio Preto - SP LaCOM Laboratório de Catálise Organometálica e Materiais

Área: CAT

Designing bio-based materials for organophosphate neutralization: exploring alginate chemical functionalization

Willian Hideki Takarada (PG),[1*] Rilton A. de Freitas (PQ)[2] and Elisa S. Orth (PQ)[1]

***hidetak10@gmail.com;**

[1]*Department of Chemistry and* [2]*Departament of Pharmacy, Universidade Federal do Paraná (UFPR) – Curitiba, PR, Brazil.*

Keywords: *Biopolymer, Dephosphorylation, Detoxification, Hydroxamic Acid, Amidoxime, Pesticide.*

Highlights

Alginate-derived biocatalysts were developed anchoring reactive amidoxime and hydroxamic acids groups. The two materials efficiently neutralize organophosphates.

Resumo/Abstract

Organophosphates comprise hazardous chemicals employed as pesticides and chemical warfare. Dephosphorylation reactions that lead to detoxification are hindered due to highly stable P-O bonds, making the neutralization process challenging. Alpha-nucleophiles (*e.g.,* amidoximes and hydroxamic acids) are very reactive and promising to promote dephosphorylation but present some disadvantages – such as non-selectivity and non-recycling. Anchoring these groups on biopolymeric templates can improve the neutralization, promoting a catalytic path. Alginate is a brown seaweed-derived, water-soluble, and harmless biopolymer. Furthermore, it is a remarkable and versatile material that can be processed in many ways (like colloid, gel, and membrane). Herein, amidoximates- and hydroxamate-derived bio-based materials from alginate were developed aiming organophosphorus degradation. Amidoximates were obtained from hydroxyls groups on alginate (leading to the sample ALG-AMI). On the other hand, carboxylic acids groups on the template were functionalized into hydroxamate (resulting in ALG-HDA), according to Figure 1A. Chemical modification was confirmed by several techniques (*e.g.,* FTIR, potentiometric titrations, TGA) (Figure 1C). Then, the samples were evaluated as biocatalysts in the neutralization process of diethyl 2,4-dinitrophenyl phosphate (DEDNPP) (Figure 1B), promoting rate enhancements up to 10^4-fold compared to the spontaneous reactions, results among the best reported (Figure 1D). Thus, these materials enable several applications and further development of green, efficient, selective, and low-cost (bio)sensors, neutralizing gels, filter membranes and other detoxifying agents for organophosphates, a worldwide concern.

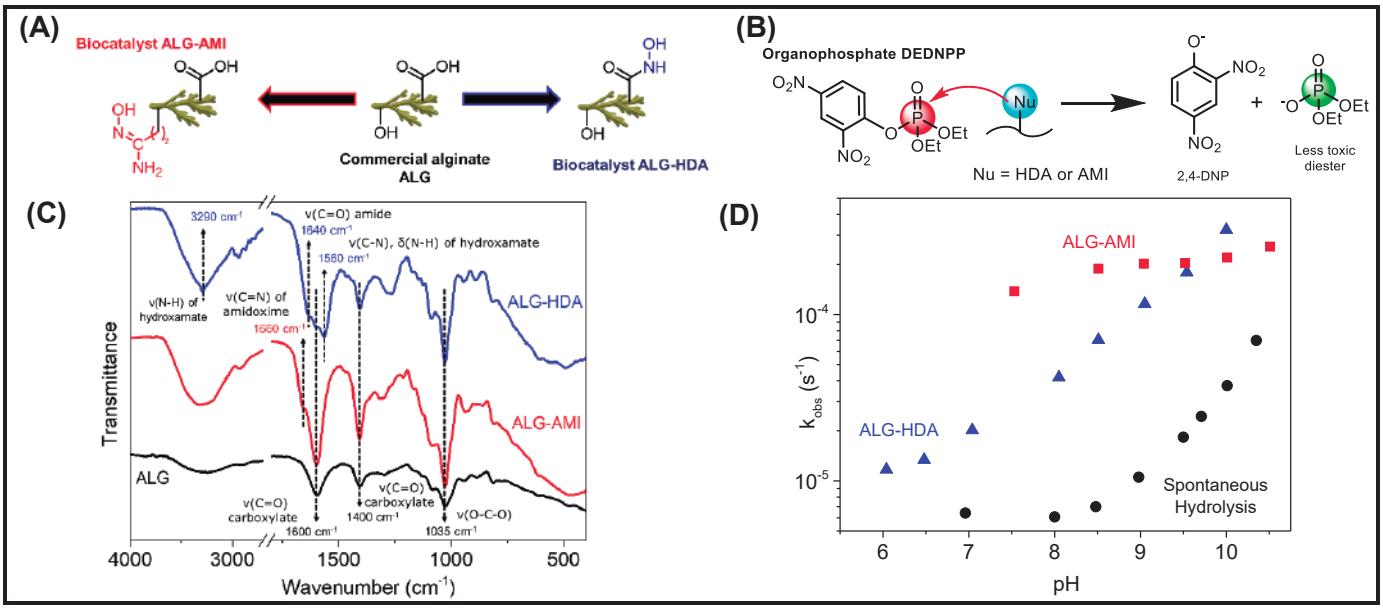


Figure 1. (A) Functionalization route for the biocatalysts; **(B)** DEDNPP neutralization reaction; **(C)** FTIR spectra of the samples; **(D)** pH rate profile of the samples reactions with DEDNPP at 21ºC

Acknowledgements: UFPR, CAPES, CNPq, L'Oréal UNESCO-ABC, PhosAgro/UNESCO/IUPAC, INCT NanoVida, INCT Nanocarbono, Fundação Araucária, FINEP.

Área: CAT

DUAL FUNCTIONALIZATION OF COVALENT ORGANIC FRAMEWORKS FOR THE DEVELOPMENT OF HETEROGENEOUS CASCADE CATALYSTS

Luiz O. M. Nogueira [1](IC), Gabriel Almeida Mendonça da Silva [1](IC), Mirian Lippi[1](PG), Leticia Dobler [1](PQ), Pierre M. Esteves [1]*(PQ), Raoni Schroeder B. Gonçalves [1]*(PQ),

1: Instituto de Química – Universidade Federal do Rio de Janeiro (IQ-UFRJ)
** raoni.schroeder@iq.ufrj.br, pesteves@iq.ufrj.br*

Keywords: COFs, Enzymes, Palladium Nanoparticles.

Highlights

Covalent Organic Frameworks (COFs) are used as supports for palladium nanoparticles and *Candida Antartica* Lipase B for the development of efficient heterogeneous dual catalyst systems.

Resumo/Abstract

The immobilization of different catalytically active sites or incompatible catalytic groups on a single material, while preserving their individual catalytic activities, has attracted substantial interest for the development of new heterogeneous catalysts. Referred as cascade catalysts, these systems act cooperatively to catalyze several reactions in a multistep sequence, without isolation of intermediates and self-quenching of catalysts. Thus, cascade catalysts present substantial economic advantages by streamlining reaction processes and minimizing resource consumption[1]. On the other side, enzymatic dynamic kinetic resolution stands out as one of the most efficient methodologies for obtaining enantiomerically pure products[2].

In this way, the present work aims to develop cascade heterogenous catalysts through the immobilization of palladium nanoparticles (Pd NPs) and *Candida Antartica* Lipase B (CalB) onto Covalent Organic Frameworks (COFs). It is expected that the Pd NPs will promote the racemization of chiral primary amines while CalB will promote the enzymatic kinetic resolution of these substrates. Moreover, by employing COFs as supports for both Pd and enzymes, it is expected that the anchoring of Pd NPs will occur within the material's pores, unlike the enzyme immobilization, which should take place on its surface.

To date, we have performed the immobilization of Pd NPs and CalB on six different materials: RIO-12, RIO-13, RIO-17, Pd@RIO-12, Pd@RIO-13, Pd@RIO-17 (all prepared by our research group through standard procedures)[3]. Immobilization of Pd NPs was performed using the double solvent method (DSM), through the addition of a $PdCl_2$ aqueous solution in a suspension of the respective COF in hexane. Then, $PdCl_2$ was reduced with $NaBH_4$ in ethanol. After that, enzyme immobilization was achieved through the adsorption of CalB in a buffered aqueous medium. The success of enzyme immobilization and the enzymatic activity was verified by measuring the hydrolytic activity of the composite material in the degradation of 4-methylumbelliferyl heptanoate (MUF-hept), which generates a fluorescent product. A selection of the obtained results is illustrated in Figure 1.

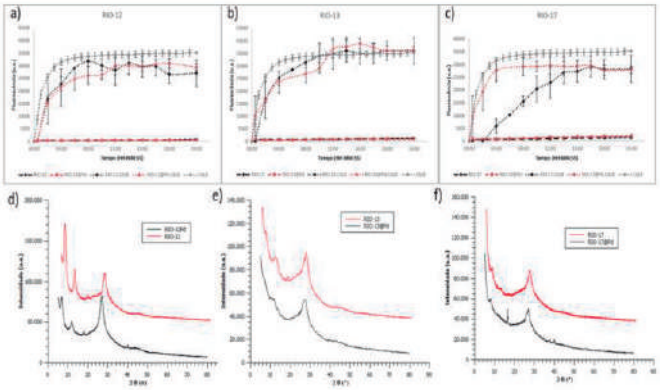


Figure1: Kinetic study of MUF-hept's degradation for RIO-XX COFs, both with and without Pd NPs and/or enzymes and the COFs XRD characterisation.
a,d) RIO-12; b,e) RIO-13; c,f) RIO-17

The results indicate that most of the enzyme was successfully adsorbed onto the materials, without loss of activity. In the new phase of the project, the use of these materials in kinetic resolutions of chiral amines will be studied.

Agradecimentos/Acknowledgments

To CNPq, FAPERJ, CAPES for their financial support.

[1]**GÖRBE**, T. *ACS Catalysis*, 2017, 7, 1601.
[2]**PELLISSIER**, H. *European Journal of Organic Chemistry*, 2022, 7.
[3]**MAIA**, R. et al. *Crystal Growth and Design*, 2018, 18. 5682

Área:____CAT_____ Nº de Inscrição: __271___

Enzymatic degradation of small poly(ethylene terephthalate) (PET) oligomers mediated by commercial lipases

Larissa W. Terrabuio (IC), Laerte Ganéo Neto (PG), Laíza A. de Almeida (PQ), Humberto M. S. Milagre (PQ)

larissa.terrabuio@unesp.br

Institute of Chemistry, São Paulo State University (UNESP), 14801-970 Araraquara, SP, Brazil

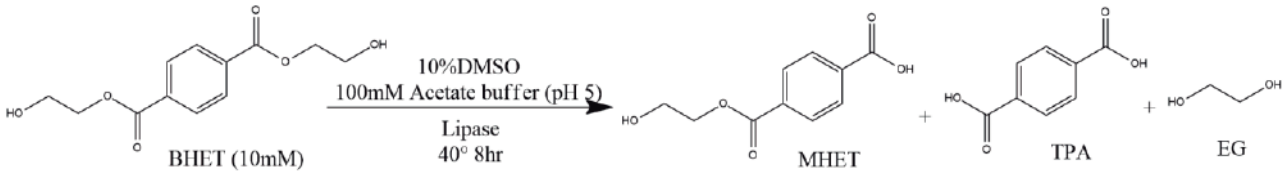
Key words: *Biocatalysis, Lipase, Plastic degradation, Enzymatic hydrolysis.*

Highlights

This work is the first screening of commercial immobilized lipases for the enzymatic hydrolysis of the PET oligomer bis-(hydroxyethyl) terephthalate (BHET) into mono (2-hydroxyethyl) terephthalate (MHET), terephthalic acid (TPA) and ethylene glycol (EG).

Abstract

PET is one of the most used polymers in the world. However, alongside its incredible versatility comes a significant challenge: developing cost-effective PET recycling processes. The current routes mainly involve mechanical and chemical methods, which can affect the quality of the material structure[1]. Aiming for more eco-friendly processes that lead to highly pure monomers, enzymatic degradation of PET is a rising strategy.[2] Thus, this study describes the first screening of commercial immobilized lipases for the enzymatic hydrolysis of PET oligomer BHET into MHET, TPA, and EG. The reaction conditions were defined based on the optimal temperature and pH of the selected lipases and using as reference a pioneer work of PET degradation catalyzed by *Candida antarctica* lipase B (CAL-B)[2] immobilized in acrylic resin (Scheme 1). Table 1 shows the percentages of BHET, MHET, and TPA after 8 hours of reaction with different lipases and indicates the potential of the enzymatic approach for BHET hydrolysis. Future studies of enzymatic immobilization with nontoxic supports and more active lipases can provide a highly efficient method to degrade the ever-growing plastic waste, opening the possibility of a better total PET recycling process through the repolymerization of TPA and EG[3] for establishing a circular economy.



Scheme 1: BHET enzymatic hydrolysis in 100mM Acetate Buffer (pH 5).

Table 1. Results of BHET enzymatic hydrolysis with commercial immobilized lipases.

Entry	Lipases[a]	BHET (%)[b]	MHET (%)[b]	TPA (%)[b]
1	CAL-B (immobilized in acrylic resin)	0	1,305	98,70
2	CAL-B (immobilized in Immobead 150)	0	3,758	96,24
3	*C. rugosa* (immobilized in Immobead 150)	0	90,46	9,545
4	*T. lanugimosus* (immobilized in Immobead 150)	4,236	93,31	2,451
5	*R. miehei* (immobilized in Immobead 150)	96,16	3,837	0
6	*R. oryzae* (immobilized in Immobead 150)	97,74	2,265	0

[a]Immobilized lipases purchased from Sigma-Aldrich. [b]Determined by HPLC (C18 column, eluents: 0.1% Formic acid in water (A), and methanol (B), gradient: 25–68.5% of B).

References: [1]Ghosal, K.; Nayak, C. *Mater. Adv.,* **2022**, *3(4),*1974–1992.
[2]Świderek, K. et al. *Nat. Commun*., **2023**, *14(1),* 3556, 2023.
[3]PENG, Y. et al. Nat. Commun., v. 14, n. 1, p. 3249, 2023.

Acknowledgments

FAPESP CNPq CAPES periódicos

Área: CAT
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Estudo de obtenção de açúcares por sacarificação de biomassa lignocelulósica

Vinicius G. C. Madriaga (PG)[1], Daniel G. S. Quattrociocchi (PQ)[1], Saulo B. Pinheiro (IC)[1], Maria Clara O. Ribeiro (IC)[1], Fabio B. Passos (PQ)[2], Thiago M. Lima (PQ)[1]

tmlima@id.uff.br; vinicius_madriaga@id.uff.br

[1]*Instituto de Química, Universidade Federal Fluminense, Outeiro São João Batista, s/n, Campus do Valonguinho, Centro, Niterói, Rio de Janeiro, Brasil, 24020-141.*
[2]*Departamento de Engenharia Química e de Petróleo, Universidade Federal Fluminense, Rua Passo da Pátria, 156, Niterói, Rio de Janeiro, Brasil, 24210-240*
Palavras Chave: *biomassa lignocelulósica, sacaraficação, Gigoga, Singônio*

Highlights

Obtention of sugars from lignocellulosic biomass through saccharification. This work investigates the saccharification process from two different biomasses: Gigoga (*Eichhornia crassipes*) and Singônio (*Syngonium podophyllum*), performing the characterization of these biomasses and evaluating the total sugar concentration by dinitro salicylic acid method (DNS).

Resumo/Abstract

A biomassa lignocelulósica emerge em um contexto de busca por fontes renováveis que possam servir como alternativa para complementar as fontes de origem fóssil. Através da conversão química da biomassa é possível obter uma série de compostos, denominados moléculas plataforma, que servem como ponto de partida para uma série de produtos de química fina. A biomassa lignocelulósica é composta por três biopolímeros: a celulose, a hemicelulose e a lignina, sendo os dois primeiros compostos por unidades de açúcares. Para a obtenção das moléculas plataforma, uma série de etapas reacionais são necessárias, dentre elas a sacarificação, que busca converter a celulose e hemicelulose em seus açúcares constituintes, e que pode ser realizada por diferentes métodos.[1] Com isso, o objetivo deste projeto é investigar diferentes métodos de sacarificação a Gigoga e o Singônio, duas biomassas que são conhecidas por ocuparem ambientes urbanos, gerando transtorno por seu descarte. Inicialmente, as biomassas cruas foram caracterizadas pela sua parte orgânica e composição inorgânica. Utilizando dados da análise elementar e da análise térmica, observa-se que a Gigoga possui um teor de lignina menor (26%) quando comparado ao Singônio (39%). A parte inorgânica foi avaliada através de Espectroscopia de Fluorescência de Raios X (FRX) e Difração de Raios X observa-se que as cinzas dessas biomassas apresentam altos teores de carbonatos e fosfatos de cálcio, bem como cloreto de potássio, porém os valores foram mais elevados para Gigoga dos dois sais (11% para a Gigoga e 8% para o singônio).[1,2] As duas biomassas (300 mg) foram então submetidas ao procedimento de sacarificação, utilizando solução aquosa de ácido sulfúrico 5% em refluxo a 120°C durante 4h. Através do método de quantificação utilizando ácido dinitrossalícilico, foi possível quantificar o teor de açúcares totais em ambas as biomassas, e os resultados revelam que a Gigoga apresentou teores de açúcares de 0,03 g/L enquanto o singônio apresentou um teor dez vezes maior (0,33 g/L), essa diferença pode estar relacionada a maior recalcitrância da Gigoga, o que, embora seu teor de lignina seja menor, torna mais difícil a remoção e aproveitamento dos açúcares das outras frações.[3] Como perspectiva deste trabalho, outros métodos ainda devem ser investigados e o uso da cromatografia líquida será realizado para quantificação de cada açúcar isoladamente.

Bibliografia: **(1)** Singh, J. K.; Chaurasia, B.; Dubey, A.; *et. al. Sustainability (Switzerland)* **2021**, 13. (2) Gaurav, G. K.; Mehmood, T.; Cheng, L.; *et. al. J Clean Prod*. **2020**, 277. (3) Wood, I. P.; Elliston, A.; Ryden, P; *et.al. Biomass Bioenergy* **2012**, 44, 117–121.

Agradecimentos/Acknowledgments

UFF, FAPERJ, CAPES, PPGQ-UFF.

Área: CAT

Europium mandelate: catalytic efficiency in mechanochemical synthesis of C–C bond.

Cristiane Kelly de Oliveira (FM),[1] José Robson da Silva Filho (PQ) [2], Thiago Muniz de Souza (PQ) [3], Severino Alves Júnior (PQ),[2] Ricardo Luiz Longo (PQ),[2] Ivani Malvestiti (PQ).[2]

ckoliveira@gmail.com

[1]Escola de Referência em Ensino Médio Professor Ernesto Silva, [2]Departamento de Química Fundamental, UFPE.; [3]Universidade Federal Rural de Pernambuco, UFRPE

keywords: *Catalysis, cyanosilylation, europium, epoxides, ketones, mechanochemistry.*

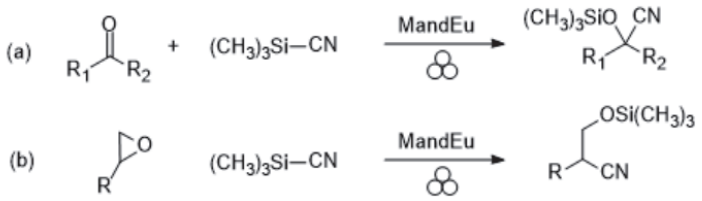
Highlights

Europium Mandelate proved to be an efficient catalyst in the mechanochemical cyanosylilation and epoxide opening. It was reused for 8 cycles in the cyanosylilation without loss of catalytic activity.

Resumo/Abstract

Green catalytic synthetic C–C bond formation protocols involving the easy recovery and reuse of catalysts are of great interest in the pharmaceutical industry. From this perspective, the present work developed a robust mechanochemical method of C–C bond formation from ketones and epoxides as electrophiles, using solid europium mandelate (MandEu) as catalyst and TMSCN as electrophile. Tests to determine the reaction conditions were performed with two aromatic ketones: 4-NO_2-acetophenone (solid) and 4-F-acetophenone (liquid). The conversion results were quantitative for the two ketones using 5% catalyst and 25% excess TMSCN in 1 hour of milling (Scheme 1a). Also, the physical state of the organic substrate did not affect the mechanochemical synthesis. The most promising result, however, was the reuse of MandEu, which until the eighth cycle of catalysis did not show any loss of catalytic activity, leading to 97% conversion of 4-NO_2-acetophenone in the last cycle. The most promising result, however, was the reuse of MandEu, which after the eighth cycle of catalysis did not show significant loss of catalytic activity, leading to 97% conversion of 4-NO_2-acetophenone in the last cycle. To reuse MandEu, the catalyst was only washed twice with ethyl acetate, centrifuged, and dried under vacuum. These results suggest that the mechanochemical synthesis of solvent-free silylated cyanohydrins is efficient, indicating the potential of MandEu as a catalyst in organic reactions. The catalytic activity of MandEu was also tested in the epoxide opening (e.g., cyclohexene oxide) with TMSCN, with 96% conversion in 90 minutes and 5% catalyst (Scheme 1b). The opening reaction of 1,2-epoxybutane led to only one of the possible regioisomers with 95% conversion. These results indicate that the mechanochemical method of C–C bond formation catalyzed by MandEu is fast, robust, and efficient with excellent catalyst reuse property without decreased of activity or need for reactivation. The perspectives consist of broadening the scope of the carbonyl addition and epoxide opening reactions, as well as testing the mechanochemical synthesis of the catalyst.

Scheme 1: Mechanochemical synthesis of cyanohydrin (a) and opening of epoxides (b) catalyzed by europium mandelate (MandEu).



Agradecimentos/Acknowledgments

CNPq CAPES FACEPE dQF Universidade Federal de Pernambuco Sociedade Brasileira de Química

Área: CAT

Explorando silanóis na superfície dos mesoporos de zeólitas NaX hierárquicas: síntese de catalisadores anfifílicos para reações de condensação.

Gabriela Fontolan (IC),[1*] Leandro P. Martins (PQ),[1] Iago W. Zapelini (PQ).[1]

gabriela.fontolan@unesp.br

[1]*Departamento de Engenharia Física e Matemática, UNESP*

Palavras-Chave: *Zeólita, Faujasita, Mesoporos, Catálise Básica, TPOAC, Reação de Condensação de Knoevenagel.*

Highlights

Exploring silanols on the surface of mesopores in hierarchical NaX zeolites: synthesis of amphiphilic catalysts for condensation reactions.

Synthesis of FAU zeolite structure containing mesopores by the surfactant templated method using the organosilane surfactant [3(trimethoxysilyl) propyl] octadecyldimethylammonium chloride (TPOAC).

The mesopores improves the accessibility to the catalytic sites.

The zeolite containing mesopores provided higher conversions in the Knoevenagel condensation reaction.

Resumo/Abstract

Zeólitas são aluminossilicatos cristalinos e microporosos (poros menores que 2nm) amplamente utilizados na indústria, já que possuem a capacidade de separar e processar diversas moléculas. Entretanto, os microporos são frequentemente associados com limitações difusionais, pois reduzem o acesso aos sítios catalíticos de moléculas muito volumosas, diminuindo as possíveis aplicações industriais. A fim de solucionar as limitações difusionais é possível criar poros maiores. A geração de mesoporos (diâmetros de 2 a 50 nm) melhora, em muitos casos, o acesso aos sítios catalíticos e os aspectos difusionais se comparado com uma zeólita convencional. Um dos métodos para a formação de mesoporos em zeólitas é o *bottom-up*, onde substâncias moldantes moles ou duras são utilizadas para geração de mesoporosidade desde o início da síntese. O organossilano utilizado para gerar mesoporos neste trabalho é o [3-(trimethoxysilyl) propyl] octadecyldimethylammonium chloride (TPOAC). Quando mesoporos são gerados, superfície apresenta grande quantidade de grupos silanóis, os quais são centros de modificação da zeólita, que podem ancorar outras moléculas por meio de ligações químicas. Assim, é possível aumentar sua hidrofobicidade ancorando grupos hidrofóbicos. Essa característica pode melhorar a conversão da reação de condensação de Knoevenagel. Essa reação ocorre em três etapas, sendo a última a eliminação de uma molécula de água. A água liberada na reação pode permanecer nos sítios catalíticos da zeólitas devido ao seu caráter hidrofílico. Assim, a modificação da zeólitas com a criação de mesoporos e o aumento da hidrofobicidade deve aumentar a conversão da reação ao liberar os sítios catalíticos reduzindo o efeito nocivo da reação. Diante disso, neste trabalho foram sintetizadas duas amostras de zeólita faujasita do tipo X, uma convencional (puramente microporosa) e outra hierárquica (contendo mesoporos). Pela técnica de difratometria de raios-X foi possível confirmar a formação de uma estrutura do tipo FAU, livre de contaminação. Além disso, através da fisissorção de nitrogênio foi possível confirmar a formação de mesoporos no material sintetizado com TPOAC, indicando a eficiência do seu uso como moldante de mesoporos na zeólita. Foram realizados testes catalíticos utilizando-se essas zeólitas como catalisadores básicos na reação de condensação de Knoevenagel entre o benzaldeído e cianoacetato de etila. A amostra contendo mesoporos foi mais eficiente na reação, como resultado do aumento da acessibilidade dos sítios catalíticos promovida pela presença dos mesoporos. A amostra contendo mesoporos será utilizada para ancoragem de grupos hidrofóbicos nos silanóis, visando a expulsão de água do meio reacional, elevando-se ainda mais a atividade.

Agradecimentos/Acknowledgments

Os autores agradecem a FAPESP pelo financiamento deste trabalho em termos da bolsa de iniciação científica (processo 2023/10974-4) e pós-doutorado (processo 2022/10732-8).

Área: CAT

Glycerol conversion by employing nano-zeolite catalyst produced by bead milling

Adonay R. Loiola (PQ),[1] Ingrid A.L. Azevedo (PG),[1] Nathalia S. Teixeira (PG),[2] Marcos A. Nascimento Junior (PG),[2] Fernanda F.A. Macedo (IC),[1] Tiago P. Braga (PQ),[1] Sibele B.C. Pergher (PQ),[2]

adonay@ufc.br

[1]*Laboratory of Nanostructured Materials, Department of Organic and Inorganic Chemistry, Federal University of Ceara*
[2]*Laboratory of Molecular Sieves, Institute of Chemistry, Federal University of Rio Grande do Norte*

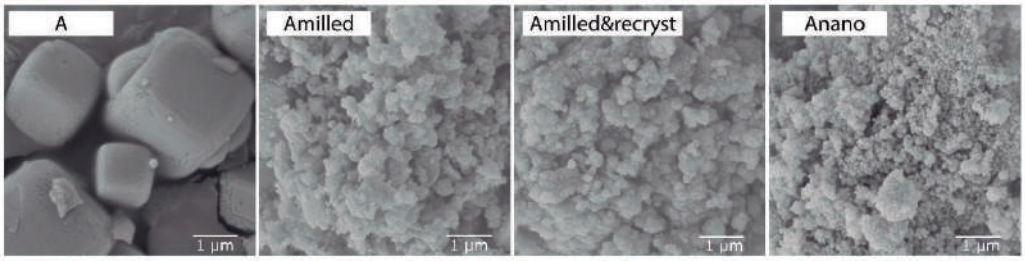
Keywords: *Nanozeolite, Bead Milling, Top-Down, Glycerol Conversion.*

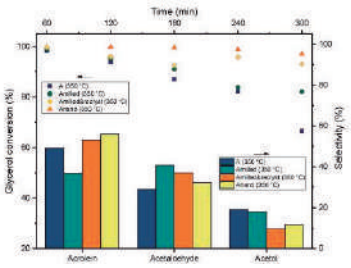
Highlights

Nanozeolite crystals were produced by employing dry milling. Their performance as a catalyst in the glycerol dehydration is better than that observed for the conventional zeolite and similar to the one obtained with nanozeolite produced with structure directing agent.

Resumo/Abstract

Mechanochemistry has been regarded as a reemerged technique that can be particularly useful in tackling issues related to conventional synthesis routes, such as the use of huge amounts of solvents. Besides, fabrication of nanoparticles can be achieved via milling approaches. Zeolites are crystalline aluminosilicates, with well-organized porous systems, and are employed in several important industrial applications, including catalysis, gas separation, and adsorption. The production of nano-zeolites involves numerous challenges. Their synthesis is usually carried out via wet methods, known as bottom-up routes, which are both laborious and expansive. In this context, high-energy milling processes are being employed to produce nanozeolites. Herein, we present the preparation of zeolite type A via a conventional hydrothermal method, and its conversion to nanoparticles by means of processes of bead milling and recrystallization. Zeolite samples were confined in 12 mL containers together with either zirconia beads stabilized with ceria or inox steel beads and treated in a planetary mill (Retsch, model PM-100). The best milling conditions were determined by studying the following parameters: the ratio between the milling agent and the zeolite (2, 3.5, 5, 10, and 20), time (1, 3, 6, and 12 h), rotation speed (200, 400, and 600 rpm) and milling agent diameter (1, 5, and 10 mm). One particular sample underwent a further recrystallization step, employing the thermal treatment with a diluted alkaline silica and alumina source. All the samples were characterized by using X-ray diffraction, scanning electron microscopy, infrared spectroscopy, and particle size measurements. The conventional zeolite A (**A**), the chosen milled zeolite (Amilled), its recrystallized form (**Amilled&recryst**), as well as a sample of nanozeolite, for reference purposes, obtained via a bottom-up method, with structure directing agent (**Anano**) were evaluated as catalysts for the dehydration of glycerol, indicating that the zeolite in form of nanocrystals produced by milling presents performance comparable to the zeolite nanocrystals obtained by bottom-up approach.





Agradecimentos/Acknowledgments

CAPES, CNPq, and FUNCAP

Área: CAT

Graphene-based nanocatalyst for the sequential two-step reaction of total neutralization of organophosphates and nitrophenol byproducts.

Gabriel C.B. Gomes (IC),[1]* Mayara G. Gonçalves (PQ),[1] Sergio H. Domingues (PQ),[2] Aldo J. G. Zarbin (PQ),[1] Elisa S. Orth (PQ).[1]

ggomesgabriel@gmail.com

[1]Departamento de Química UFPR; [2]Instituto Mackenzie de Pesquisas em Grafeno e Nanotecnologias MackGraphe, Mackenzie.

Palavras Chave: *graphene oxide, functionalization, nanomaterials, reduction reaction, pesticides*

Highlights

A new graphene oxide derived material was designed through the functionalization with cysteamine and anchoring of silver nanoparticles that is capable of the total neutralization of organophosphates.

Resumo/Abstract

The indiscriminate use of organophosphates derived agrochemicals poses a high risk due to its stability and toxicity. Some organophosphorus agrochemicals, such as paraoxon, parathion, and fenitrothion, contain nitrophenol in their formulation, which enhances their toxicity. Despite the prohibition of these agrochemicals in several countries, they are still in circulation, particularly in the Global South countries. With that in mind a new graphene oxide-based material was designed to perform the dephosphorylation of pesticides and detoxification of the generated byproduct, through the conversion of nitrophenol to aminophenol. The graphene oxide was first functionalized at the epoxide site via epoxide ring opening reaction with cysteamine and through the hanging thiol group it was anchored silver nanoparticles. The final composite was named Ag-GOSH. The material was characterized by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD), thermogravimetric analysis (TGA), Fourier transformed infra-red spectroscopy (FTIR). The multimodal material obtained was able to break the phosphorous bond through a nucleophilic attack as well as catalyzing the reduction of the nitrophenol byproduct (Figure 1.1), thus completely neutralizing the organophosphate by two consecutive one-pot reactions (Figure 1.2). The kinetics of the first step (dephosphorylation) was obtained utilizing an organophosphate simulant DEDNPP monitoring through UV-Vis spectroscopy with the surge of a 400nm band that indicates the nitrophenolate formation. The second step (nitrophenolate to aminophenolate reduction with sodium borohydride) was monitored by the disappearance of the same band, and the formation of a new band around 350 nm.

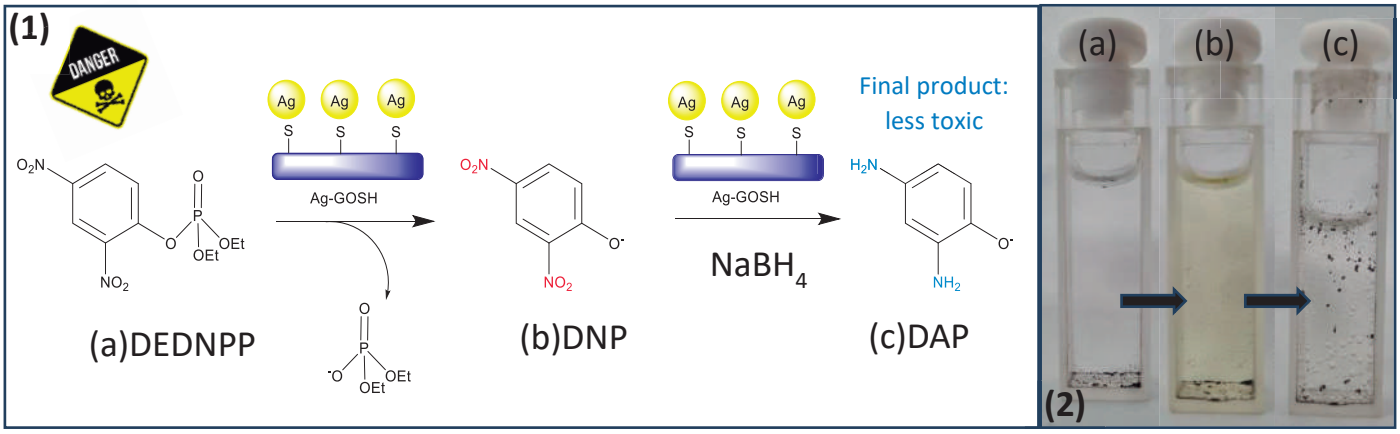


Figure 1. (1) DEDNPP neutralization reaction followed by DNP reduction with $NaBH_4$; **(2)** Cuvette pictures undergoing DEDNPP total neutralization reaction.

Acknowledgements: UFPR, CNPq, CAPES, L'Oréal-UNESCO-ABC, PhosAgro/UNESCO/IUPAC, National Institute of Science and Technology of Nanomaterials for Life (INCTNanovida) and National Institute of Science and Technology of Carbon Nanomaterials (INCTNanocarbon).

Área: CAT

Green Catalysis: Carbon Nitrides in Sustainable Chemistry

Mariana Baptista Marques (IC),[1] Danielly Tamires (PG),[1] (PG),[1,2] Ivo F. Teixeira (PQ),[1]

marianabaptistam@gmail.com; daniryidh@gmail.com.

[1]Department of Chemistry, Universidade Federal de São Carlos

Key words: Carbon Nitride, Poly(heptazine imide), Allyl Alcohol

Highlights

This study approaches the application of modified-carbon nitrides for the selective photocatalytic oxidation of allyl alcohol to acrylic acid. Using mild conditions, we obtain an 90% yield with H-PHI photocatalyst. This research contributes to the advancement of non-metal catalysts for efficient biomass conversion.

Resumo/Abstract

Acrylic acid is an important raw material for the production of super-adsorbent polymers. Currently, acrylic acid is produced industrially using propylene, which is derived from petroleum. An alternative pathway is the oxidation allyl alcohol, which can be obtained from biomass to acrylic acid. Crystalline carbon nitrides, with poly(heptazine imide) (PHI) units, have demonstrated efficiency to selectively oxidize alcohols avoiding its overoxidation into CO_2. In this study, different PHI-materials were applied to photocatalytic allyl alcohol oxidation. In Figures 1a and 1b, the catalyst synthesis process is depicted, wherein the precursor melamine with sodium chloride undergoes ionothermal treatment, generating charged poly(heptazine imide) structures that are stabilized by the Na^+ cation. Subsequently, cation exchange of the catalyst in an aqueous medium is performed with the addition of concentrated hydrochloric acid, in the case of H-PHI. Figure 1c shows the XRD of H-PHI and Na-PHI, revealing high crystallinity in Na-PHI, whereas the former only presents a signal at 27° related to layer stacking. The high crystallinity of Na-PHI is confirmed by HRTEM analysis (Figure 1d). Furthermore, in figure 1e, FTIR spectra demonstrate structural differences between the materials, particularly around the region of 1000 cm^{-1} associated with the presence of negative nitrogen in the structure. Finally, in Figure 1f, different catalytic results employing variations of PHI cations are presented, and H-PHI stands out, achieving a conversion of approximately 90%, well above the results of other metallic catalysts, which do not exceed 10% conversion, establishing it as an efficient catalyst for the allylic alcohol oxidation reaction.

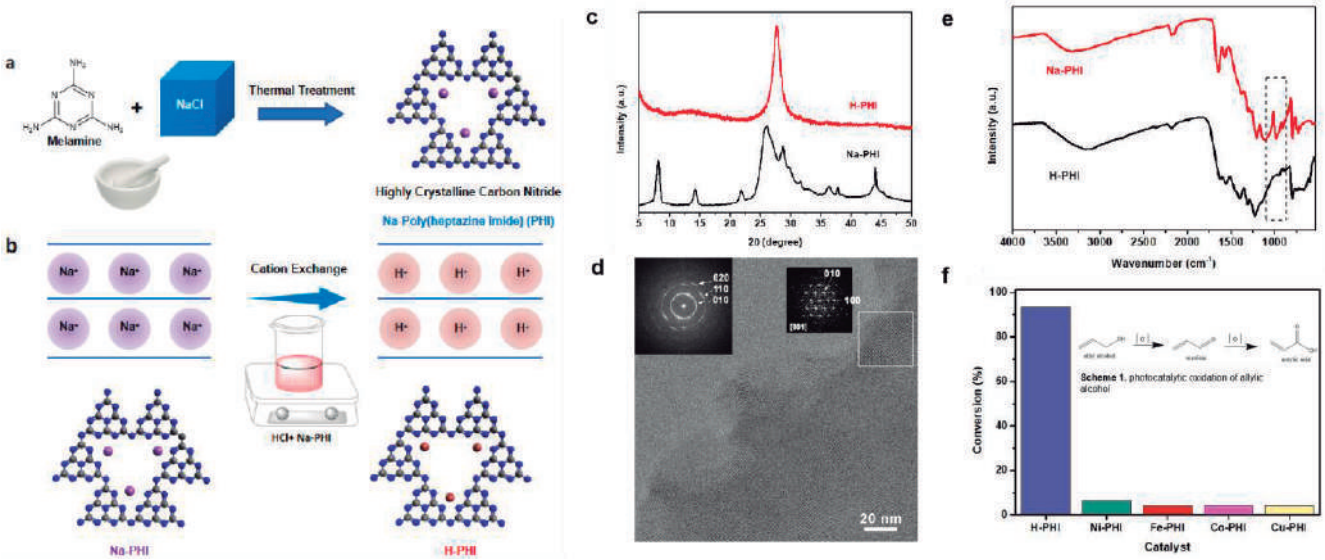


Figure 1.(a) Synthesis of the Na-PHI. (b) Cation exchange to obtain H-PHI. (c) XRD analysis of the Na-PHI and H-PHI catalysts. (d) HRTEM characterization of Na-PHI. (e) FTIR analysis of both catalysts.(f) Catalytic conversion results employing different cations in Poly(heptazine imide) with reaction conditions: Allyl alcohol (30 µL), Catalyst (25 mg), CH3CN (2 mL), Flush - O2 (4 bar), HCl (10 µL), room temperature, duration of 24h, lamp 410 nm 50 W.

Agradecimentos/Acknowledgments

FAPESP – Fundação de Amparo à Pesquisa do Estado de São Paulo

CNPq – Conselho Nacional de Desenvolvimento Científico e Tecnológico

Área: CAT

Hidrólise do amido nativo da amêndoa da manga (*Mangifera Indica*) e do amido comercial utilizando catalisador heterogêneo ácido

Alannah Montenegro Calazans (PG)[1,2*], Simone Canhaci de Jesus (PQ)[2]; Marco A. Fraga (PQ)[1,2*].

alannahcalazans@gmail.com; marco.fraga@int.gov.br

[1]*Instituto militar de engenharia, IME;* [2]*Instituto Nacional de Ciência e Tecnologia, INT.*

Palavras Chave: *Fontes renováveis, Biomassa, Amido nativo, $NbOPO_4$, Glicose, 5-HMF.*

Highlights

Hydrolysis of native mango almond starch (Mangifera Indica) and commercial starch using heterogeneous acid catalyst.

The sequential reaction of native starch and commercial starch for the formation of glucose depends on a catalyst with Brønsted acidity.

Resumo/Abstract

Os impactos negativos ao meio ambiente ocasionados pelo uso desenfreado de recursos fósseis contribuíram para que fontes renováveis, como por exemplo a biomassa amilácea, fossem cada vez mais estudadas. Sendo assim, fontes alternativas como a amêndoa da manga (*Mangifera indica*), que são consideradas como resíduos pelas indústrias de processamento, podem ser utilizadas para a obtenção de bioprodutos como a glicose e 5-HMF.[1] Nesse sentido, esse trabalho teve como objetivo a obtenção de glicose a partir do amido residual extraído da amêndoa da manga (*Mangifera indica*) da variedade Tommy Atkins sobre catalisador ácido $NbOPO_4$. Os amidos nativo e comercial (Sigma-Aldrich) foram caracterizados através de análises de TG, DRX, CHN e MEV, e submetidos a testes catalíticos realizados em reator batelada e os produtos foram analisados utilizando HPLC. Dentre os resultados das caracterizações, pôde-se observar, a partir das análises no MEV, que os formatos dos grânulos de amido comercial variavam entre esféricos e elipsoidais, enquanto do amido nativo variavam entre esféricos e ovais. Além disso, a análise de DRX do amido nativo exibiu picos em ângulos (2θ) característicos de uma estrutura cristalina do tipo A, usualmente encontrada em cereais, e o amido comercial exibiu picos em ângulos (2θ) característicos de uma estrutura cristalina do tipo B, usualmente encontrada em tubérculos. Com relação aos resultados dos testes catalíticos, os rendimentos de malto-oligossacarídeos (MOS), glicose e 5-HMF podem ser observados na Figura 1. Observa-se que tanto o amido nativo quanto o comercial foram convertidos a bioprodutos, sugerindo que o catalisador utilizado apresenta acidez necessária para realizar a hidrólise. Contudo, o amido comercial apresentou MOS como principal produto e um maior rendimento a 5-HMF (20%) do que o amido nativo (5%). No caso do amido extraído da manga, a glicose foi o principal produto. Essas diferenças sugerem que a cadeia carbônica dos MOS obtidos na hidrólise do amido nativo são menores, permitindo sua hidrólise até glicose, ao passo que o grau de polimerização dos MOS formados a partir do amido comercial é maior. Nesse caso, a fração de glicose formada por hidrólise é desidratada a HMF. Esses resultados trazem informações importantes sobre a qualidade dos bioprodutos que podem ser obtidos a partir da biomassa amilácea disponível no setor agroindustrial brasileiro.

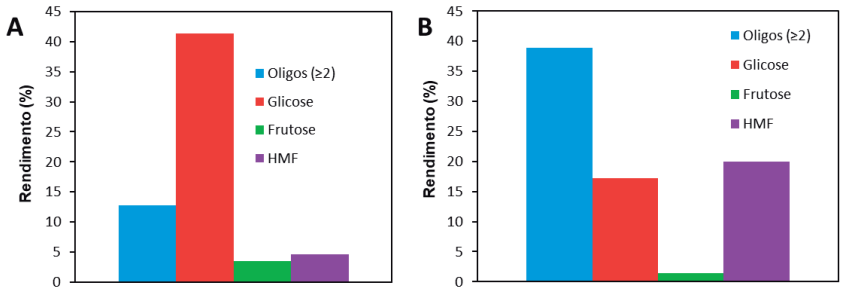


Figura 1: Rendimento dos produtos obtidos pela hidrólise do (A) amido nativo e (B) amido comercial sobre $NbOPO_4$.

[1]Tesfaye, T. et al. Clean Technologies and Environmental Policy, 20, 2018,81-94

Agradecimentos/Acknowledgments

Os autores agradecem o apoio financeiro do CNPq. AMC agradece ao CNPq pela bolsa de mestrado concedida.

Área: CAT

HO-functionalized 1,2,3-triazole-based ionic liquids as an efficient single component, bifunctional, metal, and solvent-free catalysts to CO_2 conversion.

Julia P.S.C.Leal[1](IC), João Victhor R. G. Queiroz[1](IC), Rafael P. Chagas [2](PQ), Jorge Luiz Sônego Milani[1](PQ).

juliaroots87@gmail.com

[1]*Departamento de Química, UFJF;* [2]*Departamento de Química, UFG.*

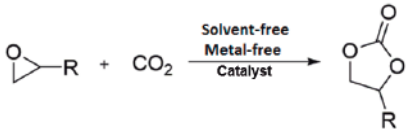
Keywords: *Organocatalysis, CO_2, Cyclic carbonates, Cycloaddition reaction.*

Highlights

Synthesis, characterization and application as bifunctional catalysts of 1,2,3-triazoles in CO_2 cycloaddition reaction.

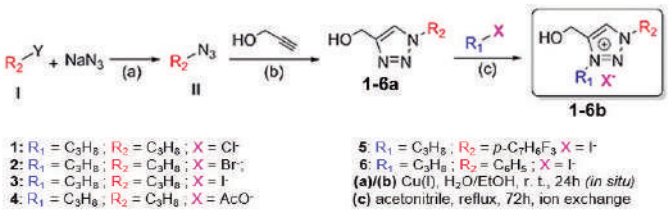
Resumo/Abstract

Carbon dioxide is the most abundant waste generated by anthropological processes. Its emissions are constantly increasing, becoming the most environmental concern. It is the main responsible for the greenhouse effect and the consequent adverse global climate changes. Therefore, in the last decades, the use of CO_2 as renewable feedstock has received a lot of attention from scientists to capture and fixate this greenhouse gas and transform it in high value-added products. One of the most promising classes of CO_2-derivatives is the organic carbonates. These eco-friendly compounds have a wide range of applications such as electrolytes in Li-ion batteries or chemical intermediates.



Scheme 1. CO_2 cycloaddition reaction.

Hence, we report the synthesis, characterization and catalytic performance of six organocatalysts based on 1,2,3-triazole-based ionic liquids with different alkyl groups in positions 1 and 3 eith different nucleophilic anions in their structure.



Scheme 2. Synthesis of ionic liquids.

The catalytic performance was evaluated using styrene oxide (SO) as standard epoxide, under 1 bar of CO_2, 90 °C using 5 mol% of **1-5b** as catalysts. Compound **6b** is not characterized yet. The conversions shown in Table 1 support the strong counter anion role in the catalytic reactions due their nucleophilic and leaving group abilities which act in different determining-steps in mechanism. As shown in entry 3, the iodide analogue (**3b**) had the highest conversion. The HO- groups could interact stronger with Cl and Br, decreasing their nucleophilicity. Moreover, the strong C-Cl bond should hamper the ring closure, while when iodide is present, the ring-closure is favored. As **3b** presented the best conversion, it was chosen to perform the optimization and the kinetic study.

In entries 3, 6-10 it was observed the strong reaction temperature dependence, also, the system presented excellent conversion even in 60 °C (95 %). The reaction under 1 bar at 35 °C presented 68% of product, showing the potential of the catalyst.

Table 1. Conversions and parameters of the cycloaddition reactions performed.

Entry	Catalyst[a]	Temperature (°C)	Conversion (%)[b]	TOF (h^{-1})[c]
1	**1b**	90	68	2
2	**2b**	90	88	2
3	**3b**	90	99	3
4	**4b**	90	22	1
5	**5b**	90	88	2
6	**3b**	80	99	3
7	**3b**	70	99	2
8	**3b**	60	95	3
9	**3b**	50	86	2
10	**3b**	40	56	1
11	**3b**[d]	35	68	1

Reactions conditions: [a]0.3 mmol of catalyst (5 mol%), SO (6.25 mmol), P = 1 bar, t = 8 h. [b]Conversion determined on basis of ^{1}H NMR analysis. [c]Turnover frequency (TON.h^{-1}). [d]Catalyst (10 mol%)

In summary, a series of triazoles-based ionic liquids was synthesized in high yields using simple and well-known methodologies. The catalytic results showed the strong temperature and anion dependence.

The next steps will be to evaluate catalyst activity in various epoxides and exchange the anion by acetate and lactate, becoming metal and halogen-free catalysts.

Agradecimentos/Acknowledgments

CNPq and FAPEMIG

Área: CAT

Hydrogen Evolution Reaction Employing Low-Cost Poly (Heptazine Imide) Photocatalysts

Bruna R. Serino (IC),[1]* Gabriel A. A. Diab (PG)[1], Ivo F. Teixeira (PQ)[1].

bruna.serino@estudante.ufscar.br; gabrieldiab@estudante.ufscar.br.

[1]*Department of Chemistry, UFSCar.*

Keywords: *Photocatalysis, Poly(Heptazine Imide),Green Hydrogen, Hydrogen Evolution Reaction, Noble metal-free.*

Highlights

Poly(heptazine imide)-based materials were embedded with Ni as cocatalyst for hydrogen evolution reaction (HER) as an alternative to noble metals. The results demonstrate that Ni nanoparticles as an efficient system yielding 70 $\mu mol.g^{-1}.h^{-1}$ and AQY around 1%.

Resumo/Abstract

The heavy dependence on fossil resources over the past decades has resulted in considerable impacts on the planet's natural balance. An alternative and promising approach to conventional fossil fuels lies in energy conversion through photocatalysis, utilizing semiconductor-based photocatalysts directly fueled by solar energy to produce green hydrogen. Poly(heptazine imide), a recent organic crystalline polymer, has been intensively investigated for photocatalytic energy conversion due to its non-toxicity, easy fabrication, bad gap active on visible light range and mainly due to the efficient excitons mobility, as well as charge transference.[1] Although, thanks to the high rate of recombination, these class of materials relies on noble metals cocatalyst. In this work, we demonstrated a simple and controlled method for developing an efficient photocatalyst, based on highly crystalline carbon nitrides decorated with Ni metals, as reductive sites for photocatalytic H_2 production, instead of noble metals. The semiconductor support (Na-PHI) was synthesized by the ionothermal polymerization of melamine in the presence of NaCl. Then, Ni metals were introduced within the Na-PHI framework though a simple cation exchange.[2] Different metal loadings were prepared and applied for HER to compare to the conventional system. PXRD analysis of the photocatalysts shows characteristic layered sheet structure with high organization that remains after nickel introduction. The infrared spectra of all samples confirms the PHI nature formation and also typical bands related to the metal interaction. Still, DRS shows a single band with a maximum absorption around 463 nm, presenting a band gap of 2,68 e.V. As evidenced in the photocatalytic tests, the saturated sample stands out as the most active, yielding 70 $\mu mol.g^{-1}.h^{-1}$ and 1% of AQY. A clear trend is observed indicating that nanoparticles are more active compared to single-atoms environment for HER. Although, Ni-PHI is much less active when compared to the noble metal system, it is estimated that the Ni-PHI is 100-fold more economical in terms of mol of H_2 produced per US$ of metal.

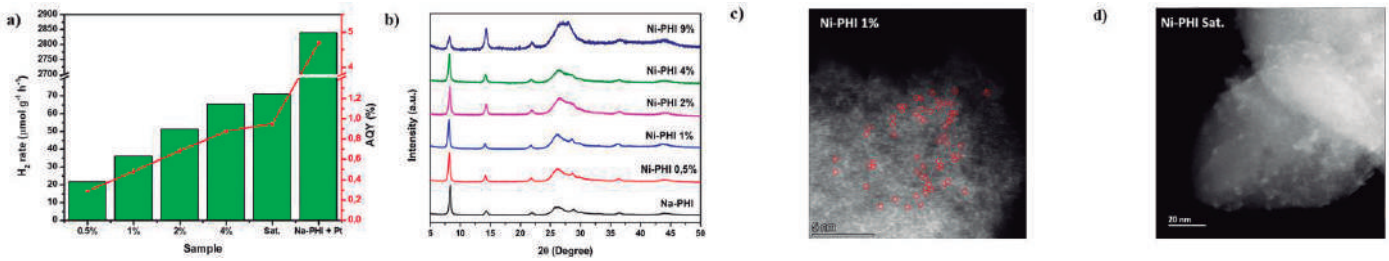


Figure 1. (a) H_2 rate production; **(b)** PXDR; **(c)**; AC-HAADF-STEM of NI-PHI 1% **(d)** AC-HAADF-STEM of Ni-PHI Sat.

(1) Rocha, G. F. S. R.; da Silva, M. A. R.; Rogolino, A.; Diab, G. A. A.; Noleto, L. F. G.; Antonietti, M.; Teixeira, I. F. Carbon nitride based materials: more than just a support for single-atom catalysis. *Chemical Society Reviews* **2023**, 10.1039/D2CS00806H. DOI: 10.1039/D2CS00806H.

(2) da Silva, M. A. R.; Silva, I. F.; Xue, Q.; Lo, B. T. W.; Tarakina, N. V.; Nunes, B. N.; Adler, P.; Sahoo, S. K.; Bahnemann, D. W.; López-Salas, N.; et al. Sustainable oxidation catalysis supported by light: Fe-poly (heptazine imide) as a heterogeneous single-atom photocatalyst. *Applied Catalysis B: Environmental* **2022**, *304*, 120965. DOI: https://doi.org/10.1016/j.apcatb.2021.120965.

Agradecimentos/Acknowledgments

The authors are thankful for FAPESP, CAPES, CNPQ and UFSCar.

Área:CAT

Hydrogen production by Ruthenium (II) complex bearing a bulky PNP-ligand: a catalyst for the decomposition of formic acid and/or ammonium formate

André L. Bogado (PQ),[1*] Leon K. Paschai Darian (PG),[2] David Bürgy (PG),[2] Lutz H. Gade (PQ),[2]

bogado@ufu.br

[1]Instituto de Ciências Exatas e Naturais do Pontal, UFU; [2]Inorganic Chemistry Institut, Heidelberg University.

Palavras Chave: *Formic acid decomposition; Ammonium formate decomposition, Hydrogen production, Homogeneous catalysis.*

Highlights

The present complex catalyzed total decomposition of formic acid and/or ammonium formate.

An associative pathway was found for the catalyzed reaction of formic acid.

Resumo/Abstract

The five-coordinate complex [$RuCl_2$(PNP)] was synthesized from the binuclear [$RuCl_2$(*p*-cym)]$_2$ (0.245 mmol) with a PNP-type ligand (PNP = 3,6-di-tert-butyl-1,8-bis(di*iso*propylphosphino)methyl)-9H-carbazole – Cbzdi*i*PrH; 0.514 mmol) in toluene solution (10 mL) in 20h at 110°C. Afterwards, the solvent was pumped off until dry for at least 1h, and the crude green solid was precipitated with a 1/1 mixture of *n*-pentane/HMDSO. $^{31}P\{^1H\}$ NMR data (242.9 MHz, C_6D_6, rt) showed only a singlet signal at δ 66 ppm, confirming the trans positions of the P-donor groups, and ^1H NMR data (600.1 MHz, C_6D_6, rt) showed the signal from the coordinated N-protonated ligand at δ 8.19 ppm. Mass spectroscopy (LIFDI): m/z (%) was calculated for $C_{34}H_{55}Cl_2NP_2Ru^+$ 710.77, found 710.23 (100). Cyclic voltammetry has shown E_{pa} and E_{pc} = -0.25 and -0.44 V respectively (ΔE_p = 0.19 V), and I_{pa}/I_{pc} = 1.01. These values are lower than ferrocene, ΔE_p = 0.86 V and I_{pa}/I_{pc} = 0.83. A linear relationship between I_p against square root of the scan rate ($sr^{1/2}$), obtained in the range of 0.1 – 0.8 V/s, confirmed a reversible diffusion-controlled process. The complex [$RuCl_2$(PNP)], loaded with 0.08%, catalyzed the decomposition of ammonium formate (AF) in NH_3, CO_2 and H_2 in THF solution at 80°C, with 94% of H_2 and TOF = 206 h^{-1} (molar ratio [Ru] / AF = 1 / 1204). The catalytic activity increased remarkably for the decomposition of formic acid (FA) as substrate to produce H_2 and CO_2. In the HMDSO solution at 80°C, a conversion of 100% was obtained in relation to H_2, and TOF = 3010 h^{-1} (molar ration [Ru] / FA / NEt_3 = 1 /1204 / 843). In an equimolar mixture of AF/FA in HMDSO solution at 80°C, without additives, the complex [$RuCl_2$(PNP)] catalyzed the decomposition of both with 100% of H_2 and TOF = 987 h^{-1} (molar ratio [Ru] / AF / FA = 1 / 602 / 602). In the last experimental condition, carbamic acid [$HO(C{=}O)NH_2$] was obtained as a co-product by a side reaction between NH_3 and CO_2 (Yield = 50 % in relation to the amount of AF). The remarkable catalytic activity of the [$RuCl_2$(PNP)] complex in the decomposition of FA encouraged us to develop a kinetic study in the range of 60 – 100°C, which provided $\Delta S^{\neq}$ = - 9.7 *e.u*; $\Delta G^{\neq}$ = 13.35 k*J* mol^{-1} and E_a = 64 k*J* mol^{-1}. These results suggest a no-spontaneous reaction with an associative pathway, in the transition state, to decompose the FA.

Agradecimentos/Acknowledgments

UNIVERSITÄT HEIDELBERG ZUKUNFT SEIT 1386 · DAAD Deutscher Akademischer Austauschdienst German Academic Exchange Service · FAPEMIG · CNPq · UFU Universidade Federal de Uberlândia

Identifying Metal Single-Atoms in Carbon Nitrides Supports by CO DRIFT-FTIR

Larissa Yukari Takagi Aya (IC) [1]Isadora Guedes Farias (PG)[1], Ivo Freitas Teixeira (PQ)[1].

isadoragfarias@gmail.com

[1]*Departamento de Química, Universidade Federal de São Carlos (UFSCar).*

Keywords: Carbon nitride, adsorption, photocatalysts, DRIFT-FTIR

Highlights

- Single-atom catalysts (SACs) characterization by DRIFT-FTIR with CO as a probe molecule.
- Identification of metal single-atoms in crystalline carbon nitride supports by their CO adsorption modes.

Resumo/Abstract

Carbon nitrides (C_3N_4) represent highly promising semiconducting polymers, widely employed in energy conversion reactions through photocatalysis, owing to their stable two-dimensional structure and excellent electronic properties. These materials, especially the most crystalline ones, offer exceptional coordination sites for stabilising isolated atoms, making them particularly well-suited for use as photocatalysts in single-atom catalysis. This study employed the DRIFT-FTIR technique to investigate the adsorption of CO molecules on supported metals, specifically Ni-PHI and Fe-PHI, prepared from sodium poly(heptazine imide) (Na-PHI), a very crystalline carbon nitride support. The aim was to comprehend the impact of different metal loadings on the coordination mode of the CO probe molecules. The experimental process involved heating the sample to 350°C using helium, introducing CO, and then purging it with helium. The resulting spectra exhibited distinct bands indicating chemisorbed CO. The resulting spectra for both samples (i.e. Fe-PHI and Ni-PHI) revealed distinct bands, indicating the presence of chemisorbed CO with different coordination modes. Lower wavenumbers (below 2100 cm^{-1}) suggested CO coordination with multiple metals (coordination in bridge), especially in samples with a high metal load, indicating cluster formation. Conversely, higher wavenumbers (above 2150 cm^{-1}) indicated CO monocoordinated, suggesting the presence of isolated metallic atoms. Additional studies with different metals and concentrations are planned to validate these findings, potentially revolutionizing the characterization of single-atom catalysts.

Keywords: Carbon nitride, adsorption, photocatalysts, DRIFT-FTIR.

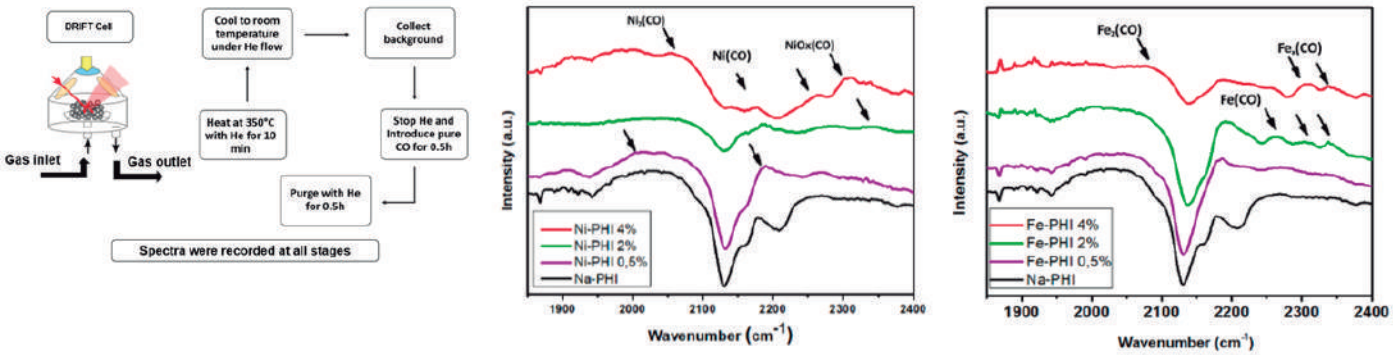


Figure 1: a) Experimental process of CO adsorption on the catalyst; b) FTIR-DRIFT spectra of Ni-PHI (0.5, 2 and 4%) and Na-PHI with chemisorbed CO and c) FTIR-DRIFT spectra of Fe-PHI (0.5, 2 and 4%) and Na-PHI with chemisorbed CO.

Agradecimentos/Acknowledgment

CNPq
FAPESP
FUNDAÇÃO DE AMPARO À PESQUISA DO ESTADO DE SÃO PAULO
ufscar
LNNano
Laboratório Nacional de Nanotecnologia

Área: Cat

Influence of carbon nitride decomposition on the photocatalytic production of ammonia

Hamilton A.S. Junior (IC),[1*] Luis F.G. Noleto (PG),[1] Ivo F. Teixeira (PQ)[1].

hasjunior@estudante.ufscar.br

[1]*Departamento de Química, UFSCar.*

Keywords: *Photocatalytic production of ammonia, Poly(heptazine imide), Carbon nitride decomposition.*

Highlights

Challenges for photocatalytic production and ammonia detection employing poly(heptazine imide) based catalysts.

Abstract

This work aims to make viable the photocatalytic synthesis of ammonia (NH_3) using highly crystalline carbon nitride, specifically known as sodium poly(heptazine imide) (Na-PHI). The synthesis of Na-PHI involved the thermal treatment of melamine and sodium chloride under a nitrogen atmosphere. NH_3 production tests were conducted by combining Na-PHI with deionized water under an N_2 atmosphere in the presence of light (410 nm). Ammonia quantification was performed using the Salicylate colorimetric technique.

Results indicated that the synthesized Na-PHI exhibited a commendable level of short-range ordering, leading to high crystallinity and efficient energy absorption in the visible region (Figures 1a and 1b). NH_3 production tests initially conducted under an argon atmosphere are depicted in Figures 1c, where a sequence of tests is presented in which the same catalyst is consecutively reused. In the first two tests, conducted without light and with washes between tests, the aim is to promote the degradation of the catalyst, aiming for a lower degradation in the third test (with light). However, even in this third test, the presence of NH_3 was identified in the absence of nitrogen gas in the reaction system, suggesting that the degradation of Na-PHI persists. As for Figure 1d, tests were carried out with H-PHI which has more stable terminals, giving it a lower susceptibility to degradation, which would discourage the generation of ammonia. However, the analysis using the detection method revealed an even greater presence of NH_3 compared to the test conducted with Na-PHI.

Consequently, it is evident that the decomposition of carbon nitride-based materials, such as Na-PHI and H-PHI, during photocatalytic reactions for NH_3 production presents a significant challenge that requires thorough understanding and resolution. Despite this challenge, these photocatalysts exhibit substantial potential for such reactions.

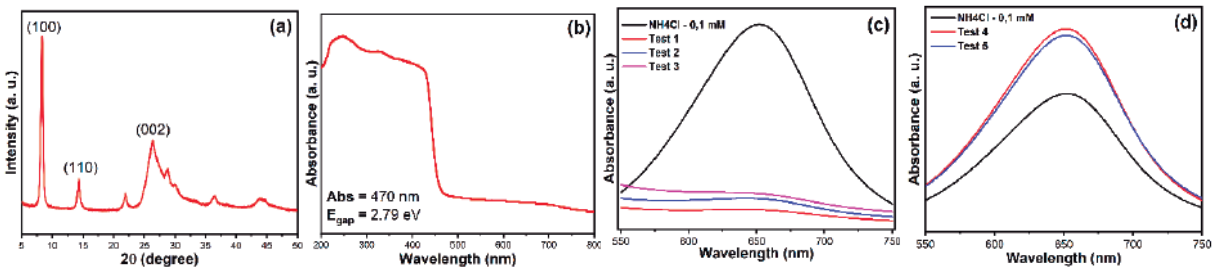


Figure 1. (a) XRD pattern and (b) UV-Vis spectra of the Na-PHI. NH_3 production using argon gas under the (c) Na-PHI and (d) H-PHI catalysts.

Acknowledgments

Universidade Federal de São Carlos (UFSCar) e Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP).

Área: CAT

LDH-catalyzed preparation of polyol diesters for application as gelators in environmental remediation

Alan José Corrêa Manso (PG)[1*], Gabriel Francisco Souza da Silva (IC)[1], Luiz Phelipe de Souza Tomaso (PG)[2], Luiz Fernando B. Malta (PQ)[2], Jaqueline Dias Senra (PQ)[1*].

***alanjcmjcm@gmail.com; jdsenra@gmail.com.**

[1]*Department of General and Inorganic Chemistry, IQ/UERJ;* [2]*Department of Inorganic Chemistry, IQ/UFRJ.*

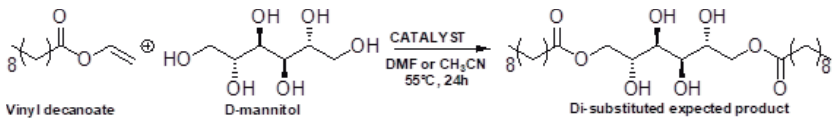
key words: *Organogels, Transesterification, Ester, Carbohydrate, Layered double hydroxides.*

Highlights

Transesterification reactions between vinyl decanoate and D-mannitol were prepared catalyzed by different heterogeneous bases. The selectivity of the expected disubstituted product was higher in the presence of Cu/Al layered double hydroxide (LDH Cu/Al) and DMF as solvent.

Abstract

Supramolecular organogels are highlighted in the literature as advanced soft materials for the environmental remediation, including the case of oil spills at sea. In general, the viscoelasticity can be due to their capacity to form selective intermolecular interactions under appropriate conditions (e.g. pH and solvents). This work aimed to combine a simple and low-cost catalytic route for the production of new esters derived from D-mannitol as potential new gelators for application in future environmental remediation. Heterogeneous base catalysts offer a number of advantages over homogeneous systems. Transesterification reactions between vinyl decanoate and D-mannitol were carried out with different solid base catalysts, in DMF at 55ºC and 24h (Scheme 1). The main yields and catalytic selectivities in DMF are shown in Table 1.



Scheme 1: General catalytic reaction between vinyl decanoate and D-mannitol.

Entry	Catalyst	Selectivity		Yield	
		Mono	Di	Mono	Di
1	$CaCO_3$	31,26	43,69	30,86	43,13
2	$MgCO_3$	7,94	56,04	7,94	56,04
3	NaH_2PO_4	100	0	18,28	0
4	$NH_4H_2PO_4$	71,57	28,43	64,92	25,79
5	HDL Cu/Al	11,82	82,54	11,31	78,96

Table 1: Selectivities and yields of the mono- and disubstituted products in DMF.

In general, the reactions in DMF showed better selectivities for the expected disubstituted product, even though sodium and ammonium dihydrogen phosphate showed full or predominant selectivity for the monosubstituted product (Entries 3 and 4, respectively). On the other hand, the low yield involving the sodium dihydrogen phosphate reveals its low basicity. When using Cu/Al LDH, the results showed the best selectivities and yields for the disubstituted product, both in DMF and acetonitrile (Entry 5). From these results, it is possible to presume that the surface basicity and the LDH layers have a main role in the transesterification mechanism. Deprotonation and adsorption of the polyol at the Cu/Al LDH surface seems favorable by considering electrostatic effects from the charge density of the lamellae. The synthetic scope and the LDH composition effect are underway.

Acknowledgments

We thank CAPES, CNPq and FAPERJ for funding.

[1]Sun, Y. *et al*. *Industrial & Engineering Chemistry Research*, 2019, v. 58, p. 7937-7947.

[2]Chen, A. *et al*. *New journal of chemistry*, 2019, v. 43, p. 7950-7961.

Área: CAT

Mechanistic and surface studies of CO_2 hydrogenation on $CoCu/MgAl_2O_4$ catalysts

Larissa E. R. Ferreira (PG),[1]* **Liane M. Rossi** (PQ),[2] **Daniela Zanchet** (PQ)[1]

larissaerf@hotmail.com;

[1]*Departamento de Química, UNICAMP;* [2]*Departamento de Química, USP.*

CO_2 hydrogenation, ethanol steam reforming, reverse water-gas shift, cooper, cobalt, magnesium aluminate

Highlights

Understanding CO_2 hydrogenation mechanism as a function of pressure by insights of reverse water-gas shift and steam reforming of ethanol over $CuCo/MgAl_2O_4$ catalyst.

Abstract

Looking for alternatives to reduce the CO_2 concentration in the atmosphere, the CO_2 hydrogenation forming ethanol emerges as an alternative to mitigate this important greenhouse gas. From the chemistry point of view, the high CO_2 stability associated with the C-C coupling and selectivity control required to produce high alcohols, remains a challenge. On the other hand, the knowledge acquired at ambient pressure, which favors the reverse water-gas shift reaction producing CO and H_2, and in the reverse reaction of CO_2 hydrogenation, i.e., the steam reforming of ethanol, represent an opportunity to speed up the understanding of the reaction mechanisms to obtain high alcohols from CO_2. The catalysts are based on $Co_xCu_y/MgAl_2O_4$ (varying the Co:Cu ratio (wt.%) in 5:5, 9:1, 0:10 and 10:0), with the $5Co5Cu/MgAl_2O_4$ catalyst showing 2.8 $mg_{alcohols}/g_{cat}.h$ (95:5 methanol: ethanol) that can be improved to 5.1 $mg_{alcohols}/g_{cat}.h$ previously reducing the catalyst at 400°C (batch reactor, 200°C, 100 bar, CO_2:H_2 ratio 1:4), Fig. 1. While CO is formed at atmospheric pressure, both CH_4 and methanol selectivities significantly increased with pressure. This indicated the important role pressure in favoring the hydrogenation step. Ethanol was also formed at high pressures, but the C-C coupling is still limited at the moment. Ongoing studies includes the optimization of the reaction parameters and the study of steam reforming of ethanol. By understanding the catalytic sites behavior under the different reaction conditions, we seek to achieve the sustainable production of ethanol from CO_2 hydrogenation and assisting in the transition to renewable energy sources.

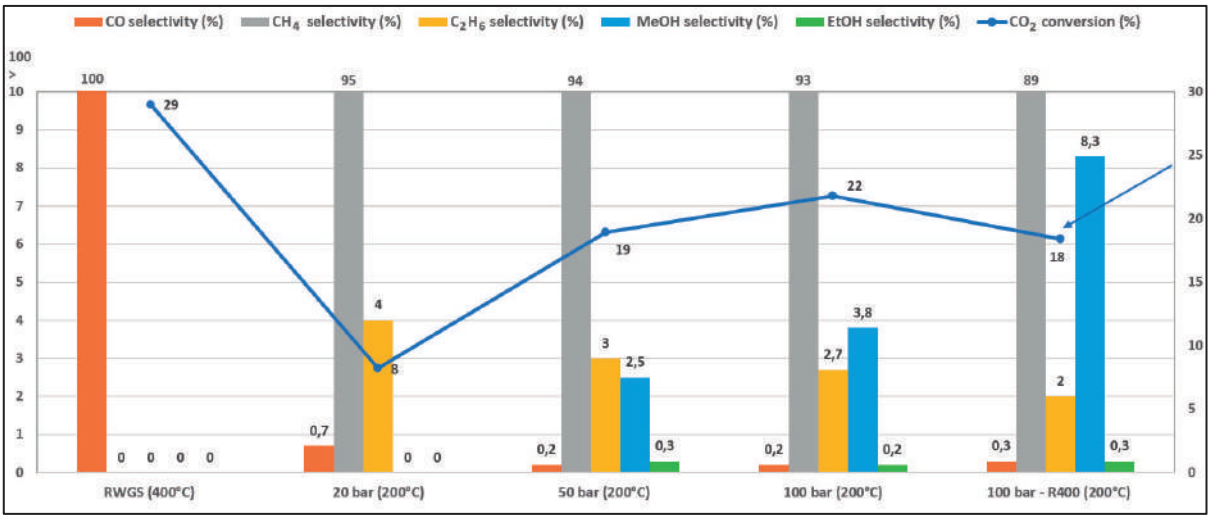


***Figure 1**: Conversion and selectivity of the $5Co5Cu/MgAl_2O_4$ catalysts in reverse water-gas shift reaction in fix-bed reactor at 400°C and batch reactor at 200°C, at 20 bar, 50 bar and 100 bar. H_2/CO_2 ratio= 4 for both reactions.*

Acknowledgments

UNICAMP · Instituto de Química · GCN · CNPq · CAPES · FAPESP · Research Centre for Greenhouse Gas Innovation

Área: CAT

Mesoporosity and hydrophobicity of FAU zeolites boosting glycerol ketalization

Leonardo H. Pazin (IC),[1*] Iago W. Zapelini (PQ),[1] Silvia H. Santagneli (PQ),[1] Leandro Martins (PQ),[1*]

leandro.martins@unesp.br; leonardo.pazin@unesp.br

[1] *Instituto de Química, UNESP - Universidade Estadual Paulista, Prof. Francisco Degni 55, 14800-900 Araraquara, SP (Brazil)*

Palavras Chave: *USY zeolites, reversible reactions, SiOH defects, two-phase reaction.*

Highlights

Dealumination of FAU zeolite enhanced accessibility and hydrophobicity and generated silanol groups. Accessibility and hydrophobicity of zeolite catalysts are key factors for glycerol ketalization.
Silanol healing and grafting of hydrophobic groups on mesopores of hierarchical FAU enhanced its hydrophobicity, boosting the catalytic activity.

Abstract

Faujasite (FAU) zeolite is widely used as a catalyst due to its mesoporosity derived from dealumination processes, which also enhances its thermal stability. The process generates silanol (SiOH) groups in the zeolite that can be used to anchor several chemical functionalities. The removal of aluminum and generation of silanol groups can be used to tailor the hydrophilic-hydrophobic balance of the catalyst, which is useful for catalyzing reactions in immiscible systems such as glycerol ketalization. This is a two-phase reaction involving bulky molecules, thus boosted by the ordinary mesoporosity of the hierarchical faujasite zeolite. Besides, the formation of water as a byproduct requires a fine-tuned hydrophobic-hydrophilic balance. This work evaluated several FAU zeolites with different framework Si/Al ratios (from 2.5 to 250) as catalysts in the glycerol ketalization. Pore size distribution from nitrogen physisorption isotherms confirmed the ordinary mesoporosity of the solids. Hydrophobicity was estimated in terms of water adsorption capacity, measured by thermogravimetry. Measurements of the contact angle of zeolites with glycerol showed only a slight increase with the increase in the Si/Al ratio due to a rise in SiOH groups, as confirmed by ^{29}Si NMR. Despite the high concentration of hydrophilic SiOH groups, the accessibility and hydrophobicity of isolated Brønsted acid sites improved the performance of these catalysts in the reaction. The silanols were also used as anchor points for octyl groups, improving the surface's hydrophobicity and boosting the zeolite's catalytic activity even with more hydrophobic ketones.

Acknowledgments

The authors are grateful for the financial support granted by the São Paulo Research Foundation - FAPESP, grants #2018/01258-5, #2019/12486-1, #2022/13453-2, #2022/10732-8, #2023/03158-6 and #2023/10544-0. In addition, we acknowledge the GFQM/UNESP for contact angle and N_2 physisorption measurements and the LCE/UFSCar for scanning electron microscopy images.

Área: CAT

Nitreto de carbono grafítico dopado com Nb para redução fotocatalítica de N_2 a amônia

Guilherme R. Farias (PG),[1] Eudes Lorençon (PQ)[1*]

rodriguesguilherme92@gmail.com; eudeslorencon@cefetmg.br

[1]*Departamento de Química, Centro Federal de Educação Tecnológica de Minas Gerais, Belo Horizonte-MG.*

Palavras-chave: Síntese de amônia, Redução de N_2, Nitreto de Carbono Grafítico, Nióbio(V), Catálise Heterogênea.

Highlights

Nb-doped graphitic carbon nitride for photocatalytic reduction of N_2 to ammonia.

- Nb(V)-doped g-C_3N_4 materials were prepared and extensively characterized by several techniques.
- The materials were applied as heterogeneous catalysts towards photorreduction of N_2 to ammonia.

Resumo

A síntese da amônia tornou-se um processo de grande atenção mediante a grande consumo energético, alta emissão de CO_2 oriundo de matriz fóssil, e também, difícil instalação fabril. O até então utilizado, processo Haber-Bosch esbarra em muitos problemas, dentre eles, o ambiental e econômico.[1,2] Diante dessa perspectiva, os catalisadores baseados em semicondutores para fixação de nitrogênio surgem como proposta de processos de baixo consumo energético, e possível aplicação da Química Verde.[2,3] Alguns trabalhos apresentam o nitreto de carbono grafítico, CN, como possibilidade de aplicação para a síntese de amônia, devido ao seu baixo custo, disponibilidade, boa resposta à luz, e estabilidade química adequada. A busca de materiais por meio de modificações do CN, como, dopagem, formação de hétero-estrutura, torna-o ainda mais promissor a aplicação na redução fotocatalítica de N_2 a amônia.[3,4] Em contribuição, preparamos uma série de materiais à base de nióbio e nitreto de carbono grafítico pelo método de pirolise do precursor melamina. Em seguida, os materiais foram caracterizados pelas técnicas de microscopia eletrônica de varredura e transmissão, espectroscopia FTIR e Raman, difração de raios X, espectroscopia de absorção atômica, espectroscopia por energia dispersiva. Os materiais foram aplicados como catalisadores heterogêneos para a redução fotocatalítica de N_2. As reações foram conduzidas à temperatura ambiente, estudando a variação de radiação no espectro de luz visível e ultravioleta, e a concentração de NH_3 foi acompanhada utilizando reagente de Nessler e espectroscopia UV-Vis.

1. JIAO, F.; XU, B. Electrochemical Ammonia Synthesis and Ammonia Fuel Cells. **Advanced Materials**, v. 31, n. 31, p. 1–5, 2019.
2. WU, T. et al. Electrochemical synthesis of ammonia: Progress and challenges. **Materials Today Physics**, v. 16, p. 100310, 2021.
3. VESALI-KERMANI, E. et al. Nitrogen photofixation ability of g-C3N4 nanosheets/Bi2MoO6 heterojunction photocatalyst under visible-light illumination. **Journal of Colloid and Interface Science**, v. 563, p. 81–91, 2020
4. HU, S. et al. Fe3+ doping promoted N2 photofixation ability of honeycombed graphitic carbon nitride: The experimental and density functional theory simulation analysis. **Applied Catalysis B: Environmental**, v. 201, p. 58–69, 2017.

Agradecimentos

CEFET-MG, FAPEMIG, CNPq, CAPES, and CBMM.

Área: CAT

Photocatalytic metal-free synthesis of Quinolines from nitrobenzene and short-chain alcohols

Guilherme F. S. R. Rocha (PG),[1]* Marcos A. S. Ribeiro (PG)[1], Ivo F. Teixeira (PQ)[1].

Guilherme.rocha@estudante.ufscar.br; marcosgusto96@gmail.com .

[1]*Department of Chemistry, UFSCar.*

Keywords: *Photocatalysis, Carbon Nitride, Green chemistry*

Highlights

Use of crystalline carbon nitride based on protonated PHI, applied for the sustainable synthesis of simple substrates such as nitrobenzene and short-chain linear alcohols under light irradiation and mild conditions.

Resumo/Abstract

Quinolines are a class of molecules with a wide range of applications as natural products, its derivatives are used as scaffolds for pharmaceuticals and agrochemical compounds. The most established methods for synthesis of quinolines involves the use of aniline and reactive aldehydes and ketones, in the presence of strong acids (e.g H_2SO_4) and at boiling temperatures. Therefore, cheaper, and mild approaches are highly desirable to lower economic and environmental costs. Crystaline carbon nitride is simple in composition, yet a promising type of semiconductor that can be applied as photocatalyst in several chemical transformations or combined with nanoparticles or metal single-atoms. Herein, we propose an alternative green approach by utilizing protonated crystalline carbon nitride (H-PHI) as photocatalyst and using ethanol and nitrobenzene as simple building blocks for quinaldine. Crystalline carbon nitride (PHI) is usually produced by the ionothermal polymerization of melamine in the presence of NaCl, the Na^+ ions in the structure can be easily exchanged by other cations.[1] In this work, hydrochloric acid in different concentrations, from 2 $mol.L^{-1}$ up to 12 $mol.L^{-1}$, was used as a H^+ source, resulting in H-PHI (acid modified PHI), which possess the photocatalytic properties of PHI while attaining properties of an acid catalyst. This photocatalyst was characterized by a wide range of techniques such as XRD, FT-IR and UV-Vis. Finally, this material was employed in a single pot conversion of nitrobenzene into quinaldine in ethanolic media, using light as energy source and mild heating up to 40 ºC. From the XRD results shown in **figure 1a** it is possible to notice the acid treatment leads to a loss of crystallinity by the converging of bands around 27º and diminishing band in 8º which means a loss of orderly stacking of the PHI sheets, while maintaining the overall 2D structure. In **figure 1b,** the catalytic results over a twelve-hour period are summarized, although the conversion does not follow a linear trend, the selectivity for quinaldine is kept above 35% reaching and overall yield of 32.6% at 12 hours. The results, while satisfactory for this type of reaction, can possibly be optimized with more selective control over side products and increasing conversion. We also strongly believe that by selecting different alcohols, other types of quinolines might be synthetized by this system.

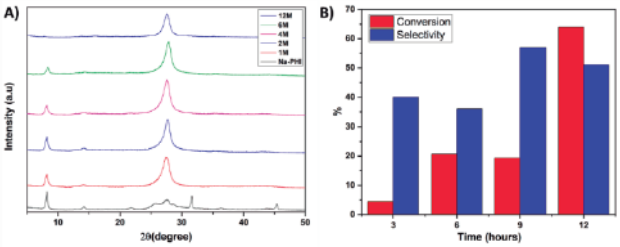


Figure 1: a) X-ray diffraction profile of Na-PHI and the different synthetized H-PHIs. **b)** Catalytic results over a 12-hour period for the conversion of nitrobenzene into quinaldine.

(1) da Silva, M. A. R.; Silva, I. F.; Xue, Q.; Lo, B. T. W.; Tarakina, N. V.; Nunes, B. N.; Adler, P.; Sahoo, S. K.; Bahnemann, D. W.; López-Salas, N.; et al. Sustainable oxidation catalysis supported by light: Fe-poly (heptazine imide) as a heterogeneous single-atom photocatalyst. *Applied Catalysis B: Environmental* **2022**, *304*, 120965. DOI: https://doi.org/10.1016/j.apcatb.2021.120965.

Agradecimentos/Acknowledgments

The authors are thankful for FAPESP, CAPES, CNPQ and UFSCar.

Área: CAT

Ru^{II}/Pd^{II} complexes as versatile multifunctional catalysts for Heck coupling, ROMP, and vinyl polymerization

Poliana C. Mello[1*] (IC), Thais R. Cruz[1] (PG), Pedro Ivo S. Maia[2] (PQ), Lionel Delaude[3] (PQ), Beatriz E. Goi[1] (PQ), Valdemiro P. Carvalho-Jr[1] (PQ)

***poliana.campagnoli@unesp.br**

[1] Faculdade de Ciências e Tecnologia, UNESP – Univ. Estadual Paulista, Presidente Prudente 19060-900, SP, Brazil; [2] Institute of Exact Sciences, Naturals and Education, Federal University of Triângulo Mineiro (UFTM), 38064200, Uberaba,Minas Gerais, Brazil; [3] Laboratory of Organometallic Chemistry and Homogeneous Catalysis, University of Liege, Allée du six août 13, 4000 Liège,Belgium

Keywords: Multifunctional catalyst, Palladium, Ruthenium, Dual catalysis.

Highlights

Pd and Ru/Pd complexes were successfully synthesized. New Ru/Pd complexes were able to mediate different reactions mechanisms. Phenyl-Norbornene were obtained in quantitative yields.

Abstract

The heterobimetallic complexes have emerged as a versatile tool in the development of new multifunctional catalyststo couple different polymerization mechanisms through a dual catalysis. In this work, new complexes based on heterobimetallic complexes combining a Ru metal center to Pd, were developed as pre catalysts for different reactions: ROMP andvinyl polymerization of norbornene and for Heck reaction of norbornadiene.
The Pd monometallic complexes [Pd(4-aminopyridine)(TSC)] were synthesized from the reaction of the respective thiosemicarbazone ligands (TSC), and 4-aminopyridine in the presence of Et_3N. The heterobimetallic complexes of the type [$RuCl_2$(*p*-cymene)(μ-4-aminopyridine)Pd(TSC)] were synthesized from the equimolar reaction between [$RuCl_2$(*p*-cymene)]$_2$ and the respective palladium complexes. The synthesized complexes were characterized by ^1H NMR. Initial tests on Heck reactions of norbornadiene (NBD) proved to be successful. Quantitative conversions were achieved for Pd-1 complex when molar ratios of [Cat.]/[PhI]/[NBD] = 1/418/1344 were employed at 120°C for 16h. Research investigations into the mechanism of Heck reactions mediated by palladium complexes have revealed that the oxidative addition of PhI at the metal center occurs associatively, leading to the formation of a hexacoordinate complex.

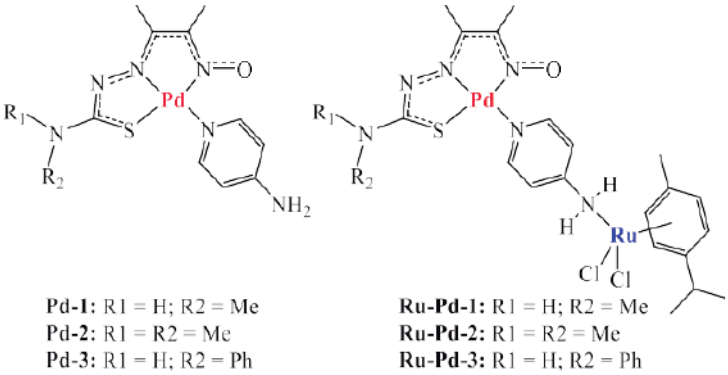


Fig. 1. The Ru-Pd heterobimetallic complexes and their monometallic palladium fragments.

Acknowledgments

CAPES FAPESP CNPq LaCOM

Área:CAT

Síntese e caracterização do complexo [NiI(aril-Ebib)(N,N)] para o acoplamento de reações de polimerização de etileno e ATRP

Matheus P. Neves (IC),[1] Gustavo H. C. Masson (PG),[1] Douglas Henrique Nunes Santos,[1] Beatriz E. Goi (PQ),[1] Valdemiro P. Carvalho-Jr. (PQ),[1*] matheus.p.neves@unesp.br; valdemiro.carvalho@unesp.br

[1]*Departamento de Química e Bioquímica, FCT-UNESP, Presidente Prudente.*

Palavras Chave: *Níquel, Polimerização, Etileno, ATRP.*

Highlights

The present work reports the synthesis of a NiII complex potentially active in ethylene polymerization reactions. The complex incorporates an α-diimine ligand and a functionalized ligand to initiate Atom Transfer Radical Polymerization (ATRP) reactions, thereby connecting the reaction mechanisms.

Resumo

Complexos contendo centro metálico de Ni^{II} têm atraído a comunidade científica devido às suas grandes possibilidades de reações catalíticas e seu custo mais acessível. A exemplo, a polimerização de etileno mediada por complexos de Ni^{II} produz polímeros com baixa distribuição de massa molar e estrutura bem definida. Outra reação em que complexos de Ni^{II} são amplamente empregados é a polimerização radicalar por transferência de átomo (ATRP), a principal vantagem, é a capacidade de controlar a taxa de polimerização, sendo útil para aplicações onde a uniformidade e a previsibilidade das propriedades do polímero são essenciais. Desta forma, o complexo [NiI(aril-Ebib)(N,N)] foi planejado para conter uma base de Schiff bidentada do tipo N,N, configurando estabilidade e modulando os efeitos eletrônicos do complexo. Pensando no acoplamento dos mecanismos (polimerização de etileno e ATRP), um ligante funcionalizado foi inserido no centro de Ni^{II}, contendo um iniciador para as reações de ATRP (**Figura 1**). O ligante 2-bromo-2-metil propanoato de *p*-iodo fenilila (aril-Ebib) foi sintetizado seguindo a esterificação de Steglich modificada. Para isso, reagiu-se 4-bromo-fenol com 1,5 mol de 2-bromo-2-metil-ácido-propanoico, na presença de 1,5 mol de N,N'-Diciclohexilcarbodiimida (DCC) e 1,5 mols de 4-dimetilaminopiridina (DMAP) em acetonitrila por 48 horas a 45° C. O complexo precursor de Ni^{II}, foi obtido em duas etapas. Primeiro reagiu-se o precursor $[Ni(PPh_3)_2Cl_2]$ com 3,5 equivalentes de PPh3, na presença de n-butil-Lítio em tolueno, sob agitação por 2 horas, obtendo o complexo $[Ni(PPh_3)_4]$. A adição oxidativa de 3 equivalentes do ligante I-Aril-BMA ao complexo de Ni^0 resultou no produto $[Ni(aril\text{-}Ebib)(PPh_3)_2I]$. O complexo obtido foi reagido com N1,N2-bis(2,6-diisopropilfenil)etano-1,2-diimina (DABi-propil) por 12 horas a temperatura ambiente, resultando no complexo [NiI(aril-Ebib)(N,N)]. Todos os complexos e precursores foram analisados e caracterizados por FTIR, UV-Vis e RMN de H^1, para posterior aplicação.

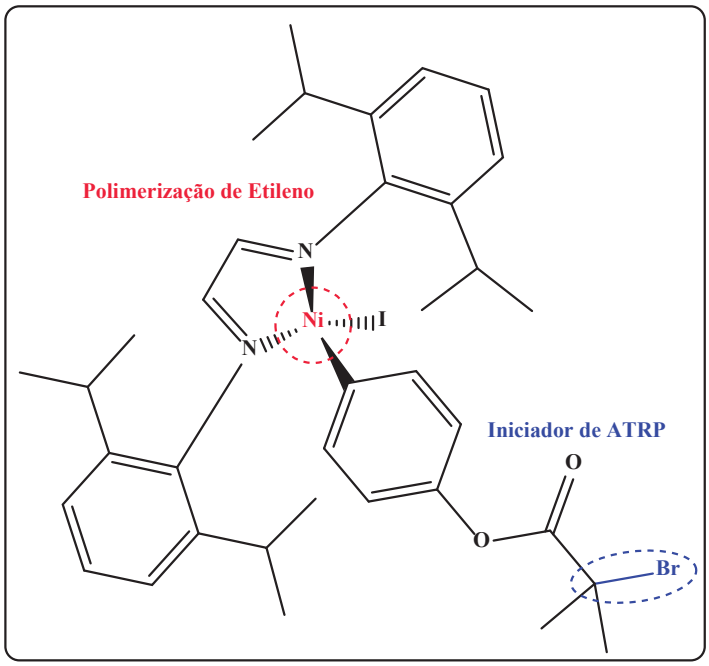


Figura 1. Complexo de Níquel multifuncional

Agradecimentos

Proc.: 2021/11873-1 e 2021/13128-1

Área: CAT

Sínteses de *p*-cimeno-complexos de rutênio com fosfitos e polimerização via metátese de olefinas

Gabriel P.F. Santos (IC),[1] Renan B.G. Caetano (PG),[1] Pedro H.O. Santiago (PQ), [2] Javier A. Ellena (PQ), [2] Benedito S. Lima-Neto (PQ)[1*]

gabrielpasianferreira@usp.br; * benedito@iqsc.usp.br

[1] *Instituto de Química de São Carlos, USP;* [2] *Instituto de Física de São Carlos, USP*

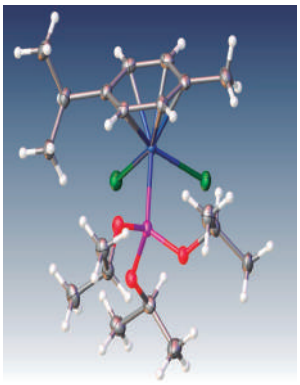
Palavras Chave: *Complexos de rutênio; Ligantes ancilares; Fosfitos; Catálise homogênea; Metátese de olefinas; ROMP*

Highlights

Syntheses of p-cymene-complexes of ruthenium with phosphites and ring opening metathesis polymerization: Arene complexes as precursor of synthesis. Phosphite as ancillary ligand. Development of ruthenium complexes for ROMP.

Resumo/Abstract

Reações de polimerização via metátese de olefinas cíclicas (ROMP) têm tido um grande avanço no desenvolvimento de polímeros funcionais [1,2]. Um fator primordial para tanto foi o desenvolvimento de complexos para catalisar as reações que são essenciais para as etapas de iniciação e propagação da polimerização [3]. A razão de velocidade entre as duas etapas deve ser idealmente igual a um para que todas as cadeias sejam propagadas de maneira uniforme [1,3]. A espécie catalítica é um carbeno-complexo inicialmente presente no complexo ou gerado no meio da reação [1-3]. Quando gerado *in situ*, isso ocorre em um período de indução o qual tem que ser eficiente quanto à formação da esfera de coordenação na espécie catalítica [1]. Assim, planejar um complexo precursor é parte do desenvolvimento de complexos eficientes para gerar polímeros almejados, com baixo custo e resistências à oxidação, à luz e a grupos orgânicos que possam desativá-lo [1]. Nessa direção, temos estudado complexos de rutênio-areno coordenados a ligantes fosfitos do tipo [$RuCl_2$(*p*-cimeno)(P(OR_3))], sendo R = fenil, etil, isopropil ou *n*-butil, para uso em ROMP de norborneno (NBE). A seleção se faz por diferenças quanto ao efeitos eletrônicos e estéreos dos fosfitos junto ao complexo. As sínteses dos complexos são em meio de metanol entre o complexo precursor [$RuCl_2$(*p*-cimeno)]$_2$ com o fosfito em proporções de 1:5, precursor:fosfito, por 2 h a 40 °C, em atmosfera de argônio, seguido de precipitação por 16 h em geladeira, lavado com hexano gelado e filtrado via cânula. Entre os complexos já desenvolvidos, o complexo com P(O^iPr)$_3$ formou um cristal vermelho que foi analisado por difração de raios-X, além de ser devidamente caracterizado por análise elementar (CHN), FTIR, RMN (^{1}H; ^{31}P) e espectrofotometria UV-Vis. Os primeiros experimentos de ROMP de norborneno (NBE) em 3 mL de $CHCl_3$, sob argônio, foram adicionado subsequentemente o monômero (razão [NBE]/[Ru] = [1000]), 1 mg de complexo e etildiazoacetato (5µL) como fonte de carbeno, em diferentes temperatura (20 50 °C) e tempo de reação (2; 4 h). Ao final de cada reação é adicionado ao balão 5 mL de metanol, utilizado como agente terminante, precipitando o polímero formado e seco em estufa a vácuo. Nas reações por 2 h (20; 50 °C) não houveram formações de polímeros. Reações por 4 h à 50 ºC obteve-se 6% de rendimentos de poliNBE. Pode-se dizer que o complexo é composto latente e estudos com irradiação com lâmpadas de 350 e 450 nm são promissores.



[1] V.P. Carvalho Jr, C.P. Ferraz, J.L. Silva Sá, Lima-Neto B.S., ROMP como um método versátil para a obtenção de materiais poliméricos diferenciados, Quim. Nova 2012,35,791; [2] I.M. Andreas F.M. Kilbinger, Practical Route for Catalytic Ring-Opening Metathesis Polymerization, JACS Au 2022, 2, 12, 2800; [3] C.W. Bielawski, R.H. Grubbs, Living ring-opening metathesis polymerization, Prog. Polym. Sci. 2007, 32, 1.

Agradecimentos/Acknowledgments

À FAPESP (2023/09286-6) pela bolsa de IC a GPFS; Ao CNPq e CAPES.

Área: CAT

Selenoxide-Pillar[5]arenes: new efficient catalysts in aqueous media reaction.

Victor H. M. Costa*(IC)[1], Pâmella Cordeiro (PG)[1], Alix Y. B. Angel (PG)[2], Eduardo E. Alberto (PQ)[2], Vanessa Nascimento (PQ)[1].

vhmenezescosta@id.uff.br, nascimentovanessa@id.uff.br

[1] *Laboratório SupraSelen, Universidade Federal Fluminense, Niterói, RJ, Brasil*

[2] *Universidade Federal de Minas Gerais, Belo Horizonte, MG, Brasil*

Keywords: Organoselenium, Supramolecules, Catalysis, Aqueous medium.

Highlights

This work presents promising results obtained from the application of selenoxide pillararenes as supramolecular strategic promises in obtaining nitrile compounds under green conditions.

Resumo/Abstract

The Pillar[n]arenes, supramolecular macrocyclics, has demonstrated great relevance in several applications mainly as important catalysts. This due to their unique properties such as easy functionalization and cavities capable of establishing non-covalent bonds with different reagents among others characteristics[3]. On the other hand, organoseleniums have consolidated importance in chemistry because of the wide range of applications in different areas, including the area of catalysis in which they showed excellent results in the catalysis of nucleophilic substitution reactions and transfer of alkyl groups. In this way, this work demonstrates the unique catalytic potential of a macrocycle formed from the union of the characteristics of pillar[5]arenes with organoselenium. After obtaining the catalyst, it was tested in obtaining nitrile 2a-l from benzyl bromide (**Fig.1a).** The best result was obtained under the following conditions: 1 mol% **P[5]SeO**, r.t. and 16h. From this optimization condition it was possible to obtain a series of 10 different nitrile structures with yields ranging from 35 to 75%. **P[5]SeO** was also efficient when different leaving groups and nucleophiles were used (**Fig 1a**). It is important to highlighted that both the recycling of the catalyst and its reaction in larger quantities presented very positive results (**Fig. 1b)**. Furthermore, the values of the Turn-off number and Turn-off frequency stand out, 75 and 4.5 respectively, for the optimized conditions. These results confirmed the need for our catalyst in these reactions, given its high interaction with the substrates. Furthermore, studies regarding the mechanism are being investigated, however, primary achievements already demonstrate that there is a strong contribution from both the macrocycle cavity and chalcogen **Fig.1c**.

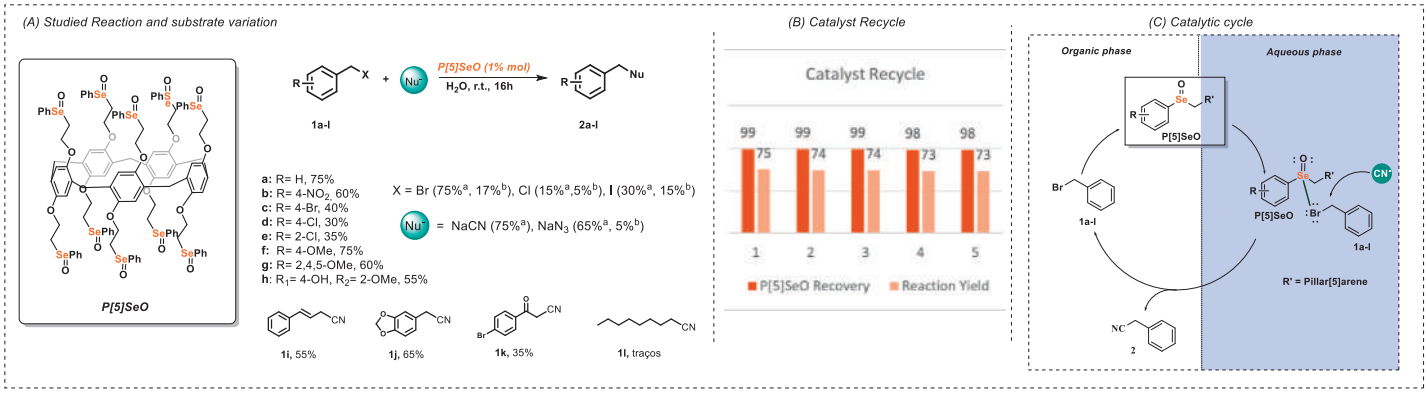


Figure 1. A) Better Efficiency parameters and substrate variation; B) Catalyst Recycle; C) Catalytic Cycle; [a]Reaction with P[5]SeO, [b]Reaction without catalyst

Agradecimentos/Acknowledgments

CAPES, FAPERJ, UFF, UFMG

[1] BALLESTER, P et al. **Chem. Mol. Sci. and Chem. Eng.**, Elsevier, 2015. [2] MONDAL, B. et al.**Supramol. Coord. Comp.**, Elsevier, 2023. p. 387–420. [3] WANG, K. et al. **Ang. Chem. Int. Ed.**, 2020, v. 59, n. 33, p. 13712–13721. [4] MAMGAIN, R. et al. **Med. Chem.**, 2023, v. 30, n. 21, p. 2421–2448,

Área: CAT

Study of BAS/LAS activities on H-[Al]-RUB-18 by cascade reactions from dihydroxyacetone to lactic acid

Paulla B.F. Sousa (PG)*[1,2], Elise M. Albuquerque (PQ)[2], Marco A. Fraga (PQ)[2,a], Heloise O. Pastore (PQ)[1,b]

***p203756@dac.unicamp.br; [a]marco.fraga@int.gov.br; [b]lolly@unicamp.br**

[1]*Micro and Mesoporous Molecular Sieves Group (GPM3), Institute of Chemistry, University of Campinas, 13083-970, SP/Brazil.*
[2]*Instituto Nacional de Tecnologia - INT, 20081-312, RJ/Brazil.*

Keywords: *Na-RUB-18, lamellar aluminosilicate, BAS, LAS, Biomass*.

Highlights

The lamellar catalysts H-[Al]-RUB-18 were active in converting dihydroxyacetone to lactic acid. The conversion and selectivity were affected by the ratio of Al_{Td}/Al_{Oh} species.

Abstract

Lamellar silicates are known by their ion exchange properties due to the existence of (-SiO^-)-type sites. The isomorphous substitution of Si^{4+} by T^{+3}-atoms in the structure confers acidic properties to the 2D-materials, which can be applied in catalytic processes that demand accessibility of bulky molecules to the acidic sites , such as those involved in biomass conversion (1). In this work, lamellar H-[Al]-RUB-18 catalysts (with nominal Si/Al molar ratios = 15, 30, 60, ∞) were synthesized and characterized by XRD, XRF and ^{29}Si- and ^{27}Al-MAS-NMR. The conversion reactions of dihydroxyacetone (DHA) and pyruvaldehyde (PA) to lactic acid (LA) were performed to investigate activity of Brönsted and/or Lewis acid sites in a continuous flow reaction system in aqueous medium (130 °C, 10 bar, 300 mg catalyst, [substrate] = 0.2 mol.L^{-1}, 0.3 mL.min^{-1} flow, 6 h) (2). Products were analyzed every 1 h of the reaction on an HPLC system (Agilent Technologies - 1110, RID detector, column HPX-87H - 65 °C). The synthesis of lamellar Na-[Al]-RUB-18 yielded materials with Q^3/Q^4 ratios > 2, indicating structural defects due to a large presence of $(SiO_4)_3Si\text{-}OH/(SiO_4)_3Si\text{-}O^-$ groups (1). This influenced the process of isomorphic substitution with the incorporation of tetrahedral (Al_{Td}) and octahedral (Al_{Oh}) species in different proportions into its structure. The acidic solids showed intrinsic structural ordering characteristics to α-H-RUB-18 (3). However, ion exchange caused a variation in the final proportion of the Al^{3+} species. The Al_{Td}/Al_{Oh} ratio values decreased with an increase in aluminum content: 3.4 (H-[Al32]-R18); 0.8 (H-[Al29]-R18); 0.5 (H-[Al16]-R18). The acidic properties of the catalysts were confirmed by the increased conversion rates in both model reactions in comparison to autothermal reactions or using H-R18 (non acidic) as catalyst. Dehydration of DHA to PA occurs on BAS (4), and a better performance was observed over H-[Al32]-R18 (higher content of Al_{Td}), with ~50% of selectivity to PA. Also, the catalysts exhibited a relative selectivity for LA, indicating that the Al_{Oh} sites acted as LAS. To demonstrate this fact, we performed reactions from PA to LA, which requires exclusively LAS for the Cannizaro reaction (3). Thus, the Al_{Oh} sites $[(SiO_4)_3Al\text{-}(OH)(H_2O)_2]$ in RUB-18 structure played an important role in this reaction, making the H-[Al_{15_16}]-R18 sample more active and selective to this product (>70% of selectivity to lactic acid).

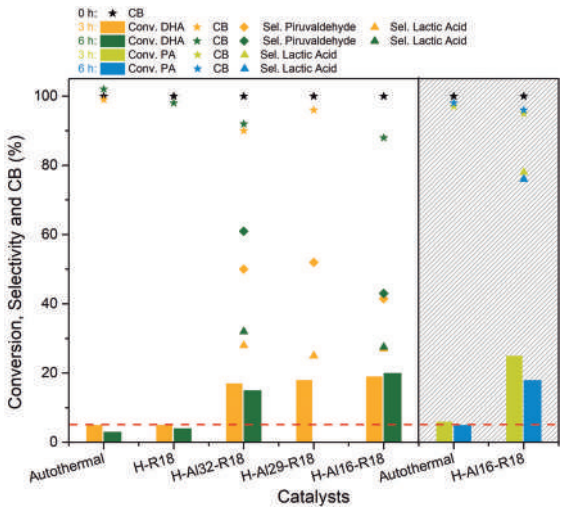


Figure 1: The conversion, selectivity, and carbon balance values to DHA (orange and green colors) and PA (blue and light green colors - shaded region) reactions at 3 h and 6 h.

Acknowledgments

This work was supported by the FAPESP (grant 2022/05743-0, project n° 2021/12058-0). The authors thank the LIRMN (IQ-UNICAMP) for the NMR analyses. MAF also acknowledges FAPERJ for financial support and HOP thanks CNPq for the scholarship. CAPES code 01 is also acknowledged.

(1) Báfero, G.B.; *et al.*, ***Mol. Catal.***, 2023, 535, 112870.
(2) Borowski, M.; *et al.*, ***Z. Krist.***, 2002, 217, 233–241.
(3) Santos, K.M.A;. *et al.*,***Biomass Convers. Biorefin.***, 2023, 13, 11865–11878.c.

Area: CAT

STUDY OF PHOTOCATALYTIC DEGRADATION OF EMERGING CONTAMINANTS IN SURFACE WATER BY SILVER TUNGSTATE

Otávio A.P. Pereira (PG)[1*]; Kelvin C. Araújo (PQ)[2], Ailton J. Moreira (PQ)[3]; Ernesto C. Pereira (PQ)[2], Elaine C. Paris (PQ)[4], Gian P. G. Freschi (PQ)[1]; Tania Regina Giraldi (PQ)[1] Roberto Bertholdo (PQ)[1]; roberto.bertholdo@unifal-mg.edu.br; otavio.pereira@sou.unifal-mg.edu.br

[1]MACAA - Instituto de Ciência de Tecnologia, Universidade Federal de Alfenas (UNIFAL-MG); [2]LIEC - Departamento de Química, Universidade Federal de São Carlos (UFSCar); [3]UNESP – Instituto de Química de Araraquara; [4]EMBRAPA Instrumentação

Key Words: *Photocatalysis, Silver Tungstate; Emerging Contaminants.*

Highlights

- Silver tungstate semiconductor synthesis by hidrotermal method using microwave energy
- Conventional water and sewage treatments aren't efficient in organic pollutants removal
- Efficient photocatalytic remotion of the Fluoxetine an Ofloxacin

Abstract

Studies on emerging pollutants, their risks to different ecosystems and to humans have increased, in addition to potential processes of treatments for environmental remediation of these compounds. Water is the main route for these contaminants to access ecosystems. So, these substances are found in domestic and industrial sewage, and even after treatment, they persist in the treated effluent and reach different biomes. Heterogeneous photocatalysis is one of the most studied processes for degradation of emerging pollutants and their mechanism can be summarized by the activation of a material semiconductor by sunlight or artificial light to generate the oxidizing species. Silver tungstate Ag_2WO_4 is a semiconductor with outstanding photocatalytic properties because when it is irradiated by ultraviolet (UV) or visible (Vis) light it is able of producing hydroxyl radicals, peroxides and/or superoxide that feature high oxidation potential of organic pollutants, besides its bactericidal action. In this research, silver tungstate particles were synthesized at by hydrothermal method assisted by microwave radiation. After the material characterization, their potential application in the photodegradation of Fluoxetine (FLX) and Ofloxacin (OFX) in surface water was studied. In the silver tungstate synthesis, 20 mL of a 2 mmol solution of silver nitrate was added to 100 mL of a 1 mmol solution of sodium tungstate under magnetic agitation at room temperature. Then, the suspension was transferred to 4 PTFE vials, hermetically closed and put in a Mars 6 microwave oven. The reaction was managed at 126 ºC during 50 minutes. The obtained beije precipitate was separated by centrifugation, washed 3 times with Milli-q water and dried in an oven at 65ºC until constant mass. The material was analyzed by powder XRD, that made it possible to verify the α-Ag_2WO_4 formation, mainly, which is the photactive phase. SEM-FEG images shows the presence of orthohombic end rods was noticed, confirming the presence of α-Ag_2WO_4. By DRS spectra, it was verified that the material presented a band gap value of 3,3 eV, and the analysis of surface area showed a non-porous material (0,6 $m^2.g^{-1}$). In the application of Ag_2WO_4 in the degradation of FLX and OFX, photocatalytic essays were done using 10 mL of the aqueous mixture of FLX 4000 $\mu g.L^{-1}$ and OFX 240 $\mu g.L^{-1}$ containing 5 mg of Ag_2WO_4, equilibrium time of adsorption of 30 minutes and 1-30 minutes of exposure to UV-C light in an reactor. The obtained solutions were filtered and analyzed by molecular fluorescence for quantification of remaining FLX and OFX from photodegradation. It was verified that FLX and OFX removal, after adsorption equilibrium, were 49% an 62%, respectively, in 30 minutes.

Acknowledgments

The authors would like to thank the FAPEMIG, CNPq, CAPES, ICT/UNIFAL, EMBRAPA INSTRUMENTAÇÃO and LIEC/UFSCar.

Área: CAT

Study of the catalytic activity of ceria nanorods for the hydrogenation of α,β-unsaturated compounds under flow and batch conditions, and investigation of the catalyst surface

Gustavo D L de Andrade (IC)*,[1] Antonio Leyva-Perez (PQ)[2], Italo Odone Mazali (PQ) [1]

g171282@dac.unicamp.br, mazali@unicamp.br

[1] *Universidade Estadual de Campinas, Instituto de Química, Laboratório de Materiais Funcionais, Campinas, SP, Brazil.*
[2]*Instituto de Tecnología Química, The Valencia Polythecnic University – Spanish Research Council (ITQ, UPV-CSIC) – Valencia, Spain.*

Palavras Chave: *Heterogeneous Catalysis, Cerium Oxide, α,β-Unsaturated Carbonyls, Surface charaterization, Oxygen vacancies*

Highlights

CeO_2 nanorods were used for hydrogenating α,β-unsaturated carbonyls in batch and flow conditions. The study revealed insights into the roles of oxygen vacancies and the hydrogen cleavage pathway.

Resumo/Abstract

Cerium oxide exhibits intricate redox properties, positioning it as a promising catalyst for a diverse range of reactions.[1] This catalyst is notably recognized for its high capacity to form oxygen vacancies, a feature that can be further enhanced through the utilization of nanostructured morphologies. Recent investigations have identified ceria nanorods as a specific catalyst for the hydrogenation of crotonaldehyde to crotyl alcohol.[1] In this study, the hydrogenation of different α,β-unsaturated carbonyls have been evaluated in flow and batch conditions. The investigation of the selective hydrogenation of such compounds holds significant importance in the field of catalysis, particularly for industries involved in the production of pharmaceuticals, flavorants, and fragrances.[2] Furthermore, the adoption of a heterogeneous catalysis system represents a pivotal step toward enhancing the sustainability of these processes.

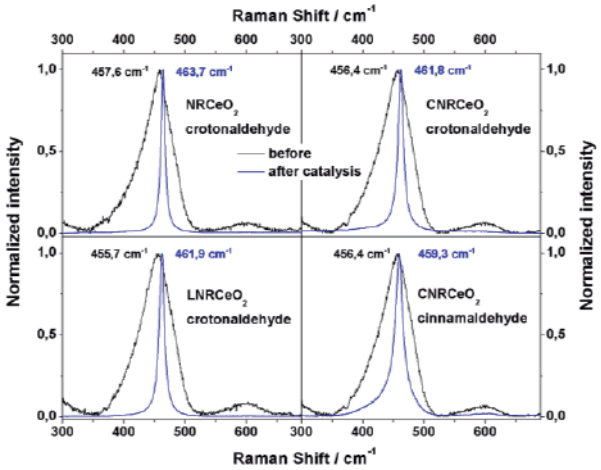


Figure 1: *Raman spectra of the catalyst used in flow conditions.*

The nanorods have been treated by comminution and acid leaching to achieve a highly defective material.[3] Raman spectroscopy, Fourier Transformed Infrared (FTIR) and X-Ray Photoelectron Spectroscopy (XPS) have been applied to evaluate the interaction between the α,β-unsaturated compounds and the surface of the ceria. Notable differences have been observed between the activity of ceria in batch and flow conditions, leading to the formation of hydrogenolysis or hydrogenation products depending on the specific system employed. The outcomes from Raman (Fig. 1) and XPS analysis substantiate the close correlation between the concentration of oxygen vacancies on the ceria surface and its catalytic activity. An in-depth exploration of the underlying pathways elucidates the pivotal role played by the cleavage mechanism of hydrogen on the surface of cerium oxide (Fig. 2).

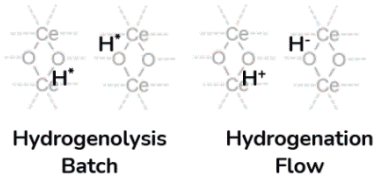


Figure 2: *Representation of the reaction pathways in flow and batch conditions.*

References:

1. Z. Zhang, et al. *ACS Catal.*, 2020, **10**, 14560–14566.
2. M. Zielinski, W. Juszczyk and Z. Kaszkur, *RSC Adv.*, 2022, **12**, 5312–5323.
3. I. de C. Silva, F. A. Sigoli and I. O. Mazali, *J. Phys. Chem. C*, 2017, **121**, 12928–12935.

Agradecimentos/Acknowledgments

UNICAMP · Instituto de Química · Laboratório de Materiais Funcionais · EMMU · FAPESP · CNPq · LNNano · ITQ Instituto de Tecnología Química · Universitat Politècnica de València

Área: CAT

Supported Ionic Liquid Phases for Carbon Dioxide Fixation

Jonas X. Torres (IC),[1] Vinicius K. Tomazett (PG),[1] Rafael P. das Chagas (PQ),[1] Muhammad Irfan Qadir (PQ)[1*]
jonas_torres@discente.ufg.br; irfan@ufg.br
[1]*Laboratório de Síntese e Catálise Organometálica (LABSINCO), Instituto de Química, Universidade Federal de Goiás - UFG;*

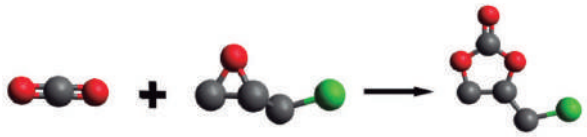
Keywords: *Carbon dioxide, Cyclic carbonate, Epichlorohydrin, Ionic liquid.*

Highlights

Utilization of carbon dioxide (CO_2) is crucial to mitigate greenhouse effect. CO_2 fixation with epoxides yields cyclic carbonates, promoting sustainable chemical materials, enabling economically viable green chemistry.

Resumo/Abstract

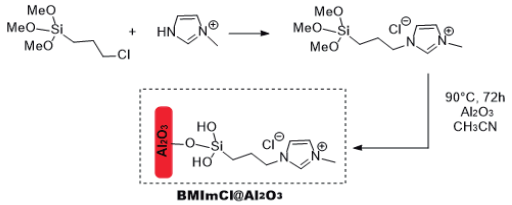
The mitigation of atmospheric CO_2 is one of the main goals for the research community. In this regard, it is possible to capture and convert CO_2 into value-added chemicals such as methanol, carbon monoxide, fuels, and cyclic carbonates. Among them, the fixation of CO_2 with epoxides has emerged as a promising approach due to its sustainability and potential for environmentally beneficial economic processes. This method has garnered considerable interest due to the use of cyclic carbonates as intermediates in the synthesis of polycarbonates.



Scheme 1. Cycloaddition reaction of CO_2 and epichlorohydrin

The model reaction involves the cycloaddition between CO_2 and epichlorohydrin (ECH) at a pressure of 1 bar (Scheme 1). A supported ionic liquid on aluminum oxide was employed as a catalyst (Scheme 2). The reaction was tested under different temperature conditions ranging from 25 to 70°C and time durations from 2 to 24 hours, while maintaining constant parameters such as pressure, epoxide quantity, and catalyst amount. This system results in the production of the aforementioned cyclic carbonates.

Through the conducted experiments and analyses, especially proton nuclear magnetic resonance (NMR) analysis, it was possible to compile and assess the yields and selectivity in obtaining cyclic carbonate. The experiment was based on two parameters: time variation and temperature variation.



Scheme 2. Synthesis of Ionic Liquid (IL) catalyst

Both parameters showed a trend of increased conversion concerning both temperature and time, with the best result achieved under conditions of 24 hours at 70°C, reaching a conversion of ~92%. All results showed a high rate of selectivity, which is positive in obtaining a specific product, as in the case of cyclic carbonates.

Cyclic carbonates have proven to be environmentally friendly solvents. Therefore, the fixation of CO_2 with epoxides represents a promising approach to reduce the amount of CO_2 in the atmosphere, leveraging its potential in the production of sustainable chemical materials.

Agradecimentos/Acknowledgments

The authors express their gratitude to CNPq (406422/2022-2) and the Institute of Chemistry IQ-UFG.

Área: CAT

Synthesis of copolymers via coupling of ROMP and addition polymerization mediated by a bifunctional Ru^{II}/Ni^{II} heterobimetallic catalyst

Douglas Henrique Nunes Santos (PG),[1] Gustavo Henrique Cícero Masson (PG),[1] Eliada Andrade da Silva,[2] Beatriz Eleutério Goi (PQ),[1] Valdemiro Pereira de Carvalho Júnior (PQ).[1]*

douglas.santos@unesp.br; valdemiro.carvalho@unesp.br

[1]*Departamento de Química e Bioquímica, FCT – UNESP, Presidente Prudente.*
[2]*Instituto de Química de São Carlos, Universidade de São Paulo, São Carlos, SP, Brazil.*
Keywords: *(Bimetallic complex, bifunctional catalyst, ROMP, polymerization via addition, norbornene).*

Highlights

The study showcases the catalytic potential of the heterobimetallic complex Ru-Ni in ring-opening and addition polymerization reactions, achieving significant yields and acting as bifunctional catalysts in the synthesis of advanced copolymers.

Abstract

With the need for new polymeric materials that could satisfy the advances in technology, the search for polymers with sophisticated properties and architectures has become increasingly attractive. Heterobimetallic catalysts have been gaining great ascension in recent years due to their multifunctionality in catalysis, as well as the mechanistic synergism that such systems can provide. In this work, a ruthenium(II) and nickel(II) heterobimetallic catalyst $[RuCl_2(\eta^6\text{-}p\text{-cymene})][(\mu\text{-Schiff-pip})Ni(Aryl\text{-}NBE)(PPh_3)]$ (Ru-Ni) and its catalytic activity was evaluated in ROMP and addition polymerization reactions using norbornene (NBE) as monomer. Ru-Ni was shown to be active for metathesis ring opening polymerizations (ROMP), reaching a yield of 40% at 50 °C, using a molar ratio [NBE]/[Ru] = 5000, [EDA]/[Ru] = 10 and a reaction time of 60 minutes. The heterobimetallic complex was also active in NBE polymerization reactions via addition, using methylaluminoxane (MAO) as cocatalyst, obtaining a yield of 92% using the molar ratio Al/[Ni] = 2500 at 30°C, with a TOF (turnover frequency) of 6.96×10^6 g.mol^{-1} Ni. h^{-1}.

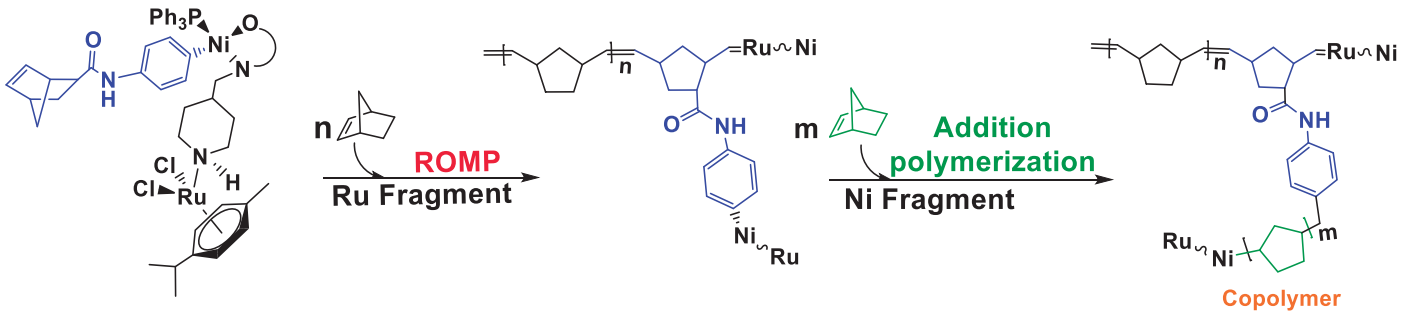


Figure 1. Bifunctional catalyst acting as mediator in two reactions distinct mechanistically.

1. Das, D., Mohapatra, S. S. & Roy, S. Recent advances in heterobimetallic catalysis across a "transition metal–tin" motif. Chem. Soc. Rev. 44, 3666–3690 (2015).

2. Masson, G. H. C. et al. Ruthenium–nickel heterobimetallic complex as a bifunctional catalyst for ROMP of norbornene and ethylene polymerization. New J. Chem. 45, 11466–11473 (2021).

Acknowledgments

Proc: 2022/12417-2, 2021/11873-1 and 2021/13128-1

Área: CAT
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Synthesis of Supported Photocatalysts on *Lucina pectinata* Shell Powder for applying in Solar Hydrogen Generation

Adnaildo M. Mota (PG),[1*] Raiane M. dos Santos (IC),[1] Cesário F. das Virgens (PQ),[2] Luciana A. da Silva (PQ),[1,3]

Adnaildo.mota@gmail.com

[1]Instituto de Química, Universidade Federal da Bahia- UFBA; [2]Departamento de Ciências Exatas e da Terra I, Química, UNEB; [3]Instituto Nacional de Ciência e Tecnologia - INCT - de Energia e Ambiente, Universidade Federal da Bahia- UFBA, Brasil

Key Words: *Solar Hydrogen, Photocatalysis, Water Splitting, Lucina pectinata.*

Highlights

This work used solid waste to support a photoactive material (CdS) for application in H_2 generation assisted by sunlight. The results indicated that the support/semiconductor interaction improved the photocatalytic activity.

Resumo/Abstract

The search for clean and sustainable energy sources has driven the investigation of new technologies, with the production of green hydrogen currently being highlighted. A possible approach to this production involves water splitting through photocatalytic processes using sunlight-assisted semiconductors. Metal sulfides, especially CdS, are considered promising materials because they absorb visible light efficiently. However, these materials face challenges related to photocorrosion and environmental concerns associated with cadmium. Given this scenario, this study proposed a less explored approach to mitigate such issues, promoting the sonochemical incorporation of CdS in a 1:3 ratio in supports originating from solid waste, such as powder from the shell of *Lucina pectinata* (L), usually known as *lambreta* in northeastern Brazil. Exploring this shellfish constitutes an important source of income for traditional populations in the coastal area. However, inadequate disposal of solid waste is also considered an environmental problem.

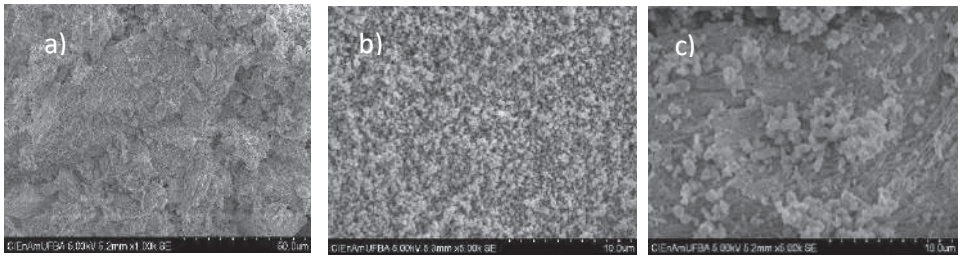


Figure1: Micrographs: a) support (L); b) CdS; c) composite CdSL

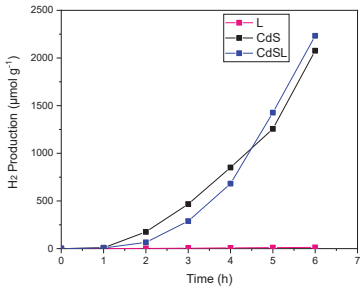


Figure 2: H_2 production profile

The results obtained by SEM (Figure 1) showed the effectiveness of the method used in promoting the deposition of CdS on the surface of the *Lucina Pectinata* shell powder (L). Photocatalytic tests were conducted in a solar simulator and the S^{2-}/SO_3^{2-} pair in an alkaline medium was used as a sacrificial reagent in the presence of Pt (cocatalyst). Figure 2 shows the H_2 production profile of support L, pure CdS and composite CdSL, with H_2 production rates of 2 μmol h^{-1} g^{-1}; 346 μmol h^{-1} g^{-1} and 372 μmol h^{-1} g^{-1}, respectively. The results highlight the significant potential of the supported material for use in photocatalytic processes for hydrogen generation. When considering only the mass percentage of the photoactive material (25%) in the CdSL sample, the average hydrogen production reaches 1488 μmol h^{-1} g^{-1}, approximately 4 times higher than pure CdS.

[1] I. S, Barros, et al. JOURNAL OF THERMAL ANALYSIS AND CALORIMETRY, v. 137, p. 1-10 (2019)
[2] P. A. L. Lopes, A. J. S. Mascarenhas, L. A. Silva, *Materials Latters*. **111-113**, 136 (2014).

Agradecimentos/Acknowledgments

Programa de Pós-Graduação
CNPq Conselho Nacional de Desenvolvimento Científico e Tecnológico
FOTOMS
Estado da Bahia
fapesb Fundação de Amparo à Pesquisa do Estado da Bahia

Área: CAT

Tailoring supported iron oxide catalysts for the acetone HDO reaction

Pedro B. de M. Nunes (IC),[1*] **Gabriel B. Báfero (PG),[1] Daniela Zanchet (PQ).[1]**

[*]**p236605@dac.unicamp.br**

[1]*Institute of Chemistry, University of Campinas, UNICAMP, Campinas, SP, Brazil*

Keywords: *Nanomaterials, Heterogeneous Catalysis, Supported catalysts, Iron oxide*

Highlights

Dispersing iron oxide on high-SA supports increased the active phase accessibility and the hydrodeoxygenation yield.

Resumo/Abstract

Supported catalysts are composed of active phases dispersed or immobilized on a porous matrix. The support enhances active phase stability, dispersibility, and overall performance by offering a higher surface area and promoting unique metal-support interactions, leading to charge transfer and/or creation of specific interfacial catalytic sites. Previously[1], we investigated γ-Fe_2O_3 nanopowder as an interesting bulk catalyst candidate for the hydrodeoxygenation (HDO) reaction, a biomass upgrading process that reduces the oxygen content of bio-oils by selectively cleaving C-O bonds under a hydrogen-rich atmosphere. We showed that the fine tuning of $Fe^{3+}/Fe^{2+}/Fe^0$ sites by pretreatments optimized the HDO reaction of acetone, a model compound for bio-oils. In this work, we synthesize FeO_x supported catalysts to enhance the active sites' accessibility and modulate their properties by metal-support interaction. The catalysts were synthesized by incipient wetness impregnation, with 3.6 at% Fe loadings, using $Fe(NO_3)_3$ as the precursor and SiO_2 (380 m^2/g), γ−Al_2O_3 (78 m^2/g), and $MgAl_2O_4$ (130 m^2/g) as supports. XRD analysis, Fig. 1(a), presented only peaks related to the supports, for $MgAl_2O_4$ and γ-Al_2O_3, or an amorphous halo, for SiO_2, indicating that the FeO_x species were well dispersed on the support's surface. Catalytic screenings were carried out from 100 to 450 ºC, by 50 °C isothermal steps, 30 min/step for each catalyst, using fresh catalysts and equivalent Fe loading taking 14.3 mg of γ-Fe_2O_3 nanopowder as reference. Below 300 °C (not shown), the catalysts generated only undesired oxygenated products. Regarding the bare supports, SiO_2 was not active under the HDO conditions, while $MgAl_2O_4$ and γ−Al_2O_3 yielded up to 2.7% of propylene (C3) and isobutene (C4) at 450 ºC. Fig. 1(b) shows that the FeO_x supported catalysts showed superior dehydrogenation capability in comparison to the bare supports and γ-Fe_2O_3 nanopowder, the latter reaching a maximum of 2.5% yield towards C3 and C4. Regarding the overall selectivity, γ-Fe_2O_3 nanopowder was more selective toward C-C cleavage products (e.g. methane and ethylene), while the bare supports and FeO_x supported catalysts produced mostly aldol condensation products (e.g. mesityl oxide), and only C3 and C4 as deoxygenated products. So far, we can conclude that the increase in C3+C4 yield is probably related to a higher accessibility to the iron oxide domains provided by the supports, while the selectivity to these products in detriment of C-C cleavage ones (as seen in the bulk material), could be related to synergistic interactions between the iron oxide and the supports, which are yet to be explored. *(1) Nunes, et al.,* ***2024,*** *doi:10.26434/chemrxiv-2024-7cbsd*

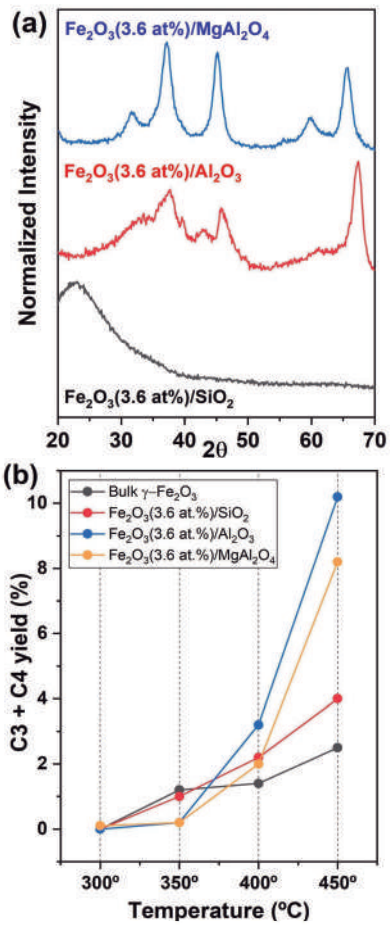


Figure 1.(a) XRD patterns and (b) deoxygenation yield (C3+C4) of FeO_x supported catalysts.

Agradecimentos/Acknowledgments

We thank FAPESP (2023/15042-2 and 2018/01258-5), CNPq (140849/2020-3 and 311226/2022-1) and CAPES (001) for funding.

Área: CAT

Transesterification of propylene carbonate and glycerol catalyzed by tetrabutylammonium salts

Dion C. M. Filho (IC),[1] Vinicius K. Tomazett (PQ),[1] Jorge L. S. Milani (PQ),[2] Rafael P. das Chagas (PQ)[1*]

dion_carlos@discente.ufg.br; rpchagas@ufg.br

[1]Laboratório de Síntese e Catálise Organometálica (LABSINCO), Instituto de Química, Universidade Federal de Goiás – UFG; [2] Departamento de Química, Universidade Federal de Juiz de Fora – UFJF.

Keywords: *CO_2 conversion, Glycerol carbonate, Homogeneous catalysis, Tetrabutylammonium salts.*

Highlights

Conversion of waste material into a high-value chemical product. Use of catalysis to overcome thermodynamic stability of CO_2. One-pot synthesis of glycerol carbonate from CO_2, epoxide and glycerol.

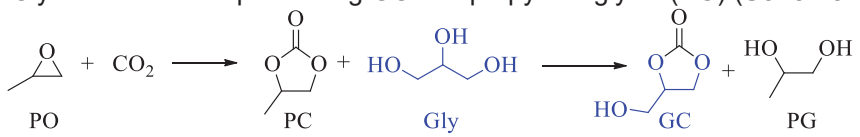
Abstract

The chemical conversion of carbon dioxide (CO_2) to value added and fine chemicals is an important topic in green and sustainable chemistry because CO_2 is an abundant, nontoxic, and renewable C1 resource. Glycerol (Gly) is another interesting, renewable, abundant and cheap raw material. The simultaneous utilization of both to produce glycerol carbonate (GC) represents an innovative strategy with significant potential for sustainable chemical synthesis.

GC poses a variety of applications as a green solvent, solvent for electrolyte in lithium-ion batteries and chemical intermediates for the pharmaceutical, polymer and cosmetic industries.

The direct synthesis of GC from CO_2 and Gly is an attractive process; however it suffers from the high thermodynamic stability of the two substrates, not to mention equilibrium limitations.

The present work describes the use of tetrabutylammonium salts (TBAX, X = Cl, Br and I) as catalysts for the synthesis of GC. Two processes were investigated: the transesterification of propylene carbonate (PC) with Gly, and the one-pot reaction, where CO_2, Gly and epoxide (PO) were mixed, generating propylene carbonate (PC) *in situ*, which then reacts with Gly in a second step affording GC and propylene glycol (PG) (**Scheme 1**).



Scheme 1: Synthesis of glycerol carbonate (GC) from CO_2.

Table 1. GC production from CO_2.

	Cat		Conv (%)		
	Gly :Subs		GC	PG	PC
1	TBABr [a]	1 : 2	50	45	-
2	TBABr [a]	1 : 4	95	95	-
3	TBABr [b]	1 : 4	59	46	30
4	TBACl [b]	1 : 4	17	35	11
5	TBAI [b]	1 : 4	67	98	36

Table 1 shows the results of the reaction conducted at 100 ºC, 4 h, 2 mol % of catalyst based on Gly. Conversion results were obtained from 1H-NMR of the reaction mixture using 1,4-diclhorobenzene as internal standard. **Condition a,** entry (1 and 2), transesterification of PC into GC, using TBABr as catalyst, performed by varying the amount of PC and Gly in the following ratios Gly : PC (1:2) and (1:4) and the respective conversion of GC were 50 %, and 95 %.

The greatest conversion obtained was using 4 equivalents of substrate.

The one-pot reaction was conducted under the same conditions. **Condition b,** One-pot reaction using 4 equivalents of PO 1 equivalent of Gly and 10 bar of CO_2.

For the one-pot reaction different catalysts were tested, in addition to **TBABr** who gave 59 % GC conversion, and their conversion were, **TBACl** 17 % and **TBAI** 67 %, (entries **3 - 5**). So far, the catalysts tested presented good results, and the target is to maximize the yield of glycerol carbonate, by evaluating other reaction parameters such as temperature, catalyst load and CO_2 pressure.

Acknowledgments

The authors are grateful for the financial support and scholarships from CNPq, FAPEG and CAPES.

Área: CAT

Transfer hydrogenation of ketones using Ru-Phenanthroline derivatives: an improvement of the reaction combining photo and thermal conditions

Gustavo Henrique Cicero Masson (PG) [1], Beatriz Eleutério Goi (PQ)[1], Maurizio Ballico (PQ)[2], Walter Baratta (PQ)[2]*, Valdemiro Pereira de Carvalho Júnior (PQ).[1]*

gustavo.masson@unesp.br

[1]*Departamento de Química e Bioquímica, FCT – UNESP, Presidente Prudente (Brasil)*
[2]*Dipartimento di Scienze AgroAlimentari, Ambientali e Animali (DI4A) – Università di Udine, Udine (Italy)*

Keywords: *(Excited state, photochemistry, photo-TH, photo-trasfer hydrogenation).*

Highlights

The study addresses new Ru^{II} catalytic systems (mono- and homobimetallic) in hydrogen transfer reactions of ketones, using both thermal and photochemical pathways.

Abstract

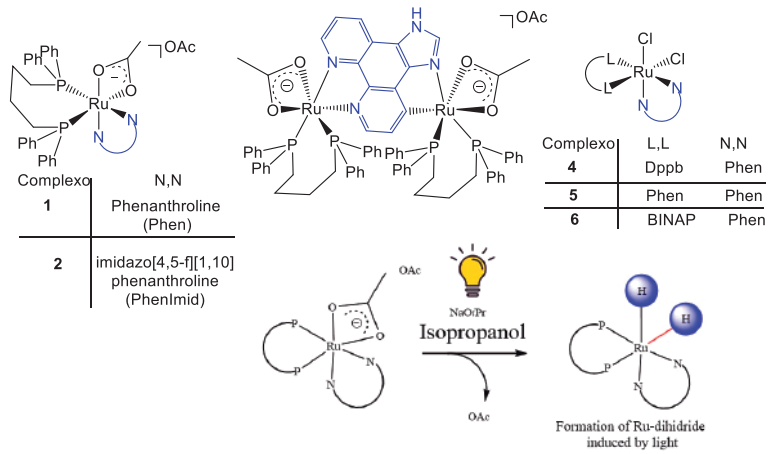


Figure 1. Molecular structure of the six Ru(N,N) complexes for thermal and photo-Transfer Hydrogenation and the formation of RuH_2 induced by light.

Three novel cationic Ru(II)/OAc/dppb complexes incorporating phenanthroline derivatives as ligands were synthesized. The complexes [Ru(OAc)(dppb)(NN)]OAc, where NN represents phenanthroline (**1**) or imidazo[4,5-f][1,10]phenanthroline (**2**), were synthesized by reacting $[Ru(OAc)_2dppb]$ with the corresponding NN ligand. Additionally, complex [(dppb)(OAc)(Ru(μ-N,N-PhenImid-C,N)Ru(OAc)(dppb)]OAc (**3**) was obtained by the reaction of complex 2 with $[Ru(OAc)_2(dppb)]$. To provide reference points for comparison in transfer hydrogenation (TH) reactions, the complexes $[RuCl_2(phen)(LL)]$, where LL denotes dppb (**4**), phen (**5**), and BINAP (**6**) were prepared. The characterization of the complexes involved FTIR, UV-Vis, and NMR spectroscopies, elemental analysis, molar conductivity measurements, and cyclic voltammetry.

The catalytic performance of complexes **1-6** was evaluated in photo-induced TH (photo-TH) of acetophenone (ACP) at 30 °C, utilizing 2 mol% of NaO*i*Pr in isopropanol under a 300 W Xenon Arc Lamp light source. Notably, complex **1** displayed the highest Turnover Frequency (TOF) of 85 h^{-1}, achieving a 93% conversion of ACP. Furthermore, complexes **1-3** were tested for thermal TH at 60 °C under the same conditions (and light irradiation), showing enhanced catalytic activity compared to solely photo-induced reactions, reaching TOF values up to 6 times higher when compared with thoso at 30 °C. Complex **1** also demonstrated efficacy in the reduction of various ketones to alcohols. Additionally, we investigated the mechanism of active species formation through NMR, observing the generation of the dihydride species $[RuH_2(phen)dppb]$ under light irradiation.

Acknowledgments

Proc: 2021/11873-1 and 2021/13128-1

This work was supported by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – Brasil (CAPES) – Finance Code 001.

EDU

Ensino de Química

Sociedade Brasileira de Química

Área: EDU

A construção de um produto educacional: SOS – Ensino de Química para alunos com deficiência visual

Taís Cristina de Lima Guimarães (PG),[1]* Marta Eloísa Medeiros (PQ).[1]

taiscristina0412@gmail.com

[1]*Instituto de Química, UFRJ*

Palavras Chave: *Ensino de química, Produto educacional, Deficiência Visual, PROFQUI*

Highlights

The construction of an educational product: SOS – Teaching Chemistry to students with visual impairments
This work consists of presenting the construction of an educational product designed to assist basic education chemistry teachers in preparing their classes for students with visual impairments.

Resumo/Abstract

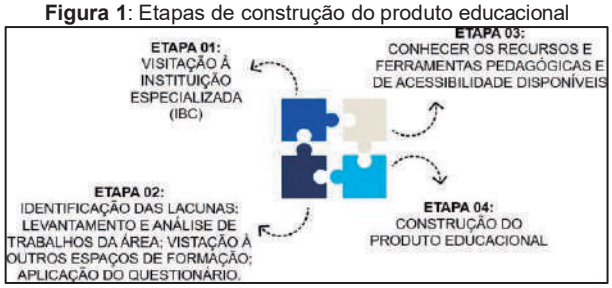
O produto/processo educacional (PE), dentro da área de ensino, de acordo com Rizziatti *et al.* (2020), "deve ser elaborado com o intuito de responder a uma pergunta ou problema oriundo do campo de prática profissional, podendo ser um artefato real ou virtual, ou ainda um processo".

A Organização Mundial da Saúde (OMS) classifica a deficiência visual em algumas categorias que vai desde a baixa visão até a ausência total de visão, sendo que elas se baseiam em valores quantitativos de acuidade visual e eficiência visual (CID – 11), onde os sujeitos que possuem as variações desse tipo de deficiência têm direito à Educação Inclusiva e o professor que os atende deve possuir conhecimentos e recurso para auxiliar o estudante com necessidades educacionais especiais.

Ao fazer um levantamento e análise de trabalhos publicados na área de ensino de química para pessoas com deficiência visual, durante o ano de 2023, em bases de dados, constatou-se que não há um número expressivo de produções acerca desta linha de atuação se comparada a outras.

Diante desta problemática, foi idealizado e construído um produto educacional, onde as etapas para o seu desenvolvimento estão representadas na figura 1, que tem por objetivo ser um documento instrucional, para docentes de química que os auxilie na reflexão e construção de suas aulas, para alunos com deficiência visual, no formato de um E-book interativo, com links e QR codes para redirecionamentos, e confeccionado através de recursos tecnológicos para o seu design, como o *CANVA* e o *Microsoft PowerPoint*.

Figura 1: Etapas de construção do produto educacional



Este material, que tem por título: SOS – Ensino de Química para alunos com deficiência visual, foi estruturado então em 4 capítulos onde: no capítulo 01 é apresentado aos professores alguns conceitos técnicos e a legislação vigente, importantes para um entendimento geral da temática do produto; no capítulo 02 são fornecidas orientações gerais e específicas para professores para a inclusão de alunos com deficiência visual em escolas regulares, como também é apresentado recursos pedagógicos e de acessibilidade existentes para tal fim; nos capítulos 03 e 04, são expostos materiais didáticos desenvolvidos na área de ensino de química para alunos com deficiência visual, de forma categorizada por assunto, sendo o enfoque do capítulo 03 em material téorico e o do capítulo 4 de propostas experimentais.

Agradecimentos/Acknowledgments

Ao PROFQUI – UFRJ e à Capes pelo apoio financeiro para a realização da pesquisa.

RIZZATTI, I. M.; MENDONÇA, A. P.; MATTOS, F.; RÔÇAS, G. SILVA, M. A. B. V. da; CAVALCANTI, R. J. S.; OLIVEIRA, R. R. Os produtos e processos educacionais dos programas de pós-graduação profissionais: proposições de um grupo de colaboradores. **ACTIO**, Curitiba, v. 5, n, p. 1-17. 2020.

Área: EDU

A cooperative learning approach using the Jigsaw method as a teaching strategy in elementary public schools of Fortaleza (CE)

Gisele S. Lopes (PQ),[1,2] Magno F. de Melo Junior (PG/FM),[2,3] Arlete da Cunha de Oliveira (PG/FM),[2,4]

gslopes@ufc.br; magno.melo@educacao.fortaleza.ce.gov.br

[1]Departamento de Química Analítica e Físico-Química, UFC; [2]Mestrado Profissional em Ensino de Ciências e Matemática, Centro de Ciências, UFC; [3]Escola Municipal Conego Francisco Pereira da Silva, Fortaleza, CE; [4]Escola Municipal José Bonifácio de Sousa, Fortaleza, CE.

Palavras Chave: cooperative learning, jigsaw method, elementary school.

Highlights

The jigsaw method was used with as a teaching strategy. The theme “Climate changes” was used as subject in elementary public schools. Students were actively involved in sharing ideas and work cooperatively to complete the tasks.

Resumo/Abstract

In this work we present some strategies for didactic activities based on the precepts of cooperative learning (Jigsaw format) associated with other didactic teaching tools. The pedagogical potential of using the Jigsaw cooperative learning method (FATARELI et al, 2010) can reinforce a more active participation of students in classes, as well as promote the collective socialization of students. This technique associated with discussions about relevant topics of climate change was evaluated. Taking into account that “Climate change will likely increase the frequency and strength of extreme events (such as floods, droughts, and storms) that threaten human health and safety. Climate changes may expose more people to diseases. Some groups of people (e.g., the very young and very old) are especially vulnerable to health impacts. The preparation for the application of the jigsaw class associated with “climate change” discussion was divided into 3 stages organized as follows, 1st stage: fragmentation of the content to be worked on (climate change) to generate the specific contents of the groups of specialists with the proper elaboration or selection (if the teacher has access to didactic material that fits the requirements of the jigsaw method) of supporting texts; 2nd stage: formation and distribution of functions of the base group; 3rd stage: preparation of the discussions related to the theme. Two semi-structured questionnaires were used to evaluate the strategy, one to analyze the contributions of the students in the proposed model and another one considering the acceptance of the method. The students of the 8st grade of public elementary school (Escola Municipal Conego Francisco Pereira da Silva) in Fortaleza actively participated of the jigsaw method. Five groups with 7 students in each one received the topics for the application of the jigsaw method. The topics were: global warming, greenhouse effect, heat islands, thermal inversion and acid rain. The students exposed their perceptions about the influence of the cooperative work in their learning, organization and relevance of the stages, didactic resources used and the topics addressed. The observed results show that the proposed strategy caused significant advances in the acquisition of knowledge by the students, about the theme addressed, and it was very well accepted, including reducing the resistance of students to perform reading activities. The second strategy is in progress and guides the use of the jigsaw method in classes on current issues in environmental education for students to set up “podcasts” in the groups to present the proposed topics in environmental education. Through interaction the students learn to interrogate issues, share ideas, clarify differences, and construct new understandings. Therefore, it is concluded that combining different didactic methods with the teaching and learning process can result in an important instrument for stimulating learning.

Ref.: FATARELI, E. F.; FERREIRA, L. N. A.; FERREIRA, J. Q.; QUEIROZ, S. L. **Método cooperativo de aprendizagem jigsaw no ensino de cinética química**. Química Nova na Escola, v. 32, n. 3, p. 161–168, 2010.

Agradecimentos/Acknowledgments

Secretaria Municipal de Educação de Fortaleza (SME) and Universidade Federal do Ceará (UFC).

Área: EDU

Adequação de tecnologias sustentáveis para produção de kits didáticos com experimentos de química: uma interação entre universidade e escolas

Davi G. Dutra (IC),[1] Rita C. O. Sebastião (PQ),[1*] Natália R. S. Araujo (PG),[1*] Janaína P. Silva (PG),[1] Ana Tereza G. Jesus (IC),[1] Júlia M. X. Leite (IC),[1] Maria Clara S. Oliveira (IC),[1] Alfredo L. M. L. Mateus (PQ),[2] Andréa H. Machado (PQ),[2] Fernando A. Moreira (FM),[3] Lucimar V. Amaral (PG),[4] Marina P. N. Correa (PG),[1] Isabela T. Lima (TC),[1] Juliana A. S. Oliveira (PQ),[1] Wladmir T. Silva (PG).[1]

davidutra@ufmg.br; ritacos@ufmg.br; nataliarsaraujo@ufmg.br

[1]Departamento de Química, UFMG; [2]Colégio Técnico da Universidade Federal de Minas Gerais, Coltec; [3]Colégio Professor Roberto Herbster Gusmão; [4]Escola de Engenharia, UFMG.

Palavras Chave: *Inspirati, Divulgação científica, Objetivos da Química para o Desenvolvimento Sustentável, Experimentos de química, Tecnologias sustentáveis, Kits didáticos.*

Highlights

Adequacy of sustainable technologies to produce teaching kits with chemistry experiments: an interaction between university and schools
Promotion of actions to contribute for the Chemistry Sustainable Development Goals in basic education.
Adequation of sustainable technologies for teaching kits.

Resumo/Abstract

O projeto “Inspirati” é uma iniciativa do Programa de Extensão 1000 Futuros Cientistas (1000FC) e é atualmente realizado em parceria com o Instituto Nacional de Ciência e Tecnologia Midas (INCT Midas). O principal objetivo dessa iniciativa é aproximar a universidade e a sociedade por meio da divulgação científica. Utilizando experimentos de química, atividades didáticas e oficinas, as tecnologias desenvolvidas pelos pesquisadores da universidade são levadas aos estudantes da Educação Básica (EB) e à sociedade. Além disso, o projeto visa colaborar com o cumprimento dos Objetivos da Química para o Desenvolvimento Sustentável (OQDS), no que tange proporcionar educação de qualidade, reforçando a centralidade da Química no enfrentamento de problemas sociais e ambientais. As atividades principais são: (I) Mapear e adequar tecnologias sustentáveis produzidas por pesquisadores do INCT Midas, em forma de experimentos de química, alinhados ao conteúdo previsto pela Base Nacional Comum Curricular (BNCC) para o Ensino Fundamental II e Ensino Médio. (II) Produzir vídeos e propor atividades didáticas que auxiliem na compreensão de tais experimentos, tendo professores da EB como participantes. (III) Divulgar os materiais e práticas elaboradas em plataformas digitais e eventos promovidos pelos autores da iniciativa. (IV) Adaptar os experimentos desenvolvidos no formato de kits didáticos e distribuí-los para professores da EB. Como resultados, no ano de 2023, foram elaborados dois experimentos com suas respectivas atividades didáticas e vídeos. O primeiro experimento, denominado “Meu xixi é adubo!”, baseia-se na tecnologia “P4Tree”, que é uma pastilha capaz de adsorver o fósforo presente na urina para ser utilizado como fertilizante. O experimento visa discutir o funcionamento do “P4Tree”, tratando o conceito de solubilidade. O segundo experimento, “Tinta de isopor”, envolve a reciclagem de poliestireno expandido a partir da dissolução em solventes verdes. Nessa atividade são abordados os conteúdos de interações intermoleculares e solubilidade. Ambos experimentos foram adaptados no formato de kits didáticos e demonstrados em eventos promovidos pelo 1000FC e INCT Midas, como o I Workshop para professores da EB sobre experimentação no ensino de Química. Esse evento teve 69 participantes, sendo a maioria atuante em escolas públicas. Em seu encerramento, foi aplicado um questionário por meio de um formulário eletrônico para que os participantes o avaliassem. Todos os avaliadores consideraram o evento muito útil e 76,9% afirmaram que aplicariam os experimentos em sala de aula se tivessem os recursos disponíveis. Em suma, o projeto “Inspirati”, no ano de 2023, cumpriu com seus objetivos no que diz respeito à elaboração de novas práticas, materiais didáticos e divulgação de suas atividades. Além disso, cumpriu com os eixos do primeiro OQDS, promovendo ações relacionadas à sustentabilidade através da Química na EB.

SILVA, Ingrid F. et al. Movimento Química pós 2022: construção de um plano de ação para que a Química e Seus Atores impactem a Sustentabilidade e Soberania no Brasil. Química Nova, v. 45, p. 497-505, 2022.

Agradecimentos/Acknowledgments

INCT Midas, Proex, FAPEMIG, CAPES e CNPq.

Área: EDU

A IMPLEMENTAÇÃO DA LEI 10.639/03 NO ENSINO DE QUÍMICA ESPERANÇANDO SUPERAR OS ESTIGMAS ÉTNICO-RACIAIS EM SALA DE AULA

Marilene Barcelos Moreira* (PG)[1], Drª. Anna M. Canavarro Benite (PQ)[2].

[1]Departamento de Química, CEPAE-UFG; Coletivo Ciata-Laboratório de Pesquisa em Educação Química e Inclusão (Ciata-LPEQI), Instituto de Química (IQ), Universidade Federal de Goiás (UFG).
[2] Núcleo de Pesquisa em Ensino em Ciências (NUPEC); Coletivo Ciata-Laboratório de Pesquisa em Educação Química e Inclusão (Ciata-LPEQI), Instituto de Química (IQ), Universidade Federal de Goiás (UFG).

Palavras-Chave*: Educação Antirracista; Cultura; Educação Libertadora; Lei 10.639/03; Ensino de Química.*

Highlights

The implementation of law 10.639/03 in chemistry education aiming to overcome ethnic-racial stigmas in the classroom.

Brazilian education is based on traditional models. The demands of Law 10.639/03 have led us to develop tools that can construct an anti-racist and liberating education in the teaching of chemistry.

Resumo/Abstract

O sistema educacional brasileiro, está pautado nos modelos: tradicional, conservador, alienante, padronizador de mentes e de comportamentos. Esses modelos são características herdadas da colonização, que por muito tempo utilizaram dos ditames da monocultura eurocêntrica, que valida um único e exclusivo “saber científico”, excluindo da dinâmica social, os saberes de outros povos do cenário educacional, especialmente, o conhecimento africano e afro-brasileiro. Infelizmente, esses elementos vedaram nossos olhos, para que não pudéssemos compreender as assimetrias e problemáticas sociais presentes nas salas de aula e que são causadas por essa exclusão. Contudo, as exigências da Lei 10.639/03, trouxe para a educação o nosso despertar para as relações étnicas-raciais, ao passo que nos ensinou a construir o nosso “*ser mais*”. Pensando nos dizeres de bell hooks, sobre a educação antirracista, de Paulo Freire, sobre a educação libertadora, e nas intervenções pedagógicas (IP) desenvolvidas no Coletivo CIATA, buscamos responder: “é possível ensinar Química por meio de uma disciplina eletiva que tem por contexto elementos da diáspora africana?”. Para esse fim, desenvolvemos a disciplina eletiva “Química na cozinha: alimentação e a diáspora africana” na unidade escolar CEPAE/UFG, ofertada no ano de 2019, que contou com o desenvolvimento de um material instrucional nos moldes antirracistas. É válido ressaltar que, mesmo havendo diversos materiais instrucionais com perspectivas antirracistas para o ensino de ciências, foi elaborado um, que abarcasse a triangulação do conhecimento químico e os três pilares freirianos: culturalidade, politicidade e dialogicidade. A presente pesquisa apresenta elementos da pesquisa participante, que segundo Brandão e Borges (2007, p.54) é capaz de “construir e reconstruir a teoria a partir de uma sequência de práticas refletidas criticamente”, pois pressupõe que os sujeitos da pesquisa e todas as culturas que circunscrevem o meio são fontes originais de saberes. Nesse sentido, a pesquisa contou com a participação de trinta (30) estudantes da 2ª e 3ª séries do Ensino Médio da própria instituição escolar. Todas as aulas foram gravadas e, posteriormente, transcritas, sendo refletidas à luz da Análise da Conversação. Nessa pesquisa, apresentamos as razões para implementação da lei 10.639/03 no ensino fundamental e médio; as perspectivas freirianas por uma educação antirracista; e, entrelaçamento do ensino de Química, da alimentação e da cultura africana e afro-brasileira. No desvelar da trama, explicamos sobre o desenvolvimento (planejamento e elaboração) do material instrucional, bem como as reflexões obtidas do desenvolvimento de duas IPs em sala de aula. Os resultados foram refletidos em torno dos três pilares freirianos - ao qual chamamos de circularidade – e em referenciais teóricos da ciência/ensino de Química e da educação antirracista. Os dados alvitram mostrar que o “ser mais” é uma ação mútua, no qual os sujeitos (o eu e o outros), se percebam e se formem, à medida que os discursos-dialógicos vão sendo tecidos. Para tanto, a nossa práxis pedagógica ao ser estruturada nos moldes antirracista e libertador deve ser capaz de recolocar os coletivos subalternizados da sociedade brasileira num discurso profícuo e multicultural no ensino de ciências, que se contextualize com a realidade dos estudantes, mostrando-lhes que somos seres incompletos, que por colaboração, podemos construir uma educação antirracista e libertadora.

Agradecimentos/Acknowledgments

Ao Centro de Ensino e Pesquisa Aplicada À Educação (CEPAE) e ao Coletivo Ciata (LPEQI/IQ/UFG).

Área: EDU

APPLICATION OF ACTIVE METHODOLOGIES AS AN ALTERNATIVE FOR IMPROVING LEARNING: A STUDY OF THE SUBJECT OF CHEMISTRY

Marcelle B. Xavier (IC) [1], Ana P. Contelli (IC) [1], Gustavo C.F. Santos (IC) [1], Gustavo N. De Araújo (IC) [2], Camila K. Fenner (IC) [1], Cássia G. dos S. Ferreira (IC) [1], Mayara O. dos Santos (IC) [1], Nathalia S. Campanatti (IC) [1], Beatriz de O. Gomes (IC) [1], Eliane C. Pedrozo (PQ) [1]*

marcellexavier@usp.br; ecpedrozo@usp.br

[1]Department of Chemical Engineering, Lorena School of Engineering – EEL/USP; [2]Department of Biochemical Engineering, Lorena School of Engineering – EEL/USP

Keywords: *Active Methodology, Experimental Activities, Undergraduate Teaching In Engineering.*

Highlights

Verification of the applicability of Problem Based Learning (PBL) and Team Based Learning (TBL) active methodologies for new chemistry students at the Lorena School of Engineering.

Abstract

Teachers face a number of challenges during their classes, which one is to make teaching more dynamic in order to improve student learning. In turn, they find it difficult to relate the theoretical content taught to the practical part of the course. In order to overcome this problem, this study analyzed the applicability of active methodologies. This encourages critical thinking, problem-solving and the practical application of knowledge. These activities have been conceptualized in Problem Based Learning (PBL), where students learn by solving situations, and Team Based Learning (TBL), where students exercise their communication and argumentation skills in groups.

During the last few years, a series of activities were used for 28 General Chemistry I and II classes, from 6 engineering courses at EEL-USP, totaling 1228 students. From the first results obtained, it was found that the sequence of activities presented below is the one that resulted in the best performance of the classes in terms of improving grades and passing the course, in addition to greater student satisfaction with the classes: **(1)** Initial assessment of prior knowledge in chemistry: two activities, one individual and one in a group, are applied in the first week of class. Based on the results obtained, a series of reinforcement exercises are offered to students. The student can monitor the improvement in their performance in relation to the rest of the class throughout the semester. **(2)** Videos of theoretical classes and experimental practices are available on the Propaga Química YouTube channel. **(3)** During classes, demonstrative experiments are presented so that students can relate theoretical content with practice. **(4)** Students work in groups with simulations available online to answer specific questions from chemistry content previously studied in theory only. These simulations were used to assist in the understanding of topics related to the content of the discipline and to exemplify experiments that could not be carried out in our classroom, due to the complexity of the necessary experimental apparatus. **(5)** Before assessments, a group (for P1) and individual (for P2) preparatory activity is carried out with the content corresponding to the exam, using the Kahoot platform as a tool. This way, students were able to check whether they had sufficient knowledge to carry out the assessment and whether they were able to answer them in the appropriate time. **(6)** Students form groups to present a seminar, before the final exam, involving a case study. An experimental practice must necessarily accompany the presentation. The final project involves researching scientific articles where the application of theoretical chemical concepts learned during the semester was studied or applied directly or indirectly in more complex research. Thus, the student realizes the importance of the content for practical and professional life. The entire practical part was discussed and carried out in the presence of the teacher in advance.

Of the activities presented previously, those that employ the PBL and TBL concepts correspond to items 4, 5 and 6. Furthermore, some of the most important soft skills for engineers were studied to develop the activities: Effective communication; Team work; Conflict resolution; Efficient negotiation; Analysis and decision making; Flexibility and resilience; Effective leadership. The poster presentation will describe the details of the activities a qualitative and quantitative analysis of the results obtained, which managed to demonstrate the good receptivity of students to the use of active methodologies, and a significant improvement in performance when compared to previous classes where ABP and PBL were not used.

Acknowledgments

Programa Unificado de Bolsas da USP (PUB) and Lorena School of Engineering – EEL/USP

Área: EDU

APPROACHING THE COLIGATIVE PROPERTIES OF SOLUTIONS WITH HIGH SCHOOL STUDENTS THROUGH RESEARCH TEACHING

Laís Araújo de Almeida (PG)*,[1] Ivoneide L. C. Barros (PQ)[2], Ângela Fernandes Campos (PQ)[2]
ivoneide.lopes@ufrpe.br; laislsa20@gmail.com
[1]*Programa de Mestrado Profissional em Rede Nacional – PROFQUI/UFRPE;* [2]*Departamento de Química UFRPE*

Palavras Chave: Ensino por investigação, Química, Propriedades coligativas.

Highlights

Teaching the coligative properties of solutions with high school students through research teaching
Approach to colligative properties through an investigative teaching sequence.

Resumo/Abstract

No contexto escolar, são necessidades formativas atuais desenvolver autonomia, reflexão, postura, pensamento coletivo e trabalho cooperativo, com a adoção de protagonismo na construção do conhecimento. Sob esse olhar surge o ensino por investigação, que permite ao estudante agir de forma autônoma e cooperativa, priorizando a investigação de algo a ser resolvido, com ou sem orientação de um mediador (a depender da sua maturidade com esse tipo de abordagem), o que promove sua inserção de forma ativa nas atividades. Há de se mencionar ainda a dificuldade que os estudantes apresentam para aprender Química, sendo justificada a necessidade da elaboração de estratégias que observem e trabalhem com o tripé dos níveis do conhecimento químico: fenomenológico, teórico e representacional. O ensino por investigação possibilita essa articulação. Nessa perspectiva foi desenvolvida uma pesquisa com estudantes do ensino médio de uma escola pública do agreste de Pernambuco, a partir da proposição de uma Sequência de Ensino Investigativa (SEI) com ênfase no ensino das propriedades coligativas das soluções. Para justificar o tema escolhido foi realizado um levantamento bibliográfico dos últimos cinco anos (2019 - 2023) em 10 periódicos nacionais, sendo identificado entre os 24 artigos pesquisados uma escassez de temas relacionados a físico química e apenas um deles mencionando uma das propriedades coligativas, a osmose. A fim de obter um panorama das concepções dos estudantes sobre os conceitos correlatos da temática "propriedades coligativas" foi elaborado e aplicado um questionário para levantamento dos conhecimentos prévios. A SEI foi elaborada com base nas características fundamentais que devem estar presentes nas atividades investigativas mencionadas por Zômpero e Laburú (2011) e Gil-Pérez et al (1988). Assim, a SEI foi concebida com elementos da experimentação investigativa, com grau três de liberdade, na qual o professor fornece o problema, consistindo de cinco etapas: questionário diagnóstico; proposição de problema; levantamento de hipóteses e planejamento; execução procedimental e sistematização do conhecimento (CARVALHO et al, 2018). Para analisar os limites e potencialidades da abordagem didática foram elaboradas categorias a fim de verificar as habilidades investigativas desenvolvidas pelos estudantes, quanto a aprendizagem conceitual, procedimental e atitudinal. A análise do questionário para levantamento dos conhecimentos prévios mostrou que uma minoria (3%) sabia o que são as forças intermoleculares e como elas influenciam nas temperaturas de fusão e ebulição; sendo que apenas um estudante mencionou a propriedade crioscopia com confusão do conceito, o que permitiu constatar desconhecimento dos conceitos. Quanto à resolução dos problemas sugeridos pela SEI, houve formação de grupos e efetiva participação dos estudantes em todas as etapas da proposta. A partir da análise das respostas ao problema, no que diz respeito ao aspecto conceitual, notou-se que a maioria compreendeu que o soluto não volátil influencia no cozimento e congelamento das soluções, e na salada que murcha, porém não conseguiram utilizar a linguagem química, aludindo as propriedades coligativas tonoscopia, ebulioscopia, crioscopia ou osmose. Quanto ao aspecto atitudinal, mostraram-se colaborativos em todos os momentos, pois seguiram as recomendações, ativos e curiosos na execução de suas propostas e na apresentação de suas observações. Já no aspecto procedimental, curiosamente, alguns utilizaram materiais que não haviam sido delimitados, como panela de pressão, sendo aceitável pois foram criativos e testaram outros vieses. A maioria deles conseguiu pensar em algo dentro da proposta. Resultados da análise mostraram que a proposta da SEI, em colocar o estudante como protagonista, se utilizando da observação de fenômenos para compreensão de aspectos teóricos e representacionais foi bem aceita, pois se mostraram engajados e motivados, o que contribuiu para aprendizagem do tema propriedades coligativas, mesmo apresentando dificuldade em transpor para os termos científicos.

Referências

ZÔMPERO, A. F.; LABURÚ, C. E. ATIVIDADES INVESTIGATIVAS NO ENSINO DE CIÊNCIAS: ASPECTOS HISTÓRICOS E DIFERENTES ABORDAGENS. **Ensaio Pesquisa em Educação em Ciências (Belo Horizonte)**, v. 13, n. 3, p. 67–80, 2011.

GIL, D.; MARTÍNEZ-TORREGROSA Y SENET, F. El fracaso en la resolución de problemas de Física : una investigación orientada por nuevos supuestos. **Enseñanza de las Ciencias Revista de investigación y experiencias didácticas**, v. 6, n. 2, p. 131–146, 2006.

CARVALHO, A. M. P. Fundamentos teóricos e metodológicos do ensino por investigação. **Revista Brasileira de Pesquisa em Educação em Ciências**, p. 765-794, 2018.

Agradecimentos/Acknowledgments

Ao Programa de Mestrado Profissional em Química em Rede Nacional – PROFQUI/UFRPE e à CAPES.

Área:
EDU
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

A Química da Maionese

Nadia M. Comerlato* (PQ), Raoni S.B. Gonçalves (PQ), Claudia M. Rezende (PQ), José C. Barros Neto, (PQ), Rosa C. D.Peres (PQ), Raquel, Raquel F. Oliveira (FM), Pedro Henrique R. Conceição (IC), Giovanna L. V. Fonseca (IC), Flavia, R. Alvares (PG), Gustavo, Z. M. G. Oliveira (PG)

nadia.comerlato@iq.ufrj.br

[1]*Instituto de Química, UFRJ*

Palavras Chave: *Colóides, Emulsão, Culinária, Maionese.*

Highlights

The chemistry of mayonnaise. Experimental activity for pedagogical guidance on chemistry knowledge for high school students through culinary. Educational method to bring students closer to science in a daily and accessible way.

Resumo/Abstract

Neste trabalho é apresentado o relato de experiências didáticas no âmbito do projeto de extensão “Química na Cozinha”, do Instituto de Química da Universidade Federal do Rio de Janeiro (IQ/UFRJ). Este projeto tem como objetivo o direcionamento pedagógico acerca do conhecimento da química para alunos do ensino médio, associando-o a saberes e processos da culinária. Esse formato permite, de maneira conciliada, o entendimento de termos e assuntos da química, de forma mais palpável e dinâmica, aproximando os alunos da ciência de forma cotidiana e acessível. O projeto teve início em 2020, em meio à pandemia de COVID-19, sendo realizada uma série de oficinas remotas que permitiram com que os alunos realizassem “experimentos de química na cozinha” em suas casas e discutissem a ciência por trás das observações, com professores e alunos de graduação participantes do projeto. A partir de 2022, iniciou-se a realização de oficinas presenciais em escolas da rede pública estadual nas cidades do Rio de Janeiro e Duque de Caxias. Inicialmente, o ovo foi escolhido para a elaboração dos experimentos nas oficinas pois trata-se um ingrediente que permite investigar uma série de transformações químicas e físicas, bem como é utilizado numa infinidade de receitas corriqueiras presentes na alimentação dos estudantes, como a maionese, merengue e bolos.[1] Para as oficinas, o tema utilizado foi o da química da maionese. Cada oficina contou com a participação de 30 alunos, com o preparo da maionese executado por grupos de 5 ou 6 alunos, totalizando 5 oficinas. A cada grupo foram fornecidos os ingredientes (ovo, óleo de cozinha, sal e vinagre) e um liquidificador, juntamente com a receita para o preparo da maionese. Após a finalização do preparo, iniciou-se uma discussão com os alunos na qual foram abordadas as transformações que ocorreram após misturar os ingredientes e submetê-los a agitação, sendi possível investigar o processo de formação de um sistema coloidal, que no caso específico da maionese trata-se de uma emulsão. O aprofundamento da discussão foi realizado abordando-se os temas ligação química, polaridade das ligações químicas, interações intermoleculares e miscibilidade de líquidos, todos ligados à unidade temática matéria e energia da BNCC[2], explorando os objetos de conhecimento: misturas, transformações reversíveis e não reversíveis e propriedades físicas dos materiais e as habilidades (EF04CI01) Identificar misturas na vida diária, com base em suas propriedades físicas observáveis, reconhecendo sua composição; (EF04CI02) Testar e relatar transformações nos materiais do dia a dia quando expostos a diferentes condições (aquecimento, resfriamento, luz e umidade); (EF05CI01) Explorar fenômenos da vida cotidiana que evidenciem propriedades físicas dos materiais – como densidade, condutibilidade térmica e elétrica, respostas a forças magnéticas, solubilidade, respostas a forças mecânicas, entre outras. Com isso, foram destacados aspectos relativos ao comportamento de coloides, como a natureza das partículas em sua fase dispersa, e o comportamento termodinâmico da mistura, além de propriedades como a distribuição de tamanho e formato das partículas de óleo na emulsão, destacando-se a importância do entendimento de cada um. Durante as oficinas, constatamos que os alunos demonstraram muito interesse no tema escolhido e participaram ativamente da discussão acerca das transformações observadas. Espera-se que este tipo de atividade contribua para que os alunos desenvolvam um pensamento científico no estágio inicial de aprendizado da química.

1. Mc Gee, H., Comida e Cozinha: Ciência e Cultura da Culinária, 2ª Edição, Editora WMF Martins Fontes, 2014, pg. 651-70.

Agradecimentos/Acknowledgments

À Pró-Reitoria de Extensão da UFRJ pela concessão de uma bolsa PROFAEX no período 2022-2023.

Área: EDU

Artificial intelligence and Chemistry teaching: reflections on Bard and ChatGPT in the description of chemical concepts

Bruno Silva Leite (PQ).[1]*. brunoleite@ufrpe.br

[1]*Departamento de Educação, UFRPE*

Keywords: *Artificial intelligence, Chemistry teaching, Bard, ChatGPT, Chemical concepts.*

Highlights

An investigation was carried out on the ability of Bard and ChatGPT to answer questions about the definitions of chemical concepts, identifying their potential and limitations.

Abstract

Contemporary society in the year 2023 has been significantly impacted by the advancement of Artificial Intelligence (AI). In education, it was no different, the impact that AI had and its implications on the teaching and learning process were observed. The emergence of Bard (a large language model chatbot developed by Google AI, trained on a massive dataset of text and code) and the evolution of ChatGPT (a large language model that generates convincing sentences by mimicking the statistical patterns of language in a vast database of text collated from the internet) caused great excitement and concern among teachers, educational managers, and students. In this context, this research aimed to investigate the potential and limitations of the Bard and ChatGPT tools. We evaluated their performance in terms of their ability to answer questions about chemical concepts. For this, we analyzed Bard and ChatGPT's responses about five chemical concepts (Covalent Bond, Substance, Isomerism, Stoichiometry, and Atom) and compared them with definitions present in literature (scientific articles and books) and on the internet. The results show that Bard's answers present more objective and understandable explanations, inserting extra topics and explanations. Regarding ChatGPT responses, it is observed that this AI presents a compilation of definitions already available in the literature and on the internet, such as websites, digital repositories, scientific articles published in virtual journals, and books. Concerning the definition of the five chemical concepts, Bard presented explanations that were more coherent with the concepts found in the literature. ChatGPT presented, the investigated chemical concepts, and definitions that can be used for the process of building chemical knowledge. However, ChatGPT had difficulties in elucidating the concepts of chemical bonding (presenting a new type of bonding), isomerism (mixing planar and geometric isomerism), and chemical equilibrium. Of the five concepts, Bard superficially presented the definition of isomerism; however, ChatGPT also had difficulties in defining this concept. In an overview, texts written by Bard are more easily identified as non-human language, unlike ChatGPT, which has the ability to generate fluent language, churning out sentences that are increasingly hard to distinguish from texts written by people. Regarding limitations, Bard, in his answers, presented simple and objective topics, in which, in some cases, details about the definition of the respective concept were missing. One of the limitations observed is that ChatGPT's answers may present plagiarism, raising concerns about whether the student/teacher will be able to recognize a copied text or if the AI will recognize the ethical nuances of scientific research. The Bard and ChatGPT have excellent linguistic capabilities but are limited in logic, abstraction, and high-level reasoning, and are not capable of maintaining a coherent discussion that can be achieved through teacher-student and student-student interaction. Alongside these concerns are also questions about how students can use chatbots to build their knowledge and how teachers can make use of AI for teaching. That said, we understand that more studies need to be conducted in-depth on the real impact of AI on teaching, especially in Chemistry teaching. These are challenges that come with the advent of technologies in education.

Acknowledgments

To CNPq (proc. 422587/2021-4), FACEPE (proc. APQ-0916-7.08/22), LEUTEQ, UFRPE.

Área: EDU

As abordagens utilizadas por professores/as da área de ciências da natureza após os resultados das avaliações em uma escola pública em Minas Gerais

Edson Luiz Campos Cruz (IC)[1*]; Juliana Maria Sampaio Furlani (PQ)[1]

yuyidage05@gmail.com; jufurlani@unifei.edu.br

[1]*Instituto de Física e Química, Universidade Federal de Itajubá*

Palavras Chave:*(Avaliação, Ciências da natureza, Ensino Médio, Objetivos avaliativos).*

Highlights

The approaches used by teachers in the area of natural sciences after the results of assessments in a public school in Minas Gerais.

"When a student does not perform as expected on an assessment, how do you address that situation?" The data showed three types of teaching approaches: student-centered, teacher-centered and pedagogical intervention-centered.

Resumo/Abstract

A avaliação educacional desempenha um papel crucial nos processos de ensino e aprendizagem da educação formal, fornecendo informações valiosas para orientar o planejamento de ensino e as práticas pedagógicas em sala de aula. Realizou-se uma pesquisa exploratória com o objetivo conhecer estratégias e procedimentos de professores da área de ciências da natureza em relação às suas escolhas de tipos de avaliação e dos instrumentos avaliativos. Foi aplicado um questionário on-line contendo onze perguntas, que foi respondido por cinco dos seis docentes da referida área, que trabalham em uma escola pública estadual de um município localizado no Sul de Minas Gerais. Os dados foram analisados por meio da Análise Textual Discursiva (Moraes; Galiazzi, 2011). Os professores foram identificados pela letra P e as professoras por Pa, seguidos de um número de 1 a 5. Neste resumo, apresentam-se os resultados relacionados a apenas uma das perguntas do questionário.

Pergunta apresentada: *"Quando um aluno não atinge o desempenho esperado em uma avaliação, como você aborda essa situação?"* A partir da leitura das respostas, categorizou-se três tipos de abordagens em relação à recuperação da aprendizagem. A abordagem centrada no aluno foi a mais prevalente, com três das cinco respostas, nas quais os professores/as enfatizam a importância de identificar as dificuldades e necessidades específicas dos alunos. Por exemplo, a resposta do P1: *"Conteúdo direcionado a dificuldade (revisão/ recuperação)"* sugere que o professor deve adaptar o conteúdo e as atividades de aprendizagem para atender às necessidades dos alunos. Já a Pa2 respondeu que *"Faço correção acompanhada, e oriento a estudar e se dedicar um pouco mais"* sugere uma intervenção mais individualizada, com base na análise conjunta das respostas consideradas erradas na avaliação aplicada. P3, por sua vez, respondeu que *"Tentando verificar as dúvidas. Ajudando com consulta. Mas não tem muita efetividade por falta de interesse dos alunos"*. Nota-se que o professor, apesar de retomar o assunto da avaliação, não tem considerado que essa ação está contribuindo para a melhoria da aprendizagem de seus estudantes, apontando que eles têm pouco interesse no processo. A abordagem centrada no professor foi assim identificada a partir da resposta de P5: *"Sim. Faz-se novas intervenções com objetivo de recompor a aprendizagem do aluno"*. Diferentemente das respostas anteriores, nesta categoria o professor se percebe como o responsável pela aprendizagem. Por fim, identificou-se uma abordagem centrada na intervenção, com uma resposta destacando a importância da intervenção pedagógica para ajudar os alunos que estão com dificuldades. Assim, a resposta da Pa4: "Realizo a recuperação e, quando necessário, intervenção pedagógica" sugere que a professora deve fornecer aos alunos oportunidades adicionais de aprendizagem e suporte pedagógico.

Pretende-se dar continuidade a esta pesquisa a partir de entrevistas com os professores/as respondentes, visando ampliar o entendimento das relações entre os processos avaliativos e o planejamento de ensino desses docentes.

Referência: MORAES, Roque; GALIAZZI, Maria do Carmo. Análise textual discursiva. Ijuí, RS: Ed. da UNIJUÍ, 2011)

Agradecimentos/Acknowledgments

Às professoras e professores que dedicaram seu tempo para responder ao questionário e contribuir para a pesquisa em ensino de ciências.

Área: EDU
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Assessment of environmental perception and education on Climate Change within the population of the city of Rio de Janeiro

Cleyton Martins da Silva (PQ),[1,2] Dalton Domingues de Carvalho Neto (PG).[1]

martins.cleyton@gmail.com; daltondomingues63@gmail.com

[1]Universidade Veiga de Almeida, UVA; [2]Instituto Nacional da Propriedade Industrial, INPI.

Palavras-chave: greenhouse effect, global warming, cities, environmental impacts, extreme weather events.

Highlights

Climate change has serious impacts on cities. Part of the population does not correctly understand climate change, its causes, consequences and control and mitigation measures. Environmental education and the role of Chemistry are fundamental to understanding and finding solutions to today's major environmental issue.

Abstract

Several evidences show that climate change and its impacts constitute one of the biggest environmental issues today, directly affecting different segments of society in addition to having consequences for the environment and biodiversity. Climate change is mainly due to the intensification of the Greenhouse Effect, caused by the increase in greenhouse gas emissions, especially carbon dioxide (CO_2), arising from various anthropogenic activities, especially those involving the burning of fossil fuels (production and use of energy, transport, industrial processes) and deforestation from fires. Climate change has brought numerous impacts to the environment and its biodiversity.[1] In cities, in particular, it is possible to observe the occurrence of floods, storms, landslides, fires, waves and heat islands, among other consequences.[2] However, some of these impacts may also be associated with other natural or anthropogenic issues, and are not always understood or easily correlated to climate change by the entire population, highlighting the need for environmental education so that the population could understand its individual and collective contribution. In this context, the role of Chemistry and its knowledge in understanding environmental phenomena that occur with human influence stands out. Based on this, the main objective of this study was to evaluate the climate change perception of the Rio de Janeiro population, as well as to understand the role of environmental education and Chemistry in this issue. The study was carried out through survey research using online questionnaires (project submitted and approved by the research ethics committee - CAAE 65501922.1.0000.5699).

182 valid responses were considered for the questionnaires administered, and the socioeconomic profile observed is shown in Table 1. Approximately 98% of the population understands human actions as the main causes of climate change and the severity of its consequences, with emphasis on the city of Rio de Janeiro, the increase in the frequency and intensity of rain, as well as such as extreme heat waves. In spite of that, about 50% of the responses showed that important environmental chemical concepts, such as stratospheric ozone depletion and urban air pollution, are misunderstood and often mistakenly associated with the greenhouse effect and climate change. It is also observed that there is a lack of correct knowledge regarding the nomenclature of Greenhouse Gases (GHG), their chemical representations and emission sources.

Table 1 - Socioeconomic profile

Age Group (%)		Gender (%)	
16 - 25 years	12.0	Feminine	49.4
26 - 45 years	58.0	Masculine	48.4
46 - 75 years	26.0	Others	1.6
above 75 years	4.0		
Education (%)		**Social Class (%)**	
Primary	0.5	A	10.0
High Scholl	8.8	B	49.0
University	45.1	C	35.0
Postgraduate	45.6	D	6.0

The study pointed out that the level of education is directly correlated with a greater and more assertive understanding of climate change, highlighting the need and urgency for environmental education actions, especially those conducted in educational institutions. Chemistry teaching regarding GHG, its physical-chemical characteristics, emission sources and impacts, and scientific research and dissemination are fundamental for a better and greater depth of understanding about the phenomenon and awareness of the population in searching concrete and effective actions to solve today's major environmental problem. Also, atmospheric chemical processes, as well as the main atmospheric pollutants and its effects, in troposphere and stratosphere should be further discussed in formal and informal education.

References:

1. IPCC, 2022 https://doi.org/10.1017/9781009325844;
2. Sattherwaite, D. Cidades e mudanças climáticas. Newspaper Essay, 2008.

Acknowledgments

Authors would like to thank FAPERJ, FUNADESP and Veiga de Almeida University (UVA).

Área: EDU

Atividade de extensão como ferramenta para desmistificar o uso de produtos domissanitários

Luísa H. R. O. Vargas (IC)[1*], Maria Júlia N. Pegorelli (IC)[1], Caroline Y. Fukuti (IC)[1], Bruno R. Feitosa (IC)[2], Beatriz M. Santos (IC)[3], Leonardo Sitta (IC)[1], Erika Watanabe (TC)[2], Janksyn Bertozzi (PQ)[2], Alessandra Stevanato (PQ)[2]

luisahelenavargas@alunos.utfpr.edu.br; stevanato@utfpr.edu.br

[1]Departamento Acadêmico de Engenharia de Materiais, UTFPR – Campus Londrina; [2]Departamento Acadêmico de Química, UTFPR – Campus Londrina; [3]Departamento de Engenharia Química, UTFPR – Campus Londrina.

Palavras-Chave: *Pandemia, Vírus, Escola, Higiene, COVID-19.*

Highlights

Extension activity as a tool to demystifiy the use of hosehold cleaning products. Promoting post-pandemic hygiene, curbing viral spread, enhancing quality of life.

Resumo/Abstract

Durante a pandemia de SARS-CoV-2, evidenciou-se o aumento expressivo nas vendas de álcool 70%, sabão líquido e antisséptico para as mãos em 2020. Assim, destaca-se a importância de compreender como esses produtos são utilizados no combate ao coronavírus por meio do aprofundamento dos estudos de química, oficinas de ensino e campanhas informativas. Ressalta-se a necessidade de persistir tais ações mesmo após o fim da emergência de saúde declarada pela Organização Mundial da Saúde (OMS) em 2023, justificada pelo histórico de surtos virais e potencial de contaminação, especialmente em ambientes como escolas. Esse projeto de extensão propõe o desenvolvimento de estratégias de educação sobre hábitos de higiene na comunidade local, visando impacto social e utilizando a experimentação no ensino de ciências como ferramenta de transformação. O trabalho foi dividido em 3 etapas: 1) montagem de materiais didáticos e dos produtos a serem distribuídos nas escolas; 2) divulgação e apresentação da oficina e 3) análise dos dados. Na primeira etapa, os materiais didáticos construídos foram cartilhas contendo informações sobre a diferença entre pandemia e epidemia, a função do álcool 70% e do sabão (a base), e como estão presentes nos produtos domissanitários causando a destruição do vírus, além de questionários sobre os assuntos abordados pelo projeto para avaliação prévia e pós-apresentação. Além disso, foram preparados os produtos distribuídos, que incluem álcool 70%, sabonete líquido e sabonete em barra. Para dar início a segunda fase, foi realizada uma conversa com a equipe pedagógica de quatro colégios públicos da cidade de Londrina – PR para o atendimento das turmas de ensino médio. Foram aplicadas três questões*: "1) Quais doenças são causadas por vírus"; "2) Qual produto domissanitário é recomendado para a limpeza de superfícies" e "3) Como as bases agem na estrutura dos vírus"*. Os questionários foram aplicados antes e após as oficinas. O primeiro colégio visitado foi o Colégio Estadual Josemaria Escrivá, onde foram atendidos 88 alunos das turmas de 1º, 2º e 3º anos do ensino médio, houve um aumento da porcentagem de acertos de 75,38% para 83,71% após a oficina. A Escola Estadual Fernando de Barros Pinto foi a segunda a ser atendida, na qual inicialmente obtivemos uma porcentagem de acertos de 68,67% e de 88,67% após a aplicação da oficina. A terceira escola visitada foi a Escola Estadual Professora Behair Edna Mendonça, na qual obtivemos uma porcentagem de acertos prévios de 59,52%, aumentando para 75,60% e por fim, aplicamos a oficina em uma turma de Ensino de Jovens e Adultos (EJA) do Colégio Estadual Professor José Carlos Pinotti, obtendo uma porcentagem de acertos inicial de 55,00%, aumentando para 60,00%. Desta forma, no ano de 2023, o projeto impactou um total de 214 alunos. Assim, foi possível observar que o método de avaliação e as estratégias desenvolvidas pelo projeto para o aprendizado desses alunos quanto a importância e conscientização da higiene foram relevantes, ressaltando a motivação por parte dos alunos em participar de atividades lúdicas e em grupo.

Agradecimentos/Acknowledgments

Agradecemos ao Edital 01/2023 – Conjunto PROREC/PROGRAD pela concessão da bolsa para o desenvolvimento do projeto, a Universidade Tecnológica Federal do Paraná – Campus Londrina e ao Departamento Acadêmico de Química, ao Colégio Estadual Josemaria Escriva, à Escola Estadual Fernando de Barros Pinto, à Escola Estadual Professora Behair Edna Mendonça e ao Colégio Estadual Professor José Carlos Pinotti pela disponibilidade e por abraçarem esse projeto.

Área: EDU
Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Attributes of games for learning and their relationship with Roger Caillois' taxonomy of games: an analysis of pedagogical games published in scientific journals.

Sara Romeiro Rodrigues dos Santos (IC), Larissa Garcia Velasco (PG), Felipe Augusto de Mello Rezende (PQ), Nyuara Araújo da Silva Mesquita (PQ) e Márlon Herbert Flora Barbosa Soares (PQ)*

marlon@ufg.br; nyuara@ufg.br

Laboratório de Educação Química e Atividades Lúdicas – Instituto de Química – Universidade Federal de Goiás.

Palavras Chave:*(atributos dos jogos; jogos pedagógicos; taxonomia de jogos).*

Highlights

We analyzed the attributes of games present in scientific articles and how they can improve the educational potential of a pedagogical game in chemistry teaching.

Resumo/Abstract

A partir de uma pesquisa empírica, Bedwell et al. (2012) fazem uma proposição de taxonomia abrangente dos jogos na qual se permite uma relação do processo de ensino e aprendizagem com os *Atributos* presentes nos jogos. Para os autores, esta proposta de taxonomia pode fornecer aos pesquisadores que trabalham com o uso da ludicidade na educação, uma ferramenta importante para organizar os trabalhos de investigação, uma vez que analisadas, as relações *Atributo*-resultado identificadas em aplicações dos jogos em salas de aula, elas podem auxiliar a comunidade científica a construir um modelo integrado de aprendizagem em jogos pedagógicos e conduzir a esforços consolidados no âmbito da aprendizagem baseada na ludicidade. Bedwell et al. (2012) nos trazem 19 *Atributos*, a saber: Adaptação, Avaliação, Desafio, Conflito, Controle, Fantasia, Interação (equipamento), Interação (interpessoal), Interação (social), Linguagem/comunicação, Localização, Mistério, Peças ou jogadores, Progresso, Surpresa, Representação, Regras/objetivos, Segurança e Estímulos sensoriais. A partir destes *Atributos*, Rezende e Soares (2023) fizeram uma articulação teórica entre estes *Atributos* e as características filosóficas na perspectiva de Roger Caillois, mostrando as possibilidades didáticas para o ensino de química e como estas diminuem o paradoxo do jogo educativo. A partir destes estudos, o objetivo deste trabalho foi determinar, por meio de uma análise documental, quais *Atributos* dos jogos estão presentes em artigos científicos que fizeram proposição de jogos pedagógicos para o ensino de química nas revistas Química Nova na Escola (2014-2023) e Revista Eletrônica Ludus Scientiae (2017-2023) e se estes se relacionam com a taxonomia de Roger Caillois (2017). A análise dos artigos selecionados foi realizada por meio da Análise de Conteúdo de Bardin. Foram selecionados 27 artigos em Química Nova na Escola e 38 artigos na Revista Eletrônica Ludus Scientiae. Os *Atributos* 'regras', 'controle', 'localização', 'desafio', 'interação (equipamento)', 'linguagem/comunicação', 'peças ou jogadores' e 'progresso' foram identificados em todos os trabalhos analisados. Entendemos que isso ocorreu, pois estes são atributos que estão intrinsecamente ligados às características dos jogos, conforme definido por Caillois: *Alea* (jogos de sorte/azar), *Agon* (jogos de competição), *Mimicry* (jogos de representação) e *Ilinx* (jogos de vertigem). No entanto, observamos que *Atributos* tais como 'avaliação' e 'conflito' estão ausentes, principalmente em jogos de *Agon* e de *Alea*. Tal aspecto prejudica a interação entre jogadores e pode diminuir o potencial educativo do jogo proposto. Dentre as classes de Caillois, a que apresenta maior número de atributos é a Mimicry, o que implica que se deve fazer maior proposição de jogos de representação, considerando-se que quanto maior o número de *Atributos* presentes, maior o potencial educativo do jogo pedagógico.

REZENDE, F. A. M.; SOARES, M. H. F. B. **Ensino & Multidisciplinaridade**, p. e1023, 2023.
BEDWELL, W. L. et al. **Simulation and Gaming**, v. 43, n. 6, p. 729–760, 2012.
CAILLOIS, R. **Os jogos e os homens**. Petrópolis: Vozes, 2017.

Área: EDU

Can I picture what you see? Visualizing mental representations of molecules

Guilherme A. Marson (PQ),[1] Rodrigo A. Consoli (PG), Eduardo Colli(PQ),[2] Raimundo da S. Soares Jr (PG),[3] João R. Sato (PQ)[3]

gamarson@iq.usp.br

[1]Depto de Química Fundamental, IQUSP; [2]Depto de Matemática Aplicada IME USP; [3]CMCC - UFABC

Palavras Chave: cognition, visualization, visual representations, eye-tracking, mental rotation.

Highlights

Images of the likely mental representation of molecular models were generated from a novel method combining 3D mapping of quantitative measurements of physical rotation and gaze fixation.

Abstract

INTRODUCTION: The mental processes involved in the perception, manipulation, and understanding of molecular models are an ongoing topic of research in chemistry education. One challenge is to examine the mental models related to the interpretation of external models[1]. In this work we use eye-tracking measures to obtain an image that we believe approximates the internal representations of molecular models. We rely on the fact that eye movement is controlled by internal cognitive processes that integrate the sensorimotor system, the nature of the objects observed, and the context in which the observation takes place [2,3]. Therefore, visual attention data of an external molecular model may provide a good measure of its internal counterpart. **METHODS:** We recorded physical rotation and gaze fixation (GF) during a task involving two representations of the same 3D molecular model: a static one, as **r**eference, *Rs*, (Fig A) e an interactive one, the **w**orking model, *Wi*. The task was rotating *Wi* so it got as close as possible to *Rs*. An ordinary laptop equipped with a mouse and eye-tracking device was used. A novel method developed by our group was used to map GF data over the 3D model and generate images of the likely internalized models (Figs B1 and B2, colored in transparency scale).

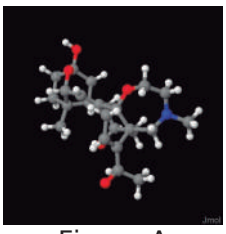


Figure A

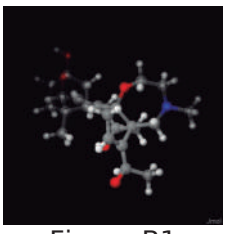


Figure B1

Figure B2

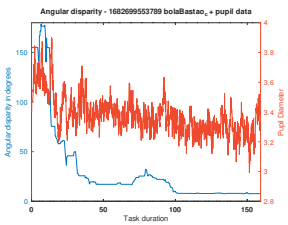


Figure C1

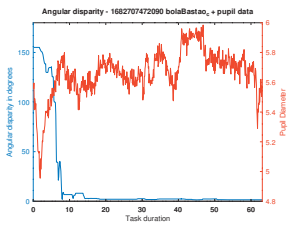


Figure C2

RESULTS AND DISCUSSION: Data from the task solving process for two individuals (1 and 2) are shown in Figures B1, B2, C1, and C2. The images of the cumulative GF for *Wi* (Figs. B1 and B2) indicate that each person internalizes distinct regions of the same external model. Relevant differences are also observed in the interaction with the model (blue line - rotational difference between *Rs* and *Wi* over time) and pupil dilation (red line - related to cognitive effort), shown in Fig. C1 and C2. The process analysis (click and see an animation of the task solving process in the supplemental material) suggests that solving the task with interactive models apparently requires recursively repeating steps similar to those involved in tasks with static images[3]: searching and comparing regions in *Rs* and *Wi*, followed by interacting with *Wi* for adjustment. However, this is still to be tested in broader studies. **CONCLUSION:** the present method is a promising addition to the repertoire for studying the role of molecular models in chemical education. We consider combining qualitative research methods focusing on interpreting chemical information from virtual and physical molecular models.

REFERENCES: 1: Harle & Towns, *J. Chem. Ed.*, 2011, 88(3) 351; Stieff et al. *J. Ed. Psychol.*, 2018, 110(8), 1160; 2:, Kümmerer M.& Bethge M., *Ann. Rev. Vis Sci* 2023, 9(1), 269; 3: Xue et al., *Sci. Reports* 2018,7, 10076.

Acknowledgments

The authors are thankful to CAPES, USP and UFABC. João R. Sato received support from FAPESP (Grants Nos. 2018/21934-5, 2018/04654-9, and 2023/02538-0).

Área: EDU

Changing students' perception of nature of Science by a Freirean's Three Pedagogical Moments teaching intervention

Sancler C. Vasconcelos (PG)[1], Marcelo M. Marques (PQ-FM)[2], Joana G. Aguiar (PQ)[3*]

sanclervasconcelos@id.uff.br; joana_aguiar@id.uff.br

[1]Programa de Pós-Graduação em Química, UFF; [2]Colégio Universitário Geraldo Reis, UFF; [3]Programa de Pós-Graduação em Ensino de Ciências da Natureza, UFF

Keywords: *Nature of Science, Science education, Freirean's Three Pedagogical Moments, Inquiry-based learning*

Highlights

This work discusses the changes in students' perception regarding the nature of science before and after a teaching intervention structured in the Freirean's Three Pedagogical Moments.

Abstract

Although we live in a society that is widely dependent on science and technology, the increase in scientific illiteracy is a fact among the younger generations. The deficiency in the dissemination of the diverse topics in science and the lack of comprehension on how science is made are key factors that contribute to the growth of pseudoscience, meaning that it is necessary to bring science closer to the population, allaying the authoritarian and dogmatic views on science, thus making learning more feasible.[1] In that matter, the Freirean's Three Pedagogical Moments (3 PMs)[2] was chosen as teaching methodology to involve high school students in an active manner for the construction of knowledge and critical thinking. This work uses a didactic sequence based on an inquiry-based activity to help students to comprehend the scientific method and the nature of science. The sequence was structured in: 1st PM – Problematization: a dialogued expository class focused on pseudoscience; 2nd PM – Knowledge Organization: an inquiry-based task called "Black Box", which the students had to formulate hypothesis and to perform tests to discover the shape of a material inside a sealed recipient; 3rd PM – Application of Knowledge: creation of a podcast with the themes discussed in class. The students (n = 19) were asked to judge 10 statements (Table 1) using a five-item Likert scale (from totally disagree to totally agree) applied before and after the teaching intervention. Data analysis were conducted through the weighted average of the scale, depicted in a bar chart (Figure 1). Results indicated a decreasing belief that science cannot be changed, a dogmatic view on science, and a better understanding about the importance of a scientific community and their non-empirical bias. In contrast, students had problems to assimilate the topics related to the neutrality of the science.

Table 1: Summarized Statements

	Summarized Statements
S1	Science cannot be modified nor challenged
S2	Science brings absolute truths
S3	Science is an ongoing process that goes through revisions
S4	Scientific theories are based on the opinion of scientists
S5	Scientists personal experiences are not considered during research
S6	Scientific explanations of natural phenomena are obtained using rational evidence
S7	Theories based on personal beliefs can be considered scientific theories
S8	Scientific discoveries are useful in making people's lives easier
S9	A theory is only scientifically proven when verified by different groups of scientists
S10	Most scientific theories can be experimentally proven and replicated

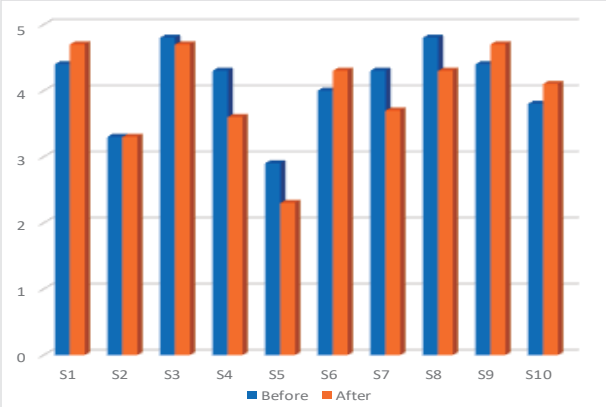


Figure 1: Average agreement level

[1]Miguel, M. L.; Santos, L. J. dos; Souza, L. A. M. de. Algumas percepções de estudantes do ensino médio sobre ciências, pseudociência e movimentos anticientíficos. *Investigações em Ensino de Ciências* **2022**, *27* (1), 191. [2]Urel, D. E. Paulo Freire e os Três Momentos Pedagógicos. *Scientia Naturalis* **2022**, *4* (1), 49–59.

Acknowledgments

JGA acknowledges FAPERJ for the funding (Process SEI 260003/013046/2021); CNPq;

Área: EDU

Chemistry in the final years of Elementary School: union between BNCC and the Curricular Document of the State of Pará

Danielle R. M. Costa (PQ),[1] Marília M. Sagica (PG),[2]*

danymont@uepa.br; marilia.sagica@aluno.uepa.br

[1]Departamento de Ciências Naturais, UEPA, Campus VII- Marabá; [2]Mestranda do Programa de Pós-Graduação em Educação em Ensino em Ciências na Amazônia, UEPA.

Keywords: Basic Education, Guiding document, Pedagogical practices, Chemical knowledge.

Highlights

The present work aims to link the BNCC and the Curricular Document of the State of Pará in relation to chemical knowledge present in the final years of Elementary School.

Resumo/Abstract

A abordagem dos conhecimentos químicos no âmbito da disciplina de Ciências da Natureza (CN), anos finais do Ensino Fundamental (EF), é de grande importância que esteja relacionada a outras áreas curriculares e seja fundamentada para compreender as interações e aplicações da química no mundo real. O presente estudo visa realizar a articulação entre os preceitos estabelecidos pela Base Nacional Comum Curricular (BNCC) e o conteúdo curricular proposto pelo Documento Curricular do Estado do Pará, com foco na esfera dos conhecimentos químicos referentes aos anos finais do EF. De acordo com a BNCC a área de Ciência da Natureza apresenta competência especificas para o desenvolvimento dos alunos associados ao componente curricular. Nessa perspectiva, o EF segundo a BNCC divide-se em anos iniciais e anos finais que possui três unidades temáticas: Matéria e Energia, Vida e Evolução e Terra e Universo, os quais que estão relacionados a objetos de conhecimento e habilidades (Brasil, 2018). O Estado do Pará possui seu próprio documento de referência curricular, que tem como objetivo orientar a prática pedagógica nas escolas estaduais considerando as especificidades locais e as demandas educacionais do estado. Na área de CN, assim como em outras áreas do EF, foram definidos em eixos estruturantes. Cada um desses eixos é subdividido em subeixos que direcionam os objetivos de aprendizagem e as habilidades a serem desenvolvidas pelos alunos. Mediante a revisão dos documentos notou-se que a articulação do documento do estado com a BNCC, para o ensino dos conceitos químicos, é observada quando analisado os 4 grandes eixos estruturantes que compõem o documento do estado com as competências específicas de CN para o EF da BNCC. Um exemplo é o eixo 1 (Espaço/tempo e suas transformações). Essa abordagem visa compreender a natureza como um sistema dinâmico, destacando o papel dos seres vivos, especialmente os humanos, como agentes de transformação no mundo (DCEIEFEPará, 2019). Além disso, busca-se o entendimento do funcionamento do corpo humano, suas transformações e os impactos de substâncias prejudiciais à saúde, bem como a exploração do sistema solar, a composição da Terra, fenômenos atmosféricos e suas influências na dinâmica da vida. As competências específicas da BNCC (2018, p. 324) de CN são observadas no eixo 1 são as competências 2 e 3. As articulações entre os documentos possibilitam adaptar as diretrizes nacionais às necessidades locais, garantindo uma educação alinhada com a realidade da comunidade e promovendo um ensino mais eficaz.

BRASIL. Ministério da Educação. **Base Nacional Comum Curricular. Brasília**, 2018.
PARÁ, Governo do Estado do**. Documento Curricular para Educação Infantil e Ensino Fundamental do Estado do Pará**. CEE: Belém. 2019.

Agradecimentos/Acknowledgments

Área: EDU

Chemistry teaching and review study: RASBQ abstracts review.

Ana Caroline Ferreira Garcia (PG)[1], Rodrigo Campos dos Santos (PG)[2], Keila Bossolani Kiill (PQ)[3]

ana.garcia@sou.unifal-mg.edu.br;

[1]*Programa de Pós-Graduação em Educação - UNIFAL-MG*
[2]*Programa de Pós-Graduação em Química - UNIFAL-MG*
[3]*Instituto de Química - UNIFAL-MG*

Palavras-Chave: estudo de r*evisão, anais, RASBQ, ensino de química.*

Highlights

Over 18 years, 17 review investigations were found, representing 1.2% of the total 2,060 reviews. Some of the themes covered include argumentation, games, and gender.

Resumo/Abstract

Os estudos de revisão têm apresentado relevância pela possibilidade de retomar ou expandir as investigações, permitindo aos pesquisadores identificar lacunas sobre a temática. Além disso, apresentam como objetivo principal o levantamento, o mapeamento e a análise do que está publicado na literatura, com o intuito de promover novas discussões e abordagens relacionadas às necessidades para um determinado tema (CRUZ; FERREIRA, 2023). Diante disso, este trabalho objetiva realizar o levantamento e identificar quais são as temáticas dos estudos de revisão publicados nos anais das Reuniões Anuais da Sociedade Brasileira de Química (RASBQ), especificamente na área de Ensino de Química (EDU). Considerando a importância desses estudos para o reconhecimento de temáticas a serem revisadas, pontua-las permite evidenciar quais as possibilidades para futuros estudos de revisão. Para traçar o panorama dos estudos de revisão, foi conduzido um levantamento nos anais das reuniões disponíveis *online*, ou seja, a partir da 29ª edição, referente ao ano de 2006. O levantamento seguiu por meio da busca com as palavras-chave: "revisão", "análise", "levantamento", "estado da arte" e "panorama". O Quadro 1 detalha a relação entre o número total de trabalhos publicados e a quantidade de trabalhos sobre revisão para cada ano.

Quadro 1: Número de trabalhos de revisão publicados nos anais das reuniões da SBQ por ano.

Ano	Nº de documentos				
	publicados nos anais	de Revisão		publicados nos anais	de revisão
2006	130	0	2015	108	**1**
2007	164	**1**	2016	71	**3**
2008	**INDISPONÍVEL***		2017	**INDISPONÍVEL***	
2009	173	0	2018	66	0
2010	183	**1**	2019	72	**1**
2011	432	**1**	2020	61	**3**
2012	150	**1**	2021	16	0
2013	158	0	2022	61	**1**
2014	161	**2**	2023	54	**2**
Quantidade total de trabalhos: 17					

Fonte: das autoras.
*arquivo indisponível. Acesso em: 16/01/24.

Pelo levantamento na área EDU, identificou-se 17 trabalhos de revisão no período de 2006 a 2023. Os arquivos dos anos de 2008 e 2017 não estão disponíveis para acesso. Se comparado ao número total de trabalhos publicados, esse número representa 1,2%, ou seja, menos de 5%, o que pode ser considerado um número reduzido diante da relevância dos trabalhos de revisão para a identificação de lacunas para futuras investigações. Outro resultado relevante é a identificação das temáticas abordadas nestes estudos de revisão, sendo eles: a. produção de conhecimento (2007); b. argumentação (2010); c. pesquisa no Ensino de Química (EQ) da USP (2011); d. jogos em meio ambiente (2012); e. ensino de quimiometria (2014) e produção acadêmica PPGEC (2014); f. Biotecnologias (2015); g. Gênero (2016), experimentação (2016) e ensino de reações redox (2016); h. aspectos pedagógicos na seção de experimentação da QNESC (2019); i. orientação na pós-graduação (2020), formação docentes indígena e as Ciências da Natureza (2020) e estudo de caso (2020); j. viés do enfoque contextual dos artigos da seção Química e Ciências da QNESC (2022); k. realidade aumentada e virtual (2023) e interdisciplinaridade (2023). Os resultados evidenciaram a possibilidade de ampliação de temáticas para serem abordadas na forma de revisão, como por exemplo, abordar o cenário das investigações sobre a formação de professores de química e o uso de sequências didáticas nas publicações dos anais das RASBQ.

CRUZ, F. R.; FERREIRA,J. L. Estudos de revisão em educação: estado da arte e revisão sistemática. **Revista Espaço Pedagógico**, v. 30, e11512, 2023. Disponível em: https://doi.org/10.5335/rep.v30i0.11512.

Agradecimentos/Acknowledgments

Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – Brasil (CAPES) – Código de Financiamento 001. Programas de Pós-Graduação em Educação e Química da UNIFAL-MG e LAPEQUIM.

Área: EDU

Ciência e arte: histórias em quadrinhos e oficinas artísticas sobre o tema formigas cortadeiras

Adriana Y. Iwata (PQ)*[1], Maria Fatima G.F. Silva (PQ),[2] Karina O. Lupetti (PQ),[3].

adrianaiwata@gmail.com

[1,2,3]*Departamento de Química, UFsCar.*

Palavras Chave: Histórias em quadrinhos, Divulgação Científica, Meio ambiente, Formigas cortadeiras.

Highlights

Science and art: comic books and art workshops about leaf-cutter ants. This project proposed using comics to inform the public about leaf-cutter ants. The activities involved the creation of comic strips and short-time workshops with 9th year elementary school students.

Resumo/Abstract

A divulgação científica tem como um de seus principais objetivos comunicar a ciência de forma eficiente ao público, sendo as Histórias em Quadrinhos (HQs) uma ferramenta em potencial para informar de forma clara concisa, tópicos relacionados à ciência por meio da união entre imagem e texto, utilizando uma linguagem descontraída e leve. Com isso, o projeto, que faz parte das atividades de ensino/divulgação científica do INCT-CBIP (Instituto Nacional de Ciência e Tecnologia de Controle Biorracional de Insetos Praga e Fitopatógenos), propôs utilizar as HQs para informar ao público de Ensino Fundamental sobre diferentes temas relacionados com as pesquisas desenvolvidas, sendo um deles sobre formigas cortadeiras. Desta forma, foram elaboradas tirinhas (HQs curtas) para divulgação online e oficinas de curta duração (60 minutos) para a elaboração de ilustrações e textos científicos com alunos do 9º ano do Ensino Fundamental de diferentes escolas públicas na cidade de São Carlos-SP. As tirinhas foram elaboradas em formato de curiosidades, utilizando-se o estilo mangá (quadrinhos japoneses) e coloridas, geralmente com cerca de até 6 quadros cada uma. Elas estão disponibilizadas no endereço: https://tirinhascbip.wordpress.com. A Figura 1 a seguir ilustra um recorte da tirinha sobre o assunto.

Figura 1.Tirinha sobre formigas cortadeiras.

As oficinas foram realizadas na biblioteca comunitária da universidade com 7 turmas de duas escolas (quatro turmas da escola 1 e três turmas da escola 2), totalizando 174 alunos. Foram discutidas informações sobre formigas cortadeiras para auxiliar os alunos na confecção dos textos. Devido ao número de alunos em cada turma, os alunos foram orientados a se dividir em grupos. Por fim, constatou-se que as tirinhas são um formato de HQs adequado para o uso em divulgação científica por ser possível abordar conteúdos em formato de curiosidades, além de ser um material de rápida leitura. Atividades envolvendo ciência e arte possuem o potencial para despertar o interesse do público em geral, conforme se constatou pelo grande interesse dos alunos na maioria das oficinas realizadas.

Agradecimentos/Acknowledgments

DQ – UFSCar, CNPq.

Área: EDU **Nº de Inscrição: 0320**

Contributions to the teaching-learning process of chemistry contents for quilombola's students in engineering courses at IGE - Unifesspa

Tatiani da L. Silva (PQ),[1] Alexandre R. P. da Silva (IC),[1] Adria M. R. Matos (IC),[1] Enelly K. G. de S. Fontes (IC),[1] Emmanuelly S. Feitosa (PQ),[1] Elias F. Neto (PQ),[1] . tls1981@hotmail.com; alexandre.silva@unifesspa.edu.br

[1]*Instituto de Geociências e Engenharias, Unifesspa-Pará*

key words: *Active methodologies; inclusion; quilombola's students; engineering.*

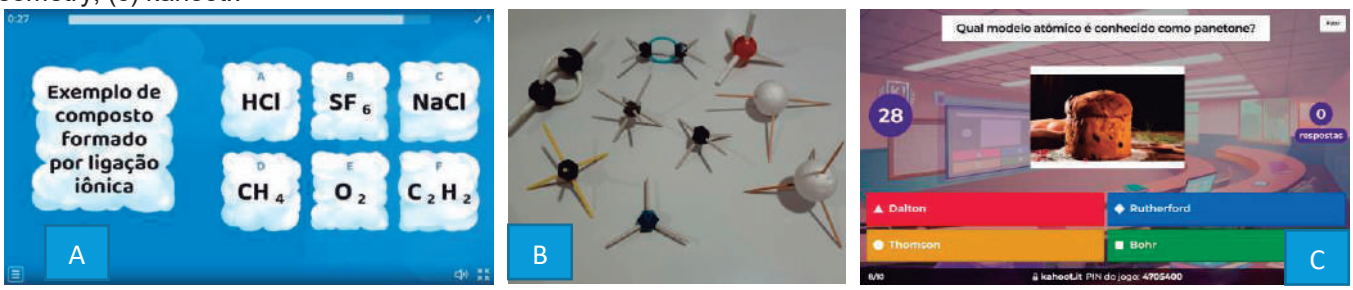
Highlights

This work sought to contribute to the chemistry teaching-learning process of quilombola students at the Institute of Geosciences and Engineering of the Federal University of South and Southeast of Pará, since it is a basic subject in several engineering courses.

Abstract

Of the 5,568 municipalities in Brazil, 1,696 have a quilombola's population (IBGE, 2022). According to data from the 2022 Census, the country's quilombola population is 1.32 million people, or 0.65% of the country's total inhabitants. Pará is the fourth Federation Unit with the largest number of quilombolas: 135,033 people (counted quilombola population) and has 1.66% of quilombolas in the State's population. Pará is one of the few states in the Legal Amazon where universities have a selection process with specific vacancies reserved for quilombolas. It is necessary to understand that access to higher education for students from quilombola communities through affirmative actions is not understood as a solution in itself. In the case of access to higher education by quilombola peoples, such actions must be accompanied by the dimensions of permanence and academic progress, especially because they are social actors with ways of seeing and understanding the world from different logics than what constitutes the university. There are few studies related to the teaching and learning of chemistry content by quilombola students. Thus, this work aims to contribute to the permanence of quilombola students at university through personalized assistance in chemistry subjects, which are basic subjects common in the curriculum of most engineering courses. In order to achieve this purpose, the project was organized in stages. First, a meeting was held with project collaborators to prepare an initial work plan. Bibliographic research began on quilombolas and their historical educational context. Subsequently, information was sought on the number of quilombola students working on IGE undergraduate courses. With this information, we try to contact students to present the project and encourage participation in it. Therefore, a first diagnostic questionnaire was prepared for quilombola students to collect fundamental information, to assist the team in developing activities with students and to begin preparing teaching materials and planning applications. Then, based on the data obtained, personalized support materials were developed, including reinforcement classes with individual resources for each student, as several difficulties were reported in the questionnaire regarding the basic subjects of engineering and geology courses. Focusing on chemistry subjects, we began our activities by selecting some links available on YouTube, which are short videos with experiment schemes that help in understanding the atomic structure chapter (cathode ray tubes, Millikan experiment, Rutherford experiment). The websites wordwall.com and Kahoot.com were used to create games that helped with the content of chemical bonds, acids and bases and thermochemistry. The resource of experimentation was also used to help understand the content of thermochemistry and acids and bases. For these, some experiments were selected that were easy to manipulate and an experimental script was created. A workshop was also held to assemble three-dimensional geometric structures to assist in the molecular geometry chapter – chemical bonds.

Figure 1: Use of active methodologies in the construction of chemical knowledge. (a) wordwall; (b) molecular geometry; (c) kahoot!.



Acknowledgments

Thanks to PROGEP/Unifesspa and NUADE/Unifesspa for the financial support (scholarship).

Área: EDU

Experimental determination of vitamin C in orange juice as a proposal for an alternative methodology for teaching chemistry

Samuel D Guimarães (IC)[1], Ana Paula A. Borges (PG)[1], Jocélia Pereira de C. Oliveira (PQ)[1]

[1]*Instituto de Química, UFCAT*

samueldias@discente.ufcat.edu.br

Palavras Chave: *Ensino, Método Balentine, Frutas.*

Highlights

The determination of vitamin C content in orange juice using the Balentine method was carried out as a pedagogical proposal to teach redox by iodometric titration. The procedure was effective for application in experimental chemistry classes.

Resumo/Abstract

A vitamina C, também conhecida como ácido ascórbico, é um composto amplamente reconhecido, pois desempenha um papel crucial na proteção do organismo contra infecções e doenças. Devido à sua ausência na síntese corporal humana, ela precisa ser adquirida por meio da ingestão de alimentos, especialmente frutas e legumes, sendo sua presença predominante em frutas cítricas. A ingestão diária recomendada para um adulto é aproximadamente 70 mg. A deficiência de vitamina C na alimentação pode resultar em escorbuto, uma condição que afligiu marinheiros durante o período do descobrimento do Novo Mundo.[1] A maior parte das funções bioquímicas do ácido ascórbico decorre de sua capacidade de doar um ou dois elétrons.[2] Além disso, ele desempenha um papel importante na biossíntese de 17 aminoácidos, reduz a suscetibilidade a infecções, contribui para a cicatrização de feridas, fraturas, contusões e sangramento gengival, participa da formação de dentes e ossos, melhora a absorção de ferro e previne o escorbuto.[1] Neste trabalho, determinou-se o teor de vitamina C em suco (*in natura*) de laranjas do tipo pêra comercializadas no município de Catalão - Goiás, por meio do método de Balentine. Esse método consiste na titulometria de óxidorredução iodométrica, fundamentada na conversão de iodo molecular em íon iodeto.[2] A reação entre iodo e vitamina C é rápida e quantitativa, é nesse fato que se baseia a titulação iodométrica para determinação de vitamina C. O ponto final da reação é visualmente obtido através da solução de amido, que adquire coloração azul escuro após toda vitamina C ter reagido. A técnica apresenta a vantagem de ser de baixo custo e utilizar materiais de fácil acesso. O objetivo desse trabalho foi elaborar uma proposta pedagógica, como uma metodologia alternativa para o Ensino de Química, com a possibilidade de se trabalhar a contextualização, por exemplo, com a parte bioquímica, além de estudos de estereoquímica, relação entre a estrutura e propriedade química e cálculos químicos utilizando o raciocínio proporcional onde é possivel determinar a quantidade da vitamina por gramas da fruta. Esse procedimento para determinação de vitamina C pode ser realizado em escolas que possuam laboratório de Ciências. O uso de propostas pedagógicas experimentais como ferramentas de ensino é de grande importância para assegurar a qualidade no ensino, e também contribui para uma melhor fixação dos conteúdos trabalhados de maneira teórica em sala de aula, como por exemplo, ao mostrar a importância da vitamina C para a saúde. Nesse estudo, foi realizada uma titulação pelo método de Balentine,[2] utilizando solução de iodato de potássio com concentração de 0,02 mol/L como titulante em uma bureta com volume de 25 mL. Em um erlenmeyer de 250 mL, foram adicionados 15 mL de suco de laranja *in natura* como titulado, juntamente com 50 mL de água destilada e 10 mL de solução de ácido sulfúrico a 20%, 1 mL solução de iodeto de potássio a 10%, e 1 mL solução de amido a 1%. Esse procedimento foi repetido em duplicata. A titulação permitiu a determinação do teor de vitamina C nas amostras da laranja testada. Verificou-se que, em média, 15 mL de suco da fruta *in natura* consumiram 0,5 mL do titulante. Com os cálculos pela fórmula: Vitamina C (mg por cento m/m) = 100 x V x F / P, onde V = volume de iodato de potássio gasto na titulação; F = 8,806 ou 0,8806, respectivamente para KIO_3 0,02 ou 0,002 mol/L e P = g ou mL da amostra utilizada, constatou-se que o teor de vitamina C em 15 mL de suco foi de 29,35 mg%. Dessa forma, foi possível determinar a concentração de vitamina C através da titulação iodométrica em amostras de suco de laranja, e verificar que a adaptação desse método para ser utilizado no Ensino de Química é possível, inclusive com a possibilidade de aplicação para outros tipos de frutas, com a participação dos próprios estudantes que podem sugerir outras opções de frutas para a realização de testes.

Agradecimentos/Acknowledgments

Ao PIBIC-UFCAT pela bolsa e ao Instituto de Química pelo apoio.

Referências

[1]COSTA, J. O. Determinação do teor de vitamina C em polpas de frutas congeladas por iodimetria: uma opção para o controle de qualidade? Trabalho de Conclusão de Curso – UFPE – Vitória de Santo Antão, 2016.

[2]TAVARES, J. T. de Q.; SANTOS, C. M.; DE CARVALHO, L. A.; DA SILVA, C. L. Determinação volumétrica de ácido ascórbico pelos métodos de tilmans e balentine. Magistra, v. 7, jan./dez., p. 1-8, 1999.

Área: EDU

Ensino de Química: Uma Educação no Novo Ensino Médio - O Movimento CTS/CTSA nos Livros Didáticos

Antonio Geilson M. Monteiro (FM),[1] Irlane Maia de Oliveira (PQ),[2] Adriana Dantas G. de Freitas (PQ),[3]

geilsontonho@gmail.com; irlanemaia@uol.com.br: adrianadantas1@gmail.com

[1]Secretaria de educação e disposto do Amazonas, SEDUC/AM; [2]Institutode Ciências Biológicas – ICB/UFAM; Instituto de Ciências Biológicas- ICB/UFAM

Palavras Chave: *reforma curricular, educação básica, unidades temáticas*

Highlights

Ensino de Química: Uma Educação no Novo Ensino Médio - O Movimento CTS/CTSA nos Livros Didáticos: O estudo consiste em uma análise por meio dos livros didáticos, embasando-se conjuntamente na Base Nacional Comum Curricular (BNCC) e no Referencial Curricular da Amazônia (RCA).

Resumo/Abstract

A Aprovações da Base Nacional Comum Curricular do Ensino Médio (BNCC-EM) e do Referencial Curricular Amazonense do Ensino Médio (RCA-EM) aprovados e com datas de aplicação em todas as escolas públicas e particulares levantaram debates sobre a implementação do novo Ensino Médio, que por sua vez foi adiada para 2022 no Amazonas (AMAZONAS, 2021; BRASIL, 2017) devido à pandemia de COVID-19, com calendário proposto até o ano de 2024 para o último ciclo de implementação e com a primeira turma a se formar no novo sistema de educação básica. O contexto da aprendizagem através das normativas veio estruturar a educação, e nesse sentido se questiona, é possível através do movimento de ciências, tecnologia, sociedade e meio ambiente criar conteúdo de ensino aprendizado para ou nas unidades curriculares proposta pelo novo ensino médio? Este estudo teve como objetivo analisar como o movimento Ciências, Tecnologia e Sociedade (CTS/CTSA) (STRIEDER,2008) pode criar contextos de aprendizagem no novo Ensino Médio, destacando sua importância diante das mudanças curriculares e da realidade pandêmica. Analisar a criação de contextos de aprendizagem a partir do movimento CTS/CTSA, teorizando à luz da perspectiva de Levi Vygotsky, com foco no itinerário formativo como eixo estruturante. Privilegiamos duas dimensões específicas: a implementação do novo Ensino Médio e as relações entre CTS/CTSA mencionadas na normativa, abordando a educação CTS no itinerário formativo. Utilizamos análise de conteúdo de Bardin (BARDIN, 1995) e análise textual discursiva (ATD) (MORAES, 2003) para explorar artigos e livros didáticos pertinentes, considerando a homologação da BNCC e do RCA de 2018 a 2022. Como resultado não foi apontado sobre o desenvolvimento em sala de aula pelo qual o ciclo de implementação ainda está ocorrendo de tal maneira a aplicação da proposta depende da aprovação escolar prévia, mas ainda é cedo para avaliar seus impactos (ALVES, 2018). A análise revelou a possibilidade de criação de contextos de aprendizagem na formação básica, evidenciando a importância do diálogo entre teorias educacionais, especialmente a de Vygotsky (VYGOTSKY, 2010), e ressaltando a relevância de uma abordagem interdisciplinar e multidisciplinar para incentivar uma aprendizagem mais conectada e significativa. Permitido perceber que através dos artigos e das normativas tem-se muito a se destacar, tais como a importância da abordagem interdisciplina e multidisciplinar nos livros didáticos analisado, pois os próprios documentos ressaltam essa relevância. Assim incentivando os alunos a explora conteúdo de forma interligada com a sociedade.

ALVES, Felipe Fabian dos Santos. O impacto da perspectiva ciência, tecnologia e sociedade (CTS) na disciplina de Biologia no ensino médio tecnológico. 2018. Dissertação (Mestrado em Ensino de Ciências e Matemática) - Programa de Pós-Graduação em Ensino de Ciências e Matemática, Universidade Federal do Amazonas, Amazonas. 2018.
AMAZONAS. Referencial Curricular Amazonense – Ensino Médio. Manaus: Secretaria de Estado de Educação do Amazonas, 2021.
BARDIN, Laurence. Análise de conteúdo. Lisboa: Edições 70, 1995.
BRASIL. Lei 13.415, de 16 de fevereiro de 2017. Base Nacional Comum Curricular. Diário Oficial da União, de 17 de fevereiro de 2017.
MORAES, Roque. Uma tempestade de luz: a compreensão possibilitada pela análise textual discursiva. Ciência & Educação (Bauru), v. 9, n. 2, p. 191-211, 2003.
STRIEDER, Roseline Beatriz. Abordagem CTS e ensino médio: espaços de articulação. Tese de Doutorado, Universidade de São Paulo, 2008.

VYGOTSKY, LEV Semionovich; IVIC, Ivan; COELHO, Edgar Pereira. Recife: Fundação Joaquim Nabuco. Editora Maisagama, 2010.

Agradecimentos/Acknowledgments

FAPEAM Fundação de Amparo à Pesquisa do Estado do Amazonas
CAPES
CNPq Conselho Nacional de Desenvolvimento Científico e Tecnológico

Área: Ensino de Química
EDU

Environmental Education in Chemistry Teacher Training: resonances of a collaborative collage activity

Maria Cecília dos S. Vieira (PG)[1], Márlon Herbert F. Barbosa Soares (PQ)[2], Nyuara Araújo da S. Mesquita (PQ)[2].

nyuara@ufg.br; mariaceciliavieira4@gmail.com.

[1,2] *Laboratório de Educação Química e Atividades Lúdicas, Instituto de Química - UFG.*

Palavras Chave: *Modernidade Líquida, Licenciatura em Química, Educação Ambiental.*

Highlights

Environmental Education in Chemistry Teacher Training: resonances of a collaborative collage activity. Considering liquid modernity, a didactic activity was carried out in a chemistry course on consumerism, environmental degradation and human exploitation associated with the context of Chemistry.

Resumo

A inserção da dimensão ambiental no contexto da formação docente em química (FDQ) é constantemente desafiada, principalmente quando se fundamenta na perspectiva crítica da Educação Ambiental. Um dos desafios é a apatia e o desinteresse em relação à realidade socioambiental, que dificulta a interação dos envolvidos no processo de formação ambiental crítico, que requer um debate profundo e permanente[1]. Estes comportamentos - assim como a tendência ao individualismo, a compulsão pelo ter e a competitividade - são características da modernidade líquida mencionada por Bauman[2]. Considerando a importância de ampliar o repertório de atividades e discussões ambientais voltadas para o Ensino de Química e tendo em vista a promoção do envolvimento e participação dos sujeitos, este trabalho apresenta as ressonâncias de uma atividade desenvolvida em um contexto específico de FDQ. A atividade integra uma proposta formativa fundamentada no referencial baumaniano que foi desenvolvida no âmbito de uma disciplina de Química Ambiental, envolvendo a participação de 17 estudantes. Após serem problematizadas questões existenciais e políticas que acometem a sociedade e o ambiente, os estudantes foram orientados a confeccionar colagens em grupos, buscando articular em alguma medida: a) Questões socioambientais que possuam relação com a química e; b) Aspectos ou características da modernidade líquida discutidos anteriormente. No total foram apresentadas sete colagens, de modo que os estudantes escolheram e problematizaram temas emergentes e de seu interesse, tal como o da indústria da moda (uma das mais poluidoras do mundo com Gases do Efeito Estufa, etc.), associando ao consumismo (reflexo da lógica do capital que paira na modernidade líquida), à exploração humana (trabalho análogo à escravidão nas fábricas) e à degradação ambiental (descarte de roupas usadas no deserto do Atacama, Chile). As colagens e os temas foram discutidos com a turma e as discussões foram gravadas e transcritas. A proposta promoveu ressonâncias, isto é, a movimentação de todos os estudantes para participar das discussões, a criatividade no processo de confecção das colagens e a colaboração por meio da interpretação conjunta das criações dos grupos. Percebeu-se o caráter multifacetado da dimensão ambiental e as influências neste contexto a partir da atividade que também foi um convite à mudança de uma posição desinteressada e apática à crítica e participativa, que se faz necessária, principalmente porque vivemos em um cenário de interações superficiais e maleáveis.

[1] VIEIRA, M.C.S.; MESQUITA, N.A.S. Educação Ambiental Crítica e Formação de Professores de Química em Tempos de Modernidade Líquida. In: Anais do 21º Encontro Nacional de Ensino de Química. **Anais...**Uberlândia (MG), Universidade Federal de Uberlândia, 2023.

[2] BAUMAN, Z. **Modernidade Líquida**. Tradução: Plínio Dentzien. 1º ed. Rio de Janeiro: Zahar, 2021.

Área: EDU

Experimentos químicos I: abordando a prática no ensino médio como forma de consolidação do ensino de química

Júlia R. Marques (TM),[1*] Marccus Victor A. Martins (FM),[1]

julia.marques1@estudante.ifgoiano.edu.br

[1] *Gerência de Ensino, IF GOIANO-Campus Catalão*

Palavras Chave: *Ensino de química, Experimentos, Prática no ensino.*

Highlights

Practical classes in high school are a highly didactic mechanism for consolidating learning. In this sense, this work proposed the creation and execution of practical itineraries combined with the contents of the first year of high school chemistry. The final product developed by the high school student will be a chemistry practice booklet for high school.

Resumo

O ensino médio é uma nova etapa na vida de qualquer estudante, tanto no contexto social quanto acadêmico. Do ponto de vista de inserção no mundo científico, a realização de aulas práticas dentro do ensino médio corresponde a um mecanismo extremamente importante para atingir tal objetivo. Neste sentido, é de fundamental importância o professor, responsável pela mediação deste ensino, criar mecanismos didáticos a fim de tornar o ensino de química muito mais consolidado e atraente.[1] Em vista disso, esse trabalho propôs a criação de dois roteiros práticos de química associados aos conteúdos ministrados geralmente na primeira parte curricular do primeiro ano do ensino médio. Assim, a Figura 1(A) apresenta uma fotografia mostrando o resultado do experimento proposto e conhecido como "produção de gás hidrogênio", onde 1 grama de bolinhas de alumínio (papel alumínio) são colocados dentro de um tubo de ensaio contendo 20 mL de solução de NaOH (1 M). Nesta figura, observa-se nitidamente uma chama, como produto da reação química entre o alumínio metálico e a solução de NaOH. A combustão do gás hidrogênio evidencia um fenômeno químico. Já na Figura 1(B), foi proposto e executado o processo de separação de uma mistura heterogênea com um funil de decantação entre água (50 mL) e óleo (50 mL) contendo corante alimentício de cor azul. Neste experimento, observa-se a capacidade de fácil separação entre dois líquidos imiscíveis.

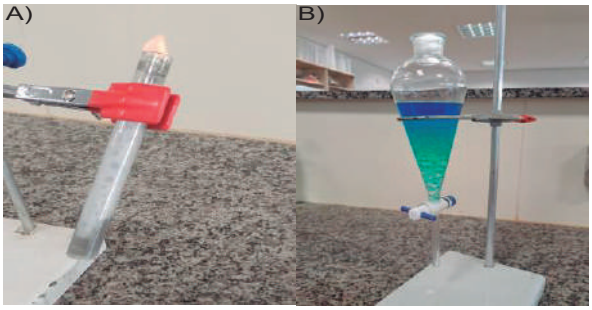


Figura 1. (A) experimento: "produção de gás hidrogênio" e (B) separação da mistura água e óleo.

Para ambos os experimentos propostos foi possível criar uma forma didática, prática, fácil e atraente para melhorar e potencializar o ensino especificamente de fenômenos químicos e de misturas heterogêneas. Assim, a implementação dessas práticas consiste em sair da simples memorização de conteúdos dentro do ensino médio.

Referências

1. BRAGA, M.N.S.; PRESTES, C.F.; OLIVEIRA, V.G.; MENEZES, J.A.; CAVALCANTE, F.S.; LIMA, R.A. A importância das aulas práticas de química no processo de ensino-aprendizagem no PIBID. Diversitas Journal, v.6, n.2, p.2530- 2542, 2021.

Agradecimentos/Acknowledgments

Ao programa de Iniciação Científica de Ensino médio do IFGoiano (PIBIC-EM).

Área: EDU

Experimentos químicos II: abordando a prática no ensino médio como forma de consolidação do ensino de química

Maria Rita R. Ataíde (TM),[1*] Marccus Victor A. Martins (FM),[1]

maria.ataide1@estudante.ifgoiano.edu.br

[1] *Gerência de Ensino, IF GOIANO-Campus Catalão*

Palavras Chave: *Ensino de química, Experimentos, Prática no ensino.*

Highlights

Experimentation in chemistry teaching; Practical classes on chemical reactions and geometry of molecules for high school.

Resumo

A formação de profissionais na área da química tem grande influência ainda dentro do ensino médio. Neste sentido, é de fundamental importância o professor, responsável pela mediação deste ensino, criar mecanismos didáticos a fim de tornar o ensino de química muito mais consolidado e atraente.[1] Em vista disso, esse trabalho propôs a criação de dois roteiros de química associados aos conteúdos ministrados geralmente na última parte curricular do primeiro ano do ensino médio (fenômenos químicos e Geometria Molecular). Assim, a Figura 1(A) apresenta uma fotografia mostrando o resultado do experimento proposto e conhecido como "camaleão químico". Nesta figura, observam-se nitidamente diferentes colorações no interior da proveta. Cada cor está associada aos diferentes estados de oxidação do íon permanganato em meio básico, devido à reação de óxidorredução. Já na Figura 1(B), foi proposta e executada a criação de modelos práticos em três dimensões (3D) com o uso de palitos e jujubas.

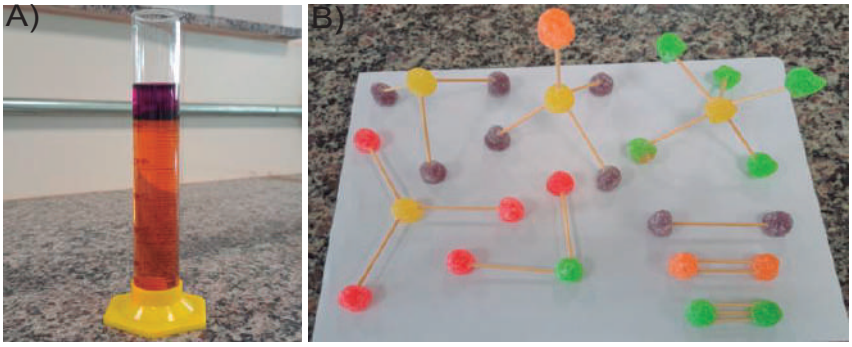


Figura 1. (A) experimento do "camaleão químico" e (B) modelos em 3D de diferentes geometrias moleculares.

Para ambos os experimentos propostos foi possível criar uma forma didática, prática e atraente para melhorar e potencializar o ensino especificamente de reações químicas e de geometria molecular. O desenvolvimento dos dois roteiros estabelece a dinâmica da não memorização teórica, além de serem de fácil execução para fins de ensino médio. Além disso, a realização da experimentação no ensino médio desperta o estudante para o mundo científico. Neste sentido, tais roteiros não foram aplicados em sala de aula por fazerem parte de uma sequência de outros roteiros que estão em fase de preparação para a construção de uma apostilha de práticas para o ensino médio da disciplina de química.

Referências

1. BRAGA, M.N.S.; PRESTES, C.F.; OLIVEIRA, V.G.; MENEZES, J.A.; CAVALCANTE, F.S.; LIMA, R.A. A importância das aulas práticas de química no processo de ensino-aprendizagem no PIBID. Diversitas Journal, v.6, n.2, p.2530- 2542, 2021.

Agradecimentos/Acknowledgments

Ao programa de Iniciação Científica de Ensino médio do IFGoiano (PIBIC-EM).

Área: EDU
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

EXPLORANDO A ESTEQUIOMETRIA: UM GUIA POGIL COM ABORDAGEM DE DESIGN-THINKING

Roberto P. Santos (PQ)[1], Priscilla S. A. Côrtes (PG)[1,2]*.

roberto.santos@ifes.edu.br; priscilla.cortes@educador.edu.es.gov.br

[1]Instituto Federal do Espírito Santo – Campus Vila Velha – Programa de Mestrado Profissional em Química em Rede Nacional - PROFQUI; [2]EEEFM Caboclo Bernardo – Secretaria de Estado de Educação do Espírito Santo.

Palavras Chave: *Design-based learning, DBL, POGIL.*

Highlights

Exploring Stoichiometry: A POGIL Guide with a Design-Thinking Approach. Implementing a POGIL Guide for Stoichiometry using Design-Thinking to promote meaningful learning. Student-centered approach with empathy, definition, idea, modelling, and test steps, applied to chemistry teaching. Outcomes include increased student engagement and applied understanding of stoichiometry in real-world contexts.

Resumo/Abstract

Este estudo propõe a criação de um Guia POGIL (*Process Oriented Guided Inquiry Learning*) para o ensino de Estequiometria, aplicando a metodologia de *Design-Thinking* (DT) com o objetivo de oferecer uma aprendizagem mais significativa e contextualizada aos estudantes. O DT é uma abordagem inovadora que envolve entender as necessidades dos usuários (no caso, os estudantes), definir os problemas de maneira clara, gerar ideias criativas, modelar as soluções e testá-las.

O projeto vem sendo desenvolvido com alunos da 2ª série do Ensino Médio da Escola Estadual de Ensino Fundamental e Médio Caboclo Bernardo, em Aracruz/ES, considerando uma população estudantil com idades entre 16 e 18 anos, sendo 40% do sexo feminino e 60% do sexo masculino. Iniciamos com a construção do **Mapa de Empatia** para compreender as experiências, necessidades e desafios dos alunos em relação ao aprendizado. Seguiu-se a **determinação do problema**, onde identificamos as principais barreiras para o aprendizado da disciplina. Na fase de **ideação**, foram geradas várias soluções, culminando com a **criação de atividades didáticas** significativas (modelagem), que vêm sendo incorporadas ao Guia POGIL, a ser validado em sala de aula.

Os resultados obtidos até o momento demonstram aumento no engajamento dos estudantes, melhorando não só a compreensão teórica dos fenômenos, mas também a aplicação do conhecimento em situações cotidianas, como interpretação de rótulos comerciais e realização de experimentos simples. A abordagem DT permite que os alunos se sintam mais conectados ao processo de aprendizagem, evidenciando a eficácia desta metodologia na educação em química.

Assim, o DT, além de ser utilizado como ferramenta pedagógica no ensino de química, tem se mostrado como uma abordagem eficiente para envolvimento dos alunos e tornar o aprendizado mais relevante e aplicado à realidade.

Agradecimentos/Acknowledgments

Ao Instituto Federal do Espírito Santo (IFES) – Campus Vila Velha e Secretaria de Estado de Educação do Espírito Santo (SEDU/ES).

Área: EDU

Exploring the Conceptions and Perceptions of Public High School Students Regarding Scientists and Their Scientific Endeavors

Leonardo L. Silva (PG), Luana Caroline Tonhetti Maester (IC), Amadeu M. Bego (PQ).

leonardo.l.silva@unesp.br

São Paulo State University (UNESP), Institute of Chemistry, Araraquara, Brazil.

Keywords: Scientists; Drawings representations; Stereotypes.

Highlights

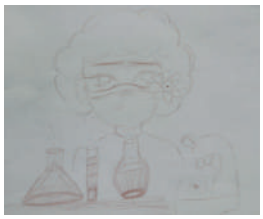
We investigated high school students' conceptions and perceptions regarding scientists and their work through drawings and interviews in order to analyze the impact of an extension design.

Resumo/Abstract

An extension activity, which involved collaboration from three distinct university groups, was carried out aimed to strengthen the relationship between the university and society and to promote the dissemination of science produced in universities. The activity, lasting an average of five hours, took the form of a guided tour of high school students who visited the Institute of Chemistry (IQ) at Unesp. The design was crafted to provide students with a comprehensive extension experience, encompassing informative, interactive, stimulating, and collaborative activities. 93 students from a public school participated in the activity. At the outset, students were asked to "draw a representation of a scientist" on a sheet of paper, using colored pencils provided to them. Subsequently, students engaged in informative, experimental, and playful activities related to a scientific research project led by a female professor of the IQ.

At the conclusion of the visit, as part of the data collection process, 29 students were selected for a reflective interview using a stimulated recall protocol. The aim was to access participants' memories and experiences based on stimuli (drawings made at the beginning of the intervention) and reflective questions, allowing students to express their own conceptions and ideas about the subject, thus seeking to understand the occurrences and meanings attributed by students to the scientific enterprise and scientists.

Analyzing the students' representations, 55 drawings depicted a person as a scientist, of which 69% were white men and 31% were women, with 71% being white and 29% black. During the interview, 65.5% of the students stated that they would keep their drawing unchanged even after the intervention; however, 34.5% of the students proposed modifications to the drawing, including more people and different settings.



Thus, compared to the literature, we observed the predominance of the association of scientists with experimental activities and white men engaging in them. However, this study revealed a higher percentage of female scientists, including black female scientists, drawn by high school students which can point out a possible auspicious and new landscape regarding public perception of scientists.

Agradecimentos/Acknowledgments

The authors would like to thank CNPq, the Research and Innovation Network in teaching of Chemistry (RIPEQ, abbreviation in Brazilian Portuguese for “Rede de Inovação e Pesquisa do Ensino de Química”), the Tutorial Education Programme (PET, abbreviation in Brazilian Portuguese for “Programa de Educação Tutorial”); the Applied Metal-Organic Frameworks Research Group and the Institute of Chemistry, located in Araraquara, at the State University of São Paulo.

Área: EDU

Fermentation process in discussion: a curricular analysis

Rodrigo Campos dos Santos (FM)[1]*, Ana Caroline Ferreira Garcia (PG)[1], Keila Bosolani Kiill (PQ)[1]

rodrigo.santos@sou.unifal-mg.edu.br; rodrigo.santos@sou.unifal-mg.edu.br

[1] *Departamento de Química, Universidade Federal de Alfenas – UNIFAL-MG*

Palavras-chave: *Modelo, Currículo, Fermentação.*

Highlights

The process of forming the concept of fermentation is simplistic in terms of the curriculum, in addition to being recommended in a decontextualized way.

Resumo

O ato de contextualizar assuntos pertinentes as Ciências Naturais exige o uso de temas relacionados ao cotidiano dos estudantes. Nesse sentido, o café surge como uma possibilidade temática promissora, uma vez que este produto se relaciona com a vida dos estudantes, devido ao fato de seu cultivo ser muito difundido.

Dentro da versatilidade de conceitos que poderiam ser discutidos a partir desta temática, os processos fermentativos se destacam, porque o consumo dos cafés especiais fermentados teve um crescimento a nível mundial (PEREIRA *et al.*, 2016). Assim, o objetivo deste trabalho foi investigar como que os currículos da Educação Básica e Superior preconizam a construção do conceito de fermentação nas aulas de Química e os seus possíveis efeitos sensoriais na bebida do café.

O *corpus* avaliado foi o Currículo Referência de Minas Gerais, por meio dos Planos de Curso de 2023, e os programas de ensino das disciplinas de Bioquímica e de Tecnologia de Fermentações, ambas ofertadas no curso de Química Bacharelado com Atribuições Tecnológicas da Unifal-MG. A leitura analítica destes documentos foi realizada, buscando por palavras-chave que possuíam relação direta com o conceito de interesse e/ou com o fenômeno de estudo. A análise dos dados se deu à luz do Modelo Científico Escolar de Arribo (LÓPEZ y MOTA, 2019), por meio da construção do Modelo Curricular (Mcu).

Os documentos analisados indicam a ausência de abordagens contextualizadas do processo fermentativo. Metabolismo, carboidratos, fermentação, microrganismos, etanol, anaeróbio, ácidos orgânicos, leveduras, bactérias e meio de cultura foram as entidades encontradas nos documentos que se relacionam com a fermentação no grão de café e que foram utilizadas na construção do Mcu e do seu diagrama de causalidade (figura 1).

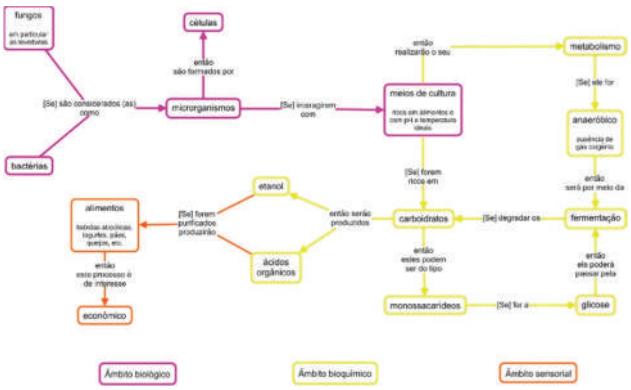


Figura 1: Diagrama de causalidade para o MCu (do autor).

O Mcu possui uma complexidade intermediária no que tange a discussão conceitual, estando bem longe do que seria considerado o ideal. As inferências que podem ser obtidas por meio das informações que ali se encontram ainda são consideradas superficiais o que, por sua vez, denota ao processo de fermentação um caráter simplista. Dessa forma, o processo de formação do conceito de fermentação é deficitário na Educação Básica e Superior, por motivos de negligências não só da prática docente, mas também curricular.

Referências

LÓPEZ y MOTA, A. D. **Modelos científicos escolares**: el caso de la obesidade humana. México: UPN, 2019.

PEREIRA, G. V. M.; CARVALHO NETO, D. P.; MEDEIROS, A. B. P.; NETO, E.; SOCCOL, V. T.; WOICIECHOWSKI, A. L.; SOCCOL, C. R. Potential of lactic acid bacteria to improve the fermentation and quality of coffee during on-farm processing. **International Journal of Food Science and technology**, v. 51, p. 1689-1695, 2016.

Agradecimentos

O presente trabalho foi feito com apoio da CAPES.

Área: EDU

Investigative experimentation: a proposal for teaching gases in experimental stations

Claudia Braga (PQ),[1] Emelly Suelen de F R Santos(IC),[1*] Saloana Santina Gomes Santos(FM)[2]

claudiafbraga@gmail.com; suelenemelly2@gmail.com

[1]Departamento de Química, UFPB; [2]ECIT João Goulart, SEPB.

Palavras Chave: *experimentação investigativa, estudo dos gases, ensino de química.*

Highlights

Experimentation in chemistry teaching brings students closer to science. Investigation possible to relate the knowledge acquired with reality. Experimentation classes contribute to the students' scientific literacy process.

Resumo/Abstract

A química possui características macroscópicas, submicroscópicas e representacional (fórmulas e equações) e a abordagem apenas representacional dificulta sua compreensão pelos estudantes. Em contrapartida, a experimentação simula a realidade e pelo seu caráter observatório, visual e instigante aproxima os conteúdos da realidade do aluno. Neste contexto, apresenta-se o relato de sala de aula, a partir do desenvolvimento de experimentos de caráter investigativo para estudo dos gases, realizados na ECIT João Goulart no município de João Pessoa-PB. Inicialmente foi realizada uma abordagem geral expositiva sobre o que são os gases, para em seguida realizar uma prática experimental de caráter investigativo sobre as propriedades dos gases. Para a experimentação, o laboratório foi dividido em quatro estações, sendo estas: 1 - expansão e contração do gás, 2 - reação com liberação de gás, 3 - volume ocupado, 4 - pressão exercida (Figura 1). Os alunos foram separados em quatro grupos, desta forma, cada prática foi realizada por todos os grupos de forma alternada. Cada estação de trabalho continha o título da estação, materiais dispostos em uma caixa e um monitor. Os alunos deveriam realizar a montagem do aparato, realizar o experimento, registrar suas observações e em seguida propor explicações para os fenômenos observados relacionados às propriedades dos gases. Os registros das práticas foram realizados através de diários de bordo realizados pelos monitores, assim como registros fotográficos. Também foi solicitado a entrega de relatórios experimentais sobre as conclusões dos alunos com relação às práticas como avaliação formal da disciplina. A experimentação investigativa possibilitou a autonomia dos estudantes, assim como, o desenvolvimento da curiosidade e motivação dos mesmos em estudar química, contribuindo assim para a formação/alfabetização científica dos alunos. Foi possível observar também a melhora no desenvolvimento do trabalho em grupo e das relações interpessoais, visto que, as práticas foram desenvolvidas coletivamente e valorizando o trabalho em grupo.

Figura 1 – Estações experimentais: 1- expansão e contração do gás, 2-reação com liberação de gás, 3-volume ocupado, 4-pressão exercida.

[1] SOUZA, K. A. de F. D. de; CARDOSO, A. A. Aspectos macro e microscópicos do conceito de equilíbrio químico e de sua abordagem em sala de aula. Química Nova na Escola, São Paulo, n. 27,p. 51-6, fev. 2008.
[2] NUNES, A. S.; ADORNI, D. S. O ensino de química nas escolas da rede pública de ensino fundamental e médio do município de Itapetinga-BA: O olhar dos alunos. Enditrans, 2010, Vitória da Conquista,BA.

Agradecimentos/Acknowledgments

As autoras agradecem à Universidade Federal da Paraíba e à ECIT João Goulart pelo suporte ao trabalho.

Área: EDU
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Low-Cost Calorimeter for Remote Experimentation Using the ESP8266 Platform.

Daltamir Justino Maia (PQ),[1] Sarah Stefany Monteiro dos Santos (IC),[1] Edson Anício Duarte (PQ),[1] Márcio André Miranda (PQ).[1]*

daltamir.maia@ifsp.edu.br; m_amiranda@ifsp.edu.br.

[1]*Instituto Federal de Educação, Ciência e Tecnologia de São Paulo – Campus Campinas, IFSP-CMP.*

Palavras Chave: Calorimeter, low-cost, remote rxperimentation, physical-chemistry.

Highlights

Construction of a low-cost calorimeter, associated with the ESP8266 platform, to control functions and collect data in cloud for remote experimentation in physical chemistry teaching.

Resumo/Abstract

The proposal was to build a low-cost calorimeter, associated with the Arduino platform to control functions and collect data for application in remote experimentation. The methodological proposal was aimed at experimental practice, the automation of teaching laboratories, with a view to innovation, interdisciplinarity and contextualisation, enhancing the learning of physical-chemical concepts, making classes attractive and motivating. There is no product on the market with the characteristics of this calorimeter under development. Technological advances in microelectronics and the internet have made it possible to bring resources into the classroom and enrich students' practical lessons, having a positive impact on classroom and distance learning. Considering the importance of practical experience in education, Remote Experimentation has stood out as a tool for Learning Objects, as it allows students and interested parties to have access to virtual laboratories with real experiments, using internet resources and other technological means capable of providing remote access (Kinshuk *et al.*, 2016). The calorimeter developed is aimed at experimental activities in Basic Education (High School) in the subject of Chemistry for the teaching of Physical Chemistry. As well as in undergraduate courses, with a focus on Chemistry and an emphasis on the Licentiate Degree, as an example of a teaching object (Assumpção *et al.*, 2010). An operational, microcontrolled prototype was obtained, with local and remote monitoring of temperature variation and cloud storage. Didactic experiments are currently being developed and will be compiled into a workbook to instruct students and teachers in the proper use of the prototype.

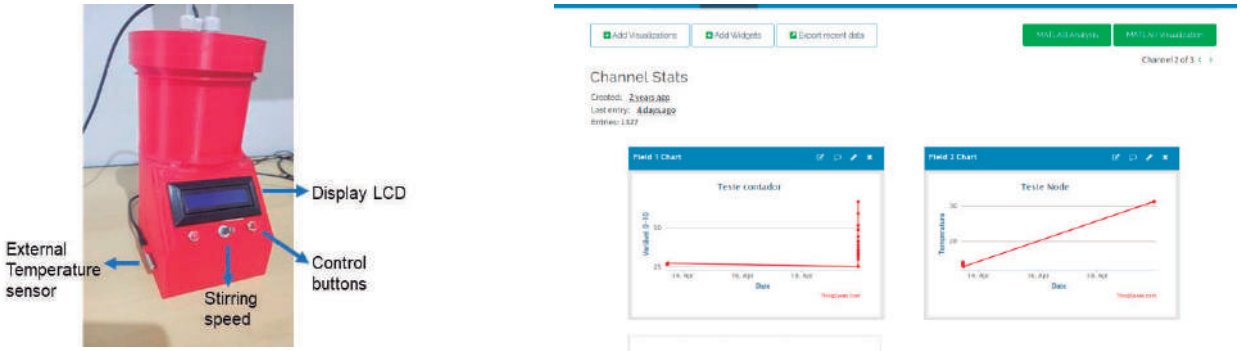


Figure. Representation of the finalised Prototype and the results collected in the cloud.

Assumpção, M. H. M. T., Wolf, L. D., Bonifácio, V. G., & Fatibello-Filho, O. Construção de um calorímetro de baixo custo para a determinação de entalpia de neutralização. Eclética Química, v. 35, p. 63-69, 2010.

Kinshuk; Chen, Nian-Shing; Cheng, I-Ling; Chew, Sie Wai. Evolution is not enough: Revolutionizing current learning environments to smart learning environments. International Journal of Artificial Intelligence in Education, v. 26, p. 561-581, 2016.

Agradecimentos/Acknowledgments

INSTITUTO FEDERAL São Paulo

CNPq Conselho Nacional de Desenvolvimento Científico e Tecnológico

PIBIC / PIBITI / PIBIC-EM

Área: EDU

Marie Curie's visit to Brazil and her relationship with Brazilian scientific societies

Juliete S. Neves (PQ)[1]*, Valéria T. Carraro (PG)[1], Ana Paula Biaobok (PG),[1] Camila Silveira (PQ)[1]

***julieteneves@ufpr.br**

[1]*UFPR, Departamento de Química, PROFQUI*

Palavras-chave: *Women scientists, Marie Curie, Irène Curie, Chemistry, Brazilian Academy of Sciences.*

Highlights

Chemistry Society of São Paulo, Brazilian Academy of Sciences and Pharmacy and Chemistry Society of São Paulo award honorary membership to Marie Curie
Marie Curie visits Brazil

Abstract

At the beginning of the 20th century, Brazil and France established an important cooperation agreement for scientific development, involving exchanges between universities with exchanges between French and Brazilian scientists, promoted by the Franco-Brazilian Institute of High Culture. In this context, in 1926, the Franco-Polish scientist Marie Curie (1867-1934) came to Brazil to give a series of lectures on radioactivity[1]. She came assisted by her eldest daughter and fellow researcher, Irène Curie, and was accompanied by an entourage of scientists, doctors and politicians in all her activities. During her time in the country, she visited cities in Rio de Janeiro, São Paulo and Minas Gerais. This historical episode is of great importance for understanding the role that the scientist played for Brazilian science and the context in which the visit took place. With this in mind, this paper analyzes Marie Curie's relationship with Brazilian scientific societies in the year of her visit to the country. To do this, we carried out historical research by analyzing documentary sources from 1926. In the scientist's travel documents, kept by the National Library of France[2], we found documentary records that point to the honors and tributes Marie received, which are indicators of this relationship. When we collected all this data, we opted to make a second selection, which concerned those linked to the sciences[3]. After delving deeper into the Brazilian Academy of Science (ABC), we found that Marie played an important role in consolidating the ABC. Her visit to Brazil as a scientist of great international renown, winner of two Nobel Prizes, reinforced the institution's role in promoting science in Brazil, as well as raising an important gender issue, the participation of women in science, being the first woman to receive the honor of corresponding member of the ABC. In addition to her lectures on radioactivity, Marie also contributed by hosting Brazilian scientists at the Paris Faculty, such as Adalberto Menezes de Oliveira, president of the ABC between 1937 and 1939, who studied in France with the Polish scientist[4]. Thus, the results show that Marie Curie's visit to Brazil had a positive influence on the promotion of Brazilian scientific culture, as her lectures were broadcast by Rádio Sociedade, a radio station created with the aim of promoting scientific dissemination in the country. In addition, at a time when Brazil was seeking to consolidate its scientific culture, the presence of a renowned female figure encouraged other women to play a role in the scientific community that was being formed. After inducting Marie Curie, the ABC awarded Emília Snethalage, a German ornithologist who lived in Brazil and was one of the first women to be part of a Brazilian research institution, the honor of corresponding member of the Brazilian Academy of Sciences.

[1] HAMBURGER, A. I. A Ciência nas relações Brasil-França, 1850-1950. Edusp,1996
[2]Source gallica.bnf.fr/Bibliothèque nationale de France. Pierre et Marie Curie. Papiers. II — PAPIERS ET CORRESPONDANCE. CII-CVII Marie Curie. Correspondance et documents concernant ses voyages. CII Voyages et conférences. 1911-1931
[3]CURIE, E. Madame Curie. Tradução de Monteiro Lobato. São Paulo: Ed. Nacional, 1946.
[4]CARVALHO, J. M.; Moreira, I. C. Ciência no Brasil: 100 anos da ABC, 2017.

Acknowledgments

CNPq – Processo 409697/2023-0

Área: EDU

Marie Curie em Águas de Lindóia/SP e a popularização científica na mídia jornalística

Camila Silveira (PQ)[1*], Ana Paula Biaobok (PG)[1], Valéria Teixeira Carraro (PG)[1], Alessandra Nakonetchnei (PG)[2], Lucas Albuquerque do Nascimento (PG)[3], Vinicius Jacques (PQ)[4], Juliete S. Neves (PQ)[1]

***camilasilveira@ufpr.br**

[1]UFPR/PROFQUI; [2]UFPR/PPGECM; [3]UFSC/PPGECT; [4]IFSC/São José

Palavras-chave: Mulheres Cientistas, Correio Paulistano, Águas Radioativas.

Highlights

Marie Curie in Águas de Lindóia/SP and the scientific popularization in the journalistic media: addresses news from the newspaper Correio Paulistano from 1926 revealing the technical-scientific approach, facts of the scientist's life and work and the impacts of her research on society.

Resumo

A cientista franco-polonesa, ganhadora de dois prêmios Nobel, Marie Sklodowska Curie (1867-1934) esteve no Brasil no ano de 1926 por meio do Instituto Franco-Brasileiro de Alta Cultura para proferir uma série de conferências e participar de outras atividades científicas e culturais. Por sua grande notabilidade, esse importante episódio da história da ciência foi bastante divulgado na mídia jornalística da época. Marie Curie esteve em cidades do Rio de Janeiro, São Paulo e Minas Gerais durante o período em que passou no Brasil, cumprindo uma programação de viagem repleta de compromissos junto a pessoas cientistas, médicas, políticas e outras personalidades da sociedade. Neste trabalho, analisamos a passagem de Marie por Águas de Lindóia/SP - na época Thermas de Lindoya - a partir das notícias divulgadas no jornal *Correio Paulistano*, relevante periódico do Estado de São Paulo no contexto investigado, na perspectiva da popularização científica[1,2]. A partir dos pressupostos da pesquisa documental, consultamos a Hemeroteca Digital da Biblioteca Nacional, selecionando o período de 1920-1929 do periódico mencionado, usando como descritores: Marie Curie, Madame Curie, Curie. Obtivemos 30 notícias de jornal sobre a visita de Marie no ano de 1926 e, destas, cinco focam/citam Águas de Lindóia (publicadas em 13, 14, 15, 16 e 17 de agosto). Na sequência, o conteúdo dessas notícias foi lido e sistematizado em categorias temáticas, a saber: a) abordagem técnico-científica; b) fatos da vida e carreira; c) impactos da pesquisa na sociedade. O itinerário da cientista é detalhado no jornal, assim como as pessoas da comitiva que a acompanhavam (Bertha Lutz, Carlota Pereira de Queiroz, Adelino Leal, Celestino Bourroul, entre outras personalidades). Grande ênfase foi dada à relação com o médico proprietário das termas, Francisco Tozzi, e a visita às fontes de águas termais “ficando encantada com a quantidade de rádio encontrada na água” (15/08/1926) e “que muito bem a impressionaram” (16/08/1926). Inferimos que a disseminação da visita de Marie Curie à Águas de Lindóia na mídia impressa contribuiu para o processo de popularização da ciência, ao destacar os atores sociais participantes de práticas científicas, os interesses envolvidos na visita, bem como aspectos técnico-científicos, a exemplo das fontes de águas radioativas.

[1]GERMANO, M. G.; KULESZA, W. A. Popularização da ciência: uma revisão conceitual. *Caderno Brasileiro de Ensino de Física*, Florianópolis, v. 24, n. 1, p. 7-25, 2007. [2]MOREIRA, I. C. A inclusão social e a popularização da ciência e tecnologia do Brasil. *Inclusão Social*. Brasília, v. 1, n. 2, p. 11-16, 2006.

Agradecimentos

CNPq – Processo 409697/2023

Área: EDU

Níveis de compreensão da Química Orgânica no Ensino Médio: reflexões sobre currículo.

Eduardo Dias Albino* **(PG)[1], Drª. Daniela Gonçalves de Abreu Favacho (PQ)[1].**

eduardo.albino@usp.br ; danielaga@ffclrp.usp.br

[1] *Universidade de São Paulo, Faculdade de Filosofia, Ciências e Letras de Ribeirão Preto, Departamento de Química, Programa de Mestrado em Química em Rede Nacional, Ribeirão Preto.*

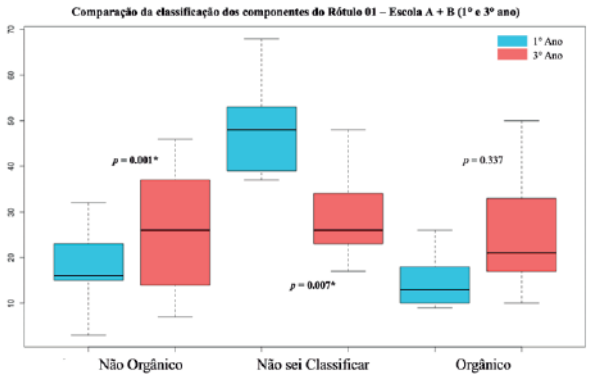
Palavras-Chave: *Química Orgânica, Educação Científica, Formação Cidadã , Currículo escolar.*

Highlights

Levels of understanding of Organic Chemistry in High School: reflections on the curriculum. Interpretation of organic compounds on commercial product labels. The school curriculum does not provide high school graduates with the ability to classify organic compounds present in everyday life.

Resumo/Abstract

A intencionalidade docente pode propiciar um ensino de química em que seja possível associar nomes, fórmulas às situações comuns do dia a dia das pessoas. Ático Chassot (2018) em sua síntese sobre "*fazer educação por meio da química*" enfatiza que o ensino de química deva possibilitar cada vez mais uma aprendizagem que forneça suporte para se fazer educação, ou seja, essa interpretação nos aponta uma direção de compreensão de que não basta a simples transmissão de conteúdos químicos, mas a elaboração de uma proposta que subsidie a instrumentalização para melhor se fazer educação. Segundo o autor, a maior responsabilidade do ensino de Ciências é formar pessoas críticas, que sejam agentes de transformação. Embora os compostos de carbono façam parte da constituição de muitos produtos utilizados por adolescentes, é notável uma redução na abordagem de conteúdos de Química Orgânica desde os Parâmetros Curriculares Nacionais para Ensino Médio até a recente Base Nacional Curricular Comum. Este trabalho é um recorte de uma Dissertação e teve como objetivo investigar a compreensão de alunos concluintes do Ensino Médio (EM) sobre Compostos Orgânicos presentes no cotidiano, por meio da interpretação da composição química descrita em rótulo de produtos comerciais. Adotou-se o rótulo de Creme Dental pelo uso cotidiano e por apresentar substâncias orgânicas e inorgânicas. O questionário foi diagramado em caixa de seleção na plataforma SurveyMonkey, podendo o entrevistado para cada substância selecionar uma opção entre "não orgânico", "não sei classificar" e "orgânico". O questionário foi aplicado para dois grupos de alunos Grupo 1 (80 alunos de 1ºEM público/privado) e Grupo 2 (80 alunos de 3ºEM público/privado). Foi aplicado o teste T de Welch pelo software R e os resultados apresentados em forma de *Boxplot* comparativo conforme a figura. O valor de p é uma medida estatística que indica a probabilidade de obter os resultados observados ou mais extremos, assumindo que não há diferença real entre os grupos comparados. Os resultados obtidos foram para a categoria "Não Orgânico", a significativa diferença (p = 0.001*) nas médias entre os grupos o que sugere amplia-se o entendimento sobre o tema, os estudantes conseguem identificar e classificar os compostos inorgânicos à medida que progridem do 1° para o 3° ano. Da mesma forma, na categoria "Não sei classificar", constatou-se diferença significativa (p = 0.007) nas médias entre os grupos, o que indica a falta de conhecimento na classificação dos componentes em alunos do 1ºEM e um aumento na assertividade classificatória em alunos do 3ºEM. Por outro lado, na categoria "Orgânico", não se observou diferença estatisticamente significativa (p = 0.337) nas médias entre os grupos. Tal fato sugere uma estabilidade na compreensão e na classificação dos componentes orgânicos ao longo dos anos escolares. Ou seja, é possível concluir que o currículo escolar não possibilita ao aluno concluinte a compreensão significativa em classificar os compostos orgânicos presentes no cotidiano e consumidos diariamente pelos adolescentes.



CHASSOT, A. **Para que(m) é útil o ensino?**. 4ª ed. Canoas: Editora ULBRA, 2018.

Agradecimentos/Acknowledgments

Ao Programa de Mestrado em Química em Rede Nacional da FFCLRP

Área: EDU

O ensino de macromoléculas através do Jogo da Memória: uma alternativa de aula diversificada

Ana Júlia N. da Costa (IC),[1*] Talita C. Marques (IC),[1] Maryana V. B. da Silva (IC),[1] Priscila A. R. Sousa (FM),[1] Júlio S. P. Ortiz (PQ),[2] Jocélia Pereira de C. Oliveira (PQ).[1]

nascimentoanajulia952@gmail.com

[1]*Instituto de Química, UFCAT,* [2]*Instituto de Física, UFCAT*

Palavras Chave: *Jogo lúdico, Bioquímica, PIBID.*

Highlights

Teaching macromolecules through the Memory Game: a diverse class alternative

The proposed work was developed with high school and EJA classes, awakening students' curiosity about Macromolecules in everyday life using the memory game as an alternative methodology.

Resumo/Abstract

A bioquímica é uma ciência que aborda fenômenos presentes nos sistemas vivos, sendo considerada como a ciência química da vida. Dentre os inúmeros assuntos abordados pela bioquímica destaca-se as macromoléculas (proteínas, carboidratos, ácidos nucléicos e lipídios) que são estudadas considerando a estrutura e funções que exercem no metabolismo, além de reações químicas que ocorrem no organismo vivo. Por ser um assunto com características, muitas vezes, abstratas, é necessário a utilização de atividades diferenciadas para facilitar a compreensão dos alunos. Nesse contexto, esse trabalho foi desenvolvido por bolsistas do subprojeto Interdisciplinar de Química e Física do Programa Institucional de Bolsas a Iniciação à Docência (PIBID) da UFCAT, direcionado para turmas da 3º série do Ensino médio regular e 3º EJA (Educação de Jovens e Adultos), ambas do período noturno de uma escola pública na cidade de Catalão-Goiás. As atividades propostas foram realizadas em três aulas na disciplina de Química sendo divididas em: primeira etapa – realização de aula expositivo-dialogada, apresentando os principais conceitos sobre macromoléculas destacando-se a classe dos lipídeos. Nessa etapa os alunos conheceram exemplos do cotidiano e curiosidades relacionadas ao assunto. Após a aula os alunos foram instruídos a responderem um questionário sobre os lipídeos, a fim de se verificar os conhecimentos adquiridos, realizando-se ao final a correção do questionário com os alunos, gerando uma ampla discussão. Na segunda etapa os alunos foram divididos em grupos e foi aplicado um jogo da memória sobre os lipídeos. O jogo (Figura 1) foi produzido considerando as características e principais informações sobre as estruturas e compostos químicos que foram estudados na primeira etapa. Ao final realizou-se a terceira etapa com os mesmos grupos que foram divididos para aplicação do jogo. Foram feitas perguntas sobre a classe de macromoléculas estudada e o grupo que respondeu a maioria das questões ganhou um brinde como forma de premiação. Ao final foi possível concluir que um processo de ensino aprendizagem aliado a práticas pedagógicas diferenciadas torna-se suporte para atrair a atenção dos alunos, uma vez que metodologias diferenciadas possibilitam atender as diversidades de uma sala de aula facilitando a aprendizagem.

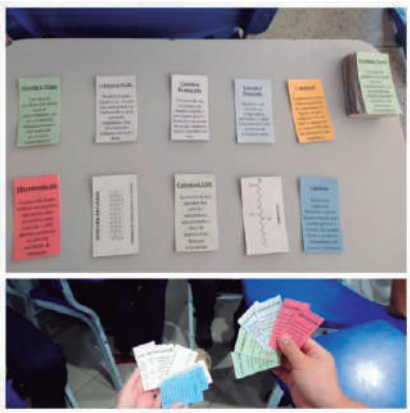


Figura 1: Jogo da memória aplicado nas turmas de Ensino médio Regular e EJA.

Agradecimentos/Acknowledgments

Á CAPES, Ao PIBID, à UFCAT e ao Instituto de Química.

Área: EDU

O ENSINO DE QUÍMICA NA PERSPECTIVA DE ALFABETIZAÇÃO CIENTÍFICA: metodologias disruptivas para a formação de professores de Ciências

Dayanne Dailla da Silva Cajueiro (PG) [1*], Danielle Rodrigues Monteiro da Costa (PQ)[2].

***dayanne_dailla@hotmail.com**

[1]*Programa de Pós-graduação em Educação em Ciências e Matemática- PPGECM-UNIFESSPA*
[2]*Programa de Pós-graduação em Educação em Ciências e Matemática- PPGECM-UNIFESSPA*
Palavras-Chave: Ensino de Química, Alfabetização científica, formação de professores.

Highlights

THE TEACHING OF CHEMISTRY FROM THE PERSPECTIVE OF SCIENTIFIC LITERACY: disruptive methodologies for the training of teachers of Natural Sciences.

The Teaching of Chemistry; Scientific literacy; Teacher training; Science education.

Resumo/Abstract

Este trabalho é um recorte de uma pesquisa cujo objetivo é evidenciar estratégias didáticas no Ensino de Química que viabilizem a alfabetização científica na formação de professores com perspectivas de metodologias ativas que, também, desenvolvam a formação cidadã de seus futuros alunos. Com isto, buscou-se, por meio da pesquisa qualitativa, na perspectiva narrativa, analisar o processo formativo de futuros professores das várias áreas das Ciências da natureza (Química, Física, Biologia...) em um curso de formação docente (de curta duração) que ocorreu no contexto de um evento regional, em parceria, com instituições de Ensino Superior - cuja temática norteadora se pautava na formação de professores e o Ensino de Química na Educação Básica. Na ocasião participavam 30 licenciados (que consentiram a participação na pesquisa em questão), que tiveram suas narrativas registradas por meio de relatos escritos ao final de cada atividade. Para análise das informações adotou-se a Análise Textual Discursiva (ATD) em que, após o processo de desmontagem das narrativas dos sujeitos, organizou-se as mesmas em categorias de análise - categoria 1: o ensino investigativo na perspectiva do ensino de Química; categoria 2: o ensino de Química a partir da alfabetização Científica com vistas a formação cidadã. De acordo com a interpretação, dos dados levantados, observou-se que na categoria 1 foram expressas evidências de que o ensino investigativo possibilita que o conhecimento científico seja vivenciado a medida que o sujeito tem contato com o conhecimento de modo construtivista, isto é sinalizado, dentre os discursos, quando o sujeito 1 cita que “as grandezas químicas fizeram mais sentido quando se pôde enxergá-las dentro de nossa realidade”; Já na categoria 2 os professores destacaram para a prática da alfabetização científica como impulsionadora da formação cidadã quando levantaram inúmeras problemáticas ambientais da região que, por falta de conhecimento da população, agridem o meio ambiente, como citam o sujeito 2 e 3: “temos rios que são afetados diretamente pelo óleo de embarcações que muitas vezes são oriundos dos próprios ribeirinhos que são as pessoas que mais precisam dele e eles acham que aquilo um dia sumirá do rio e não é bem assim, mas acho que agiriam diferente de soubessem o que acontece...”; “As pessoas gostam de almoçar nos restaurantes flutuantes daqui, mas não imaginam como esse turismo sem controle pode afetar a fauna e flora local e com esse conhecimento acredito que iriam visitar os locais de maneira mais responsiva”, tais narrativas demonstram a preocupação docente com a formação cidadã- um aspecto expectado pela alfabetização científica como habilidade. Os resultados evidenciam que a estratégia didática se pauta em despertar o interesse dos participantes - futuros professores de Ciências em metodologias de ensino com enfoque ao ensino investigativo, visando a alfabetização científica no ensino de Química, de alunos da educação básica, a partir de problemáticas socioambientais para atuação responsiva na sociedade e de maneira crítica reflexiva com vistas a formação científica e cidadã.

Agradecimentos/Acknowledgments

A UNIFESSPA e a CAPES pelo financiamento desta pesquisa.

Área: EDU

Oficina temática "Energia e Sustentabilidade" para alunos do ensino médio: possibilidade de aprendizagem de conhecimentos químicos

Maria Eunice Ribeiro Marcondes (PQ),[1] Fabio Luiz de Souza (PQ),[1] Luciane Hiromi Akahoshi (PQ),[1].

mercarco@iq.usp.br

[1]*Instituto de Química da USP*

Palavras Chave: *Oficina Temática, Atividade Experimental, Energia, Sustentabilidade, Abordagem CTSA.*

Highlights

Learning chemistry from energy and sustainability: a workshop for high school students.

In this paper we present the results of an investigation of concepts related to energy and sustainability presented by high school students, based on experiments offered in the workshop.

O GEPEQ (Grupo de Pesquisa em Educação Química do IQ-USP) oferece oficinas temáticas para estudantes do ensino fundamental e médio, abordando temas que relacionam ciência, tecnologia, sociedade e ambiente (CTSA), tendo em vista a compreensão de conceitos e o julgamento e tomada de decisões em relação à realidade social (SANTOS; AULER, 2019). Neste trabalho, investigamos possíveis impactos de uma oficina temática envolvendo a produção, uso e problemas ambientais de diferentes fontes de energia (carvão, álcool, gasolina, solar) na aprendizagem de química de estudantes do ensino médio.

A metodologia utilizada foi dividida em três etapas: 1 - desenvolvimento e aplicação da oficina sobre o tema "Energia e Sustentabilidade"; 2 - construção e aplicação de um instrumento de coleta de dados contendo questões a respeito dessa temática, tanto para participantes como para não-participantes da oficina; 3 - análise qualitativa dos dados obtidos.

Desenvolvimento e aplicação: a oficina "Energia e Sustentabilidade" é constituída por quatro experimentos: produção de carvão vegetal; aquecimento solar; poder calorífico de combustíveis e simulação da chuva ácida. A discussão dos experimentos, promovida pelos monitores (estudantes de graduação), envolve aspectos CTSA

Aplicação do questionário: O questionário elaborado pelo grupo continha 7 questões de múltipla escolha, 1 questão aberta e 5 afirmações com escala Likert de 5 pontos (discordo totalmente até concordo totalmente). Ele foi aplicado via google formulário para 110 estudantes de ensino médio de escolas públicas, dos quais 26 participaram da oficina temática.

Resultados e análises:

Enquanto 65% dos participantes da oficina compreendem que os gases formados na produção artesanal de carvão vegetal são prejudiciais ao ambiente, este índice é de apenas 23% entre os não participantes da oficina. Apenas 23% dos participantes consideraram o carvão vegetal como recurso não renovável, sendo esta compreensão errônea manifestada por 54% dos não participantes. 62% dos participantes diferenciaram um aquecedor solar de um painel fotovoltaico, enquanto 44% dos não participantes identificaram corretamente esses dispositivos. 85% dos participantes sabiam que etanol é um combustível renovável obtido da cana-de-açúcar ou milho e que a gasolina é derivada do petróleo e não renovável. Esse acerto cai para 69% entre os não participantes.

Os resultados mostram que, de maneira geral, a oficina temática "Energia e Sustentabilidade" tem contribuído para aprendizagem de conteúdos CTSA relativos aos diferentes modos de produção e uso de energia, bem como para a reflexão sobre aspectos sociais e ambientais ligados ao tema.

Referência: SANTOS, R. A.; AULER, D. Ciência & Educação, Bauru, v. 25, n. 2, p. 485-503, 2019.

Agradecimentos/Acknowledgments

A todas as escolas e seus alunos que participaram da atividade no IQUSP.

Área: EDU

O Jogo de Realidade Alternada Curto (Short ARG) na Temática de Café: Um Relato de Experiência na Educação Básica

Jonatan Pinto Cavalcante (PG),[1]* Marlon Herbert Flora Barbosa Soares (PQ),[2] Claudia Moraes de Rezende (PQ).[1]

jonatanpcavalcante@gmail.com

[1]Instituto de Química, UFRJ; [2] Instituto de Química, UFG

Palavras Chave: ARG; Jogo pedagógico; *Ensino de química, Café*

Highlights

The Short Alternating Reality Game (Short ARG) on the Coffee Theme: An Experience Report in Basic Education

This work aims to present an experience report on the application of a Short ARG pedagogical game on the coffee theme for high school students.

Resumo/Abstract

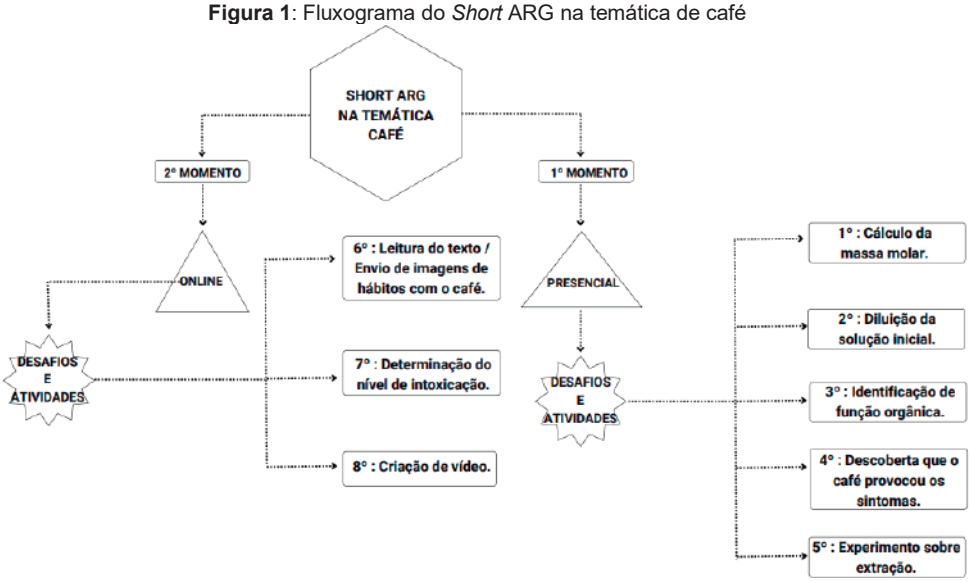
O jogo pedagógico do tipo *Short* ARG utiliza características enigmáticas combinando elementos digitais com o mundo real numa narrativa, nos quais os alunos são os próprios jogadores. Esse jogo promove uma aprendizagem colaborativa e utiliza a Tecnologia Digital da Informação e Comunicação – TDIC.

Desse modo, este trabalho tem por objetivo apresentar um relato de experiência da aplicação de um jogo pedagógico desse tipo na temática de café para trabalhar conteúdos de química para alunos do ensino médio.

A escolha do café como temática desse jogo se justifica pelo fato de que essa bebida é amplamente consumida pelos jovens e representa um assunto que pode ser explorado de maneira interdisciplinar no ensino. É possível explorar os conceitos dos conteúdos de separação de misturas, unidades de concentração de soluções, diluição de soluções, solubilidade de sólidos em água e identificação de funções orgânicas relacionando com a história, biologia e estabelecendo uma ligação com o cotidiano dos estudantes.

O jogo, que teve como o público-alvo os estudantes da segunda série do Ensino Médio, foi elaborado seguindo a sequência descrita no fluxograma da figura 1.

Figura 1: Fluxograma do *Short* ARG na temática de café



O jogo na temática de café permitiu a abordagem, nos dois primeiros desafios, de cálculos químicos dentro do assunto de soluções, como o da massa molar da cafeína, a partir de uma concentração molar de uma solução conhecida, e de diluição; no assunto de química orgânica os alunos identificaram as funções orgânicas presentes na molécula da cafeína, conforme no 3° desafio; já no 5º desafio, os alunos realizaram um experimento do método de extração sólido-líquido para a compreensão da temperatura da água no preparo da bebida café. Desse modo, o *Short* ARG na temática de café é um potencial auxiliador no processo de ensino e aprendizagem para o ensino de química, em que possibilitou com que os alunos estivessem imersos na aventura do jogo, proporcionando um debate entre os membros dos grupos para as resoluções dos desafios, ao qual pôde promover uma aprendizagem colaborativa.

Agradecimentos/Acknowledgments

Ao Colégio CIEP 170 – Gregório Bezerra, localizado na baixada fluminense, no município de São João de Meriti, RJ

Área: EDU

Orgânica Experimental na graduação: Novas abordagens para o ensino de Química Verde para educação do cidadão

Juliana A. Francisco (IC),[1] Thuany B. S. Aguiar (IC),[1] Matheus B. Guimarães (IC),[1] Erica N. D. Figueiredo (IC),[1] Pedro A. R. Lessa (IC),[1] Tiago R. Navarro (PG),[1] Patrick P. Pimentel (PG)[1,2] Evanoel Crizanto de Lima (PQ)[1*]

juamerica@ufrj.br; evanoel.crizanto@gmail.com

[1]Laboratório de Catálise e Síntese de Substâncias Bioativas, Centro Multidisciplinar UFRJ-Macaé, Pólo Ajuda, Macaé-RJ; [2]Laboratório de Catálise e Síntese (CSILab), sala 413, Instituto de Química, Campus do Valonguinho, Universidade Federal Fluminense, Centro, Niterói-RJ.

Palavras Chave: *Química verde, Sonoquímica, Mecanoquímica, Ftalimida.*

Highlights

Experimental Organic Chemistry at undergraduate level: New approaches to teaching Green Chemistry for citizen education. Experiments were carried out using ultrasound and mechanochemistry with phthalic anhydride.

Resumo/Abstract

A Química sempre esteve presente no desenvolvimento científico, tecnológico e do bem-estar da sociedade, seja através de insumos utilizados na alimentação, no vestuário ou mesmo na obtenção de medicamentos para as mais diversas enfermidades. Ultimamente, tem havido um crescimento da preocupação da comunidade científica em se promover ações para o desenvolvimento sustentável do planeta. Neste contexto, a Química Verde é considerada uma área multidisciplinar que cria, desenvolve e aplica produtos e processos químicos que visam à redução ou eliminação do uso e da geração de substâncias nocivas ao meio ambiente e ao homem.[1] Possui 12 princípios, dentre os quais estão a prevenção da geração de resíduos, o uso de solventes mais seguros e a busca pela eficiência energética.[2] Embora tais princípios sejam de vital importância para o desenvolvimento e bem estar-social das próximas gerações, uma consulta *on line* às ementas da disciplina de Química Orgânica Experimental dos cursos de Química de algumas das principais Universidades do país evidencia que este tema não tem sido explorado nas aulas práticas, desta forma, os profissionais que tem se formado terão uma pronunciada deficiência neste tema de extrema relevância. Uma das poucas aulas práticas que aborda estes princípios é a síntese da ftalimida, experimento que tem seu potencial subestimado e poderia ser mais explorado. Neste experimento não se utiliza solvente orgânico, porém, há o emprego de elevadas temperaturas. No contexto da sustentabilidade, o emprego da sonoquímica (uso de ultrassom em síntese) e da mecanoquímica são abordagens quimicamente verdes e que não são exploradas nas aulas práticas de Química Orgânica. Este trabalho tem como objetivo o uso de sonoquímica e mecanoquímica para se abordar metodologias verdes nas aulas de Química Orgânica Experimental, revisitando o experimento de obtenção da ftalimida e propondo um novo experimento para a graduação, empregando a oxidação de anidrido ftálico. Inicialmente, foram realizados 3 experimentos de mecanoquímica, macerando-se ureia e anidrido ftálico, utilizando-se gral e pistilo, com diferentes tempos reacionais: 1h, 1,5h e 2h. O acompanhamento da reação por CCF pareceu indicar o término da reação, além de se sentir o odor de amônia que é liberado durante o consumo do anidrido ftálico. Porém, o espectro de CG-EM indicou a presença de uma única substância que era o anidrido, material de partida. Outra reação foi feita utilizando água como solvente empregando-se ultrassom, com e sem catálise. A catálise foi realizada com uma gota de HCl ou APTS (0,1 eq.). As análises mostraram que o produto não foi obtido, o que nos conduziu a uma nova abordagem experimental. Reações preliminares utilizando rearranjo de Curtius para oxidação de alguns anidridos empregando irradiação com ultrassom apresentaram resultados satisfatórios e serão explorados com anidrido ftálico. Ademais, outros parâmetros como diferentes tempos reacionais e catalisadores serão utilizados com o intuito de otimizar a reação e seu rendimento.

Todos os discentes participaram da síntese por mecanoquímica e/ou emprego de ultrassom.

Referências:

[1] Júnior, C. A. S. *et. al.*. *Quím. Nova* **2022**, *45*, 1010; [2] Marques, C. A. *et. al.*. *Quím. Nova* **2020**, *43*, 1510.

Agradecimentos/Acknowledgments

Authors thank Faperj and CNPq for financial support and Farmanguinhos for analytical data.

Área:EDU
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

PERIÓDIBELA: UM JOGO DIDÁTICO PARA ENSINAR TABELA PERIÓDICA

Maryana Victória B. da Silva (IC),[1] Bianca Amoras B. Tavares (IC),[1] João Felipe M. de Abreu (IC),[1] Ana Júlia N. da Costa (IC),[1] Gabriela da Costa Ribeiro (FM) ,[1] Julio S. E. Ortiz (PQ),[2] Jocélia Pereira de C. Oliveira (PQ).[1*]

maryana.silva@discente.ufcat.edu.br; joceliapereira@ufcat.edu.br

[1]Instituto de Química, UFCAT; [2]Instituto de Física UFCAT

Palavras Chave*: Metodologia Alternativa, Lúdico, Ensino de Química.*

Highlights

PERIÓDIBELA: A TEACHING GAME TO TEACH THE PERIODIC TABLE

A didactic game covering the Periodic Table was applied to a 1rd grade high school class. After applying the game, a conversation was held to evaluate the methodology applied.

Resumo/Abstract

O Ensino/aprendizagem de Química tem sido um desafio, por abordar temas considerados de difícil compreensão pelos estudantes. Isso ocorre, porque os conteúdos podem envolver conceitos abstratos, como também, uma grande variabilidade de fórmulas e nomenclaturas.[1] Muitas escolas públicas no Brasil são carentes de materiais para melhorar o aprendizado e por fazer parte do Programa Institucional de Bolsas de Iniciação à Docência (PIBID) da UFCAT, vimos uma oportunidade de levar metodologias alternativas de ensino para uma escola estadual no município de Catalão – Goiás. O conteúdo indicado pela professora foi Tabela periódica, e por se tratar de uma escola com turmas grandes, surgiu a proposta de aplicar-se um jogo didático, pois embora já se tenha uma grande quantidade desse tipo de jogos na literatura, pensou-se em um jogo de tabuleiro de fácil manuseio e aplicação por professores de turmas com grandes quantidades de alunos, não necessitando de cartas, pois as perguntas e desafios ficam descritos diretamente nas casas do próprio tabuleiro, sendo cada cor um tipo de pergunta e com nível diferente de dificuldade. O tabuleiro foi produzido com impressão em papel cartão e plastificado para ter maior durabilidade. Os pinos de cores diferentes e dados foram obtidos em comercio local. O jogo foi aplicado em quatro turmas da 1ª série do Ensino Médio do período matutino. Inicialmente o conteúdo foi ministrado em sala de aula e a aplicação do jogo surgiu como proposta de fixação do conteúdo. Os alunos foram divididos em seis grupos de cinco alunos, cada grupo recebeu um tabuleiro com pinos coloridos e um dado para iniciar o jogo e tinham também tabelas periódicas para utilização como consulta (Figura 1). O jogo foi denominado de “Periódibela” e após as intervenções pedagógicas realizadas pelo PIBID, todos os kits com os materiais para aplicação do jogo foram doados para escola.

Figura 1: Jogo didático “Periódibela”.

Após a aplicação do jogo iniciou-se uma roda de conversa para avaliar a metodologia utilizada. De maneira geral, não se constatou dificuldades, visto que foi observada grande aceitação por parte dos estudantes, pois além do aspecto lúdico também se incentivou o trabalho em equipe e as interações socioemocionais ao promover discussões dentro dos grupos na tentativa de responder corretamente as perguntas. Além do conteúdo de Tabela periódica, realizou-se também uma contextualização com exemplos de elementos químicos do cotidiano e a introdução da temática da importância das mulheres na descoberta de elementos químicos. Esse trabalho soma-se a outros que demonstram a importância dos jogos didáticos como mediadores do processo de ensino e aprendizagem, auxiliando também, na prática, no desenvolvimento das habilidades e competências dos bolsistas do PIBID e futuros docentes.

Agradecimentos/Acknowledgments

Á CAPES pelas bolsas, à UFCAT e ao Programa *Institucional de Bolsas de Iniciação à Docência* (*PIBID*).

[1]MARTINS, M. S. P.; CAVALCANTI, H. L. B. Quím. nova esc. v. 45, N° 3, p. 187-194, 2023.

Área: EDU

Programa Qui+S: química sustentável no ensino médio: ampliando horizontes educacionais

Germano M. C. Fagundes (IC)[1], Maryna M. Barros (PG)[1], Valeska P. da S. R. Pardi (PQ)[1], Thais A. Silva (FM)[1], Izabella C. N. P. Andrade (PG)[1], Rochel M. Lago (PQ)[1], Ana Paula C. Teixeira (PQ)[1]*, Alfredo L. M. L. Mateus[1], Márlon H. F. B. Soares[2]

thaisalves.profquimica@gmail.com; anapct@ufmg.br

[1]*Departamento de Química, ICEx, UFMG,* [2]*Instituto de Química, UFG*

Palavras Chave: *Sustentabilidade, Curso, Qui+S, Educação básica*

Highlights

Qui+S Program: course for High School Chemistry teachers

Qui+S has developed a course for High School Chemistry teachers that purposes a different approach to catch the attention of students and improve the image of Chemistry and Sustainability among them.

Resumo/Abstract

A SBQ está trabalhando no Programa Qui+S, que tem como objetivo principal impactar a sustentabilidade no país por meio da química. Este é formado por dois Objetivos de Química para o Desenvolvimento Sustentável (OQDS) e respectivos eixos de ação, além de cinco desafios direcionadores, os quais norteiam todos os projetos e ações executados dentro do Qui+S. Dentro do OQDS 1, uma importante inciativa em execução é o curso "química sustentável no ensino médio: ampliando horizontes educacionais"(Figura 1). Assim, este trabalho tem como objetivo apresentar o conteúdo desse projeto.

O desenvolvimento do curso "química sustentável no ensino médio: ampliando horizontes educacionais" é uma ação em parceria com o CFQ. A partir dessa, almeja-se apresentar conteúdos sobre química e sustentabilidade para professores da educação básica utilizando como exemplos os grandes desafios em sustentabilidade no contexto brasileiro. Espera-se que os professores possam utilizar esses conteúdos para trabalharem esses assuntos em sala de aula, ampliando o conhecimento dos alunos e impactando a sustentabilidade no Brasil a longo prazo.

Para atingir os objetivos citados, o projeto foi divido, em um primeiro momento, em dois módulos: "química para a transformação de resíduos" e "química para o uso sustentável da água". Nesses módulos, encontram-se aulas chamadas de "contextualizando" e outras de "experimenta(ação)". O primeiro tipo corresponde àquelas com conteúdo textual, o qual apresenta a base técnica do conhecimento em questão. O outro tipo é formado por experimentos e atividades práticas que podem ser realizadas em sala de aula sem necessidade de materiais complexos. Desta forma, os professores podem facilmente replicar a proposta para os seus alunos.

A iniciativa está hospedada no site www.quimaiss.com.br, no qual os professores têm acesso gratuito a 33 aulas por meio de um cadastro simples. Atualmente, são 221 (08/02) professores inscritos distribuídos por todo o Brasil (Figura 2). Em uma próxima etapa do projeto, os professores que quiserem poderão submeter práticas sobre sustentabilidade que realizaram em sala de aula e concorrer a uma viagem para a 47ª Reunião Anual da Sociedade Brasileira de Química, na qual serão premiados.

Figura 1: Banner de divulgação do curso "química e sustentabilidade no ensino médio".

Figura 2: Mapa de inscritos no curso por estado do Brasil – quanto mais escuro, maior o número de inscritos.

Agradecimentos/Acknowledgments

Capes, CNPq, FAPEMIG, INCT Midas, SBQ, CFQ e UFMG.

Área: EDU

Projeto "De Olho na Química": experimentação e divulgação científica no Sul do Piauí

Kaio H.S. da Silva (IC),[1*] Fernando C. Damasceno (PQ),[1] Vanessa N. dos Santos (PQ),[1] Aparecida M.S. Mimura (PQ).[1]

kaiosoares201@gmail.com

[1]*Colegiado de Licenciatura em Química, Universidade Federal do Vale do São Francisco - UNIVASF*

Palavras Chave: *experimentação, química, divulgação científica.*

Highlights

"De Olho na Química" Project: Experimentation and scientific divulgation in South Piauí

Problematizing experimentation can help the teaching-learning process, linking theory and practice.

Resumo/Abstract

O curso de licenciatura em Química da Universidade Federal do Vale do São Francisco (UNIVASF), implementado em 2017 no Campus Serra da Capivara, em São Raimundo Nonato – PI, atua na formação de profissionais com conhecimentos científicos e tecnológicos na área de Química. No entanto, no ensino médio, a Química ainda é considerada uma ciência abstrata e de difícil compreensão por partes dos alunos. Assim, torna-se necessário promover atividades que envolvam a química do cotidiano na explicação de conceitos e fenômenos químicos, relacionando aspectos microscópicos e macroscópicos. Nesse sentido, a experimentação se apresenta como uma alternativa norteadora, pois através da experimentação problematizadora é possível relacionar a atividade prática realizada com os conteúdos abordados em aula, o que possibilita a construção das relações entre teoria e prática.[1,2] Assim, realizar atividades experimentais contextualizadas é de suma importância para fazer a ponte entre o conhecimento prévio do aluno e o conhecimento científico, além de possibilitar uma interação entre os estudantes, motivando-os a compreender os fenômenos que ocorrem no seu cotidiano e a buscar explicações para os mesmos. Dessa forma, este trabalho teve como objetivo realizar atividades de experimentação em cinco escolas da microrregião de São Raimundo Nonato, como uma estratégia de divulgação científica. As atividades desenvolvidas fazem parte do projeto de extensão "De Olho na Química", devidamente cadastrado na UNIVASF e em execução desde 2019. Em 2023, foram promovidas diversas atividades, como a realização de cinco atividades envolvendo experimentação nas escolas Francisco Antônio da Silva (em São Braz do Piauí), Margarida da Silva Costa (em Coronel José Dias), Antônio Soares Rocha (em Caracol), Iraci Gomes de Sá Soares (em Jurema) e Letícia Macêdo Anísio de Abreu (em Anísio de Abreu). Participaram das atividades professores e alunos do curso de licenciatura em Química e alunos vinculados ao Programa Institucional de Bolsas de Iniciação à Docência (PIBID). Em cada atividade nas escolas, foram realizados três experimentos envolvendo ácidos e bases e indicadores químicos. Também foram discutidas reações químicas, evidências de reações e características dos ácidos e bases comuns no cotidiano, como o vinagre (ácido acético) e a soda cáustica (hidróxido de sódio). Todos os experimentos realizados foram abordados de forma investigativa. Além disso, foram apresentadas informações sobre o curso de Química da UNIVASF e relatos de experiência por parte dos graduandos. Foi possível atingir um público de aproximadamente 700 alunos de ensino médio nas cinco escolas e observou-se ampla interação entre os envolvidos. Todas as atividades desenvolvidas foram também postadas nas páginas das redes sociais no perfil @deolhonaquimica (Instagram, Facebook, YouTube e TikToK), atingindo um público ainda maior (cerca de 4900 seguidores, no total). Assim, bons resultados foram alcançados, uma vez que as atividades tiveram caráter de extensão, a fim de divulgar o curso de Química nas cidades vizinhas, além de despertar o interesse dos alunos, relacionando a experimentação com o cotidiano dos mesmos.

[1]FRANCISCO JUNIOR., W. E.; FERREIRA, L. H.; HARTWIG, D. R. Experimentação Problematizadora: Fundamentos Teóricos e Práticos para a Aplicação em Salas de Aula de Ciências. **Química Nova na Escola**, v. 30, nov. 2008.

[2]MACHADO, P. F. L.; MÓL, G. S. Experimentando química com segurança. **Química Nova na Escola**, v. 27, fev. 2008.

Agradecimentos

UNIVASF e PROEX.

Área: EDU

Químico por um dia: extração de antocianinas como um experimento para a Educação Básica

Sinésio Boaventura Júnior (PQ), Adriana da Silva Santos de Oliveira (PG), Marili Villa Nova Rodrigues (PQ)*

sinesio@unicamp.br; marilivn@unicamp.br

Centro de Pesquisas Químicas, Biológicas e Agrícolas (CPQBA), Universidade Estadual de Campinas (UNICAMP)

Palavras-Chave: *Antocianinas, ensino de ciências, ensino de química, extração, cromatografia*

Highlights

Chemists for a day: Extraction of anthocyanins as an experiment for Basic Education. Encouraging young talents for cientific research.

Resumo/Abstract

As antocianinas são um grupo de pigmentos de origem vegetal responsáveis pelas inúmeras tonalidades de cores encontradas em flores, frutas e folhas. Nos vegetais apresentam funções de antioxidantes, de proteção contra a luz ou de mecanismo de defesa. Essa classe de compostos também é responsável por inúmeras atividades farmacológicas, além do crescente interesse em utilizá-las como corantes naturais. O fenômeno da cor sempre é algo fascinante para os alunos da Educação Básica. Neste trabalho, realizado com estudantes do 2º e 3º ano do ensino médio de escolas públicas da região de Campinas, extraiu-se antocianinas das frutas amora, mirtilo e morango com o objetivo de ensinar ao aluno os conceitos de rendimento, solvente extrator, composição química e cromatografia. Inicialmente, os alunos prepararam os solventes que foram utilizados nas extrações (tabela 1). Em seguida, pesou-se sete amostras de 5,00 g de cada uma das frutas selecionadas, em tubos tipo Falcon de 50mL, adicionou-se 20mL de solvente extrator e obteve-se os extratos após 1 minuto com o auxílio de um dispersor (figura 1). Os extratos foram centrifugados e concentrados em evaporador rotativo à vácuo. A avaliação das antocianinas presentes nos extratos foi realizada por cromatografia em camada delgada (CCD), utilizando-se, como fase móvel, uma solução de acetato de etila, ácido acético glacial, ácido fórmico e água (100:11:11:26). O revelador foi NP e Macrogol, UV 366 nm.

Tabela 1: Composição dos solventes

Extrato	Solvente extrator
1	Água destilada
2	Água ácida (0,2% de Ácido fosfórico)
3	Água básica (0,2% de Hidróxido de amônio)
4	Água e Etanol (70:30)
5	Água ácida e Etanol (70:30)
6	Água básica e Etanol (70;30)
7	Etanol absoluto

Figura 1: Estudantes do ensino médio – CAF 2024

Os alunos calcularam os rendimentos das extrações e analisaram os dados de CCD, verificando que o melhor solvente extrator foi a mistura de água ácida e etanol (70:30), pois seus extratos apresentaram a maior quantidade de antocianinas representado pela intensa tonalidade de cores. O experimento foi realizado no laboratório da Divisão de Química Orgânica e Farmacêutica do CPQBA / UNICAMP. A interação entre as escolas e as Universidades é de suma importância para despertar o interesse dos alunos pelas Ciências da Natureza, em especial, pela Química, normalmente vista como uma ciência muito difícil e pouco atrativa. O presente trabalho desenvolveu um experimento viável, o qual proporcionou o contato com os equipamentos de laboratório, com a metodologia do trabalho científico, com os desafios atuais da ciência e o ambiente humano dos laboratórios de pesquisa. Isso mostra a importância de programas de extensão que promovam essa oportunidade do aluno da educação básica vivenciar um dia no laboratório de química, como protagonista na condução do experimento em um ambiente real de trabalho do profissional da química.

Agradecimentos/Acknowledgments

Pró-Reitoria de Pesquisas da Unicamp pelo financiamento – projeto CAF 2024 (FAEPEX 519292)

Área: EDU

Rede de apoio ao ensino de química e ciências na educação básica brasileira

Janaína de Paula e Silva (PG),[1] Wladmir T. Silva (PG),[1] Mikaelly V. S. Magalhães (IC),[1] Bárbara R. Vicensoni (IC),[1] Alfredo M. Lameirão (PQ),[2] Márlon H. F. B. Soares (PQ),[3] Nyuara A. S. Mesquita (PQ),[3] Ana P. C. Teixeira (PQ)[1], Maria H.de Araújo (PQ)[1], Rochel M. Lago (PQ)[1], Rita C. O. Sebastião (PQ),[1*]
janainapaulasilva@ufmg.br; ritacos@ufmg.br
[1]Departamento de Química, ICEX, UFMG; [2] Colégio Técnico, UFMG, [3]Instituto de Química, UFG
Palavras-Chave: *Educação básica, Química e ciências, Inovação e melhoria educacional, Formação inicial e continuada, Tecnologia educacional, Colaboração educacional*

Highlights

CREATION OF A SUPPORT NETWORK FOR TEACHING CHEMISTRY AND SCIENCE IN BASIC EDUCATION
Continuing training and incentive for basic education teachers
Development of educational resources for chemistry and science classes
Promotion of academy-school partnership

Resumo/Abstract

O Programa Internacional de Avaliação de Estudantes (PISA) é um programa da Organização para a Cooperação e Desenvolvimento Econômico (OCDE) que avalia, a cada 3 anos, o desempenho de estudantes de 15 anos em diferentes países. Segundo o último relatório, 55% dos alunos não alcançaram o patamar mínimo de aprendizagem em ciências. Nesse cenário, o Brasil ocupa a posição 61 entre os 80 países avaliados. Dentre as carências no ensino de ciências no Brasil, identificamos: dificuldades de aprendizagem; falta de incentivo à permanência na educação; escassez na oferta e incentivo da formação continuada de professores; falta de integração com a tecnologia e escassez na promoção da educação inclusiva. O objetivo principal deste trabalho é criar uma rede de apoio para impactar positivamente a qualidade do ensino de química e ciências, contribuindo com o desenvolvimento de estudantes e professores da educação básica (EB) brasileira. Esta rede é composta por especialistas em educação e inovação tecnológica de universidades federais, organizações não-governamentais e professores da educação básica. Os principais eixos de atuação são: formação continuada de professores, desenvolvimento de recursos educacionais, implementação de laboratórios virtuais, promoção da inclusão e diversidade, integração de inovação e tecnologia, desenvolvimento de experimentos químicos com foco em tecnologia e sustentabilidade, parcerias com instituições de ensino superior e pesquisa, estímulo à participação em eventos científicos, apoio às escolas com IDEB abaixo de 6 e monitoramento e avaliação contínua das ações. Os principais produtos desenvolvidos e resultados obtidos são apresentados no Quadro 1.

Quadro 1. Eixos de atuação, produtos desenvolvidos e resultados obtidos.

Eixo de atuação	Produtos/Resultados
Formação Continuada de professores	1 plataforma com cursos online 2 workshops de formação 6 equipes de desenvolvimento
Recursos Educacionais (RE)	23 Recursos Educacionais (RE) (jogos, experimentos e vídeos)
Laboratórios Virtuais	Em desenvolvimento
Inclusão e Diversidade	2 RE para PCD 1 canal de podcast para EB 3 perfis de divulgação científica
Inovação e Tecnologia	3 maratonas de inovação 1 startup com estudantes da EB

Eixo de atuação	Produtos/Resultados
Comunidade de professores da EB	Comunidade no whatsapp com 70 prof.de química e ciências da EB
Parcerias	1 parque tecnológico 32 escolas públicas
Eventos científicos	3 congressos academia-EB
Apoio às escolas	2 polos de Empréstimos de RE 20 labs. para compartilhar infraestrutura com a EB
monitoramento e avaliação	2 encontros anuais da rede 4 formulários de avaliação de satisfação

Com o desenvolvimento deste trabalho, destacamos os principais impactos esperados: estímulo à curiosidade científica, desenvolvimento de habilidades, inclusão e equidade, melhoria das práticas pedagógicas, integração de tecnologia e inovação nos experimentos, aumento do engajamento dos estudantes, compartilhamento de recursos e promoção do letramento científico. Referências: BRASIL. Instituto Nacional de Estudos e Pesquisas Educacionais Anísio Teixeira (Inep). Notas sobre o Brasil no Pisa 2022. Brasília, DF: Inep, 2023.

Agradecimentos/Acknowledgments

INCT Midas, CNPq, FAPEMIG and UFMG/PRPq/Proex for financial support.

Área: EDU

Sherlock Holmes vai à praça

Railda Neyva M. Araújo (FM),[1*] Francisco Carlos dos Santos (FM),[1] Antonia Eliana C. Nogueira (FM)[1], Reinaldo Viziney S. Moreira (FM)[2], Manoel L. Lopes Junior (PQ),[3] Lourivaldo S. Santos (PQ).[4]

raildamoreira@hotmail.com; lsslouri@gmail.com

[1]E.E.E.M. Agostinho Moraes de Oliveira/SEDUC/PA; [2]SEMED/Inhangapí; [3]UFPA-Campus Cametá; [4]Programa de Pós-graduação em Química/ICEN/UFPA.

Palavras Chave: *Sherlock Holmes, Feira de Ciências, Inhangapi.*

Highlights

Sherlock Holmes goes to the square. A staging of a murder was presented at a high school science fair, with the aim of demonstrating the importance of “forensic chemistry” in the elucidation of crimes.

Resumo/Abstract

As Feiras de Ciências de Escolas Municipais e Estaduais têm como objetivo oferecer um espaço de divulgação e cultura científica, que se constitui por meio de projetos de Pré-Iniciação Científica, implicando relações pedagógicas que promovam a formação acadêmica dos estudantes. Os projetos de pesquisa buscam a resolução de problemas baseados na realidade cotidiana, envolvendo análise crítica e tendo como princípio, interferir positivamente nesse contexto, trazendo benefícios à escola e à sociedade. Os projetos devem dialogar com temáticas que busquem atrair a atenção de alunos, professores, pais e a comunidade em geral. A Escola Estadual de Ensino Médio Agostinho Moraes de Oliveira, localizada no município de Inhangapí no estado do Pará, realiza anualmente uma Feira de Ciências, Arte e Cidadania na praça (FECACI), o evento tem consagrado-se como de muita relevancia, tanto para a Escola Agostinho Moraes de Oliveira, quanto para o municipio, já que, engloba, todas as demais escolas da cidade, as secretarias municipais, escolas visitantes de municipios vizinhos, e outras instituições parceiras. Em sua terceira edição, em novembro de 2022, o evento ocorreu com grande participação de alunos, escolas, professores, e comunidade em geral, com apresentação de projetos científicos, culturais e artísticos. Dentre os diversos projetos apresentados, destaca-se o projeto “Ciências Forenses: É elementar meu caro aluno” coordenado pelos professores de Química e Biologia da referida escola e desenvolvido com 20 alunos das três séries do ensino médio. Neste projeto foi trabalhado, a importância das ciências forenses, conceito, campo de atuação e orientações aos alunos que têm interesse de seguir nessa área. Nas semanas que antecederam o evento, foram realizadas palestras, pesquisas e testes experimentais simples, relacionados à química forense, como a revelação da impressão digital por vapor de Iodo (I_2). Também foi produzida uma encenação que simulava uma cena de crime, na qual, os alunos interpretavam os personagens, como: policiais, peritos e repórteres. O crime em questão, tratava-se do assassinato de uma pessoa da comunidade, e objetivava demonstrar a importância das ciências forenses, especialmente a química, na elucidação de crimes, como um verdadeiro mistério solucionado por Sherlock Holmes. Na cena, foi narrado pelos repórteres, que o corpo da vítima, foi encontrado às margens do rio Inhangapí, e que a perícia recolheu materiais e provas, encontrados no local, inclusive uma faca, que mais tarde se constatou ser a arma do crime. Os alunos que representavam os peritos, realizaram o teste que revela as impressões digitais por vapor de Iodo (I_2), e explanaram sobre a adsorção do vapor de iodo, pelos “ácidos graxos”, do suor, que aliado a outras técnicas, possibilitou desvendar o crime. As apresentações foram realizadas em uma sala, e contaram com 4 sessões de 30 minutos cada, com plateia de 25 pessoas por sessão. Após cada sessão, houve um diálogo com a plateia, esclarecendo alguns pontos até então desconhecidos para os ouvintes. Foi observado que o assunto despertou grande interesse. Dessa maneira, os objetivos do trabalho foram plenamente atingidos.

“É elementar meu caro aluno!”

Agradecimentos/Acknowledgments

À SEDUC-PA, à Direção da Escola Agostinho Moraes de Oliveira, à Universidade Federal do Pará e aos alunos envolvidos no projeto.

Área: EDU

TEACHING TOOLS TO ENCOURAGE THE LEARNING OF CONCEPTS OF CHEMISTRY AIMING AT THE CURRICULARIZATION OF EXTENSION

De Araujo, Gustavo N. (IC) [1], Contelli, Ana P. (IC) [1], Ferraz, Gustavo C. (IC) [1], Fenner, Camila K. (IC) [1], Ferreira, Cássia G. dos S. (IC) [1], Xavier, Marcelle B. (IC) [1], dos Santos, Mayara. O. (IC) [1], Campanatti Nathalia S. (IC) [1], Pedrozo, Eliane C. (PQ) [1*]

gustavo.araujo07@usp.br; ecpedrozo@usp.br

[1]*Department of Chemical Engineering, Lorena School of Engineering – EEL/USP*

Keywords: *General chemistry, teaching methodologies, practice experiments, curricularization of extension*

Highlights

Propaga Química bridges the gap between theoretical and practical learning, enhancing the understanding of fundamental chemistry concepts, by developing educational content on social media platforms, at schools and directly with society, aiming at the curricularization of extension for EEL students.

Abstract

Inspired by Johnstone's (1993)[1] approach, the project acknowledges the significance of interconnection between the observation of natural phenomena, representations in scientific language and the understanding of the microscopic universe. The methodology encompasses the development of didactic, practical, and accessible content, coupled with an active presence on social media.

The division of activities followed three main lines of action (Figure 1):

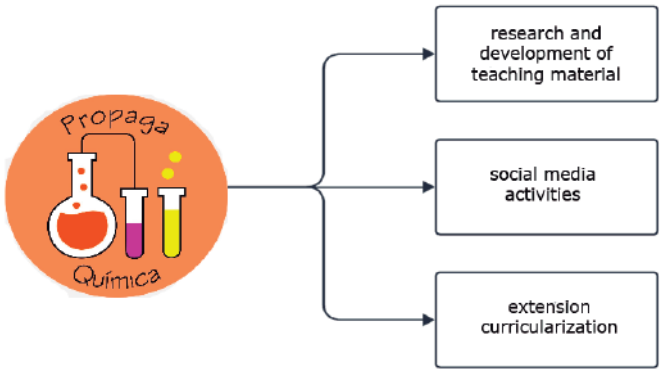


Figure 1: Division of project activities.

Understanding the importance of joint learning between the theoretical and practical, Propaga Química acted directly on connections between these interfaces. With a reach of more than thousands of internet users on its social networks and hundreds of students from different cities and states through the teaching and university extension projects developed, this project demonstrates how videos and posts can be used as a technology for pedagogical and how the dissemination of Chemistry acts as a great ally in the process.

Furthermore, the involvement of the undergraduate students who make up the project with elementary and secondary students within the schools brings active collaboration to the learning of both parties, reflected in the extension curricularization for undergraduate students.

[1]JOHNSTONE, A. H. The development of chemistry teaching: A changing response to changing demand. Journal of chemical education, ACS Publications, v. 70, n. 9, p. 701, 1993

Acknowledgments

PROGRAMA UNIFICADO DE BOLSAS DE ESTUDO PARA ESTUDANTES DE GRADUAÇÃO

EEL USP Escola de Engenharia de Lorena

PRCEU pró-reitoria de cultura e extensão universitária

Área: EDU

The potential of a popular science text (PST) into a humanizing approach to green chemistry (GC) education

Nayana B. Nery Monção (TM),[1,2*] Marcelo Carlos de C. Dino Junior (IC),[3] Luciana Nobre de A. Ferreira (PQ).[2,3]

brunanery@ufpi.edu.br

[1]Colégio Técnico de Floriano, UFPI; [2]Programa de Pós-Graduação em Química, UFPI; [3]Departamento de Química, UFPI

Palavras Chave: GC education, humanizing approaches, popular science text.

Highlights

Using the PST to contribute to a critical and humanizing GC education. Analysis of a PST. PST has elements that allow its association for use in humanizing approaches to the teaching of GC.

Resumo/Abstract

The GC provides the Chemistry and science in general with ways to practice them with the aim of reducing or eliminating the use or generation of hazardous, polluting, and/or harmful substances to human health and/or the environment [1]. To bring about this change, education must be valued as the fundamental basis [2]. Considering what steps have already been taken to implement the GC teaching, [3] presented there is a predominance of actions focused on laboratory activities. Although this should be part of the training, the authors highlight the importance of discussing the social role of chemistry and the responsibility of chemists, through GC education aligned with didactic objectives consistent with a critical and humanizing approach, which is able to intertwining its history, values and principles and the way society could/can instrumentalize it to progress. Therefore, we believe that GC can be incorporated into chemistry education, enhanced using PST to contribute to critical and humanizing GC education. A representation for teaching knowledge around GC even suggested changing of the term “humanist” to “humanizing” and was proposed by [4]. It involves aspects of human, social and environmental well-being, but also highlights the commitment to humanity through humanizing practices. This qualitative research searched for texts in the Brazilian magazine “Ciência Hoje” that mentioned the term "química verde" (2013 to 2022). Among the data found, we selected the PST "Quando toda a química será verde?" for analysis, considering the elements of humanizing approaches to GC teaching, as proposed by [4]. In the PST in question there is no evidence of a conceptual deepening in relation to the central objective of GC and its principles. However, we suggest that this can be justified by the fact that the author does not necessarily seek to "teach GC", but to problematize it. In this way, the analysis suggests that the PST in question has aspects that support its association with a humanizing approach to GC teaching. This is because, in the problematization raised, the scientific knowledge in the material in question was presented in a historical context, highlighting temporal markings and movements/entities that contributed to the emergence of GC. Furthermore, the textual production is surrounded by persuasive elements with the aim of promoting awareness. The title of the PST under analysis is also significant. The use of a rhetorical question suggests that the author is inviting the reader to reflect on the future of GC and can also be interpreted as a way of attracting young people and/or stimulate changes in attitudes among those who already work in the area. We suggest that the PST in question has the potential to be used in humanizing approaches to the teaching of GC, particularly from the perspective of reflective critical green chemistry. It addresses GC through its future uncertainties. Therefore, the use of this resource in didactic proposals can encourage discussions about the limitations/impasses that have impeded the development of this knowledge field.

References: [1] Armstrong et al., *Chem. Educ. Res. Pract.*, 2024; [2] Zuin et al., *Green Chem.*, 2021; [3] Marcelino; Marques, *Educ. Cienc. Mat.*, 2023; [4] Marcelino, *PhD thesis*, 2020.

Agradecimentos/Acknowledgments

To the UFPI for the financial apport and scholarship awarded.

Área: EDU

The production of bioplastic by high school students: an experience in scientific iniciation

Nikolas B. Gargani* (PQ),[1] Jordana E.P de Souza (PQ),[1] Pablo H.F Duarte (PQ)[1], Arthur D.D Oliveira (PQ),[1] Beatriz D.B Torres (PQ),[1] Douglas C da Silva (PFM)[1]

douglas.c.silva@ufv.br; nikolas.7078570@aluno.mg.gov.br;

[1]Escola Estadual Madre Carmelita - Secretaria de Estado de Educação de Minas Gerais

Palavras Chave:(Iniciação científica na educação básica; Bioplástico, Casca de banana, Plástico, Sustentabilidade).

Highlights

Madre Carmelita State School's scientific project addresses plastic pollution, with students creating sustainable bioplastics from materials like banana peels, aiming to mitigate environmental damage.

Resumo/Abstract

Pensando nos danos causados pelos plásticos convencionais no meio ambiente, a equipe da Escola Estadual Madre Carmelita decidiu incluir em seu ambiente escolar o projeto de iniciação científica na educação básica, no qual os alunos do ensino médio teriam a oportunidade de praticar a pesquisa científica, desenvolvendo eles mesmos o seu próprio material sustentável, assim encontrando uma forma de conscientizar a comunidade escolar da importância de um plástico sustentável, e ao mesmo tempo, contribuir para o desenvolvimento sustentável. Já é de conhecimento geral que os plásticos convencionais vêm causando inúmeros problemas ao meio ambiente, como a poluição do solo, rios e lagos e a morte de diversos animais. Com base nisso, os pesquisadores da iniciação científica da educação básica têm como objetivo procurar um meio de produzir um bioplástico através de análises de artigos na literatura, como uma possível solução para esses problemas, visto que diferentemente dos plásticos convencionais, o bioplástico demora menos tempo para se decompor e pode ser feito com materiais biodegradáveis. De início, os pesquisadores decidiram utilizar plataformas como o Periódicos Capes e o Google Acadêmico usando “Bioplásticos” e “Plásticos biodegradáveis” como palavras-chave com o intuito de encontrar artigos sobre bioplásticos para obterem conhecimento sobre o assunto. Logo em seguida, alguns dos artigos foram selecionados para serem analisados mais cautelosamente por meio da criação de resumos e confecção de uma tabela, na qual informações sobre os artigos foram inseridas como: informações como a matéria prima utilizada, a metodologia, os reagentes utilizados, os autores e o ano de publicação de cada um afim de facilitar a comparação e a análise dos artigos. Após isso, foram feitas reuniões tanto presenciais quanto online com o objetivo de discutir quais metodologias, matéria prima e reagentes seriam mais acessíveis tanto para nossa pesquisa quanto para o ambiente e, com isso, foi decidida a metodologia e a matéria prima principal do nosso experimento, que será a casca de banana, por ser de fácil acesso, ter bom custo-benefício e não competir no mercado alimentício por ser algo que tende a ser descartado. O próximo passo foi repetir os processos anteriores, porém focando agora na biodegradação dos bioplásticos, a fim de estudar metodologias de biodegradação e como tal ato acontece em diferentes tipos de solo, clima e tempo, assim decidimos, por análise similar, qual será a metodologia para análise da biodegradação que utilizaremos. Com a conclusão dessa parte do projeto, chegamos a uma nova etapa, na qual serão colocadas em prática nossas descobertas e conhecimentos. A produção experimental do bioplástico será feita em laboratório, assim como a análise e a comparação da degradação desse plástico com os plásticos convencionais. Com todo o processo de desenvolvimento do projeto, os integrantes adquiriram diversos conhecimentos, entre eles estão: fazer pesquisas de artigos científicos, construir e manipular tabelas compartilhadas e outros tipos de tecnologias, fazer citações, trabalhar em equipe, o funcionamento de feiras científicas, danos causados pelos plásticos convencionais e os pontos positivos e negativos da substituição do plástico convencional pelo bioplástico, além de que os conhecimentos obtidos pelos mesmos durante a iniciação, poderão ser usados por aqueles que gostariam de ingressar nessa área.

Agradecimentos/Acknowledgments

Agradecemos ao programa de Iniciação Científica na Educação Básica (ICEB) e à equipe da Escola Estadual Madre Carmelita.

Área: EDU

Trabalhando aspectos da Química Verde por meio de um material didático sobre pesticidas.

Luan F. M. de Oliveira (IC),[1] Cristina V. M. do Carmo (IC),[1] Eliane do R. Alberti (PQ),[1] Guilherme S. Machado (PQ).[1]*

luan.massocato@ufpr.br; *guimachado@ufpr.br

[11]Laboratório de Bioinorgânica Marinha e Química Verde, Campus Pontal do Paraná, Centro de Estudos do Mar, Universidade Federal do Paraná, Unidade Mirassol, Balneário Mirassol, Caixa-Postal: 61 CEP: 83255-000, Pontal do Paraná, Paraná, Brasil.

Palavras Chave: *Ensino de química, Estratégias de ensino, Sustentabilidade.*

Highlights

Working on aspects of Green Chemistry through a teaching material about pesticides. Teaching material on pesticides containing Green Chemistry concepts. Use with high school class and pre-university course. Possibility of working on sustainability aspects.

Resumo/Abstract

A Química Verde (QV) é um conceito que pode ser empregado em todas as etapas de produção na indústria química, desde as matérias-primas, processos de produção e até o produto final [1]. A QV possui grande interação com os princípios de desenvolvimento sustentável, buscando-se uma eficiência maior dos processos químicos, com geração cada vez menor de subprodutos nocivos ou perigosos ao meio-ambiente e ao homem. Neste sentido, o presente trabalho teve por objetivo a preparação e aplicação de um material didático para abordagem dos conceitos de QV, para isto foi escolhido o tema sobre pesticidas (também chamados de agrotóxicos) como base. No desenvolvimento do material, a partir da conceituação do tema, com seus principais exemplos e com a descrição dos conceitos químicos envolvidos, bem como informações sobre os impactos do uso inadequado de tais substâncias, foram inseridas questões e informações acerca da QV, por exemplo, foi apresentado o conceito de feromônio [2], feromônios são sinalizadores químicos de atuação entre indivíduos da mesma espécie, como, por exemplo, substâncias emitidas por fêmeas de insetos para a atração do inseto macho visando a reprodução. Tais substâncias podem ter análogos sintetizados em laboratório e serem empregadas na agricultura para o manejo dos insetos, por exemplo, por meio do monitoramento e captura com armadilhas, sem a necessidade de utilização de pesticidas para o controle das pragas, indo de encontro ao que diz o 4º Princípio da QV [1]: Produtos químicos devem ser projetados visando a preservação de sua eficácia, mas com redução da toxicidade. O material preparado também contém questões para que os estudantes possam responder sobre o que entenderam do tema, bem como questões do ENEM (Exame Nacional do Ensino Médio) sobre a temática, considerando-se que a QV e seus conceitos já apareceram em edições deste exame [3]. O material foi utilizado em uma turma do 2º ano do Ensino Médio em um colégio estadual na cidade de Paranaguá - PR, ao todo 12 estudantes participaram da atividade e responderam as questões propostas, sendo que a maioria das questões foram respondidas dentro do tempo disponível, com respostas satisfatórias, como, por exemplo, para a seguinte questão: "*Como os agricultores podem reduzir o uso de pesticidas e agrotóxicos sem comprometer a produtividade ou a qualidade dos cultivos?*", uma das respostas foi: "*Podem reduzir através da adoção de práticas de manejo integrado de pragas, como rotação de culturas e controles biológicos e o monitoramento constante de pragas*". O material também foi aplicado junto à turma do curso pré-vestibular solidário *E-CurSo*, na cidade de Pontal do Paraná - PR, 11 alunos matriculados no *E-CurSo* participaram da atividade e foi possível resolver todas as questões de ENEM que complementaram o material, trabalhando-se os conceitos de QV com os estudantes. Os resultados obtidos indicaram que a estratégia de abordagem da QV por meio do material sobre pesticidas (ou agrotóxicos) foi viável e útil para discussão com os estudantes, visando contribuir na formação destes como cidadãos também comprometidos com aspectos de sustentabilidade e preservação do meio ambiente.

Referências

[1] P.T. Anastas, M.M. Kirchhoff. Accounts of Chemical Research, 35 (2002) 686-694.
[2] C.J. Arioli, M. Botton, A.M. Neto, F. Molinari, R. Borges, P.L. Pastori, Feromônios sexuais no manejo de insetos-praga na fruticultura de clima temperado. Florianópolis: Epagri, 2013. 58p.
[3] J.M. Mondadori, G.C. Mesquita, E.R. Alberti, G.S. Machado. V SLEC, Matinhos: UFPR, 2022. 184-185.

Agradecimentos/Acknowledgments

À Universidade Federal do Paraná e ao Programa Licenciar – PROGRAD/UFPR.

Área: *EDU*

Uma proposta de aula experimental lúdica com contação forense como ferramenta didática motivacional para o ensino de química direcionada ao Ensino Médio

Jaqueline da Rocha (PG),[1] Aloísio Diogo Martins Coelho (PG),[1] Cláudio Eduardo Rodrigues-Santos (PQ)[1,2]

profjaqueline@yahoo.com; claudioers@ufrrj.br

[1]Programa de Mestrado em Química em Rede Nacional (PROFQUI - Polo-UFRRJ); [2]Departamento de Química Orgânica, Instituto de Química, Universidade Federal Rural do Rio de Janeiro (UFRRJ)

Palavras Chave: *Experimento lúdico, Kit forense, Câmara escura.*

Highlights

A proposal for a ludic experimental lesson with forensic storytelling as a motivational didactic tool for chemistry education targeted at high school.
A ludic experimental class with alternative materials and forensic connotation was planned, executed, and assessed in a school science laboratory.

Resumo/Abstract

Os experimentos podem ter três categorias distintas de atividades. A primeira categoria engloba as atividades em que o professor desempenha um papel preponderante, executando ações enquanto os alunos se limitam à observação, caracterizando-se como atividades de experimentação por demonstração. A segunda categoria refere-se às atividades destinadas à confirmação de leis ou teorias, são fundamentais para a validação experimental de conceitos. Por último, a terceira categoria engloba atividades nas quais os alunos desempenham um papel ativo na interpretação, participação e resolução de problemas, tais atividades são denominadas de experimentações investigativas, propiciam aos alunos a oportunidade de explorar, compreender e solucionar desafios científicos de forma participativa e reflexiva. Segundo Leite (2018), a partir da análise do Programa Nacional do Livro Didático (PNLD), aponta que que os livros didáticos adotados possuem lacunas na experimentação, e suas atividades experimentais estão destinadas exclusivamente para comprovação da teoria na prática. Este trabalho relata uma proposta de aula experimental lúdica simples com contação forense como ferramenta didática motivacional para o ensino de química direcionada ao ensino médio a partir de materiais de baixo custo. Inicialmente, foi elaborado um kit forense composto por uma câmara escura, um borrifador contendo ninidrina, um recipiente contendo areia e gotas de solução de iodo comercial (2% m/v), um catálogo de impressões digitais das mãos e dos pés, caixas de medicamentos revestidas com papel sulfite contendo impressões digitais, cartolinas com impressões digitais, “amostras de sangue” (guardanapos contendo [$(K_3Fe(CN)_6$] + batom vermelho) e um roteiro detalhado da atividade forense lúdica.
Uma câmara escura foi preparada a partir de uma caixa de *pet* para revelação da reação de fluorescência entre o luminol e água oxigenada catalisada por íon de Fe (III), com o intuito de observar a coloração azul brilhante, era necessário que o ambiente estivesse completamente escuro, também preparou-se um borrifador contendo ninidrina, cujo o jato era espalhado e fino, favorável para a revelação de digitais. Para a elaboração da câmera reveladora digitais, preparou-se uma mistura de 10 gotas de iodo comercial com aproximatamente 20g de areia, a sublimação do iodo foi mais controlada e proporcionou a revelação das digitais. A “amostra de sangue” foi elaborada a partir de ferricianeto de potássio que foi inserido juntamente com batom vermelho em um guardanapo. Alguns pontos foram cruciais na preparação da prática, como a construção da câmara escura, que, a princípio, seria fácil, porém, a qualquer traço de luz, refletia na observação da reação de quimiluminescência, dificultando o processo. A escolha de um borrifador que conseguisse aspergir de forma suave também foi fundamental na revelação das digitais sem danificá-las. Por meio da observação empírica e por meio de aplicação de um questionário, a atividade lúdica forense alcançou resultados significativos, entre estes destacam-se: desafiou os alunos, uma vez que tiveram que refletir e buscar informações, permitiu a troca de experiências entre grupos, além disso, a experimentação investigativa permitiu também que os alunos refletissem sobre a relação direta de sociedade e ciência, pois o experimento forense, de certa forma, cultiva a ideia de que o desenvolvimento de uma sociedade justa perpassa necessariamente pela ciência para a tomada de decisão.

Agradecimentos/Acknowledgments

Os autores agradecem ao PROFQUI, CAPES e CNPq.

Área: EDU

Uma sequência didática envolvendo a produção artístico-visual para potencializar o aprendizado ambiental e químico

Rodrigo Alves de Souza (FM)[1]

rodrigo.alves.souza@ifb.edu.br

[1] *Instituto Federal de Educação, Ciência e Tecnologia de Brasília (IFB), Campus Planaltina, Brasília/DF, Brasil.*

Palavras Chave: CTSA, Sequência didática, Produção artístico-visual, Ensino Médio, Ambiental, Aprendizado.

Highlights

A didactic sequence involving artistic-visual production to enhance learning environmental and chemical *Science-Technology-Society-Environment conception, into a didactic sequence with an artistic mediation, showed a potential to increment the learning and criticiality of Environmental Chemistry.*

Resumo

Em 2015 ocorreu o maior desastre ambiental da história brasileira, com a ruptura de uma barragem de rejeitos da Samarco Mineradora: 32.600.000 m^3 de rejeitos extravasaram, passando por sucessivas barreiras e por Bento Rodrigues, distrito da cidade de Mariana/MG, atingido por 1/3 dos resíduos iniciais [1]. O local foi devastado, assim como uma ampla porção de fauna/flora na extensão do rio doce, afetando 39 municípios. Foram mortas 19 pessoas.

Outro rompimento de barragem (Brumadinho/MG, 2019), com impactos ambientais relativamente menores, ceifou 270 vidas [2]. E, ao final de 2023, outro caso problemático da mineração estampou os noticiários, fruto da condução irregular de extração promovida pela empresa Braskem, em Maceió/AL [3].

Tais casos ilustram a frágil legislação brasileira, bem como a fiscalização ineficaz, acerca da mineração, alertando-nos para a necessidade de rever os rumos da extração mineral no Brasil. Cabe, então, gerar uma ampla conscientização sobre o tema, para se antecipar aos desastres "anunciados" ou evitáveis, levando-se em conta a preservação ambiental e a vida. A escola, portanto, é um local indispensável para abordar esta temática.

Assim, este trabalho utilizou, por mediação das artes, a concepção Ciência-Tecnologia-Sociedade-Ambiente (CTSA), envolvendo uma sequência didática (SD) sobre 'produção, descarte e consumo consciente', objetivando verificar o aprendizado em Química e a perspectiva crítica e ambiental de 39 estudantes da 1ª série do Ensino Médio de uma escola estadual de Araraquara/SP, em 12 aulas (10 h).

Estabeleceu-se a SD segundo os preceitos de Zabala, como um "conjunto de atividades ordenadas, estruturadas e articuladas para a realização de certos objetivos educacionais, que têm um princípio e um fim conhecidos tanto pelos professores quanto pelos alunos" [4], pautando-se em investidas contra o Meio Ambiente do entorno escolar ao caso Mariana/MG. Ocorreram aulas teóricas, práticas, leitura coletiva de um texto sobre lixo, leitura e uma breve análise de um poema de Drummond [5], passando por momentos de observação da circunvizinhança escolar – com o descarte inadequado de rejeitos – até debates, aulas dialógicas e a culminância em uma mostra artística, produzida pelos estudantes. Foram exploradas habilidades que envolveram, além da Química, aspectos ambientais, sociais, econômicos, tecnológicos e atitudinais (sociabilização, coletividade, argumentação e criatividade), consonantes com as habilidades previstas no Currículo Paulista [6] para a 1ª série do Ensino Médio.

Sobre a produção artístico-visual, de livre escolha, estabeleceu-se que a obra contivesse elementos que retratassem aspectos críticos envolvendo os resíduos oriundos da mineração ou da área urbana, possíveis soluções para a problemática e/ou mensagem abordando a conscientização quanto aos problemas gerados pelos rejeitos.

A concepção artística, sua apresentação e as relações envolvendo conteúdos químicos serviram de instrumentos avaliativos. Foi possível notar uma considerável evolução no aprendizado do alunado no 3° bimestre com a SD aplicada. Além da percepção subjetiva e das observações docente, para citar, estudantes abaixo do básico (notas de 0 a 4) passaram de sete no 1° bimestre para zero no 3° bimestre, enquanto dobrou o número de discentes nos níveis adequado/avançado (notas entre 7 e 10) do 2° bimestre (13) para o 3° bimestre (26).

[1] Reparação. **SAMARCO**. Disponível em: <https://www.samarco.com/reparacao/>. Acesso: 17 fev. 2024.
[2] POLIGNANOI, M. V; LEMOS, R. S. **Ciência e Cultura**, v. 72, n. 2, p. 37–43, 2020. http://dx.doi.org/10.21800/2317-66602020000200011.
[3] FERREIRA, I. R.; BUFREM, L. S. **Diversitas Journal**, v. 8, n. 4, p. 3128–3138, 2023. https://doi.org/10.48017/dj.v8i4.2814.
[4] ZABALA, A. **A prática educativa**: como ensinar. Porto Alegre: Artmed, p. 18, 1998.
[5]. WISNIK, J. M. **Maquinação do mundo**: Drummond e a mineração. São Paulo: Companhia das Letras, p. 40–41, 2018.
[6] GOVERNO DO ESTADO DE SÃO PAULO. **Currículo do Estado de São Paulo**: Ciências da Natureza e suas tecnologias. São Paulo: SE, 2011.

Área: EDU

Undergraduate Chemistry Students' Difficulties and Misconceptions in Learning about Acid-base Titrations

Lara Luciano da Silveira (PG),[1*] Brenno Ralf Maciel Oliveira (PQ).[1]

silveiralarals@gmail.com; brenno.oliveira@udesc.br

[1]*Departamento de Química, UDESC/CCT*

Keywords: *Difficulties, Misconceptions, Learning, Acid-base, Titration, Chemistry.*

Highlights

Difficulties and/or misconceptions of chemistry undergraduate students from public higher education institutions in Santa Catarina in relation to acid-base titrations.

Resumo/Abstract

Understanding acid-base titrations requires the exploration of the three levels of chemical representation (macroscopic, submicroscopic (or microscopic), and symbolic),[a] the integration of chemical concepts with concepts from other sciences, the use of chemical language, as well as a consolidated scientific knowledge base. However, these requirements are reported in the literature as the matrix of the difficulties and/or misconceptions encountered in the process of teaching and learning chemistry.[b-e] Furthermore, research into the process of teaching and learning the content of acid-base titrations in higher education is still relatively recent, especially at national level. Therefore, this work is a part of a master's research project that aims to identify the difficulties and/or misconceptions of students in relation to learning the content from a specific context in higher education in Santa Catarina and contribute to reflections in the research scenario with an educational focus on the content. To this end, a questionnaire was administered to students enrolled in Quantitative Analytical Chemistry at two public higher education institutions in Santa Catarina who already had contact with the content of acid-base titrations and who signed a consent form. A total of 13 students took part in the research. The questionnaire included 3 characterization questions, which sought to find out the age of the undergraduates, the city/state in which they live, as well as how long ago they had finished high school. It also included 5 true or false objective questions, 4 questions with a Likert-type scale and 8 discursive questions, which sought to understand the teaching and learning context of acid-base titrations and involved the interpretation of titration curves, the definition of acids and bases, the differentiation of terms commonly used in a titration (e.g. analyte, titrant, equivalence point, end point, etc.), among others. The results revealed that the main difficulties and/or misconceptions encountered in the process of learning the content of acid-base titrations are mainly due to the lack of integration and/or exploration of the three levels of chemical representation by the students. To illustrate this, when asked about the definition of acids and bases, although they gave correct answers, the students had difficulty expressing characteristics beyond the macroscopic and symbolic level: "*Acid is when it has a pH below 7 and is considered sour. Base is when it has a pH above 7 and is compared to soap*". In addition, most students were unsure whether a buffer solution is formed in a titration of a weak base with a strong acid (or vice versa) from the first addition of strong acid (or strong base) until just before the equivalence point. These and other answers were gathered in the category *Representational Levels*, following the Content Analysis Method. Answers that evoked new meanings were organized into four other categories: *Conceptual confusion*; *Operational aspects*; *Lack of previous concepts*; *Mechanical treatment*. Overall, this study provides relevant information about learning the content of acid-base titrations in Chemistry degree courses at public higher education institutions in Santa Catarina, which may lead teachers to reflect on their teaching practice in order to help them plan teaching strategies aimed at clarifying, minimizing or overcoming the difficulties and/or misconceptions encountered in this process, given that some of them were presented even after the students received instructions from the teachers. **References:** [a] Johnstone, A. H. Chemistry Education: Research and Practice in Europe, **2000**, Vol. 1, No. 1, p. 9–5. [b] Treagust, D. F.; Chittleborough, G.; Mamiala, T. L. International Journal of Science Education, **2003**, Vol. 25, No. 11, 1353–1368. [c] Moyo, C. Texila International Journal of Academic Research, **2018**, V. 5, Issue 2. [d] Rossi-Rodrigues, B. C. Oliveira, E. A; Galembeck, E. Quim. Nova, **2009**, 32, 1059. [e] Cardellini, L. Educación Química, **2012**, 23, 305–310.

Agradecimentos/Acknowledgments

UDESC UNIVERSIDADE DO ESTADO DE SANTA CATARINA · fapesc Fundação de Amparo à Pesquisa e Inovação do Estado de Santa Catarina · CAPES · GIDQuim Grupo de Investigação em Didática e Química

Field: EDU

Undergraduates' perceptions of the environmental impacts of burning plastics: experimental activity.

***Víviam Cristina Costa Silva Santos (PG),[1] Elaine Angelina Colagrande (PQ).[1]**

viviam.santos@sou.unifal-mg.edu.br; elaine.colagrande@unifal-mg.edu.br.

[1]*Instituto de Química, UNIFAL-MG.*

Keywords: *Environmental Education, Experimental Activity, Plastic Waste.*

Highlights

Experimental activities help construct concepts, contributing to the teaching and learning process, and, when developed with questions, it becomes more investigative and reflective.

Resumo/Abstract

Guimarães (2020) reports that in today's society, humanity is increasingly moving away from nature, reaching the extreme of individualism, which generates socio-environmental imbalances. Therefore, environmental education that involves the formation of citizenship, ethics, and justice is essential. To achieve this, it is necessary to resize the social role of the school to promote an education that is concerned with forming more aware citizens in the face of socio-environmental problems often caused by our lifestyle (NASCIMENTO et al., 2021). In the context of teacher training, an experimental activity containing questions related to the burning of plastics was developed in one of the classes in the discipline “Socio-environmental Issues and Teaching” with eight undergraduate students from the Chemistry and Biology course at UNIFAL-MG. According to Passos et al. (2022), the experimental activity helps visualize a situation, making the students observe and analyze the results and be more reflective. This activity was planned to verify the characteristics of the gases produced when burning different types of plastic waste (in this case, PVC and PE) and whether licensees recognize the environmental impacts generated from this burning. Then, using universal indicator paper, they noted the pH before and after the reaction (burning of the plastic), being encouraged to present their conclusions through this analysis. Table 1 summarizes the undergraduate students' responses, identified by L1 to L8.

Table 1. Responses from the eight undergraduate students participating in the experimental activity.

Answers – pH analysis.	L1 simply responded that there was a change in the pH of the samples without specifying, and the others responded that the pH decreased, which characterizes an acidic environment.
Answers - toxicity of the gases released and reaction with water.	All students stated that chlorine gas, in contact with water, produces HCl, which is a toxic gas.
Answers – socio-environmental impact from burning plastic waste.	All students understand that burning this waste releases toxic gases that are harmful to both the environment and human beings.
Answers - the destination of plastic waste.	All students agree that recycling would be the best option. L6 cites landfill as an option when recycling cannot be done, pointing it out as a long-term problem, and L7 explains the difficulty and lack of investment in the recycling process. L7 and L8 also comment on the need to raise awareness to reduce the use of these materials.

Source: the authors.

The experimental activity sought to contribute to the training of more reflective graduates, as it addressed the burning of plastic waste, a practice often used to dispose of this type of material that negatively impacts the environment and living beings that are part of it.

GUIMARÃES, M. A dimensão ambiental na educação. Papirus Editora, 2020. 112 p.

NASCIMENTO, L. M. B. et al. A emergência do educador ambiental crítico a partir da formação docente: importância do saber socioambiental na construção de projetos de intervenção coletivos. **Revista Brasileira de Educação Ambiental (RevBEA)**, *[S. l.]*, v. 16, n. 2, p. 212–231, 2021.

PASSOS, B.; VASCONCELOS, A. K.; SILVEIRA, F. Ensino de Química e Aprendizagem Significativa: uma proposta de Sequência Didática utilizando materiais alternativos em atividades experimentais. **Revista Insignare Scientia - RIS**, v. 5, n. 1, p. 610-630, 16 mar. 2022.

Agradecimentos/Acknowledgments

CAPES, UNIFAL-MG, LAPEQUIM – Chemical Education Research Laboratory (*Laboratório de Pesquisa em Educação Química*) – UNIFAL-MG.

Área: EDU

Use of the Free Word Association Test (TALP) to verify changes in undergraduate students' conceptual representations of chemical equilibrium

Flavio Antonio Maximiano (PQ),[1] Camilla Midori Peroni (PG).[1]

famaxim@iq.usp.br

[1]*Departamento de Química Fundamental, Instituto de Química da USP.*

Palavras Chave: *representação social, representação conceitual, teoria do núcleo central, teste de associal livre de palavras, equilíbrio químico.*

Highlights

The methodological framework of the Theory of the Central Nucleus (TNC) of Social Representations (RS) can detect changes in the conceptual structure shared by students in a learning situation.

Resumo/Abstract

Neste trabalho aplicamos a técnica de associação livre de palavras (TALP) para investigar possíveis alterações na estrutura do conhecimento conceitual de alunos de uma disciplina de Química Geral submetidos a uma abordagem do tema equilíbrio químico a partir das leis da termodinâmica. Os dados foram coletados e analisados de acordo com o referencial teórico-metodológico da Teoria do Núcleo Central (TNC) das Representações Sociais (RS). A RS busca compreender como um determinado objeto ou assunto é compartilhado por um grupo social. A TNC busca captar e analisar a estrutura cognitiva e afetiva das RS, destacando o núcleo central, formado pelos conceitos e ideias mais centrais e estáveis que organizam as demais ideias, e o sistema periférico, formado por conceitos mais suscetíveis às influências externas. Como estamos no contexto de uma situação de ensino específica e não num contexto social mais amplo, optamos aqui por adotar o termo representação conceitual (RC) no lugar de representação social (RS).

A TALP consiste em pedir para que cada aluno liste as seis primeiras palavras que lhe vêm à mente diante do termo indutor (equilíbrio químico), hierarquize as palavras em ordem de importância e escreva uma justificativa para cada citação. Considerando apenas as palavras mais frequentes, foram calculadas a frequência (F) e ordem média de evocação (OME - a média da posição de cada palavra após a hierarquização das mesmas). Conceitos com baixa OME e alta F são considerados os mais salientes. Já a conectividade indica como conceitos mais centrais aqueles mais conectados (citados conjuntamente) com outros conceitos. Um possível núcleo central (NC) é obtido pela intersecção entre saliência e conectividade.

Resultados: 1) O número de conceitos mais frequentes caiu de 17 para 10 após o ensino indicando uma homogenização promovida pelo ensino; 2) O possível NC antes do ensino era composto por: K (F=10, OME=2,2), deslocamento (F=11, OME=3,6) e reação reversível (F=8, OME=1,6). Após o ensino, como possível NC: K (F=19, OME=1,6) e ΔG (F=12, OME=3,7). O aumento de F e diminuição de OME em K também indicam uma homogeneidade maior na RC pós ensino. 3) Quanto à conectividade os resultados mostram importantes mudanças. Antes do ensino, os alunos associavam K principalmente como uma ferramenta matemática, sendo utilizado muitos exemplos como K_a e K_b nas explicações. Após o ensino, houve uma compreensão mais avançada e integrada, aplicando os conceitos termodinâmicos como ΔG, entalpia e Princípio de Le Chatelier. Os alunos passaram a relacionar a ΔG ao equilíbrio químico e K indicando uma mudança RC próxima à apresentada nas aulas.

Agradecimentos/Acknowledgments

Aos alunos da disciplina QFL1103 Química Geral II do segundo semestre de 2022.

Área: EDU

Utilização do Software *Blender 3D* para a realização de instrução em conteúdos que requerem habilidade espacial em Química Orgânica

Kerlyn K. M. Hiraga (PG),[1] Antonio Aprigio da Silva Curvelo (PQ)[2].

kerlynk@usp.br; aprigio@iqsc.usp.br

[1]*Instituto de Química de São Carlos- IQSC-USP*

Ensino de Química, Ensino e aprendizagem de Química Orgânica, Competência Representacional, Representações Estruturais, Estágio PAE.

Highlights

Utilization of Blender 3D Software to provide learning that requires spatial skills in Organic Chemistry.Utilizando o software *Blender 3D* foram elaboradas intervenções com o objetivo de instruir significativamente estudantes de um curso de Química Orgânica, em conteúdos que requerem o desenvolvimento de habilidades espaciais.

Resumo/Abstract

Apesar de importantes para a ciência química, os modelos são também caracterizados como de difícil assimilação pelos estudantes. (Eunice Ribeiro Marcondes, Fabio Luiz Souza, n.d.; Kozma & Russell, 1997). A química Orgânica, por ser uma ciência intensamente visual, tem nesta temática relevante destaque.(Graulich, 2015). Diversas Representações Estruturais são utilizadas durante seu processo de ensino e aprendizagem, e como consequência seu domínio está diretamente relacionado com a capacidade de escrever e interpretar os mecanismos de reação, compondo desta forma, a linguagem pela qual é expressa a química Orgânica. Entretanto, partindo do pressuposto de que tarefas tais como desenhar, interpretar e realizar a interconversão entre as variadas representações estruturais não são triviais, e requerem a utilização de habilidades cognitivas tais como Competência Representacional e Habilidade Espacial, foi elaborado um projeto de Estágio PAE, para a disciplina de Química Orgânica I de um curso de Bacharelado em Química de uma universidade pública brasileira, cujo objetivo foi o de fornecer andaimes que favorecessem a Aprendizagem Significativa dos diferentes tipos de representações, utilizando uma construção ativa de conhecimento, investigação e desenvolvimento de habilidades espaciais. Tal projeto contou com cinco etapas: levantamento dos conhecimentos prévios dos estudantes, levantamento dos conhecimentos prévios em relação às suas habilidades espaciais, averiguação das suas habilidades espaciais em conceitos da disciplina, intervenção com a utilização do *software Blender 3D*, durante as próprias aulas e em monitorias expositivas dialogadas (principalmente em conteúdos com características tridimensionais) e por fim, a coleta das impressões estudantis. A vantagem de utilizarmos a projeção do programa consistiu na possibilidade da promoção de manipulações, como rotações e aproximações das moléculas (objetos construídos) nos eixos X, Y e Z, simultaneamente ao diálogo com os estudantes, facilitando assim a observação dos compostos por meio de diferentes perspectivas. Além disso, em softwares de construções de moléculas tridimensionais já conhecidos, uma dada molécula, por exemplo, já é apresentada em sua conformação mais estável, não havendo a possibilidade de representarmos e compararmos a estabilidade de diferentes Confôrmeros. Também, não é possível visualizar íons, como, por exemplo, ilustrar que em um mecanismo de reação S_N1, que ocorre via formação de intermediários carbocátions, o ataque nucleofílico pode ocorrer em ambas as faces. Com o *Blender 3D* essas ilustrações foram possíveis, (figura 1). Concluímos que apesar de a habilidade espacial apresentada pelos estudantes ser favorável, ela deve ser investigada com maior profundidade e orientada à aprendizagem da disciplina de Química Orgânica, ou seja, é necessário dar sequência a atividades que promovam a integração das **habilidades espaciais** às **habilidades conceituais**, contribuindo desta forma para a aprendizagem da disciplina.

Figura 1: Interface do programa *Blender 3D* e exemplo de algumas moléculas construídas e apresentadas.

Fonte: Autoria própria.

Agradecimentos/Acknowledgments

Instituto de Química de São Carlos (IQSC-USP), Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq).

Área: EDU

Xciência.org: uma plataforma de compartilhamento de recursos educacionais para professores de Química

Alfredo Luis Mateus* **(PQ),[1] Pedro Reis Araújo Fernandes (IC),[2] Karollyne Costa Silva (IC),[2] Fernanda dos Santos Mattos (IC)[1] .**

almateus@gmail.com

[1] Colégio Técnico da UFMG; [2] Departamento de Química, Instituto de Ciências Exatas da UFMG

Palavras Chave: experimentação no ensino de química, formação de professores, fabricação digital.

Highlights

Xciência.org: a website for sharing educational resources with chemistry teachers
Xciência.org is a website created for sharing experiments and resources with high school chemistry teachers. We have developed more than 20 experimental kits that can be borrowed by teachers that come to the university and be used several times.

Resumo/Abstract

Professores de Química têm de superar muitas dificuldades para a realização de experimentos nas suas aulas. Muitas escolas não possuem um laboratório ou um técnico para auxiliar o professor. Os professores não têm acesso aos materiais numa forma pronta para seu uso em aula. Além disso, muitas vezes os professores não têm familiaridade com os experimentos já existentes na literatura.

Para estimular o uso da experimentação por professores de Química, o projeto XCiência iniciou em 2023 um serviço de desenvolvimento e empréstimo de materiais para professores, similar a iniciativas como a Experimentoteca[1]. Todos os experimentos são documentados no site, com fotos e vídeos. O professor reserva o material por meio de mensagens eletrônicas, pega os kits no laboratório do projeto e devolve após a realização das atividades com seus alunos. A equipe do projeto então realiza a manutenção dos kits para futuros empréstimos. Muitos dos kits foram produzidos com o auxílio do corte a laser e impressão 3D, o que facilita a sua reprodução. Dentre os mais de 20 recursos disponíveis para empréstimo (**http://www.xciencia.org/catalogo-de-experimentos-e-recursos/**), temos kits para o teste de chama, evidências de reação em microescala, modelos moleculares e indicadores da condutividade elétrica de soluções. As visitas dos professores têm sido usadas como oportunidades para capacitar os professores no uso dos experimentos em sala de aula, e para conhecer as suas práticas e a realidade onde estão inseridos e com isso melhorar a oferta de materiais.

De acordo com depoimentos dos mais de 20 professores que utilizaram o serviço, o empréstimo dos kits possibilitou a realização de experimentos em suas aulas, atingindo um número estimado de 3.000 alunos.

Figura 1. Imagens de alguns dos kits disponíveis para empréstimo.

Agradecimentos/Acknowledgments

Os autores gostariam de agradecer ao INCT Midas, FAPEMIG e CNPq pelo apoio financeiro.

1Experimentoteca. Disponível em https://cdcc.usp.br/experimentoteca/ Acesso em 10 de março de 2024.

ELE

Eletroquímica e Eletroanalítica

Sociedade Brasileira de Química

Área: ELE

3D-printed aluminum oxide/graphite/polylactic acid electrochemical platform: A cost-effective alternative for sulfamethoxazole sensing

Natalia M. Caldas (IC)*[1], Lucas V. de Faria (PQ)[1], Luana M. Villafuerte (IC)[1], Suéllen F. L. do Nascimento (PQ)[1], Fernanda N. Feiteira (PQ)[1], Daniel G. S. Quattrociocchi (PQ)[1], Thiago de M. Lima (PQ)[1], Renato C. Matos (PQ)[2], Diego P. Rocha (PQ)[3], Felipe S. Semaan (PQ)[1], Wagner F. Pacheco (PQ)[1], Rafael M. Dornellas (PQ)[1].**

***nataliamarinho@id.uff.br, **rafaeldornellas@id.uff.br**

[1]Departamento de Química Analítica, Instituto de Química, Universidade Federal Fluminense, 24020-141, Niterói-RJ, Brazil; [2]Departamento de Química, Universidade Federal de Juiz de Fora, 36026-900, Juiz de Fora, MG, Brazil; [3]Instituto Federal do Paraná, Pitanga, PR, 85200-000, Brazil.

Palavras Chave/ Key words: *Conductive composite filament; additive manufacturing; 3D-pen; antibiotic; food analysis.*

Highlights

Conductive composite material to manufacture 3D-printed sensors;

Al_2O_3 drastically improves the electrochemical properties of the sensors;

Sulfamethoxazole is determined in honey samples;

Resumo/Abstract

Composite materials with properties intended for the additive manufacture of affordable electrochemical sensors have received special attention from the scientific community. In this context, we proposed a new composite material based on alumina oxide (Al_2O_3) and graphite (Gpt) dispersed in polylactic acid (PLA) biopolymer. Various proportions between the materials were studied, and a compromise between printability and electrochemical performance was obtained using Gpt/Al_2O_3/PLA (30:10:60 % w/w). All the electrodes were produced using a 3D pen, a low-cost portable tool. Characterizations by Raman and infrared spectroscopy, X-ray photoelectron spectroscopy and scanning electron microscopy indicated that the production process was successful. In addition, preliminary studies using species with well-known electrochemical behavior, such as the redox probe ferri-iron and dopamine, revealed that Al_2O_3 has a positive impact on the electrochemical response of the sensor. As a proof of concept, sulfamethoxazole (SMX), a low-cost antibiotic widely used in beekeeping practices, was selected as the target analyte, and a simple, fast and selective method using square wave voltammetry was proposed. Figure 1 illustrates the cyclic voltammogram obtained from 400µmol/L of SMX in 0.12mol/L Britton-Robinson (BR) buffer (pH7.0) using the unmodified and modified 3D printed electrodes. Using the 3D printed Gpt/Al_2O_3/PLA electrode, a wider linear range (2.0 to 40.0 µmol/L), a 6.5-fold increase in sensitivity, better limits of detection (LOD = 0.4 µmol/L) and quantification (LOQ = 1.2 µmol/L) were achieved compared to the free Al_2O_3 electrode (Gpt/PLA). In addition, the proposed sensor was selective against other antibiotics commonly used in beekeeping practices. Three honey samples were analyzed after simple dilution in 0.12 mol/L BR buffer, pH 7.0 (background electrolyte), and recovery results close to 100% certified the accuracy and reliability of the method. Therefore, this strategy is valuable for contributing to the progress of additive manufacturing in electroanalytical proposals, especially in the detection of antibiotic species in food, a public health challenge.

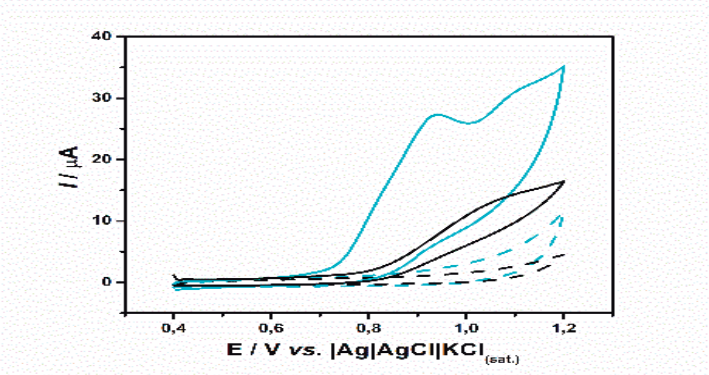


Fig 1: CVs obtained for 400 µmol/L SMX in 0.12 mol/L BR buffer medium (pH 7.0) using Gpt/PLA (black line) and Gpt/Al_2O_3/PLA (30:10:60, blue line). The dashed lines indicate the respective blanks

.

Acknowledgments

The authors would like to thank the support from CAPES, FAPERJ, and CNPq.

Área: ELE

3D-printed hyphenated sensor using dual extrusion for catechol detection.

Vinícius A. O. P. da Silva (PG),[1*] Lucas C. Duarte (PQ),[2] Rafael R. Silva (IC),[2] Wendell K.T. Coltro (PQ),[2] Bruno C. Janegitz (PQ).[1]

vinicius.silva@estudante.ufscar.br;

[1] *Department of Nature Sciences, Mathematics and Education, Federal University of São Carlos*
[2] *Chemistry Institute, Federal University of Goiás*

Palavras Chave: *Additive Manufacturing, dual extrusion, hyphenated, electrochemistry, microfluidic, colorimetric.*

Highlights

Dual extrusion additive manufacturing was employed in the construction of a hyphenated device for catechol detection. Electrochemical, colorimetric, and microfluidic techniques were combined to produce more complete results.

Resumo/Abstract

With the continuous evolution of dual extrusion additive manufacturing technologies, and printing with two extruders simultaneously, the field of electrochemical detection has seen advancements in the construction of sensors with enhanced functionality [1]. Hyphenated techniques involve the combination of two or more analytical methods, aiming to achieve a more efficient device, yielding more comprehensive and rapid results [2]. Electrochemical detection exhibits good quantitative performance, enabling miniaturization and integration of new materials [3]. Microfluidics allows the processing or manipulation of fluids in small portions through micrometer-scale channels [4]. On the other hand, quantitative colorimetric detections respond through color reflection in the test zones and require few materials and simple equipment [5]. In this work, a hyphenated device was proposed with static and fluidic electrochemical sensors and colorimetric detection, constructed through dual extrusion additive manufacturing using polylactic acid (PLA) and PLA/carbon-black filaments for p-catechol detection. The electrochemical sensors were treated with dimethylformamide and then immersed in ethyl alcohol, subsequently subjected to an ultrasonic bath in ultrapure water [6]. The characterization of electrochemical impedance spectroscopy (EIS) demonstrated that after treatment, the system exhibited two phases, represented by two Nyquist semi-circle. While untreated the static and fluidic sensors showed R_{ct} values of 2.3769 and 9.3803 kΩ, respectively. After treatment, the R_{ct1} and R_{ct2} values were 0.021 and 1.609 kΩ, and 0.115 and 1.832 kΩ, respectively, indicating a decrease in resistances. The increase in response current was confirmed through cyclic voltammetry analysis. Fourier-Transform Infrared Spectroscopy (FTIR) analysis indicated the presence of the same functional groups on the material surface before and after treatment, demonstrating no alteration in the material composition. Optimization studies for catechol detection with 4-aminoantipyrine indicator were performed. The device was applied for voltammetric and colorimetric detection of catechol, which has been provided to be an effective alternative for phenols determination.

[1] M. Schouten, G. Wolterink, A. Dijkshoorn, D. Kosmas, S. Stramigioli, G. Krijnen, IEEE sensors journal, (2020) 2112900-12.
[2] M.V.N. Rodrigues, V.L.G. Rehder, A. Sartoratto, S.B. Júnior, A.d.S. Santos, MultiCiências: Construindo a história dos produtos naturais, (2006) 7.
[3] J.L. Hammond, N. Formisano, P. Estrela, S. Carrara, J. Tkac, Essays in biochemistry, 60(2016) 69-80.
[4] G.M. Whitesides, Nature, 442(2006) 368-73.
[5] T. Bhattacharjee, H.R. Jiang, N. Behdad, IEEE Sensors Journal, 15(2015) 819-26.
[6] A.K. Au, W. Lee, A. Folch, Lab on a Chip, 14(2014) 1294-301.

Agradecimentos/Acknowledgments

FAPESP (2017/21097-3 e 2021/03179-8), CAPES (financial code 001 and CAPES 09/2020 Epidemias 88887.504861/2020-00), FINEP (01.22.0179.00) and CNPq (301796/2022-0), Brazil for all the financial support.

Área: ELE

A CB/PLA-based 3D printed electrode to detect tyrosine in simulated urine

Amanda Morais (PG),[1*] Maria Lurdes Felsner (PQ),[1,2] Diego Pessoa Rocha (PQ),[3] Andressa Galli (PQ).[1]

am.morais534@gmail.com

[1]Departamento de Química, UNICENTRO; [2]Departamento de Química, UEL, [3]Departamento de Química, IFPR

Palavras Chave: L-tyrosine sensor, portability of analyses, brain diseases.

Highlights

Novel electroanalytical method for biomarker detection;

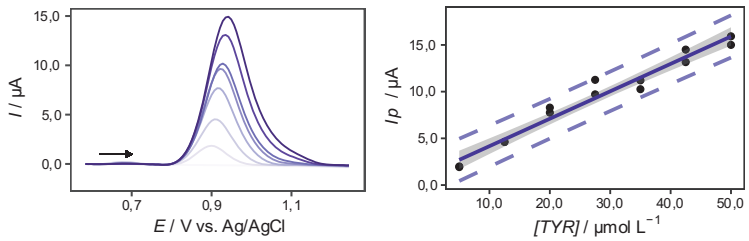
Validation of methodology developed;

Fast, affordable, eco-friendly, and cheap methodology.

Abstract

Biomarkers play a crucial role in the investigation and diagnosis of diseases. L-tyrosine shows promise as a biomarker for Alzheimer's disease, depression, and other illnesses[1]. To overcome the challenges of cost and complexity associated with conventional analytical methods, a new electroanalytical methodology was developed. This methodology combines a 3D printed carbon black/polylactic acid (CB/PLA) electrode with square wave voltammetry. Before measurements, the electrode surface was activated through a simple and quick step[2], followed by bubbling with N_2 above the electrode. The validation study demonstrated that the electroanalytical methodology is linear within the range of 5 to 50 µmol L^{-1} (Figure 1), with low LOD and LOQ values of 2.0 and 5.1 µmol L^{-1}, respectively. Good estimates of accuracy and precision were verified in the LOQ, and the low, medium, and high levels of the analytical curve in the presence of the simulated urine matrix, achieving RSD values (%) ranging from 4.0 to 9.6% (n = 5)[3]. This work proposes the development of 3D printed electrodes for the detection of L-tyrosine in urine. The aim is to apply analytical methodologies with better accessibility and portability characteristics than conventional methods.

Figure 1 – (A) Voltammograms obtained to the calibration curve, (B) Linear regression with confidence and prediction interval



1 - AN, M.; GAO, Y. Urinary Biomarkers of Brain Diseases. **Genomics, Proteomics & Bioinformatics**, China, v. 13, n. 6, p. 345–354, 2015.

2 - RICHTER, E. M. et al. Complete Additively Manufactured (3D-Printed) Electrochemical Sensing Platform. **Analytical Chemistry**, v. 91, n. 20, p. 12844–12851, 2019. ISSN 0003-2700, 1520-6882.

3 - FDA. FDA M10 BIOANALYTICAL METHOD VALIDATION AND STUDY SAMPLE ANALYSIS. p. 55, 2022.

Acknowledgments

CAPES CNPq ARAUCARIA UNICENTRO PARANÁ GEMN Unicentro Grupo de Eletroanalítica e Materiais Nanoestruturados

Área:
_____ELE_____
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Ammonia electro-oxidation reaction on platinum and magnetic iron oxide nanoparticles via MagnetoElectroCatalysis

Júlio César M. Silva (PQ),[1*] Caio M. Fernandes (PQ),[1] Eduardo M. Rodrigues (PG),[1] Evelyn C. S. Santos (PQ),[2] Yutao Xing (PQ),[3] Odivaldo C. Alves (PQ),[1] Flávio Garcia (PQ).[2]

juliocms@id.uff.br

[1]Departamento de Físico-Química, UFF; [2]Centro Brasileiro de Pesquisas Físicas; [3]Instituto de Física, UFF.

Palavras Chave: *Electrocatalysis, Magnetic hyperthermia, Ammonia electro-oxidation.*

Highlights

Use of alternating magnetic field to generate localized heat in magnetic iron oxide nanoparticles to boost the ammonia electro-oxidation reaction on platinum nanoparticles.

Resumo/Abstract

The ammonia electro-oxidation reaction (AmER) has attracted considerable attention because ammonia is a toxic substance that causes a series of problems for the environment [1]. It is reported that ammonia electrolysis requires 95% less energy than water electrolysis to produce hydrogen gas [2]. However, in this process electrocatalysts are essential. Although platinum is the metal with the highest electrocatalytic activity towards AmER, its nanoparticles surface suffers poisoning by N_{ads}, which limits the AmER process. One of the ways to make the AmER process more efficient is to combine Pt with a second material, e.g. $PtSnO_2$ [2]. Another strategy to accelerate the rate of REAm is increasing the temperature of the reaction process. However, the large amount of energy expended to heat the entire catalytic bed limits this approach. In this sense, promoting an increase in temperature only in the catalytic sites, where the reaction actually occurs, without expending a large quantity of energy is extremely relevant to increase the kinetics of the AmER process. This can be done using the magnetic hyperthermia technique, which with the use of magnetic nanoparticles such as magnetite (Fe_3O_4), for example, heat is generated when these nanoparticles are under an alternating magnetic field (AMF) [3]. Thus, in this work, binary Pt-Fe_3O_4 electrocatalysts nanoparticles were synthesized and used as catalysts for AmER under an AMF, this process is called MagnetoElectroCatalysis. For this process, the Pt-Fe_3O_4 nanoparticles were supported on a carbon cloth electrode which was uses as working electrode, the reference and auxiliary electrodes were Hg|HgO and a Pt plate, respectively. Chronoamperometry (CA) and cyclic voltammetry (CV) experiments were carried out in 0.5 mol L^{-1} ammonia solution in 1.0 mol L^{-1} NaOH under the AMF with amplitude varying from 14.9 mT to 133.5 mT and frequency of 224.7 kHz. It was observed in the CA experiments (at 0.55V for 60 min.), that under the AMF the current from AmER increases abruptly, obtaining current increase values from 2 to 51% with lowest to highest AMF. In CV experiments, in addition to the increase in peak current density from AmER under the AMF, the onset potential of the reaction was shifted to more negative overpotential values. Therefore, AMF boosted AmER on Pt-Fe_3O_4.

References

[1] W. Xu, *et al.* Appl. Catal. B: Environ, v. 237, 2018, 1101.
[2] J. R. Barbosa, *et al.* Appl. Catal. B: Environm. v. 264, 2020, 118458.
[3] E. M. Rodrigues, *et al.* Int. J. Hydrog. Energy, v. 51, 2024, 1460.

Agradecimentos/Acknowledgments

FAPERJ (E-26/211.371/2019, E-26/201.435/2021, E-26/211.389/2021, E-26/210.793/2021), CBPF, CNPq, CAPES.

Área: ELE

Ammonia electrosynthesis via nitrate reduction in basic medium catalyzed by copper single-atom catalyst

Daniel S. Braga (PG),[1,2] Thiago M. Mariano (PQ),[1,2] Jesús Barrio (PQ),[3] Angus Pedersen (PQ),[3] Ifan E. L. Stephens (PQ),[3] Maria-Magdalena Titirici (PQ),[3] Raphael Nagao (PQ)[1,2*]

d271144@dac.unicamp.br; nagao@unicamp.br*

[1]Institute of Chemistry, Unicamp; [2]Center for Innovation on New Energies; [3]Imperial College London

Keywords: *Single-atom catalyst, Green ammonia, Nitrate reduction*

Highlights

- Cu-NC has a stable 42 ± 3% faradaic efficiency to ammonia between −0.2 and −0.6 V (vs RHE);
- 165 ± 19 μmol·h^{-1}·cm^{-2} yield rate was observed at −0.6 V (vs RHE).

Abstract

Ammonia (NH_3), a cornerstone of modern agriculture and fertilizers, currently faces an unsustainable production process. The dominant Haber-Bosch process uses high temperatures and fossil fuels, contributing significantly to greenhouse gas emissions. Single-atom catalysts (SACs) show promise for the electrochemical reduction of nitrate (NO_3RR) to NH_3. This approach has advantages over the Haber-Bosch process, including more efficient conversion without nitrogen coupled products, reduced energy consumption, cleaner production without fossil fuels while also removing the water pollutant nitrate, and flexibility to scale the system. NO_3RR with SACs can enable simpler, more accessible NH_3 production for small agricultural communities while addressing nitrate contamination.[1] Cu-NC was prepared via pyrolysis of inexpensive 2,4,6-triaminopyrimidine and Mg^{2+} as an active site template and porogen.[2] Electrochemical performance was evaluated in a H-type cell in 0.1 M NaOH with 0.5 M $NaNO_3$ under argon flow. Linear sweep voltammetry displayed onset at 0.15 V vs RHE and higher current in the presence of NO_3^- (Fig. 1a). NH_3 quantification revealed a stable 42 ± 3% faradaic efficiency starting at the low overpotential of −0.2 V vs RHE and increasing yield rates with more negative potentials (Figs. 1c-d), with higher nitrite concentration (Fig. 1b). Therefore, the material appears to be a good alternative for eliminating nitrate and producing NH_3 at low overpotentials.

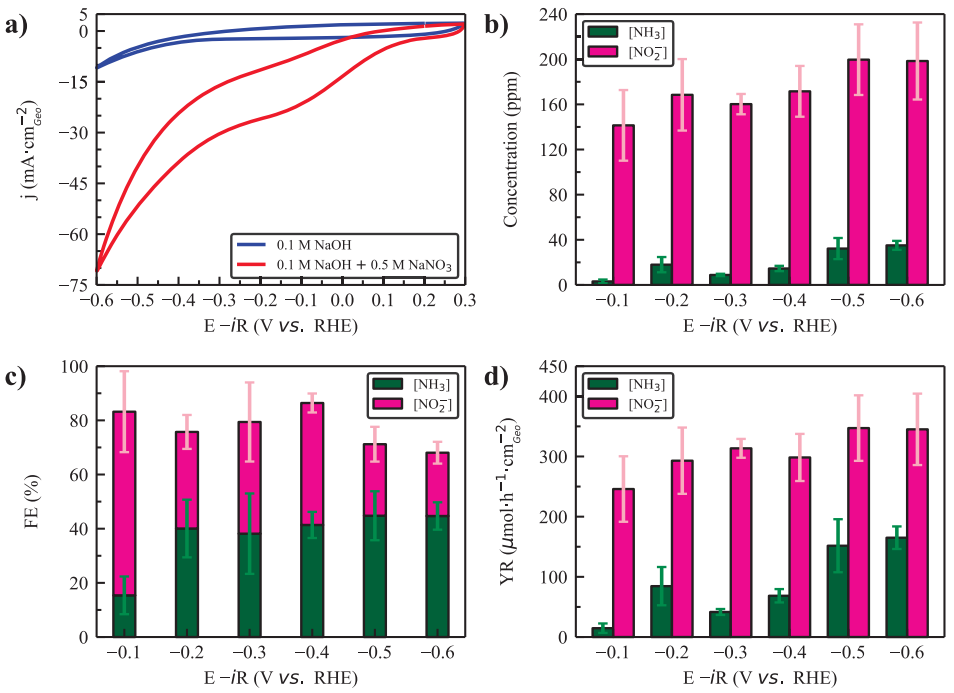


Figure 1: (a) Cyclic voltammograms of Cu-NC in 0.1 M NaOH with (red line) and without (blue line) 0.5 M $NaNO_3$ at 20 mV·s^{-1}. **(b)** Concentration in ppm, **(c)** Faradaic efficiency and **(d)** yield rate of NH_3 (green bar) and NO_2^- (pink bar) in the potential range of −0.1 to −0.6 V *vs.* RHE, with 85% ohmic drop compensation.

[1]Wu, L., Guo, W., Sun, X. & Han, B. **Pure and Applied Chemistry** 93, 777-797 (2021).
[2]Barrio, J. et al. **Advanced Materials** 35, 2211022 (2023).

Acknowledgments

This work was supported by Shell, FAPESP, CNPq and CAPES.

Área: ELE

Analysis of electrocatalytic ammonia oxidation reaction on PtRu/C with online electrochemical mass spectrometry

Geraldo N. Tessaro (PG),[1*] Rodrigo G. de Araujo (PG),[1] Seiti I. Venturini (PG),[1] Joelma Perez (PQ).[1]

geraldotessaro@usp.br

[1]*Instituto de Química de São Carlos, IQSC-USP*

Keywords: *Electrocatalysis, Ammonia oxidation reaction, Platinum, Ruthenium, OLEMS, Alternative fuel.*

Highlights

Adding Ru into the catalyst demonstrates enhanced conversion to N_2, the major product, at lower potentials. The PtRu/C catalyst showed an onset reduction of 100 mV in the ammonia oxidation reaction.

Abstract

Ammonia plays a significant role in the transition to renewable and carbon-free fuels. With 17.6 wt.% of hydrogen in the molecule, it becomes possible to solve the transportation and storage problems of hydrogen fuel.[1] Another application would be a fuel in the anode of a direct ammonia fuel cell. Thus, ammonia oxidation reaction (AOR) studies are required to develop a more efficient conversion. In this work, the AOR was studied in alkaline medium with a commercial PtRu catalyst supported on carbon. The experiment was conducted with online electrochemical mass spectrometry (OLEMS) to identify differences in the product distribution when compared with Pt catalyst. The PtRu/C catalyst reduced the onset of AOR in 100 mV, with N_2 being the major product. Other products like NO, N_2H_4, NH_2OH, HN_3, N_2O, NO_2 were identified during the experiments on both catalysts, similar to recent studies on the mechanism of AOR on Pt/C.[2] Integrating the current signal from OLEMS, indicated that in lower potentials the conversion to N_2 is greater in PtRu/C than Pt/C. Figure 1 demonstrates the detection of products N_2 (m/z 28) and NO (m/z 30) by applying a potential sweep in the direction of high potential in both catalysts analyzed. No hysteresis was observed in the N_2 signal before the onset of NO production, indicating a poisoning effect of the NO.

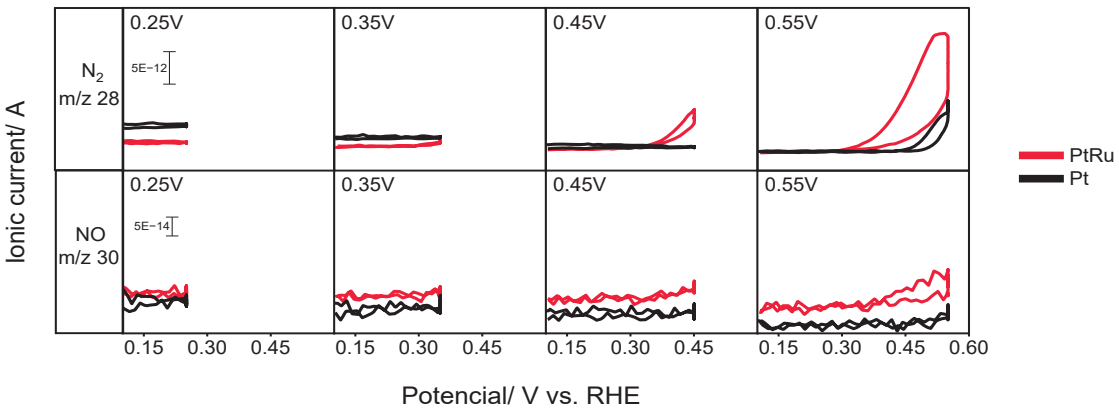


Figure 1: OLEMS analysis for nitrogen and nitric oxide through cyclic voltammetry in 1 mol L^{-1} NH_4OH and 1 mol L^{-1} NaOH.

REFERENCES

[1] X. Xi, Y. Fan, K. Zhang, Y. Liu, F. Nie, H. Guan, J. Wu. Carbon-free sustainable energy technology: electrocatalytic ammonia oxidation reaction. *Chem. Eng. J.*, 435 (2022), 134818.

[2] S. Venturini, D. Godoi, J. Perez. Challenges in Electrocatalysis of Ammonia Oxidation on Platinum Surfaces: discovering reaction pathways. *ACS Catalysis* 13 (2023), 10835-10845.

Acknowledgments

Thanks to CAPES, CNPq and FAPESP for the financial support.

Área: ELE

Analysis of secondary products resulting from the breakdown of xylene in an ethanol environment, using a mixed metal oxide anode

João Paulo A.D. Guardia (PG)[1]*, Thays S. Lima (PQ) [1], Artur J. Motheo (PQ)[1]

joao.guardia@usp.br; artur@iqsc.usp.br

[1]*Departamento de Físico-Química, Instituto de Química de São Carlos; USP.*

Palavras Chave: *Water treatment; electro-oxidation; degradation; xylene.*

Highlights

-Eletrooxidation of xylene using dimensionally stable anodes. – Proposal route for orto, meta, para-xylene oxidation. -Forming added-value products.

Resumo/Abstract

Atmospheric contamination is a pervasive issue with direct implications for the well-being of all living organisms, including humans. One significant contributor to this concern is xylene, a compound known for its high risk to both human health and the environment [1]. Traditional treatment methods are inefficient in addressing this issue, prompting the exploration of alternative, sustainable approaches such as electrochemical methods [2]. This study focuses on the electrochemical degradation of xylene isomers in an ethanol medium, utilizing an anode featuring a combination of metal oxides ($Ti/Ru_{0,3}Ti_{0,7}O_2$). The investigation includes an assessment of various water percentages in the process. In this manner, for water contents of 0%, 5%, and 10%, the corresponding removal rates were: for p-xylene, 89.9%, 91.9%, and 84.6%; for m-xylene, 77.3%, 82.0%, and 79.4%; and for o-xylene, 90.0%, 91.6%, and 87.7%. The removal of xylene isomers is presented as a function of the applied charge in Fig. 1. The results of o-, m-, p-xylene degradation were accompanied by GC-MS, enabling the proposition of the degradation route for each xylene isomer, as shown in Fig. 2. When xylene was oxidized with H_2SO_4 in ethanol/methanol, it was possible to observe the formation of 2-chloro-o-xylene from o-xylene, 2-chloro-m-xylene from m-xylene, and 4-chloro-p-xylene from p-xylene [3]. It has been noted that water content significantly facilitates the degradation of xylene, leading to the production of valuable compounds with substantial potential for industrial applications [4].

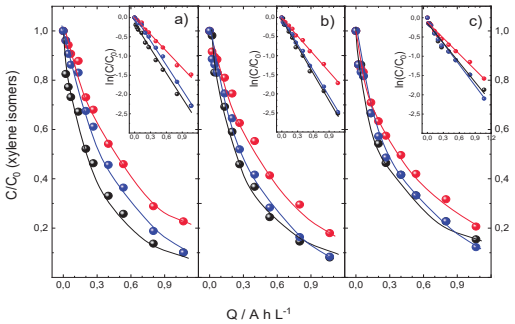


Figure 1. Concentration decay of xylene isomers during electrolysis in ethanol medium with different water content: p-xylene (●), m-xylene (●), and o-xylene (●) in a) 0; b) 5 and c) 10% H_2O ([Xylene] = 140 mg L^{-1}, [H_2SO_4] = 0.05 mol L^{-1}, ethanol).

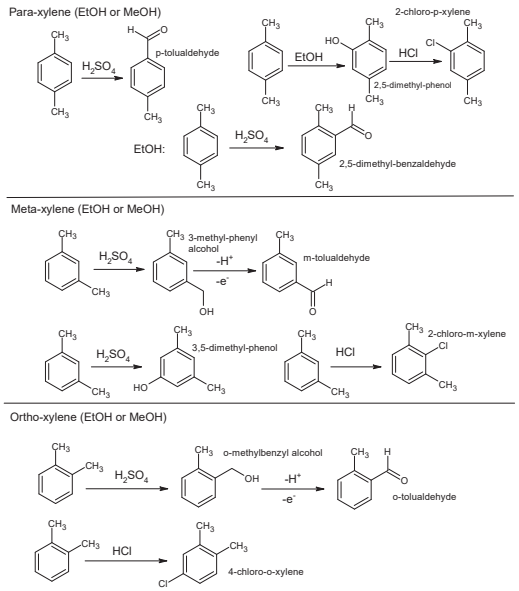


Figure 2. Byproducts formed from xylene isomers degradation.

References

[1] FRANCIS, W.; PETER, M. C. Data Sheet No. 172. Fuels and Fuel Technology (Second (SI) Edition) (1980) 645-649.
[2] SILVA, D. R.. Quím. Nova, São Paulo, v. 39, n. 5 (2016) 559-565.
[3] GAVINDARAJAN, M.; KARABACAK. M. B. Spec. 94 (2012) 36-47.
[4]LUO, K.; FENG, M.; HELLIER, P.; FENG, W.; ZENG, W.; JIAN, X. Fuel. 235, (2019) 515-521.

Agradecimentos/Acknowledgments

This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – Brasil (CAPES) – Finance Code 001.

Área: ELE

Assessing The Electro-oxidation of Ethanol in Alkaline Media – Assisting anions *vs.* Chaotropic Effects in SO_4^{2-}/ClO_4^- Electrolytes

Pedro L. Hermes-Lima (IC)[1]*, Thiago V. B. Ferraz (PG)[2], Hamilton Varela (PQ)[2]

plhlima@estudante.ufscar.br; thiagovbferraz@usp.br; hamiltonvarela@usp.br

[1]*Departamento de Química, UFSCAR;*[2]*Instituto de Química de São Carlos, USP*

Palavras Chave:*Ethanol, Electro-oxidation, Platinum, ElectrolyteEffects*

Highlights

Current density enhancement was observed for the electro-oxidation of 1 M ethanol (pH 13) over pc-Pt with increasing $Na_2SO_4/NaClO_4$ ratio up to 75% (Mol/Mol) and was accompanied by a change in the RDS.

Resumo/Abstract

Currently, the global warming crisis is by far the main environmental challenge faced for humanity as a whole. Caused by society's chronic dependency on fossil fuels for power generation, its solution requires the development of alternative processes capable of large-scale efficient production and storage of clean energy. Under this aspect, aiming to increase the reach and applications of negative CO_2 emission technologies, catalytic energy conversion processes, such as the H_2 evolution reaction (HER), have been heavily studied due to the great opportunities they present. However, even the most promising systems (e.g., fuel cells) tend to display clear limitations when the thermodynamical and kinetic hindrances associated to the water oxidation counter reaction (OER) are taken into account. The introduction of low molecular weight organic compounds in these devices, particularly alcohols (e.g., ethanol), as substitute to the OER, and in the presence of assisting anions could, in principle, both help to bypass most of the key kinetic issues as well as to modulate selectivity of the organic oxidation towards more economically interesting products. In the case of the ethanol, its electro-oxidation over platinum (Pt) electrodes demonstrates a distinguished performance in the presence of SO_4^{2-} compared to when they are absent in the medium, which was attributed to variations in the alcohol adsorption energies (-0.3424 eV and -0.7193 eV, respectively), emphasizing how the Pt/ethanol control the overall rate of the alcohol oxidation[1,2]. However, even under alkaline conditions (for which anionic electrosorption is considerably smaller) it is observed that the SO_4^{2-} species near the system's interface exhibits a hydrophobic behaviour that also promote catalytic enhancement, but which is explained by the presence of a *q* chaotropic media which leads to a greater anion/metal stabilization [3]. In order to better assess the extent of these two distinct effects, electrochemical measurements were performed in a conventional three-electrode cell using a polycrystalline platinum (pc-Pt) bead (1 mm radius) as work electrode, a platinum coil as counter electrode and a reversible hydrogen electrode (RHE) as reference. The results for the electro-oxidation of 1 M ethanol at pH 13 indicate that an increase in the SO_4^{2-} content induces a steady increment in the average current of the main oxidation process up to 75% ($Na_2SO_4/NaClO_4$), after which a pronounced decay is observed. The Tafel analysis performed on the LSV data show that, for the 50% and 75% systems, the observed enhancement can be associated to a kinetic favouring of the reaction (average Tafel angular coefficient of 82 mV dec^{-1}) compared to what is seen for the higher $NaClO_4$ concentrations (average of 161 mV dec-1) and for 100% Na_2SO_4 (128 mV dec^{-1}) – also indicative of a change in the rate determining step). Finally, the observation of an optimum condition suggests that, while heavily diminished, the inhibiting character of adsorbed sulphate ions on the pc-Pt surface still plays a role on the final response of the system to the catalytic process, being other important variables, such as the pH, further explored subsequent works.

References:

[1]X. You, M. Niu, V. Del Colle, X. Sun, J. Han, C. Ji, C. Pan, J. Zhang, Q. Gao, J. Phys. Chem. C 2022, 126, 3397–3403; **[2]**X. You, Y. Xu, J. Han, Y. Chang, V. Del Colle, C. Ji, C. Pan, J. Zhang, Q. Gao, J. Phys. Chem. C 2023, 127, 5743–5753; **[3]**A. H. B. Dourado, N. A. Silva, R. L. Munhos, V. Del Colle, M. Arenz, H. Varela, S. I. Córdoba de Torresi, ChemElectroChem 2020, 7, 1843-1850.

Agradecimentos/Acknowledgments

The authors would like to thank FAPESP (#2019/22183-6, #2020/15230-5, and #2022/06405-1), USP, RCGI/USP & Shell Brasil for the funding and infrastructure provided for this project, ANP (Agência Nacional de Petróleo, Gás Natural e Biocombustíveis) for the support provided through the R&D levy regulation, and CCET/UFSCAR for the financial support provided for participation in this event.

Área: ELE

Benzene bioremediation in microbial fuel cell using mixed culture present in mangrove sediment

João Carlos de Souza (PQ)[1,3]*, Ana Clara Bonizol Zani (PG)[1], Maria Valnice Boldrin Zanoni (PQ)[2,3], Valeria Reginatto (PQ)[1], Adalgisa Rodrigues de Andrade (PQ)[1,3]

ardandra@usp.br; souza_jc33@yahoo.com.br

[1]Department of Chemistry, Faculty of Philosophy, Science and Letters at Ribeirão Preto, University of São Paulo (USP); [2]Institute of Chemistry at Araraquar, São Paulo State University (UNESP);[3]National Institute of Alternative Technologies for Detection,Toxicological Evaluation and Removal of Micropollutants and Radioactive*Substances (INCT-DATREM)*-UNESP.

Palavras Chave: *(Benzene, Microbial fuel cell, Mangrove sediment, Biorremediation, Energy generation).*

Highlights

- MFC was developed to degrade benzene and generate energy simultaneously;
- An electroactive and conductive biofilm was formed;
- The MFC degraded 98.7% of benzene and generated 390 mW m^{-2} of electricity.

Resumo/Abstract

Benzene is present in oil and its derivatives, and it is extremely toxic, genotoxic and mutagenic, even at low concentrations, it can cause serious damage to the environment and the human health [1]. A very attractive alternative for the bioremediation of this compound is through the use of microbial fuel cells (MFC), which in addition to degrading, simultaneously produces clean energy [2]. In this sense, this work aims to develop an MFC to adequately and efficiently degrade benzene and simultaneously generate energy. For this, a two-compartment MFC with a capacity of 50 mL was constructed. The anode consisted of a carbon fiber brush (3.0 cm x 2.0 cm) connected to a titanium metal rod and the cathode of a carbon cloth modified with 40% Pt (area 15 cm^2) pressed into Nafion® proton exchange membrane. The voltages generated by the MFC were recorded in real-time, every 15 minutes, using an Arduino Mega 2560 microcontroller board programmed in the C++ language. To obtain the biofilm, a mixed microbial culture with mangrove sediment was used. A volume of 50.0 mL of a 20.0% (m/v) suspension composed of sediment and Lovley and Philips culture medium was transferred to the anode compartment. As the primary substrate for microorganisms, sodium acetate 1000 mg L^{-1} was used, being gradually replaced by benzene until the final concentration of 330 mg L^{-1}. Finally, the MFCs were closed and a resistance of 1000 Ω was connected between the anode and cathode. The developed MFC showed high efficiency, removing 98.7% of total benzene, after 96 hours of system power cycle, and reduced the toxic potential. The benzene increased the output voltage of the MFC from 568 mV (sodium acetate) to 902 mV (benzene). A maximum power density of 390 mW m^{-2} was obtained, a relatively higher value compared to most values reported for the remediation of benzene, toluene, xylene, and other compounds using similar devices. A reduction in solution resistance (Rs) was observed, where in the MFC without biofilm an Rs value of 7.7 Ω was found, and in the MFCs fed with sodium acetate and benzene, the Rs values were 1.25 Ω and 1.16 Ω, respectively. This indicates that the presence of the biofilm also made the solution less resistive, facilitating the migration of electroactive species into the medium. The evaluation of the microbial community showed a distinct microbial diversity when fed with sodium acetate and benzene. When fed with sodium acetate, there genera predominant were *Arcobacter* (20.23%) and *Comamonas* (11.03%), and with benzene, the genera *Bacillus* (32.93%) and *Arcobacter* (30.28%) predominated. Given the results, the developed MFC is an excellent, promising, and attractive alternative for benzene bioremediation and simultaneous energy production.

Agradecimentos/Acknowledgments

National Institute of Alternative Technologies for Detection, Toxicological Evaluation and Removal of Micropollutants and Radioactive Agents (INCT-DATREM - FAPESP process number 2014/50945-4, CNPq process number 465571/2014-0) and São Paulo Research Foundation (FAPESP – process number 2021/12866-9). Prof. J. Ribeiro, Centro de Ciências Exatas, Departamento de Química, UFES to collect and provide the initial sludge.

[1] SOUZA, J. C. et al. High J. Environ. Chem. Eng., v. 12, 2024, 111703.
[2] RABAEY, K.; VERSTRAETE, W. Trends Biotechnol., v. 23, p. 291–298, 2005.

Área: ELE

Capacitive electrochemical lab-made immunosensor modified with Au microflowers for the determination of PARK7/DJ-1

Luiz O. Orzari (PG)[1,2]*, Bruno C. Janegitz (PQ)[1].

l.o.orzari@gmail.com

[1] *Department of Nature Sciences, Mathematics and Education, UFSCar;* [2] *Department of Physics, Chemistry and Mathematics, UFSCar*

Keywords: *Au microflowers*, *Electrochemical immunosensor*, *Parkinson's disease*, *Lab-made conductive ink*, *carbon black*, *PVA*

Highlights

The surface modification with Au microflowers werewas extensively studied

Design of Experiments was employed to optimize immunosensor modifications

Bode plots were investigated to describe the device behavior

An analytical curve correlating surface capacitance and PARK7/DJ-1 concentration was obtained

Abstract

Parkinson's disease has a well-explained mechanism by the scientific community, with considerable advances since its first publication by James Parkinson in 1817. Among its functions, the disease damages the motor system, causes sleep disorders, and is related to depression and hyposmia [1]. An interesting protein that has been considered an emerging biomarker for Parkinson's is the DJ-1 protein. It has different functions in the body and plays a fundamental role in protecting against oxidative stress. The protein is produced by the PARK7 gene and was initially categorized as an oncogene [2]. The level of DJ-1 tends to be an important signal, especially in patients with Parkinson's, where DJ-1 has its gene sequence oxidized in its cysteine residues (position 106) [3]. Perhaps the most common modifier in electrochemical biosensors, Au nanoparticles stand out in terms of the high stability of the nanoparticles and low cellular toxicity. Also, these particles are able to immobilize biomolecules, while adding electrical properties and surface charge, facilitating electronic transfers between electrode and electrolyte [4]. The device was morphologically characterized with scanning electron microscopy, in which the presence of floral structures was detected, with an average area of 413 nm. These systems were modified with 3-MPA, EDC, AntiPARK7/DJ-1, and BSA to prepare them for an antigen-antibody interaction. By optimizing the self-assembly parameters for 3-MPA and AntiPARK7/DJ-1 with chemometrics, it was possible to obtain a calibration curve of the inversely linear relationship between the concentration of immobilized PARK7/DJ-1 and the system capacitance, corresponding to the range of 20 to 120 ng mL^{-1}, with R^2 of 0.981 and LOD and LOQ of 0.207 and 0.689 ng mL^{-1}, respectively. The data indicates that platforms modified with Au microflowers, despite being complex structures, have attractive behavior and responses for monitoring Parkinson's disease biomarkers.

Acknowledgments

The authors are grateful for the financial support provided by Brazilian agencies Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP, #2019/23342-0), Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES, 88887.504861/2020-00 and 001), Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq #380632/2023-3; 301796/2022-0) and Financiadora de Estudos e Projetos (FINEP, MARTMA, #01.22.0179.00).

References

[1] W. Poewe, et al., Parkinson disease, Nature Reviews Disease primers, 3(2017) 17013.
[2] H. Ariga, S.M.M. Iguchi-Ariga, DJ-1/PARK7 Protein: Parkinson's Disease, Cancer and Oxidative Stress-Induced Diseases: Springer; 2017.
[3] Y. Saito, et al., Oxidation and interaction of DJ-1 with 20S proteasome in the erythrocytes of early stage Parkinson's disease patients, Scientific reports, 6(2016) 1-11.
[4] V.Q. Khue, et al., Electrochemical stability of screen-printed electrodes modified with Au nanoparticles for detection of methicillin-resistant Staphylococcus aureus, Materials Chemistry and Physics, 255(2020) 123562.

Area: ELE

Chlorine Evolution Reaction for Tetracycline Hydrochloride Electrooxidation: effect of NaCl concentration

Maria T. P. de Farias (PG)[1], Evanny L. dos Santos (PG)[1], Adeildo J. de Oliveira (PQ)[2], João P. T. da S. Santos (PQ)[1], Vinicius Del Colle (PQ)[1,3]
maria.thalia@arapiraca.com.br; viniciusdelvdc@fab.mil.br
[1]*Programa de Pós-graduação em Agricultura e Ambiente, Universidade Federal de Alagoas – Campus Arapiraca.*
[2]*Universidade Federal de Alagoas, Núcleo de Ciências Exatas (NCEx) – Campus de Arapiraca.*
[3]*Instituto Tecnológico de Aeronáutica. Departamento de Química..*

Keywords: Dimensionally-stable anodes, Antibiotics Oxidation, Advanced Oxidation Processes.

Highlights

DSA® electrodes are highly efficient for PEC electro-oxidation in chloride medium, and the ion concentration affects directly rates of pollutant degradation. The lower Cl^- concentration showed the best global efficiency since presented the lower relative absorbance byproduct formation.

Abstract

The conventional treatments are not enough to eliminate the so-called pollutants of emerging concern (PEC). The electrochemical advanced oxidation process (EAOP) is versatile, environmentally compatible, has a good cost-benefit, and generates oxidative species *in situ*.[1,2] This study aimed to investigate the effect of the different NaCl concentrations (1.0, 0.5, and 0.1 mol L^{-1}) using a commercial DSA® electrode (nominal composition: $Ti/Ru_{0.3}Ti_{0.7}O_2$) for the degradation of tetracycline hydrochloride (TCH) in a concentration of 200 mg L^{-1}, applying a constant current density of 100 mA cm^{-2} during 720 min (Fig. 1(a)). The increase in chloride ions concentration enhances the production of the so-called active chlorine which favors a quicker TCH degradation presenting the following apparent first-order kinetic constants: $k_{0.1\ mol/L}$= 1.5 min^{-1}, $k_{0.5\ mol/L}$= 1.5 min^{-1} and $k_{1\ mol/L}$= 1.9 min^{-1}. For each studied concentration, it was possible to observe the formation of a stable byproduct which appears in the UV-Vis spectrum, *c.a.* 290 nm (Fig. 1(b)). The global energetic consumption (EC) values observed were 0.00094, 0.00060, and 0.00052 kW h $(g_{TCH})^{-1}$. Although TCH disappeared more quickly with a higher concentration of NaCl, we observed that only the lowest chloride concentration (0.1 mol L^{-1}) showed the smaller byproduct relative absorbance which suggests a minor rate of production, moreover just in this concentration the byproduct was also degraded.

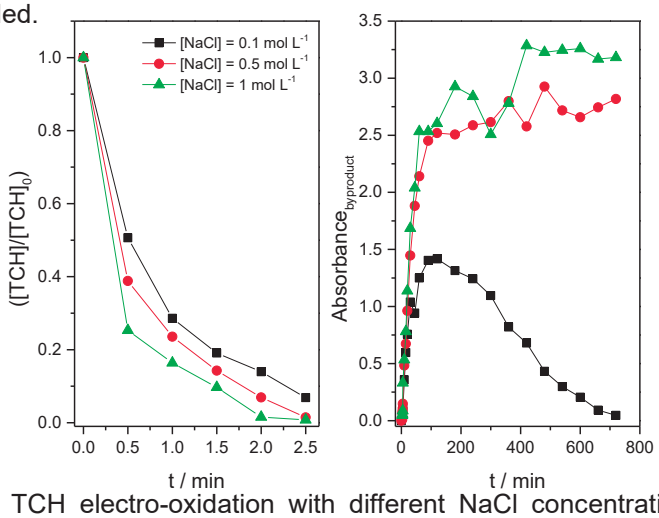


Fig. 1. (a) Kinetic curves for TCH electro-oxidation with different NaCl concentrations: 1.0, 0.5 and 0.1 mol L^{-1}. (b) Byproduct relative absorbance curves.

Acknowledgments

FAPEAL and CNPq.

References

1. LIM, Hyun Woo et al. Rational design of dimensionally stable anodes for active chlorine generation. **ACS Catalysis**, v. 11, n. 20, p. 12423-12432, 2021.
2. MALPASS, Geoffroy Roger Pointer; DE JESUS MOTHEO, Artur. Recent advances on the use of active anodes in environmental electrochemistry. **Current Opinion in Electrochemistry**, v. 27, p. 100689, 2021.

Área: ELE

Co_3O_4 nanowires supported on TiO_2 for the electroreduction of nitrate to ammonia

Kauan L. Gomes (PG),[1] Manuel E.G. Winkler (PQ),[1] Thiago M. Mariano (PQ),[2] Juliano A. Bonacin,[1,2] Raphael Nagao (PQ).[1,2*]

k271143@dac.unicamp.br; nagao@unicamp.br

[1]Institute of Chemistry, UNICAMP, [2]Center for Innovation on New Energies.

Keywords: *(Nitrate reduction reaction, Ammonia generation, Co_3O_4 nanowires).*

Highlights

- Higher yield rate (6.69 ± 0.818 μmol h^{-1} cm^{-2}) at 0.0 V vs RHE indicates a low overpotential for NO_3RR;
- Maximum faradaic efficiency reaches 66.0 ± 5.77% at -0.3 V vs RHE.

Abstract

Ammonia (NH_3) is widely used in industry as a raw material for synthesis of reagents, drugs and fertilizers. Furthermore, due to its high volumetric energy density (4.32 kWh L^{-1}) and carbon-free composition, it has the potential to be a carrier of renewable energy.[1] In search of alternatives to the well-established Haber-Bosch process, the electrochemical synthesis of ammonia from the nitrate reduction reaction (NO_3RR) has attracted interest, because it use clean and renewable energy, exploring the mitigation of nitrate contamination in water resources, without emitting pollutants. To minimize the energy cost of NO_3RR, catalysts with performance similar to that of noble metals are being developed.[2] Therefore, in this work, Co_3O_4 nanowires on TiO_2 were synthesized as a catalyst using a methodology consisted of cobalt electrodeposition followed by calcination. The performance of the catalyst was evaluated in an H-type electrochemical cell in Ar-saturated $NaNO_3$ 20 mmol L^{-1} and NaOH 1.0 mol L^{-1}. The cyclic voltammogram of the catalyst immersed in electrolyte without the presence of nitrate (Figure 1A) shows activity characteristic of the hydrogen evolution reaction at potentials near to -0.3 V vs RHE. However, with the catalyst immersed in electrolyte containing nitrate, the current density increases at less negative potentials, associated with nitrate reduction. To evaluate the catalytic performance, potentiostatic electrolysis was carried out, followed by product quantification. The maximum faradaic efficiency reached 66.0 ± 5.77% at -0.3 V vs RHE (Figure 1B), and in relation to the yield rate (Figure 1C), the maximum was reached at 0.0 V vs RHE (6.69 ± 0.818 μmol h^{-1} cm^{-2}), indicating that the catalyst has a low overpotential for NO_3RR. Given the considerations above, Co_3O_4 nanowires on TiO_2 have demonstrated to be promising catalysts for NO_3RR.

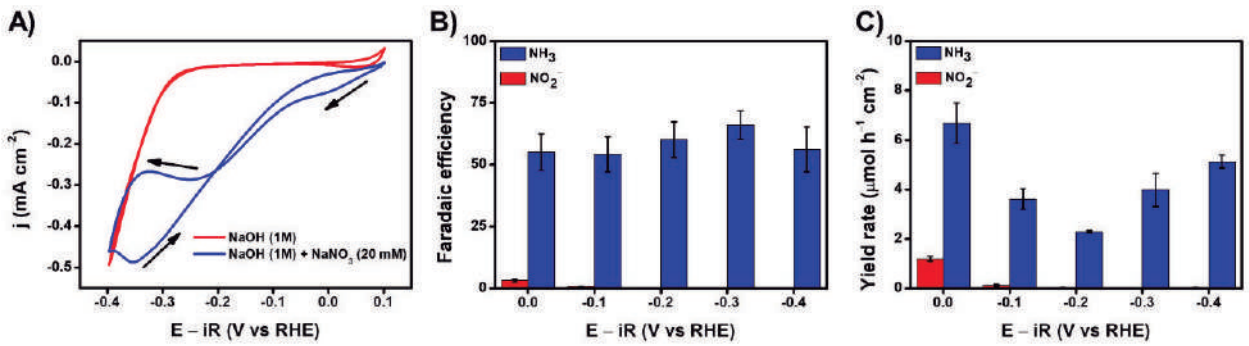


Figure 1. A) Cyclic voltammetry curves (20 mV s^{-1}) of the catalyst in NaOH (1.0 M) without and with $NaNO_3$ (20 mM), B) faradaic efficiency and C) yield rate for NH_3 and NO_2^- at different potentials.

[1] D. Yao, C. Tang, P. Wang, H. Cheng, H. Jin, L.-X. Ding, S.-Z. Qiao, *Chem Eng Sci* **2022**, *257*, 117735.
[2] G. Zhang, X. Li, K. Chen, Y. Guo, D. Ma, K. Chu, *Angew Chem Int Ed* **2023**, *62*, e202300054.

Acknowledgments

CAPES
Instituto de Química
UNICAMP

Comparative Study of the Influence of Protonic Ionic Liquid Properties on the Determination of Carbendazim

Maria Eduarda da Conceição Vieira Nascimento (IC),[1*] José Fernando de Macedo (PG),[2] Brenda Rafaela Lima Freire (PG),[2] Eliana Midori Sussuchi (PQ)[1]

mariaeduardacvn2@gmail.com

[1]Departamento de Química, UFS, [2]Programa de pós-graduação em Química, PPGQ-UFS.

Keywords: *Electrochemical sensors, Ionic liquids, Pesticide.*

Highlights

Carbendazim (CBZ) possible reproductive toxicity and persistence in the environment for long periods.

The use of LIP in electrode modification for voltammetric techniques.

Abstract

Protonic ionic liquids (PIL) are promising as modifiers for electrochemical sensors due to their accessibility, easy obtainability, and low toxicity, aiding in the development of electrodes with increased sensitivity and selectivity for detecting analytes such as carbendazim (CBZ), a widely used fungicide in agriculture for controlling a variety of diseases in various crops, with high persistence in the environment for long periods, leading to contamination of soils, surface waters, and groundwater. In this study, two carbon paste electrodes modified with the PILs Citrate 2-hydroxylammonium (2HECit) and Ascorbate 2-hydroxylammonium (2HEAsc) were developed to investigate the diffusion process, which has different properties such as viscosity and electrical characteristics that may influence CBZ determination. The characterization of the electrodes was carried out using voltammetric techniques of Electrochemical Impedance Spectroscopy (EIS) and Cyclic Voltammetry (CV) in the presence of 10.00 mL of $[Fe(CN)_6]^{3-/4-}$ solution (1.00 mmol L^{-1}) in KCl (1.00 mol L^{-1}). The EIS results demonstrated that the E/Cit 10% (52.9 Ω) and E/Asc 10% (NaN Ω) electrodes (**Fig. 1a**) exhibited lower charge transfer resistance compared to the EPC (850 Ω) for the $Fe^{2+/3+}$ redox pair (**Fig. 1b**). The E/Asc 10% did not present a numerical resistance value, which may be related to the viscosity of 2HEAsc (33.10 Pa s^{-1}), which is higher than 2HECit (13.50 Pa s^{-1}) at 25°C, hindering the charge transfer process but resulting in an increase in active sites due to the presence of PIL, leading to the E/Cit (0.25 mm^2) and E/Asc (0.30 mm^2) electrodes presenting a larger effective area compared to the EPC (0.20 mm^2) and geometric area (0.18 mm^2), facilitating the diffusional process with $Fe^{2+/3+}$ redox species. The E/Asc 10% (**Fig. 1c**) and E/Cit 10% (**Fig. 1d**) electrodes exhibited voltammetric behavior similar to EPC (**Fig. 1e**), with a linear relationship between peak anodic and cathodic currents as a function of the square root of the scan rate, characterizing quasi-reversible systems and diffusion-controlled processes. The present work is still ongoing; however, the E/Asc and E/Cit electrodes show promising characteristics for future determination of carbendazim at low concentrations and environmental monitoring.

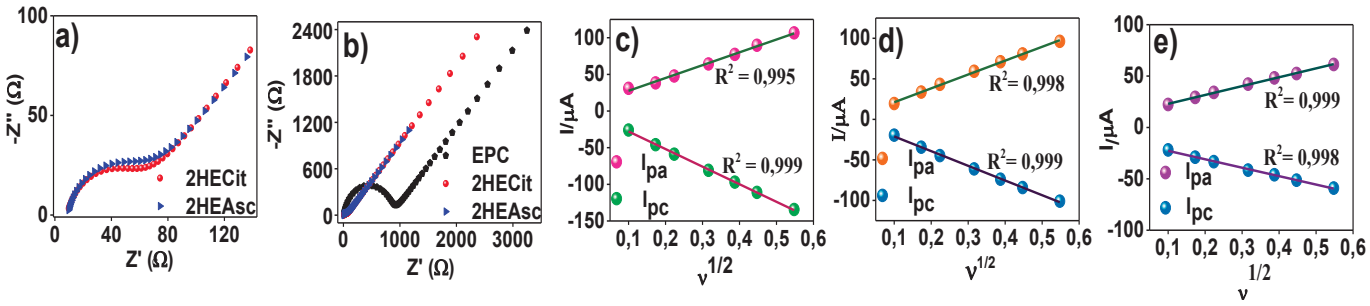


Figure 1. a) Electrochemical Impedance Spectroscopy (EIS) of 2HECit and 2HEAsc **b)** EIS of EPC, 2HECit, and 2HEAsc **c)** Peak anodic (I_{pa}) and cathodic (I_{pc}) currents as a function of the square root of scan rates ($n^{1/2}$) for E/Asc **d)** Peak anodic (I_{pa}) and cathodic (I_{pc}) currents as a function of the square root of scan rates ($n^{1/2}$) for E/Cit **e)** Peak anodic (I_{pa}) and cathodic (I_{pc}) currents as a function of the square root of scan rates ($n^{1/2}$) for EPC.

Agradecimentos/Acknowledgments

CCET ufs PPGQ SEnM SergipeTec CAPES CNPq FAPITEC|SE

Área: ELE

Cost-effective 3D-printed electrode for nitrite electrochemical sensing

Ariel Dayan (PG),* Lauro A. Pradela-Filho (PQ), Thiago R. L. C da Paixão (PQ)

dayan.ariel@usp.br

Institute of Chemistry, Department of Fundamental Chemistry, University of São Paulo, 05508-900, São Paulo-SP, Brazil.

keywords: *Fused Deposition Modeling, 3D-printing pen, electrochemical sensors, alkaline treatment, fouling resistance.*

Highlights

Developing affordable electrodes using a 3D printing pen. Evaluating the alkaline electrochemical treatment on the analytical signal. Exploring the electrode potentiality for nitrite quantification.

Resumo/Abstract

Fused Deposition Modeling (FDM), a three-dimensional (3D) printing technique, enables the rapid fabrication of electrochemical sensors. The printing process involves using a heated nozzle to extrude a molten thermoplastic composite. The 3D structure is generated right after filament deposition. This project aims to produce electrodes using a 3D printing pen, an acrylic mold, and a commercial conductive filament, which is composed of polylactic acid (PLA) and carbon black (CB). The resulting sensors were initially tested with $[Ru(NH_3)_6]^{3+}$, providing well-defined and consistent voltammetric profiles for this redox probe (Figure 2). Subsequently, the sensors were subjected to an alkaline electrochemical treatment, evaluating their electrochemical signal for nitrite oxidation (Figure 2). For the treatment, ten cyclic voltammograms were recorded over +1 to -1 V in 0.5 mol L^{-1} NaOH. Figure B shows that the treatment enhanced the analytical signal (1.5-fold) for nitrite oxidation and the electrode's ability to resist the fouling effect. The signal enhancement is related to partially removing the PLA from the electrode surface, exposing the electroactive carbon sites. Additionally, the stability enhancement is probably due to the changes in the electrode surface hydrophobicity, minimizing the deactivation process. Once characterized, the nitrite oxidation was evaluated at different pH (from 2 to 8), selecting pH 4 as an optimum condition. Next, a calibration curve was constructed for nitrite (Figure C), generating a linear range from 10 to 200 µmol L^{-1}. These results bring encouraging findings for nitrite quantification. Therefore, the next step will involve analyzing water, soil, and sausage samples.

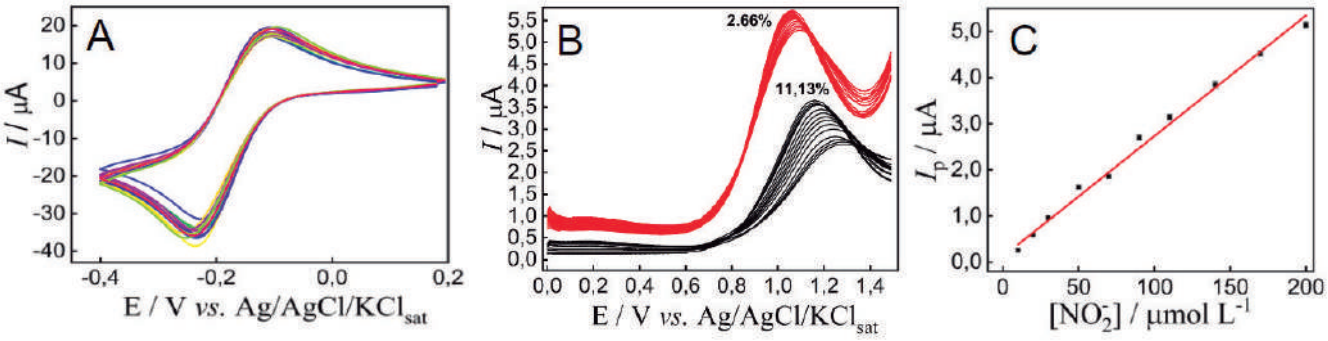


Figure 1 – A) Cyclic voltammograms for twenty different non-treated electrodes recorded in 5 mmol L^{-1} $[Ru(NH_3)_6]^{3+}$ and 0.1 mol L^{-1} KCl at 100 mV s^{-1}; B) Square wave voltammograms recorded with electrodes before (black) and after (red) performing electrochemical treatment. The measurements were recorded in 100 µmol L^{-1} nitrite and 0.1 mol L^{-1} Britton-Robinson buffer pH 4. C) Calibration curve for nitrite determination using the treated electrodes.

1.PRADELA-FILHO et al. Patterning (Electro)chemical Treatment-Free Electrodes with a 3D Printing Pen. Analytical Chemistry, 22 June 2023.

Agradecimentos/Acknowledgments

Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - CAPES (PROEX 88887.925954/2023-00) and São Paulo Research Foundation - FAPESP (2021/00205-8, 2022/11346-4 and 2018/08782-1).

Área: ELE

Current Density Influence in Active Chlorine Production for Tetracycline Hydrochloride Electro-oxidation

Evanny L. dos Santos (PG) [1], Maria Thalia P. Farias (PG)[1], Adeildo J. de Oliveira (PQ)[2], João P. T. da S. Santos (PQ)[1], Vinicius Del Colle (PQ)[1,3]
evanny.santos@arapiraca.ufal.br, viniciusdelvdc@fab.mil.br*
[1]*Programa de Pós-graduação em Agricultura e Ambiente, Universidade Federal de Alagoas – Campus Arapiraca.*
[2]*Universidade Federal de Alagoas, Núcleo de Ciências Exatas (NCEx) – Campus de Arapiraca.*
[3]*Instituto Tecnológico de Aeronáutica. Departamento de Química.*

Keywords: Electrochemical Parameter, Electrocatalysis, Advanced Oxidation Processes.

Highlights

The use of DSA® rapidly degraded TCH in different current densities. There was byproduct formation which was also electro-oxidized. Considering the global process, the J = 50 mA cm^{-2} presented the best global efficiency.

Abstract

RuO_2 is an important component material in commercial dimensionally stable anodes (DSA®) for chlorine evolution which makes it a very promising electrocatalytic material for active chlorine production to degrade pollutants of emerging concern, such as antibiotics. The electrochemical advanced oxidation process (EAOP) is versatile, environmentally compatible, has a good cost-benefit, and generates oxidative species *in situ*.[1,2] The current density (J) is an important key parameter that influences directly degradation efficiency. This study aimed to investigate the effect of the increase in current density (J =12.5, 25, 50, and 100 mA cm^{-2}) applied to a commercial DSA® electrode (nominal composition: $Ti/Ru_{0.3}Ti_{0.7}O_2$) for active-chlorine production to degrade tetracycline hydrochloride (TCH) in a concentration of 200 mg L^{-1}. The increase in current density enhances the production of the so-called active chlorine which favors a quicker TCH degradation at higher current densities (Fig. 1 (a)). We found the following apparent first-order kinetic constants for TCH oxidation: $k_{12.5\ mA\ cm^{-2}}$ = 0.16 min^{-1}, $k_{25\ mA\ cm^{-2}}$ = 0.28 min^{-1}, $k_{50\ mA\ cm^{-2}}$ = 0.66 min^{-1}, $k_{100\ mA\ cm^{-2}}$ = 1.00 min^{-1}. All current densities used favored the formation of a stable byproduct which appears in UV-Vis spectrum, *c.a.* 290 nm (Fig. 1(b)), the byproduct formation occurred less pronounced in lower current densities, however, we observed that just with J = 50 and 100 mA cm^{-2} the subproduct was also electro-oxidized. The global energetic consumption (EC) values observed were 0.46, 0.92, 0.73, and 0.94 (x 10^{-3}) kW h (g_{TCH})$^{-1}$, respectively.

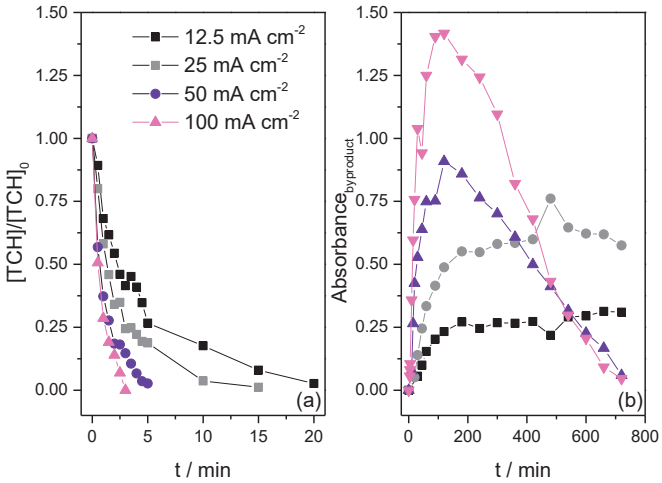


Fig. 1. (a) Kinetic curves for TCH electro-oxidation with different current densities (J): 12.5, 25, 50 and 100 mA cm^{-2}. (b) Byproduct relative absorbance curves.

Acknowledgments

FAPEAL and CNPq

References

1. LIM, Hyun Woo et al. Rational design of dimensionally stable anodes for active chlorine generation. **ACS Catalysis**, v. 11, n. 20, p. 12423-12432, 2021.
2. MALPASS, Geoffroy Roger Pointer; DE JESUS MOTHEO, Artur. Recent advances on the use of active anodes in environmental electrochemistry. **Current Opinion in Electrochemistry**, v. 27, p. 100689, 2021.

Área: ELE

Design and Fabrication of an Electrochemical Sensor for Accurate Nicotine Measurement in E-Liquids

Antonio Gomes dos Santos Neto (PG),[1]* Camila Silva de Sousa (PG),[1] José Antonio de Oliveira Junior (PG),[1] Marco Aurelio Suller Garcia (PQ),[2] Cristiane Luisa Jost (PQ)[1].

cristiane.jost@gmail.com; santos.antonio@posgrad.ufsc.br

[1]Chemistry Department, UFSC; [2]Chemistry Department, UFMA

Keywords: *Nicotine, Voltammetry, Electrochemical sensor, Gold, TiO_2 based materials, E-liquids.*

Highlights

Development of a nanocomposite comprised of TiO_2 supported by elongated gold nanostructures. Design and fabrication of Au-TiO_2-based electrochemical sensor for cost-effective nicotine (NIC) quantification. Detailed electrochemical characterization of the proposed sensor. Direct electroanalysis of e-liquid samples through SWV with accuracy and proper sensitivity.

Abstract

This research presents a novel electrochemical sensor based on a nanocomposite of TiO_2 supported by elongated gold nanostructures, providing an economical (only 2.0 wt.% of Au) and highly sensitive voltammetric method for measuring nicotine (NIC). Solid gold elongated nanostructures were synthesized through a seed-mediated growth method. The process involved mixing a prepared gold solution with a polyvinylpyrrolidone aqueous solution and stirring at 50°C. Aqueous citrate and gold chloride solutions were added sequentially. The growth of the nanostructures was monitored by quenching the reaction at different time intervals. The nanostructures were isolated and washed with ethanol via centrifugation, then immobilized on TiO_2 through a wet-impregnation technique. NIC, a stimulant and addictive purine alkaloid found in the *Nicotiana genus* plants, is consumed in various forms; currently, smoking has been replaced by NIC-delivery alternatives such as electronic cigarettes (e-cigarettes). E-liquid, also referred to as e-juice or vape juice, is the flavoured mixture used in e-cigarettes by several brands, offering a tailored vaping experience. The European Union has set a limit of 20 mg/mL of NIC in these products.[1] Thus, accurate and cost-effective methods for determining NIC content are crucial. In this regard, our investigation encompasses the sensor's development, characterization, and successful application, accentuating its potential for extensive utilization in analytical domains.[2] Comprehensive material analysis utilized transmission electron microscopy, X-ray photoelectron spectroscopy, and X-ray diffraction. Voltammetric studies were conducted to explore the response of NIC in a Britton Robinson-supporting electrolyte by varying the pH, with the maximum current response obtained at pH 7.0. The electrochemical process was characterized as irreversible and diffusion-controlled.[3] In light of this, the analysis of half-width ($W_{1/2}$) during low-intensity pulses, following the methodology proposed by Tafel,[3] suggests the involvement of one electron in the oxidation process. The square wave voltammetry (SWV) technique was chosen and optimized for analytical purposes. Two linear ranges of 1.99 to 108.9 and 159.3 to 900.8 μmol L^{-1} were achieved; the limit of detection (LOD) was calculated as 0.149 μmol L^{-1}. The accuracy was notably high, with a recovery range of 99% to 110%. The e-liquid samples were examined without any sample preparation or dilution. Quantification in different e-liquid real samples exhibited no significant differences compared to molecular absorption spectroscopy, endorsing the sensor for monitoring NIC through electroanalysis. The intraday and interday tests emphasized the remarkable stability of the electrochemical sensor, suggesting its applicability for at least five days. In conclusion, the facile fabrication of the nanocomposite has yielded a highly sensitive voltammetric method for NIC quantification. Its analytical performance underscores its potential as a valuable tool in routine protocols.

[1] Report from the Commission to the European Parliament and the Council on the potential risks to public health associated with the use of refillable electronic cigarettes. European Commission, 2016. [2] Mehmeti, Eda *et al*. Microchemical Journal, v. 158, p. 105155, 2020. [3] Bard, A. J.; Faulkner, L. R. Electrochemical Methods Fundamentals and Applications; Wiley: New York, 2001.

Acknowledgments

CNPq, CAPES, FAPESC and Prof. Dr. Adailton J. Bortoluzzi (UFSC) for his X-ray diffraction expertise.

Area: ELE

DETERMINATION OF CHLORAMPHENICOL IN MILK USING AN ELECTROCHEMICAL SENSOR WITH A GLASS CARBON ELECTRODE MODIFIED WITH CARBON BLACK

Déborah de Oliveira Lopes (IC),[1]* Felipe Magalhães Marinho (PG),[1] Geiser Gabriel de Oliveira (PQ).[1]

oliveira.lopes@uft.edu.br

[1]*Federal University of Tocantins, 77402-970, Gurupi, Tocantins, Brazil.*

Keywords: *Carbon black, Chloramphenicol, Milk, Differential Pulse Voltammetry.*

Highlights

Chloramphenicol (CAP) is an antibiotic, which is extremely harmful to health and the environment. Thus, this work was to develop a simple and sensitive electroanalytical method for the determination of CAP.

Abstract

Antibiotic residues from agricultural and pharmaceutical products represent a serious problem for the environment and health [1], recent studies have found CAP residues in dairy products, such as milk [2]. In this study, the use of a modified electrochemical sensor with carbon black (CB) to detect CAP in milk samples was investigated. Initially, the characterization studies of GCE and CB/GCE were effectuated in a redox probe $[Fe(CN)_6]^{3-}$. The values of the electroactive areas were 0.084 and 0.194 cm^2; while the heterogeneous electron transfer rate constants (k^0) values were 1.0×10^{-3} and 5.2×10^{-2} cm s^{-1}, for the GCE and CB/GCE, respectively. It was observed that the modification of the electrode with CB was viable to improve the electrochemical characteristics of GCE, demonstrating improvement in the analytical signal, conductivity, and electron transfer kinetics, proving its potential for the determination of CAP.

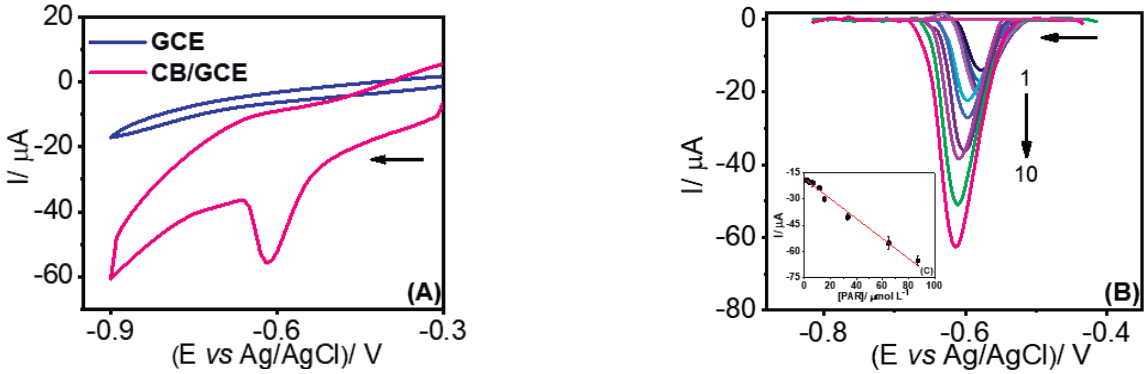


Figure 1. (A) Cyclic voltammograms obtained in the presence of 1.0×10^{-6} mol L^{-1} of CAP in BR buffer pH 7.0 with a scan rate of 50 mV s^{-1}. (B) Differential pulse voltammograms obtained using CB/GCE with different concentrations of CAP and (C) Insert image corresponds to the analytical curve.

Initially, studied the behavior of CAP in relation to CB/GCE and observed the occurrence of a reduction peak, as illustrated in Figure 1 (A), whereas GCE exhibited no signal. The objective of incorporating CB into the GCE surface was to improve electron transport efficiency, thereby offering a valid justification for its application. The analytical performance of CB/GCE for the determination of CAP was investigated using differential pulse voltammetry (DPV). Under optimum conditions, the linear concentration response of CAP ranged from 1.0×10^{-6} to 8.7×10^{-5} mol L^{-1} and obtained a low limit of detection of 1.7×10^{-7} mol L^{-1} with satisfactory results of reproducibility and repeatability performances of 5.1 and 4.7%, respectively. Recovery percentages in the range of 97 to 108% were attested to in the sample milk. Thus, the developed methods are reliable and promising for implementation in antibiotic residue monitoring in milk.

[1] M. Govindasamy, S.M. Chen, V. Mani, R. Devasenathipathy, R. Umamaheswari, K.J. Santhanaraj, A. Sathiyan. J., Colloid Interface Sci., 485 (2017) 129-136.
[2] T. Sniegocki, M. Gbylik-Sikorska, A. Posyniak. Food Control, 57 (2015) 411-418.
[3] N. Sebastian, W.-C. Yu, D.Y. Balram, Inorg. Chem. Front., 6 (2019) 82-93.

Acknowledgments

UFT Universidade Federal do Tocantins · UFT PPGQ Programa de Pós-Graduação em Química · FAPT · CAPES · CNPq Conselho Nacional de Desenvolvimento Científico e Tecnológico

Área: ELE
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Development and Characterization of Polycaprolactone-Polypyrrole Microneedle Biosensors for Enhanced Analyte Monitoring and Healthcare Accessibility

Ana Carola De La Via (PG),[1] Jose E. Rollas (PQ),[1] Ana C. Honorato (PQ),[1] Randy Burns (PG),[3] Dylan Chiaro (PG),[3] Suchi Guha (PQ),[3] Gavin M. King (PQ),[3] Vivian L. Oliveira (PQ),[2] Daniele R. de Araújo (PQ),[1] Wendel A. Alves (PQ)[1]

ana.carola@ufabc.edu.br

[1]*Centro de Ciências Naturais e Humanas, Universidade Federal do ABC, Av. dos Estados, 5001, Santo André - SP 09210-580.*
[2]*Laboratorio de Imunologia, INCOR, Hospital das Clínicas HCFMUSP, Faculdade de Medicina, Universidade de São Paulo.*
[3]*Department of Physics and Astronomy, University of Missouri, Columbia, MO 65211, USA.*

Keywords: polymeric microneedles, conductive polymers, non-invasive monitoring, healthcare, polycaprolactone-polypyrrole.

Highlights

This study presents the development of minimally invasive polymeric microneedle arrays combining polycaprolactone (PCL) and polypyrrole (PPy) for safe healthcare applications. Optimizing PPy concentration achieved a balance between conductivity and biocompatibility, enhancing antibody retention and precise antigen detection without negative control interference. This innovation highlights the potential of conductive polymeric microneedles for non-invasive analyte monitoring and treatment adherence via wearable biodevices.

Abstract

Creating advanced biosensors for real-time analyte monitoring is crucial in the evolving healthcare technology landscape. These tools facilitate immediate health assessments and aim to make medical diagnostics more accessible, affordable, and beneficial for patient health. Recent advancements have extensively utilized the capabilities of metallic microneedles; however, their application is limited by rigidity and cost. This work focuses on developing flexible, polymeric-based microneedle (MN) devices that enable scalable production using polycaprolactone (PCL). These semi-flexible MNs, integrated with polypyrrole (PPy) arrays, serve as innovative dry conductive electrodes, creating intrinsically conductive polymer surfaces. Our research produced MNs with various PPy proportions (9 to 27% w/w) in their matrix. Through thorough testing, a PPy concentration of 18% was found to be most effective, balancing conductivity and biocompatibility, as evidenced by four-point probe resistivity measurements, electrochemical impedance spectroscopy, and cytotoxicity analysis. This formulation significantly enhances antibody retention and precisely differentiates between target antigen concentrations unaffected by a negative control. MNs with an 18% PPy concentration exhibited a 56% increase in electrochemical signal, indicating their effectiveness in antibody anchorage. Furthermore, we optimized the antigen-antibody interaction time to 30 minutes, enhancing detection capabilities as evidenced by the highest R_{ct} values. With a detection limit of 0.23 ng mL^{-1} for cytokines, our MNs demonstrate strong potential for sensitive biosensing applications. Detailed examination of the MN base and surface was crucial for understanding the interaction between PCL and PPy. Scanning electron microscopy (SEM) provided in-depth views of this relationship, while atomic force microscopy (AFM) analysis was conducted along the sample's edge due to the small size of the needles and spaces between them. Compared to BET measurements, the correlation between porosity and surface roughness were analyzed in relation to the variation in the conductive polymer's concentration on the PCL microneedles' surface. The molecular structure of the resulting PPy, synthesized by oxidizing pyrrole with iron(III) chloride in an aqueous medium, was characterized using Raman and UV-visible spectroscopy. Excitation with a 785 nm laser wavelength resonates with the energy of delocalized polarons and bipolarons in the conductive polypyrrole structure, resulting in minimal penetration depth of the laser beam and no spectral features of PCL observed for high PPy concentrations on MN. The interaction between the conductive polymer and the PCL matrix was only observed at a 9% PPy/PCL concentration. Thermogravimetric analysis (TGA) revealed the thermal behavior and decomposition characteristics of the PCL-PPy composite. Additional in vitro tests using the Strat-M membrane to simulate human skin confirmed the biosensor's effectiveness in a simulated setting. Our research introduces efficient electrochemical biosensors based on PCL with the addition of PPy, potentially transforming patient monitoring and healthcare with technologies that are accessible and economically viable.

Acknowledgments

This work was supported by FAPESP (grant number 2022/14753-0), CAPES (grant number 88887.898711/2023-00), CNPq (grant number 305574/2023-0), and the National Institute of Science and Technology in Bioanalytics (FAPESP grant number 2014/50867-3 and CNPq grant number 65389/2014-7).

Área: ELE
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Development and validation of low-cost portable biosensors for dengue diagnosis

Maria Angélica de Camargo (PG),[1*] Débora Gonçalves (PQ)[1]

maria_angelica@usp.br

[1]*Instituto de Física de São Carlos – IFSC-USP*

Key words: *Screen-printed electrodes, Dengue, POC test*

Highlights

Develop biosensors with characteristics of simplicity, precision, high sensitivity and low cost as a promising alternative in the diagnostic scenario. Design commercial antibody biosensors for the detection of dengue virus markers based on printed interdigitated electrodes using ferrocene and chitosan film. Design and characterize antibody biosensors using biomarkers of dengue virus. Obtain biosensors for dengue, testing ten different antibodies by ELISA, two antibody immobilization techniques: simple adsorption and covalent bonding (chemical adsorption), optimization of antibody concentration and immobilization time. Validation with control and clinical samples to obtain a POC test.

Abstract

Despite technological advances around the world and in the most diverse areas, developing countries still face numerous challenges in the area of health. Clinical and laboratory diagnoses are generally limited and inaccessible for the majority of patients, which can result in high rates of mortality due to neglected diseases. A promising alternative in the diagnostic scenario is the use of biosensors due to their simplicity, precision and high sensitivity characteristics. Despite increasing advances in the academic field in relation to biosensors, aiming to increase the sensitivity of the technique and make it cheaper comparing to the chemiluminescence, gold standard method for Dengue, there are still no commercial tests using this methodology on the market. In this project we aimed to develop and validate a disposable device based on electrochemical techniques. Ten anti-Dengue NS1 from three different companies, national and international, were tested with ELISA to select the best antibodies capable of detecting Dengue NS1 positive and negative control samples. Then, carbon screen printed electrodes containing Carbon Black were modified with films containing a redox probe Ferrocene (Fc) 4 mg mL^{-1} and a solution containing chitosan (Qs) 5 mg mL^{-1}. After the film electrodes modification, the two antibodies selected by ELISA were then immobilized over the film using three different conjugation methods: simple absorption, glutaraldehyde covalent bonding and EDC/NHC covalent bonding. The glutaraldehyde covalent bonding showed better results and therefore was selected for the next tests. At that moment was also selected the best antibody, from an international company. Further, were tested antibody concentration, in a range of 50 to 150 µg mL^{-1}, being selected 100 µg mL^{-1}, and some other electrode optimization parameters, such as time for antibody immobilization, in a range of 2 to 14 hours, being selected 2 hours as the best. The electrochemical characterization was made by using cyclic voltammetry and differential pulse voltammetry techniques and the results were compared to chemiluminescence values, used to characterized previously the commercial positive and negative controls, in a confidence level of 95%. The biosensors were characterized by electronic and vibrational spectroscopy techniques (UV-VIS and FT-IR) and microscopy. The validation is ongoing and so far, the test presented a good repeatability and reproducibility, a high sensitivity compared to the tests available on the market, with LOD of 0,01 ug mL^{-1} NS1 protein and a low cost, estimated price less than two dollars. The next step is testing the prototype with positive and negative clinical samples and perform shelf-life stability tests. In summary, protocols and techniques used in the biosensor preparation were optimized in order to have simpler and faster methodologies aiming at obtaining specific, selective, sensitive and low-cost point-of-care test for detection of dengue disease.

Acknowledgments

This work was supported by CAPES (Finance code 001) (proc. 88887.837887/2023-00), CNPq (proc. 402816/2020-0), and FAPESP (proc. 2018/22214-6).

Development of an electrochemical Screen-Printed sensor using a new Carbon Black Super P® Water-Based Ink for Tryptophan Detection

Jéssica R. Camargo (PG)[1,2,3]*, Elena Bernalte (PQ)[3], Robert D. Crapnell (PQ)[3], Craig E. Banks (PQ)[3], Bruno C. Janegitz(PQ)[1,2]

Jessica.10.camargo@gmail.com

[1]Laboratory of Sensors, Nanomedicine and Nanostructured Materials, Federal University of São Carlos, Araras,13600-970, Brazil
[2]Department of Physics, Chemistry, and Mathematics, Federal University of São Carlos, Sorocaba, São Paulo, Brazil, 18052-780
[3]Faculty of Science & Engineering, Manchester Metropolitan University, John Dalton Building, Chester Street, Manchester M1 5GD, UK

Palavras Chave: *Screen-printed, Electrochemical sensor, Carbon black super P®, Conductive water-based ink, Tryptophan*

Highlights

Creation of a disposable sensor featuring a water-based ink formulation using Carbon Black Super P® for a Screen-Printed Electrode (SPE), designed for the diagnosis of tryptophan.

Abstract

Conductive inks have gained prominence in the manufacture of sensors due to their design flexibility, ease of manufacture, and cost efficiency[1]. Carbon-based materials, with their cost efficiency and advantageous properties such as increased electrical conductivity and large electroactive area, are proving to be excellent alternatives for the development of conductive inks. Carbon Black Super P® (CBSP®) stands out as an under-researched carbon-based material[2]. It offers additives that increase conductivity and optimize electron transfer properties, making it ideal for the construction of disposable electrochemical sensors. In addition to the conductive material, the choice of a suitable polymer matrix is also crucial. Previous studies have shown the advantages of using chitosan (CH) and polyvinylpyrrolidone (PVP) in water-based conductive inks. The present work focuses on optimizing the preparation of a water-based conductive ink by determining the optimal ratio between CBSP® and the polymer matrix to achieve increased conductivity in the final electrode. Tryptophan (TRP) is a significant biomarker with pleiotropic effects on biochemical and physiological responses[3]. Freely traded as a pharmaceutical, it acts as a potent sleep aid, appetite suppressant, and antidepressant, showing efficacy in addressing conditions like headaches and obesity. Its detection is crucial due to its presence in various sources, including food, pharmaceuticals, and human samples. Firstly, the CBSP-PVP-CH/PES electrode underwent testing using differential pulse voltammetry in a 0.1 mol L^{-1} phosphate buffer medium (pH 7.0) with 50 µmol L^{-1} TRP. An anodic peak current was observed at 0.6 V vs. Ag/AgCl ink. Following an investigation into physical-chemical and operational parameters, an analytical curve was constructed, revealing an increase in anodic peak current with rising TRP concentration (0.5 to 300 µmol L^{-1}) and detection limit of 0.06 µmol L^{-1}. The proposed electrode demonstrated TRP determination in pharmaceutical samples (tablets) and spiked beverages (apple juice and cow milk), with recovery values ranging from 86.2 to 114%. In this sense, the work presents the development of screen-printed electrodes using a new conductive water-based CBSP® ink, which were applied for TRP detection in pharmaceuticals and spiked beverages.

Acknowledgments

Fundação de Amparo à Pesquisa do Estado de São Paulo, FAPESP-Brazil (grant# 2023-00321-3, grant# 2019/23177-0). Coordenação de Aperfeicoamento de Pessoal de Nível Superior - Brazil (CAPES-Brazil) - Finance Code 001 and 88887.504861/2020-00 and Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) (301796/2022-0).

[1]P. Lakhera et al., **Materials Today Chemistry**, 26(2022) 101129.
[2]Cho, J. et al., **RSC Advances**, 5(2015) 95073-8.
[3]C. Delgado-Andrade et al. **Food Chemistry**, 98(2006) 580-5.

Área: ELE

Development of a portable and autonomous potentiostat for field analytical applications

Rafael Silva Santos (IC),[1*] Gabriel Negrão Meloni (PQ),[1] Thiago Regis Longo Cesar da Paixão (PQ).[1]

rafael.ss@usp.br

[1]*Departamento de Química Fundamental, IQUSP*

Keywords: Instrumentation, Low-cost, Electroanalytical, Field applications, 3D-printing.

Highlights

Portable, autonomous potentiostat with a microcontroller and 3D printing. The user-friendly interface allows untrained users to perform multiple electroanalytical techniques with a single button press.

Abstract

Several electrochemical methods have been developed promising application on the field, leveraging on the simple and affordable instrumentation involving electrochemistry. Despite this, most fail to prove this capability, as they still rely on expensive experimental infrastructure in research settings. Although affordable electrochemical sensor fabrication has developed greatly, the instrumentation aspect hasn't followed, particularly in the skill set needed to acquire, treat, and interpret data, which is still done by specialized users even when an affordable potentiostat is used.[1] Here we present the development of an affordable potentiostat, using simple components and an *Arduino Nano* microcontroller board, which can perform several electrochemical methods, including amperometry, cyclic voltammetry (Figure 1A), and square wave voltammetry. Further, the program running in the microcontroller, which controls the potentiostatic circuit, can acquire and store the data in its internal memory, process the signal and interpolate it against a pre-loaded calibration plot, reporting the sample concentration value in an OLED screen (Figure 1B). An internal battery powers the potentiostat, and this entire operation is autonomously performed after the press of a single button, allowing untrained users to perform complex measurements in remote locations. The potentiostat is coupled with a fully 3D printed integrated electrode system (Figure 1C), encompassing the working, pseudo reference, and counter electrode, which can be further modified for selective electrochemical sensing.[2] The combination of an affordable potentiostat with a fully 3D printed sensor allows the entire ensemble to be fabricated in a maker space or a "hobbyist garage," making this a legitimate, affordable platform for performing electrochemical methods at the cost of less than $ 72 per equipment + sensor. Together with the autonomous operation, this affordable instrumentation will help bring many of the developments in "field deployable" electrochemical sensing to fruition.

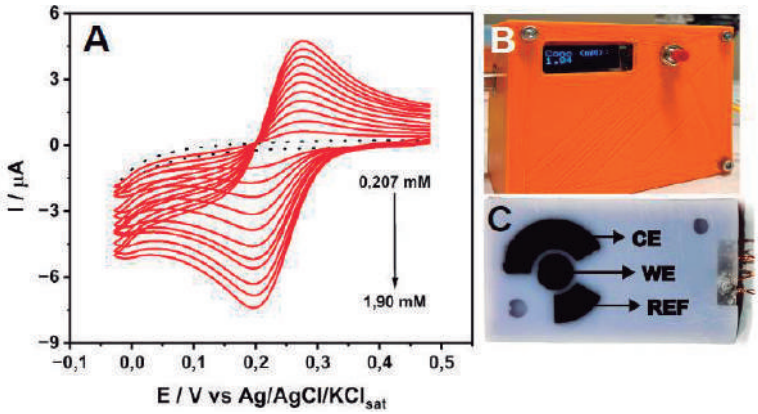


Figure 1: (A) Cyclic voltammograms recorded with the equipment for increasing concentrations of potassium ferricyanide in a 0.2 M KCl solution. The scan rate is 50 mV/s. (B) Quantification of potassium ferricyanide as a proof of concept. The reported value is 1.84 mM, with a nominal concentration of 1.90 mM. (C) 3D-printed integrated electrode system.

References: (1) Meloni, G. N. 3D Printed and Microcontrolled: The One Hundred Dollars Scanning Electrochemical Microscope. *Anal. Chem.* ***2017****, 89 (17), 8643–8649.* **(2)** Veloso, W. B.; Ataide, V. N.; Rocha, D. P.; Nogueira, H. P.; de Siervo, A.; Angnes, L.; Muñoz, R. A. A.; Paixão, T. R. L. C. *Microchim. Acta* **2023**, *190* (2), 63.

Acknowledgments

FAPESP CNPq 117016/2023-3 CAPES

Área: ELE

Development of miniaturized electrochemical sensors for carbendazim detection in drinking water

Lauanne Rocha Silva (IC),[1] Pedro Victor Valadares Romanholo (PG),[2] Lívia Flório Sgobbi (PQ).[1]*

lauannerocha@discente.ufg.br; livia_sgobbi@ufg.br

[1]*Instituto de Química, Universidade Federal de Goiás.*

Palavras chaves: Disposable electrodes, Electrochemical sensors, conductive inks, pesticides.

Highlights

Lab made- and conductive carbon ink for the fabrication of screen-printed electrodes on flexible substrates. Disposable electrochemical sensor for carbendazim pesticide detection in drinking water.

Resumo/Abstract

The development of printing technologies for the manufacture of electronic devices has aroused great interest, being a field in the area of materials science that has been gaining prominence [1]. In this scenario, electrochemical devices stand out in the production of sensing platforms for different applications [2]. Portable and miniaturized devices are fundamental for real-time and *in situ* analysis. Screen-printed electrodes (SPEs) have been widely applied in the fabrication of electrochemical sensors, due to their simplicity, mass production and reduction of sample volumes to microliters [3]. One of the critical issues in manufacturing SPEs consists of feasible conductive inks. Herein, various conductive material, binders and solvents were investigated, with the aim of improving the cost-effective and large-scale production of SPEs. The, the optimized SPEs were used to electrochemically detect carbendazim pesticide, as a proof-of-concept. The ink was made with graphite (3 brands) as the conductive material, which is cheap, non-toxic and stable. The different solvents were also evaluated, and the optimal condition was obtained with diacetone alcohol. Shellac, a natural polymer, biodegradable and insoluble in water, was used as the binder. Different binder:graphite proportions were evaluated, as well as the ink adherence on the substrate. The electrochemical behavior of the lab made-electrodes was compared with that obtained with SPEs made with commercial through cyclic voltammetry (CV) in the presence of $[Fe(CN)_6]^{3-/4-}$ probe. Subsequently, the electrodes were used to detect carbendazim in BR buffer pH 9.0. The cyclic voltammograms exhibited an irreversible process with an irreversible oxidation peak at +0.60 V (vs Ag), which is a much lower potential when compared with those reported in several previous approaches using complex electrochemical sensor [5-7]. Afterwards, the electrochemical detection of carbendazim will be evaluated over a wide pH range; then, square wave voltammetry will be used in the subsequent analytical validation steps.

[1] KAMYSHNY, A.; MAGDASSI, **Chem. Soc. Rev**., v. 48, n. 6, p. 1712-1740, 2019.

[2] CAMARGO, J. R.; SILVA, T. A.; RIVAS, G. A.; JANEGITZ, B. C. **Electroch. Acta**, v. 409, p. 139968, 2022.

[3] LI, M; LI, D. W.; XIU, G., LONG, Y. T. **Curr. Opin. Electroch**., v. 3, p. 137-143, 2017.

[4] POULIN, A.; AEBY, X.; SIQUEIRA, G.; NYSTRÖM, G. **Sci. rep**., p. 2, 2021.

[5] DONG, W.; YANG, L.; ZHANG, L. **J. Agric. Food Chem**., v. 65, p. 727-736, 2017.

[6] XIE, Y.; GAO, F.; TU, X.; MA, X.; DAI, R.; PENG, G.; YU, Y.; LU, L. **J. Electroanal. Chem**., v. 855, p. 113468, 2019.

[7] XU, D.; LI, R.; WANG, G.; ZHU, H.; LI, Z. **New J. Chem**., v. 45, p. 21308-21314, 2021.

Agradecimentos/Acknowledgments

LEES IQ/UFG and CNPq.

Área: ELE
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Effect of different morphologies of nickel-magnetic iron oxide nanoparticles towards urea electro-oxidation reaction via MagnetoElectroCatalysis

Eduardo M. Rodrigues (PG),[1] Caio M. Fernandes (PG),[1] Evelyn C. S. Santos (PQ),[2] Flávio Garcia (PQ),[2] Yutao Xing (PQ),[3] Odivaldo C. Alves (PQ),[1] Júlio César M. da Silva (PQ).[1*]

ed_rodrigues@id.uff.br; juliocms@id.uff.br

[1]Departamento de Físico-Química, UFF; [2]Centro Brasileiro de Pesquisas Físicas; [3]Laboratório de Microscopia Eletrônica de Alta Resolução

Palavras Chave: *Nanoparticles, Nickel-magnetic iron oxide, Hyperthermia, Electrocatalysis, Urea electro-oxidation.*

Highlights

Use of an alternating magnetic field to generate localized heat in nickel-magnetic iron oxide nanoparticles during the urea electrooxidation reaction. Different morphologies of iron oxide nanoparticles were evaluated. A new approach to the field of electrocatalysis.

Resumo/Abstract

Urea is a compound commonly found in water bodies and can be naturally degraded into ammonia, which is toxic [1]. Nickel (Ni)-based electrocatalysts obtained high electrocatalytic activity towards urea electro-oxidation reaction (UER) [2]. One parameter that can improve UER is the increase in temperature [3]. Magnetic iron oxide nanoparticles (MNP) have attracted considerable attention due to their ability to generate heat when exposed to an alternating magnetic field (AMF) [4]. The objective of this work is to study the effect of MNP morphology on Ni-MNP nanoparticles, aiming its application as electrocatalysts for UER under the influence of an AMF in order to generate localized heating improving the process. This new approach was named MagnetoElectroCatalysis by the authors of this work. MNP were synthesized via co-precipitation methods for spheres (MNP) and hydrothermal methods for nanorings (MNR), and nickel nanoparticles (Ni) via chemical reduction by sodium borohydride [1-4]. Ni-MNP and Ni-MNR were synthesized (mass ratio 3:2) via chemical reduction by sodium borohydride using previously synthesized MNP and MNR. All materials were supported on carbon cloth (CC). XRD patterns demonstrated the presence of Ni, NiO, Fe_3O_4 and/or γ-Fe_2O_3. The images obtained by TEM confirmed the morphologies and displayed Ni, MNP and MNR nanoparticles with average diameters of 3, 20 and 100 nm, respectively. Hyperthermia tests demonstrated that MNP, MNR, Ni-MNP and Ni-MNR generated heat, while Ni did not. Cyclic voltammetries performed on 1 mol L^{-1} NaOH from 0 to 0.7 V *vs* Hg|HgO exhibited characteristic peaks of the Ni^{2+}/Ni^{3+} transition for all nickel-containing materials [1]. Chronoamperometry experiments at 0.55 V *vs* Hg|HgO in NaOH 1 mol L^{-1} and urea 0.33 mol L^{-1} were carried out to investigate the effect of AMF (56.6 mT and 244 kHz) on the electrode containing nanoparticles during UER. The results showed that immediately after turning on the AMF, the current density obtained using the electrodes containing Ni-MNP and Ni-MNR grew dramatically (28% and 12%, respectively) demonstrating that the electrocatalytic activity of the material was improved due to the heat generated locally. The influence of the AMF amplitude (from 14.9 to 88.9 mT) on the studied process was investigated and a linear relationship was observed between the current gain and field amplitude for the electrode containing Ni-MNP and an exponential relationship for the electrode containing Ni-MNR.

[1] J. R.Barbosa et al. **Electrochimica Acta**. 355, (2020), 136752.
[2] LIU, D. et al. **Journal of Colloid and Interface Science**. 529, (2018), 337.
[3] N.A.M. Barakat, et al. **Journal of Advanced Research**. 16, (2019), 43.
[4] NIRAULA, G. et al. **ACS Applied Nano Materials**. 4, (2021), 3148.

Agradecimentos/Acknowledgments

CBPF, CNPq, CAPES, Capes-PrInt (88887.310269/2018-00), FAPERJ (E-26/211.371/2019, E-26/201.435/2021, E-26/211.389/2021, E-26/210.793/2021, E-26/210.145/2022, E-26/010.000978/2019).

Área: ELE
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Effects of Molybdenum modification on the performance of $BiVO_4$ photoanode for light-assisted glycerol electrooxidation

Ícaro Levi Tomaz Nascimento (PG), Henrique Pena Verinaud (IC), Leonardo Carvalho Soares (PG), Pablo Sebastián Fernández (PQ) and Claudia Longo (PQ).

Departamento de Físico-Química, UNICAMP.

Palavras Chave: Photoelectrochemistry, molybdenum modification, $BiVO_4$, Glycerol, photoanode.

Highlights

Photoanodes based on $BiVO_4$ were used for light-assisted glycerol oxidation reaction (GOR).
Molybdenum modification enhanced the charge carrier transport in $BiVO_4$ films, improving this performance for GOR.

Resumo/Abstract

The use of light-assisted glycerol electrooxidation (GOR) as the anodic reaction in solar-driven reactors for CO_2 conversion or for H_2 production brings higher current density at lower bias when compared with the oxygen evolution reaction.[1] This contribution reports on the effects of Mo modification on the performance of $BiVO_4$ electrodes for photo-assisted GOR .[2] The $BiVO_4$ photoanode was obtained by a three-step process: (i) Deposition of a BiOI film on FTO by Successive Ionic Layer Adsorption Reaction (SILAR); (ii) thermal treatment with a vanadium precursor; and (iii) chemical etching with NaOH aqueous solution. Fig. 1a shows the porous surface of FTO|$BiVO_4$. The electrodes exhibited an anodic photocurrent under irradiation, intensified after the addition of 1 mol L^{-1} glycerol in aqueous 0.5 mol L^{-1} $NaHCO_3$ (Fig. 1b). For FTO|$BiVO_4$:Mo, j increased from 0.37 mA cm^{-2} to 1.63 mA cm^{-2} at E_{app} = + 0.5 V RHE, and this value was maintained to more than 6 hours. The screening intensity-modulated photocurrent spectroscopy (IMPS) revealed that the modification with Mo reduced the superficial recombination of the charge carriers (Fig. 1c). The influence of molybdenum modification in the stability and charge carrier dynamics on $BiVO_4$ are under investigation through IMPS and Photoelectrochemical Impedance Spectroscopy (PEIS).

a) b) c)

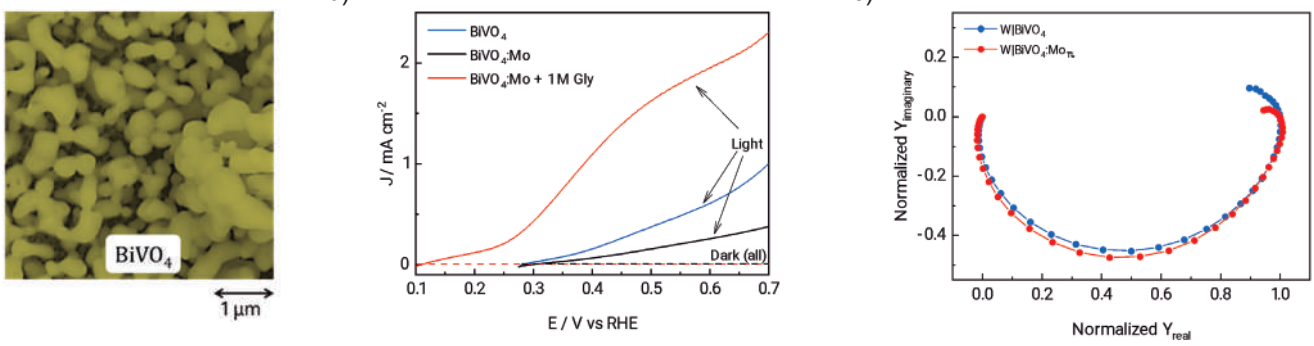


Figure 1 – Scanning electron microscopy of the FTO|$BiVO_4$ surface; b) Linear sweep voltammetry (20 mV s^{-1}) of the photoanodes in $NaHCO_3$ aqueous solution in the dark and under irradiation(100 mW cm^{-2}, 5700 K); c) intensity-modulated photocurrent spectroscopy at 0.5 V vs RHE

References

[1] P. V. B. Santiago, S. P. Raju, K. Akkiraju, R. A. Vicente, M. A. da Silva, S. Yuan, D. Zanchet, Y.Shao-Horn, P. S. Fernández. ACS Applied Energy Materials 2023 6 (13), 7025-7051
[2] D. Chen, Z Xie, Y Tong, Y Huang. Energy Fuels 2022, 36, 17, 9932–9949.

Agradecimentos/Acknowledgments

The authors gratefully acknowledge support from CINE, FAPESP, Faepex-UNICAMP, CNPq and CAPES.

Área: ELE

Electroanalysis of glutathione and piceatannol on different electrode surfaces

André F. A, Xavier (PG),[1] Raul S. Pereira (IC),[1] Jadriane A. Xavier (PQ)[1*], Marília O. F. Goulart (PQ)[1*]

andre.xavier@iqb.ufal.br; mofg@qui.ufal.br

[1]*Instituto de Química e Biotecnologia, UFAL.*

Key words: Piceatannol. *Glutathione, Antioxidants.*

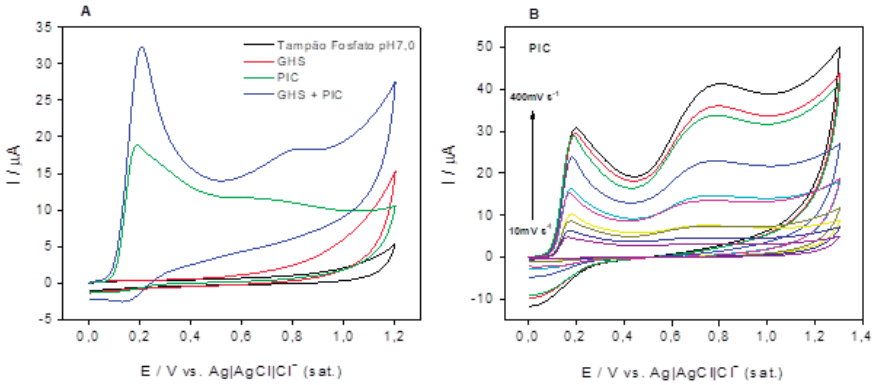
Highlights

GSH increases the functional capacity of other antioxidants. PIC has antioxidant and biological activities superior to those of resveratrol. The addition of GSH increases the PIC anodic current, a possible synergistic effect.

Abstract

Antioxidants play important roles against damage resulting from oxidative stress. The oxidizing processes resulting from oxidative stress result in damage to biomolecules, especially DNA. Piceatannol (PIC) is a structural analogue of resveratrol, belonging to the stilbenes group. It is found in natural sources and mainly in grapes and passion fruit. Studies show that piceatannol has antioxidant activity and other biological activities superior to those of resveratrol. Glutathione (GSH), is a tripeptide that is present in different tissues, it is a very important physiological antioxidant, which acts both in combating reactive species and also increases the functional capacity of other crucial antioxidants, such as vitamins E and C. Among the various analytical methods existing in the study of bioactive compounds, electrochemical methods stand out with applications in different areas, through the use of a wide variety of techniques, as they have the following important characteristics: rapid detection, high sensitivity, low cost and selectivity. Thus, the objective of the present work is to develop electroanalytical methodologies with high sensitivity, selectivity and stability for determining biologically active phenolic and thiolated derivatives using different electrolytic surfaces. The electrochemical studies were carried out in protic medium (0.1M phosphate buffer pH7.0), on a Glassy Carbon (GC) and Boron-Doped Diamond (BDD) electrode by cyclic voltammetry. PIC has a peak oxidation potential of around 0.18V, which corroborates its high antioxidant potential. It was observed that after the addition of GSH it causes an increase in the anodic PIC current, showing a possible synergistic effect. Verifying the effect of scan speed on the PIC, scans were performed varying the speed in the range of 10 to 400 mV s^{-1}. It was observed that the oxidation peak current increased with increasing scanning speed, without shifting the peak potential. The results indicate that there is a linear relationship between the anodic peak current of the PIC and the square root of the scan rates, while increasing the sweep rates of the peak currents resulted in a deviation from linearity. Therefore, the process was diffusion controlled.

Figure 1. The cyclic voltammograms recorded at the GV electrode, in Phosphate buffer 0.1 mol L-1, pH 7 (A) blank, GSH, PIC, GSH+PIC; (B) PIC at different sweep speeds 10 to 400mV.



[1]MORDECAI et al. **International Journal of Molecular Sciences**, p. 6979, 2023.

[2]ZOMER, A. P. L.; RODRIGUES, C. A.; MALDANER, L. **Society and Development**, v. 11, n. 9, e49211932221, 2022.

[3]DRÖGE, W. et al. **Immunobiology**, v. 172, p. 151–156, 1986.

Acknowledgments

CAPES, CNPq, FAPEAL and LEEO.

Área: ELE

ELECTROCHEMICAL AU ELECTRODES NANOSTRUCTURING FOR PLASMONIC ENHANCED ELECTROCHEMISTRY

***Gustavo F. Oliveira (IC) André H. B. Dourado (PQ)**

gustavo.favero@unesp.br.

[*] *Instituto de Química de Araraquara da Universidade Estadual Paulista "Júlio de Mesquita Filho"*

Palavras-Chave: Eletrochemistry, Nanostructuring, Plasmonic.

Highlights

Electrochemical Au Electrodes Nanostructuring for Plasmonic Enhanced Electrochemistry. Plasmonic is the study of the interaction of light and electrons in some metal nanostructures. Plasmonic can be used to improve the performance of electrocatalytic systems by the combination of localized surface plasmon resonance (LSPR) excitation, which can improve systems like Plasmonic Enhanced Water Splitting. In this process, it is possible to have plasmonic enhanced hydrogen and/or oxygen evolution reactions.

Resumo/Abstract

In search of new energy technologies, explore redox reactions to convert earth-abundant renewable feedstocks into value-added fuels, became an important study. This is because renewable energy sources are dependent on weather conditions, such as PV and wind energy. Because of this, energy storage is essential to generate. In this sense, the use of plasmonic assisted water electrolysis, using nanostructured Au electrodes, can be used to produce hydrogen as a solar fuel, a way to chemically store renewable energy. Plasmons are the result of the interaction of some metal nanostructures with electromagnetic waves at resonant frequency. This resonance creates oscillating localized electrons (plasmons – localized surface plasmon resonance – LSPR) and by such movements, these electrons are excited and generate the so-called hot charge carriers. In the present work, we propose the use of electrochemical processes, that allows high level of control by the electric variables, such as current and potential, and it is a low-cost process. We investigated the nanostructuration of Au bulk electrodes, using a standard three-electrode electrochemical cell, a platinized titanium net as the counter electrode and a encapsulated H_2 bubble as the reference. The electrolyte was sulfuric acid, 0.5 mol L^{-1}.

The experiments were planned through factorial planning, considering the potential window, scan rate and number of voltametric cycles. The literature shows that for the sulfate adsorption region there is an area increment, due to a surface nanostructuration. Using the factorial plan, it is possible to relate multiple variables at the same time and to obtain a mathematical model that could relate these input variables to the output, the plasmonic response checked by *in situ* spectroelectrochemistry in the UV-vis region. The obtained the results, we were able to observe an increase in the electrode surface area, as expected. This area increment is a result of the corrosion-redeposition cycles observed in this potential window, and extimulated by the adsorption-desorption of the anion. As a consequence, the electrode has become nanstructurated, and by so, plasmonic active, as observed by *in situ* spectroelectrochemical measurements in the UV-Vis region.

Agradecimentos/Acknowledgments

FAPESP

2022/06405-1

ELE

Electrochemical behavior of the bioactive and interaction with β-CD of the EHMM of the mangaba fruit (Hancornia speciosa gomes)

Luciene Conceição Esteves Souza (PG),[1]* Taislane Santos de Oliveira (IC),[1] Acácia Maria dos Santos Melo (PQ),[1]

taislanesanoliveira@gmail.com; luciene13cl@gmail.com; acacia@academico.ufs.br;

[1]*Departamento de Química, Universidade Federal de Sergipe (UFS)*

Palavras Chave:*Mangaba, betacyclodextrin, Electrochemistry*

Highlights

Bioactivity and interaction with the β-CD of EHMM of mangaba's fruit. Identification of bioactivity by VC. Production of β-CD complex with EHMM and characterizations by VC, FTIR and MEV, respectively.

Resumo/Abstract

Plants are a source of bioactives used as remedies, as mangaba (Hancornia speciosa) has antifungal, healing and even anticarcinogenic properties (OLIVEIRA et al., 2020). In view of this, the aim of the work is to determine the bioactives present in the EHMM (hydromethanolic extract of mangaba), by cyclic voltammetry (CV), observing the electrochemical behavior of the species present in the EHMM and verifying their interaction with beta-cyclodextrin (β-CD), a molecule that plays an important role in nanotechnology, and complexing by coprecipitation. A 10 mL electrochemical cell was used, containing Britton-Robinson electrochemical solution with ph 3, glassy carbon electrodes (working), hydrogen electrode (reference) and a platinum wire (counter electrode). FTIR was used to characterize the complex, in the 4000 to 400 cm-1 region, using an IR source with a KBr beam splitter, and 100-, 500- and 1000-fold magnification lenses were used for SEM.

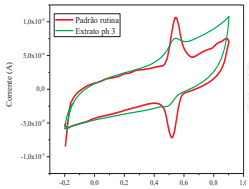


Figura 1

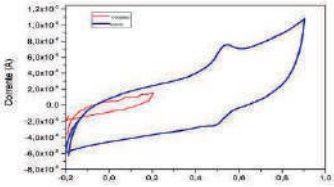


Figura 2

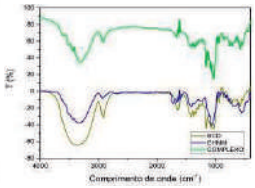


Figura 3

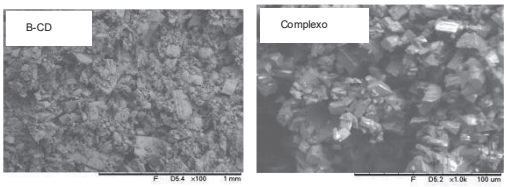


Figura 4

The voltammetric profile of the extract and pure rutin, when compared, figure 1, showed two peaks, +0.543 V and +0.493 V, due to the existence of a reversible redox process, the extract showed a lower current intensity, justified by the presence of other antioxidant compounds. The VC of the complex, figure 2, showed low current intensity and a shift in the oxidation peaks to more negative potentials, 0.0078V, 0.078V and 0.15V and 0.18V and 0.075V, which are irreversible in nature. Comparing the FTIR absorption spectra of the complex with the extract and pure β-CD, figure 3, shows an increase, decrease or appearance of bands, associated with changes in the energy of the vibrational modes, disturbances in the dipole moments of the chemical bonds of the functional groups involved in the interactions between the molecules. The photomicrographs of β-CD, figure 4, showed particles with a porous appearance of varying sizes and disorganized on the surface, while in the complex, the particles have defined crystalline forms, with aggregates of different sizes and shapes. The analysis confirms the presence of rutin in the EHMM, as well as indicating the insertion of the active molecule of the EHMM into the interior cavity of the β-CD, indicating intense interaction between the molecules.

Agradecimentos/Acknowledgments

PROBIO Universidade Federal de Sergipe

CNPq

Área: ELE

Electrochemical detection of the explosive 2,4,6-trinitrotoluene using a 3D-manufactured sensor based on graphite-aluminum oxide incorporated into a polylactic acid matrix

Raíssa R. D. Brum (PG)*[1], Lucas V. de Faria (PQ)[1], Natalia M. Caldas (IC)[1], Robson P. Pereira (PQ),[2] Felipe S. Semaan (PQ)[1], Wagner F. Pacheco (PQ)[1], Rafael M. Dornellas (PQ)[1].**

***raribeiro@id.uff.br and **rafaeldornellas@id.uff.br**

[1]*Departamento de Química Analítica, Instituto de Química, Universidade Federal Fluminense, 24020-141, Niterói-RJ, Brazil.*
[2]*Instituto Militar de Engenharia, 22290-270, Urca-RJ, Brazil.*

Keywords: *composite electrodes; forensic analysis; electroanalysis; explosives.*

Highlights

- A new 3D-printed electrochemical platform is proposed to detect the explosive trinitrotoluene (TNT);
- The synergistic properties between graphite and alumina allowed the detection of TNT residues;
- Promising tool for forensic police intelligence.

Resumo/Abstract

The detection of explosives is of great importance in the forensic scenario, since they are widely used in terrorist attacks. Many of these explosives are composed of nitroaromatic compounds, where 2,4,6-trinitrotoluene (TNT) can be highlighted. Therefore, developing of cheap, simple, sensitive, and portable analytical devices is very relevant for forensic applications. With this in mind, we propose a 3D-printed electrochemical sensor using a composite material composed of graphite (G), alumina oxide (Al_2O_3), and polylactic acid (PLA) for TNT electrochemical sensing. Various combinations between the materials were carefully examined in terms of mechanical stability, printability, and electrochemical response. Spectroscopic and morphological analyses confirmed the presence of G and Al_2O_3 in the thermoplastic matrix (PLA). Interestingly, when the G/Al_2O_3/PLA electrode (30:10:60 % w/w) was used, a well-defined electrochemical profile with a higher peak current was achieved for TNT (Figure 1, black line) compared to the free-Al_2O_3 electrode (Gpt/PLA) (Figure 1, red line). Electrochemical impedance spectroscopy also revealed the faster electron transfer for the ferri-ferro redox probe on the 3D-printed G/Al_2O_3/PLA. The square wave voltammetry (SWV) technique was selected to develop a fast and sensitive method for TNT determination. The analysis conditions were checked in detail. Better peak resolution, peak current, and precision were achieved using 60 mV amplitude, 20 Hz frequency, 10 mV step potential, and Britton-Robinson buffer pH 2.0 (background electrolyte). The synergistic properties between G and Al_2O_3 resulted in a detection limit of 0.16 µmol L^{-1} with a linear range of 0.5-10.0 µmol L^{-1}, with analytical performance comparable to expensive and sophisticated electrodes. This new sensor is simple, affordable, and robust, and could be a useful tool for detecting TNT residues in forensic analysis.

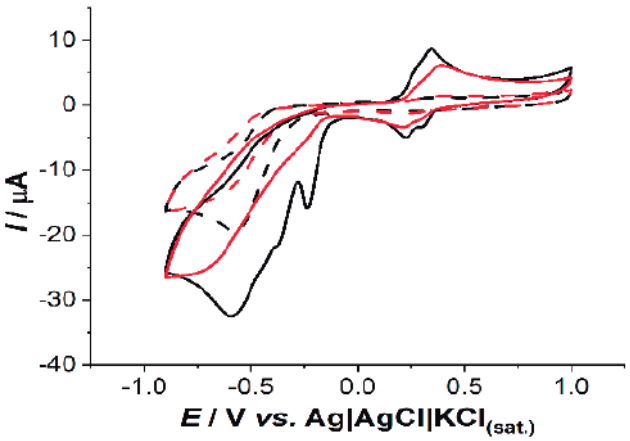


Figure 1. Electrochemical responses recorded using 0.4 mmol L^{-1} TNT in 0.12 mol L^{-1} BR buffer (pH 2.0) solution on the G/PLA (red line) and G/Al_2O_3/PLA (30:10:60, black line). The dashed lines indicate the respective blanks.

Agradecimentos/Acknowledgments

The authors would like to thank the support from CNPq, CAPES, FAPERJ, and PPGQ-UFF.

Área: ELE

ELECTRO-OXIDATION OF LIGNIN MODEL MOLECULES ON Ni ELECTRODES

***Fabio A. Diniz (IC)[1], Antonio A. S. Curvelo(PQ)[2], Hamilton Varela(PQ)[2], André H. B. Dourado(PQ)[1].**

fabio.a.diniz@unesp.br.

[1]*Instituto de Química de Araraquara da Universidade Estadual Paulista "Júlio de Mesquita Filho".*
[2]*Instituto de Química de São Carlos da Universidade de São Paulo.*

Keywords: *Biorefinary, Assisted water electrolysis, Model molecules.*

Highlights

Lignin Model Molecules Oxidation on Ni Electrodes. Lignin is a vast source of phenolic compounds. Electrochemical oxidation has been explored for the degradation of lignin. Lignin model molecules in alkaline medium using Nickel electro-catalyst for oxidation.

Resumo/Abstract

In a context of climate crisis, sustainable development and the environment have been frequently discussed nowadays, especially regarding fossil fuels applications. In this sense, biofuels are a promising alternative, however, the application of biomass residues from that fuels' generation has still room for improvement since their main use is still the burning for thermoeletricity. Lignin is the main source of aromatic carbons in biomass, following cellulose and hemicellulose. This macromolecule has, as monomers, phenolic structures and is an interesting renewable aromatic chemicals source. However, due to the complexity of the monomer connections, the depolymerization of lignins is still not optimized and this reaction mechanism is still under debate. Electrocatalysis was selected as the main tool for this work because it is an easy to control approach that can be applied for the lignin depolymerization by oxidation under ambient conditions, or close to them, and can easily provide kinetic and mechanistic information. For substrate simplification, in this work we proposed to use of model molecules based on the phenolic monomers structure containing a carbonic chain in the *para* position with sizes between one and three carbons, and equivalents containing a metoxyl group in *meta* position were selected as model molecules to comprehend the electrochemical behavior of lignins during oxidation processes. As electrocatalyst, Ni plate electrodes were selected due to the low cost and stability in alkaline conditions.

The experimental procedure was carried out using a standard three-electrode electrochemical cell. For the proposal of an experimental model, the experiments were initially proposed based on a factorial design. The planning relates NaOH concentrations, cyclic voltametric potential, sweep rates and window. The plan also considered the carbonic chain size in para and the presence or absence of the metoxyl group in *meta*. For example, peak currents are expected to be highest at sweep rates of 100 mV/s. We could see that the currents increased or decresead based on the conformation of the carbon chain, increasing when in *para* conformation and decreasing in other conformation. Furthermore, changing the methoxy of the carbon chain causes oxidation in the negative direction.

Agradecimentos/Acknowledgments

The authors thank FAPESP (#2019/22183-6, #2020/15230-5 e #2022/06405-1), USP, RCGI/USP & Shell Brasil, and ANP (Agência Nacional de Petróleo, Gás Natural e Biocombustíveis) for regulating the R&D fee.

Área: ELE

Electroreduction of nitrite mediated by Co_3O_4 and $NiCo_2O_4$ nanoplates – a comparative study.

Matheus P. Sales (PG),[1] Manuel E. G. Winkler (PQ),[1] Thiago M. Mariano (PQ),[2] Ítalo O. Mazali (PQ),[1] Raphael Nagao de Sousa (PQ).[1*]

nagao@unicamp.br

[1]Institute of Chemistry, UNICAMP ,[2]Center for Innovation on New Energies, CINE.

Keywords: ammonia, energy conversion, electrocatalysis, cobalt, nickel, electrochemistry.

Highlights

- Methodology for synthesizing Co_3O_4 and $NiCo_2O_4$ nanoplates.
- 91.5% NH_3 faradaic efficiency achieved for Co_3O_4 at -0.2 V vs RHE.
- 45 μmol h^{-1} cm^{-2} NH_3 yield rate for Co_3O_4 at -0.5 V vs RHE.

Resumo/Abstract

The search for renewable and clean energy has been a goal key in recent decades. Within this scenario, ammonia electrosynthesis emerges as an attractive alternative as it is a dense source of carbon-free energy, with the possibility of being produced from renewable electricity[1]. Both Co_3O_4 and $NiCo_2O_4$ nanoparticles were synthesized by hydrothermal treatment followed by a calcination step[2]. HRTEM and SEM illustrates a hexagonal morphology with sizes of 213 ± 45 nm and 68 ± 19 nm for Co_3O_4 and $NiCo_2O_4$, respectively. Both electrocatalysts performances for NO_2RR were evaluated in a H-type electrochemical cell in 15 mmol L^{-1} $NaNO_2$ and 1 mol L^{-1} NaOH in Ar flow. Figure 1a displays the cyclic voltammograms of both catalysts for nitrite activity *vs* blank from 0.1 V to - 0.6 V vs RHE, underlining better activity for Co_3O_4. Both figures 1b and 1c shows that NH_3 is produced in each potential evaluated, where its faradaic efficiency for NH_3 peaks at - 0.2 V (91.5 ± 8.5%) and -0.4 V (38.9 ± 3.6%) vs RHE for Co_3O_4 and $NiCo_2O_4$, respectively. Co_3O_4 nanoplate electrocatalysts are thus seen as a promising solution to reduce energy costs in ammonia production, due to their structure that allows higher conductivity and surface area, as well as the synergy between Co^{2+} and Co^{3+} in nitrite reduction.

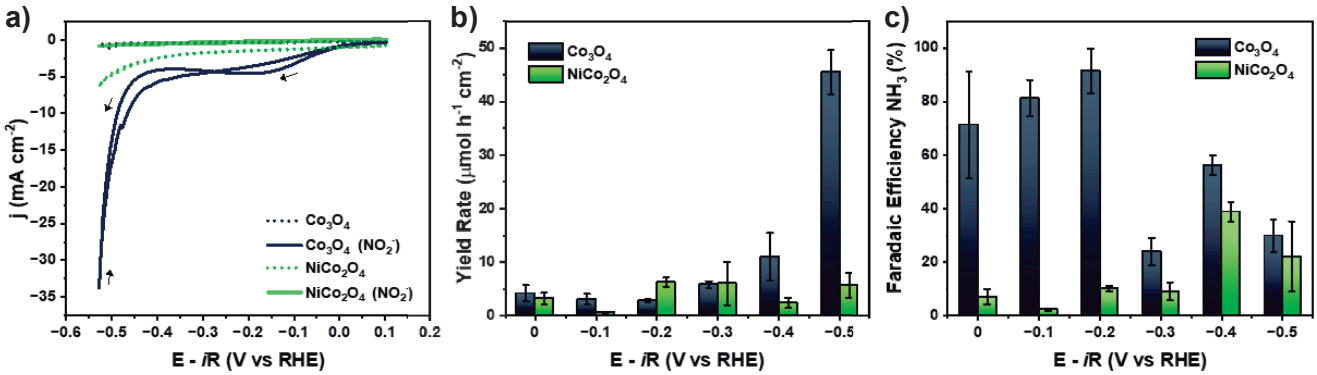


Figure 1. a) Cyclic voltammogram with and without $NaNO_2$, b) and c) yield rate and faradaic efficiency for NH_3 production from 0 to - 0.5 V vs RHE (*i*R compensated 85%).

(1) Claxton, L. D. Reviews in Mutation Research 2014, 762, 76–107.

(2) Carneiro, N. M.; Mazali, I. O. Unicamp, Campinas, SP, 2012.

Agradecimentos/Acknowledgments

This work was supported by Shell, FAPESP, CNPq and CAPES.

Área: ELE

Electro-refinery technology with effluents of biomass processing

[1] Herbet L. Oliveira (PG)*,[1] Karen G. D. Magalhães (PG),[1] Amanda D. Gondim (PQ),[1] Carlos A. Martínez-Huitle (PQ),[2] Suely S. L. Castro (PQ),[1] Elisama V. Santos (PQ)

herbet.lima.097@gmail.com, elisama.vieira@ufrn.br

[1]Grupo de Pesquisa em Energias Renováveis e Sustentabilidade Ambiental, Instituto de Química, Universidade Federal do Rio Grande do Norte, Campus Universitário, Av. Salgado Filho 3000, Lagoa Nova, CEP 59078-970, Natal, Rio Grande do Norte, Brasil

Palavras Chave: *Cashew-nut shell liquid, Electrochemical oxidation, Value-added chemicals, Green hydrogen, Free-carbon.*

Highlights

Proof of concept of an electro-refinery process with a real waste. Creating a solution containing carboxylic acids by the breakdown of waste materials. The electrochemical conversion of biomass effluent into high-value-added products and energy vector was sustainably accomplished

Resumo/Abstract

In alignment with global sustainability initiatives such as the United Nations Agenda 2030, Circular Economy, and Nexus (Water-Food-Energy), the concept of electrorefinery emerges as a promising solution for producing clean energy and valuable chemicals. This study focuses on utilizing cashew nut shell liquid (CNSL), typically considered industrial waste, as a prototype for electrorefinery, aiming to produce green hydrogen and carboxylic acids. In this study, an anion exchange membrane (AEM) electrolyzer with boron doped diamond (BDD) anode and Fe-Ni stainless steel mesh cathode was employed. The effects of current density, *j* (40, 70, and 100 mA cm^{-2}), and CNSL concentration (0.01, 0.05, and 0.10%) were investigated. Life-cycle assessment (LCA) software assessed global warming potentials (GWP) over a 100-year period, focusing on CO_2 emissions. During a 240-minute process, with 40 mA cm^{-2} current density and 1 mol L^{-1} NaOH electrolyte, increasing CNSL concentration to 0.05% and 0.10% enhanced carboxylic acid production due to increased substrate availability. Particularly, acetic acid exhibited high selectivity (557.74 mg L^{-1}), while other acids like formic and tartaric were detected in lower concentrations (57.97 and 50.37 mg L^{-1}, respectively). Higher *j* (100 mA cm^{-2}) with steady CNSL concentration (0.01%) favored tartaric acid production, increasing from 20.00 to 81.24 mg L^{-1}, while acetic acid concentration remained stable around 40.00 mg L^{-1}. A coupled electrochemical process with an electrodialysis system promotes the separation of the acids generated, concentrating them in electrodialysis and excluding them from oxidation, improving reactor efficiencies, and increasing acid production. This generates an environmentally sustainable integration that represents an emerging concept for the production and recovery of value-added products and for the recovery of waste. On the other hand, LCA demonstrate that the technique effectively decreases CO_2 emissions in terms of their GWP100. This reduction is achieved by increasing the concentration of CNSL, resulting in a decrease in CO_2 emissions from -0.037 to -0.37 kg CO_2, corresponding to 0.01% and 0.10% of CNSL, respectively. Regarding the variable *j*, there was a noticeable effect on the production of green H_2. As *j* increased, the emission of CO_2 also increased, reaching a value of $5.6x10^{-5}$ for a current density of 40 mA cm^{-2} and $1.4x10^{-4}$ for 100 mA cm^{-2}. However, the production of H_2 increased as well, with the amount of H_2 generated rising from 0.7 to 1.8 L, respectively.

Agradecimentos/Acknowledgments

Financial supports from Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq, Brazil) (306323/2018-4, 312595/2019-0, 439344/2018-2, 315879/2021-1, 409196/2022-3, 408110/2022-8),

Área: ELE

Enhancing the performance of a glycerol-fed microbial fuel cell through pyocyanin addition using *Clostridium pasteurianum* as a biocatalyst.

Ana Clara Bonizol Zani (PG),[1*] João Carlos de Souza (PQ),[1,2] Adalgisa Rodrigues de Andrade (PQ),[1,2] Valeria Reginatto (PQ).[1]

anabonizolzani@usp.br; anabonizolzani@usp.br

[1]Department of Chemistry, Faculty of Philosophy, Science and Letters at Ribeirão Preto, University of São Paulo (USP); [2]National Institute of Alternative Technologies for Detection,Toxicological Evaluation and Removal of Micropollutants and Radioactive Substances (INCT-DATREM)-UNESP.

Keywords:*(mediators, bioenergy, improved performance, extracellular electron transfer).*

Highlights

- Pyocyanin has proven to be a promising electron mediator to assist and enhance energy generation;
- *Clostridium pasteurianum* exhibited low extracellular electron transfer, necessitating the use of mediators;
- The presence of glycerol influences the electron transfer of pyocyanin and *Clostridium pasteurianum*.

Abstract

The effective interaction between microorganisms and electrode surfaces, through extracellular electron transfer (EET), plays a crucial role in advancing the application of mediator-based microbial fuel cells (MFCs). The genus *Clostridium* sp. is commonly found in MFC bioanodes and has been reported to be capable of electron uptake, significantly inducing NADH consumption pathways and altering product profiles [1]. Phenazines are nitrogen-containing heterocyclic compounds produced by some bacteria and are described to facilitate EET [2]. In this study, we separately investigated the electroactive activity of *Clostridium pasteurianum* and pyocyanin, a phenazine-type molecule extracted from a strain of *Pseudomonas aeruginosa*, with the purpose of subsequently combining them to enhance the catalytic performance of the system. The MFC comprises an anodic compartment (36 mL), with a carbon cloth (3x3 cm) utilized as the anode. The air-cathode, in turn, consists of a platinum-impregnated carbon cloth pressed with a Nafion® 117 membrane, and the medium as described by Lovley and Phillips (pH = 7) served as the supporting electrolyte. Moreover, pyocyanin was used at a concentration of 10 µmol for the experiments. Electrochemical tests were conducted in the MFC itself using an AUTOLAB PGSTAT 30 potentiostat/galvanostat (NOVA 2.1 software) and an $Ag/AgCl_{(sat)}$ reference electrode. Pyocyanin extraction followed the method outlined by Feghali and Nawas (2018), with characterization performed through infrared (IR) and UV-Vis spectroscopy. The IR spectra obtained for pyocyanin showed bands at 1612 and 1712 cm^{-1}, characteristic of the stretching of the C=C bonds in the aromatic ring. UV-Vis spectra at pH values of 2 and 7 demonstrated different peaks, at 205, 242, 280, 385, and 520 nm (pH = 2) and 234, 309, 379, and 695 nm (pH = 7), indicating the reduced and oxidized forms, respectively. Furthermore, cyclic voltammetry (CV) performed at different scan rates suggest that the electrochemical process of this molecule is reversible and diffusion-controlled. The power curve obtained for 10 µmol of pyocyanin, both in the presence and absence of glycerol, was 9.6 and 10.7 mW m^{-2}, respectively. On the other hand, for *C. pasteurianum*, the power curve was 2.2 mW m^{-2} in the presence of glycerol and 0.3 mW m^{-2} in its absence. Therefore, it is observed that the presence of glycerol resulted in a slight decrease in the electronic transfer of pyocyanin, while it enhanced the performance in the presence of *C. pasteurianum*. This suggests that the combination of these components could lead to a more efficient system, as *C. pasteurianum* would be capable of consuming glycerol, degrading it, while pyocyanin carries out the electronic transfer to the electrode. Additionally, the results of chronoamperometry in the presence of glycerol for pyocyanin and *C. pasteurianum* revealed an increase of 36.2 and 22.0 times compared to the control (Lovley and Phillips), resulting in a charge of 181 mC and 110 mC, respectively. Our results indicate low EET performed by *C. pasteurianum*. Thus, the introduction of pyocyanin is not only an effective strategy but also promising for establishing efficient electronic mediation in bioelectrochemical systems and enhancing the overall performance of the MFC related to current generation and energy production.

Acknowledgments

São Paulo Research Foundation (FAPESP – process number 2022/04024-0, 2021/12866-9) and National Institute of Alternative Technologies for Detection, Toxicological Evaluation and Removal of Micropollutants and Radioactive Agents (INCT-DATREM - FAPESP process number 2014/50945-4, CNPq process number 465571/2014-0).

[1] Choi, O. *et al. Sci Rep*. v. 4, 2014, 6961.
[2] Simoska, O. *et al. ACS Sustainable Chem. Eng*. v. 11 (32), p. 11855–11866, 2023.
[3] El Feghali, P. A. R.; Nawas, T. *MOJ Toxicol*. v. 4 (6), p. 417–422, 2018.

Área: ELE

Estudo da Eletro-oxidação de Etanol Comercial sobre Eletrodos de Platina

Caio A.C. Bertolini (IC),[1] Murilo G. de Oliveira (PG),[1] André H.B. Dourado (PQ),[2] Hamilton Varela (PQ).[1*]

caio.augusto28@usp.br; hamiltonvarela@usp.br

[1]Instituto de Química de São Carlos, Universidade de São Paulo; [2]Instituto de Química de Araraquara, Universidade Estadual Paulista Júlio de Mesquita Filho

Palavras Chave: *Oxidação eletroquímica de etanol, Instabilidades cinéticas, Oscilações de regeneração, Eletrodos de platina.*

Highlights

A Study of Commercial Ethanol Oxidation on Platinum Electrode

Regeneration oscillations occur at low currents, are influenced by the chemical composition of commercial ethanol, and allow the sample to oscillate for a longer period during tests.

Resumo/Abstract

Motivado pela possibilidade de empregar etanol como fonte de energia em células a combustível e/ou sua reforma eletrocatalítica para produção de H_2 verde, propõe-se a utilização de etanol combustível comercial, disponível em postos de combustíveis na cidade de São Carlos - SP, para verificar a influência de aditivos e contaminantes no comportamento eletroquímico do etanol. Para tal, o presente estudo analisa quatro diferentes amostras de etanol: o álcool etílico para análise (PA), com título de 96,5% (m/m); e três amostras comerciais (1, 2 e 3) provenientes de diferentes postos de combustíveis. O estudo ocorreu em uma célula eletroquímica convencional de três eletrodos, sendo o de trabalho e o auxiliar uma esfera e uma rede de platina, respectivamente; e o referência uma bolha encapsulada de H_2. O eletrólito suporte foi H_2SO_4 0,1 mol L^{-1}. Para cada amostra, testes como varreduras galvanodinâmicas foram realizados em concentrações de 0,05; 0,50; 1,00 e 2,00 mol L^{-1} de etanol comercial. Em condições de maiores concentrações de etanol comercial, correntes muito baixas (ordem de 1E-5 A) e concentração de cloreto relativamente alta, as amostras 1 e 3 apresentam oscilações de regeneração ou regenerativas (Figura 1), fenômeno em que o sistema oscila até cerca de 1.1 V, depois tem uma queda brusca de potencial e então volta a oscilar ao invés de tender a maiores potenciais sem que novas oscilações aconteçam.

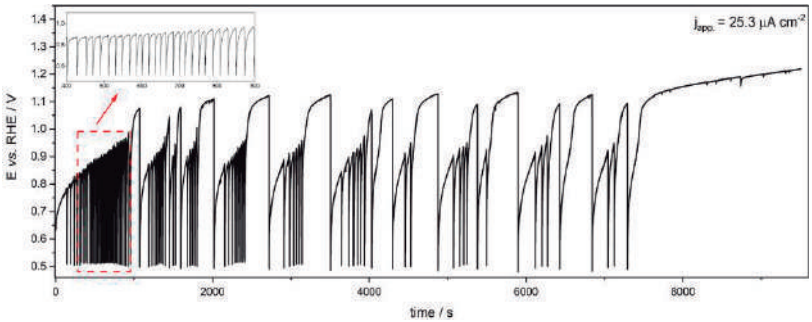


Figura 1. Oscilações de regeneração para amostra 3 (2 mol L^{-1}).

Testando as quatro amostras, o estudo indica que, quanto maior a concentração do etanol comercial, é cada vez menor a densidade energética deste em comparação com a do etanol PA em mesma concentração. Além disso, os resultados obtidos para as amostras 1 e 3 são semelhantes entre si, mas diferentes da amostra 2, cujos resultados assemelham-se mais ao etanol PA. É plausível que as propriedades das amostras de etanol sejam influenciadas pelos aditivos presentes nesses. No momento, análises de cromatografia gasosa estão sendo realizadas para identificar e quantificar essas substâncias.

Agradecimentos/Acknowledgments

Os autores agradecem à FAPESP (#2019/22183-6, #2020/15230-5 e #2022/06405-1), USP, RCGI/USP & Shell Brasil, e ANP (Agência Nacional de Petróleo, Gás Natural e Biocombustíveis) por meio da regulamentação da taxa de P&D.

Área: ELE

Estudo da Influência Heterojunção Metal-Suporte na Eletroquímica Intensificada por Plasmônica

Victor G. Pereira (IC)[1], Paulo F. M. Oliveira (PQ)[2], André H. B. Dourado (PQ).

victor.g.pereira@unesp.br

[1]Instituto de Química de Araraquara da Universidade Estadual Paulista "Júlio de Mesquita Filho". [2]Instituto de Química da Universidade de São Paulo.

Palavras-Chave: *Produção de gás hidrogênio, Electrocatálise, Plasmônica, Heterojunção, Mecanoquímica.*

Highlights

Study of the Influence of Metal-Support Heterojunction on Electrochemistry Enhanced by Plasmonics. Plasmonic-assisted water electrolysis for enhanced green hydrogen production. Increase in "hot" carriers' half-life time due to defects created in the semiconductor-catalyst interface. Use of mechanochemistry, a sustainable means of syntheses without the use of solvents.

Resumo/Abstract

A sociedade moderna enfrenta diversas dificuldades devido ao uso abusivo de combustíveis fósseis na produção de energia. Por isso, problemas como o esgotamento desses e a degradação ambiental gerada pelo seu uso, que agrava situações climáticas extremas vistas nos últimos anos. Com isso, vê-se a necessidade de conseguir novas fontes de energia duradoura e limpa, como a solar e a eólica. Essas fontes possibilitam uma produção de energia maior que o uso imediato, porém, devido a sua sazonalidade também necessitam de estratégias de armazenamento. Uma estratégia para isso é a geração de gás hidrogênio, um combustível de combustão livre de compostos carbonados e de alto poder energético. Esse gás pode ser obtido pela eletrólise da água, onde no ânodo há a formação de O_2 e no cátodo, H_2. O processo anódico possui uma forte limitação cinética e uma estratégia para diminuir essa limitação é a eletroquímica intensificada por plasmônica. Nesse processo, os elétrons presentes em nanopartículas metálicas (Au, Ag ou Cu) de tamanho coerente com a luz incidente entram em ressonância com o campo magnético (plásmons), excitando os elétrons energeticamente, gerando os portadores de cargas "quentes". Nesse processo, os elétrons vão para níveis de energia mais altos e, consequentemente, também há a geração de buracos de baixa energia. Esses portadores de carga "quentes", por serem mais energéticos, auxiliam na catálise redox, aumentando a atividade eletroquímica e/ou diminuindo a sobretensão. No geral, esses portadores podem se recombinar e gerar um efeito fototérmico convertendo a energia luminosa em calor e impedindo seu uso em catálise. Para otimizar a aplicação desses portadores em catálise, é proposto o uso de suporte em materiais semi-condutores, o que gera uma barreira Schotkky na região interface metal-suporte. Essa heterojunção normalmente é composta de defeitos estruturais, como vacâncias de oxigênio, e aumentam o tempo de meia-vida dos portadores "quentes", intensificando sua aplicação na eletrocatálise. Por isso, este trabalho propõe-se a analisar a influências dos defeitos de heterojunção na interface metal-suporte Au/óxidos de tungstênio. O material foi obtido a partir do processo mecanoquímico, controlando o aumento da população desses defeitos, em fase sólida, descartando o uso de solventes e outros compostos que pudessem bloquear algum sítio ativo dos materiais. Na análise, a eletrólise da água foi considerada como um todo, os processos de redução e oxidação, no qual foi avaliada a importância dessa população de defeitos antes e depois dos processos no claro e no escuro.

Agradecimentos/Acknowledgments

Os autores agradecem à FAPESP (#2022/06405-1, 2020/14955-6) pelo auxílio financeiro

Área: ELE

Estudo eletroquímico da formação do complexo picloram-Ferro (III)

Nataly I. C. Rodrigues IC)[1], Lucia Codognoto (PQ)[1], Eliana Valle (PQ)[1]*.

lucia.codognoto@unifesp.br; *emavalle@unifesp.br

[1]*Departamento de Química Unifesp – Campus Diadema*

Palavras Chave: *Picloram, Complexo de ferro, Voltametria de onda quadrada, Voltametria cíclica.*

Highlights

- Electrochemical study of the formation of the picloram-Iron (III) complex
- Formation of pesticide complexes with metal ions in the environment
- Voltammetric study of the interaction of metal ions with pesticides

Resumo/Abstract

À medida que a sociedade cresceu e se desenvolveu, surgiu a necessidade de se fazer uso de substâncias, conhecidas por pesticidas, para aumentar a produtividade de alimentos, bem como garantir seu armazenamento. A prática de uso dessas substâncias, faz com que ocorra acúmulo dos mesmos no ambiente, causando consequências graves. Tais substâncias, ao entrar em contato com diferentes espécies no ambiente, podem interagir e alterar suas propriedades. Um pesticida comum e que é amplamente utilizado, é o picloram, um herbicida da família dos organoclorados que possui uma alta persistência no ambiente e, devido a sua estrutura química (Fig. 1), pode formar complexos com íons metálicos. Tendo em vista que o ferro é um dos elementos mais abundantes da crosta terrestre, neste trabalho utilizou-se as técnicas de voltametria cíclica e voltametria de onda quadrada para estudar a complexação do picloram com o íon metálico ferro em meio aquoso. Nas condições estudadas (medidas realizadas em KCl 0,1 mol L^{-1}, sobre o eletrodo de carbono vítreo) o Fe (III) apresentou características de um sistema irreversível e controlado por difusão das espécies. Foi possível constatar a formação de complexo entre o pesticida picloram e o íon metálico Fe (III) por meio das observações das alterações de suas respostas eletroquímicas. Nas análises por voltametria cíclica, foi possível observar uma diminuição na intensidade de pico do Fe (III) com a adição de picloram, e a partir da proporção de 1:1,5 (Fe-pic) foi observado deslocamentos dos potenciais de pico para potenciais mais negativos, que foram de 0,0 V para -0,02V e -0,04 V (Fig. 2). Constatou-se também que o complexo Fe (III) – picloram tem um processo controlado por difusão com contribuição adsortiva. Nos estudos por voltametria de onda quadrada, observou-se um aumento na intensidade de pico e deslocamento do pico de redução das correntes direta e resultante do Fe (III) com as adições de picloram. Na corrente reversa também se observou um aumento do potencial de pico, que suspostamente é devido ao excesso de Fe (III) e a presença de Fe (II). Por espectroscopia de UV-visível pode-se comprovar o que foi observado pelas medidas eletroquímicas, uma vez que o espectro do picloram apresentou um aumento de intensidade de absorção e um sutil deslocamento para comprimentos de onda maiores quando em presença do Fe (III), indicando a formação de um complexo.

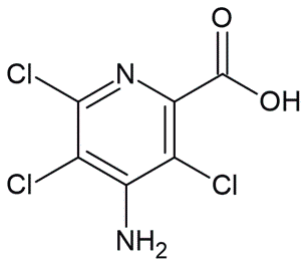


Fig.1. Estrutura do herbicida picloram

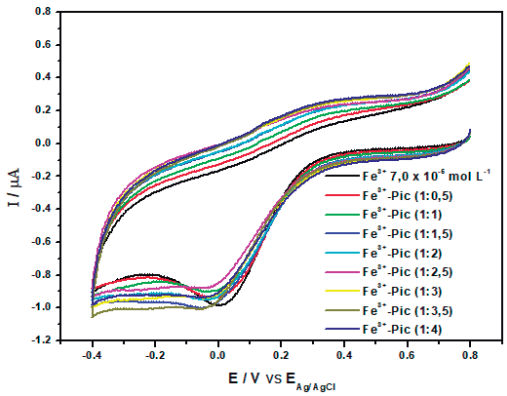


Fig.2: Voltamogramas cíclicos de Fe (III), concentração 7,0x10^{-5} mol L^{-1}, com alíquotas de picloram, em KCl 0,1 mol L^{-1}; v = 100 mV s^{-1}.

Agradecimentos/Acknowledgments

FAPESP, CNPq, CAPES.

Área: ELE

Estudo Nanogravimétrico da Influência da PANI nas Instabilidades Cinéticas de Moléculas Orgânicas Pequenas

Tifany L. R. Guercia (IC)[1], André H.B. Dourado (PQ)[2], Hamilton Varela (PQ)[1].

tifanylaila@usp.br; hamiltonvarela@usp.br

[1]Instituto de Química de São Carlos, USP - Av. Trabalhador São Carlense, 400- São Carlos, SP, 13566-590; [2]Instituto de Química, UNESP - Av. Prof. Francisco Degni, 55, Jardim Quitandinha, Araraquara - SP, 14800-900

Palavras Chave: *Nanogravimetria, oscilações*

Highlights

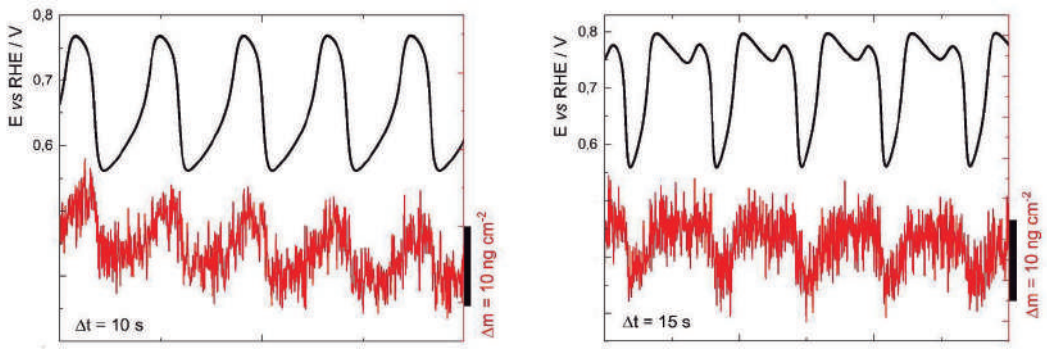
Nanogravimetric Study of the Influence of PANI on the Kinetic Instabilities of Small Organic Molecules

The methanol oscillations on Pt shows profile change with time, and oscillatory period increase proportion current applied. The mass variations oscillate in phase with potential.

Resumo/Abstract

A polianilina (PANI) é um polímero condutor que pode ser utilizado como matriz de dispersão para catalisadores em células eletroquímicas, por sua alta estabilidade e seu perfil redox reversível entre 0,3 e 0,4 V, janela na qual está presente em seu estado de oxidação mais condutor e estável ,esmeraldina. Estudos apontam que a PANI possui a capacidade de diminuir a forte adsorção de CO em catalisadores de Pt. Essa característica é de grande interesse para aplicações em conversão de energia, como a oxidação de pequenas moléculas orgânicas, metanol, por exemplo. A eletro-oxidação de metanol sobre Pt é conhecida por apresentar instabilidades cinéticas, que podem ser exploradas durante os processos de conversão de energia, para aumentar a vida útil do catalisador. Essas instabilidades cinéticas também auxiliam na elucidação de mecanismos reacionais, por necessitarem de etapas específicas para ocorrerem. As instabilidades são amplamente reconhecidas por serem relacionadas à espécies adsorvidas. Portanto, a utilização de técnicas gravimétricas como a nanobalança eletroquímica de cristal de quartzo (EQCN, em inglês), pode auxiliar nesta investigação, e ainda relacionar o comportamento oscilatório com a existência dessas espécies, sendo assim, uma ferramenta capaz de relacionar a adsorção de CO com a resposta eletroquímica. Por esse motivo, foram estudadas as oscilações galvanostáticas de potencial , juntamente com perfil nanogravimétrico durante a oxidação de metanol sobre Pt e Pt modificada com PANI, para verificar a influência da PANI como suporte catalítico no processo de envenenamento do eletrodo. Foi observado que as oscilações no eletrodo de Pt apresentam mudanças no perfil com o tempo, indicando mudança no mecanismo de envenenamento do eletrodo, há também um aumento na duração do período oscilatório proporcional à corrente aplicada. Os perfis de variações de massa oscilam em fase com o potencial, tendo magnitude de 10 ng cm^{-2}.

Figura 1. Oscilações de potencial (em preto) e massa (em vermelho) para o sistema contendo 0,5 mol L^{-1} de H_2SO_4 e 0,5 mol L^{-1} de H_3COH. j = 1,08 mA cm^{-2}.



Agradecimentos/Acknowledgments

FAPESP (#2019/22183-6, #2020/15230-5 e #2022/06405-1), USP, RCGI/USP & Shell Brasil, e ANP (Agência Nacional de Petróleo, Gás Natural e Biocombustíveis) por meio da regulamentação da taxa de P&D.

Área: ___ELE_____

Evaluation of the Effect of Functionalized Graphene Oxide on Hydrogen Permeation During Acid Pickling of SAE 1020 Steel

Larissa T. Cardoso* **(IC),[1] Diego P. Sangi (PQ),[1] Elivelton A. Ferreira (PQ).[1]**

Larissa_cardoso@id.uff.br *

[1]*Universidade Federal Fluminense, Instituto de Ciências Exatas, Departamento de Química, Volta Redonda, RJ, Brasil.*

Keywords: *(Hydrogen permeation, Corrosion, Inhibitors, Functionalized graphene).*

Highlights

Permeation studies of hydrogen in carbon steel using the Devanathan-Satachurski (D-S) cell; Investigation of GO-functionalized inhibition of corrosion and hydrogen penetration in SAE 1020 steel.

Resumo/Abstract

In steel industries, specifically during the hot rolling stage, the steel surface comes into contact with humid air at high temperatures, forming an oxide layer known as “scale”. This scale layer must be removed by dissolution in an acid bath so that the steel can then be hot-dip galvanized [1]. However, in addition to the steel corrosion process during acid pickling, atomic hydrogen generated during the corrosion process can penetrate the steel and cause hydrogen embrittlement [2]. One way to minimize metal attack and acid consumption during pickling is by adding corrosion inhibitors to the solution. Recently, functionalized graphene oxides, also known as “organically modified nanomaterials,” have been used as effective corrosion inhibitors due to the presence of hydroxyl, carboxyl, epoxide and carbonyl groups on their surfaces, making them soluble in aqueous media [3]. In this study, the inhibitory effect on corrosion and hydrogen permeation using 49.8 mg of functionalized graphene oxide (Fig. 1.a) with *p*-phenylenediamine (Fig 1.b) on SAE 1020 steel during pickling in 5.4 mol L^{-1} HCl was proposed. Mass loss and atomic hydrogen permeation tests were conducted using the D-S cell. In this cell, atomic hydrogen is generated during steel pickling in one cell compartment. This atomic hydrogen passes through the steel plate and is then electrochemically detected in the other compartment of the cell. The procedures for these measurements were based on the work of Silva *et al.* [2]. It can be observed in Figure 1.c that up to 15 min of steel immersion in solutions with or without the presence of functionalized graphene oxide (GO-func.), the hydrogen permeation transients through the 2.0 mm steel plate were equal, however, from approximately 15 min onward, the steel immersed in the solution with GO-func showed current densities higher than those of the steel immersed in the solution without GO-func., indicating that the modified nanomaterial increased the injection of atomic hydrogen into the steel plate. On the other hand the GO-func. inhibited the steel corrosion process (Fig. 1.d).

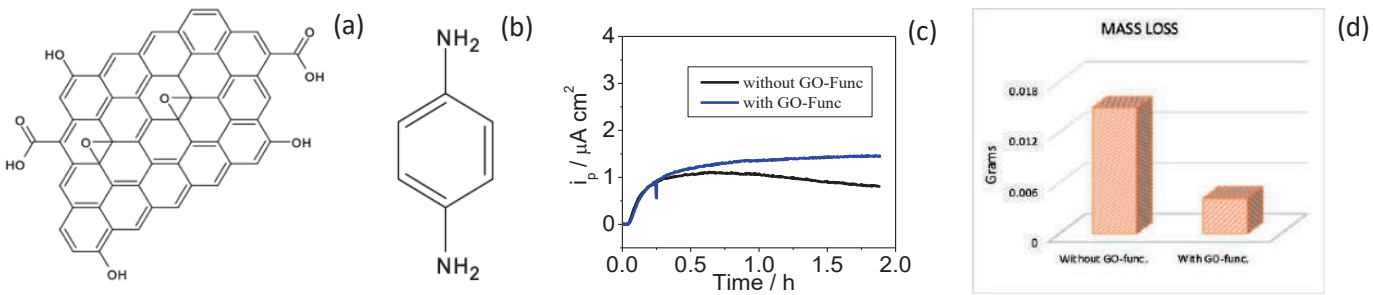


Figure 1. (a) Structural representation of graphene oxide; **(b)** Structural representation of *p*-phenylenediamine; **(c)** Hydrogen permeation transients (i_p) for a 2.0 mm SAE 1020 steel plate immersed in acid solution with and without functionalized graphene oxide (GO-func.); **(d)** Mass loss of steel in acidic solutions with and without functionalized GO.

[1] Zaferine, S. H. *et al.* Application of eco-friendly products as corrosion inhibitors for metals in acid pickling process – A review, **Journal of Environmental Chemical Engineering**, Virginia, p. 652–657, 2013.
[2] Silva, M. G. *et a*l. Inhibition effects of ionic and non-ionic derivatives of imidazole compounds on hydrogen permeation during carbon steel pickling. **Journal of Materials Research Technology**, New York, 2022.
[3] Gupta, R. K. *et al*. Functionalized graphene oxide as a new generation corrosion inhibitor for industrial pickling process: DFT and experimental approach. **Materials Chemistry and Physics**, New York, v. 236, p. 121727, 2019.

Agradecimentos/Acknowledgmentes

The authors thank the CNPq and PIBIC-UFF for financial support.

Área: ELE
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Evaluation of the potential of MoS_2 thin films obtained at liquid-liquid interface in the development of electrochemical biosensors.

Patricia S. Araújo (PD),[1] Luiz H. Marcolino Jr. (PQ),[1] Marcio F. Bergamini (PQ),[1] Aldo J. G. Zarbin (PQ) ,[1]*

patricia.araujo1@ufpr.br; aldozarbin@ufpr.br*

[1]Departamento de Química, UFPR;

Electrochemical biosensors, Molybdenum disulfide, Transition metal dichalcogenide, Voltammetric sensors

Highlights

MoS_2 samples of commercial origin and synthesized in the laboratory were used in the preparation of films through the liquid/liquid interfacial route. The films were characterized and tested as electrodes for biosensors in the determination of K^+.

Resumo/Abstract

Since the isolation of Graphene, the development of 2D materials has been of great importance in scientific studies. An example are nanomaterials based on MoS_2, in which their structural and semiconductor properties depends on the number of stacked layers, allowing different applications such as in catalysis, batteries and photovoltaic devices, among others. These characteristics highlight its high potential for use in the immobilization of different biomarkers and the development of biosensors. [1] The properties of MoS_2 in its 2D format are strongly influenced by its morphological and structural characteristics, with its synthesis method being an important means of controlling these parameters. This work is about the preparation of MoS_2 films through the liquid/liquid interface route (LLIR). This method allows obtaining thin, homogeneous films with a high surface area in a simple and economical way [2,3]. Due to the importance of detection techniques applied to the area of health and human well-being, films produced using this method were investigated for their potential use as electrodes for biosensors. MoS_2 samples of commercial origin and synthesized in the laboratory were used to prepare films by the interfacial route (LLIR), and deposited on glassy carbon electrodes by film transfer or drop-casting. After synthesis, the samples were characterized to evaluate their composition and structure using techniques such as scanning electron microscopy, x-ray diffraction, Raman scattering spectroscopy, ultraviolet spectroscopy. The electrochemical characterization was carried out using cyclic voltammetry to evaluate the response obtained with the modified electrodes, which were also evaluated using the K^+ biomarker, observing the stages of development and validation of analytical methodologies for determining the analyte. Through characterizations using microscopic and spectroscopic techniques, the presence of MoS_2 in the form of flakes arranged in layers was observed. Through cyclic voltammetry, better electrochemical responses were observed for electrodes modified by the LLIR and film transfer method. The results obtained with MoS_2 samples produced in the laboratory are compatible, in comparison with samples of commercial origin, demonstrating that electrodes modified by MoS_2 have the potential for application in the production of efficient and low-cost biosensors.

[1] SOHAIL, Muhammad et al. Trends in Analytical Chemistry, 169, 117398, 2023.

[2] SCHIMIDT, Ariane, ZARBIN, Aldo J. G. Journal of Colloid and Interface Science, 554, 80-90, 2019.

[3] ZARBIN, Aldo J. G. Materials Horizons, 8, 1409-1432, 2021.

Agradecimentos/Acknowledgments

UFPR, FINEP Nanobiosen, CNPq, CAPES, INCT Nanocarbono, INCT NanoVida.

Área: ELE

Explorando o papel da dopagem de nióbio em hidróxido de níquel na atividade eletrocatalítica para a reação de evolução de oxigênio

Rafaela Barreto da Silva Alves (IC),[1*] Gabriel Christiano da Silva (PQ).[1]

gabriel.christiano@ufv.br; rafaela.barreto@ufv.br

[1]*Departamento de Química, UFV.*

Palavras Chave: *Nióbio, Evolução de oxigênio, Eletrólise, Dopagem, Hidrogênio verde.*

Highlights

Effect of niobium doping in nickel hydroxide on electrocatalysts for the oxygen evolution reaction.

- The effect of niobium atom doping on nickel hydroxide ($Ni(OH)_2$) is investigated;
- The synthesized materials are studied for the oxygen evolution reaction in an alkaline medium.

Resumo/Abstract

A produção de hidrogênio verde através da eletrólise da água tem sido amplamente reconhecida nos últimos anos como uma estratégia para mitigar as consequências ambientais associadas ao uso de fontes de energia fósseis. No entanto, as barreiras cinéticas relacionadas à reação de evolução de oxigênio continuam a ser um desafio significativo. Neste estudo, investigamos o impacto da dopagem de nióbio no hidróxido de níquel para aprimorar a eficiência da reação de evolução de oxigênio em meio alcalino.

Os eletrocatalisadores foram sintetizados pela precipitação dos precursores metálicos com hidróxido de potássio, visando uma concentração nominal de 5% do dopante. As medidas eletroquímicas foram conduzidas em células de três eletrodos. A caracterização eletroquímica dos materiais foi realizada através da técnica de voltametria cíclica (Fig. 1a), enquanto a atividade frente à reação de evolução de oxigênio foi avaliada por meio de experimentos de varredura linear (Fig.1b).

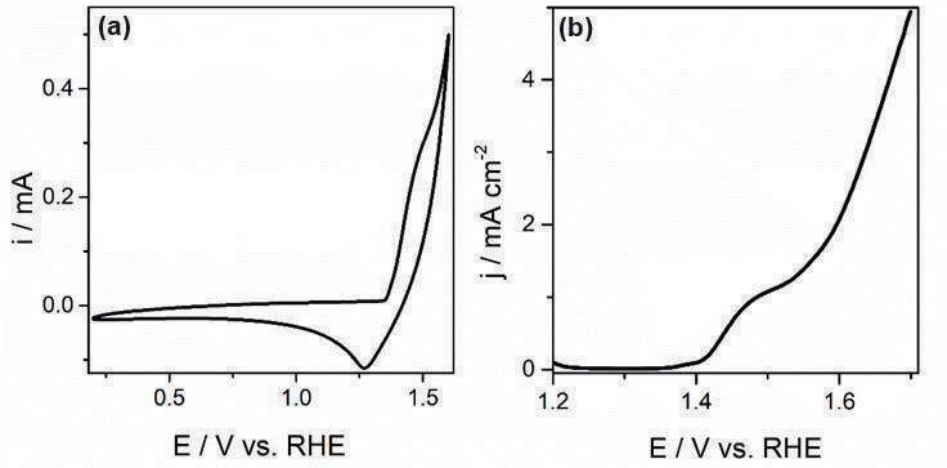


Fig. 1 – (a) Voltamograma cíclico, a 50 mV s^{-1}, e (b) voltametria de varredura linear, a 10 mV s^{-1}, para o material Nb-$Ni(OH)_2$, em eletrólito de KOH 1 mol L^{-1} a 25°C.

Agradecimentos/Acknowledgments

Os autores agradecem o Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) pelo financiamento (Processos: 405819/2022-6 e 408069/2022-8).

Área: ELE_____
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Flexible and sustainable plant-wearable sensors for on-site and fast decentralized pesticide detection toward precision agriculture and food safety

Rafaella T. Paschoalin (PQ)[1], Nathalia O. Gomes[2], Gabriela F. Almeida (PG)[3], Stanley Bilatto (PQ)[3], Cristiane S. Farinas (PQ)[3], Sergio A.S. Machado (PQ)[2], Luiz H.C. Mattoso (PQ)[3], Osvaldo N. Oliveira Jr. (PQ)[1], Paulo A. Raymundo-Pereira (PQ).[1*]

pauloaugustoraymundopereira@gmail.com

[1]São Carlos Institute of Physics, University of São Paulo, CEP 13560–970, São Carlos, SP, Brazil; [2]São Carlos Institute of Chemistry, University of São Paulo, CEP 13566-590, São Carlos, SP, Brazil; [3]Nanotechnology National Laboratory for Agribusiness (LNNA), Embrapa Instrumentation, 13560-970, São Carlos, SP, Brazil

Keywords: *Wearable sensor, Carbendazim, Diquat, Precision agriculture and food safety, Sustainable and biodegradable device, poly(lactic acid) fibers.*

Highlights

Simple method for fabrication of flexible, biocompatible and biodegradable sensors. Plant-wearable sensor can detect carbendazim and paraquat directly on lettuce and tomato skin for food safety.

Resumo/Abstract

On-site monitoring the presence of pesticides on crops and food samples is essential for precision and post-harvest agriculture, which demands nondestructive analytical methods for rapid, low-cost detection that is not achievable with gold standard methods. The synergy between eco-friendly substrates and printed devices may lead to wearable sensors for decentralized analysis of pesticides in precision agriculture. In this paper we report on a wearable non-enzymatic electrochemical sensor capable of detecting carbamate and bipyridinium pesticides on the surface of agricultural and food samples. The low-cost devices (<US$ 0.08 per unit) contained three-electrode systems deposited via screen-printing technology (SPE) on solution-blow spinning mats of poly (lactic acid) (PLA). The flexible PLA/SPE sensors can be used on flat, curved and irregular surfaces of leaves, vegetables and fruits. Detection was performed using differential pulse voltammetry and square wave voltammetry with detection limits of 43 and 57 nM for carbendazim and diquat, respectively. The wearable non-enzymatic sensor can discriminate and quantify carbendazim and diquat on apple and cabbage skins with no interference from other pesticides. The use of such wearable sensors may be extended to other agrochemicals, including with incorporation of active bio (sensing) layers for online monitoring of any type of agricultural products and foods.

Agradecimentos/Acknowledgments

This work was supported by São Paulo Research Foundation (FAPESP) [grant numbers 2017/18725-2, 2020/09587-8, 2018/10899-4, 2016/10636-8, 2019/01777-5, 2018/22214-6, 2016/01919-6 and 2023/09685-8], Brazilian National Council for Scientific and Technological Development (CNPq) (Grant 309370/2021-3, 423952/2018-8, 164569/2020-0, 307070/2022-0, 151200/2022-0 and 151113/2023-8). The authors are especially grateful to Mr. Marcio de Paula (CAQI/IQSC/USP) for the SEM micrography. LSCM images were made at LNNano - Brazilian Nanotechnology National Laboratory, CNPEM/MCTIC.

Área: ELE

Gold-modified electrochemical sensor for detection and quantification of nitrite in tap water

João Vitor Fernandes Paiva (PG),[1] Daniel A. de Azevedo (PG),[2] Pedro V. V. Romanholo (PG),[1] Sergio A. S. Machado (PQ),[3] Maria L. Felsner (PQ),[4,5] Andressa Galli (PQ),[4] Lívia F. Sgobbi (PQ).[1*]

livia_sgobbi@ufg.br

[1]Instituto de Química, UFG; [2]Instituto de Física, UFG; [3]Instituto de Química de São Carlos, USP; [4]Departamento de Química, UNICENTRO; [5] Departamento de Química, UEL.

Palavras Chave: *Disposable eletrochemical sensor, Nitrite, Screen-printed electrodes, tap water, Analytical validation*

Highlights

Disposable electrochemical sensor based on screen-printed electrodes modified with gold nanostructures to detect nitrite in drinking water.
Extensive analytical validation of the sensor in real sample.

Resumo/Abstract

High concentrations of nitrite, a naturally occurring compound, can cause significant environmental and health issues. It is primarily generated from the decomposition of organic matter and human activities such as excessive use of nitrogen-based fertilizers, as well as, industrial, and agricultural discharges. Nitrite, whether ingested directly or produced from ingested nitrate, is acutely toxic and causes methemoglobinemia, cyanosis, and vascular collapse in infants. Therefore, it is crucial to monitor and control nitrite levels in water to protect both human health and aquatic ecosystems. The Ministry of Health and the National Council for the Environment (CONAMA) defined the maximum limit of nitrite in drinking water as 1.0 mg L^{-1}. Traditional methods of analysis, such as chromatography and spectrophotometry, provide accurate results and exhibit high specificity. However, they come with significant drawbacks, including costly, time consumption, and the need for specialized personnel. As a result, electrochemical sensors have emerged as promising analytical tool, offering simplicity in construction, portability, affordability, high sensitivity, and rapid analysis at the point-of-care. A disposable electrochemical sensor has been developed for the detection and quantification of nitrite in drinking water. It is based on the electrodeposition of gold nanostructures on carbon screen-printed electrodes. The gold electrodeposition was performed through chronoamperometry, applying -0.3 V for 600 s in a 1.5 mM tetrachloroauric acid solution with 0.1 M H_2SO_4. The modified electrode was characterized using cyclic voltammetry, scanning electron microscopy and energy dispersive spectroscopy. The detection process involved chronoamperometry, which monitored the oxidation of nitrite in a solution containing $NaClO_4$ (0.1 M) and H_2SO_4 (pH 2). The parameters for chronoamperometry were optimized to apply 0.576V for 20s. The analytical curve for nitrite was prepared using standard addition of tap water. It demonstrated a linear range from 1.0 µM to 24.0 µM. The limit of detection and the limit of quantification were 0.72 µM and 2.18 µM, respectively. Precision estimates were obtained through repeatability tests, in which 5 replicates were carried out in a single day using the same electrode (RSD =12.54%). Regarding the intermediate precision tests, 5 measurements on 3 different days and nine different electrodes were performed obtaining a RSD value of 23% [1,2]. The developed electroanalytical methodology appears promising based on the analyzed figures of merit, demonstrating good precision, low limits, and adequate linearity [1,2]. The next step will evaluate the accuracy through the comparison with the standard method.

[1] AOAC OFFICIAL METHODS OF ANALYSIS. GUIDELINES FOR STANDARD METHOD PERFORMANCE REQUIREMENTS, 20ª ed., Appendix F, p. 6 – 9, 2016.
[2] INMETRO. Instituto Nacional de Metrologia. Normatização e Qualidade industrial. (2018). DOQ-CGCRE-008. Orientações Sobre Validação de Métodos Analíticos.

Agradecimentos/Acknowledgments

CNPq Conselho Nacional de Desenvolvimento Científico e Tecnológico
UFG
Sociedade Brasileira de Química
LEES

Área: ELE

Hierarchical structure of TiO_2 and rGO for photoelectrochemical H_2 production

Francisco A.S. Ribeiro (PG),[1,2*] Denilson V. Freitas (PQ),[2] Leonardo J. L. Maciel (PQ)[2], Joanna E. Kulesza (PQ)[1], Giovanna Machado (PQ)[1,2]

francisco.ribeiro@cetene.gov.br;

[1]Programa de pós graduação em ciência de materiais, UFPE; [2] Centro de Tecnologias Estratégicas do Nordeste.

Key words: Hydrogen, TiO_2, Photoelectrocatalysis, rGO.

Highlights

Increased efficiency through the addition of GO in the anodizing process, being easy to execute and low cost;

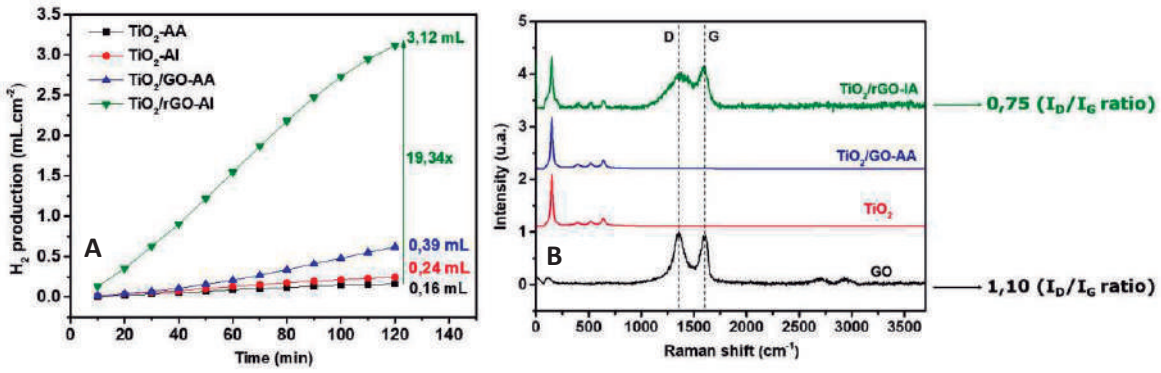
In situ reduction of GO in an inert atmosphere is essential for photoelectrochemical efficiency;

Production of 1.56 $mL.cm^{-2}.h^{-1}$ of hydrogen through TiO_2/rGO.

Abstract

The production of green hydrogen via photoelectrochemistry is a promising energy alternative.[1] We report the synthesis of TiO_2 via electrochemical anodization, with *in situ* reduced graphene oxide. We investigated the effect of thermal reduction of graphene oxide on the photoelectrocatalytic properties of the TiO_2/rGO composite, to improve hydrogen production performance. When the TiO_2/rGO composite was formed, the GO reduction was carried out through heat treatment in an ambient and inert atmosphere (controlled Ar flow). The photoanodes produced were characterized by Raman, SEM, in addition to photoelectrochemical evaluation and hydrogen production by gas chromatography. The TiO_2/rGO composite heat-treated in an inert atmosphere showed a decrease in electron transfer resistance of 74.3%, and an increase in photocurrent of 177.8%, compared to pure TiO_2. Hydrogen production showed improvements of 1830%, with a maximum value of 3.12 $mL.cm^{-2}$ of hydrogen, as seen in Figure 1A. These high improvements were not evident in composites treated in ambient atmosphere, suggesting that rGO can be obtained in situ only in an inert atmosphere with flow control. Figure 1B shows Raman, where a decrease in the degree of structural disorder of TiO_2/rGO is noted, indicating the in-situ reduction of rGO, while for composites treated in an inert atmosphere, the D and G bands of graphene are not identified.[2] These results suggest a simple and innovative methodology for in situ reduction of rGO, which promotes a significant increase in hydrogen production.

Figure 1. (A) H_2 production and (B) Raman spectroscopy for TiO_2 and TiO_2/rGO photoelectrodes.



[1]Zheng, et al., (2019)/ Appl. Surf. Sci. 512, 144549; [2]Wang, et al., (2020)/ Symmetry, 12(9), 1420.

Acknowledgments

CETENE UNIDADE DE PESQUISA DO MCTI · UFPE · FACEPE Fundação de Amparo à Ciência e Tecnologia do Estado de Pernambuco · MINISTÉRIO DA CIÊNCIA, TECNOLOGIA E INOVAÇÕES

Área: ELE

Impact of the electrochemical process on the morphology of photoanodes developed for green hydrogen production

Luana B. C. Oliveira (PG),[1,2*] Felipe L. N. Sousa (PQ),[2] Denilson V. Freitas (PQ),[2] Marcelo Navarro (PQ),[1] Giovanna Machado (PQ).[2]

luana.oliveira@cetene.gov.br

[1]Departamento de Química Fundamental, UFPE; [2] Centro de Tecnologias Estratégicas do Nordeste.

Key words: *Nanomaterials, Electrosynthesis, Green Hydrogen, BiOI, $BiVO_4$*

Highlights

Evaluation of the electrochemical synthesis process in the morphology of BiOI;

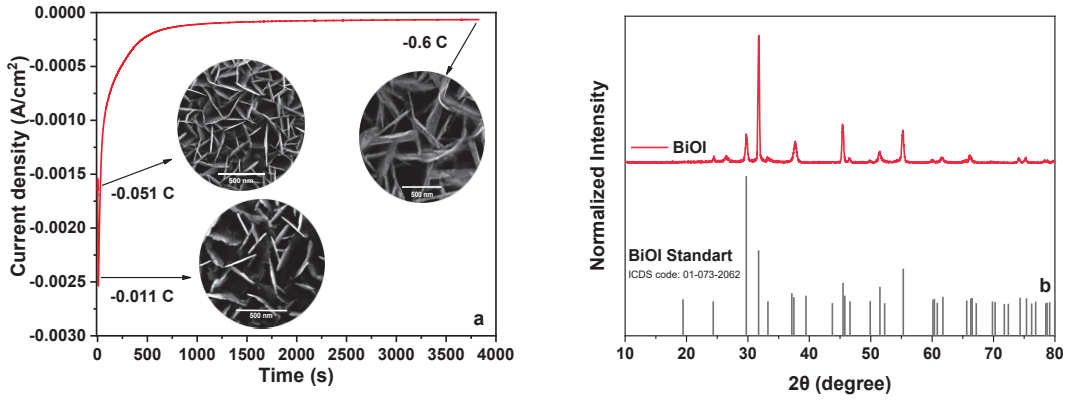
Effect of charge on film growth;

Use of a simple and scalable route for the production of photoanodes.

Abstract

Aiming at the synthesis of $BiVO_4$ and its subsequent application in the production of H_2, a series of routes were evaluated, among which electrodeposition was selected. This methodology was used for its simplicity and for scaling the material. The process consists of electrodeposition of BiOI and, subsequently, thermal conversion to obtain $BiVO_4$[1]. From this perspective, it is inferred that the BiOI thin film directly impacts the performance of $BiVO_4$.The effect of the applied charge in electrochemical synthesis on the morphology of the bismuth oxyiodide film was evaluated. In figure 1.a, the BiOI electrodeposition curve and the morphology of the semiconductor can be seen, through micrographs, at different points of the curve. It can be seen that the thickness of the nanoplate is directly related to the applied charge. Calculating the thicknesses (n=100) and corroborating the micrographs, it was noted that the greater the applied charge, the greater the thickness of the nanoplates, ranging from 18.9 to 56.9 nm with applied charges from -0.011 to -0.6 C respectively. This occurs due to the increase in the degree of interconnection between the microstructures, which leads them to connect with overall structure [2]. In figure 1.b, there is the XRD of the material obtained after the electrochemical process and it is noted that the peaks observed in the sample are relative to the crystalline planes of BiOI, indicating its formation. It is concluded that the applied charge to the system impacts the morphology of the material, obtaining thicker nanoplates with a greater applied charge.

Figure 1. Electrodeposition curve (a) e X-ray diffractogram (b) of BiOI.



[1]McDonald, K., Choi, K. Energy Environ.Sci.,2012,5, 8553; [2]Yu, Z. *et al.* Nano Energy,2021,89,106419.

Acknowledgments

MINISTÉRIO DA CIÊNCIA, TECNOLOGIA E INOVAÇÃO
GOVERNO FEDERAL BRASIL UNIÃO E RECONSTRUÇÃO
CNPq
CETENE CENTRO DE TECNOLOGIAS ESTRATÉGICAS DO NORDESTE
UNIVERSIDADE FEDERAL DE PERNAMBUCO
dQF Departamento de Química Fundamental

Área: ELE

Lab-made graphite/silver/polylactic acid filament: A new material for additively manufacturing affordable electrochemical sensors

Natália M. Caldas (IC)[1*], Amanda G. Batista (IC)[1], Daniel M. L. Alves (IC)[1], Anderson O. Alves (IC)[1], Lucas V. de Faria (PQ)[1], Fernanda N. Feiteira1(PQ), Felipe S. Semaan (PQ)[1], Wagner F. Pacheco (PQ)[1], Rafael M. Dornellas (PQ)[1]

amanda_batista@id.uff.br; Nataliamarinho@id.uff.br

[1]*Departamento de Química Analítica, Universidade Federal Fluminense (UFF), Niterói/RJ, Brazil;*
Keywords: Composite electrodes, Acid polylatic, Silver particles, Electrochemistry.

Highlights

- Incorporating silver into the material considerably improved the electrochemical performance of the sensor;
- Pyridoxine is determined in pharmaceutical samples using the BIA-AD method.

Abstract

3D printing technology has been gaining enormous prestige in the field of electrochemistry, especially in sensing applications, as numerous electrochemical cell and electrode designs have been proposed. However, the conductive filaments available have not been produced exclusively for electrochemical sensing, due to the low content of conductive material. Faced with this situation, we have produced a new material based on graphite (G), silver (Ag), and polylactic acid (PLA) to be employed as a working electrode. In this combination, PLA offers printability and mechanical stability, while G and Ag provide electrical properties and electrocatalytic sites, respectively. Different proportions were studied in the production stage of the composite materials, and the best compromise between printability and electrochemical performance was achieved using G/Ag/PLA (30:10:60 % w/w, respectively). The electrodes were manufactured in a cylindrical format using acrylonitrile butadiene styrene (non-conductive filament) and an FDM 3D printer, while the proposed conductive filament was inserted using a 3D pen. All the electrodes were characterized by electrochemical, spectroscopic, and morphological techniques which revealed a successful incorporation of G and Ag into the polymer matrix. The device fabrication process was reproducible (% relative standard deviation (RSD) inter-electrodes < 8.15). As a proof of concept, pyridoxine (PYR), a B-complex vitamin, also known as vitamin B6, was selected as the target analyte. Figure 1 illustrates the cyclic voltammogram obtained from 1mmol/L of PYR in 0.1mol/L phosphate buffer (pH 2.0) using the unmodified and modified 3D printed electrodes. Thus, the 3D-printed sensor was combined with batch injection analysis, a high-throughput tool for amperometric determination of PYR in pharmaceutical products. The results obtained using the G/Ag/PLA electrode showed wider linear behavior (0.1 to 400 μmol L^{-1} and appropriate limits of detection (LOD = 0.03 μmol L^{-1} L) and quantification (LOQ = 0.1 μmol L^{-1}). In addition, surface fouling and memory effects were not pronounceable. Consecutive measurements using different PYR concentration levels attested to the precision of the method (RSD < 2,41). When pharmaceutical samples were analyzed, recoveries close to 100% certified the accuracy and reliability of the analyses. Therefore, it is possible to infer that the platform proposed here could be a valuable low-cost strategy for other routine electrochemical applications in places with minimal infrastructure.

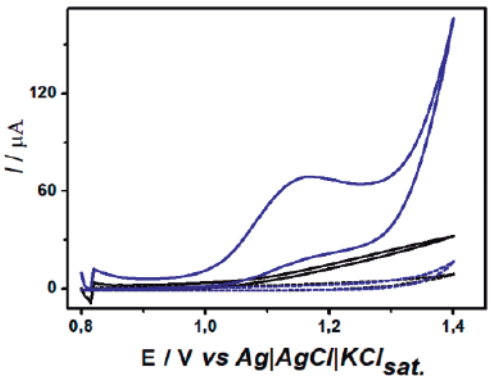


Figure 1: CVs obtained for 1 mmol/L PYR in 0.1 mol L-1 phosphate buffer (pH 2.0) using G/PLA (black line) and G/Ag/PLA (30:10:60, blue line). The dashed lines indicate the respective blanks.

Acknowledgments

The authors would like to thank FAPERJ and CNPq for their financial support.

Área: ELE

Nickel electrocatalysts supported on functionalized graphene for efficient glycerol electro-oxidation

Lízia A. X. Bulin (PG),[1*] Brenda Koch (IC),[1] Eduardo G. C. Neiva (PQ),[2] Daniela Z. Mezalira (PQ)[1]

lizia.alana@posgrad.ufsc.br*

[1]*Chemistry Department, UFSC, Florianópolis, SC, Brazil;* [2]*Chemistry Department, FURB, Blumenau, SC, Brazil*

Keywords: *nickel electrocatalyst, graphene functionalization, polyol method, Fleischmann mechanism.*

Highlights

Nickel catalysts supported on graphene for glycerol electro-oxidation. Functionalized graphene to assess increased reaction efficiency. Electrocatalysts maintaining activity over time.

Abstract

Efficient catalysts are essential for glycerol oxidation reactions, with potential applications in electrical energy generation and high-value byproducts production.[1] Nickel, a non-noble metal, has been investigated as an electrocatalyst for these reactions, utilizing graphene supports to enhance electrical conductivity and surface area properties. The functionalization of graphene with oxygenated and nitrogenated groups intensifies support reactivity and facilitates Ni deposition. This study investigates the catalytic activity of Ni electrocatalysts synthesized via the polyol method (Ni/G, Ni/GO, and Ni/NGO) for glycerol electro-oxidation. Characterization techniques including XRD, TGA, AAS, SEM and TEM were employed, with some results shown in Figure 1.

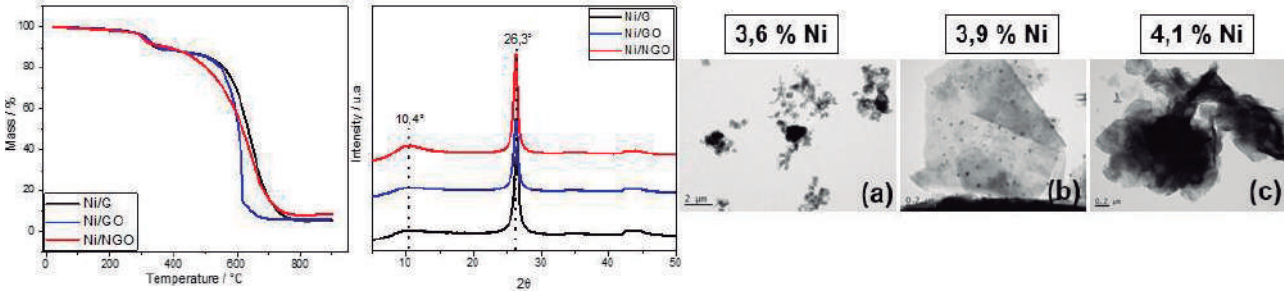


Figure 1. TGA, XRD, TEM, and AAS results for (a) Ni/G, (b)Ni/GO, and (c) Ni/NGO

Electrochemical studies employing cyclic voltammetry (CV) with 1.0 mol L^{-1} KOH as the electrolyte (Figure 2a) revealed redox peaks corresponding to $Ni(OH)_2$/NiOOH species, with NiOOH responsible for glycerol oxidation, according to the Fleischmann mechanism[1]. The introduction of 0.1 mol L^{-1} glycerol (Figure 2b), induced changes in the voltammetric profile, confirming the success of the reaction. Additionally, chronoamperometry (CA) measurements (Figure 2c) were performed at 0,5 V to monitor the stability of electrocatalysts during glycerol electro-oxidation over 1 hour, revealing sustained current with notable fluctuations over time.

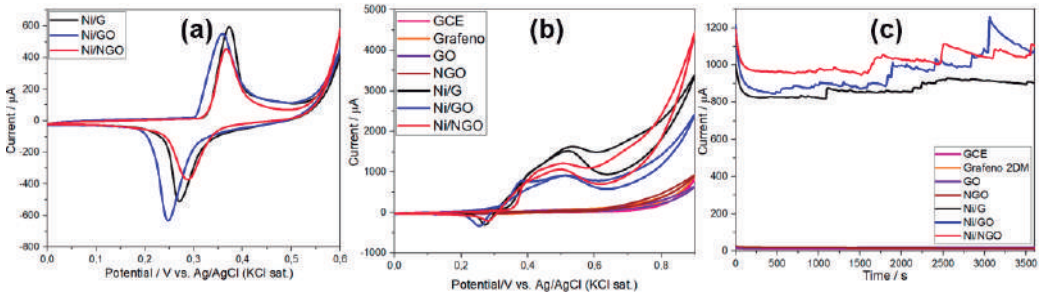


Figure 2. (a) CV without glycerol, (b) with glycerol, and (c) CA measurements result for all materials

[1] Ghaith, M. E., Abd El-Moghny, M. G., Alalawy, H. H., El-Shakre, M. E. & El-Deab, M. S. ***RSC** Adv.* **13**, 10893–10902 (2023).

Acknowledgments

CNPq, CAPES, FAPESC, UFSC, FURB, LCME-UFSC, LEMA/LARES, Central de Análises QMC-UFSC.

Área: ELE

Photobioelectrochemical sensor based on chloroplast for Simazine detection in water sample

Marina C. Dias (IC),[1*] Caio C. G. Silva (PG),[1,2*] Saulo S. Garrido (PQ),[2] Maria V. B. Zanoni (PQ),[1]

mc.dias@unesp.br; ccg.silva@unesp.br

1 São Paulo State University (UNESP), Institute of Chemistry, Department of Analytical, Physicochemical and Inorganic Chemistry, Rua Professor Francisco Degni, 55, Araraquara 14800-060, São Paulo, Brazil
2 São Paulo State University (UNESP), Institute of Chemistry, Department of Biochemistry and Organic Chemistry, Rua Professor Francisco Degni, 55, Araraquara, 14800-060, São Paulo, Brazil

Palavras Chave: *Photosynthesis, chloroplast, photobioelectrochemical system, biosensor, herbicide, water.*

Highlights

Photoelectrochemical biosensor based on chloroplasts to detect herbicide simazine. The light source used was a white LED. The biosensor in the presence of simazine reduces the photocurrent by inhibiting electron transfer in photosynthesis.

Abstract

Due to population growth and the development of industries and agriculture, the scientific and technological scenario faces significant challenges for the 21st century: the energy crisis and the increasing pollution of environmental resources, especially water resources. In this context, photosynthesis is a vital and complex natural process, capable of transforming solar energy into chemical energy with remarkable efficiency. Its successful integration into photobioelectrochemical (PBE) devices has paved the way for technological advances in diverse areas [1]. Given this, we designed a chloroplast-based PBE biosensor to monitor the herbicide simazine (SMZ) in water samples.

To build the biosensor, we used the previously optimized parameters [2]. The WO_3 substrate was used due to its compatible characteristics, such as low band gap, chemical stability, absorption in the visible region, and biocompatibility. The electrode was synthesized by anodizing a W sheet at 40 V for 15 minutes in 0.1 M Na_2SO_4 with 0.7% (w/v) NH_4F and calcined at 450°C for 2 hours. The substrate was modified with a PDA film with 5 mg mL^{-1} of dopamine in 10 mM Tris-HCl pH= 8.5 at 4ºC for 4 hours. Then, using drop-casting, 25µL of a solution of 150µg mL^{-1} of chloroplasts was dripped on the electrode surface and dried at room temperature. The performance of the construction steps of the described PBE device was carried out in 0.1 M PBS medium pH 7.0, using chronoamperometry curves with on/off cycles using a low-power white-LED system at + 0.3 V, proved to be satisfactory for carrying out the measurements. Verifying that the use of PDA contributes to an increase in photocurrent by 30% about the WO_3 substrate, this is due to its absorption in the visible region. Furthermore, the photocurrent signal continues to increase by 50% with the immobilization of chloroplasts, showing its versatile properties such as strong adhesion, biocompatibility, and the presence of functional groups (quinones and semiquinones) that facilitate charge transfer. Furthermore, we evaluated the influence of 10uM of SMZ on the photocurrent signal, and there was a decrease of 90% in the signal. Therefore, we explored signal protection to build a linear relationship between photocurrent and SMZ concentration from 5.0×10^{-9} M to 1.0×10^{-5} M and detection and quantification limits of 0.461 and 1.4, respectively. Other parameters were optimized, such as the influence of light intensity, with the best efficiency being 15.2 mW cm^{-2}. Finally, the method was applied to detect SMZ in water.

Acknowledgments

CAPES and INCT-DATREM (grant number: CNPq 465571/2014-0, grant number: FAPESP 2014/50945-4)

References

[1] Zanoni, M. V. B., **Braz. J. Anal. Chem.** 2023, 10, 10-12.

[2] Silva, C.C.G., Torquato, L.D.de M., de Araújo, B.C., Mantilla, H.D.R., Zanoni, M.V.B., Garrido, S.S. **Bioelectrochemistry** 2022, 147, 108177.

Área: ELE
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Photoelectrochemical Glycerol valorisation over SILAR-deposited $BiVO_4$ photoanode.

Leonardo Carvalho Soares (PG),[1] Ícaro Levi Tomaz Nascimento (PG),[1] Sarayute Chansey (PQ),[2] Christopher Hardacre (PQ),[2] Pablo Sebastián Fernández (PQ)[1], Claudia Longo (PQ)[1].

[1]Departamento de Físico-Química, UNICAMP; [2] School of Natural Science, MECD, University of Manchester,UK

Palavras Chave: Photoelectrochemistry, $BiVO_4$, Glycerol, photoanode.

Highlights

Photoanode based on $BiVO_4$ were used for Light-assisted glycerol oxidation.
Under 100 mW cm^{-2} white LED irradiation, FTO|$BiVO_4$ in aqueous $NaHCO_3$ provided 6.2 mA cm^{-2} at 1.0 V vs RHE.
After 2 h, Glycolate, glycerate and formate as products of glycerol oxidation.

Resumo/Abstract

Bismuth vanadate ($BiVO_4$) is a n-type semiconductor widely investigated for application as a photoanode for photoelectrochemical oxidation reactions. In this work $BiVO_4$ photoanodes were used for production of value-added chemicals from light-assisted oxidation of glycerol, a waste from biodiesel production.. $BiVO_4$ films deposited on FTO were synthesized using the BiOI template, by a combination of Successive Ionic Layer Adsorption Reaction (SILAR) and thermal treatment. This methodology produces porous structures with a controllable thickness, and geometrical areas ranging from 1 to 25 cm^2 (Figure 1a) . All experiments were recorded under irradiation provided by a white LED (5700 K) calibrated at 100 mW cm^{-2} at the electrode surface. Irradiation of FTO|$BiVO_4$ electrode from the FTO side promoted an increment of the photocurrents in 30%, from 0.85 to 1.10 mA cm^{-2} at + 1.0 V vs RHE, in supporting electrolyte, aqueous 0.5 mol L^{-1} $NaHCO_3$ (pH 8.2). Furthermore, the presence of 0.5 mol L^{-1} glycerol enhanced the photocurrents densities in 6 times at 1 V vs RHE (Figure 1b). The long-term measurements under different applied potentials (Figure 1c) revealed that the photocurrent densities are strongly impacted by the ex ternal electrical bias, with reliable stability up to 2 hours. Analysis of the electrolyte by HPLC-DAD-RID revealed the presence of glycolate, glycerate and formate as products of partial glycerol oxidation.

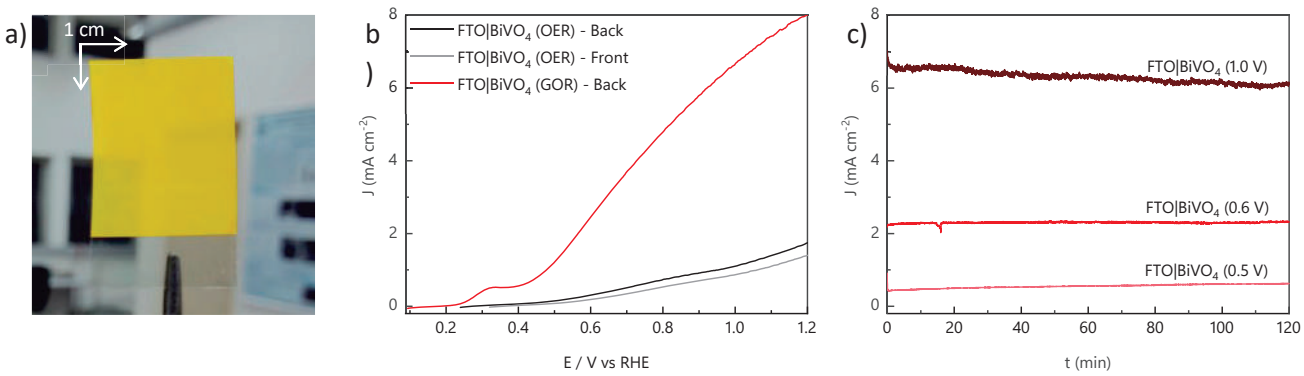


Figure 1 - (a) photography of FTO|$BiVO_4$ electrodes, (b) Linear sweep voltammetry (20 mV s^{-1}) in aqueous $NaHCO_3$ illuminated from front side (gray), back side (black), and in presence of glycerol (red), (c) chronoamperometry profile under different applied pontentials.

Agradecimentos/Acknowledgments

The authors gratefully acknowledge support from CINE, FAPESP, Faepex-UNICAMP, CNPq, CAPES and the University of Manchester.

Área: ELE

REFORMA ELETROCATALÍTICA DE LIGNINA EM MEIO ALCALINO: INVESTIGAÇÃO DOS EFEITOS DA FORMA E TEMPERATURA SOBRE ELETRODOS DE Ni

Leticia Fernandes (IC),[1] André H. B. Dourado (PQ),[1,2] Hamilton Varela (PQ)[1]

leticia.f2@usp.br; andre.dourado@unesp.br ; hamiltonvarela@usp.br

[1]Instituto de Química de São Carlos, USP [2]Instituto de Química de Araraquara, UNESP

Palavras Chave: *Lignina, eletro-oxidação, efeito da temperatura, vanilina .*

Highlights

Electrocatalytic reforming of lignin in alkaline media: Investigation of shape and temperature effects on Ni electrodes; this work is dedicated to investigating the electro-oxidation of kraft lignin from eucalyptus, waste from the paper and cellulose industry on nickel plate and nickel foam electrode, emphasizing the analysis of the products generated and carrying out a brief comparison between them.

Resumo/Abstract

A emissão antropogênica de dióxido de carbono (CO_2) não é compensada pelos ciclos biogeoquímicos, gerando acúmulo deste na atmosfera e gerando efeitos ambientais nocivos, como as mudanças climáticas. Uma alternativa a esse cenário seria a utilização de biocombustíveis como fonte de energia por terem emissão zero de CO_2, devido ao ciclo biológico das plantas. Porém, a biomassa gerada como resíduo dessa produção é subutilizada, pois seu principal uso é a geração de energia termoelétrica. Nesse processo, a lignina, macromolécula conhecida por ser a maior fonte renovável de compostos aromáticos, e terceiro maior componente em título da biomassa, acaba por ser queimada. Neste trabalho, sugere-se o uso de técnicas eletroquímicas para a geração de produtos monoaromáticos através da despolimerização oxidativa de lignina kraft de eucalipto proveniente da indústria de papel e celulose.

Nesse estudo, verificou-se a dependência cinética frente à morfologia do eletrodo utilizando eletrodo de Ni placa e esponja. Para tanto, voltametrias cíclicas em regime *quasi*-estacionário foram realizadas a diferentes temperaturas, entre 12 e 80°C. Assim, foi possível notar que a forma dos perfis j-E é fortemente afetada pela morfologia do eletrodo. Posteriormente, foram realizadas eletrólises de 3 horas em diferentes potenciais e temperaturas para cada eletrodo, para verificar se as diferenças observadas nos perfis j-E eram resultados de diferentes caminhos reacionais. Para tanto, o licor obtido ao final de cada eletrólise era tratado para que os produtos fenólicos pudessem ser isolados e posteriormente analisados pela técnica de cromatografia gasosa com detector por ionização de chama. Notou-se uma maior seletividade a aldeídos, indicando uma preferência pela quebra da ligação C_α-C_β. Além disso, apesar de unidades S serem o monômero mais presente na lignina em uso, notou-se uma maior seletividade para vanilina, composto oriundo de unidades G. Dessa forma, duas hipóteses são levantadas, a inversão é devido à seletividade do eletrodo, ou à quebra da ligação entre o anel e um dos substituintes metoxila em *meta*. Adicionalmente, observou-se que 60ºC foi a temperatura de maior eficiência faradaica a esses compostos.

Agradecimentos/Acknowledgments

Os autores agradecem à FAPESP (#2019/22183-6, #2020/15230-5 e #2022/06405-1), USP, RCGI/USP & Shell Brasil, e ANP (Agência Nacional de Petróleo, Gás Natural e Biocombustíveis) por meio da regulamentação da taxa de P&D.

Área: ELE
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Solar-driven upgrading of nitrobenzene by coupled hydrogenation using electrochemically generated green H_2

Aline Maria Sales Solano (PQ), José Eudes Lima Santos (PQ), Letícia G. A. Costa (PQ), Letícia Milena Gomes da Silva (PQ), Jussara Câmara Cardozo (PQ), Marco A. Quiroz Alfaro (PQ), Aruzza Araújo (PQ), Amanda Duarte Gondim (PQ), Lívia Nunes Cavalcanti (PQ), Elisama Vieira dos Santos (PQ), Carlos A. Martínez-Huitle (PQ)*

carlos.alberto.mh@ufrn.br

Renewable Energies and Environmental Sustainability Research Group, Institute of Chemistry, Federal University of Rio Grande do Norte, Campus Universitário, Av. Salgado Filho 3000, Lagoa Nova, CEP 59078-970, Natal, Rio Grande do Norte, Brazil

Palavras Chave: *green hydrogen, integrated-hybrid processes, water splitting, sustainable approach, electrochemical oxidation.*

Highlights

Commercial aniline is an essential chemical in multiple sectors, such as pharmaceuticals, dyes, and rubber processing.

The synthesis of aniline is by transforming nitrobenzene at high-pressurized H_2 gas and temperatures requiring specialized equipment with significant costs and economic challenges for the establishment of a sustainable hydrogenation sector.

Pt and Pd catalysts have been attempted for the hydrogenation of nitrobenzene by coupling an integrated-hybrid electrochemical strategy to produce green H_2 to elucidate its benefits in comparison to the traditional pathway.

The combined electrochemical hydrogenation system may achieve high level of selectivity, leading to profitability and the production of hydrogen at a cost that is like steam methane reforming.

Resumo/Abstract

Commercial aniline is an essential chemical molecule that has extensive use in multiple sectors, such as pharmaceuticals, dyes, and rubber processing. The main process used for its manufacturing is the catalytic hydrogenation of nitrobenzene, which is an essential step in the synthesis of aniline. heterogenous hydrogenation of NB to AN is known to occur with high-pressurized H_2 gas, that is usually carried out at a H_2 pressure of 1-5 MPa and temperature of 100-200°C, consequently, requires the utilization of specialist equipment and the handling of H_2 pose possible safety concerns, resulting in significant costs and economic challenges for the establishment of a sustainable hydrogenation sector. In this work, supported platinum (Pt) and palladium (Pd) have been attempted for the hydrogenation of NB. Furthermore, the effects of the support on the physical-chemistry properties of the amount of catalysts (100, 200 and 300 mg L^{-1}) were analyzed and temperature (25, 40 and 55 °C). Hence, this reaction is appropriate as a demonstration of our integrated strategy and to elucidate its benefits in comparison to the traditional pathway. Furthermore, no deactivation was seen of catalyst. An economic feasibility analysis reveals that the combined electrochemical hydrogenation system may achieve a high level of selectivity, leading to profitability and the production of hydrogen at a cost that is like steam methane reforming. The potential, constraints, and future direction of our current paradigm are now being examined.

Agradecimentos/Acknowledgments

CNPq (306323/2018-4, 312595/2019-0, 439344/2018-2, 315879/2021-1, 409196/2022-3, 408110/2022-8), FAPESP (2014/50945-4 and 2019/13113-4) and Humboldt Foundation.

Área: ELE

Study of Ru/RuO_2 composite for nitrate electrochemical reduction

Felipe H.S. Santos (PG)[1], Gabriel F. Costa (PG)[1], Raphael Nagao (PQ)[1]*

f271139@dac.unicamp.br; nagao@unicamp.br

[1]*UNICAMP, Institute of Chemistry*

Keyword: *Electrocatalysis, Green ammonia, Ruthenium oxide.*

Highlights

- Nitrate ions are one of the main nitrogenous pollutants;
- Nitrate electroreduction is a promising alternative to these environmental problems;
- The synthesized catalyst showed activity for NO_3RR.

Abstract

Nitrate ions are one of the main nitrogenous pollutants that accumulate through the successive oxidation of ammonia.[1] The run-off of this pollutant into wastewater, mainly in agricultural fields, is an environmental problem that is evidenced by the accumulation of nitrate from industrial and biological processes, causing harmful consequences on wildlife, such as eutrophication and aquatic acidification.[2] To tackle this issue, the Nitrate Reduction Reaction (NO_3RR) is a promising alternative to these environmental problems. In this perspective, this work proposes the study of the ruthenium and ruthenium oxide (Ru/RuO_2) composite for NO_3RR. We electrodeposited Ru/RuO_2 on a gold substrate (Au) (Figure 1a) to carry out electrochemical tests. We performed cyclic voltammetries in a 1.0 mol L^{-1} NaOH solution, as well as in 1.0 mol L^{-1} NaOH + 20 mmol L^{-1} $NaNO_3$ in order to assess the electrode's activity for nitrate electroreduction. We observed a consistent fixation of the catalyst on the substrate at the applied potential of -0.2 V vs. RHE. Based on the voltammograms, the redox profile of the Ru/RuO_2 electrode in the absence (Figure 1b) and presence of nitrate (Figure 1c) can be evaluated. We detected the suppression of the hydrogen desorption peak in the presence of nitrate (red arrow, Figure 1c and d), indicating that the competition for the catalyst's adsorption/desorption site is favorable for nitrate over hydrogen. We also noted that the synthesized catalyst showed activity for NO_3RR from the potential of -0.2 V vs. RHE (Figure 1e). However, it is necessary to characterize the synthesized material to see how the structure of the catalyst influences NO_3RR, so X-ray diffraction (XRD) will be carried out to identify the crystalline phases, X-ray photoelectron spectroscopy to determine the oxidation state of Ru, as well as scanning electron microscopy with energy dispersive spectroscopy.

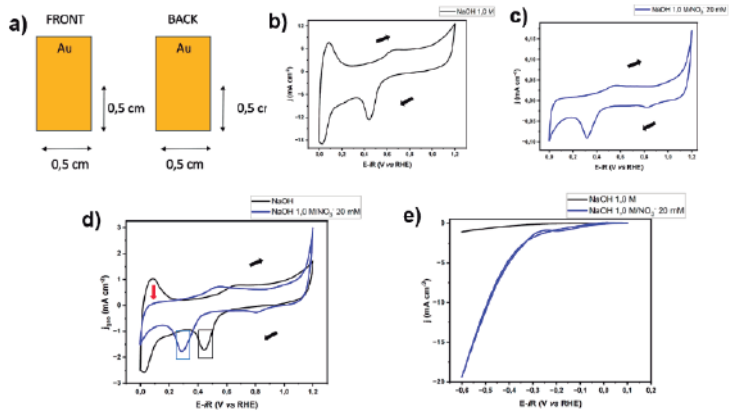


Figure 1. (a) Representation of the geometric area of electrodeposition of the catalyst on the gold substrate. (b) Voltammogram of the Ru/RuO_2 composite in 1.0 mol L^{-1} NaOH in the potential range from 0.0 V to 1.2 V vs. RHE. Scan rate 20 mV s^{-1} (c) Voltammogram of the Ru/RuO_2 composite in 1.0 mol L^{-1} NaOH + 20 mmol L^{-1} $NaNO_3$ in the potential range from 0.0 V to 1,2 V vs. RHE. Scan rate 20 mV s^{-1} (d) Overlap of voltammograms b and c. (e) Voltammogram of the Ru/RuO_2 composite in 1.0 mol L^{-1} NaOH (black line) and 1.0 mol L^{-1} NaOH 1,0 mol L^{-1} + 20 mmol L^{-1} $NaNO_3$ (blue line) in the potential range from 0.1 V to -0.6 V vs. RHE. Scan rate 20 mV s^{-1}.

Acknowledgments

CAPES, CNPQ, UNICAMP, IFRO

References

[1]P. H. Langevelde, I. Katsounaros and M. T. M. Koper, Joule 5 (2021) 290 – 294.
[2]Davidson, E.A. et al. 2011. 'Excess Nitrogen in the US Environment: Trends, Risks, and Solutions', Issues in Ecology (15).

Área: ELE

Substrate selection strategies for electrocatalysis: an analysis based on the nickel Prussian blue analogue

João P. B. de Souza (PG),[1] Juliano A. Bonacin (PQ).[1*]

J264558@dac.unicamp.br; jbonacin@unicamp.br

[1]*Instituto de Química, Universidade Estadual de Campinas (UNICAMP).*

Palavras-Chave: green hydrogen, water electrolysis, prussian blue analogue, substrate, hydrogen evolution reaction.

Highlights

The substrate plays a key role in water electrolysis but is often overlooked.

Titanium forms an oxide layer that decrease the catalyst activity

Stainless steel and FTO present promissory properties.

Resumo/Abstract

Hydrogen produced from water electrolysis powered by renewable energy, known as green hydrogen, emerges as one of the most promising alternatives for various hard-to-decarbonize sectors. However, the use of green hydrogen is limited by the high energy consumption of its production process and the dependency on rare metals (specifically platinum group metals, PGM) for electrolysis in acidic media. This demands the development of new electrolysis strategies with low energy consumption using catalysts made of more abundant elements. In this context, research in electrocatalysis tends to focus on the catalyst, but a proper understanding of the other components of the system is crucial for developing electrolyzers with maximum efficiency. An example is the substrate on which the catalysts are placed, which is not usually thoroughly studied.

In this work, four substrates were studied: titanium (Ti), stainless steel (SS-316L), fluorine-doped tin oxide (FTO). A PGM-free catalyst, nickel Prussian blue analogue (Ni-PBA), was electrodeposited on each substrate in two steps via chronoamperometry. The metal-organic framework structure of Ni-PBA allows for a lower content of metal ions per geometric area while increasing the availability of active sites for catalysis. Additionally, Ni-PBA is known to be stable over a wide pH range in acidic media. The deposition was visually confirmed and by cyclic voltammetry. Then, the activity of each electrode for the hydrogen evolution reaction (HER) in 0.5 mol L^{-1} H_2SO_4 was evaluated.

For the FTO, FTO/Ni-PBA, and SS/Ni-PBA systems, overpotentials, in modulus, of 0.54 V, 0.43 V, and 0.29 V were obtained for the current density at 5 mA cm^{-2}. In comparison, platinum, considered to have very high activity for HER, showed 0.08 V overpotential for the same current density. The Ti and Ti/Ni-PBA electrodes, although showing an increase in current related to HER, did not reach the current density of 5 mA cm^{-2}. Tafel plots confirm the observed catalytic activity trend. The low activity of the Titanium electrodes and high charge transfer resistance - as evidenced by electrochemical impedance spectroscopy (EIS) - are associated with the formation of an oxide film on the metal surface.

Agradecimentos/Acknowledgments

CAPES: Finance Code 001, CNPq: 308203/2021-6 and FAPESP- grant# 2017/11986-5; 2021/05976-2).

Área: ELE

The Electrochemistry of Nitrocompounds from a Bibliometric Approach

Mauro Aquiles La Scalea (PQ)

mauro.scalea@unifesp.br

Departamento de Química, UNIFESP, campus Diadema

Keywords: *bibliometry, nitrocompounds, electrochemistry, electroanalysis, voltammetry*

Highlights

Bibliometric analysis was used to evaluate the relationships and trends on the different applications of the electrochemistry involving the heterocyclic and aromatic nitrocompounds.

Abstract

The heterocyclic and aromatic nitrocompounds are industrially and commercially important chemicals, considering drugs, explosives, pesticides and dyes[1]. Despite their economic importance, the advent of these chemicals also brought serious human health and environmental problems due to their toxic characteristics as pollutants[1]. The nitro group is catalyzed by nitroreductases promoting a six electron reduction to form sequentially the nitro-anion radical, nitroso-, N-hydroxylamino and amino-functional groups[1,2]. This reactions sequence can be electrochemically reproduced with more different goals and applications[3]. In this sense, a preliminary bibliometric analysis has been performed based on the Web of Science Core Collection. A Boolean analysis with 98 topic terms in 21 combination steps was applied by using the operators OR, AND and NOT. The truncation search for difference among spellings, noun and adjective terms, plurals and prefixes was considered. The terms aliphatic(s), potentiometry(ic) and conductometry(ic) were excluded. This search covered entire period defined by the data base until 2023, in which 8,156 documents were registered, highlighting 7,616 original articles, 266 reviews and 391 proceeding papers. The annual register of publications (Fig. 1) clearly shows an exponential increase from 1990 until 2021 with a slight drop in the following two years (2022/23), probably as a consequence of the Covid-19 pandemic period[4]. Anyway, the cumulative data confirm an evident expansion of publications over that period. Moreover, People Republic of China was the more prolific country in publications (26.9%), followed by India (11.1%) and USA (9.41%) and Brazil reached the milestone of 3.35% correspondent to 255 published articles. Among the research fields, obviously, Electrochemistry appears as one of the highlights with 1,803 articles (23.7%), but with a smaller number than that recorded for Analytical Chemistry with 1,974 or 25.9% of all registers.The first three journals that more published in this area were: Journal of Electroanalytical Chemistry (394 articles), Electrochimica Acta (333 articles) and Electroanalysis (213 articles), but this search field is broad and diverse and more than 1,000 entries publication titles were registered. Citations can be trend indicators and this analysis was made considering the last 20 years of publications. Analyzing citations by VOSviewer software was observed that, except for the obvious citations of electrochemical techniques, nanoparticles come up with the highest citation numbers (844) and link strengths (7.445) also associated to the keywords sensor (771), electrochemical sensor (511) and degradation (503), which suggests studies of nanostructure modified electrodes having some compounds as target: 4-nitrophenol (492), p-nitrophenol (431), nitrobenzene (388), chloramphenicol (302) and metronidazole (238). This analysis made it possible to recognize the main research focuses and what is under development, providing a comprehensive overview on electrochemistry of nitrocompounds.

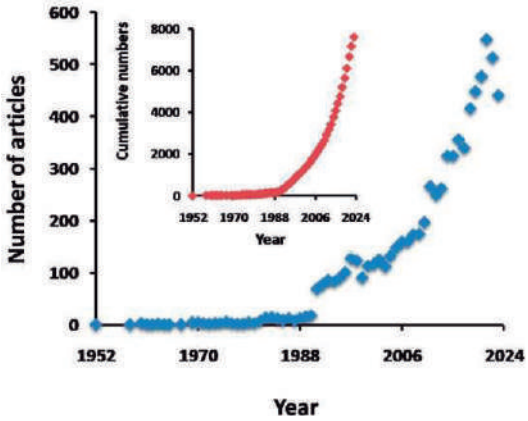


Fig. 1 – The annual register of publications

1) T.M. Penning *et al.*, Chem. Res. Toxicol. **2022**, 35, 1747; 2) N.Čénas *et al.*,Int. J. Mol. Sci. **2021**, 22, 8534; 3) O. Hammerich, In: *Organic* electrochemistry, 5th ed. CRC Press, **2015**, pp 1149; 4) S. Heo *et al.*, Humanit. Soc. Sci. Commun. **2022,** 9, 434

Acknowledgments

Capes

Área: ELE

Ultra-Sensitive Nanotube TiO_{2-X}/Cu_XO Electrochemical Sensor for Glyphosate Detection in Water Sample

Samantha Torres Ohse (PG)[1]*, Amanda Morais (PG)[1], Maria Lurdes Felsner (PQ)[1,3], Andressa Galli(PQ)[1], Mariana de Souza Sikora (PQ)[1,2]

***samanthatohse@gmail.com;**

[1]Departamento de Química, Universidade Estadual do Centro Oeste (UNICENTRO) – Campus CEDETEG; [2]Departamento de Química, Universidade Tecnológica Federal do Paraná (UTFPR) – Campus Pato Branco; [3]Departamento de Química, Universidade Estadual de Londrina (UEL)

Keywords: TiO_2NT; Mixed Copper Oxides; Glyphosate; Electrochemical Sensor; Differential Pulse Voltammetry;

Highlights

Ti^{3+} ions and mixed copper oxides incorporation lead to a decrease in TiO_2 resistance;
The TiO_{2-X}NT/Cu_XO sensor promoted an indirect measurement of glyphosate;
The TiO_{2-X}NT/Cu_XO sensor presented na LOD 100 times lower than the lowest referenced value.

Abstract

Glyphosate (GLY) is non-selective herbicide, widely used around the world for weed control, that raises significant health and environmental concerns due to its potential association with chronic diseases, cancers, and symbiotic relationships disruption, making it necessary to study and monitor this substance[1]. Hence, a novel electrochemical sensor was developed utilizing nanotubular TiO_2 films modified with Ti^{3+} ions and copper oxides to accurately detect and quantify GLY in water samples. Under optimal conditions, the method's suitability was evaluated by validation study, with the sensor exhibiting an ability to detect and quantify glyphosate traces indirectly by differential pulse voltammetry through current peak inhibition. It obtained low limits of detection (LOD = 3.44×10^{-3} pmol L^{-1}) and quantification (LOQ = 0.27 pmol L^{-1}), values lower than the lowest referenced value[2] and the 65.00 µg L^{-1} maximum waste limit established by CONAMA, for GLY in fresh water[3]. The sensor demonstrated strong stability, repeatability, and recovery rates ranging from 54.91 to 132.72%. These promising results highlight the sensor's potential for GLY quantification in real aquatic environments, contributing to environmental monitoring and health protection.

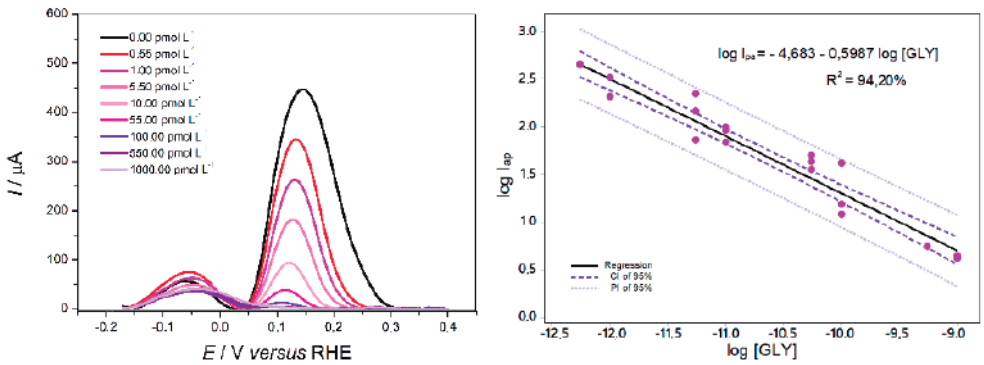


Figure 1. Differential pulse voltammograms for GLY made in linear range concentration from 0.55 - 1000.00 pmol L^{-1} in 0.10 mol L^{-1} tris-HCl buffer (pH = 7.00; v = 100.00 mV s^{-1}) (left) and corresponding calibration curve (right)

[1] FERRANTE, M.; RAPISARDA, P.; GRASSO, A.; FAVARA, C.; CONTI, G. O. Environ. Res., v. 235, 2023.
[2] GONÇALVEZ, D.A.; ALENCAR, L.M.; ANJOS, J.P.B.; ORTH, E.S.; SOUZA, V.H.R. Mater. Today Commun, v. 36, 2023.
[3] BRASIL, Conselho Nacional do Meio Ambiente (CONAMA). Resolução CONAMA nº 357, de 17/03/05.

Acknowledgments

The autors are grateful to CAPES, CNPq, UNICENTRO, and the laboratories of CMCM (UTFPR) and CME (UFPR).

Área: ELE

Uso de zeólitas como modificador de pasta de carbono e sua aplicação para a determinação de carbedazim

Cybelle C. C. M. Barbosa (PG),[1] Bárbara L. Ramos (IC),[2] Elivelton A. Ferreira (PG),[2] Mendelssolm K Pietre (PQ).[1,2]

mkpietre@yahoo.com.br

[1]PGTA- Mestrado em tecnologia Ambiental ; [2]Departamento de Química-ICEx-UFF

Palavras-Chave: *Zeólita, Voltametria, Sensor, Carbedazim, Eletrodo, Pasta de carbono*

Highlights

- Use of zeolites as a carbon paste modifier and its application for the determination of carbedazim
- Synthesis of faujasite zeolite and its functionalization with CTAB (Fau-CTAB).
- A simple modification of Fau-CTAB zeolite carbon paste electrode was proposed.
- A new electrochemical sensor with amplified response was developed to detect the fungicide carbendazim.
- Low detection limit (0.0124 µmol L-1) with wide range of linearity was achieved.
- Application of the developed sensor on real samples.

Resumo/Abstract

Neste trabalho foi realizada a síntese da zeólita Faujasita (Fau), sua funcionalização com CTAB (Fau-CTAB) e aplicação eletroanalítica ao se desenvolver um novo sensor voltamétrico, a partir da modificação de pasta de carbono, para quantificação de carbendazim em amostras de águas superficiais. As zeólitas sintetizadas foram caracterizadas por XRD, FRX, potencial Zeta e FTIR. XRD demonstrou estrutura cristalina típica das zeólitas faujasita sem impurezas [1], estrutura que se manteve após a funcionalização com o CTAB. A Fau apresentou uma razão Si/Al no valor de 1,4 característico da faujasita X, enquanto o potencial Zeta mudou de -35.8 eV da zeólita Fau para +41.8 eV após a funcionalização. Esses resultados confirmam a eficiente funcionalização do cátion CTA^+ como cadeias duplas. Após a síntese foram preparados eletrodos de pasta de carbono contendo 4% de Fau e 2% de Fau-CTAB. O acréscimo das zeólitas como modificador promoveu o aumento da área efetiva dos eletrodos, no valor de 0,129 cm^2 e 0,620 cm^2 para os eletrodos CPE/Fau e CPE/Fau-CTAB, respectivamente. Utilizando a técnica de DPV, o eletrodo CPE/Fau-CTAB foi aplicado na detecção de carbendazim em tampão Britton-Robinson em pH 6. A precisão do método desenvolvido mostrou resultados satisfatórios de repetibilidade e reprodutibilidade, dentro dos limites aceitos pelo INMETRO. A curva analítica apresentou duas faixas lineares de 0,05 a 0,35 µmol L^{-1} e de 0,35 a 3 µmol L^{-1}, os limites de detecção e quantificação calculados foram de 0,0124 µmol L^{-1} e 0,0377 µmol L^{-1}, respectivamente. O sensor proposto foi aplicado com sucesso para a determinação de CBZ em amostra de água superficial obtendo valores de recuperação na faixa de 98,91 a 103,61%.

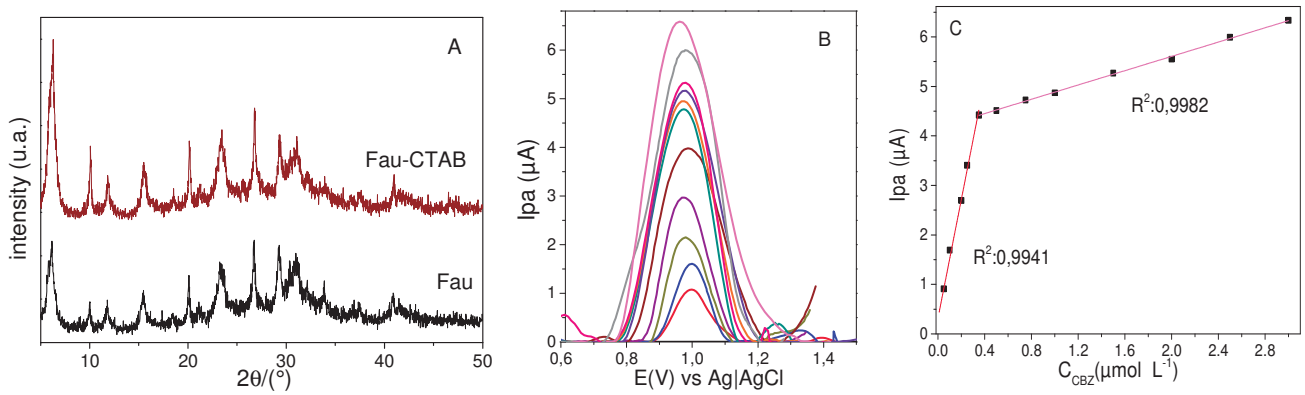


Figure 1: XRD das zeólita Fau e Fau-CTAB (A), DPV (B) e curva analítica (C) para diferentes concentrações de CBZ utilizando o eletrodo CPE/Fau_CTAB.

Agradecimentos/Acknowledgments

Os autores agradecem à FAPERJ, PROPPI e ao CNPQ pelo suporte financeiro.

[1] DAGLI, Zülfiye; ATALAY-ORAL, Cigdem; TATLIER, Melkon. Effects of using substrate heating method for the preparation of zeolite coatings containing faujasite. **Brazilian Journal Of Chemical Engineering**, v. 40, n. 3, p. 817-825, 14 nov. 2022.

Área: ELE

Voltammetric determination of lead(II) in different matrices using a 1,3-*bis*(4-ethyl-1H-1,2,3-triazol-1-yl)propan-2-one modified electrochemical sensor

Brenda R. L. Freire (PG),[1*] Maria E. da C. V. Nascimento (IC),[1] Jonatas de O. S. Silva (PG),[2] Carla L. C. Meira (PQ),[2] Mauricio Moraes Victor (PQ),[2] Eliana Midori Sussuchi (PQ).[1]

brendafreire.ufs@hotmai.com

[1]Programa de Pós-Graduação em Química, PPGQ-UFS, Departamento de Química, UFS; [2]Programa de Pós-Graduação em Química-UFBA.

Palavras Chave: *Voltammetry; Modified Electrodes; Bis-triazoles; Heavy Metals; Lead.*

Highlights

A new electrochemical sensor modified with 1,3-bis(4-ethyl-1H-1,2,3-triazol-1-yl)propan-2-one (BTE) has been developed.
BTE was used for determination of lead(II) in tap water, river water and gunshot residues.

Resumo/Abstract

The detection of heavy metals in solution is necessary due to their toxic properties, capacity for bioaccumulation, and harm to living organisms. Chemically modified electrodes have been widely used as an alternative for detecting ions due to their improved selectivity resulting from specific interactions with these analytes. Therefore, ligands derived from *bis*-triazolic compounds emerge as new materials capable of interacting with metal ions, potentially enhancing the detectability of the electrode. In this context, this study aimed to obtain an electrode modified with 1,3-*bis*(4-ethyl-1H-1,2,3-triazol-1-yl)propan-2-one (BTE) and a method for the quantification of lead(II) ions was developed, wherein differential pulse voltammetry (DPV) demonstrated that BTE possesses remarkable detectability against Pb^{2+}. Optimization of the scanning medium parameters and DPV technique resulted in approximately a 7-fold increase in the analytical signal current of Pb^{2+}. An analytical curve was obtained, and the developed method achieved a limit of detection (LOD) of 0.10 nmol L^{-1}. It was applied to quantify the analyte in tap water (Fig. 1a), river water samples (Fig. 1b), with recovery values obtained at three different concentration levels ranging from 87.80% to 118.46% and gunshot residue samples (Fig 1c and d). Consistent results were obtained compared to those obtained by Atomic Absorption Spectroscopy (AAS) for gunshot residue samples, highlighting the reliability and precision of the developed method.

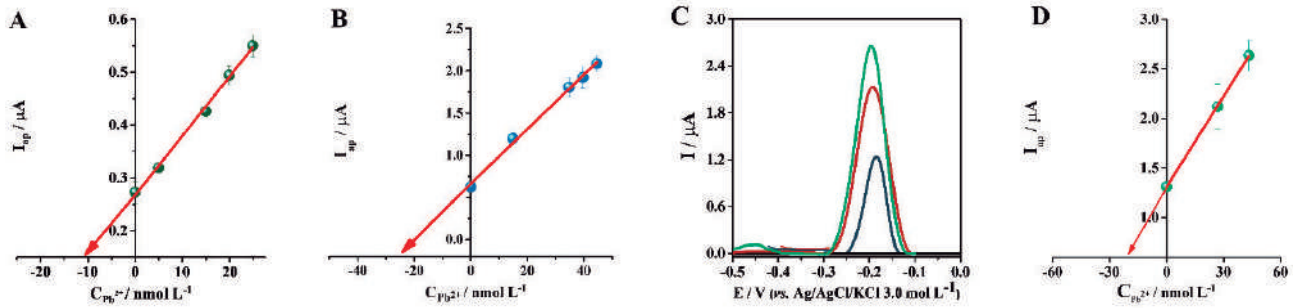


Figure 1. Anodic peak current intensities obtained as a function of Pb^{2+} concentration: **a)** in tap water; **b)** in river water; **c)** in gunshot residue; **d)** Differential pulse voltammograms corresponding to the standard addition curve obtained by BTE for the determination of Pb^{2+} in gunshot residue sample.

Agradecimentos/Acknowledgments

Área: ELE

Zeolitic Imidazole Framework-Based Materials by Mechanochemical Synthesis Applied as Positive Electrodes in Lithium-Sulfur Batteries

Heloise M. Sintaku[1*] **(IC), Breno L. Souza**[1] **(PG), Paulo F. M. Oliveira**[1] **(PQ), Roberto M. Torresi**[1] **(PQ)**

heloise.sintaku@usp.br

[1]*Institute of Chemistry (IQ), University of São Paulo*

Palavras Chave: ZIF, MOF, Mechanochemistry, Electrochemistry, Batteries, Li-S

Highlights

Improve lithium-sulfur batteries' electrochemical performance with ZIF-based materials to mitigate the *shuttle* effect. Enhance and optimize mechanochemical synthesis for porous materials in LiBSs.

Resumo/Abstract

The increasing energy demand, driven by the expansion of portable devices, has led to a search for more efficient energy storage solutions. Lithium-sulfur batteries (LiBSs) have emerged as a promising option, offering a high theoretical capacity (1675 mAh g^{-1}) and energy density (2600 Wh kg^{-1}), as well as the low cost of sulfur, its non-toxic nature and abundance. However, before LiBSs can be widely adopted, several challenges must be addressed, such as the *shuttle* effect caused by polysulfide dissolution, the expansion during lithiation, and sulfur's insulating property. Effective sulfur encapsulation and adsorption can be achieved by optimizing the positive electrode structure using metal-organic frameworks (MOFs) such as ZIF-S and conductive polymers, which are excellent sulfur hosts for Li-S batteries **[1]**. The synthesis of ZIF-S was performed in an MM400 ball mill. ZnO, 2-methylimidazole (2-MeIM), and 2-mercaptoimidazole (2-MerIM) were combined in a stainless-iron jar along with ethanol as liquid-assisted grinding solvent. Three varying ratios of 2-MeIM:2-MerIm were tested: (45:55); (40:60) and (25:75). These compounds were melted with sulfur at 155ºC for 12h, then the composites (ZIF-S:S_8) formed were mixed with CarbonBlack 65 and poly(vinylidene fluoride) in a ratio of 70:20:10 and coated in an Al-C current collector foil. Up to now, this study suggests that applying ZIF-S as positive electrodes in Li-S batteries catalyzes the formation process of long-chain polysulfides (Li_2S_x, 4<x<8), commonly seen at 2.31 V, that results in irreversible loss of sulfur and rapid capacity degradation by the polysulfide dissolution in the electrolyte. It is interesting to note that the addition of a higher amount of 2-MerIM leads to greater suppression of the formation of soluble polysulfide, as demonstrated in Figure 1b. In addition, the formation of these intermediates is shifted to lower potentials in the case of proportions of 60 and 75 wt%, in comparison to the ZIF-8 metal-organic framework. This indicates that the amount of ligand added plays a crucial role in controlling polysulfide formation and even possibly catalyzing the reaction kinetics. **[1]** Susana Chauque, Breno L. Souza, Heloise M. Sintaku, Rômulo A. Ando, Roberto M. Torresi, Unveiling the polysulfide-PPY interaction for enhanced lithium–sulfur battery performance, Electrochimica Acta, V. 475 (2024).

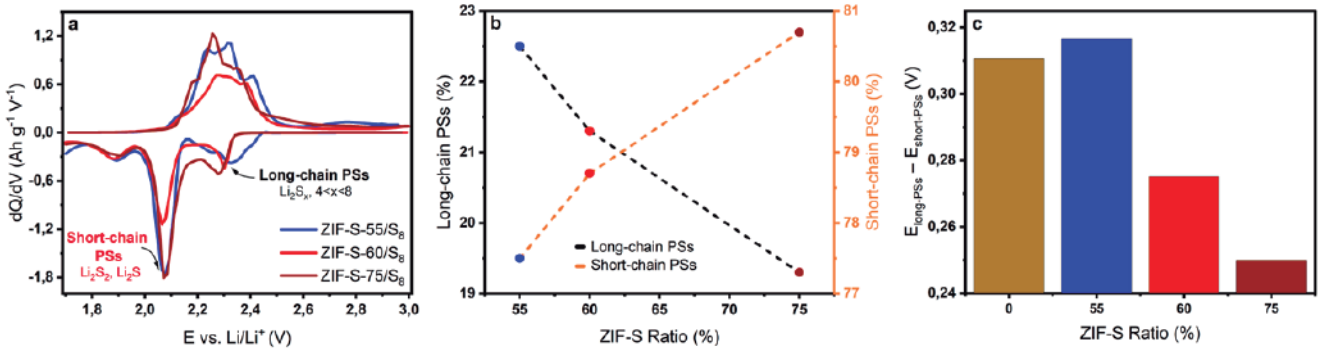


Figure 1. a) Derivate of galvanostatic curves versus potential. b) Polysulfide formation in function of ZIF-S ratio extracted from dQ/dV graph. c) ΔE between long-chain and short-chain polysulfide. All the tests were performed between 3.0 and 1.7. V vs. Li/Li^+ in an electrolyte of 1 mol L^{-1} LiTFSI - DME/DOL containing 1% of $LiNO_3$ as additive.

Agradecimentos/Acknowledgments

This work was supported by FAPESP (2022/10235-4; 2019/09341-1; 20/14955-6; 2021/00675-4 respectively); IQ-USP.

FIS

Físico-Química

Sociedade Brasileira de Química

Área : FIS

Application of Raman Spectroscopy in the Analysis of Induced Osteoporosis in Rats Subjected to Early Menopause

Luana B Regazi (IC),[1] Rafael de Oliveira (PG),[1] Camila de Souza Acosta (IC), [2] Amanda Andrade Policarpo (IC), [2] Evelise Aline Soares (PQ), [2] Silvia Graciela Ruginsky Leitão (PQ), [2] Flávia Da Ré Guerra (PQ),[2] Antonio Carlos Sant'Ana (PQ).[1]*

luana.regazi@estudante.ufjf; antonio.sant@ufjf.br

[1]*Depto. de Química, Univ. Fed. Juiz de Fora, MG;* [2] *Instituto de Ciências Biomédicas, Univ. Fed. De Alfenas, MG.*

Palavras Chave: *Vibrational Spectroscopy, Ovariectomy, Apatite.*

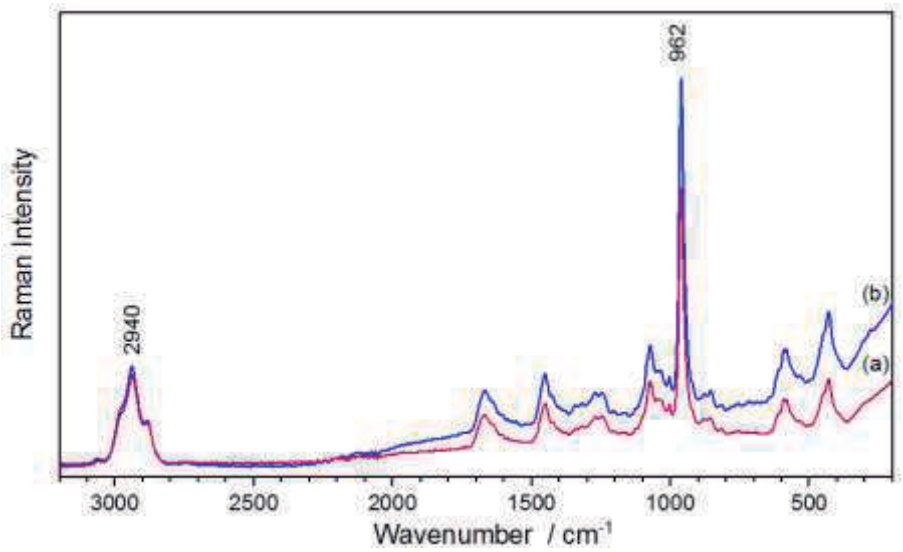
Highlights

The study of Raman spectral patterns of bones from femur of rats submitted to ovariectomy allows detecting induced osteoporosis effects, unveiling molecular findings for diagnosis and therapy.

Abstract

Menopause, a natural phase in the end of reproductive life of mammals, corresponds to the cessation of the hormonal activities, with the progressive reduction in the production of, as for instance, progesterone and estrogen. Such hormones play crucial roles in bone remodeling regulation. It is know that decreases in estrogen levels results in reduced inhibition of osteoclasts, leading to the increase of the bone mass loss, potentializing the development of osteoporosis.

This study aims to analyze the influence of menopause, induced by ovariectomy, on the development of osteoporosis effect, which can be observed in femur of rats, through Raman spectroscopy. The investigation was done on the femur diaphysis. Such a vibrational technique allows discerning the presence of mineral and organic materials in bones, as well as the proportion between them. Such results were compared with similar samples originated from female rats that were not submitted to the ovariectomy, as well as two additional set of samples from similar origin, but submitted to melatonin treatment. The observed changes in Raman spectral patterns leaded to the characterization of osteoporosis diagnostic.



As an example of the possible comparative study through Raman spectroscopy, Fig. 1 shows two spectral patterns of internal medullary channel and external diaphysis portions from a fractioned femur. The significant difference in the relative intensities of both band at 962 cm^{-1-}, assigned to PO_4^{3-} and at 2940 cm^{-1}, assigned to CH stretching of organic compounds, indicates organic mater is more abundant in the internal region of the bone.[1]

Fig. 1: Raman spectra of femur bone took in (a) internal medullary channel and (b) external portions of diaphysis.

Reference:

[1] Penel, G, et al., Calcif. Tissue Int. 1998 (63) 475.

Acknowledgments

The authors would like to thank the funding agencies CNPq, CAPES and FAPEMIG.

Área: FIS

Aqueous foams stabilized by polysaccharide nanoparticles

Priscila da C. Rodrigues (IC),[1*] Guilherme A. Ferreira (PQ),[2] .

priscilarodrigues@ufba.br

[1]*Departamento de Físico-Química, Instituto de Química, Universidade Federal da Bahia, Salvador-BA*

Palavras Chave: *(Foams, Polysaccharides, Nanoparticles).*

Highlights

Nanoparticles, due to their high adsorption energy at the air-water interface, can favor the stabilization of foams made with formulations containing them.

By controlling the solution conditions, it is possible to tune foam formation and stability.

Resumo/Abstract

Liquid-gas foams are colloidal systems formed by air bubbles separated by thin liquid films. From a thermodynamic point of view, they are metastable dispersions of two immiscible phases (gas/water) that separate over time. Since they become unstable under small disturbances, surfactants are added to these systems to increase the volume and lifetime of the resulting foams. However, their use, can be harmful, leading to human health and environmental problems considering their petrochemical origin. Nanoparticles, on the other hand, due to their high adsorption energy at the air-water interface, can favor the stabilization of aqueous foams in the absence of any added surfactant or with smaller concentrations of it. In this sense, polysaccharides are promising materials to prepare these nanoparticle owing to their availability, low cost and biocompatibility. In this perspective, the objective of this work is to investigate the stability of aqueous foams prepared different cellulose-based, nanoparticles formed either by the biopolymer or the biopolymer combined with small amounts of surfactants. Foams were prepared using the Bartch method and different solution conditions, like pH, ionic strength and biopolymer concentration, were investigated. Collectively, the results demonstrated that it is possible to control foam formation and stability by tunning these parameters and further investigation will be conducted to elucidate the mechanism behind the formation of foams.

Agradecimentos/Acknowledgments

To PIBIC for funding the research, and to the Colloids & Surfaces research group for their support.

Área: FIS

Aqueous suspensions of activated charcoal stabilized by cardanol-derived surfactants

Lucas P. Teixeira (IC),[1] Guilherme A. Ferreira (PQ),[1]

lucas.pteixeira@hotmail.com

[1]*Departamento de Físico-Química, Instituto de Química, Universidade Federal da Bahia, Salvador-BA*

Palavras Chave: *Activated Charcoal, Surfactant, Aqueous Suspension, Cardanol*

Highlights

Higher concentrations of sodium dodecyl sulfate (SDS) result in aqueous suspensions of activated charcoal (AC) with good stability.

Cardanol-based, nonionic surfactants are being studied due environmental and health concerns related to the use of SDS.

Resumo/Abstract

Most commercial surfactants, such as SDS, are harmful to the environment and to human tissue. However, countless daily products based on AC use these surfactants in order to generate long-lived aqueous suspensions. The aim of this study was to investigate the stabilizing effect of SDS and of nonionic surfactant derived from cardanol as an eco-friendly alternative. In order to determine quantitatively the capacity of SDS to stabilize aqueous suspensions of AC, absorbance as a function of time for the suspensions at different SDS concentrations was monitored (Figure 1). Small absorbance values imply in a greater AC sedimentation, thus indicating lower stability. Based on that, absorbance decrease rates were calculated and are presented in Table 1. The conclusion was that higher concentrations of SDS and lower concentrations of AC resulted in a lower rate of change, assuring better stability. After understanding this system, the next steps of this research will be to use cardanol ethoxylates to replace SDS as they are non-ionic surfactants and come from natural sources.

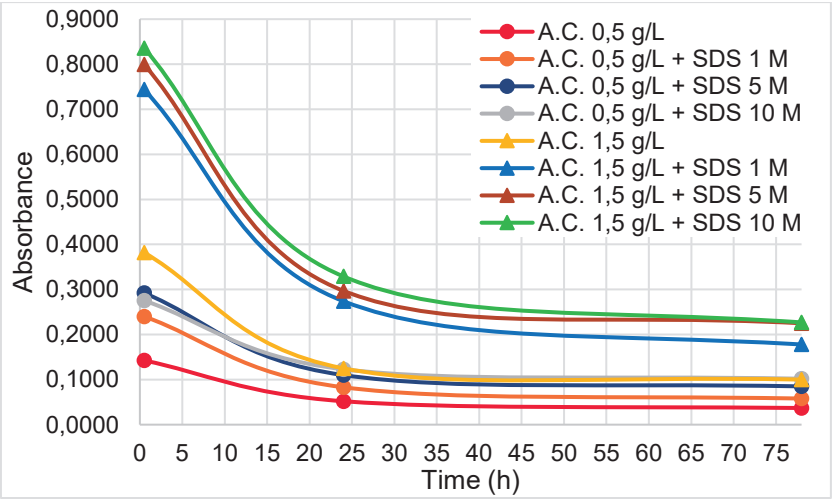


Figure 1. Absorbance of aqueous suspensions of activated charcoal with SDS at different concentrations *versus* time.

Table 1. Rate of change of suspensions of activated charcoal (AC).

Suspensions	$\lvert dA/dt \rvert$ (s^{-1}) (0 to 60 s)	R^2
AC 0,5 g/L	0,0006	0,988
AC 0,5 g/L + SDS 1 mM	0,0005	0,960
AC 0,5 g/L + SDS 5 mM	0,0004	0,976
AC 0,5 g/L + SDS 10 mM	0,0003	0,982
AC 1,5 g/L	0,0018	0,989
AC 1,5 g/L + SDS 1 mM	0,0009	0,985
AC 1,5 g/L + SDS 5 mM	0,0009	0,966
AC 1,5 g/L + SDS 10 mM	0,0011	0,965

Agradecimentos/Acknowledgments

CNPq, PIBIC UFBA, Cardolite

Área: FIS
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Artificial Intelligence Meets Quantum Computing or Quantum Active Learning for Material Design and Discovery

Maicon P. Lourenço[1*](PQ), Hadi Zadeh-Haghighi[2](PQ), Jiří Hostaš[3](PQ) and Dennis R. Salahub[2] (PQ)

maiconpl01@gmail.com

Departamento de Química e Física, UFES[1]; Department of Chemistry, University of Calgary[2]; NRC Canada[3].
Keywords: Quantum *Machine Learning, Quantum Active Learning, Experimental Design, Perovskites, Support Vector Machines.*

Highlights

A **quantum active learning** (QAL) method for experimental or material design was developed and implemented in **MLChem4D**. This **quantum artificial intelligence** (AI) technology has the potential of finding optimum solutions, within the chemical space, in materials science and in other branches of chemistry.

Abstract

Artificial intelligence (**AI**) has already met quantum computing[1]. Here, this is explored through the development of a *quantum active learning*[1] (**QAL**) method for experimental or material design. QAL uses quantum machine learning (**QML**) regressions and their epistemic uncertainties for decision making (the agent), Fig. 1-left. The QAL method was implemented in the MLChem4D[2] software and applied in perovskites, aiming to improve their properties. QML and QAL have the potential of improving the quality of inferences, making the agent "smarter" – to choose, with higher probability, the next material with enhanced properties to be synthesized/computed, with fewer experiments. Fig. 1-right shows the QAL results for double-perovskites band-gap minimization using quantum support vector regression (**QSVR**). QAL with different feature maps (Fig. 1-center) – to build QSVR models with fidelity quantum kernel – performed better than the classical **AL** – using classical **SVR**[2], with radial basis function kernel[2].

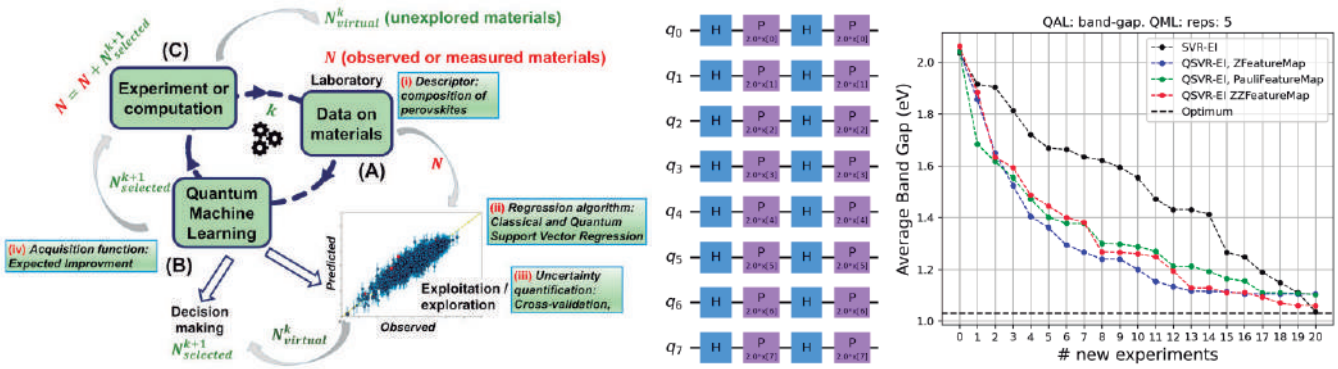


Figure 1. Left: *QAL method.* ***Center:*** *ZFeatureMap with 8 qubits circuit used to obtain the* QSVR models with fidelity quantum kernel. ***Right:*** *average $A_2BB'O_6$ (double-perovskite) band-gap minimization for 20 QAL independent runs as a function of new experiments. (Q)SVR: (Quantum) Support Vector Regression. XFeatureMap: X = Z, ZZ, Pauli. EI: expected improvement.*

QAL applied for double-perovskites proved to be efficient, bringing new perspectives in exploring QML algorithms to walk in uncharted regions of chemical space for new and efficient discoveries on-the-fly, using small data.

[1]*Huang, et al.; Power of data in quantum machine learning; Nat. Commun. 12, 2631 (2021).* [2]*Lourenço et al.; Active Learning for Optimum Experimental Design – Insight into Perovskite Oxides; Can. J. of Chem. 9, 734 (2023).*

Acknowledgments

Fundação de Amparo à Pesquisa do Espírito Santo (FAPES); Conselho Nacional para o Desenvolvimento Científico e Tecnológico (CNPq); Coordenação de Aperfeiçoamento de Pessoal de Ensino Superior (CAPES). National Research Council of Canada, Artificial Intelligence for Design program and by the Natural Sciences and Engineering Research Council of Canada, Discovery Grant (RGPIN-2019-03976).

Área: FIS

Bile salts/cellulose nanofibrils self-aggregates for potential use as hydrogels

Davi Siqueira da Silva de Souza (PG),[1] Vinícius Augusto Peixoto Tartare (IC),[2] Giovana Cristina Zambuzi (PG),[1] Brenda da Silva Bega (IC),[2] Kelly Roberta Francisco (PQ),[1,2*].

davisssouza@hotmail.com; kfrancisco@ufscar.br

[1]Material Science Graduate Program, UFSCar; [2]Department of Natural Sciences, Mathematics and Education, UFSCar

Keywords: *Self-aggregation, Biosurfactants, Nanocellulose, Rheology, Hydrogels.*

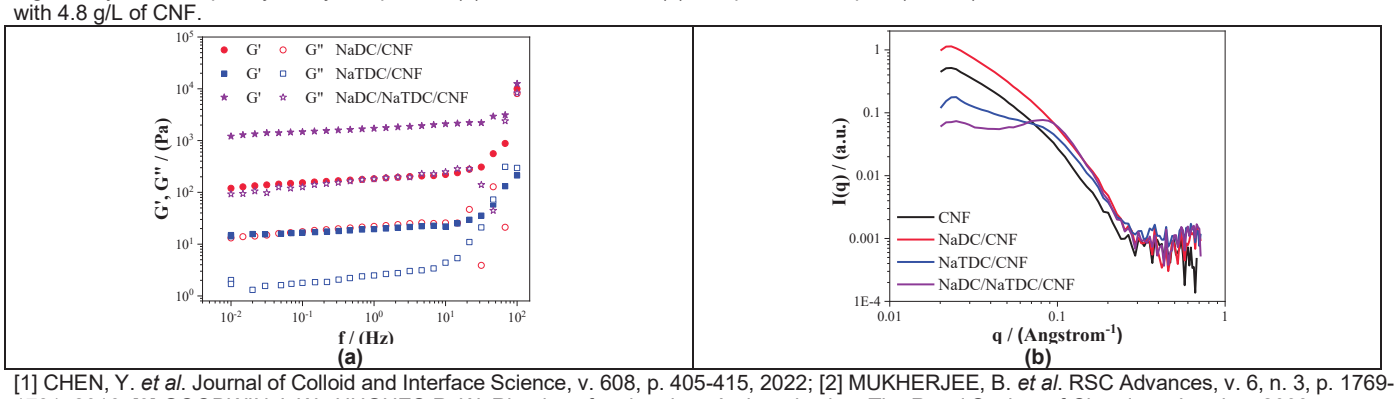
Highlights

Viscoelastic systems were formed by long self-assembling bile salts/cellulose nanofibrils aggregates. Binary bile salts system increase hydrogel force and form longer aggregates. Results have potential use as drug carriers' materials.

Abstract

Bile salts are surfactants that at concentrations above the critical micellar concentration (cmc) form aggregates spontaneously in ordered and/or disordered phases, driven by hydrophobic interactions in the aqueous phase[1]. Self-aggregated structures can be altered in the presence of certain molecules[2], such as cellulose nanofibrils (CNF), affecting the size, shape, and distribution of the aggregates, and, consequently, leading to changes in the rheological behavior of the systems. Here, aggregates formed by 50 mM of sodium deoxycholate (NaDC), 50 mM of sodium taurodeoxycholate (NaTDC), or 50 mM NaDC/ 50 mM NaTDC mixed with 4.8 g/L of CNF in aqueous medium was investigated using Dynamic Light Scattering (DLS), Zeta Potential (ZP), rheology, and Small-angle X-ray Scattering (SAXS). DLS results showed smaller particles in NaDC/NaTDC/CNF system (304,2 nm), followed by NaDC/CNF (596,1 nm) and NaTDC/CNF (1780 nm). ZP values showed stable systems, with values of -46,8 ± 8,9 mV, -68 ± 16,9 mV and -60,3 ± 3,1 mV for NaDC/CNF, NaTDC/CNF, and NaDC/NaTDC/CNF systems, respectively, and NaTDC/CNF system is more stable. Rheological curves obtained in the oscillatory mode confirm that systems are viscoelastic and G' and G" moduli did not change in a wide range of frequency (Fig. 1 *a*) suggesting gel-like behavior for all the systems[3]. NaDC/NaTDC/CNF hydrogel is more viscoelastic (G_0 = 2011 Pa) and stronger than NaDC/CNF (G_0 = 210,1 Pa) and NaTDC/CNF (G_0 = 22,58 Pa), since G'/G" are greater (8,88), in first case, followed by NaDC (8,39) and NaTDC (6,66) suggesting more entanglements between the aggregates in binary bile salts system. SAXS curves (Fig. 1 *b*) showed aggregates with cylindrical morphology, longer in NaDC/NaTDC/CNF, confirming high degree of entanglements in that case, and shorter aggregates of NaTDC/CNF, suggesting a weaker gel formation of NaTDC/CNF, as observed in rheology. Intermolecular interactions, such as hydrogen bond, electrostatic and van der Waals interactions established among NaDC/CNF, NaTDC/CNF and NaDC/NaTDC/CNF had played an important role in the formation of hydrogels with potential application in pharmaceutical and cosmetics industry.

Fig. 1 – Dynamic frequency assay comparison (a) and SAXS curves (b) of equimolar samples (50 mM) of NaDC, NaTDC and NaDC/NaTDC mixed with 4.8 g/L of CNF.



[1] CHEN, Y. *et al.* Journal of Colloid and Interface Science, v. 608, p. 405-415, 2022; [2] MUKHERJEE, B. *et al.* RSC Advances, v. 6, n. 3, p. 1769-1781, 2016; [3] GOODWIN J. W., HUGHES R. W. Rheology for chemists: An introduction. The Royal Society of Chemistry, London, 2000.

Acknowledgments

CAPES FAPESP CNPEM GFCx LaQuiMoBio

Área: FIS

Chemical modification of calabash biomass through neutralization hydrolysis: Adsorption kinetic studies of indigotine dye

Stephany B. Franceschini (IC),[1] Keller P. Nicolini (PQ),[1] Jaqueline Nicolini (PQ)*[1]

jaqueline.nicolini@ifpr.edu

[1] *Instituto Federal de Educação, Ciência e Tecnologia do Paraná – IFPR, Av. Bento Munhoz da Rocha Neto s/n, 85555-000 – Palmas - PR*

Keywords: green adsorbent, indigotine dye, kinetic parameters.

Highlights

Pseudo-second order kinetics occur to materials at 25 °C. Intraparticle diffusion occur just in 55 °C.

Abstract

The search for new environmentally friendly adsorbent materials are employed in different areas, to removal dyes and drugs[1, 2] or metals.[3] The aim of this study was investigate the effect of chemical modification through neutralization hydrolysis of calabash biomass using indigotine dye in adsorption kinetic studies. Was used as biosorbent calabash (*Lagenaria*, LG). The LG was ground, washed, dried (40-50 °C) and ground (<150 µm) (LG in natura (LG-in)). Part of LG-in was chemically modified by neutralization hydrolysis, using 0.1 mol L^{-1} NaOH solution for 24 h and washed again with water. The LG biomass was then left in a 0.1 mol L^{-1} HCl solution for 2-3 h to remove traces of NaOH (LG-a/b). The "basic phase" using NaOH solution allows delignify the biomass[4] and the use of HCl solution in addition to removing NaOH traces, promotes agglomeration of fibers of lignocellulosic materials.[5] The pH was determined using 0.1500 g±0.0003 g of LG in 20 mL of distilled water for 30 min (LG-in pH=8.4; LG-a/b pH=7.2). Kinetic tests were carried out until equilibrium (t=30 min; T=25 and 55 °C; indigotine dye (IND) concentration 3.0 x 10^{-5} mol L^{-1}) using 0.1500 g of each biomass in 20 mL of aqueous IND solution. Data fitted to pseudo-first-order model indicates physical adsorption, just to LG-in, at 25 °C. The kinetic parameters (Tab.1) demonstrate that the amount of IND adsorbed calculated at equilibrium obtained from pseudo-second-order kinetics (chemical adsorption) is equivalent to the maximum amount of IND adsorbed in equilibrium at 25 °C (Tab.1). Pseudo-second kinetics (Tab. 1) indicate that the sorption is determined by the rate of adsorption reactions, occurring at the solid/liquid interface.[6] In intraparticle diffusion, the adsorbate molecules infiltrate the interior of the adsorbent particles.[7] The data indicate that this mechanism occur just in 55 °C (Tab. 2), representing the stage of gradual adsorption by diffusion intraparticle.[8]

Table 1. Coefficients of pseudo-second-order diffusion kinetic constants

			Pseudo-first-order			Pseudo-second-order		
Material	T (°C)	$q_{e,exp}$	$q_{e,cal}$	k_1	R^2	$q_{e,cal}$	k_2	R^2
LG-in	25	1.76×10^{-2}	NF	NF	NF	1.90×10^{-2}	-29.93	0.84
LG-a/b	25	8.78×10^{-3}	1.30×10^{-2}	-4.40×10^{-2}	0.91	8.15×10^{-3}	-25.92	0.87

Pseudo-second-order:[9] q_e (mg g^{-1}): amount adsorbed in equilibrium; k_2 (g mg^{-1} min^{-1}): second-order adsorption constant. *NF = no fit.*

Table 2. Coefficients of intraparticle diffusion kinetic constants

Material	Intraparticle diffusion			
	T (°C)	C	K_p	R^2
LG-in	55	1.20×10^{-3}	1.30×10^{-3}	0.83
LG-a/b	55	4.60×10^{-3}	-2.20×10^{-3}	0.91

Intraparticle diffusion:[8] C (mg g^{-1}): constant related to diffusion resistance; K_p (mg g^{-1} $min^{-1/2}$): intraparticle diffusion coefficient.

Acknowledgments

LACOPPI, IFPR, PIBIC/CNPQ, CNPq

1. Sulak, M. T., Yatmaz, H. C. *Desalin. Water Treat.* **2012**, 37 (1-3), 169.
2. Rusu, L., et al. *Mater.* **2021**, 14 (17), 4810.
3. Dawwam, G. E., et al. *Sci. Rep.* **2023**, 13 (1), 891.
4. Santos, R. d., et al. *Cienc. Florestal* **2016**, 26, 1281.
5. Teixeira, E. d. M., et al. *Polímeros* **2010**, 20, 264.
6. Bojić, D. V., et al. *Desalin. Water Treat.* **2013**, 51 (34-36), 6871.
7. Dada, A. O., et al. *Sci. Rep.* **2021**, 11 (1), 16454.
8. Carvalho, T. E. M. d., et al. *Quim. Nova* **2010**, 33, 358.
9. Debrassi, A., et al. *Quim. Nova* **2011**, 34 (5), 764.

Área: FIS

Coacervation in hair care products formed by anionic surfactants and cationic polymers

Stephany Chaiben (PG),[1] Julia Pereira (IC),[1] Matheus Ouverney Ferreira (PG),[1] Karina Oliveira Lima (PQ),[1] Ana Maria Percebom (PQ).[1]*

apercebom@puc-rio.br*

[1]*Departamento de Química, Pontifícia Universidade Católica do Rio de Janeiro, PUC-Rio*

Keywords: *Colloids, Polyelectrolytes, Cosmetics, Liquid Crystals, Phase behavior*

Highlights

Micellar solutions of surfactants and polymers can form a liquid crystalline phase upon dilution
The deposition over hair strands is more dependent on the polymer than on the coacervation phenomenon

Abstract

Oppositely charged polymers and surfactants are very common in shampoos with a conditioning effect because they can be deposited over hair surface through a phase separation induced by dilution. This effect needs to be controlled to guarantee phase separation in adequate quantity and moment (avoiding it in the shampoo bottle, for example). The molecular structure and concentration of surfactants and polymers and the ionic strength are parameters expected to affect this phenomenon, but their effects were not fully elucidated for practical conditions. In this study, we used surfactants and polymers commonly used in the cosmetic industry: sodium lauryl ether sulfate (SLES), disodium laureth sulfosuccinate (SS), or sodium lauryl sarcosinate (LS) combined with poly(diallyldimethylammonium chloride) (PDADMAC) or cationized hydroxyethylcellulose (cat-HEC) to elucidate how molecular structure affects dilution-induced coacervation, using a typical concentration range of hair care products. Zeta potential, small-angle X-ray scattering (SAXS), and optical microscopy provided colloidal characterization of the samples. Deposition on hair strands was assessed through polarized optical and atomic force microscopy (AFM). Comparison between different surfactants showed that the coacervation depends on their chemical nature and charge density. According to SAXS results, the combination of SS or LS with PDADMAC, forms micellar solutions in concentrated samples, and a phase separation into a cubic mesophase (Pm3n) occurs upon dilution. The system formed by SLES and PDADMAC phase separates even at high concentrations. Microscopy of systems containing cat-HEC showed that efficient deposition over hair can occur even without coacervation and is mainly dependent on the polymer's chemical nature. The correlation between colloidal structures and macroscopic properties of this study provides tools to tune the properties of hair care formulations.

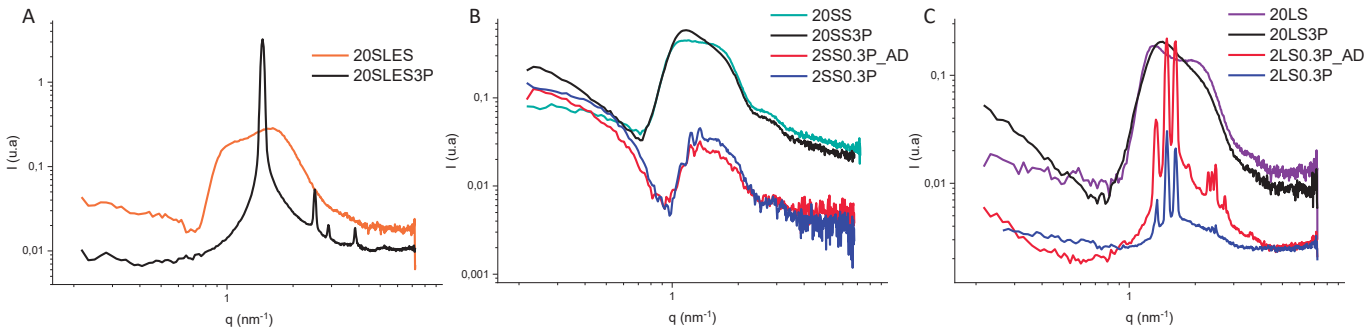


Figure 1: SAXS curves of different surfactants, SLES, SS, and LS, combined or not to PDADMAC at various concentrations. The acronym indicates the concentration and type of surfactant, followed by the concentration of PDADMAC (for example, 20SLES3P, means 20 wt% of SLES and 3 wt% of PDADMAC). When the samples were prepared by diluting a concentrated sample, _AD was added to the acronym.

Acknowledgments

Oxiteno, CNPq, FAPERJ and CAPES.

Área: FIS

Colorimetric Detection of Organophosphorus Pesticides: Rapid and Efficient Approach for Environmental Monitoring and Food Safety

Patricia M. Soares (PG),[1] Alex R. Teixeira (PG),[1] Renan B. Campos (PQ),[2] Elisa S. Orth (PQ).[1*]

patriciasoares@ufpr.br; elisaorth@gmail.com

[1]Departamento de Química, UFPR; [2]Departamento Acadêmico de Química e Biologia, UTFPR

Palavras Chave: *Agrochemicals, Derivatization, Acephate, Chemical security*

Highlights

- Promote the formation of a colored product through the derivatization reaction with simple molecules.
- Promote the colorimetric detection and monitoring of organophosphate pesticides in a fast, efficient and cost-effective way.

Resumo/Abstract

When used in excess, pesticides can pose risks to human health and the environment. Currently, in addition to the contamination of water supplies, several foods, both natural and industrialized, have presented high amounts of pesticides[1], which makes the detection and monitoring of these molecules extremely necessary. This study seeks to detect organophosphate pesticides, in this case acephate (ACF), through a rapid colorimetric method and using derivatization through simple molecules derived from nitrobenzenes. The kinetic monitoring for these reactions was monitored by the formation of colored products that absorbs in the UV-vis region (~350 nm), and which presents a different profile to that obtained for the hydrolysis of the precursors (Figure 1). Indeed, the precursors can hydrolyze and lead to colored products, but we were able to distinguish these reactions and validate the method. Therefore, the colorimetric detection of the pesticide was accomplished successfully in a few minutes. All reactions showed potential for detecting acephate in contaminated samples, which also showed to be selective. Studies using NMR spectroscopy indicate the formation of the proposed products. In summary, this study seeks a strategy for monitoring and detecting toxic and often carcinogenic substances, through a simple, direct and efficient approach.

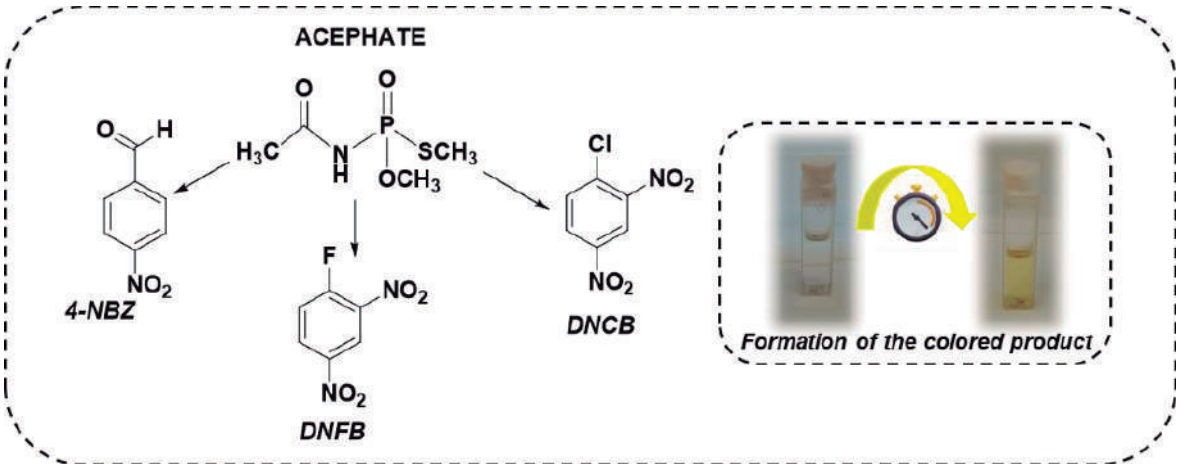


Figure 1. Kinetic profile of the colorimetric reactions (T=25°C and weakly basic aqueous medium).

Agradecimentos/Acknowledgments

UFPR, CAPES, CNPq, L'Oréal UNESCO-ABC, PhosAgro/UNESCO/IUPAC, INCT NanoVida, INCT Nanocarbono.

Área: FIS

Comparison of the rheological behavior of systems formed by lecithin, propylene glycol and different bile salts

Giovana C. Zambuzi (PG)[1]; Brenda da Silva Bega (IC)[2]; Davi Siqueira da Silva de Souza (PG)[1]; Vinícius Augusto Peixoto Tartare (IC)[2]; Kelly R. Francisco (PQ)[2]
giozambuzi@gmail.com; *kfrancisco@ufscar.br
[1]Programa de Pós-Graduação em Ciência dos Materiais, UFSCar; [2]Departamento de Ciências da Natureza, Matemática e Educação, UFSCar

Keywords: *Lecithin, Bile salt, Propylene glycol, Rheology, Self-aggregation*

Highlights

Bile salt/Lecithin systems were prepared in three different proportions, using three different bile salts and with the addition of propylene glycol. Phase separation was observed for some systems. Furthermore, the sizes of the aggregates formed were determined, as well as their rheological behavior.

Resumo/Abstract

Bile salts, such as sodium taurodeoxycholate (NaTDC), sodium deoxycholate (NaDC) and sodium cholate (NaC) are biosurfactants that have a polar face and a nonpolar face, produced in the liver and responsible for fat solubilization [1]. Lecithin is a natural zwitterionic surfactant, formed by two nonpolar tails and a polar head, found in soybeans and egg yolks[2]. Combining these two surfactants can generate the formation of different types of self-aggregated systems, which can be used for encapsulation and release of substances of interest. Propylene glycol is an aliphatic diol widely used in the pharmaceutical industry to develop drug delivery systems[3]. The systems were prepared from stock solutions of 200 mM lecithin and 100 mM bile salts (NaTDC, NaDC and NaC) solubilized in methanol. Three proportions were used: 0.2; 0.4 and 0.8 (mol/mol) Bile salt/Lecithin, stirring for 1 h. Then, the systems were placed in an oven at 35 °C for approximately 48 h to evaporate the methanol. Then, 10 mL cyclohexane and 0.001 g propylene glycol (PG) were added, and the systems remained stirring for 24 h at 100 rpm. Before the analyses were carried out, the systems remained at rest for at least 24 hours. After resting, phase separation was observed for the systems formed by NaTDC and NaDC, with the lower phase being more viscous. Aggregate sizes were measured using dynamic light scattering (DLS), for NaTDC the proportion of 0.2 presented the largest aggregates and the proportion of 0.4 presented the smallest aggregates. For NaDC and NaC, it was not possible to measure the aggregate sizes in the proportion of 0.8, due to technical limitations and, for these two salts, the smallest aggregates were observed in the proportion of 0.4. Rheological analyses showed that for the proportion of 0.2, NaTDC presented the highest zero shear viscosity value (η_0) (756.86 Pa.s), in the proportion of 0.4, NaC presented the highest value of η_0 ($2x10^3$ Pa.s) and in the proportion of 0.8, NaDC presented the highest value of η_0 ($169x10^3$ Pa.s). Through frequency sweep measurements, through the comparison between the storage (G') and loss (G") moduli, it was observed that the systems with a proportion of 0.2 for the three salts, 0.4 NaC and 0.8 NaTDC showed mostly elastic behavior. The 0.4 NaTDC, 0.4 NaDC and 0.8 NaC systems showed predominantly viscous behavior. Therefore, it is possible to conclude that the chemical structure of salts influences the behavior, size and type of aggregates formed,

References:

[1] SINGH, K. & CHAUHAN, S. Journal of Molecular Liquids. 316 (2020) 113833.
[2] CAUTELA, J. et al. Colloids and Surfaces A. 532 (2017) 411.
[3] LI, W. Z. et al. Journal of Controlled Release. 226 (2016).

Agradecimentos/Acknowledgments

CAPES
Fellowships: 88887.713913/2022; 0088887.713911/2022-00

FAPESP
Fellowships: 22/02092-9; 22/02089-8

CNPEM

Área: FIS

Degradação do corante reativo amarelo sidercron BF3RL pela oxidação com Fenton e avaliação da ecotoxicidade da reação.

[1]Maria Eduarda Santos Souza (IC), [1]João Pedro Cury Cesar (IC), [1]Paulo Cesar de Jesus (PQ)*, [1]Endler Marcel Borges (PQ).

pcj@furb.br; mess@furb.br

[1]Departamento de Química, Universidade Regional de Blumenau, FURB, Blumenau, SC; 89030-903.

Palavras-Chave: *corante, amarelo sidercron BF3RL, descoloração, degradação, Fenton, ecotoxicidade.*

Highlights

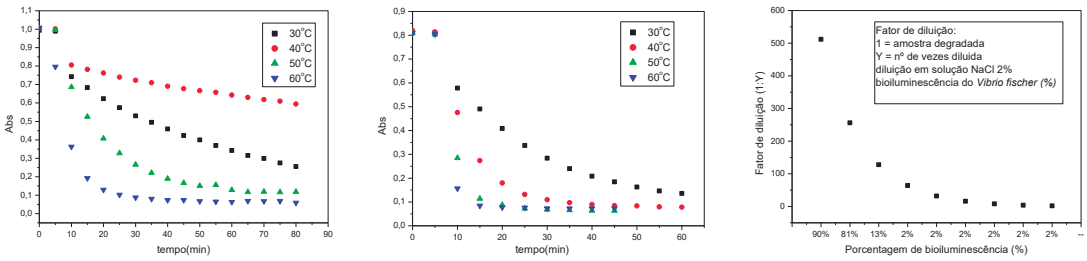
Degradation of the sidercron reactive yellow BF3RL dye by oxidation with Fenton and evaluation of the ecotoxicity of the reaction.

The efficiency of decolorization and degradation of the sidercron reactive yellow BF3RL dye by oxidation with Fenton and the ecotoxicity of the final product was evaluated. The Fenton system containing H_2O_2 3% was the most efficient, with 92% in 15 minutes. The percentage of bioluminescence decreases with increasing concentration of the final solution, increasing ecotoxicity. It is necessary to dilute the final product to dispose of it.

Resumo/Abstract

Eliminar corante residuais ainda tem sido objeto de pesquisa no mundo[1]. Neste trabalho foi estudado a degradação do corante reativo amarelo sidercron BF3RL, pela oxidação com Fenton, em diferentes concentrações de H_2O_2 (30%, 3%, 0,3% e 0,03%). Foi preparada solução de corante na concentração de 0,060 gL^{-1} e solução de Fenton ($H_2O_2/FeSO_4$) com 0,225g de $FeSO_4$ em 100mL de diferentes concentrações de H_2O_2, ajustando o pH para 2 com H_2SO_4. Foram transferidas para uma cubeta de quartzo termostatizada, 3 mL da solução de corante e 0,2 mL da solução de Fenton. Leituras da absorbância no comprimento de onda máximo do corante (λ_{max}= 415 nm) foram realizadas de 5 em 5 minutos, nas temperaturas de 30°C, 40°C, 50°C e 60°C. A eficiência de descoloração e degradação da solução do corante foi determinada. Experimentos foram realizados em duplicatas bem como os brancos. Para os ensaios de ecotoxicidade, no término dos experimentos foram efetuadas diluições das amostras com solução de NaCl 2%, e realizada as medidas da bioluminescência do microrganismo, Vibrio Fischer, utilizando o Lumistok. Diluições de 2, 4, 8, 16, 32, 64, 128, 256 e 512 vezes foram realizadas. As eficiências de degradação com diferentes concentrações de peróxidos, nas temperaturas de 30°C, 40°C, 50°C e 60°C. foram respectivamente: H_2O_2 30% (64,4%, 86%, 88% e 92%) H_2O_2 3% (86%, 90%, 92% e 92%), H_2O_2 0,3% (91%, 90%, 91% e 92%) e H_2O_2 0,03% (90%, 916%, 92% e 92%). As constantes de velocidade k_{obs} ficaram na faixa de 10^{-2} min^{-1} (r^2 ≥0,97) com $t_{1/2}$ variando entre 10min e 60min nos experimentos de 30ºC a 60ºC respectivamente. A **Figura 1** mostra o decaimento da absorbância para Fenton 30% e 3% e da ecotoxicidade. Comportamento similar foram observados nos demais experimentos, sendo o aumento da eficiência associado a diminuição da concentração de H_2O_2, nas condições experimentais estudadas. Ensaios de ecotoxicidade mostraram que o produto residual precisa ser diluído antes do tratamento e descarte, pois mesmo em baixa concentração o residual do Fenton apresenta toxicidade. A porcentagem de bioluminescência caiu de 90% com diluição acima de 100 vezes do produto final para 2% quando a diluição ficou abaixo de 50 vezes.

Figura 1 (a) decaimento da absorbância vs tempo para Fenton com H_2O_2 **(a)** 30% e **(b)** 3% em diferentes temperaturas. **(c)** porcentagem de bioiluminescência do *Vibrio Fischer.*



(a) **(b)** **(c)**

Referências e notas

(**1**) Mittersteiner, M.; Farias, N. R.; Barbieri, M.R.; Scharf, D. R.; Borges, E. M.; João, J. J.; De Jesus, P. C.; *J. Mol. Liq*. **2021**, 325.

Agradecimentos/Acknowledgments

Ao PIBIC/CNPq, INCT Catálise e FAPESC.

Área: FIS
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Effect of chitosan microsphere synthesis on the adsorption of erythrosine dye.

Bruna C. Badalotti (IC),[1] Fatima E. Borelli (IC),[1] Douglas C. Dragunski (PQ),[1] Reinaldo A. Bariccatti (PQ),[1*]

reinaldo.bariccatti@unioeste.br

[1]*Centro de Engenharias e Ciências Exatas, Unioeste*

Keywords: Biopolymer, Chromatic probe, Kinetics.

Highlights

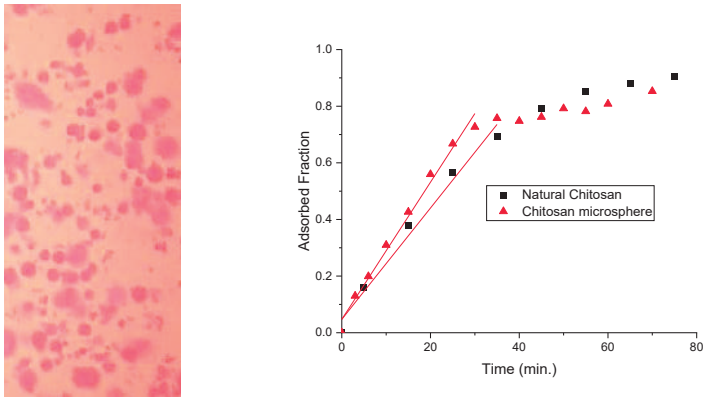
The adsorption speed of erythrosine on chitosan surface and chitosan microsphere was compared and it was found that the microsphere has an adsorption speed 20% higher than chitosan.

Resumo/Abstract

INTRODUCTION: Chitosan is derived from chitin, present in the exoskeletons of crustaceans and insects. It is abundant and renewable, has low production costs, non-toxic and functionalizable, and has chemical properties used in various areas such as: Biomedicine, Agriculture, Water treatment, Textile and Food industries. In this work we evaluated the effect of chitosan microparticle synthesis on the adsorption of erythrosine dye in relation to the starting chitosan.

PROCEDURE: The synthesis was adapted from Li et. al (RSC Adv., 10, 7163) where span 80 was replaced by Tween 80. A stock solution of 0.0221 $g.L^{-1}$ of erythrosine was prepared and 20.0 mL aliquots were placed under magnetic stirring with 0.0208 g of chitosan microsphere and with 0.0202g of chitosan. At predetermined times, absorption spectra were obtained (Shimadzu device, UV-1800).

RESULTS and DISCUSSION: Observe in Figure 1 A the chitosan microspheres in suspension (20X magnification) and in Figure 1 B the adsorbed fraction as a function of time. The fitted straight lines are shown and their angular coefficients are 0.024±0.001 $min.^{-1}$ (microsphere) and 0.020±0.002 $min.^{-1}$ (in natura chitosan), indicating that the microsphere has an adsorption speed 20% higher than the original.



(A) (B)

Figure 1 (A) Figure with chitosan microsphere and (B) Graph of the fraction of dye adsorbed as a function of time.

According to Figure 1 B, the maximum amount adsorbed is not significantly changed.

CONCLUSION: The synthesis of chitosan microspheres has an influence on the adsorption rate of the erythrosine dye.

Agradecimentos/Acknowledgments

To CNPq and Fundação Araucária for the S. I. Scholarships, to UNIOESTE and GIPeFEA for the laboratory structure.

Área: *FIS*

Experimental and computational investigation of new multicomponent solid forms of caffeic acid with nucleobases

Maria Vitória Porto (IC),[1,2*] Mário T. S. Rosado (PQ),[2] Ricardo A. E. Castro (PQ) ,[3] Flávio J. Caires (PQ).[1]

Maria Vitória Porto; mv.porto@unesp.br

[1] Departamento de Química Universidade Estadual Paulista UNESP-Bauru; [2] CQC-IMS, Departamento de Química, Universidade de Coimbra, Portugal;

Palavras Chave:*(Mechanochemical, Multicomponent solids, Caffeic acid, Nucleobases, Cocrystal, Co-amorphous).*

Highlights

Mechanochemistry was used to produce new cocrystals and co-amorphous forms of caffeic acid with co-formers cytosine and hypoxanthine. These were investigated by experimental and computational methods.

Abstract

Caffeic acid (CFA) is a insaturated phenolic acid with many potential medicinal applications, with bioavailability limited by its low aqueous solubility[1]. The search for new multicomponent solid forms is a common strategy to modulate the physico-chemical properties of substances. The supramolecular synthesis by mechanochemistry is viable for compounds that degrade upon melting while avoiding the use of solvents. In this work, caffeic acid was combined with two nucleobases: cytosine (CYT) and hypoxanthine (HPX) using different grinding conditions. The use of a drop of solvent in liquid-assisted grinding (LAG) tends to produce low-energy, ordered, crystal structures, while neat grinding (NG) favors amorphous forms, lacking long-range order. Amorphous solid phases often have improved solubility because of their high-energy, but being metastable, are prone to relax, crystalizing. Low-energy cocrystals are kinetically stable, with longer shelf life[2]. The crystalline content tends to be greater with CYT than HPX. While equimolar CFA-CYT mixtures resulted in a cocrystal by LAG, the CFA-HPX combination yielded a completely amorphous phase by NG. The new multicomponent solid forms were characterized experimentally by Powder X-ray Diffraction, Infrared Spectroscopy and Differential Scanning Calorimetry. The rationalization of the interactions stabilizing the molecular aggregation were explored by several computational methods, namely Molecular Electrostatic Potential (MEP)[3] and Independent Gradient Model (IGM-δg)[4] analyses, based on ω-B97XD DFT calculations.

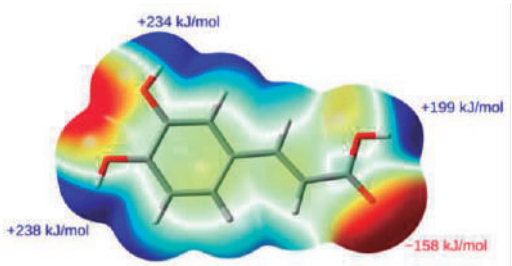


Figure 1. Molecular electrostatic potential of caffeic acid.

1 H. Mude, et al. Food Chemistry, 2022, 374, pp.1-11.
2 M.D.S.H. Mithu, et al. Journal of Drug Delivery Science and Technology, 2021, 63, pp. 1-11.
3 J.S. Murray, P. Politzer. WIREs Computational Molecular Science, 2011, 1 (2), pp. 153-163.
4 C. Lefebvre, et al. ChemPhysChem, 2018, 19 (6), pp.724-735.

Acknowledgments

Grants 2023/10545-6 and 2023/00909-0 São Paulo Research Foundation (FAPESP). CQC-IMS is funded by the Fundação para a Ciência e a Tecnologia (FCT) project UIDB/00313/2020, also co-funded by FEDER/COMPETE 2020-EU. Thanks are due to UCQFarma for the use of the PXRD facility.

Área: FIS

Exploring self-aggregated systems: rheological analysis of PEO solutions with lecithin and sodium deoxycholate"

Júlia S. Forster (PG),[2] Giovana C. Zambuzi (PG),[2] Davi S. S. Souza (PG),[2] Kelly R. Franscisco (PQ).[1]

forsterju@gmail.com

[1]DCNME - UFSCar; [2] CCTS - UFSCar

Palavras Chave: *Self-aggregated, Rheological, Poly(ethylene oxide), Lecithin, Sodium deoxycholate.*

Highlights

Bile salts/lecithin systems were prepared with different proportions of Poly(ethylene oxide) (PEO) of different molecular weights. More viscoelastic systems were obtained at higher concentrations and molecular weight of PEO.

Resumo/Abstract

The investigation of self-aggregated systems formed by lecithin and bile salt molecules has been widely studied, especially due to their physicochemical properties and relevance in various biomedical and pharmaceutical contexts.[1,2] The combination of these components makes it possible to create several structures, such as reverse micelles, liposomes or giant micelles and the addition of PEO can play a crucial role as a stabilizing agent, influencing the structural modification and packing of these aggregates.[2,3] In this context, nanoaggregates of bile salt/ lecithin were prepared using stock solutions of 200 mM lecithin and 200 mM sodium deoxycholate (NaDC) solubilized in an aqueous medium. After, PEO of 400 g/mol or 4000 g/mol was added to the systems at 1% (w/w), 2.5% (w/w) and 5% (m/w) . The systems were analyzed by rheological tests, and, comparing. systems with PEO 4000 and PEO 400 (Fig.1), systems containing PEO 4000 showed higher viscosity at low shear rates due to the formation of entanglement structures. Systems containing PEO 400 presented lower viscoelasticity (Fig. 2), since G' (storage modulus) is lower than G'' (loss modulus), while the addition of PEO 4000 produced systems highly viscoelastic. Thus, the effect of molecular weight of PEO on the rheology of lecithin/ NaDC/ PEO systems played an important role in obtaining viscoelastic systems due to the entanglement among the nanoaggregates formed.

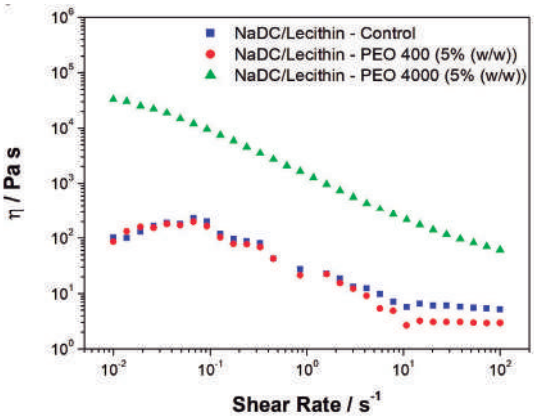


Figure 1: Flow curves of NaDC/ Lecithin systems.

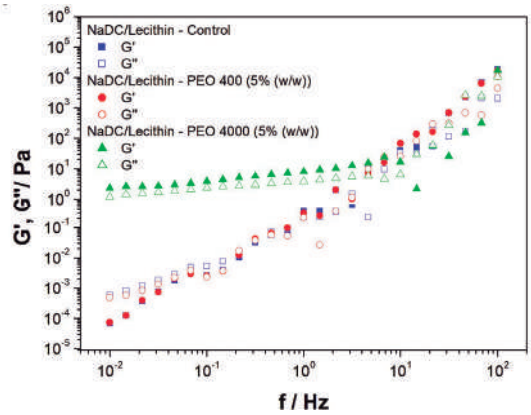


Figure 2: Oscillatory tests for NaDC/ Lecithin systems.

[1] HANIO, S. et al. Langmuir. 37 (2021) 2543.
[2] CAUTELA, J. et al. Colloids and Surfaces A. 532 (2017) 411.
[3] ORTIZ, M. et al., Journal of rheology. 38, 519 (1994).

Agradecimentos/Acknowledgments

CAPES FAPESP Embrapa

Área: FIS

Exploring the Phase Behavior of Cardanol-Based Surfactant/Water Mixtures: Influence of *n*-alcohols on Microemulsion Formation.

Hannah de A. V. Matos (PG),[1*] Guilherme A. Ferreira (PQ).[1]

hannah.vieira@ufba.br;

[1]*Department of Physical Chemistry, Institute of Chemistry, Federal University of Bahia, Salvador, BA, Brazil*

Keywords: *Microemulsion, Cardanol, Biobased surfactants, Microstructure.*

Highlights

- Microemulsions with different nanostructures can be produced using green surfactants derived from cardanol mixed with water and *n*-alcohols.
- The obtained microemulsions show promising application as dispersants for oil spills in marine environments.

Abstract

Due to environmental concerns, there is a need to adopt new surfactants sourced from renewable origins, aiming at the reduction of the environmental footprint of industrial activities. An alternative to petroleum-based surfactants is the use of surfactants derived from cardanol. This natural phenolic compound is extracted from cashew nutshell liquid (CNSL), which is a byproduct of the agroindustry in Northeast Brazil.[1,2] However, there are few studies investigating the phase behavior of these cardanol-based surfactants in water and in mixtures with other solvents. In this study, we investigated the use of a nonionic surfactant, with 12 ethylene oxide groups linked by a phenol group to a long unsaturated carbon chain, derived from cardanol to produce microemulsions and the influence of co-surfactants, ethanol, and *n*-butanol, on the formation of these systems. The microemulsion region was determined using the water titration method. The microstructure of the microemulsions was investigated using electrical conductivity, dynamic light scattering (DLS), and small angle X-ray scattering (SAXS) to determine the influence of the co-surfactant. The local dynamics of these microemulsions were also investigated using X-ray photon correlation spectroscopy (XPCS). The microemulsions were utilized as an oil spill dispersant, and their effectiveness was assessed using the LUMiSizer dispersion analyzer. The results indicate an increase in the microemulsion region when *n*-butanol is used as a co-surfactant compared to ethanol. It was observed that the type of microemulsion formed depended on the co-surfactant used, with a bicontinuous structure being only formed when *n*-butanol was present along a selected dilution line. The efficiency tests showed that there is a relationship between the type of microemulsions formed and the system's capacity to disperse heavy oil.

[1]BHADANI, A. et al.Curr. Opin. Colloid Interface Sci. **2020**, 45, 124-135.
[2]ROY, A. et al. Molecules. **2022**, 22, 1143.

Acknowledgments

CNPq, UFBA, CAPES, LNLS, Cardolite and Prof. Watson Loh (UNICAMP).

.

Área: FIS

Halogen bonding in pharmaceutical compounds: a case study

Camila B. Pinto (PQ),[1] Adilson B. Wanderley (PG),[1] Juan C. Tenorio (PQ),[2] Ihosvany Camps (PQ),[3] Christian Lehmann (PQ),[4] Javier Ellena (PQ).[1]*

camilabpinto@usp.br; javiere@ifsc.usp.br

[1]Instituto de Física de São Carlos, USP, Brazil; [2]Instituto de Física, UFRJ, Brazil; [3]Departamento de Física, Instituto de Ciências Exatas, UNIFAL, Brazil; [4]Max-Planck-Institut für Kohlenforschung, Germany.

Palavras Chave: *Crystal structure, Non-covalent interaction, Hirshfeld Atom Refinement, Hirshfeld surface.*

Highlights

Evaluation of F···F and F···H interactions in a pharmaceutical cocrystal through Hirshfeld Atom Refinement.
Topological analysis is performed to quantify the strength of these interactions.

Abstract

Halogen bonds have been studied in the past years especially due to their directionality, which enables the rational design of molecules with desired properties. When it comes to pharmaceutical active ingredients, the interest in halogen bonds is mainly due to the role they play in mediating the binding of small molecules to receptors[1]. In this manner, the understanding of the nature of halogen bonds is essential for the development of new pharmaceutical compounds with enhanced selectivity and overall properties. To contribute for the understanding of these non-covalent interactions, here we evaluate the F···H and type I F···F contacts in the pharmaceutical codrug of Isoniazid and 5-Fluorocytosine[2,3]. The cocrystal was subjected to X-ray diffraction experiment, and the obtained crystal structure was further refined via Hirshfeld Atom Refinement (HAR)[4], which is known to give a better estimate of the position of H atoms, thus enhancing the quality of the model and allowing more accurate analyses of non-covalent interactions. In the HAR method, a molecular wavefunction based on the crystal structure is calculated and then partitioned according to Hirshfeld stockholder scheme. The obtained aspherical atomic electron densities are then Fourier transformed, retrieving aspherical form factors, which are then used in the structure refinement. After the HAR procedure, the contacts were evaluated via Hirshfeld Surface analysis, and topological analysis[5] based on Bader's Quantum Theory of Atoms in Molecules.
The Hirshfeld Surface (HS) indicates both F···H and F···F contacts, seen through fingerprint plots (FP) and through the mapping of the *Curvedness* function, which delineates contact regions with blue edges. For the contacts under study, it is possible to see three regions corresponding to the non-covalent contacts and yellow/red areas, which indicate flat regions on the surface usually associated with H-bonds[6] (Figure 1b). The topological analysis of these contacts locates bond critical points and bond paths, confirming the existence of the interactions (Figure 2). Topological descriptors at the bond critical points (Table 1) indicate that the F···F interaction is weaker than those reported in literature while the F···H contacts are stronger than those found in literature[7]. However, in either case, the low electron density and positive Laplacian indicate closed-shell interactions, and the ε value for F···F indicates a higher contraction of electron density perpendicular to the bond path direction.

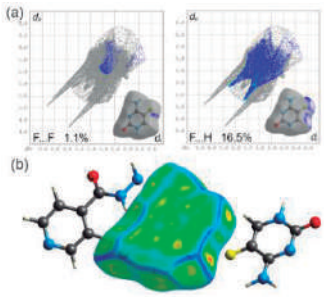


Figure 1. (a) FPs and (b) HS mapping the *Curvedness* function.

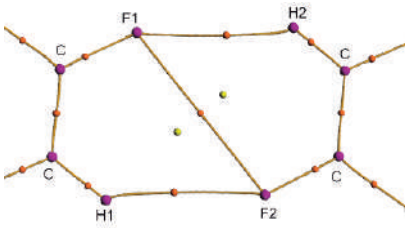


Figure 2. Bond critical points (orange), ring critical points (yellow) and bond paths for the contacts F···H and F···F.

Table 1. Topological descriptors. Values of $\rho(\boldsymbol{r}_{bcp})$ are in *e* Å^{-3}, $\nabla^2\rho(\boldsymbol{r}_{bcp})$ are in *e* Å^{-5}, and R_{ij} in Å.

Contact	$\rho(\boldsymbol{r}_{bcp})$	$\nabla^2\rho(\boldsymbol{r}_{bcp})$	ε	R_{ij}
F1···F2	0.019	0.470	0.83	3.21
F2···H1	0.049	0.751	0.05	2.48
F1···H2	0.049	0.751	0.05	2.48

References: [1] Thomas et al. *Molecules*, **27**, 3690, 2022; [2] Souza et al. *Cryst. Growth Des.*, **18**, 5202, 2018; [3] Wanderley et al. *Acta Cryst.*, A**77**, c909, 2021; [4] Kleemiss et al. *Chem. Sci.*, **12**, 1675, 2021; [5] Lu & Chen. *J. Comput. Chem.*, **33**, 580, 2012; [6] McKinnon et al. *Acta Cryst.*, B**60**, 627, 2004; [7] Hathwar & Row. *Cryst. Growth Des.*, **11**, 1338, 2011.

Acknowledgments

FAPESP (grants # 2023/10889-7; 2017/15850-0; 2016/08823-4; 2013/07581-9) and CNPq (grant # 312505/2021-3).

Área: __FSC QMC___
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

How to tackle organophosphates' toxicity? Allying selective functionalization for catalyst-by-design, reactivity trends and colorimetric detection

Patrícia Soares (PG), Willian Takarada (PG), Bernardo M. Régnier (PQ), Amanda Scheuer (IC), Gabriella A. Borim (IC), Alex R. Teixeira (PG), André H. G. Martinez (PG), Vinícius O. Costa (PG), Mariana H. Nazareno (IC), Ana Beatriz Bezerra de Lima (IC), Mayara Gabriela Gonçalves (PQ), Gabriel C. B. Gomes (IC), Valmir B. Silva (PQ), Elisa S. Orth (PQ) *

patti.ms16@gmail.com; elisaorth@ufpr.br

[1]*Departamento de Química, UFPR*

Palavras Chave: *Dephosphorylation, Agrochemicals, Chemical security, Nanocatalyst, Biocatalyst, Nucleophilic catalyst.*

Highlights

Mono- and bifunctionalized catalysts derived from nanomaterials, biopolymers and simples molecules were designed. Colorimetric reactions could effectively monitor toxic agrochemicals.

Resumo/Abstract

The organophosphates are a class of substance of alarmingly concern since they constitute many agrochemicals and chemical warfare. Hence, it has been of great interest to develop efficient methods for alerting attacks, monitoring misuse and overall neutralizing undesired stocks. Our group has been focused in: (i) selective and fast neutralization processes; (ii) catalysts-by-design (molecular, nanometric, polymeric and sustainable) and neutralizing gels; and (iii) colorimetric detectors. Several pesticides (> 5) have been efficiently neutralized with a myriad of over 30 catalysts (homogeneous and heterogeneous). Mechanistic studies and structure-reactivity relationships have shown to be valuable tools for modulating towards less toxic products. The mono- and bi-functionalization "on demand" has also been pursued on various scaffolds such as graphene oxide and cellulosic residues under mild conditions (aqueous, neutral pH, ambient condition) anchoring imidazoles, amines, hydroxamates, amidoximes, amines and thiols. The catalysts are able to act as neutralizing agents for organophosphates, accelerating the process to less than 1 day, that otherwise could take millions of years. A neutralizing gel was also obtained derived from functionalized carboxymethylcellulose, promising for preventing cutaneous intoxication. Colorimetric reactions using derivatization reactants showed to be effect for detecting agrochemicals such as Parathion, Paraoxon, Glyphosate and Acephate in a couple of minutes. Also, the effect of interferents was studies and the method showed to be selective. Finally, portable detectors (led, paper, glass) have been developed based on a colorimetric signal triggered from a reaction. In conclusion, chemical security and safety can be successfully accomplished for highly toxic compounds by combining catalytic degradation and efficient detection. The key point is surely allying sustainable practices with the strategic design of the systems, based on a comprehensive understanding of the effect of: neighboring groups, catalytic group, mechanism, support, medium, processability and optimal detection triggering.

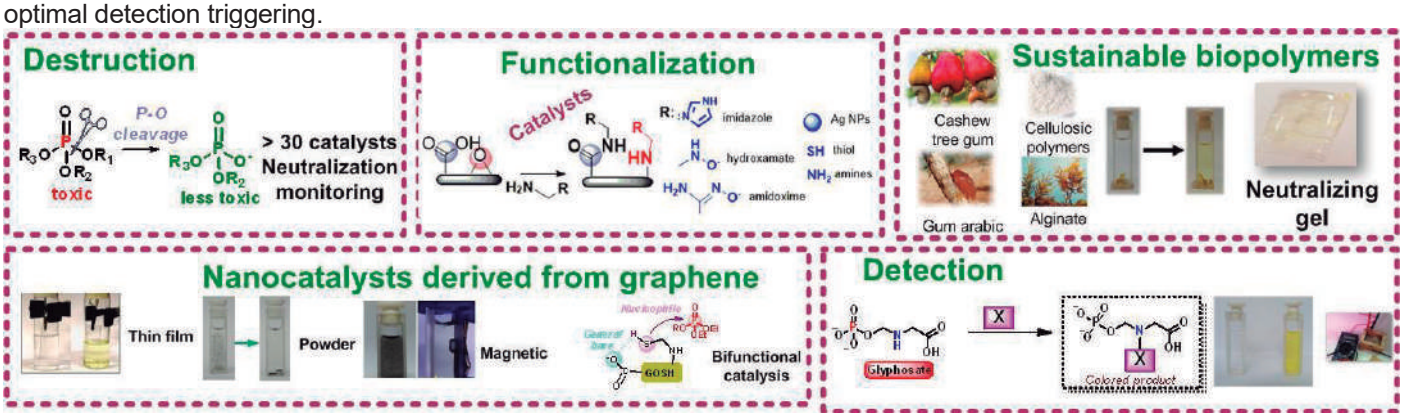


Figure 1 – Overall summary of the studies carried out herein

Agradecimentos/Acknowledgments

UFPR, CAPES, CNPq, L'Oréal UNESCO-ABC, PhosAgro/UNESCO/IUPAC, INCT NanoVida, INCT Nanocarbono

Área: FIS

Influence of Bounded Magnetic Polarons in Ferromagnetic Behavior of Ceria Nanoparticles with preferentially exposed plane (100) and (110).

Aila de O. dos Santos (PG)[1], Hozana S. C. Oliveira (IC)[1], Jilder P. Serna (PQ)[2], Noemi R. Checca (PQ)[2], André V.H. Soares (PQ)[3], Júlio César M. Silva (PQ)[1], Odivaldo C. Alves (PQ)[2*]

ailaoliveira@id.uff.br; odivaldocambraia@id.uff.br

[1]Departamento de Físico-Química, UFF; [2]CBPF; [3]Escola de Engenharia, UFF.

Palavras Chave: *Ferromagnetism, Ceria, Nanosheets, Nanorods, Oxygen Vacancy, BMP model.*

Highlights

Ceria nanoparticles and bounded magnetic polarons.

Oxygen vacancies on ceria nanosheets and nanorods.

BMP model and room temperature magnetic behavior of ceria nanoparticles.

Resumo/Abstract

The ferromagnetic behavior of CeO_2 (ceria) nanoparticles (NPs) has been extensively studied due to its potential application in spintronics [1] and optical devices [2]. Different morphologies of ceria NPs present different values of magnetic parameters associated to the structure of oxygen vacancies and the amount of Ce^{+3} ions that depend on the surface exposed [3,4] and these may be associated with the magnetic behavior of the material [5]. In this work, the synthesis of ceria NPs in rod (CeO_2 R) and hexagonal nanosheet (CeO_2 HS) morphologies was carried out and the magnetic behavior and its relationship with the surface structure were evaluated using magnetization curves, Electronic Magnetic Resonance (EMR) and X-Ray Photoelectrons Spectroscopy (XPS). Transmission Electron Microscopy (TEM), X-ray dispersive spectroscopy (EDS) and X-ray diffraction (XRD) were also performed. Through XPS data it was observed that CeO_2 HS presented higher concentration of oxygen vacancies and oxygenated species adsorbed on the surface. On the other hand, it was observed higher saturation magnetization curves for CeO_2 R. The ferromagnetic curve in EMR spectra was fitted with derivative Lorentz to obtain the value of the relative area of the spectral components C_1 (associated to isolated oxygen vacancies) and C_2 (associated to oxygen vacancies clusteres) [6]. CeO_2 R showed higher C_2 area than CeO_2 HS. Comparing these results with the XPS, it is inferred that CeO_2 HS presents an excess of oxygen vacancies that results in the depletion of the F^+ centers and a lower amount of bounded magnetic polarons, resulting in a decrease in the long-range ferromagnetism of the material, which is in agreement with magnetization data [7]. Therefore, it is suggested that the magnetic behavior of ceria NPs strongly depends on the optimal concentration of oxygen vacancies on the material surface and, consequently, on higher concentrations of BMP on the surface.

Referências/References

[1] A. N. Ribeiro and N. S. Ferreira. ***Physical Review*** *B* 2017;*95*:1-8.
[2] X. Ma, *et al*. ***Journal of Alloys and Compounds*** 2018;*734*:22-8.
[3] M.Coey, *et al.* ***Nature Physics*** 2016;*12*:694-700.
[4] F. Dong, *et al.* ***Scientific Reports*** 2019;9(1):12056.
[5] A.F.F. de Lima, *et al.* ***Applied Catalysis A, General*** 2021;6011.
[6] A.A. Marciniak, *et. al.* ***Molecular Catalysis*** 2020; 493:111053.
[7] H.R. Khakhal, *et al.* ***Journal of Alloys and Compounds*** 2020;*844*:156079.

Agradecimentos/Acknowledgments

CNPq 141454/2021-0, LNNano-CNPEM, FAPERJ e ao CBPF.

Área: FIS

In silico insight into polymer affinity for biodegradation by Cutinase from *Fusarium oxysporum*

Maycon Vinicius Damasceno de Oliveira (PG),[1*] Clauber Henrique Souza da Costa (PQ),[2] José Rogerio A. Silva (PQ),[1,3] Anderson H. Lima (PQ),[1] Jeronimo Lameira (PQ)[1]

maycon.damasceno.oliveira@icen.ufpa.br; maycon.damasceno.oliveira@icen.ufpa.br

[1]Laboratório de Planejamento e Desenvolvimento de Fármacos, Instituto de Ciências Exatas e Naturais, Universidade Federal do Pará, 66075-110, Belém, Pará, Brasil; [2]Center for Computing in Engineering & Sciences – IQ/UNICAMP; [3]Catalysis and Peptide Research Unit, University of KwaZulu-Natal, Durban 4000, South Africa

Keywords: *Cutinase, Fusarium oxysporum, Molecular Dynamic, Synthetic polymers, PET, PBAT*

Highlights

The present work demonstrated, through computational methods, the affinity of synthetic polymers (PET and PBAT) for the formation of the complex with the Cutinase from *Fusarium oxysporum*.

Abstract

Plastic poses a significant environmental threat due to its chemical resilience, leading to prolonged degradation times, and resulting in widespread adverse effects on global flora and fauna. Particularly, Cutinases (Cut), a type of serine hydrolase capable of degrading cutin—a fatty acid polyester forming the primary component of plant cuticles—have emerged as vital biocatalysts in breaking down synthetic polymers, including polyethylene terephthalate (PET) and polybutylene adipate terephthalate (PBAT), among others. Here, we employed computational techniques such as molecular docking, molecular dynamics (MD) and binding free energy calculations to investigate how PET and PBAT polymers interact with the catalytic site of the Cut enzyme from *Fusarium oxysporum* (*Fo*Cut). The 3D structure of *Fo*Cut was obtained from PDB under code 5AJH. After molecular docking procedures, 100 ns of classical MD simulations (in triplicate) were performed by using the AMBER20 package. The equilibrated ensembles were submitted to binding free energy calculation through the MM/GBSA approach. Our investigation extended to dissecting the contact interactions between the polymers and the enzyme at three intervals of 100 ns for each of the replicas, utilizing the ProLIF library to capture the evolving interaction landscape throughout the MD simulations. From structural analysis, the PET-Cut complex showed variable RMSD values (1.54 Å, 4.02 Å, and 2.51 Å across three replicas), with the notable increase in the second replica attributed to polymer bond rotation during simulation. Clustering analysis confirmed this conformational change, particularly the rotation of single bonds connecting monomers, while the other replicas exhibited minimal structural deviations, with 66% similarity to the PET structure. Conversely, the PBAT-Cut complex demonstrated consistent stability across all replicas (RMSD values of 1.95 Å, 2.04 Å, and 1.88 Å), with observed rotational and conformational changes not affecting stability. Interaction analysis of both complexes highlighted the predominance of van der Waals, hydrophobic, and hydrogen bonds (only in PBAT-Cut complex), with key residues including Thr44, Glu45, Leu82, Ala86, Tyr120, Ser121, Leu183, His189 (part of the PET/PBAT-Cut complex's catalytic triad), Leu190, and others contributing to the formation and stability of these complexes. The free energy results show that both PET (-34.26±5.51 kcal/mol) and PBAT (-22.78±5.36 kcal/mol) polymers exhibit favorable affinity for the Cut enzyme. Our findings demonstrate a successful integration of the polymers into the Cut active site, underscoring the importance of this enzyme as a natural catalyst for polymer degradation and offer valuable insights for enhancing biocatalyst production within biotechnological applications, particularly in the development of biocatalysts in Amazonia.

Acknowledgments

The authors would like to thank the Fundação Amazônica de Amparo a Estudos e Pesquisas (FAPESPA) and the Pró-Reitoria de Pesquisa e Pós-Graduação (PROPESP/UFPA) for the financial support to improve the quality of this study (PRODISCENTE-08/2024), to Coordenação de Aperfeiçoamento de Pessoal de Nível Superior for the financial support, and to the Santos Dumont Supercomputer from the Laboratório Nacional de Computação Científica (LNCC) and Centro de Computação de Alto Desempenho (CCAD), for providing the supercomputing facilities.

Área: FIS
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Estudo cinético de adsorção por Hidroxiapatita

Thaís A. Possidente (PG)[1], Luiz E.P. Borges (PQ)[1], Kátia R. de Souza (PQ)[1].

thapossidente@ime.eb.br

[1]*Departamento de Química, IME*

Palavras Chave: *Adsorção, Hidroxiapatita, Ferro, Efluente, Cinética.*

Highlights

This study shows the behavior of hydroxyapatite for adsorption in different materials, specifically in metallic species. The variables used was amount of adsorbent, time of contact, temperature, concentration of adsorbate and speed of shaking. The results were treated and used to construct de adsorption kinetics and isotherms. This experiment shows that the reaction is a second order and the Dubinin-Radushkevich isoterm best fit in the data obtained.

Resumo/Abstract

Este trabalho teve por objetivo estudar a adsorção de substâncias de diferentes naturezas em um adsorvente não convencional sintetizado previamente com uma rota simples e pouco custosa. Foi avaliada a capacidade de adsorção da hidroxiapatita (HAP) para a remoção de azul de metileno e ferro em sua forma iônica trivalente, valência incomum para que a HAP adsorva com eficiência, devido a sua estrutura química, em matrizes de águas e efluentes.

Foram utilizadas como variáveis para os testes de adsorção: massa do adsorvente, tempo de contato, velocidade de agitação do sistema e variação de temperatura. A concentração de adsorvato foi realizada para avaliar a capacidade de adsorção e o grau de saturação da HAP.

Foram realizadas três curvas de calibração, uma para azul de metileno e duas para Ferro III. Os coeficientes obtidos foram bastante satisfatórios, sendo R^2 = 0,999 para a curva de Azul de Metileno, R^2 = 0,998 para Ferro III – faixa baixa e R^2 = 0,999 para Ferro III – faixa alta.

Os experimentos realizados mostraram que a HAP é altamente eficiente na adsorção de Ferro inclusive em altas concentrações, em condições específicas, além de ser eficiente também para a molécula modelo Azul de Metileno. Os parâmetros avaliados como variáveis ótimas de adsorção, visando o melhor custo-benefício foram: massa de 50 mg de HAP, 5 minutos de tempo para a adsorção, velocidade de agitação do sistema de 50% e variação de temperatura do sistema de 45 °C. O grau de saturação da HAP para íons Ferro foi de cerca de 50 mg HAP/ 2500 mg Fe, nas condições ótimas. Foi observado que a superfície de contato é um fator determinante na capacidade de adsorção deste sistema.

Quanto à cinética de adsorção, os estudos mostraram que estas foram reações de segunda ordem, com três testes em concentrações distintas de coeficientes lineares excelentes obtidos. Para as isotermas avaliadas, foram utilizados os modelos de Langmuir com, Freundlich, Temkin e Dubinin-Radushkevich. Sugere-se que a isoterma de Dubinin-Radushkevich seja a ideal para este sistema, devido à melhor linearização obtida com seus dados. Os resultados obtidos para a energia de ativação foram de Ea = - 80,0 $KJ.mol^{-1}$, sugerindo uma reação de quimissorção.

Do ponto de vista ambiental, a HAP é um excelente adsorvente, capaz de atender aos requisitos da legislação CONAMA 430/2011, que estabelece os limites de tolerância para disposição final de efluentes com metais pesados no ambiente.

Agradecimentos/Acknowledgments

Este estudo foi financiado em parte pela Coordenação de Pessoal de Nível Superior -(CAPES)- Código Financeiro 001, FAPERJ (edital nº05/2020) e IME (Instituto Militar de Engenharia).

Área: FIS

Kinetic study of the methylene blue: adsorption in loofah biomass

Janaina Pontes da Silva (IC),[1] Jaqueline Nicolini (PQ),[1] Keller Paulo Nicolini (PQ).[1*]

keller.nicolini@ifpr.edu.br

[1]*Instituto Federal de Educação, Ciência e Tecnologia do Paraná – IFPR – Campus Palmas, Avenida Bento Munhoz da Rocha Neto, PRT 280, S/N, CEP.: 85555-000, Palmas, PR – Brazil.*

Palavras Chave: *biomass, adsorption, chemical kinetics, biochar.*

Highlights

The best fit was obtained for the pseudo-second-order kinetic model.

The data indicates chemisorption of methylene blue by biochar from biomass of *Luffa* spp.

Resumo/Abstract

Vegetable biomasses are prominent adsorbents.[1] The properties of the channel structure of vegetable loofah are unique.[2] Biochar may be prepared by simple pyrolysis of vegetable loofah.[2] The aim of this work was to study the adsorption of methylene blue (MB) in charcoal from biomass of *Luffa* spp. (BL) prepared from fruits of the plant. *Luffa* fruits were pyrolyzed at 625 °C (± 5) for 30 min. The biochar generated (BL) was crushed (≤ 0.01 mm), washed with distilled water and dried at 60 °C (± 3). The MB adsorption studies were performed using 50 mL of MB solutions (49.7 to 75.7 mg L^{-1}) at temperatures of 25, 30 and 35 °C, using 100 mg of adsorbent (BL) and stirring for 30 min. Aliquots were collected every 5 min, centrifuged at 3000 rpm for 2 min and absorbance determined at 660 nm. The pseudo-second-order kinetic model (Table 1) suggests that the rate-limiting step is chemisorption rather than mass transport limitation.[3] Pseudo-second order kinetic model suggests that chemical adsorption of MB by BL is the dominant mechanism, involving electrostatic attraction.[4]

Table 1. Adsorption of methylene blue in loofah biochar: kinetic parameters.

T	$q_{e\ (exp.)}$	Pseudo first order			Pseudo second order		
		k_1	$q_{e\ (teor.)}$	R^2	$q_{e\ (teor.)}$	k_2	R^2
25	1.39	-0.01	1.25	0.03	0.19	-1.22	0.17
30	7.03	0.08	2.63	0.55	6.99	0.13	0.99
35	6.51	0.15	2.63	0.67	6.69	0.14	0.99

T	Intraparticle diffusion			Elovich equation		
	C	K_P	R^2	α	β	R^2
25	-0,22	0.11	0.08	4.44×10^{-1}	0.28	0.06
30	1.60	1.14	0.75	2.38×10^{5}	0.45	0.63
35	1.76	1.04	0.67	1.49×10^{75}	0.04	0.00

T: °C; $q_{e\text{-}exp.}$: mg g^{-1}; k_1: min^{-1}; $q_{e\text{-}teor.}$: mg g^{-1}; k_2: g mg^{-1} min^{-1}; C: mg g^{-1}; K_P: mg g^{-1} $min^{-1/2}$; α: mg $g^{-1}min^{-1}$; β: g mg^{-1}.

Agradecimentos/Acknowledgments

LACOPPI, IFPR, PIBIC/CNPq, PIBIC/IFPR, CNPq.

References

[1]Da Costa, J.S.; Fajardo, A.R. J. Clean. Prod., **2023**, 389, 136084.
[2]Gou, G.; Huang, Y.; Wang, Y.; Liu, C.; Li, N.; Lai, B.; Xiang, X.; Li, J. Sep. Purif. Technol. **2023**, 306, 122585.
[3]S. Saikia, A. Sinharoy, P.N. Lens, Sep. Purif. Technol., **2022**, 120462.
[4]M.N. Alnajrani, O.A. Alsager, Scientific Reports, **2020**, 10, 794.

Área: FIS

Nb_2O_5 as a key material for use in advanced oxidative processes: textural, electronic, vibrational, and structural characterization of six polymorphs.

Vinícius S. Santana (IC)[1*], Michele V. C. O. Silva (PG)[2], Rodrigo De Paula (PQ)[1,2].

viniciussantana524@gmail.com

[1]Universidade Federal do Recôncavo da Bahia (UFRB), Centro de Formação de Professores (CFP); [2] Programa de Pós-Graduação em Química Pura e Aplicada (POSQUIPA), Universidade Federal do Oeste da Bahia (UFOB).

Keywords: *Niobium pentoxide, Polymorphs, Characterization.*

Highlights

Nb_2O_5 as a key material for use in advanced oxidative processes: textural, electronic, vibrational, and structural characterization of six polymorphs - In this context, the aim of this study was to perform the characterization of six samples of Nb_2O_5 polymorphs, kindly supplied by the Companhia Brasileira de Metalurgia e Mineração (CBMM).

Abstract

The niobium pentoxide (Nb_2O_5) exhibits several polymorphs, whose properties are sensitive to the thermal treatment employed during its preparation[1]. Greater crystalline purity and stability are achieved at high temperatures. Table 1 summarizes the crystallographic data of the studied polymorphs, their phases, band gap energy and wavelength for the six spectra. The results indicated that the thermal treatment play a fundamental role in crystallographic phase obtained. Figure 1 displays the spectra of Diffuse Reflectance Spectroscopy (DRS) of the Nb_2O_5 samples, showing different wavelengths concerning absorbance.

Table 1 - Results obtained by X-ray diffraction *

Sample	Temp (°C)	Crystal structure and phase				% of the Crystalline Phase	Gap energy (eV)	λ(nm)
		AM	HEX	OR	MC			
9377	≥1000				X	H (100%)	3,09	398
8071	1200				X	H (99,2%)[2]	2,98	414
8070	900			X	X	M (64,7%) e T (35,3%)[2]	3,04	389
9376	≤ 600		X	X		T (93,8%) e TT (6,2%)	3,36	379
9375	≤ 600		X	X		T (75,7%) e TT (24,3%)	3,17	385
4381	450	X				--[2]	3,65	344

* The analysis XRD conducted by CBMM; MO - monoclinic; OR - orthorhombic; HEX - hexagonal; AM - amorphous.

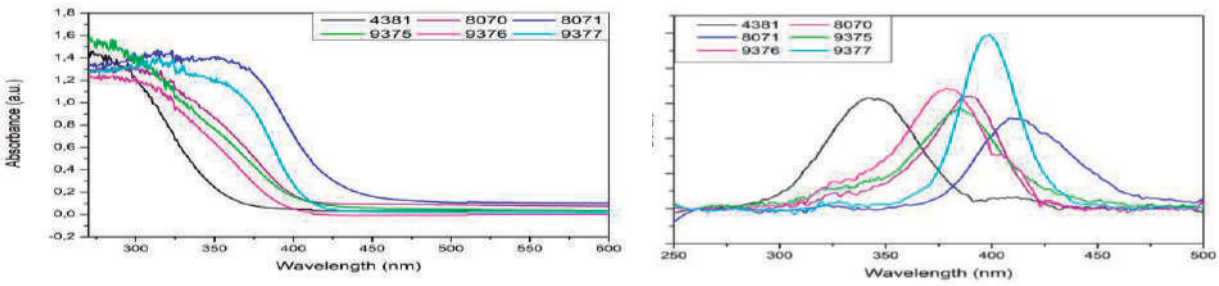


Figure 1: Diffuse reflectance spectra and differential analysis of Nb_2O_5 samples (Source: author, 2023)

[1] L. A. de Morais, Synthesis, In: *Characterization and study of the photocatalytic properties of niobium compounds in environmental matrices*, PhD Thesis,2016.
[2] M.V.C.O. da Silva, In: Niobium oxide (v): *Characterization study and evaluation of photocatalytic properties*. Master Thesis, 2022.

Acknowledgments

We are grateful to CBMM/Araxá-MG for providing all the materials studied in this work. We would also like to thank Prof. Dr. Yuji N. Watanabe (UFRB/CFP) and Dr. Gerônimo L. Lima (UFRB/CFP), as well as the personnel at LABCAT (UFBA).

Área: FIS

Oil-in-water nanoemulsions based on Beta-caryophyllene stabilized by Pluronic F-127

[1]Laysa Luana Silva de Macedo (IC), [2]Emília Celma de Oliveira Lima (PQ)

laysa.macedo@discente.ufg.br; elima@ufg.br

[1]Instituto de Química, IQ; [2]Univesidade Federal de Goiás

Palavras-Chave: *Nanoemulsion, Beta-Caryophyllene, Caprylic acid, Pluronic F-127.*

Highlights

O/W nanoemulsions based on Beta-caryophyllene presenting high colloidal stability; Pluronic F 127 as agent of dispersion; caprylic acid as adjuvant of dispersion; Low energy method of preparation.

Resumo/Abstract

O Beta-cariofileno (CAR) é um sesquiterpeno encontrado no óleo essencial de algumas plantas, e que possui efeito anti-inflamatório e antioxidante. O potencial para aplicações do cariofileno em diversas área como farmacologia, higiene e cosméticos, demanda o desenvolvimento de formulações contendo esse princípio ativo, sendo as emulsões uma forma bastante versátil de veiculação de princípios ativos hidrofóbicos para as referidas aplicações. Uma abordagem de baixa energia para a preparação de emulsão do tipo O/A, consiste em dissolver a fase oleosa juntamente com um copolímero bloco ,anfifílico, em um solvente orgânico, seguido pela evaporação do solvente e hidratação do filme com a fase aquosa. Tal procedimento permite a emulsificação do sistema sob leve agitação manual, gerando emulsões compostas de poucos componentes. Este método se demonstrou eficaz, em trabalho anterior realizado no IQ-UFG, referente à preparação nanoemulsões a base de óleo de copaíba estabilizadas somente pelo copolímero Pluronic F-127[1]. Nessa comunicação descrevemos o uso dessa metodologia para a preparação de emulsões a base de Beta-cariofileno estabilizada com o Pluronic F127. A metodologia consistiu em utilizar o método citado para produzir as emulsões variando-se a proporção cariofileno/Pluronic, e utilizando o ácido caprílico (AC) como um adjuvante no processo de emulsificação, na proporção 1:5 AC:CAR. As emulsões obtidas foram inicialmente opacas, mas após alguns dias de repouso tornam-se translúcidas ou transparentes, dependendo da relação cariofileno/Pluronic empregada. As emulsões foram analisadas por medidas de DLS e as diferentes amostras apresentaram distribuição de diâmetros hidrodinâmicos das gotículas majoritariamente monomodal, com diâmetros médios inferiores a 200 nm. As diversas amostras obtidas se mantem estáveis por mais de sete meses após a preparação. Os resultados obtidos nos estimula a prosseguir na caracterização do sistema visando compreender como o ácido caprílico, atua como agente de compatibilidade para interação do bloco polióxido de propileno do Pluronic com o cariofileno.

[1]SILVA et al., Antifungal activity of Copaiba resin oil in solution and nanoemulsion against Paracoccidioides spp. *Brazilian Journal of Microbiology*, v. 151, p. 125-134, 2020.

Agradecimentos/Acknowledgments

PIBIC - UFG

Área: FIS

Preparation and characterization of O/W nanoemulsion based on MCFA stabilized by Pluronic copolymers F127 and F68

Vinícius C. Lemes (FM),[1*] Emília C. de O. Lima (PQ).[1]

viniciuscandido@discente.ufg.br; elima@ufg.br.

[1]*Institudo de Química, Universidade Federal de Goiás (UFG).*

Palavras Chave: *Nanoemulsões, Pluronic F127, Pluronic F68, Ácido graxo de cadeia média, Liofilização.*

Highlights

O/W nanoemulsion based on MCFA stabilized by Pluronics; high colloidal stability; suitable for freeze-drying; stored in powder form; nanoemulsions reconstitution while preserving their properties.

Resumo

Nanoemulsões são amplamente utilizadas como sistemas de encapsulamento de componentes bioativos aumentando a estabilidade e a biodisponibilidade do encapsulado. Os ácidos graxos de cadeia média (AGCM) são biocompatíveis e empregados em diversas aplicações farmacêuticas, apresentando, inclusive atividade antitumoral em estudos *in vitro*. Dessa forma, o desenvolvimento de nanoemulsões à base de AGCM estabilizadas por Pluronic F127 (PF127) e por Pluronic F68 (PF68) se mostra uma boa estratégia para veiculação de princípios ativos hidrofóbicos. Nesse trabalho foram preparadas nanoemulsões com diferentes proporções mássicas fase oleosa/copolímero, de acordo com a metodologia da hidratação do filme. Na tabela 1 estão apresentadas as proporções bem como a denominação das amostras. As propriedades analisadas das nanoemulsões obtidas foram a estabilidade coloidal, por inspeção visual e o raio hidrodinâmico (R_H) , por meio da técnica DLS. As nanoemulsões estabilizadas pelo copolímero PF127 (amostras A1, A2, A3 e A4) e PF68 (amostras B2, B3 e B4) apresentaram aspecto visual límpido e translúcido, sem sedimentação ou separação de fases, mesmo após um ano de armazenamento na forma líquida, o que é indicativo da alta estabilidade coloidal das amostras. A mostra B1 não apresentou estabilidade. As figuras 1A e 1B apresentam a distribuição dos R_H das gotículas de AGCM nas emulsões originais, mostrando que excetuando-se a emulsão A1, todas as demais apresentam uma única população de gotas e com R_H inferiores a 100 nm. Verificou-se que as emulsões puderam ser liofilizadas e estocadas na forma de pó. As emulsões com maior teor de polímero quando reconstituídas a partir dos pós, aprestaram aspecto visual semelhantes aos das emulsões originais. As figuras 1C e 1D são referentes às amostras reconstituídas após a hidratação do pó (ver figura 2), nas quais se observa a presença de gotículas com R_H ainda inferiores a 200 nm. Conclui-se que os copolímeros PF127 e PF68 são adequados para a estabilização de nanoemulsões a base de AGCM, com alta estabilidade coloidal, e que as nanoemulsões com maiores proporções de copolímero preservam suas propriedades quando reconstituídas a partir do pó obtido por liofilização da nanoemulsão.

Tabela 1. Proporção mássica AGCM/Pluronic de cada amostra de nanoemulsões em 5 mL de água

Formulação	Pluronic utilizado	Massa de AGCM (mg)	Massa de Pluronic (mg)
A1	PF127	25	25
A2	PF127	25	50
A3	PF127	25	75
A4	PF127	25	100
B1	PF68	25	25
B2	PF68	25	50
B3	PF68	25	75
B4	PF68	25	100

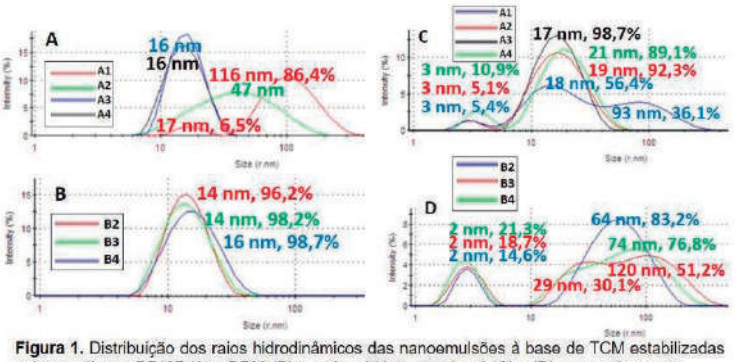


Figura 1. Distribuição dos raios hidrodinâmicos das nanoemulsões à base de TCM estabilizadas pelo copolímero PF127 (A) e PF68 (B) e após a hidratação do pó (C) e (D), respectivamente.

Figura 2. Fotografia de algumas das nanoemulsões obtidas, após a hidratação do pó.

Agradecimentos

CNPq e PIBIC-UFG.

Área: FIS

Rheological and structural modulation of bile salt self-aggregates by nanocellulose

Vinícius Augusto Peixoto Tartare (IC),[1] Davi Siqueira da Silva de Souza (PG),[2] Brenda da Silva Bega (IC),[1] Giovana Cristina Zambuzi (PG),[2] Kelly Roberta Francisco (PQ),[1,2*]

viniciustartare.ufscar@gmail.com; kfrancisco@ufscar.br

[1]Department of Natural Sciences, Mathematics and Education, UFSCar; [2]Material Science Graduate Program, UFSCar

Palavras Chave: *Rheology, Stability, CNC, CNF, Hydrogels, Wormlike micelles.*

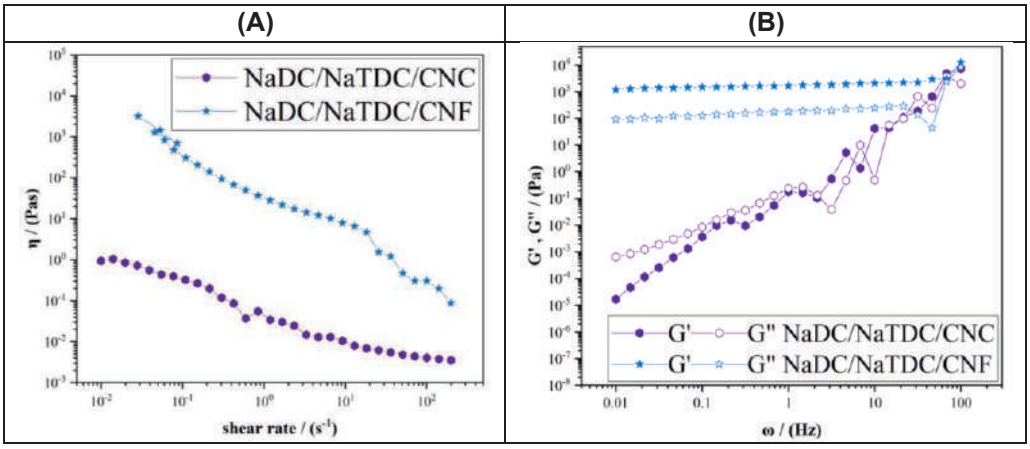
Highlights

Nanocellulose can modulate the structure of equimolar binary bile salts micelles. Bile salts aggregates can form hydrogel in presence of CNFs due to more elongated structures in comparison of bile salts/CNC aggregates.

Abstract

Sodium deoxycholate (NaDC) and sodium taurodeoxycholate (NaTDC) are biosurfactants that spontaneously form self-aggregates above their critical micellar concentration (cmc) via hydrophobic interactions in aqueous media [1]. These self-aggregates can be modulated by the addition of other molecules, such as cellulose nanocrystals (CNCs) and nanofibrils (CNFs) [2]. In this scenario, bile salt micelles with nanocellulose can exhibited different structure, size, and surface charges, as well as different rheological behaviors of the systems [3,4]. In this work, equimolar binary bile salts systems NaDC/NaTDC (50mM) were prepared in the presence of 4.80 g.L^{-1} of CNC or CNF. Systems were characterized by Dynamic Light Scattering (DLS), Zeta Potential (ZP) and Rheology. DLS results showed populations with intermediate sizes of 209.2 and 304.2 nm for the systems in the presence of CNC and CNF, respectively. ZP values were -52.3 ± 5.0 and -60.3 ± 3.1 mV for NaDC/NaTDC/CNC and NaDC/NaTDC/CNF systems, respectively, where CNF particles gave a more stable binary bile salts system in comparison with CNC system. The non-Newtonian behavior of fluids was observed for both systems, once they presented shear thinning and/or shear thickening phenomena (Fig. 1A). The zero-shear viscosity (η_0) of the system containing CNF was 3403 times greater than the η_0 of the system containing CNC. Dynamic frequency tests (Fig. 1B) indicated that CNCs induced the formation of short wormlike NaDC/NaTDC micelles in a dilute concentration regime, while CNFs induced the formation of more elongated micelles, giving a gel-like system behavior, since the storage modulus (G') is greater than the loss modulus (G") in a large range of frequency, suggesting the system is in a semi-diluted regime (more entanglements among aggregates). Results suggested NaDC/NaTDC/CNF are more structured, stable, and viscoelastic than NaDC/NaTDC/CNC systems, being promising for hydrogels formation to be applied in the controlled release of drugs and rheological modification of foods, cosmetics etc.

Figure 1. Flow curves (A) and dynamic frequency tests (B) of binary NaDC/NaTDC systems containing 4,80 g.L^{-1} of CNC or CNF.



[1] MOLDES, A. *et al*. **New and Future Developments in Microbial Bio-technology and Bioengineering**. Elsevier, p. 163-185, 2020; [2] SOUZA, D. S. S. *et al*. **Colloids and Surfaces A: Physicochemical and Engineering Aspects**, v. 682, p. 132953, 2024; [3] AZUM, N.; RUB, M. A; ASIRI, A. M. **Journal of Physical Organic Chemistry**, v. 33, p. e4015, 2020; [4] BARNES, H. A.; HUTTON J. F.; WALTERS K. F. R. S. **An Introduction to Rheology**. Elsevier Science Publishers B.V., Amsterdam, 1993.

Acknowledgments

LaQuiMoBio CNPEM FAPESP

Área: FIS

Rheological study of systems formed by bile salts, lecithin and polyethylene glycol

Brenda da Silva Bega (IC)[1]; Giovana C. Zambuzi (PG)[2]; Vinícius Augusto Peixoto Tartare (IC)[1]; Davi Siqueira da Silva de Souza (PG)[2]; Kelly R. Francisco (PQ)[1]

brendabega3@gmail.com; kfrancisco@ufscar.br*

[1]Departamento de Ciências da Natureza, Matemática e Educação, UFSCar; [2]Programa de Pós-Graduação em Ciência dos Materiais, UFSCar

Keywords: Bile salt, Lecithin, Polyethylene glycol, Rheology, Self-aggregation.

Highlights

In the present study, the objective was to obtain self-aggregate particles formed by bile salts, lecithin and polyethylene glycol. Therefore, different bile salts and different proportions were used to analyze how these parameters could interfere with the nanoaggregates formed. The systems were investigated using rheological tests and size particles (dynamic light scattering – DLS).

Resumo/Abstract

Polyethylene glycol (PEG) is a polymer that can be used for drug release [1]. Lecithin is a natural zwitterionic surfactant, found mainly in egg yolk and soybeans, and has two tails in its structure [2]. Bile salts are natural surfactants with a polar side and a nonpolar side and are produced in the liver and secreted in the intestine. Its main function is the solubilization of fats[3]. The use of lecithin and bile salts to form aggregates has been widely studied, however there is a greater need for work involving the use of organic solvents. In this work, three bile salts (sodium taurodeoxycholate, sodium deoxycholate and sodium cholate) with lecithin, in three different proportions (0.2, 0.4 and 0.8 of bile salt/lecithin in the presence of PEG molecules were studied. The systems were created from stock solutions of 100 mM bile salt and 200 mM lecithin dissolved in methanol. The samples were separated in proportions of 0.2; 0.4 and 0.8 (mol/mol) bile salt/Lecithin and remained under stirring for 1 h. Subsequently, the samples were dried in an oven for approximately 48 h, after which 10 mL cyclohexane and 0.004 g of polyethylene glycol (PEG) 400 g/mol were added to the systems and remained in agitation for 24 h. The systems were equilibrated at ambient temperature at least 24 h before analyses. NaTDC systems presented the largest aggregates in the proportion of 0.4 and the other proportions presented similar sizes, the NaDC salt presented the largest aggregates in the proportion of 0.2 and the smallest in 0.4, while NaC salt presented the largest aggregates in the proportion of 0.8 and the smallest in 0.2. Rheological analyses showed that the NaTDC and NaDC salts presented the highest values of zero shear viscosity (η_0) in the proportion of 0.8 ($1x10^3$ Pa.s and $207x10^3$ Pa.s, respectively). Meanwhile, NaC systems presented the highest value of η_0 (470.43 Pa.s) in the proportion of 0.4. The storage (G') and loss (G'') module allowed to determine whether the systems have viscoelastic behavior. Systems with a proportion of 0.4 of the three salts, a proportion of 0.2 of the salts NaDC and NaC and a proportion of 0.8 Na TDC and NaC showed viscoelastic behavior. The 0.2 NaTDC/lecithin system showed lower viscoelastic behavior. Thus, differences in the bile salt structure as well as the proportion of bile salt/lecithin can drastically affect the rheological response and the size of the nanoaggregates in the presence of PEG.

References:

[1] PAVELLI S. et al. International Journal of Biological Macromolecules. 166 (2021).
[2] CAUTELA, J. et al. Colloids and Surfaces A. 532 (2017) 411.
[3] XU, X. et al. Colloids and Surfaces A. 648 (2022) 129209.

Agradecimentos/Acknowledgments

FAPESP
Fellowships: 22/02092-9; 22/02089-8

CAPES
Fellowships: 88887.713913/2022; 0088887.713911/2022-00

CNPEM

Surface modification of cotton fabric for adsorption of essential oils

Afifeh R.F. Khader (PG),[1] Marcia M. Meier (PQ).[1]

afifehkhader@gmail.com; marcia.meier@udesc.br

[1]Departamento de Química, UDESC/CCT

Palavras-Chave: *β-cyclodextrin; Cotton fabric; Phenolphthalein; Inclusion complex; Essential oil.*

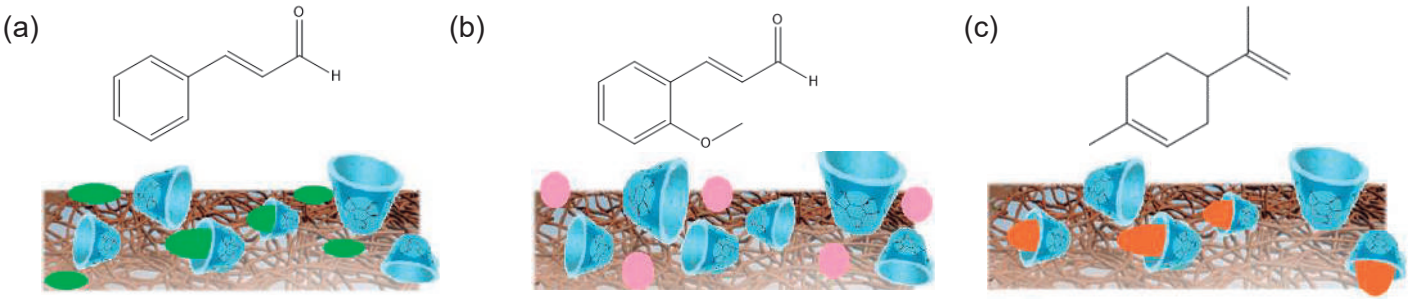
Highlights

Surface modification of cotton modified by grafting β-cyclodextrin (β-CD) fabric for adsorption of essential oils, to evaluate the adsorption capacity over time of cassia cinnamon and orange essential oils. The presence of functional groups in the chemical structures of cinnamaldehyde (aldehyde) and o-methoxy-cinnamaldehyde (aldehyde and methoxy) will promote interactions with celulose.

Resumo/Abstract

The main objective of this work was to obtain a cotton fabric modified by grafting β-cyclodextrin (β-CD) to retain essential oil fragrances and acquire bactericidal properties. The grafting of β-CD onto the fabric was confirmed by FTIR-ATR due to the appearance of the band at 1728 cm-1, the carbonyl signal, corresponding to the formation of the ester bond between the cellulose of the fabric and β-CD, mediated by a polycarboxylic acid that took part in the condensation reaction. To quantify the number of mol β-CD grafted onto the cotton fabric, the indirect spectrophotometric method was used, using phenolphthalein as a probe, quantifying 1,68 µmol g-1 of fabric. In the oil retention profile over 15 days in contact with atmospheric air, determined by GC-MS analysis, it was found that the fabric modified with β-CD did not prolong the retention of essential oils over time, but promoted a significant increase in the initial content of the main component of orange oil, D-limonene, and cinnamaldehyde for cinnamon oil. For the latter oil, another component was monitored, methoxycinnamaldehyde, and it was observed that retention for the unmodified fabric was higher than for the modified fabric. The conclusion is that adsorption can occur chemically through encapsulation in the cavity of β-CD or through the interaction of the analyte with the surface of the cellulose substrate through hydrogen bonds. Due to the presence of functional groups in the chemical structures of cinnamaldehyde (aldehyde) and methoxy-cinnamaldehyde (aldehyde and methoxy), interactions with cellulose were promoted. As D-limonene had no functional groups in its structure, its preference was to make the inclusion complex with β-CD. The figure below shows the chemical structures of the compounds in the oils and how they could interact with the modified fabric.

Figure 1 - Interaction with modified tissue for cinnamaldehyde (a), o-methoxycinnamaldehyde (b) and D-limonene (c).



Agradecimentos/Acknowledgments

CAPES
fapesc Fundação de Amparo à Pesquisa e Inovação do Estado de Santa Catarina
UDESC UNIVERSIDADE DO ESTADO DE SANTA CATARINA
NIPol Núcleo Interdisciplinar de Polímeros

Área: FIS

THERMODYNAMIC OF LYSOZYME-GOLD NANOPARTICULES INTERACTION

Hauster M. C. de Paula (PQ),[1]* Leonardo S. P. Alves (IC),[1] Yara L. Coelho (PQ),[3] Ana C. S. Pires (PQ),[2] Luis H. M. da Silva (PQ).[1]

leonardo.saulo@ufv.br; hauster.paula@ufv.br

[1]Departamento de Química, Universidade Federal de Viçosa – UFV; [2]Departamento de Tecnologia de Alimentos – UFV; [3]Departamento de Química, Universidade Federal de Alfenas – Unifal.

Keywords: Lysozyme, Gold Nanoparticules, NanoITC, NanoDSC, Thermodynamic.

Highlights

Lysozyme-gold nanoparticules interaction was driven by enthalpy with almost no electrostatic contribution. Thermodynamic parameters of interaction were independent of nanoparticules surface group.

Abstract

Gold nanoparticles (NP) have important applications in biology and medicine[1]. In biological environments, NPs are covered with biopolymers forming a protein corona, which can alter the properties and behavior of NPs. Therefore, in order to modulate the protein-NP interaction, it is essential to know the formation energy of this protein corona. The thermodynamic parameters were determinated by nanoITC and the nanoDSC. Fig. 1 shows the calorimetric isothermal titration interaction of lysozyme-NP (LS-NP) coated with citrate or PEG2000. Fitting the $\Delta H_{app-int}$ versus molar ratio curves (Fig. 1) to the model of independent binding sites, the values of the thermodynamic parameters were calculated, table 1. The interaction of NP with lysozyme (LS) was driven by the decrease of enthalpy, associating with a small entropy increase. Regardless of the chemical nature of NP surface group the thermodynamic parameters were very similar demonstrating that electrostatic interaction has a small contribution for the energetic of LS-NP interactions. These results demonstrate that the interaction of lysozyme is preferentially with the NP surface and is very little influenced by the molecules that covered the surface of the nanoparticles. Depending on the [LS/NP] ratio, protein corona is formed with different interactions and molecular packaging, producing films with different denaturation enthalpies and thermal stability (Fig. 2). However, the magnitude of the DH and the maximum denaturation temperature are dependent on the chemical nature of the gold NP coating molecules.

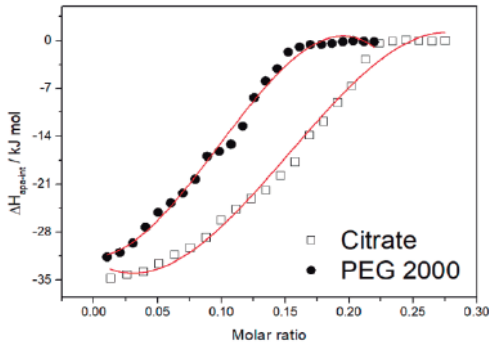


Fig. 1 - Interaction isotherm of LS-NP Citrate or PEG 2000.

Tab. 1 – Thermodynamic parameters of the LS-NP Citrate or PEG 2000 interaction.

NP	ΔH° (kJ mol⁻¹)	TΔS° (kJ mol⁻¹)	ΔG° (kJ mol⁻¹)
Citrate	-34,4	1,1	-35,5
PEG 2000	-31,9	2,9	-34,7

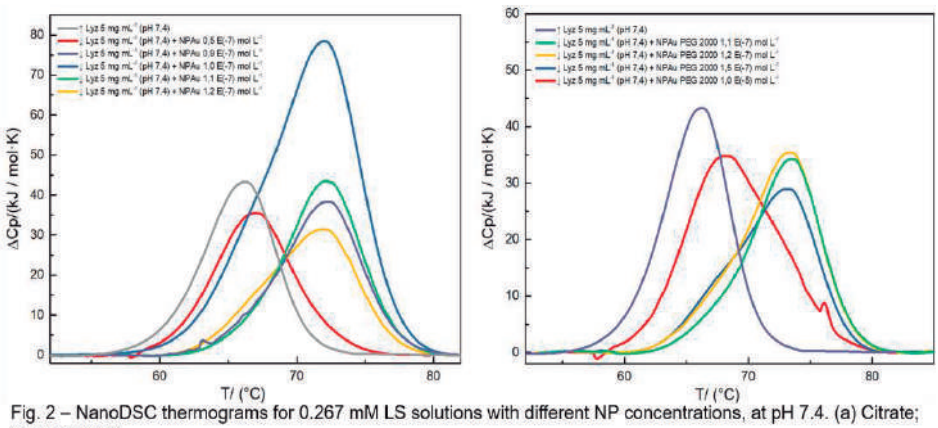


Fig. 2 – NanoDSC thermograms for 0.267 mM LS solutions with different NP concentrations, at pH 7.4. (a) Citrate; (b) PEG 2000.

[1]*J. Phys. Química. B* 2014 , 118 , 49 , 14017–14026

Acknowledgments

FAPEMIG, CNPq, CAPES, and FINEP.

Área: FIS

The use of surface-enhanced Raman scattering spectroscopy and neural network software for detection of proteins in artificial saliva.

Victória de L. Araújo[1] (IC), Daphne F. C. Lanferini[1] (PG), Héliton Martins Reis Filho[2] (PQ), Rita C. O. Sebastião[2](PQ), Nelson H. T. Lemes[3](PQ), Luciano S. Virtuoso[3](PQ), and Antonio Carlos Sant'Ana[1](PQ).

victoria07.laraujo@gmail.com; antonio.sant@ufjf.br

[1] Depto. Química, Univ. Fed. Juiz de Fora, MG; [2] Depto. Química, Univ. Fed. Minas Gerais; [3] Depto. Química, Univ. Fed. Alfenas.

Keywords*: SERS effect, biosensor, bovine serum albumin, nanoscience.*

Highlights

Raman and SERS spectra from artificial saliva samples, in the presence of gold nanoparticles and bovine serum albumin generated input for training a neural network software, as a model for diagnosis.

Abstract

Artificial saliva samples containing non-covalent íons, as chloride salts, either with or without the carboxymethylcellulose (CMC) polymer in the composition, were used as the medium for the record of both Raman and surface-enhanced Raman scattering (SERS) spectra of bovine serum albumin (BSA). Gold nanoparticles (AuNP) synthesized in aqueous medium by reducing of gold ions with borohydride were used as SERS substrate. Exciting radiation with 632.8 nm wavelength was chosen in function of the UV-VIS absorption spectrum of the metallic suspension, which presented a band from the localized surface plasmon resonance (LSPR) transition in this spectral region.[1]

The SERS technique uses metallic nanoparticles to increase the intensity of the Raman signal of molecular adsorbates, which have to be necessarily interacting with the nanostructured surface. The protein BSA was used as a biomarker, which make changes in the spectral pattern even though impressive changes may not be observed. Some set of Raman spectra taken from both artificial saliva samples, as well as SERS spectra of AuNP plus saliva in the proportion 1:1 in volume were done. In addition the set of SERS spectra taken from saliva samples mixed with AuNP and BSA were recorded. The initial set of experimentally obtained spectra gave rise to another set generated computationally by combining 15 observations in each real spectrum, resulting in 225 observations per generated spectrum. In these new spectra, the 'BSA' component could or could not be present. Those spectra containing it were considered positive, while those consisting solely of pure saliva were considered negative. The data were utilized in training a Multilayer Perceptron Artificial Neural Network with two hidden layers, which demonstrated the ability to 'learn' the training data. The group's next steps will involve the validation and optimization of the model using experimental data.

Another set of experiments will be done by using AuNP functionalized with 1-mercaptoethanol (ME), which favored the adsorption of the BSA macromolecule, anchoring her through hydrogen bonds.[2] Such a complete experimental design will be repeated by changing AuNP to silver nanoparticles (AgNP), whose synthesis is also done through the reduction of silver ions with borohydride. In this way AgNP suspension presents LSPR transition in better resonance conditions with exciting radiation with 532 nm wavelength.

The final objective is the use of a low computational cost software to be embedded in portable Raman equipment with the development of artificial neural networks (ANN) that are part of the field of study of artificial intelligence, enabling the detection of deep patterns in data sets and the generation of high-performance predictive models performance that enables accurate, automated diagnosis of viral diseases to eliminate the need for manual analysis.

References:
[1] J. A. Creighton, C. G. Blatchford, and M. G. Albrecht, J. Chem. Soc., Faraday Trans., 1989 (75) 790.
[2] L. O. Noman, and A. C Sant'Ana,. Spectrochim. Acta Part A: Mol. Biomol. Spectrosc., 2018 (204) 119.

Acknowledgments

The authors would like to thank funding agencies CNPq, CAPES, and FAPEMIG.

Área: FIS

Towards a Simple and Cost-Effective Glyphosate Detection Based on a Selective Colorimetric Reaction

Amanda C. Scheuer (IC),[1] Patricia M. Soares (PG),[1] Elisa S. Orth (PQ).[1*]

amandascheuer@ufpr.br; elisaorth@gmail.com

[1]Departamento de Química, UFPR

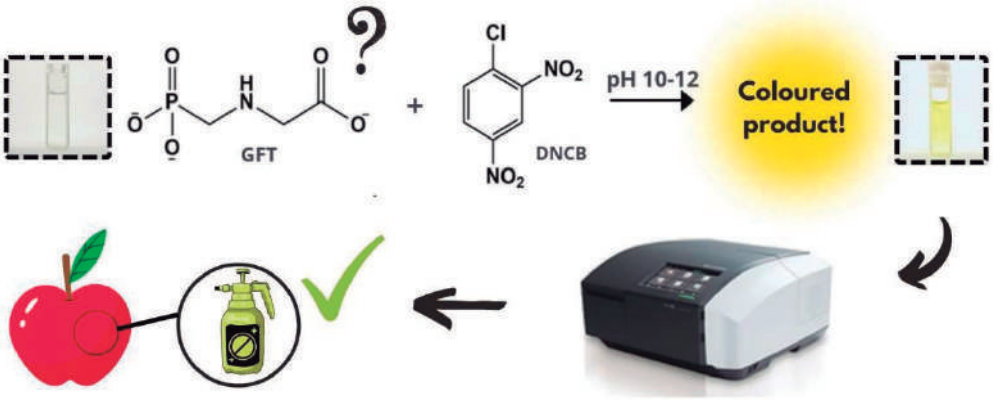
Palavras Chave: *Glyphosate, Pesticide, Derivatization, Organophosphate, Colorimetric detection*

Highlights

- Kinetic studies regarding the derivatization reaction of the organophosphate pesticide glyphosate
- Promote the monitoring of glyphosate in a simple, efficient and low-cost method

Resumo/Abstract

The residues from pesticide applications in Brazil and worldwide pose environmental risks and threats to public health linked to the toxicity of organophosphorus molecules found in pesticide formulations. Glyphosate, the most widely used active ingredient in pesticides globally, still lacks consensus-based regulations establishing its maximum residue limit[1]. The impasse in structuring these public policies is associated with the high cost and complexity of available detection methods – thus, the focus of this study is to detect glyphosate through a simple and cost-effective colorimetric method. For this purpose, the chosen technique involves the derivatization reaction of glyphosate using a nitrobenzene derivative (DNCB). Thorough kinetic studies for this reaction were conducted through UV-vis spectrometry under pseudo-first order conditions, looking for a product that absorbs in the near 400nm region. As the proposed reaction got carried out at pH 10.5, the expected UV-vis formation band was observed, and the kinetic data could be adjusted, indicating favorable conditions. Therefore, the presence of glyphosate could be detected by following the formation of a coloured product, which is stable. The effect of the medium such as concentration and pH was evaluated and with the optimal condition established, the methodology was extended to untreated commercial samples, and the kinetic studies followed the previous model, demonstrating that the additives in commercial formulations do not interfere within the analysis. Overall, the colorimetric detection reaction of glyphosate shows great potential since can be carried out in a couple of minutes and not requiring laborious equipment or pre-treatment. Altogether, the studied technique may, in the future, become accessible to the external community and be applied in a simple and efficient way.



Acknowledgments

UFPR, CAPES, Finep, CNPq, PhosAgro/Unesco/IUPAC, Fundação Araucária, L'Oréal-UNESCO-ABC, INCT NanoVida, INCT Nanocarbono.

References:

1. AMARANTE JUNIOR, O. P. D.; SANTOS, T. C. R. D.; BRITO, N. M.; RIBEIRO, M. L. Glifosato: propriedades, toxicidade, usos e legislação. Química nova, v.25, p.589. 2002.

FOT

Fotoquímica

Sociedade Brasileira de Química

Área: FOT

Caracterização e análise espectroscópica dos alcaloides naturais dicentrina, deidrodicentrina e aristolactama BII

Calvin Q. Cabello (PG),* Stephanie G. Friolani (IC), Marina M. Gonçalves (PG), Daniela C. Tristão (PG), Fernando H. Bartoloni (PQ), João Henrique G. Lago (PQ), Hueder Paulo M. Oliveira (PQ).

calvin.cabello@aluno.ufabc.edu.br

Centro de Ciências Naturais e Humanas, Universidade Federal do ABC (UFABC).

Palavras Chave: *Produtos naturais, solvatocromismo, DFT, Propriedades espectroscópicas, extração e caracterização.*

Highlights

Characterization and spectroscopy analysis of natural alkaloids dicentrine, dehydrodicentrine and aristolactam BII. This work reports the isolation and characterization of three alkaloids and the solvent effect on their absorption and fluorescence properties as well as structural changes promoted in different environments.

Resumo/Abstract

O Brasil possui uma das maiores biodiversidades florísticas mundiais, fato que está diretamente associado a ocorrência de uma elevada quimiodiversidade de produtos naturais, muitos dos quais com diversas aplicações, inclusive na indústria alimentícia, farmacêutica etc. Dentre esses, destacam-se os alcaloides, que são produtos naturais que contém ao menos um núcleo heterocíclico nitrogenado. Dentre os diversos alcaloides naturais, destacam-se os derivados aporfínicos dicentrina (**1**), deidrodicentrina (**2**) e aristolactama BII (**3**). Neste trabalho, os alcaloides **1** e **2** foram obtidos a partir do extrato metanólico de folhas de *Ocotea puberula* (Lauraceae) enquanto **3** foi isolado do extrato hexânico de galhos de *Piper truncatum* (Piperaceae). As estruturas dos alcaloides **1 – 3** (Figura 1) foram definidas por meio da análise dos espectros de RMN de ^{1}H e de ^{13}C, seguido da comparação com dados de literatura. Na sequência, as propriedades espectrais de absorção e fluorescência foram investigadas em uma série de solventes com gradiente de polaridade (clorofórmio – água), como pode ser visto na figura 2. Incialmente foi observado, nesses espectros, um deslocamento hipsocrômico na banda mais intensa dos compostos, com o aumento da polaridade do solvente, sendo essa característica de transições n – π*, permitindo inferir que o par não-ligante do nitrogênio conjugado ao sistema π, deve ser o responsável por essas bandas. Também foram feitos cálculos computacionais e realizadas correlações entre os dados teóricos e experimentais obtidos (figura 3), que permitiu a atribuição das principais transições às suas respectivas bandas, sendo para o composto **1,** H-2 → L (280 nm), H-1 → L (305 nm), para o composto **2,** H-2 → L (260nm), H-2 → L+1 (268 nm), H-1 → L (325 nm), H → L+1 (345 nm), H → L (385 nm) e para o composto **3,** H-1 → L+1 (275 nm), H → L+1 (285 nm), H-2 → L (315 nm), H → L (385 nm). Dessa forma, mapeando cada um dos orbitais envolvidos, foi possível avaliar a influência dos grupos funcionais em cada uma das bandas estudadas. Por meio da análise das correlações entre os dados obtidos para os diversos solventes e parâmetros de solvente como α,β de Reichardt, de polaridade (Δf) e E_T^N, foi possível a compreensão das interações intermoleculares realizados por esses alcaloides e seu comportamento em diferentes ambientes, o que pode auxiliar nas possíveis aplicações para esses compostos.

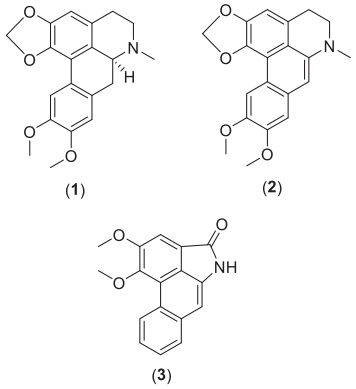


Figura 1 - Estrutura dos alcaloides **1 - 3**

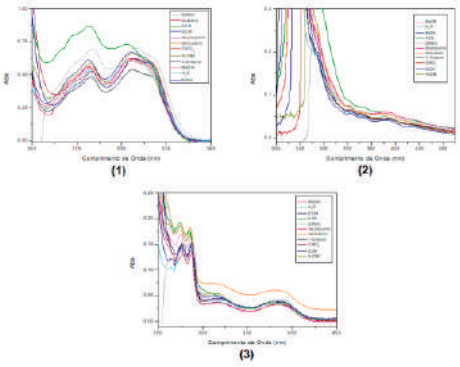


Figura 2 – Efeito do solvente nos espectros de absorção dos alcaloides **1 – 3**

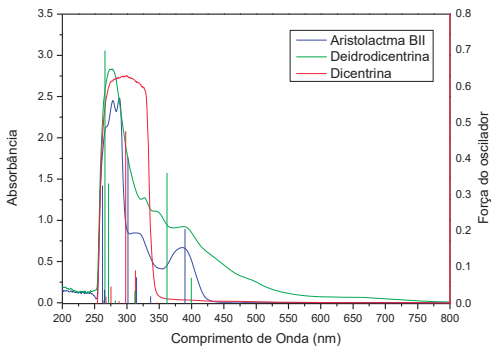


Figura 3 – Espectro de absorção comparado às transições calculadas dos alcaloides **1 - 3**

Agradecimentos/Acknowledgments

UFABC, CNPq, CAPES e FAPESP

Área: FOT

Designing a new Cu(II) complex featuring NHC ligands as a promising photoredox catalyst for CRP2 reaction

Maria L. B. de Figueiredo (PG)[1], Valdemiro P. de Carvalho Jr. (PQ)[1], Beatriz E. Goi (PQ)[1]*

*maria.botter@unesp.br; beatriz.goi@unesp.br**

Department of chemistry and biochemistry, Faculdade de Ciências e Tecnologia, Univ. Estadual Paulista - UNESP, Presidente Prudente-SP, Brazil

Palavras Chave: *N-heterocyclic carbene; CRP2; copper(II);*

Highlights

A new Cu(II) complex was synthesized with 1-methyl-3-phenyl-1H-benzo[d]imidazol-3-ium (Pmb) as the ligand and further applied as a photoredox catalyst in the Controlled Radical Photopolymerization (CRP2) of methyl acrylate (MA) using ethyldimethylaminobenzoate (EDB) and phenacyl bromide (PBr) as additives.

Resumo/Abstract

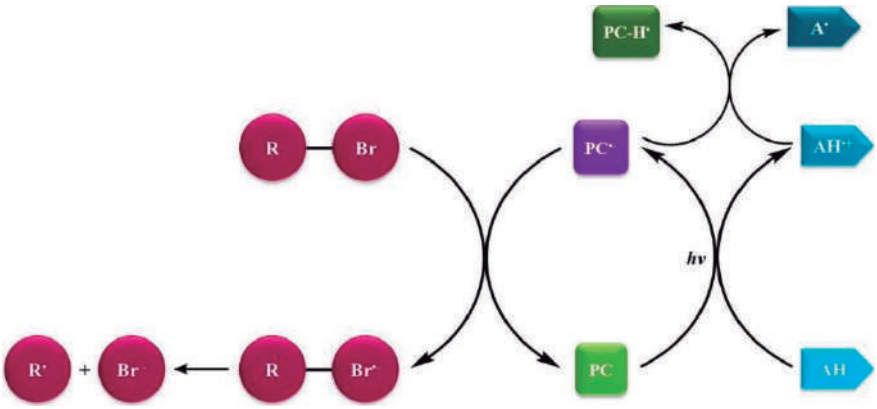


Figure 1. Reductive pathway for the CRP2 of MA catalyzed by complex in the presence of EDB and PBr.

Photoredox polymerization has been employed as a technique for obtaining precisely defined polymers. Among the extensively researched methods is Controlled Radical Photopolymerization (CRP2), which stands as one of the most studied approaches.[1,2] The Pmb ligand and its complex ([Cu(Pmb)$_2$]) were synthetized and further characterized by FTIR, UV-Vis, cyclic voltammetry, fluorescence spectroscopy and ^{1}H NMR. The synthesized complex and the ligand were additionally studied photophysically in the presence of polymerization additives under 365 nm LED light. The behavior of the complexes obtained was also monitored against irradiation at 365 nm LED light, and its sensitivity to air. The synthesized complex was active as a photocatalyst in methyl acrylate (MA) CRP2, using PBr as initiator and EDB as electron donor. The obtained polymers exhibited uniform masses with Đ < 2. The best condition for the photocatalysis was in the molar ratio of [MA/PBr/Cu(II)/EDB] = 200/1/0.12/1.

1- Federico Bella, Roberta Bongiovanni. Photoinduced polymerization: An innovative, powerful and environmentally friendly technique for the preparation of polymer electrolytes for dye-sensitized solar cells. Journal of Photochemistry and Photobiology C: Photochemistry Reviews, 16, 1-21.(2013)

2- Mao Chen, Mingjiang Zhong, and Jeremiah A. Johnson. Light-Controlled Radical Polymerization: Mechanisms, Methods, and Applications. Chem. Rev. 116, 17, 10167–10211 (2016).

Agradecimentos/Acknowledgments

FAPESP

CAPES

LaCOM

Área: FOT
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Development of new Co(II) and Fe(II) complexes bearing NHC's as potential photoredox catalysts for CRP2 reaction

Camila Bignardi (PG)[1], Naralyne M. Pesqueira (PG)[1], Yasmin de M. Shimizo,[1] Valdemiro P. de Carvalho Jr. (PQ)[1], Beatriz E. Goi (PQ)[1]*

*c.bignardi@unesp.br; beatriz.goi@unesp.br**
Department of chemistry and biochemistry, Faculdade de Ciências e Tecnologia, Univ. Estadual Paulista - UNESP, Presidente Prudente-SP, Brazil

Palavras Chave:*N-heterocyclic carbene; CRP2; iron(II); cobalt(II);*

Highlights

New Co(II) and Fe((II) complexes were synthetized from the py-mesethylimidazole and further applied as photoredox catalysts to the *Controlled Radicalar Photopolymerization (CRP2)* of the methyl acrylate using triethylamine (TEA) and phenacyl bromide (Ph-Br) as the additives

Resumo/Abstract

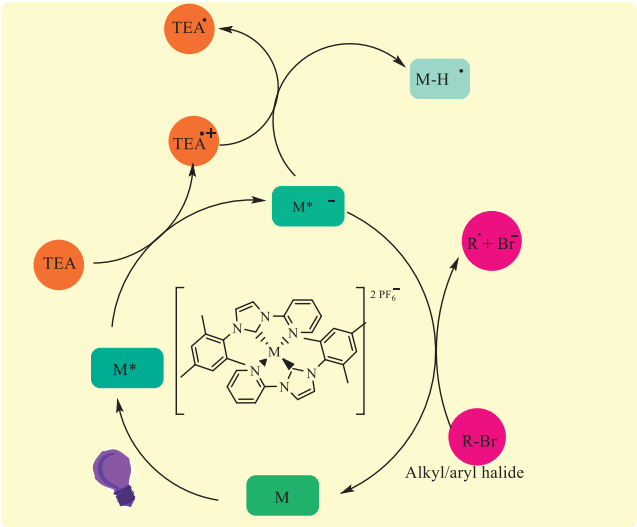


Figure 1. Reductive pathway for the CRP2 of MA catalyzed by complex in the presence of TEA and Ph-Br.

The photoredox polymerization has been used as a method to obtain well-defined polymers. One of the most studied methods is the *Controlled Radicalar Photopolimerization (CRP2)*.[1,2] The **[Co^{II}(py-mesethylimidazole)$_2$](PF$_6$)$_2$** and **[Fe^{II}(py-mesethylimidazole)$_2$](PF$_6$)$_2$** complexes were synthesized from the NHC (*N*-heterocyclic complexes), py-mesethylimidazole, and further characterized. The py-mesethylimidazole ligand was characterized by FTIR, UV-Vis, fluorescence spectroscopy and ^{1}H NMR. The complexes **[Co^{II}(py-mesethylimidazole)$_2$](PF$_6$)$_2$** and **[Fe^{II}(py-mesethylimidazole)$_2$](PF$_6$)$_2$** by FTIR and UV-Vis, cyclic voltammetry, MALDI-TOF and fluorescence spectroscopy. The synthesized complexes and the ligand were additionally studied photophysically in the presence of polymerization additives at 365 nm. The Stern-Volmer constant was estimated. The behaviour of the complexes obtained was also monitored against irradiation at 365 nm, and its sensitivity to air. The synthesized complexes were active as a photocatalyst in methyl acrylate (MA) CRP2, using phenacyl bromide (Ph-Br) as initiator and triethylamine (TEA) as electron donor. The obtained polymers exhibited uniform masses with Đ < 2. The best condition for the photocatalysis was in the molar ratio of [MA/Ph-Br/M^{II}/TEA] = 200/1/0.12/1 with $M_n \leq 190000$ g·mol^{-1} and Đ ≤ 1.4 with 56% conversion.

1- Federico Bella, Roberta Bongiovanni. Photoinduced polymerization: An innovative, powerful and environmentally friendly technique for the preparation of polymer electrolytes for dye-sensitized solar cells. Journal of Photochemistry and Photobiology C: Photochemistry Reviews, 16, 1-21.(2013)

2- Mao Chen, Mingjiang Zhong, and Jeremiah A. Johnson. Light-Controlled Radical Polymerization: Mechanisms, Methods, and Applications. Chem. Rev. 116, 17, 10167–10211 (2016).

Agradecimentos/Acknowledgments

Proc. 2021/11873-1, 2021/13128-1 and 2022/16571-6

IÁrea: FOT
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Investigation azo dyes as potencial organic photocatalysts in chemical reactions CRP2

Isabela Zago de Carvalho (IC),[1] Camila Bignardi (PG),[1] Valdemiro P. De Carvalho Jr. (PQ),[1] Beatriz E. Goi (PQ)[1]

isabela-zago.carvalho@unesp.br; beatriz.goi@unesp.br

[1]*Departamento de Química e Bioquímica, Faculdade de Ciências e Tecnologia – FCT - UNESP – Presidente Prudente, São Paulo.*

Palavras Chave: *Controlled Radical Polimerization 2, Photocatalysts, Azo dyes, Photopolimerization, Organic photocatalyst.*

Highlights

The azo dyes were synthesized according to the literature, using the 3-ethoxy-salicylaldehyde as a precursor. The azo dyes were characterized by FTIR, UV-Vis, NMR, MALDI-TOF. The catalytic activity of the azo dyes were evaluated the CRP2 of methyl methacrylate under LED irradiation in the presence of EDB and PhBr.

Resumo/Abstract

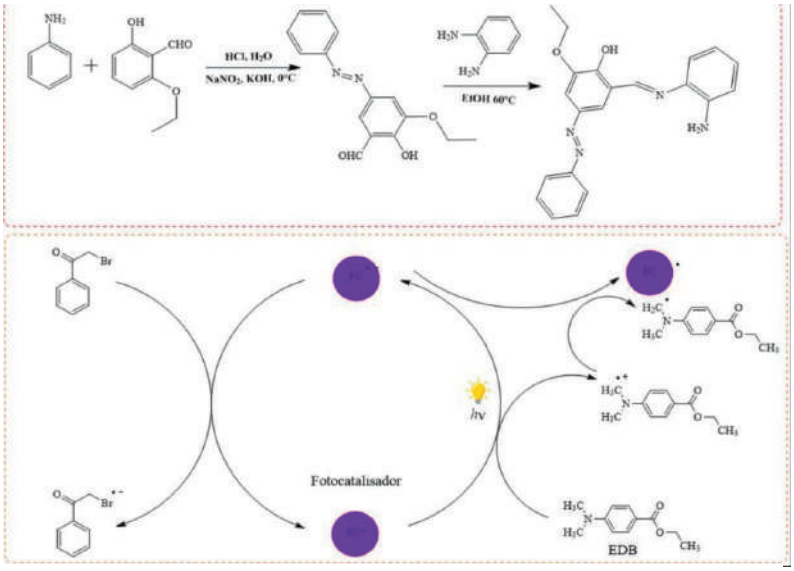


Fig.1 – Azo dyes syntnesis scheme and photopolymerization mechanism for the PCO

Despite the fact that organic chromophores have long been acknowledged for their ability to participate in photoinduced electron transfer (PET) processes, their catalytic use as applied to organic synthesis is somewhat less familiar. Topics in organic photoredox catalysis have been reviewed previously but are relatively narrow in scope or predate recent important advances in catalyst development and the discovery of new reactivity.[1] Also, organic photoredox catalysis offers far more than "metal-free" alternatives to transition metal catalyzed examples; namely, the potent reactivity afforded by many organic catalysts allows access to unique chemistries and a broad range of substrates that are unreactive in most synthetic contexts.[1] The photophysical properties of the PCO can be increased by increasing the presence of chromophore groups. In this regard, we proposed two azo dyes that were synthetized and further characterized by FTIR, UV-Vis, NRM ^{1}H and fluorescence spectroscopy. The photochemical properties were evaluated in the presence of the aditives (Ethyl 4-(dimethylamino)benzoate, EDB) and phenacyl bromide (Ph-Br) under LED irradiation. The compounds 5-azo-3ethoxy-sal and SB-5-azo-3-ethoxy were both applied in the CRP2. The monomer used was methacrylate (MMA) in the presence of EDB and Ph-Br. The polymerization kinetics was monitored by UV-vis spectroscopy to evaluate the reaction iniciation steps and by FT-IR. For both the azo dyes, the kinetics observed was a linear pseudo-first order.

1. Bonardi, A.-H.; Dumur, F.; Noirbent, G.; Lalevée, J.; Gigmes, D. Beilsteins J. ***Org. Chem***. 2018, 14, 3025–3046.
2. Nathan A. Romero and David A. Nicewicz. ***Chem. Rev.*** 2016, 116, 10075−10166

Agradecimentos/Acknowledgments

Área: FOT

Photo-CMRP of MA mediated by Co(II) complexes coordinated to *salen-type* ligands.

Larissa F. de Oliveira (PG),[1] Valdemiro P. Carvalho Jr. (PQ),[1] Beatriz. E. Goi (PQ)[1]

larissa.fazioni@unesp.br

[1]*Departamento de Química e Bioquímica, FCT-UNESP, Presidente Prudente.*

keywords: *photo-CMRP, MA, Cobalt(II) complexes, Salen-type ligands.*

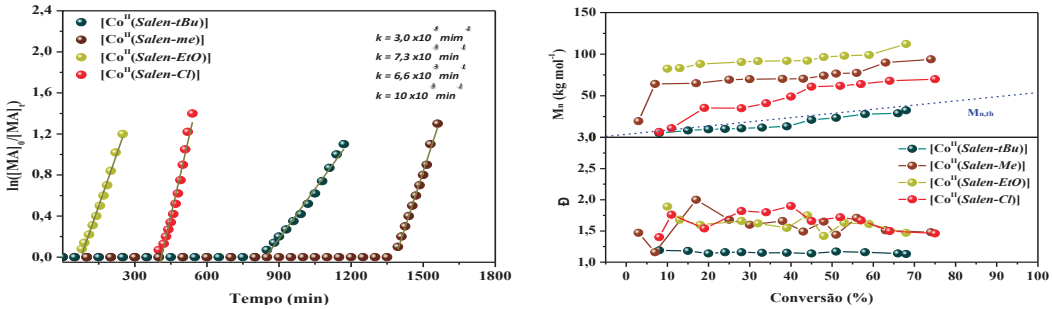
Highlights

Four Cobalt(II) complexes coordinated to Salen-type ligands were synthesized and further used as mediators in Cobalt-Mediated Radical Photopolymerization (*photo*-CMRP) of methyl acrylate (MA) in the presence of óxido de Di-fenil(2,4,6-trimetilbenzoil)fosfina (TPO).

Abstract

The *photo*-CMRP is known to promote a control in polymerization reactions. Such control can occur via Reversible Deactivation (RD) leading to the reduction of radicals through the equilibrium between active (Co^{II}) and dormant (Co^{III}) species or via Degenerative Transfer (DT) where there is an excess of radical species leading to simultaneous coupling/decoupling of the radicals to the Co(II) center. [1] In this work, four Co(II) complexes bearing Salen-type ligands were synthesized and further characterized by FTIR, UV-VIS, Cyclic Voltammetry and MALDI-TOF. Subsequently, the mediating activity of the complexes were evaluated. The complexes were used as mediators in the *photo*-CMRP of the MA using TPO as a photoinitiator, in the molar ratio [MA]/[Co^{II}]/[TPO] of 600/1/1. Also, the photolysis experiment was performed, for all the complexes, in order to obtain the K_{eq} values between Co^{II} and Co^{III} species. K_{eq} values below 10^5 indicate an incomplete conversion of Co^{II} to Co^{III}, leading to poor control in polymerization. [2]

Figure 1. Kinetic for the photo-CMRP of MA in the molar ratio [MA]/[Co^{II}]/[TPO] of 600/1/1 and evolution of molecular weight and polydispersity vs. MA conversion



The photo-CMRP mediated by the [Co^{II}(*Salen-tertButil*)] complex showed a high control throughout the polymerization, providing polydispersity index (Đ)very close to 1,00 (1,13 < Đ < 1,19) and $M_{n,exp}$ values close to the $M_{n,th}$. The K_{eq} of the species Co^{II} and Co^{III} found for this complex was 1.7 x 10^6 M^{-1}, indicating a control RD mechanism. Otherwise, the [Co^{II}(*Salen-methyl*)], [Co^{II}(*Salen-ethoxy*)] and [Co^{II}(*Salen-chloro*)] complexes provided high values of Đ and $M_{n,exp}$ deviating from the $M_{n,th}$. The K_{eq} values found for these complexes were, respectively, K_{eq} = 7.5 x 10^5 M^{-1}; 1.4 x 10^6 M^{-1} and 6.2 x 10^5 M^{-1}; justifying the low control in polymerization. Consequently, kinetic studies corroborated with photolysis studies indicate better efficiency of the [Co^{II}(*Salen-tertButil*)] complex as a mediating agent in the photo-CMRP of MA.

[1] Silva, T. T.; et al. J. Macromol Sci, Part A Pure and Applied Chemistry. v. 56, n. 12, p.1132–1140. 2019.

[2] Wang, F. S.; et. al. Macromol. Chem. Phys, 217, 422–432. 2016.

Acknowledgments

LaCOM

FAPESP FUNDAÇÃO DE AMPARO À PESQUISA DO ESTADO DE SÃO PAULO

CAPES

Área: _____*FOT*_____

Methyl acrylate CRP2 mediated by Fe(III) complexes bearing symmetric Schiff bases ligands

Yasmin de M. Shimizo (IC),[1*] Camila Bignardi (PG),[1] Naralyne M. Pesqueira (PG),[1] Valdemiro P. de Carvalho Jr. (PG),[1] Beatriz E. Goi (PG).[1]

***yasmin.shimizo@unesp.br; beatriz.goi@unesp.br**

[1]*Departamento de Química e Bioquímica, FCT-UNESP, Presidente Prudente.*

Keywords: Fe(III) complexes, Photocontrolled Radical Polymerization, symmetrical Schiff bases.

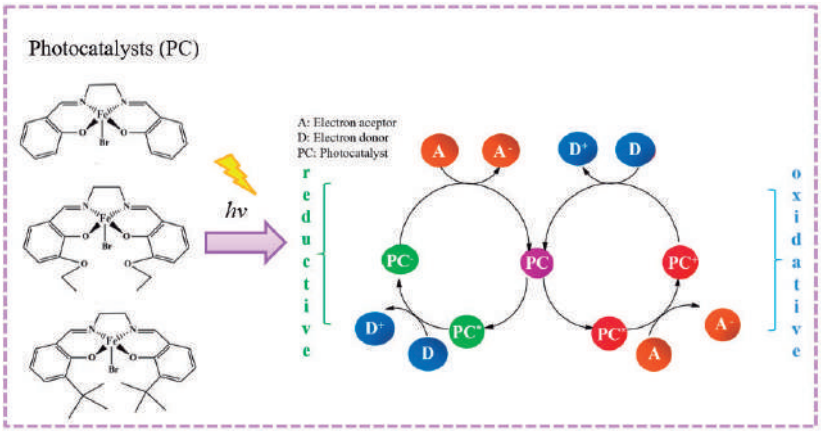
Highlights

Fe(III) complexes bearing Schiff base ligands were synthesized and further characterized by FTIR, UV-Vis, NMR, MALDI-TOF. The catalytic activity of the complexes in the CRP2 of methyl acrylate was evaluated under LED irradiation in the presence of EDB and Ph-Br.

Resumo/Abstract

First, as an alternative of thermal polymerizations, polymerization upon light irradiation offers a good alternative, because it is a greener technology. These systems do not need to be heated and no volatile organic compounds are released. It is possible to perform photopolymerizations upon soft irradiation conditions with LEDs light, for example. The photopolymerization reactions are important because they are encountered for applications in a lot of sectors[1].
Secondly, iron-based catalysts have attracted attention due to the are less toxic, inexpensive, and biocompatible catalytic systems and interesting due to the abundance of iron[2].
In this research, Fe(III) complexes bearing symmetric Schiff bases ligands were synthesized and characterized by H^1 NMR, FTIR, UV-Vis and MALDI-TOF. Thus, Fe(III) complexes were investigated as photocatalysts in the Controlled Radical Photopolymerization of methyl acrylate under LED irradiation.
Their General chemical mechanisms of CRP2 mediated by Fe(III) complexes are shown in **Scheme 1**.

Scheme 1. General chemical mechanisms of CRP2 mediated by Fe(III) complexes



Fe(III) complexes were combined with an alkyl bromide (phenacyl bromide, Ph-Br) and an aromatic amine (Ethyl 4-(dimethylamino)benzoate, EDB) under LED irradiation. The conversion degree and the respective polymerization rate were investigated by FTIR spectroscopy in conjunction with Attenuated Total Reflection, monitoring the band of the olefin in the methyl acrylate monomer at 1635 cm^{-1}. Furthermore, Fe(III) complexes were able to catalyst the photopolymerization. It was also possible to observe the increasing of molecular mass with conversion and the Đ values indicated a slightly controlled polymerization.

1. Bonardi, A.-H.; Dumur, F.; Noirbent, G.; Lalevée, J.; Gigmes, D. Beilsteins J. ***Org. Chem***. 2018, 14, 3025–3046.
2. Pan, X.; Malhotra, N.; Zhang, J. e Matyjaszewski, K. ***Macromolecules***. 2015, 48, 6948.

Agradecimentos/Acknowledgments

Proc. 2021/11873-1 and 2021/13128-1

Área: FOT
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Optimization of a closed in-line system for degradation of the 05 orange dye from wastewater

Rodrigo J. Araújo (PG)[1,2], Tiago P. Muller (IC)[1,2], Adriano V. Chagas (PG)[1,2] Aristides Pavani Filho (PG)[1], Sergio L. C. Ferreira (PQ)[1,2]

tiago.muller_ufba@hotmail.com; slcf@ufba.br

1- Universidade Federal da Bahia, Instituto de Química, Campus Ondina, 40170-270, Salvador, Bahia, Brazil

2- Instituto Nacional de Ciência e Tecnologia, INCT, de Energia e Ambiente, UFBA, 40170-115, Salvador, Bahia, Brazil.

Degradation; 05 orange dye, inline system; UV radiation; 30% hydrogen peroxide.

Highlights

An inline system was optimized for the degradation of the 05 orange dye using UV radiation.

The kinetics of the degradation reaction was studied, and the apparent kinetic constant was determined.

The dose of UV radiation necessary for degrading a mass of 05 orange dye was quantified.

Resumo/Abstract

This work proposes a closed inline system for degrading 05 orange textile dye. The system is constructed using a PTFE tube with a diameter of 0.8 mm and a 15 W UV lamp. The dye solutions circulate through the system after adding 30% hydrogen peroxide. The optimization was carried out using a 2^3 two-level full factorial design involving the factors: flow rate of the solutions in the system, photobleaching time, and the UV radiation coil size. Triplicates of the central point were performed to determine the pure error and the curvature test. The system's efficiency was evaluated through the discolorations of the solutions, measured by the absorbance in the wavelength of 520 nm. The kinetics of the degradation reaction was studied, and the apparent kinetic constant obtained was (Kap = – 0.2854x, R^2 = 0.99). The system was efficient, degrading 98% of a mass of 822 mg of dye in 12 minutes. The UV energy dose required for discoloration was also calculated as 1410 J.

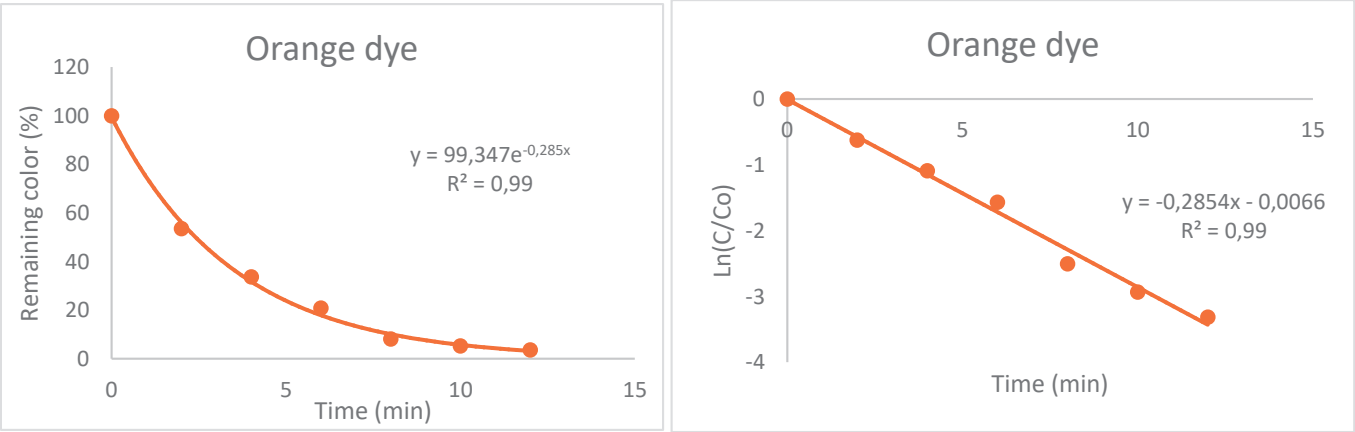


Fig. 1. Degradation test using H_2O_2 and UV lamp of for the dye orange.

gments

The authors thank the fellowships and financial support from the Brazilian agencies Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) (Finance Code 001), and Fundação de Amparo à Pesquisa do Estado da Bahia (FAPESB).

Área: FOT

Propriedades fotofísicas e cálculos químico quânticos das antraquinonas crisofanol, quinizarina e 2,6-Diaminoantraquinona

Calvin Q. Cabello (PG),[1*] Fernando H. Bartoloni (PQ),[1] João Henrique G. Lago (PQ),[1] Hueder Paulo M. Oliveira (PQ).[1]

hueder.paulo@ufabc.edu.br; calvin.cabello@aluno.ufabc.edu.br

[1] *Centro de Ciências Naturais e Humanas, Universidade Federal do ABC (UFABC).*

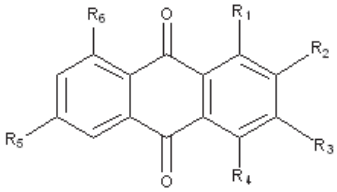
Palavras Chave: Solvatocromismo, Propriedades espectroscópicas, Tempo de vida, DFT, Cálculo estrutural

Highlights

Photophysical properties and quantum chemical calculations of anthraquinones chrysophanol, quinizarin and 2,6-Diaminoanthraquinone. This work reports the spectroscopic characterization of three anthraquinones, investigating the solvent effect on their absorption and fluorescence properties as well as structural changes.

Resumo/Abstract

As propriedades espectrais de absorção e fluorescência de três antraquinonas - crisofanol (**1**), quinizarina (**2**) e 2,6-diaminoantraquinona (**3**) (figura 1) - foram investigadas em uma série de solventes de diferentes polaridades através de técnicas espectroscópicas (figura 2) e cálculos químicos quânticos (DFT). Os corantes antraquinônicos são caracterizados por possuírem forte caráter de transferência interna de carga e as propriedades fotofísicas das hidroxiantraquinonas são governadas pelas ligações de hidrogênio intramoleculares que são formadas, como pode ser visto em sua densidade eletrônica (figura 3). Desvios no efeito de solvente esperado são observados para todos estes corantes, e são atribuídos à ligação de hidrogênio intermolecular com o solvente. Em especial para o composto (**3**), também são observados desvios em solventes de baixa polaridade em comparação com aqueles de alta polaridade devido a mudanças estruturais quando em presença de solventes de média e alta polaridade, em que a molécula adota uma estrutura planar elevando a ressonância dos pares eletrônicos não-ligantes do grupo amino com a nuvem π do sistema antraquinônico.



1. $R_1 = R_6$: OH , R_3 : CH_3 , $R_2 = R_4 = R_5$: H
2. $R_1 = R_4$ - OH , $R_2 = R_3 = R_5 = R_6$: H
3. $R_2 = R_5$ - NH_3 , $R_1 = R_3 = R_4 = R_6$: H

Figura 1 - Estrutura das antraquinonas **1 - 3**

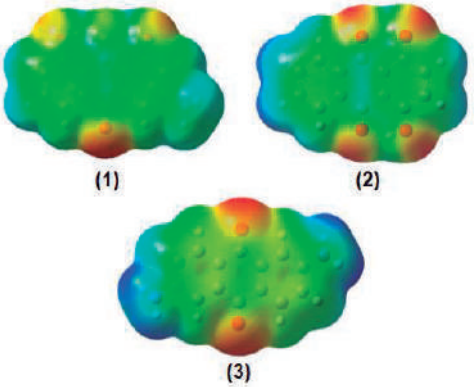


Figura 1 - Potencial eletrostático mapeado na densidade eletrônica dos compostos **1 - 3**

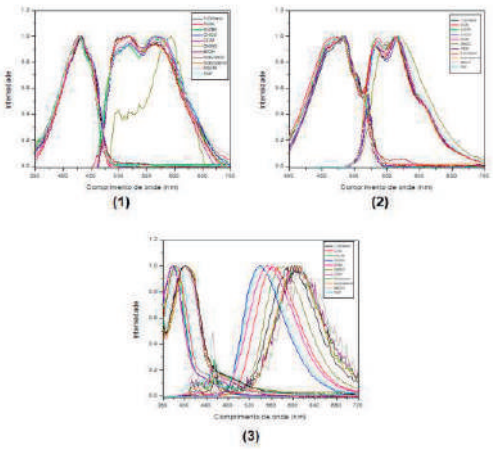


Figura 2 - Espectros normalizados de absorção e fluorescência das antraquinonas **1 - 3** em diferentes solventes

Agradecimentos/Acknowledgments

UFABC, CAPES, CNPq e FAPESP

INO

Química Inorgânica

Sociedade Brasileira de Química

Área: INO

Ag-modified ZnO structures with potential electrochemical properties

Maikon Rangel Alves Alexandre (IC),[1] Iury Horran Pereira Castro (IC),[1] Gonçalves Jotamo Marrenjo (PG),[1] Osmando Ferreira Lopes (PQ),[1] Renata Cristina de Lima (PQ)[1*].

maikonrangel@ufu.br; rclima@ufu.br

[1]*Instituto de Química, Universidade Federal de Uberlândia (UFU).*

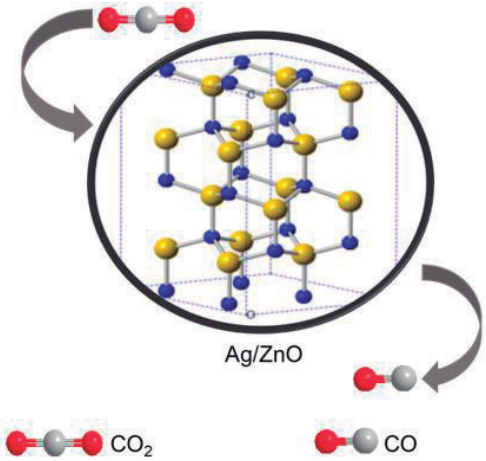
Palavras-Chave: *Zinc oxide, Semiconductor, Carbon dioxide reduction, Environment.*

Highlights

- Nanocrystalline materials of ZnO and Ag/ZnO obtained by microwave-hydrothermal.
- Effect of Ag on the structure and properties of ZnO.
- Promising materials for electrochemical applications.

Resumo/Abstract

Zinc oxide (ZnO) is a stable, non-toxic semiconductor with high chemical stability and good electrical, optical, luminescent, magnetic and piezoelectric properties. This oxide has a wide band gap of 3.4 eV, showing promise for technological and industrial applications, such as light-emitting diodes and optical devices, photovoltaic cells and photocatalytic activity. In addition, ZnO presents a significant oxidative capacity to promote the formation of reactive oxygen species, therefore being an attractive material for biological applications as antimicrobial, antifungal, biosensor modifier and as an alternative for pollutant degradation and CO_2 conversion. [1,2] The incorporation of different ions and metals in the oxide lattice, as well as, the control of synthesis parameters as pH, reaction time, temperature and used precursors has been studied by our research group for improving semiconductor properties. Due to the accumulation of CO_2 in the atmosphere and its contribution to global warming, reduction of this gas is a promising approach for recycling atmospheric CO_2 into value-added organic molecules such as carbon monoxide, methane, formic acid, ethylene and other hydrocarbons, and ZnO nanomaterials are good candidates for promoting CO_2 reduction.[3] In this work, ZnO and Ag/ZnO nanoparticles with different amounts of metallic silver (2, 4, 8 and 16 mol%) were obtained under microwave-hydrothermal conditions after 8 minutes of synthesis, a simple and ecological method that offers advantages such as fast and homogeneous heating compared to a conventional hydrothermal method, aiming to evaluate the properties of materials obtained and the effect of Ag^0 concentration in the oxide lattice for promoting CO_2 reduction. The X-ray diffractograms of pure ZnO samples confirmed the formation of a single crystalline phase corresponding to the wurtzite structure of oxide and Ag/ZnO samples showed two additional peaks related to metallic silver in the oxide lattice. The Raman spectra of the samples showed characteristic peaks of the wurtzite ZnO structure and additionally a decrease in intensity of these peaks in the silver samples, which can be attributed to the breaking of crystal symmetry due to addition of silver in the lattice. SEM images revealed clusters of nanostructures with an average size of 93 nm. Experiments on the electrochemical reduction of CO_2 to carbon monoxide and studies on the reducing properties of these materials, their efficiency and their stability are being studied.



[1]Gusmão, L. A. *et al.* Alkali influence on ZnO and Ag-doped ZnO nanostructures formation using the microwave-assisted hydrothermal method for fungicidal inhibition. *Journal of Physics and Chemistry of Solids* 158, 110234, 2021.
[2]Khan M. *et al.* ZnO microsphere synthesis for efficient sonophotocatalytic degradation of organic pollutants and CO_2 conversion. *Environmental Nanotechnology, Monitoring & Management* 18, 100711, 2022.
[3]Bhalothia D. *et al.* Reaction pathways for the highly selective and durable electrochemical CO_2 to CO conversion on ZnO supported Ag nanoparticles in KCl electrolyte. *Applied Surface Science* 608, 155224, 2023.

Agradecimentos/Acknowledgments

The authors are grateful to Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES), Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq, grant #310290/2020-1) and Fundação de Amparo à Pesquisa do Estado de Minas Gerais (FAPEMIG, grant #APQ-01661-22) for the financial support.

Área: INO

Analysis of the photocatalytic activity of doped Zinc Sulfide quantum dots in the degradation of the methylene blue molecule

Mayara F. Santos (IC)[1], Ana L.C. Doimo (IC)[1], Numbia A. Lima (IC)[1], Caterina G. C. M. Netto (PQ)[1]

mayarafs@estudante.ufscar.br; caterina@ufscar.br

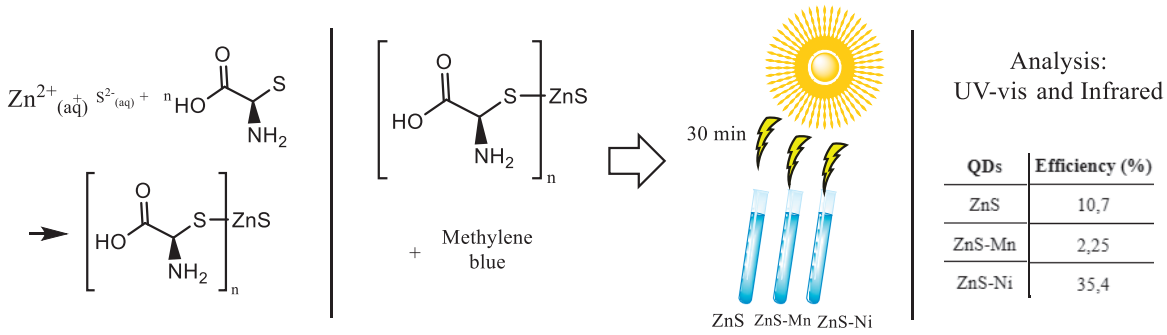
[1]*Departamento de Química, UFSCar*

Key words: Doped complexes, inorganic, photocatalysis, quantum dots.

Highlights

Analysis of the degradation of methylene blue molecules through the photocatalytic activity of zinc sulfide quantum dots, doped or undoped with Nickel or Manganese.

Resumo/Abstract



QDs	Efficiency (%)
ZnS	10,7
ZnS-Mn	2,25
ZnS-Ni	35,4

Large quantities of water contaminated with dyes are discharged into rivers by textile, paper, and cosmetic industries. These dyes can cause serious health problems and there is a need to develop methodologies for the degradation of these compounds. This study focused on analyzing the photocatalytic activity of compounds known as quantum dots (QD), which are semiconductor nanostructures possessing unique optical and electronic properties due to their extremely small size. In this case, zinc sulfide dots (ZnS QDs) were evaluated for their performance in the photodegradation of methylene blue. QDs doped with 4% Nickel or Manganese were synthesized, and it was assessed whether doping would influence the photodegradation. The synthesis of ZnS, ZnS-Mn, and ZnS-Ni QDs was conducted using a closed system with a nitrogen atmosphere, employing the chemical co-precipitation method. The QDs were analyzed by UV-Vis spectrophotometry, revealing maximum absorbance bands at 250 nm for ZnS and ZnS-Ni, and for ZnS-Mn, two main bands at 250 nm and 360 nm, indicating that doping altered the compounds' absorption compared to literature data. Additionally, methylene blue was used as a model pigment for degradation, and its degradation was evaluated by the decrease in UV-Vis absorbance, assessing whether doping with Mn^{2+} and Ni^{2+} would also influence it. It was observed that the doping of the complexes affects their photocatalytic activity, with ZnS doped with nickel exhibiting higher efficiency (35.4%) and ZnS doped with Mn showing lower efficiency (2.25%). This possibly occurs due to the difference in the electron transition from the valence band to the hole band in the doped ZnS compounds. Nickel (Ni) has more electron-hole pairs near the valence band than Manganese (Mn), allowing it to require less energy for the transition than Mn, thus being more efficient in degradation. In conclusion, doping of the compound can be efficient for methylene blue degradation, depending on the metal used.

Agradecimentos/Acknowledgments

We acknowledge FAPESP process 23/09722-0 for the financial support.

Área: INO

Atividade antifúngica de porfirinas catiônicas induzida por luz

Pedro Fonseca Pinheiro (IC),[1] Victor Augusto Teixeira Leocádio (PQ),[2] Nathany Isabelly Dias Vieira (PG), [1]Gilson DeFreitas-Silva (PQ),[1] Daniel Assis Santos (PQ),[2] Dayse Carvalho da Silva Martins (PQ)[1]*

*** daysequimica@ufmg.br; pedrofp.ufmg@gmail.com**

[1]Departamento de Química, ICEx/UFMG; [2]Departamento de Microbiologia, ICB/UFMG.

Palavras Chave: *Terapia de fotoinativação antimicrobiana, Fungos, Luz visível, Porfirinas hidrossolúveis.*

Highlights

Light-induced antifungal activity of cationic porphyrins. Free-base and manganese cationic porphyrins were studied as antifungal agents activated by light. Three species of *Candida* were efficiently photoinactivated.

Resumo

A candidíase invasiva (CI) é uma infecção fúngica grave causada por diversas espécies de *Candida*, apresentando taxas de mortalidade que variam entre 40% e 55%.[1] Infecções por *Candida* resistentes a um ou vários tipos de antifúngicos são cada vez mais diagnosticadas,[2] o que tem estimulado o desenvolvimento de abordagens alternativas e minimamente invasivas como a terapia de fotoinativação antimicrobiana, em que um fotossensibilizador é ativado por luz visível e atua na destruição do patógeno.

Neste trabalho é relatada a avaliação de duas porfirinas catiônicas base livres e seus respectivos complexos de manganês contra fungos das espécies *Candida albicans*, *Candida glabrata* e *Candida krusei*, considerando-se que esses microrganismos estão entre os cinco patógenos que mais causam CI. A 5,10,15,20-tetraquis(*N*-etil-piridinio-3-il)porfirina ($H_2T3EPyP^{4+}$), a 5,10,15,20-tetraquis(4-*N*,*N*,*N*-trimetilamôniofenil)porfirina ($H_2T4MAPP^{4+}$) e seus análogos de Mn(III) foram avaliados *in vitro*, estudando-se seu efeito inibitório contra as três espécies citadas, sob iluminação com luz verde por 30 minutos. Os valores de concentração inibitória mínima (CIM) foram determinados na presença e ausência de luz. Observa-se que a *C. glabrata* foi a espécie mais susceptível à ação de fotoinativação das porfirinas estudadas, com redução de até 64 vezes da CIM quando se comparam os resultados obtidos para os sistemas irradiados e os sistemas em ausência de luz (Figura 1).

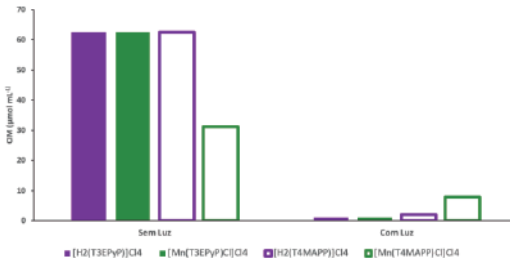


Figura 1. CIM obtido para o tratamento de *C. glabrata* com as porfirinas catiônicas fotoativadas (30 min, luz verde (519 nm), 4,5mW cm^{-2} e 8,1 J cm^{-2}). Os resultados para os outros gêneros de *Candida* serão apresentados no evento.

A determinação de espécies reativas de oxigênio (EROS) e de nitrogênio (ERNS) foi realizada para se avaliar as substâncias participantes do processo de fotooxidação.[3] As EROS e ERNS geradas na terapia de fotoinativação são citotóxicas para a célula alvo, causando desordem na parede celular e danos no DNA, levando à morte do microrganismo. A produção de EROS foi maior nos sistemas em que as porfirinas foram ativadas pela luz, como era esperado, quando compara-se com a produção de ERNS. A atividade de fotoinativação dessas porfirinas é dependente da geração das espécies reativas

Com base nos resultados obtidos, acredita-se que uma adaptação da abordagem da fotoinativação utilizando porfirinas como agentes fotossensibilizadores para terapia de infecções em mucosas e/ou cutâneas por *Candida* em humanos seja possível.

Agradecimentos

CAPES, CNPq, FAPEMIG, FINEP, INCT-CiMOL, PRPq/UFMG.

Referências:
1) Logan, C. *et al*. 2020. DOI:10.1007/s00134-020-06240-x.
2) Arastehfar, A. *et al*. 2020. DOI:10.3390/antibiotics9120877.
3) Ferreira, G.F. *et al*. 2013. DOI:10.1093/jac/dkt114.

Área: INO

Basicidade do NH_3 e geometria do PH_3 explicadas por orbitais moleculares

Ramon N.D. Costa (IC), Talis U. Silva (PQ), Sérgio P. Machado (PQ), Roberto B. Faria (PQ)

ramoncosta08@hotmail.com; faria@iq.ufrj.br

Instituto de Química - UFRJ

Palavras Chave: Basicity, Ammonia, Phosphine, Molecular Geometry, Molecular Orbitals

Highlights

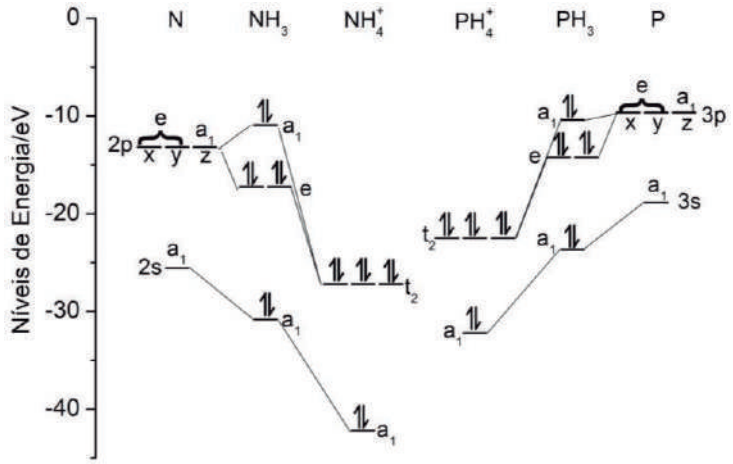
NH_3 Basicity and PH_3 geometry explained by molecular orbitals

NH_3 basicity is explained by the major energy stabilization of it's molecular orbitals.

Angular geometry of PH_3 is explained by the contribution of p atomic orbitals in HOMOs.

Resumo/Abstract

Cálculos de orbitais moleculares para as moléculas NH_3, PH_3 e suas espécies protonadas, NH_4^+ e PH_4^+, empregando a teoria da perturbação de Møller–Plesset (MP2) e base 6-311G, mostram, pela primeira vez, que a basicidade mais elevada do NH_3 se deve à maior estabilização dos seus orbitais moleculares, que ocorre após sua protonação, em comparação com a menor estabilização observada para os orbitais moleculares do PH_3 (ver Figura). As afinidades protônicas de 920 e 799 kJ mol^{-1} calculadas para o NH_3 e PH_3, respectivamente, são uma consequência do que se observa na Figura.



NH_3 % orbital p	PH_3 % orbital p
70,6 HOMO (a_1)	41,9 HOMO (a_1)
45,7 HOMO-1, 2 (e)	40,2 HOMO-1, 2 (e)
7,02 HOMO-3 (a_1)	9,72 HOMO-3 (a_1)
0,29 HOMO-4 (a_1)	**97,6 HOMO-4 (a_1)**
—	**99,7 HOMO-5, 6 (e)**
—	1,21 HOMO-7 (a_1)
—	0,03 HOMO-8 (a_1)

Com relação à geometria, o ângulo próximo de 90° para o PH_3 (93,6°) pode ser explicado, ineditamente, pela exclusiva participação dos orbitais p do fósforo nos seus orbitais moleculares HOMO-4, 5 e 6 (ver tabela), aspecto que não se observa no NH_3 (ângulo experimental 107,8°).

Agradecimentos/Acknowledgments

CNPq. CAPES, FAPERJ

Área: INO

Bis(pyrazol)-pyridine metal complexes as catalysts for the CO_2 cycloaddition with epoxides

Marcel M. Amorim (IC),[1] Álvaro F. A. da Mata (PG),[1] Jorge L. S. Milani (PQ),[2] Rafael P. das Chagas (PQ)[1*]

marcel.amorim@discente.ufg.br; rpchagas@ufg.br

[1]*Laboratório de Síntese e Catálise Organometálica (LABSINCO), Instituto de Química, Universidade Federal de Goiás - UFG;*
[2]*Departamento de Química, Universidade Federal de Juiz de Fora - UFJF.*

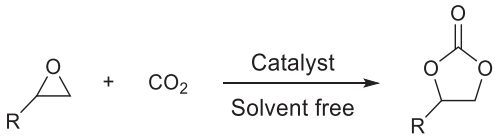
Keywords: *Metal complexes, Homogeneous catalysis, Carbon dioxide, Cyclic carbonate.*

Highlights

First row transition metal complexes with 2,6-di(pyrazol-1-yl)pyridine and 2,6-bis(3,5-dimethylpyrazol-1-yl)pyridine as catalysts for the synthesis of cyclic carbonates from CO_2 and epoxides.

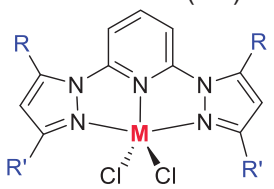
Abstract

The increase in carbon dioxide (CO_2) emissions due to human activities is causing growing concerns because of its environmental impacts. In response, there is a growing focus on studies exploring the use of CO_2 as a reagent in various chemical reactions, such as CO_2 cycloaddition (Scheme 1), aiming at the formation of cyclic carbonates, which are of great industrial relevance.



Scheme 1. Cycloaddition reaction of CO_2 and epoxides

In this work, a series of metal complexes were synthesized and tested as catalysts for this reaction. First row transition metals with ligands 2,6-di(pyrazol-1-yl)pyridine (DDP) and 2,6-bis(3,5-dimethylpyrazol-1-yl)pyridine (Me-DDP) (1-5) (Scheme 2) were combined with tetrabutylammonium bromide (TBAB) in a catalytic system for the CO_2 cycloaddition reaction with propylene oxide (PO), to produce cyclic propylene carbonate (PC).



DDP: R; R' = H
Me-DDP: R; R' = CH_3
M: 1.Zn^{II}, 2.Cu^{II}, 3.Ni^{II}, 4.Co^{II}, 5.Fe^{III}

Scheme 2. Bis(pyrazol)-pyridine metal complexes

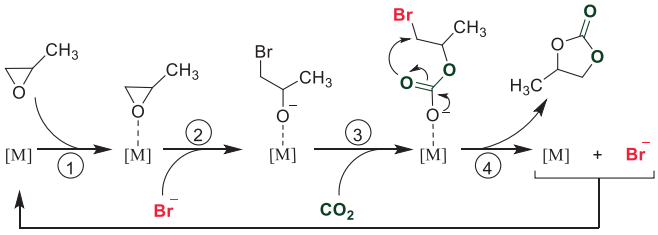
The catalytic results are shown in Table 1. A control reaction without catalyst, utilizing only TBAB, resulted in 4% of conversion (entry 1). Combination of TBAB with bis(pyrazol)-pyridine metal complexes led to increased conversion rates. Zinc catalysts emerged as superior for propylene carbonate production (entries 2 and 3), surpassing catalysts of other metals.

Table 1. Cycloaddition reactions using catalysts and PO.

Entry	Catalyst	Conv.(%)	TON[a]	TOF[b]
1	TBAB	4	50	17
2	ZnDDP	89	1106	369
3	ZnMe-DDP	70	880	293
4	CuDDP	4	51	17
5	CuMe-DDP	17	206	69
6	NiDDP	20	254	85
7	NiMe-DDP	23	290	97
8	CoDDP	31	391	130
9	CoMe-DDP	31	382	127
10	FeDDP	22	280	93

Reaction conditions: 50 mmol PO, Catalyst (0.08 mol%), Cocatalyst (0,08 mol%), temperature (100 °C), $P_{[CO2]}$ = 10 bar, time (3 hours). [a]TON = turnover number (moles of epoxide consumed)/(moles of catalyst). [b] TOF = turnover frequency TON . h^{-1}.

Previously reported works provided the basis for formulating a mechanism proposal for the CO_2 cycloaddition reaction with epoxides (Scheme 3).



Scheme 3. Mechanism proposal

All complexes produced the respective cyclic carbonate as the only product (selectivity > 99%). The catalytic activity in the reaction with ZnDDP stood out for reaching 89% conversion and a turnover number (TON) of 1106 in just 3 hours. These robust results indicate the potential of these zinc catalysts, especially ZnDDP, for the synthesis of cyclic organic carbonates. These advances demonstrate the relevance of research in zinc catalysts, offering promising perspectives for future developments.

Acknowledgments

CNPq, FAPEG, PPGQ/IQ/UFG, CAPES.

Área: _____INO_____
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Carbon Dots derived from citric acid and urea applied in the synthesis of fluorescent polymeric films and as an antioxidant agent

Anna Paula de Lima Araujo (IC),[1] Joyce Souza Nascimento (IC),[1] Ivy Santos Soares (PG),[1] Jamylle Nunes de Souza Ferro (PQ),[1] James Henrique Almeida (PG),[1] Livia Elias da Silva (IC),[1] Orlando Lucas De Lima Calado (IC),[1] Cintya D' Angeles do Espirito Santo Barbosa (PQ)[1].

anna.araujo@iqb.ufal.br

[1]*Instituto de química e biotecnologia, UFAL*

Palavras Chave: *Carbon Dots, Filmes poliméricos, Antioxidante, Viabilidade celular.*

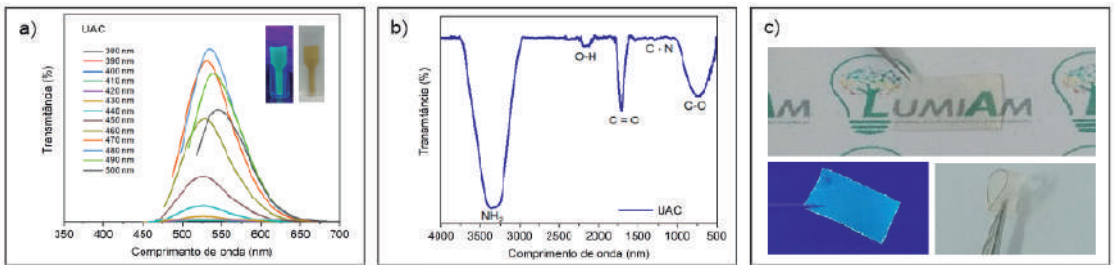
Highlights

The cell viability of CDs was approximately 80% at a concentration of 500 µg/mL; Carbon dots incorporated into flexible and photoluminescent polymeric films; Efficient action of CDs as antioxidant agents.

Resumo/Abstract

A síntese de Carbon Dots (CDs) tem despertado considerável interesse devido ao seu amplo aproveitamento em diversas áreas, especialmente as biológicas, devido ao seu custo reduzido, fluorescência sintonizável, alta dispersão em água e biocompatibilidade.[1] Considerando o contexto, este trabalho descreve a síntese de CDs derivados do ácido cítrico e ureia (UAC) via micro-ondas para avaliação da capacidade antioxidante e produção de filmes poliméricos fluorescentes a base de álcool polivinílico (PVA).[2] O UAC exibiram emissão dependente do comprimento de onda de excitação com intensidade máxima na região do verde em 537 nm (λ_{exc}= 480 nm) (Fig. 1. a)). Além disso, foi possível observar a presença de grupos nitrogenados e oxigenados (OH, NH_2, C=O, C-N, C-O) através das análises de FTIR (Fig. 1. b)). O espectro de UV-vis do UAC apresentou bandas de absorção características das transições π-π* e n-π*, associadas ao núcleo grafítico e estados de superfície, respectivamente.[3] A capacidade antioxidante foi avaliada pelo método DPPH e FRAP, apresentando uma faixa de inibição significativa em concentrações de até 50 µg/mL. Sobretudo, o UAC possui boa viabilidade celular em células de fibroblastos não tumorais (HFF-1), superior a 80%, para concentrações de até 500 µg/mL. Os filmes poliméricos (Fig. 1. c)) demonstraram transparência, flexibilidade e grau de intumescimento entre 104,34 - 166,73%. Portanto, os resultados indicam que os CDs UAC podem desempenhar um papel fundamental em aplicações biológicas no desenvolvimento de materiais antioxidantes.

Fig. 1. a) Espectro de fotoluminescência do UAC; b) Espectro de FTIR do UAC c) Filme fluorescente dos do UAC com e sem luz uv.



Agradecimentos/Acknowledgments

UFAL IQB LUMIAM Finep CAPES CNPq

1. Li, S. *et al*. **Materials Today**. doi: 10.1016/j.mattod.2021.07.028, 2021.
2. Silva, L. E. *et al*. **Journal of Bioengineering, Technologies and Health.** doi: 10.34178/jbth.v5i4.247, 2023.
3.Meierhofer, F. *et al*. **The Journal of Physical Chemistry C.** doi: 10.1021/acs.jpcc.9b11732, 2020.

Área: INO

Carbon dots derived from citric acid and urea for forensic applications: anti-counterfeiting inks and latent fingerprint development

Islaine Elí Lima Gomes (IC),[1] André Lopes Ruiz Talhari (PG),[2] Josué Carinhanha Caldas Santos (PQ),[1] Cintya D'Angeles do Espírito Santo Barbosa (PQ).[1]

islaine.gomes@iqb.ufal.br

[1]*Institute of Chemistry and Biotechnology, UFAL.* [2]*Official Expertise and Technical Identification (POLITEC).*

Keywords: *carbon dots, anti-counterfeiting ink, fluorescent powder, fingerprints.*

Highlights

Facile preparation of carbon dots from citric acid and urea; Fluorescent ink to authenticate documents based on carbon dots; Nanocomposites show high contrast in the development of fingerprints.

Abstract

Luminescent carbon nanoparticles (*Carbon dots* - CDs) have attracted attention in materials chemistry for their low toxicity, photostability, and low-cost synthesis, enabling them to be applied in biomedicine, environmental chemistry, and forensic sciences. [1]. From this perspective, carbon dots can contribute to this process as they contain ideal attributes for application, such as fluorescent inks or nanocomposite systems for papiloscopy. Thus, this work aimed to synthesize carbon dots derived from citric acid and urea (CDs_UAC) via microwaves for use as invisible anti-counterfeiting ink and fluorescent powders when incorporated into melamine-urea-formaldehyde polymer resin for revealing latent fingerprints (IDLs). The CDs_UAC exhibited energy absorption referring to the $\pi \rightarrow \pi^*$ transitions with λ_{max}= 200 nm and $n \rightarrow \pi^*$ at λ_{max} = 340 nm, characteristic of the graphitic core and surface states, respectively. In the nanocomposites, the UV-vis spectrum profile was maintained. Furthermore, the FTIR spectrum revealed the presence of oxygenated and nitrogenated organic groups between 1750 - 1000 cm^{-1}. The fluorescence spectroscopy of CDs_UAC revealed a maximum green emission at 537 nm (λ_{ex}= 480 nm), while the nanocomposites showed a maximum at 505 nm (λ_{ex}= 370 nm). These properties enable it to be used as fluorescent ink in print cartridges and writing pen refills. It is possible to see only when exposed to UV light. This function allows documents to be securely authenticated with barcodes and symbols. In addition, the fluorescent powder showed adequate contrast to reveal latent fingerprints, acting with dual functionality as a white color and green fluorescence powder when exposed to UV light, being effective for both purposes.

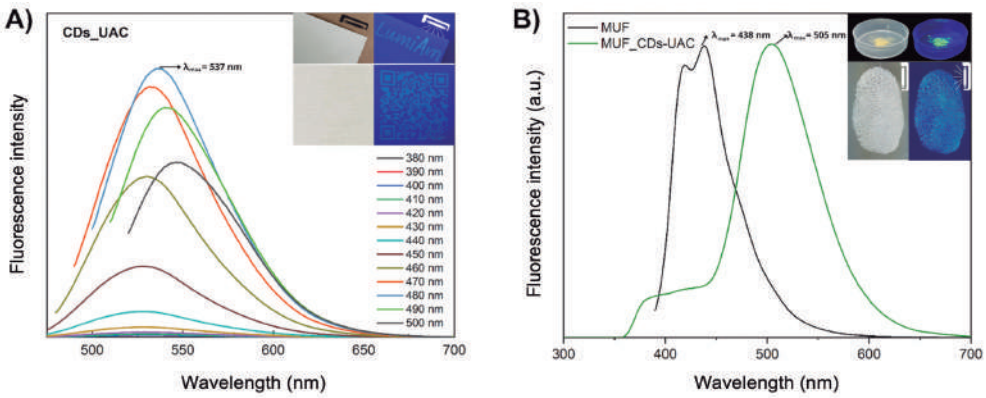


Figure 1: Photoluminescence spectra (A) of the UAC Carbon Dots and their application as an anti-counterfeiting ink and (B) of the melamine-urea-formaldehyde resin, and powder and fingerprint images on glass under natural and UV light.

Acknowledgments

LumiAm, LINQA, UFAL, PROCAD - CAPES, CNPq, FAPEAL, Finep.

[1] LI, S.; LI, L.; TU, H.; SHANG, H.; SILVESTER, D.S.; BANKS, C.E.; ZOU, G. HOU, H.; JI, X. The development of carbon dots: From the perspective of materials chemistry. Materials Today, vol 51, 188-207, ISSN 1369-7021, 2021.

Área: INO

Carbon monoxide photorelease and HSA interaction studies of a novel carbonyl trinuclear ruthenium acetate [$Ru_3O(CH_3COO)_6(THIQ)_2(CO)$]

Nathan C. Fernandes (IC),[1*] **Thuany G. Toledo** (IC),[1] **Sofia Nikolaou** (PQ)[1]

nathancamposfer@usp.br

[1]*Departamento de Química, Faculdade de Filosofia, Ciências e Letras de Ribeirão Preto, Universidade de São Paulo*

Keywords:*(Carbon monoxide, Human serum albumin, PhotoCORM, Ruthenium).*

Highlights

The photorelease of CO by the novel complex [$Ru_3O(CH_3COO)_6(THIQ)_2(CO)$] was evaluated. The interaction of the complex with HSA was studied by fluorescence titrations.

Abstract

Trinuclear ruthenium acetates of general formula [$Ru_3O(CH_3COO)_6L_3]^+$, where L = N-heterocyclic ligand, represent an important class of metal complexes due to their reversible redox chemistry and biological aplications.[1] Studies have been carried out on this class of complexes, including characterization of their reactivity, NO and CO release and interactions with biomolecules. *In vitro* antitumor and antiparasitic activities against the Chagas' disease parasite have also been reported, using 5,6,7,8-tetrahydroisoquinoline (THIQ) as a ligand.[2]

Interest in the therapeutic use of carbon monoxide has grown since the beginning of the 21st century due to its interesting biological properties at low concentrations.[3] Thus, a combination of the biological properties of THIQ with those of carbon monoxide can be reflected in the complex [$Ru_3O(CH_3COO)_6(THIQ)_2(CO)$] (**1**). The study of CO release by complex (**1**) controlled by light stimulation was carried out in ACN using 377 nm irradiation for 80 minutes, yielding a quantum yield (Φ) of 0.091 for this process.The laser intensity was determined by chemical actinometry using the standard ferrioxalate procedure.[4] The value of Φ obtained for complex (**1**) is up to two orders of magnitude higher than other carbonyl complexes in this class,[5] which is a relevant result for considering (**1**) as a photo-CORM candidate.

Furthermore, human serum albumin (HSA) is the most abundant protein in blood plasma and can be used as a natural drug carrier.[6] In this regard, the interaction between complex (**1**) and HSA was studied through fluorescence titrations of HSA solutions in PBS (pH 7.4) at different temperatures, using the Stern-Volmer equation to measure this interaction through the equilibrium constant (K_{SV}) of this process.[7] K_{SV} values in the order of 10^4 (Table 1) indicate the formation of a complex-HSA adduct, therefore, circular dichroism measurements will be carried out in the future to better understand this system.

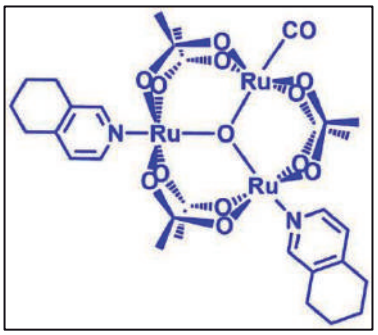


Figure 1. Structural representation of complex (1)

Table 1. Stern-Volmer constants for HSA titrations with complex (1)

Temperature (°C)	K_{SV} (10^4 M^{-1})
23	6.20
30	6.11
37	4.12
44	13.1

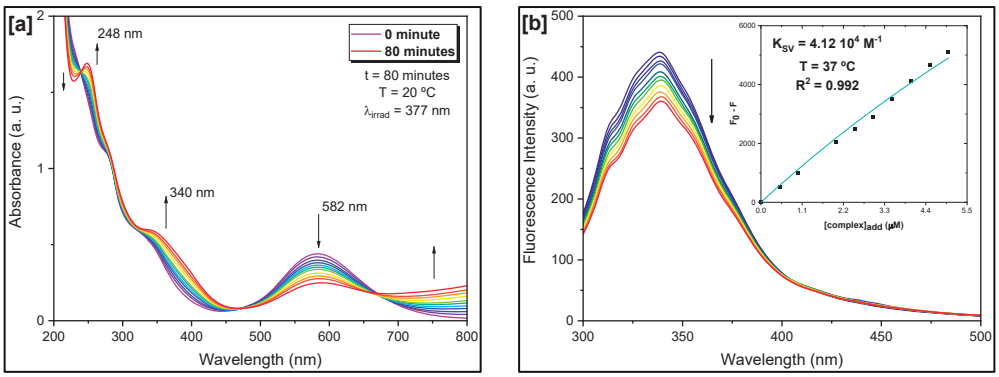


Figure 2. [a] CO-release by complex (1) using a laser irradiation at 377 nm for 80 minutes in ACN ([1] = 1.0 10^{-4} M); **[b]** HSA titration with complex (1) up to 10-fold molar excess of (1) in PBS (pH 7.4 and 0.137 M NaCl) at 37 ºC using ACN as co-solvent (0.7% v/v) ([HSA] = 0.5 mM and [1] = 0 – 5 mM); Inset: Stern-Volmer plot (F_0 – F vs. $[complex]_{add}$).[7]

[1] S. Nikolaou, L. G. A. do Nascimento, A. D. P. Alexiou, *Coord Chem Rev* **2023**, *494*, 215341. [2] B. Possato, Z. A. Carneiro, S. de Albuquerque, S. Nikolaou, *J Inorg Biochem* **2017**, *176*, 156. [3] S. W. Ryter, L. E. Otterbein, *BioEssays* **2004**, *26*, 270. [4] H. J. Kuhn, S. E. Braslavsky, R. Schmidt, *Pure Appl Chem* **2004**, *76*, 2105. [5] M. B. Moreira, C. F. N. Da Silva, R. B. P. Pesci, V. M. Deflon, S. Nikolaou, *Dalton Transactions* **2016**, *45*, 16799. [6] G. Fanali, A. Di Masi, V. Trezza, M. Marino, M. Fasano, P. Ascenzi, *Mol Aspects Med* **2012**, *33*, 209. [7] M. Van De Weert, L. Stella, *J Mol Struct* **2011**, *998*, 144.

Acknowledgments

FAPESP CAPES CNPq

Laboratório de Atividade Biológica e Química Supramolecular de Compostos de Coordenação

Área: INO

Catálise biomimética da metaloenzima monooxigenase lítica de polissacarídeos: desenho de novos catalisadores

Caterina Gruenwaldt Cunha Marques Netto (PQ), Laura Victoria Oliveira Correa (IC)

[1]*Departamento de Química, UFSCar.*

caterina@ufscar.br; laura.vitoriaoc@gmail.com

Palavras Chave:*(Catálise, Biocatalizador, LPMO, enzima.*

Highlights

- Design of new biomimetic catalysts of the metalloenzyme lytic polysaccharide monooxygenase (LPMO)
- The synthesis of LPMO enzyme mimetics is proposed to efficiently catalyze the hydrolysis of polysaccharides, aiming to contribute to the advancement of renewable energy sources

Resumo/Abstract

The use of biomass as an alternative energy source has become increasingly popular for application in industrial processes. In Brazil, energy generation from biomass is a common practice, but it often results from combustion and significant pollutant emissions. Thus, enzymes have emerged as promising alternatives due to their remarkable efficiency. A notable example is the LPMO enzyme, which exhibits degradative capacity for polysaccharides through hydrolysis and oxidation reactions. With the application of the LPMO enzyme, which catalyzes the hydrolysis of polysaccharides for energy production, it would be possible to obtain a more sustainable energy source. This approach provides significant advantages, including reducing dependence on fossil fuels and mitigating environmental impacts associated with energy generation from biomass. Furthermore, the use of the enzyme could enhance the efficiency of biomass conversion processes, resulting in cleaner and more sustainable energy production. However, as enzymes are susceptible to environmental factor, such as pH, temperature and pressure, our focus is to design a mimetic molecule of LPMO to be used in bioreactors.

This work describes the synthesis and characterization of a new ligand to be coordinated to copper and used as LPMO mimic. For that, we use the amino acid *L*-proline, which undergoes a series of five reaction steps to generate the desired ligand: *L*-proline is esterified, then alkylated with bromo-methyl pyridine, reduced with $LiAlH_4$, halogenated with thionyl chloride and finally reacted with an amine. Coordination of a copper ion to the ligand will generate the desired molecule [CuL] as a mimic of LPMO, as shown in figure 1. We envision that the synthesized complex will be able to be used as an LPMO mimetic to examine the catalytic performance of this mimetic and, subsequently, employ this catalytic system in the decomposition of polysaccharides, aiming for the generation of clean energy from biomass through hydrolysis reactions.

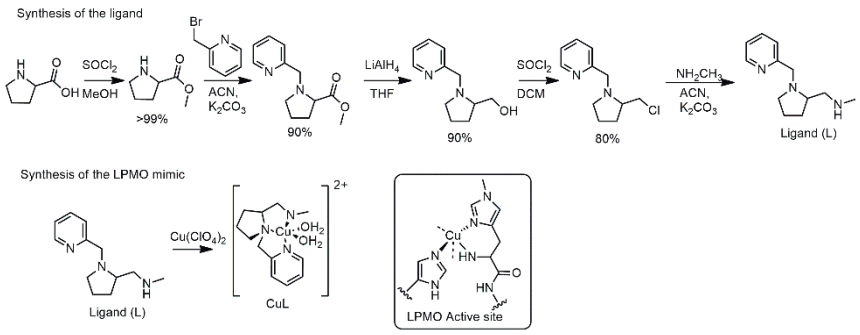


Figure 1: Synthesis of the LPMO mimic.

Agradecimentos/Acknowledgments

FAPESP 23/09722-0

Área: INO

Cobalt hydroxide chloride salt as catalyst for the Brilliant Green dye bleaching reaction

Luiz N. P. H. da Silva (IC),[1,2] Shirley Nakagaki (PQ),[1] Guilherme S. Machado (PQ).[2]*

luiznatan@ufpr.br; *guimachado@ufpr.br

[1]Bioinorganic and Catalysis Laboratory, Chemistry Department, Federal University of Paraná, Curitiba, Brazil; [2]Pontal do Paraná Campus - Center for Marine Studies, Federal University of Paraná, Pontal do Paraná, Brazil.

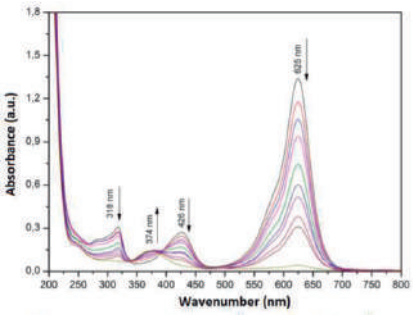
Key words: *Layered hydroxide salts, Organic dyes, Green chemistry, Heterogeneous catalysis.*

Highlights

Synthesis and characterization of the layered cobalt hydroxide chloride salt. Promising catalytic results when the solid was investigated as catalyst for the organic dye Brilliant Green bleaching reaction.

Abstract

In this work, the layered cobalt hydroxide chloride salt (HClCo), a compound from the layered hydroxide salts class [1], was synthetized, characterized and investigated as a catalyst in the Brilliant Green (BG) organic dye bleaching reaction [2], a dye with environmental relevance, using hydrogen peroxide as oxidant. The HClCo solid was synthetized by an adaptation of the ammonia diffusion method [3], in a closed desiccator, in the presence of aqueous solutions of the corresponding cobalt II nitrate salt (0.1 mol L^{-1}) and the ammonia solution (10.4 mol L^{-1}), over a period of 7 days. The obtained solid, after washing and drying, was characterized using different techniques such as: powder X-ray diffraction (basal distance = 7.99 Å), infrared spectroscopy (broad bands below 1000 cm^{-1} suggesting Co-O vibrations in the layer; broad absorption at 3498.38 cm^{-1}: O-H stretching vibration of the water in the interlayer space) and scanning electron microscopy. The analyses confirmed the HClCo preparation. The obtained solid was investigated as catalyst in the degradation of the BG dye (Figure below). It was observed an increase in the bleaching rate of the dye solutions in comparison to the control reactions without the use of catalyst, under the same preliminary reaction conditions (temperature of 25 °C, magnetic stirring, in the presence or absence of ambient light). The observed BG bleaching were very close to 100% in the investigated reactions with the HClCo catalyst. The ideal catalytic condition are under investigation.



UV-Vis electronic spectroscopy monitoring of the bright green dye bleaching reaction using H_2O_2 as an oxidant and the catalyst cobalt hydroxychloride (HClCo).

Catalysis conditions		[1]Proportion	[2]k´(s^{-1})	k´/k´b[3]
HClCo	Presence of ambient light	5000:10	1.150E-03	68.44
		5000:50	1.639E-04	71.24
		5000:100	1.256E-04	206.59
	Absence of ambient light	5000:10	1.405E-03	57.50
		5000:50	3.979E-04	86.08
		5000:100	1.896E-04	334.34

[1]Proportion: material quantity ratio 5000:X (oxidant:dye), catalyst concentration 10 x 10^{-3} m/V, 298.15 K; [2]Pseudo-first order constant in s^{-1}; [3]Relation between the constants of the catalyzed reaction and the control reaction (only H_2O_2).

[1] G.G.C. Arízaga, K.G. Satyanarayana, F. Wypych, Sol. Statelon. 178 (2007) 1143-1162.
[2] M.G. Rocha, S. Nakagaki, G.M. Ucoski, F. Wypych, G.S. Machado, J. Colloid Interface Sci. 541(2019) 425-433.
[3] Y. Du, D. O'Hare, Particuology 8 (2010) 188-191.

Acknowledgments

CAPES UFPR UNIVERSIDADE FEDERAL DO PARANÁ CNPq FUNDAÇÃO ARAUCÁRIA CIMOL

Área:INO

Heteroleptic ruthenium complex with potential use in photodynamic therapy

Francisco Hermeson de Souza Gomes (IC),[1*] Geângela F. S. Oliveira (PG),[1] Francisca Mayara S. de Alencar (PG),[1] Luiz Gonzaga de F. Lopes (PQ),[1] Eduardo Henrique S. Sousa (PQ) [1]

hermesonsouza14@gmail.com; eduardohss@dqoi.ufc.br

[1]Bioinorganic Group, Department of Organic and Inorganic Chemistry, Federal University of Ceará, Fortaleza, Ceará

Keywords: Bioinorganic, Ruthenium, Cancer, Photochemistry, ROS (Reactive Oxygen Species).

Highlights

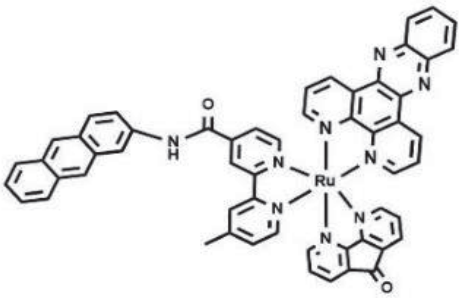
Development of ruthenium complex containing mixed polypyridinic ligands with potential use in photodynamic therapy

Synthesis and characterization of ligands and a new ruthenium complex (GHM2) as a potential photosensitizer.

Potential photogeneration of ROS and interaction with DNA.

Abstract

Ruthenium compounds are potential substitutes for platinum-based anticancer therapeutic agents, possibly with lower toxic effects, generally attributed to their similarity to iron and possible interactions with analogous biological molecules. Among these metal systems, ruthenium(II) polypyridyl complexes have received attention as promising drug candidates. This has been particularly due to the encouraging results with the compound TLD1433, currently in phase 2 of clinical trials. Motivated by such prospects, this present work aims to develop a new ruthenium complex, GHM2 ([Ru(bpy-anth)(dppz)(dfo)]Cl_2, where bpy-anth = 4'-methyl-N-(anthracen-2-yl)-[2,2'-bipyridine]-4-carboxamide, dppz = dipirido[3,2-a:2',3'-c]phenazine, and dfo = 4,5-diazo-9-fluorenone), aiming to provide photogeneration of reactive oxygen species (ROS) along with DNA interaction. The synthesis of ligands was performed, as well as a precursor dichlorido complex in the *cis* configuration, prior to the coordination of the dfo ligand, also not described in the literature, as well as the final GHM2 complex. Vibrational spectroscopy studies in the infrared region (FTIR) showed stretching modes characteristics of the carbonyl C=O present in dfo ligand at 1680 cm^{-1}, C=N at 1310 cm^{-1}, and C=C at 1570 cm^{-1} present also in the pyridinic rings and anthracenyl moiety, in addition to C-H bands at 3070 cm^{-1} and N-H bond stretching band of the anthracene amide group at 3453 cm^{-1} consistent with the synthesized structures. The electronic absorption spectrum of the ruthenium complex in the UV-vis region, in ethanol, exhibited an MLCT band at 590 nm, as well as bands at 340 nm related to the dppz ligand and at 260 nm related to the bpy-anth ligand, both attributed to intraligand transitions. Hydrogen nuclear magnetic resonance spectrum showed integrated signals consistent with the bpy-anth and dppz ligands bound for dichlorido precursor, while GHM2 is under measurement. Further studies, including stability and photoactivity assays are underway to assess the capacity of these complex to generate reactive oxygen species, as well as interactions with conventional and unconventional DNA structures.



GMH2

Acknowledgments

We are thankful to funding agencies CNPq, CAPES, FUNCAP, and FINEP, and particularly to CNPq for a studentship (PIBIC-UFC) to FHSG. Besides these funding agencies, we also wish to thank CENAUREMN for allowing us to collect nuclear magnetic resonance data.

Área: QI
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Complexos de cobalto (II) contendo ligantes diiminicos e piridínicos: Síntese, caracterização e aplicação como sensor eletroquímico.

Felipe Lopes Salerno (IC),[1*] Henrique Martinez de Andrade Orteiro (IC),[1] André Luiz Bogado (PQ),[1] Luis Rogério Dinelli (PQ).[1]

dinelli@ufu.br; felipe.salerno@ufu.br

[1]*Instituto de Ciências Exatas e Naturais do Pontal, Universidade Federal de Uberlândia.*

Palavras Chave: *Complexo diimínico, 4-vinil-piridina, sensor voltamétrico, paracetamol.*

Highlights

Cobalt complexes containing diimine and pyridine ligands: synthesis, characterization and application as electrochemical sensors.

The characterization results suggest a complex with the molecular formula [$CoCl_2$(2,4,6-trime)(py-4c)$_2$]

The synthesized complex was used as a modifier in a carbon paste electrode.

The modified electrode was successfully used for the voltammetric determination of paracetamol.

Resumo/Abstract

Complexos metálicos contendo cobalto e diiminas tem sido alvo de muitos estudos, principalmente para o uso em catalise [1] e eletrocatálise [2]. Vislumbrando essas ideias, o presente trabalho mostra a síntese, caracterização e a aplicação de um novo complexo de cobalto (II), contendo os ligantes diimina N1,N2-bis(2,4,6-trimetilfenil)etano-1,2-diimina (2,4,6-trime) e 4-piridinacarboxialdeído (py-4c), de fórmula [$CoCl_2$(2,4,6-trime)(py-4c)$_2$]. O ligante diiminico (2,4,6-trime) foi sintetizado de acordo com procedimento já descrito na literatura [3]. O complexo foi sintetizado utilizando um equivalente (200 mg, 0,84 mmol) do $CoCl_2$x6H_2O, 1,1 equivalente (270 mg, 0,93 mmol) do ligante diimínico (2,4,6-trime) e 4 equivalentes (330 µL, 3,45 mmol) do ligante piridínico (py-4c), dissolvidos na mistura metanol/diclorometano (90%/10%) sob agitação por 4 horas. O volume da solução foi então reduzido com o auxílio de um rotaevaporador e hexano foi adicionado para obtenção de um precipitado verde claro, que foi filtrado, lavado com hexano e seco em dessecador sob vácuo. O eletrodo de pasta de carbono modificado com o complexo de cobalto foi confeccionado utilizando uma mistura de 65% de grafite em pó, 31% de parafina e 4% de modificador. A mistura foi então aquecida em banho maria a uma temperatura de 80°C, até a fusão da parafina, e em seguida foi homogeneizada e transferida para uma seringa. O contato elétrico foi feito utilizando uma haste de cobre. O complexo foi caracterizado por diversas técnicas espectroscópicas. Pelo espectro no Infravermelho foi possível observar a banda característica da diimina em 1613 cm^1, referente ao estiramento C=N, e também da carbonila de aldeído em 1719 cm^{-1} referente ao ligante py-4c, mostrando que ambos os ligantes estão presentes na estrutura do complexo. Os resultados de condutividade em DMF mostraram que o complexo é neutro, portanto, os átomos de cloros ainda estão coordenados no cobalto, confirmando então a estrutura proposta. O eletrodo modificado com o complexo foi utilizado como sensor voltamétrico para a detecção de paracetamol e os resultados indicaram que o eletrodo modificado é mais sensível (maior corrente de pico) ao paracetamol do que o eletrodo não modificado.

[1] Kondori, T; Tajik, S; Akbarzadeh-T, N; Beitollahi, H; Graiff, C.; Jang, H. W. and Shokouhimehr, M. *RSC Adv.*, 2021, 11, 3049; [2] Anferov, S. W.; Filatov, A. S. and Anderson, J. S. *ACS Catal*. 2022, 12, 16, 9933–9943; [3] Hans, M.; Lorkowski, J.; Demonceau. A. and Delaude, L. *Beilstein J. Org. Chem*. 2015, 11, 2318–2325.

Agradecimentos/Acknowledgments

FAPEMIG (APQ-00372-22), CAPES e o CNPq (404435/2021).

Área: INO

Computational Study of Decapeptides Acting as MPACs Against Alzheimer's Disease

Marcela G. Silva (IC),[1] Larissa R. Pinto (PG),[1] Luiz Antônio S. Costa (PQ).[1]*

marcelagiovanadasilva@gmail.com; luiz.costa@ufjf.br

[1]*NEQC – Núcleo de Estudos em Química Computacional, Departamento de Química, ICE, UFJF*

Palavras Chave: Alzheimer's Disease, MPACs, Peptides, Molecular Dynamics

Highlights

Peptides are an excellent option as drugs due to their biocompatibility. Thus, the present work analyzes synthetic peptides proposed in combating Alzheimer's disease by DFT methods.

Abstract

Alzheimer's disease (AD) represents a challenge for society, as it is the main cause of global dementia, and lacks a definitive cure. A significant set of evidence suggested that metals, such as copper, induce oxidative stress through the production of reactive oxygen species (ROS). Furthermore, when the metal ion Cu(II) coordinates with β-amyloid (Aβ), there is an increase in the peptide's toxicity (Falco et al., 2015).

Therefore, to avoid this coordination process, the aim of this work is to computationally evaluate the peptides synthesized by Caballero et al. (2020), which can act as potential MPACs (metal-protein interaction attenuation compounds). For this, different DFT calculation protocols were analyzed for the system Cu(II)-Aβ, through the mimicking of the coordination site around copper, based on one of the structures proposed by Abelein et al. (2022) (PDB:8b9q). Firstly, by means of benchmarking, it was concluded that the B3LYP functional and the double zeta potential (LANL2DZ) provide a geometry consistent with the PDB reference. By adding an implicit water dielectric, the compound geometry did not show significant changes (Figure 1).

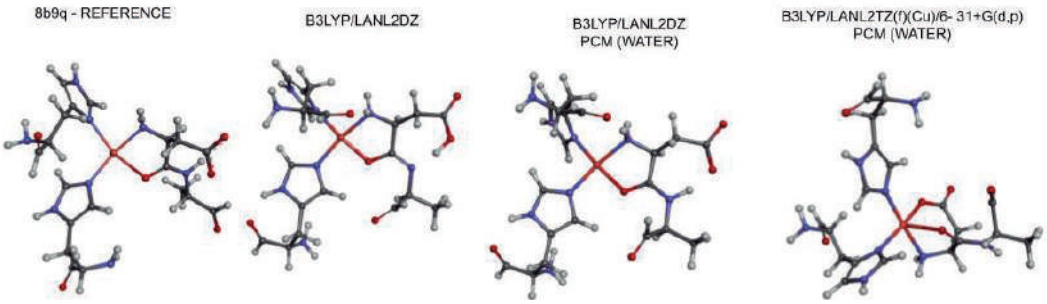


Figure 1 – Optimized geometries using different bases for the same DFT functional.

It is interesting to mention that with a triple zeta valence basis for copper(II) and double zeta valence, 6-31+G(d,p), for the other atoms, a torsion occurs in the aspartate chain, causing the metal ion to have a coordination number equal to five. Such structural differences are quite important since we look toward the stability of these peptides as MPACs coordinated to copper (Reaction: Cu-Aβ + MPAC → Cu-MPAC + Aβ). Our previous results indicate possible starting geometries to evaluate the molecular dynamics (MD) of the ligands and complexes. Such simulations are, in fact, already in development.

References

Falco AD, Cukierman DS, Hauser-Davis RA, Rey NA. Química Nova. 2015; 39(1): 63-80. doi:10.5935/0100-4042.20150152.
Caballero AB, Iranzo O, Hautier A, Sabaté R, Gamez P. Inorg Chem. 2020; 59(1):837-846. doi:10.1021/acs.inorgchem.9b03099.
Abelein, A.; Ciofi-Baffoni, S.; Mörman, C.; Kumar, R.; Giachetti, A.; Piccioli, M.; Biverstål, H. JACS 2022, 2(11): 2571–2584. doi:10.1021/jacsau.2c00438.

Acknowledgments

The authors would like to thank the support from CNPq, FAPEMIG, CAPES, and UFJF.

Área: INO

Coordination compounds containing oxazolidine-based ligands: modulation of synthetic results through controlled experimental variations

Francielle X. dos Santos (IC),[1] Brunno P. Freitas (PG),[1] Guilherme P Guedes (PQ),[1*]

franciellexavier@id.uff.br; guilherme_guedes@id.uff.br

[1]*Universidade Federal Fluminense, Instituto de Química, Departamento de Química Inorgânica*
Keywords: *oxazolidine, X-ray diffraction, crystal structure, coordination chemistry.*

Highlights

Controlled variations of a one-pot methodology were applied to afford different coordination compounds containing oxazolidine derivatives as ligands with different metal ions. All crystal structures were solved by single-crystal X-ray diffraction.

Resumo/Abstract

A combinação de ligantes orgânicos e íons de metais de transição pode levar à obtenção de materiais multifuncionais, visto que estes blocos construtores podem agregar propriedades ao sistema, tais como ópticas, magnéticas e catalíticas.[1] As oxazolidinas pertencem a uma classe de compostos orgânicos heterocíclicos de cinco membros que contém um átomo de oxigênio e um de nitrogênio nas posições 1 e 3, cujos derivados podem ser explorados na química de coordenação devido à presença de dois heteroátomos doadores de densidade eletrônica.[2]

Neste trabalho, foram obtidos sete complexos contendo ligantes derivados da oxazolidina a partir de variações de uma metodologia de síntese *one-pot* de domínio do grupo de pesquisa,[3] partindo-se de uma solução etanólica contendo 1 mmol dos reagentes 2-amino-2-(hidroximetil)-1,3-propanodiol (tris) e 2- piridinocarboxialdeído, aquecida a 50 °C durante uma hora. Para a obtenção dos compostos **1-3**, foram adicionados os respectivos sais metálicos ($Co(NO_3)_2$, $Ni(ClO_4)_2$ e $MnCl_2$) na mesma proporção; no caso do composto **4**, utilizou-se 0,75 mmol de $Co(ClO_4)_2$. Já os compostos **5-7** foram obtidos por meio da adição de 1 mmol dos sais metálicos ($CoCl_2$, $Co(ClO_4)_2$ e $CuCl_2$) a uma solução etanólica contendo 1 mmol de tris e 2 mmol de 2-piridinocarboxialdeído, também aquecida a 50 °C por uma hora, à qual utilizou-se HCl como catalisador. Após cerca de 30 dias, monocristais de todos os compostos foram obtidos e caracterizados por difração de raios X por monocristal e espectroscopia de absorção na região do infravermelho.

Nos espectros dos complexos **1-4**, foram observadas bandas características da deformação angular da ligação N–H em torno de 3225 cm^{-1}, evidenciando a formação *in situ* de um ligante contendo um anel oxazolidínico. Os dados obtidos pela difração de raios X por monocristal mostram que nos complexos **1-3** os centros metálicos são coordenados pelos átomos de nitrogênio das porções oxazolidina e piridina do ligante (**Figura 1a**). A variação na proporção estequiométrica do sal metálico produziu um composto **4**, que é trinuclear (**Figura 1b**). No caso dos compostos **5-7** (**Figura 1c**), a metodologia sintética deu origem a um ligante contendo dois anéis oxazolidínicos fundidos. Esses compostos são reportados na literatura, sendo obtidos por uma metodologia de três etapas.[4] Posteriormente, serão estudadas as propriedades espectroscópicas na região UV-visível do composto obtido em estado sólido e em solução.

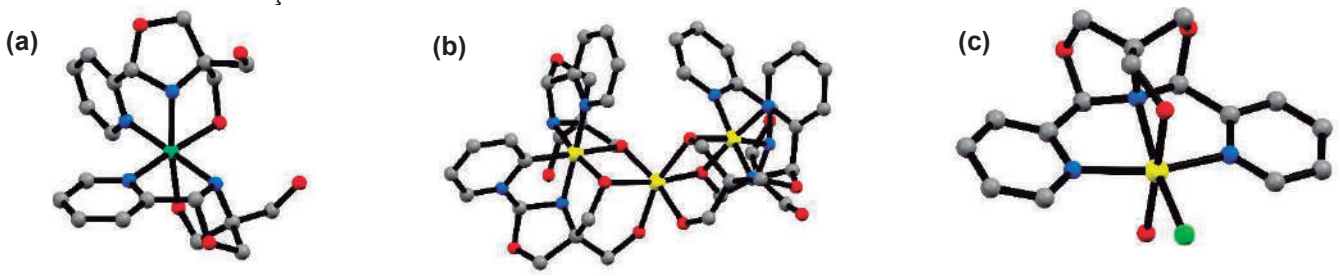


Figura 1. Estruturas resolvidas por difração de raios X por monocristal dos compostos **(a) 1**, **(b) 4** e **(c) 5**. Átomos de hidrogênio e contra-íons foram omitidos.

[1] SALEEM, A. et al., *Dalton Trans.*, **2018**, 47, 6156.
[2] SHAGHAFI, M. B., GROTE, R. E., JARVO, E. R., *Organic Letters*, **2011**, 12, 2884-2887.
[3] AREAS, E. et al., *Inorganica Chimica Acta*, **2022**, 529, 120664.
[4] NACHTIGALL, O. et al., *Z. Anorg. Allg. Chem.* **2021**, 647, 1442–1448.

Agradecimentos/Acknowledgments

CNPq, FAPERJ, CAPES, LDRX-UFF and LAME-UFF.

Área: INO

Cu(II) Complexes with Amino Acid Ligands: Superoxide Mitigation in Soybean Plants

Jennyfer C. Silva (PG),[1]* Vinycius L. Silva (IC),[2] Gustavo P. Lopes (IC),[2] Tiago Tezotto (PQ),[2] Hudson W. P. Carvalho (PQ).[2] Camilla Abbehausen (PQ).[1]

jennyfer005@hotmail.com

[1]*Institute of Chemistry, UNICAMP;* [2]*Nuclear Energy Center for Agriculture, USP*

Palavras Chave: *Superoxide, SOD, ROS, Soybean, Copper, Amino acids.*

Highlights

Cu(II) complexes with amino acid ligands ($Cu(aa)_2$) are recognized in the literature for their efficacy in dismutating superoxide in *in vitro* studies, acting as superoxide dismutase (SOD) mimetics. In the fertilizer industry, copper chelates with amino acids are employed to enhance antioxidant activity in various crops. Nevertheless, the characterization and coordination of these chelates remain inadequately understood. This study aims to investigate the impact of amino acid ligand coordination and nature on soybean cultivation, specifically addressing superoxide levels in plants subjected to saline stress.

Resumo/Abstract

As plant health is adversely affected by oxidative stress induced by both biotic and abiotic factors, it significantly hampers crop productivity[1]. During this oxidative stress process, reactive oxygen species (ROS) are generated, posing a threat to plant tissues and biomolecules, thereby impeding growth and leading to eventual cell death[2,3]. To counteract this stress and minimize productivity loss, the use of antioxidant fertilizers has become commonplace. One such commercially available solution is "Copper Chelates," a blend of flavonoids, EDTA, and amino acids. However, the specific coordination of Cu(II) within this mixture has not been fully elucidated.

In this study, we delved into the impact of amino acid coordination on Cu(II) and its efficacy in mitigating the superoxide ion. Our goal was to explore whether the nature of ligands influences this activity. To this end, we prepared and structurally characterized the complexes, evaluated their superoxide suppression activity through the indirect NBT photoreduction assay, and determined the McCord-Fridovich constant (k_{McCF}). Our findings revealed the formation of $Cu(aa)_2$ complexes with amino acids and he nature of the ligands induced noteworthy variations in superoxide suppression activity. Notably, CuTyr exhibited the highest activity with a k_{McCF} of 77.24 10^7 mol L^{-1} s^{-1}, whereas CuGly displayed the least activity with a k_{McCF} of 2.09 10^7 mol L^{-1} s^{-1}.

The most promising complexes were then tested for their ability to relieve superoxide-induced stress in soybean plants (*Glycine Max*) under conditions of salt stress. When applied to plants foliar application, the $Cu(aa)_2$ complexes with amino acids effectively mitigated the superoxide-induced stress, evaluated in the histochemistry assay, which showed low amounts of superoxide produced, with the CuHis complex exhibiting the highest leaf absorption and superior superoxide attenuating activity. It is important to emphasize that all complexes showed lower phytotoxicity in relation to the $CuCl_2$ salt, emphasizing the importance of the Cu(II) coordination sphere in this activity.

[1]. Liu, J. et al. *Jour. of Agri. and Food Chem*. **2020** 68 (47), 13608-13619.

[2]. Rene, J. et al. *Front. in Plant Sci*. **2022** 12 778270.

[3]. Oikawa, K. et al. *Nat Commun*. **2022** 13 7493.

Agradecimentos/Acknowledgments

This project was supported by Capes, FAPESP 2019/16904-2 and CNPq 404668/2021-6.

Área: ___INO_____
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Cyclohexane halogenation catalyzed by mono- and trinuclear Cu(II) complexes in the presence of trichloroisocyanuric acid as oxidant

Adolfo Horn Jr. (PQ),[1*] Monica M. de Souza (PG),[1] Christiane Fernandes (PQ),[1] Frédéric Avenier (PQ),[2] Guillot Régis (TC)[2]

adolfo.junior@ufsc.br; monicammds30@gmail.com

[1]Departamento de Química, UFSC; [2]Institut de Chimie Moléculaire et des Matériaux d'Orsay

Palavras Chave: Catalysis, Chlorocyclohexane, Copper complexes, Cyclohexane, Halogenation, TCCA.

Highlights

The copper complexes catalyzed the formation of alkyl halide.
The trinuclear species showed the highest catalytic activity.
The best performance was reached at 50° C in CH_3CN with 1% water.

Resumo/Abstract

This work delves into the catalytic activity of two Cu(II) coordination compounds in promoting cyclohexane functionalization. Complex **1** is the mononuclear compound [Cu(L)(H_2O)] synthesized with the ligand H_2L = 1,4-bis(2-hydroxybenzyl)-1,4-diazepane[1] while compound **2** is the corresponding trinuclear species [CuLCuLCu](ClO_4)$_2$, as shown in Figure 1**.** Both complexes were characterized by FTIR, UV-Vis, elemental analysis (CHN), ESI-MS and EPR. Additionally, the molecular structure of 1 was solved by monocrystal X-ray diffraction. The catalytic investigation was carried out at 25 and 50°C employing trichloroisocyanuric acid **(TCCA)** as oxidant with a ratio catalyst:oxidant:substrate of 1:333:1000 for 24 h. An evaluation was also performed to ascertain the impact of water presence within the system. The best yield (20.7%) was obtained employing complex 2 as catalyst, at 50°C, using the CH_3CN containing 1% of water. The presence of water in higher amount (5%), decreased the yield to ~12%. Spectroscopic investigation (UV-Vis and EPR) indicates a possible interaction between the Cu(II) center and the hypochlorite formed by TCCA hydrolysis. Theoretical studies showed that the interaction Cu-OCl is impaired in the presence of water, which explain the lower yield observed in the system containing 5% of water.

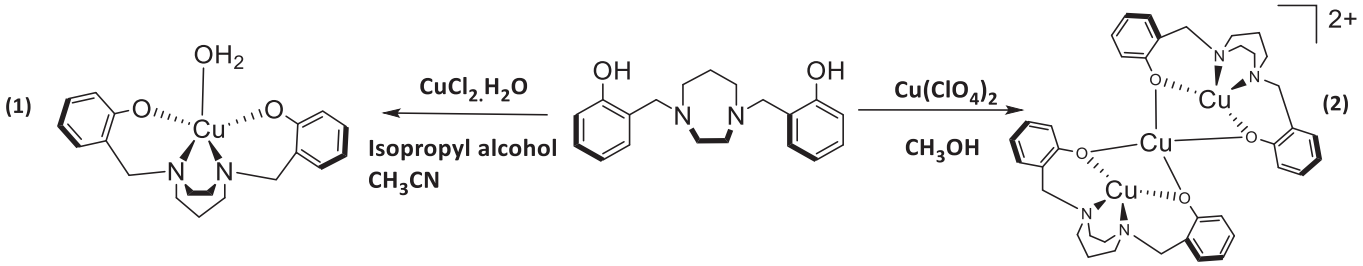


Figure 1. Scheme of synthesis for complexes **1** and **2.**

References

1. R. Mayilmurugan, H. Stoeckli-Evans, E. Suresh and M. Palaniandavar, *Dalton Transactions*, 2009, 5101–5114.
2. M. Du, X. J. Zhao, J. H. Guo, X. H. Bu and J. Ribas, *Eur J Inorg Chem*, 2005, 294–304.

Agradecimentos/Acknowledgments

CAPES UFSC Pós-Graduação QUÍMICA CAPES Print ICMMO université PARIS-SACLAY

Área: INO

Degradation of emergent compound using foamed glass as catalyst support

João F.F. Sant'Anna (PG/FM),[1*] Carlos G. Murr (PG),[1] Maria Elena P. Arrúa (PQ),[2] André V. C. de Andrade (PQ),[3] Sandra R. M. Antunes (PQ),[1] Suellen A. Alves (PQ),[1] Eder C. F. Souza (PQ),[1] Christiane P. F. Borges (PQ).[1]

cpfbores@uepg.br

[1]Programa de Pós-Graduação em Química/Departamento de Química; [2]Departamento de Química;[3]Departamento de Física /Universidade Estadual de Ponta Grossa -UEPG.

Palavras Chave: *Hematite, limestone, graphite, methylene blue, dye degradation, Advanced oxidative processes.*

Highlights

Foamed glasses functionalized with hematite were synthesized using glass waste.
The application of foamed glass as catalyst support in methylene blue dye photodegradation was evaluated.

Resumo/Abstract

The increase in population and consumption habits have led to greater waste generation worldwide. The growth in the glass waste generated, as well as the water pollution caused by emerging pollutants, is bringing more concern every year. The foamed glass is a porous material with low density that presents chemical and high-temperature thermal stability. The production of foamed glass from glass waste is a more sustainable alternative compared to the production from virgin raw materials. In the present work were studied the production of foamed glass, using waste flat glass, and its use as a photocatalyst support aiming at the degradation of emerging compound. The application of the foamed glass with the supported catalyst in the photodegradation of the methylene blue dye model was evaluated. To produce the foamed glass, the waste was comminuted and sieved up to a 200 mesh particle size. Hematite was added to the glass powder. Dolomite limestone or graphite were used as foaming agents separately. The mixture was shaped, pressed and heat-treated at 760 °C. The foamed glass obtained were characterized using X-ray diffractometry (XRD), wavelength dispersive X-ray fluorescence (WDS), UV-Vis diffuse reflectance spectrophotometry, and scanning electron microscopy (SEM). Volumetric expansion, porosity, and bulk density of the samples were also evaluated. For the degradation tests, a photoreactor with LED lamp was used. The solutions containing methylene blue had their pH adjusted. The addition of hydrogen peroxide occurred in two different ways, in one of the analysis series 30 µL of peroxide were added in a single aliquot, and in another analysis series 30 µL of H_2O_2 were added in fractions. The results of the factorial planning demonstrated that fractioning the peroxide during the degradation process and varying the pH of the solution containing the dye can optimize the process, resulting in higher rates of dye degradation. The degradation of methylene blue was close to 25% under the conditions evaluated. The results showed that obtaining foamed glass using plain glass waste is viable under the conditions used in this work, and that it is possible to use the foams produced in the degradation of an emerging pollutant using an LED lamp to perform photocatalysis.

Agradecimentos/Acknowledgments

CAPES, Fundação Araucária, CNPq, GPMFE research group; C-LABMU/UEPG

Design, Synthesis, and Evaluation of a Novel Tridentate Phosphine-Amodiaquine Palladium(II) Complex

Kevinn A. C. Guimarães (IC)[1] and Wilmer Villarreal (PQ)[1*]

kevinn.cardoso@ufrgs.br; wilmer.villarreal@ufrgs.br

[1]*Grupo de Química Inorgânica Medicinal e Reações Aplicadas, Instituto de Química, UFRGS, Rio Grande do Sul, Brasil.*

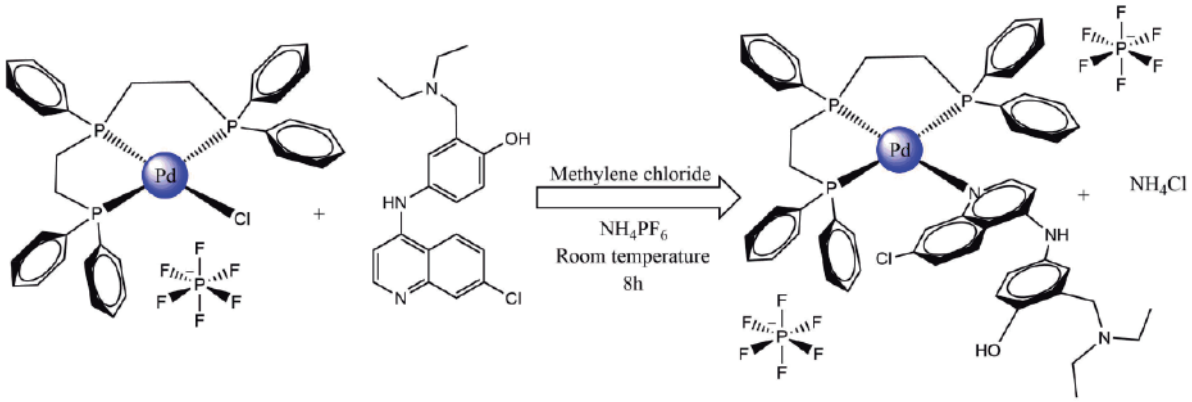
Keywords: *Metal complexes, Ferriprotoporphyrin, Antimalarial drugs, Amodiaquine-complex.*

Highlights

A new Pd (II) complex was prepared and evaluated for its interaction with the ferriprotoporphyrin group by UV-Vis titrations, demonstrating promise as a metal-based approach for malaria treatment.

Abstract

Malaria is a neglected tropical disease with a significant global impact. In 2022, there were an estimated 249 million cases in 85 countries, representing a 5 million case increase from 2021 [1]. The increase in global temperature is concerning as it may contribute to the spread of diseases transmitted by female Anopheles mosquitoes [2]. The disease is caused by the protozoa *Plasmodium sp*. and involves two cycles: hepatic and erythrocytic. In the second stage, the protozoan infects the erythrocytes and digests the hemoglobin, releasing soluble heme. This heme is toxic to the parasite and triggers a process of polymerization into hematin, forming hemozoin crystals. This process, known as heme detoxification, is the primary target of the antimalarial drug amodiaquine (AQ), which inhibits this polymerization [3]. The synthesis of a Palladium(II) complex with Bis(2-diphenylphosphinoethyl)phenylphosphine ligand (Triphos) and 4-[(7-chloroquinoline-4-yl)amino]-2-[(diethylamino)methyl]phenol (AQ) was performed as show in the Scheme 1, determining its general formula as $[Pd^{II}(Triphos)(AQ)](PF_6)_2$ (1) through UV-Vis, IR, NMR ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$. The interaction between the complex (1) and ferriprotoporphyrin was evaluated through UV-Vis absorption spectroscopic titrations [4], displayed a similar value to reported for AQ free ligand, suggesting promising potential for malaria treatment.



Scheme 1. Synthesis procedure for the complex 1

References

[1] WHO. World Malaria Report; World Health Organization: Geneva, Switzerland, 2023.

[2] U. Samarasekera, *The Lancet*, 402, 361-362, 2023.

[3] T. S. Macedo, W. Villarreal, C. C. Couto, D. R. M. Moreira, M. Navarro, M. Machado, M. Prudêncio, A. A. Batista, M. B. P. Soares, *Metallomics,* 9, 1548-1561, 2017.

[4] T. J. Egan, W. W. Mavuso, D. C. Ross, H. M. Marques. *J. Inorg. Biochem.*, 68, 137–145, 1997.

Acknowledgments

CNPq

FAPERGS

Área: INO

Development of adsorbent materials for adsorption of metal ions using *Inga edulis* biomass

Lucas dos Santos Lima (PG),[1*] Erica Porto Fernandes (PG),[1] Luiz Pereira da Costa (PQ),[1] Jefferson Arlei Freitas (PQ),[2] Eliana Midori Susschi (PQ)[1]

lsl.lucas@hotmail.com

[1]*Federal University of Sergipe, Department of Chemistry, São Cristóvão, Sergipe, 49.100-000.*

[2]*Federal University of Sergipe, Department of Environmental Engineering, São Cristóvão, Sergipe, 49.100-000.*

Keywords: *Adsorption, Biomass, Metal ions and Chemical activation*

Highlights

Adsorption of toxic metal ions such as Cr(VI) and Pb(II).
The biomass of Inga edulis has the potential for metal ion adsorption.
Activation of the biomass with acid increases the adsorption percentage.

Abstract

The applications of adsorbents derived from biomass have shown promising results in the removal of heavy metals from effluents. In this study, biomass from Inga edulis was selected due to its physicochemical properties that favor the adsorption of metal ions. Properties such as functional groups and surface area were chemically modified through treatment with sulfuric acid. The adsorbent materials were characterized using techniques such as scanning electron microscopy, vibrational spectroscopy in the infrared region, and thermogravimetric analysis, indicating that chemical activation resulted in an increase in oxygenated functional groups and a decrease in inorganic content (ashes). Inga biomass (BMIG) and activated Inga biomass (BMIGA) were introduced into solutions containing Cr(VI) and Pb(II) metal ions with a concentration of 100 mg/L, stirred for 24 hours at different pH. After the agitation time, concentrations were determined using ultraviolet-visible absorption spectroscopy. As illustrated in Figure 1a-b, the BMIGA adsorbent showed a higher percentage of removal of Cr(VI) and Pb(II) metal ions compared to the BMIG precursor, respectively, due to chemical modification with dilute sulfuric acid. The highest adsorption percentage for Cr(VI) ions was achieved at pH 2.0, while for Pb(II) ions, it was at pH 6.0. The variation in the adsorption percentage with pH is correlated with the speciation of metal ion species in aqueous media and the surface charge of the adsorbent, which changes with pH. Additional tests, such as dosage and particle size of the adsorbents, were conducted to gather information on the influence of quantity and size in the adsorption process in the presence of Cr(VI) and Pb(II) ions.

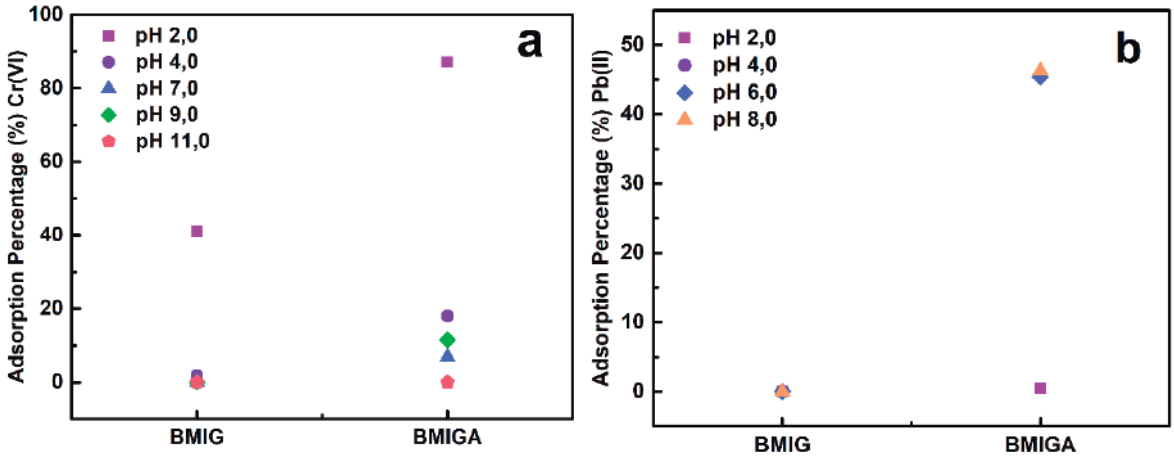


Figure 1. Metal ions removal efficiency at different pH levels.

Acknowledgments

The authors would like to thank the Multiuser Chemical Laboratories Center (CLQM), the Laboratory of Corrosion and Nanotechnology (LCNT), the Environmental Technology Laboratory (LATAM), Sergipe Technology Park (SergipeTec), and the financial support from CAPES, CNPq, and FAPITEC.

Área: INO

Ecofriendly synthesis of Portlandite from fertilizer and starch (cassava and avocado seed) applied to the rapid removal of Manganese from aqueous media

Elizandra M. de Oliveira (PG),[1]* Daiane L. da Souza (PG),[1] Anne Raquel Sotiles (PQ),[1] Fauze J. Anaissi (PQ)[1]

elimaiara540@gmail.com

[1]*Departamento de Química, Universidade Estadual do Centro-Oeste, Guarapuava, PR, Brasil.*

Keywords: Portlandite, Wastewater, Pigments, Circular Economy, Sustainability

Highlights

Portlandite [$Ca(OH)_2$] synthesized from fertilizer and different starch sources to maintain caustic properties and promote increased porosity was employed for manganese removal through adsorption.

Resumo/Abstract

Manganese a metal with high abundance and applicability in metal alloys, is potentially hazardous, and the increasing concentration of this metal in surface waters has become a cause for concern. This is because it can be bioaccumulative and affect the neurological system of humans[1,2]. The treatment of water contaminated with manganese is essential, considering water is an indispensable resource for the maintenance of life on the planet. In the quest for alternative materials that can effectively remove manganese from wastewater, calcium hydroxide was prepared using commercial fertilizer and colloidal dispersion of starch extracted from cassava (C.S.) and avocado seed (A.S.), through calcination at 900 ºC for 2 hours. The X-ray diffraction profile identified the presence of Portlandite ($Ca(OH)_2$) and Lime (CaO) phases for synthesis with C.S., and only the Lime phase when A.S. was used. Manganese removal tests were conducted using a synthetic effluent with Mn^{2+} ion concentrations ranging from 0.0047 a 0.0333 mol L^{-1}. The initial indication of effective removal is highlighted by the brownish color that the initially white solids adopted. The color is indicative of MnO_2 formation, a known pigment. Colorimetric assays following the CIELab system (Figure 1) demonstrate that as the amount of manganese is removed, there is an increase in the values of the +a* (red color) and +b* (yellow color) parameters, resulting in the brown tones observed in the pigments. The preparation of Portlandite using a sustainable and cost-effective method (starch and fertilizer) holds promise for the treatment of water contaminated with metal ions, encompassing Sustainable Development Goals (SDGs) and circular economy principles.

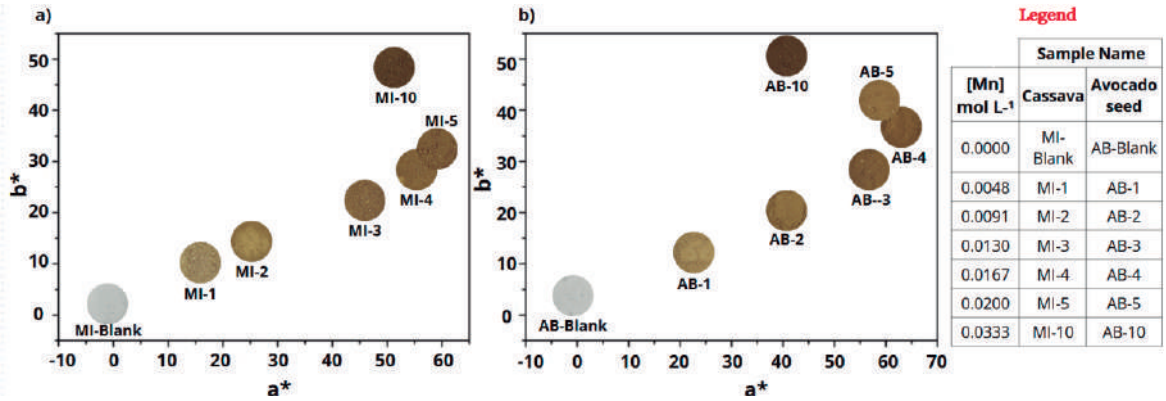


Figure 1. Relation between colorimetric parameters a* and b* in the coloration of samples using a) Cassava starch, and b) Avocado seed starch

[1] TEKERLEKOPOULOU, A. G.; PAVLOU, S.; VAYENAS, D. V. Removal of ammonium, iron, and manganese from potable water in biofiltration units: a review. Journal of Chemical Technology & Biotechnology, v. 88, n. 5, p. 751–773, 2013. John Wiley & Sons, Ltd.

[2] TOBIASON, J. E.; BAZILIO, A.; GOODWILL, J.; MAI, X.; NGUYEN, C. Manganese Removal from Drinking Water Sources. Current Pollution Reports, 1. set. 2016. Springer.

Agradecimentos/Acknowledgments

The authors express their gratitude to the funding agencies (Capes, Fundação Araucária, Finep). E.M.O. acknowledges the doctoral scholarship from PIBPG/CNPq.

Área: INO

Electrocatalysis of Oxygen Evolution Reaction by Iron Oxide Nanomaterials Synthesized with *Camellia sinensis* Extract

Samara L. Machado (IC),[1] Ana Luisa Silva (PQ),[1] Dalber R. Sánchez (PQ),[2] Mariella Alzamora (PQ),[3] Nakédia M. F. Carvalho (PQ).[1]*

nakedia@uerj.br; samara.lima.m@hotmail.com

[1]Departamento de Química Geral e Inorgânica, UERJ; [2]Instituto de Física, UFF; [3]Campus Duque de Caxias, UFRJ

Keywords: Oxygen evolution reaction, Iron oxide, Green synthesis, Plant extract.

Highlights

Iron oxide nanomaterials synthesized with the *Camellia sinensis* extract were explored as electrocatalysts in the oxygen evolution reaction, for generation of green hydrogen through water splitting.

Resumo/Abstract

The concern about the environment pollution and climate changes has brought the need to substitute the fossil fuels by clean, zero-carbon, and renewable energy and build-up a sustainable society. Transformation of solar energy in fuels based on the concept of artificial photosynthesis, is being extensively investigated and aims to come as close as possible to the process that takes place in nature. Green hydrogen can be produced from the water splitting reaction and it is considered the best option to replace the fossil fuels due to the fact that it does not generate polluting gases. In the water splitting reaction, water is reduced to H_2 and oxidized to O_2, where the water oxidation is the most demanding half-reaction and it is necessary the use of catalysts to accelerate the reaction and reduce the overpotential. The development of low-cost, Earth-abundant, active and stable electrocatalysts for the oxygen evolution reaction (OER) is an important task. Iron oxide nanomaterials are a promising option that has been explored recently for OER electrocatalysis. Synthesis of iron oxide assisted by the polyphenol-rich plant extract is a green approach to obtain nanomaterials with unique properties in a lower cost and operational simplicity. The polyphenolic compounds act as reducing and stabilizing agents of the iron nanoparticles. The main goal of this work was exploring the synthesis of iron oxides nanomaterials synthesized by the use of *Camellia sinensis* extract (black tea) to produce green and low cost electrocatalysts for OER. Four materials were synthesized exploring the order of addition of reagents and calcination, on the catalyst's properties and efficiency. The NH_4OH helps the formation and precipitation of the Fe_xO_y oxide, and two approaches were adopted: adding NH_4OH before and after the addition of the black tea extract. When NH_4OH is added before the black tea, first Fe_xO_y is formed, and the polyphenols binds to the nanoparticles surface. When NH_4OH is added after the black tea, the polyphenols first binds to the Fe(II/III) ions, and the Fe_xO_y precipitates contains the organic compounds incorporated in the bulk of the oxide. Both materials were calcined at 600 °C. The nanomaterials were characterized by XRD, SEM, SEM-EDS, FTIR, TG and Mössbauer spectroscopy, and pure iron phases were obtained, such as ferrihydrite, maghemite and hematite. The as-prepared materials presented amorphous nature, and after calcination more crystalline materials were obtained. The nanomaterials were tested in the electrocatalysis of OER in 1 mol L^{-1} KOH at pH 14. Films of the oxides were prepared over FTO for ECSA, CV and EIS and Pt RDE at 1600 rpm for OER LSV. A three electrodes cell was used, Ag|AgCl 1 mol L^{-1} KCl as reference electrode, a platinum rod as counter-electrode and FTO or Pt RDE as working electrode. Overpotential of 460 mV at current density of 10 mA cm^{-2} was obtained for the material composed of ferrihydrite prepared with the addition of NH_4OH after the iron salt and black tea extract without calcination. The most efficient electrocatalysts were those of more amorphous nature and with lower charge transfer resistance, as well as faster kinetics indicated by the lower Tafel slope.

Agradecimentos/Acknowledgments

This work was financially supported by UERJ, FAPERJ, CNPq and CAPES.

Área: INO

Evaluation of the Nitric Oxide on the Anticancer Activity of Trimethyl acetaldehyde derived Thiosemicarbazones

Emanuela da Conceição (PG)[1]*, José Clayston Melo Pereira (PQ).

***e.conceicao@unesp.br**

[1]São Paulo State University (Unesp), Department of Analytical, Physical-Chemical and Inorganic Chemistry, Institute of Chemistry, Araraquara, Brazil.

Palavras Chave: *Thiosemicarbazone; Thiadiazole; Nitric Oxide; Cyclooxidation; anticancer drugs.*

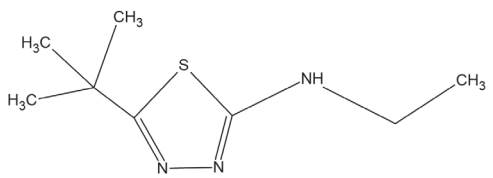
Highlights

Synthesis and characterization of trimethyl acetaldehyde derived thiosemicarbazones and thiadiazoles; investigation of the cellular viability of thiosemicarbazones and thiadiazoles in both tumor and non-tumor cells; exploration of the effectof cyclooxidation of thiosemicarbazones by nitric oxide on their anticancer activity.

Resumo/Abstract

Thiosemicarbazones (TATSC) are compounds of interest in research related to drug development for cancer treatment. Among the most promising TATSC, triapine stands out, showing excellent results in *in vitro* anticancer activity experiments[1]. Its action mechanism consists of its interaction with an enzyme present in the cellular environment, the ribonucleotide reductase (RDR), forming a metallic complex with the iron atom present in the structure of this enzyme. Researchers have suggested that triapine may be inhibited during *in vivo* treatment due to a cyclooxidation process, forming its corresponding thiadiazole (TDZ)[1]; thus, being unable to act as a chelating agent and having its neoplastic activity ceased. Our research group has been demonstrating that nitric oxide (NO) reacts, in the presence of oxygen, with TATSC through an oxidative cyclization process, forming a cyclic compound, a TDZ[2]. This could be the reason for the inhibition of the anticancer activity of TATSC, since NO is a molecule that is present in biological environments. The syntheses of the TDZ studied in this project was carried out through the oxidative cyclization of trimethyl acetaldehyde derived TATSC[2], and characterizations revealed that the proposed TDZ was in fact synthesized, as expected. The IR spectrum displays all characteristic bands present in the proposed TDZ structure, such as the bonds referring to the secondary amine present[3]. Nuclear magnetic resonance (NMR) supports the previous hypothesis; the ^{1}H spectrum shows all expected peaks along with the disappearance of two atoms of hydrogen to give origin to the TDZ ring. The ^{13}C spectrum exhibits peaks for all carbons in the proposed structure, including the C=N bond present in the cyclic structure of the TDZ, supporting our hypothesis[4]. Finally, a TDZ synthesized from TATSC-HE was obtained, and X-ray diffraction (DRX) was performed, confirming the structure previously expected. The biological experiments revealed that the TDZ-HE exhibited higher cell viability than TATSC-HE for both non-tumor lung cells (MRC5) and tumor cells (A549). That way, it's possible to conclude that the proposed TATSC-HE has a different action mechanism than those shown in literature for triapine, giving scope for future studies on the synthesized TATSCs and TDZs.

Structure of the TDZ expected derived from their respective TDZ.



Agradecimentos/Acknowledgments

I would like to thank CAPES and CNPq for funding this research project. Also, I would like to thank my research group for their support and collaboration throughout the realization of this work.

[1] Tenório, P. R.; Góes, A. J. S,; Lima, J. G.; Faria, A. R.; Alves, A. J. e Aquino, T. M.. Quim.Nova. **2005,** 1030.
[2] Zanetti, R.D. e Pereira, J. C. M. **Dinitrosilos de ferro contendo tiadiazol ou tiossemicarbazona derivada do cinamaldeído: síntese, caracterização e potencial aplicação antitumoral**, dissertação, UNESP, 2018.
[3]SILVERSTEIN, Robert M.; WEBSTER, Francis X.; KIEMLE, David J. Identificação espectrométrica de compostos orgânicos. In: **Identificação espectrométrica de compostos orgânicos.** 2007. p. 490-490.
[4]PAVIA, D. L. et al. **Introduction to Spectroscopy**. 5. ed. Stamford: Cengage Learning, 2015.

Área: INO

Evaluation of the Nitric Oxide on the Anticancer Activity of Vanillin-Derived Thiosemicarbazones

Gian Vitor Rodrigues(IC)[1]*, José Clayston M. Pereira (PQ)[1#] , Victor Marcelo Deflon (PQ)[2]

***gian.vitor@unesp.br; #jose.clayston@unesp.br**

[1]São Paulo State University (Unesp), Department of Analytical, Physical-Chemical and Inorganic Chemistry, Institute of Chemistry, Araraquara, Brazil

Palavras Chave: *Thiosemicarbazone, Tiadiazol, Nitric Oxide, Cyclooxidation, anticâncer*

Highlights

Synthesis and characterization of vanillin-derived thiosemicarbazones and thiadiazoles; investigation of the cellular viability of thiosemicarbazones and thiadiazoles in both tumor and non-tumor cells; exploration of the effect of cyclooxidation of thiosemicarbazones by nitric oxide on their anticancer activity.

Resumo/Abstract

Thiosemicarbazones (TSC) are compounds of interest in research related to drug development for cancer treatment. Among the most promising TSCs, triapine stands out, showing excellent results in in vitro anticancer activity experiments [1]. Researchers have suggested that triapine may be inhibited during in vivo treatment due to cyclooxidation, forming its corresponding thiadiazole (TD)[1]. Our research group has demonstrated that nitric oxide reacts with TSC in the presence of oxygen through an oxidative cyclization process, forming TD2. This could be the reason for inhibiting the anticancer activity of TSC. The syntheses of the worked TD in this project were carried out through the oxidative cyclization of TSC2, and characterizations revealed that the proposed TD was synthesized but with the incorporation of a NO_2 group. The IR spectrum displays all characteristic bands present in the proposed TD structures, and the addition of two signals at (1532 cm^{-1}) and (1355 cm^{-1}) corresponds to the nitro compound present in structure3. Nuclear magnetic resonance supports the raised hypothesis; the ^1H spectrum shows all expected peaks along with the disappearance of a doublet, suggesting the entry of the NO_2 group into the aromatic ring. The ^{13}C spectra exhibit peaks for all carbons in the proposed structures and a shift in the signals of carbons present in the aromatic ring, indicating support for the suggested hypothesis. Mass spectrometry and elemental analysis are essential for confirming the synthesis and the entry of the NO_2 group, matching precisely with molecular masses and percentages considering TD with a NO_2 group. Additionally, a VADTD thiadiazole was obtained, and X-ray diffraction (DRX) was performed, confirming the position of the entry of the NO_2 group, as shown in Figure 1:

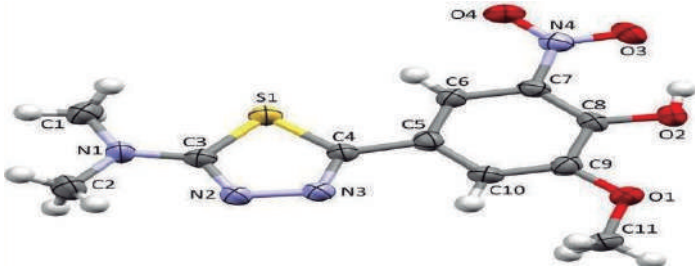


Figure 1. Structure of VADTD obtained by X-ray diffraction (DRX) technique

Biological assays have shown that TDs have a cell viability of 80% for non-tumorous lung cells (MRC5) and 70% for tumor cells (A549), whereas TSC exhibits a viability of approximately 54% for (A549) cells and 49% for MRC5 cells. It is concluded that the proposed TD aromatic rings underwent a nitration process, and due to their increased cell viability for tumor cells, the anticancer effect of TSC may be inhibited if it undergoes cyclooxidation into its corresponding TD.

Agradecimentos/Acknowledgments

I would like to thank FAPESP process number 2020/16660-3 funding the equipment. I would like to thank my research group for their support and teachings throughout the realization of this work.

[1] Tenório, P. R.; Góes, A. J. S,; Lima, J. G.; Faria, A. R.; Alves, A. J. e Aquino, T. M.. Quim.Nova. **2005,** 1030. [2] Zanetti, R.D. e Pereira, J. C. M. Dinitrosilos de ferro contendo tiadiazol ou tiossemicarbazona derivada do cinamaldeído: síntese, caracterização e potencial aplicação antitumoral, dissertação, UNESP, 2018.

[3]SILVERSTEIN, Robert M.; WEBSTER, Francis X.; KIEMLE, David J. Identificação espectrométrica de compostos orgânicos. In: Identificação espectrométrica de compostos orgânicos**.** 2007. p. 490-490.

Área: INO

Experimental DNA interactions of four new tetra-cationic ruthenium(II) porphyrin –The PRAP compounds

George Bueno Santana Pereira (PG),*[1] Alzir Azevedo Batista (PQ),[1] Fillipe Vieira Rocha (PG),[1]

george.bsp3@gmail.com

[1]*Departamento de Química, UFSCar*

Keywords: synthesis, porphyrin, ruthenium, coordination compounds, characterization, DNA interactions.

Highlights

Synthesis and characterization of PRAP compounds;
Two mechanisms of DNA interaction were proposed: electrostatic and covalent bonding;
A new class of compounds for DNA interaction and other applications.

Abstract

Cancer is a disease group characterized by uncontrolled cell growth and represents one of the leading causes of mortality worldwide[1]. Chemotherapy is a conventional treatment for cancer, especially for metastatic cases. However, chemotherapy drugs still have side effects and tumor resistance. Therefore, many chemotherapy candidates have been developed to expand this treatment and solve adverse problems. In this context, ruthenium complexes can act as candidates for chemotherapy[2]. One of the best-known classes is the RAPTA compounds. In addition to ruthenium, these coordination compounds are derived from organometallic arene and phosphine PTA and target DNA[2]. On the other hand, cationic porphyrins interact with DNA[3]. Positive charge is a crucial characteristic in the interaction with DNA[3]. Therefore, this work synthesized hybrid compounds of porphyrins coordinated to four peripheral ruthenium, arene, and phosphine complexes called PRAP compounds, Fig 1. This structural combination may be known as a new class of complexes with great biological applications. In this work, four new PRAP compounds derived from *meso*-tetra-(4-pyridyl)porphyrin, *meso*-tetra-(3-pyridyl)porphyrin and zinc(II) analogue metalloporphyrin containing four complexes of ruthenium(II), p-cymene, and triphenylphosphine in the periphery were synthesized. The compounds were characterized by UV-vis and IR spectroscopy, fluorescence, ^{1}H NMR, COSY, ^{31}P{^{1}H}, and molar conductivity. The complexes do not aggregate at 50 μM in DMF/Trizma buffer (1:4). Interactions with DNA were evaluated by spectrophotometric titration with ct-DNA, electrophoretic mobility, and photocleavage of plasmid pUC19, viscosity assay and interaction with guanosine by ^{31}P{^{1}H} NMR. These experiments proposed two modes of interaction: first, an electrostatic interaction providing aggregation; second, a covalent bond from the interaction with guanosine. The obtained results open perspectives on the applicability of PRAP compounds in the interaction with DNA and new applications in biomaterials science due to photoactive compounds such as porphyrins.

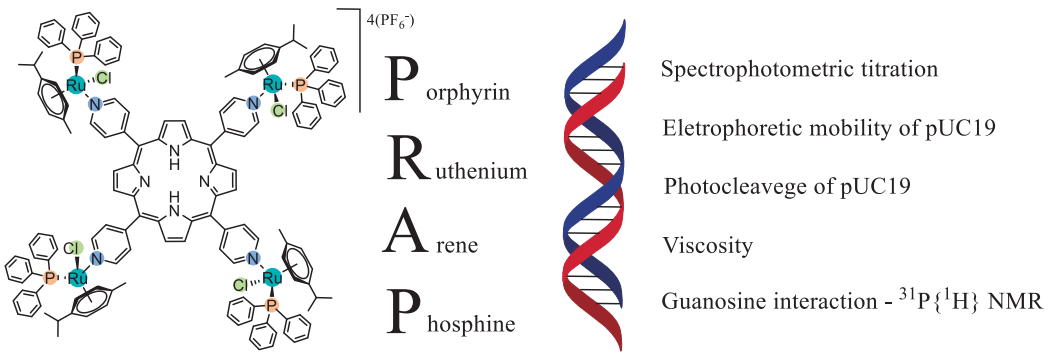


Fig 1: PRAP compound system and experimental techniques of DNA interaction.

[1] https://www.who.int/news-room/fact-sheets/detail/cancer
[2] Lee, Sang Yeul, Chul Young Kim, and Tae-Gyu Nam. *Drug design, development and therapy* (2020): 5375-5392.
[3] Pratviel, Geneviève. *Coordination Chemistry Reviews* 308 (2016): 460-477.

Acknowledgments

CAPES, CNPq (401681/2023-8), and FAPESP (2022/02876-0).

Área: _INO_____
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Exploring a quinoline derivative as an ionic sensor: Development and Applications

Janail R. Silva[1] (PG), Izilda A. Bagatin (PQ).[1]

janail.rodrigues@unifesp.br[1];

Instituto De Ciências Ambientais, Químicas e Farmacêuticas – ICAQF – UNIFESP – Diadema - SP
Laboratório de Química de Calixarenos, Espectroscopia Molecular e Catálise LQCEMC

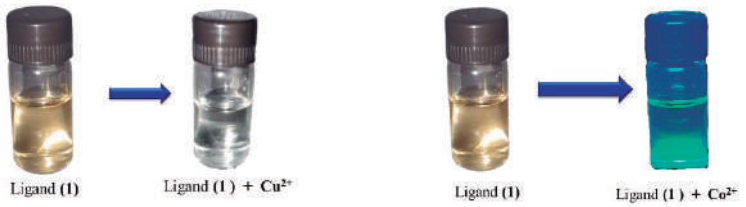
Keywords: *Chemosensor, hydrogen bond, colorimetric*

Highlights

Potential probe for F^-, Cu^{2+}, and Co^{2+} ions. Amide-bonded working groups and associated luminescent groups. Ligand has solid potential to recycle high-value materials.

Resumo/Abstract

With the advancement of technology and the need for environmental preservation, society has turned to creating innovative solutions. Scientific research on developing sophisticated chemosensors [1] has been crucial in this context. In this sense, a new chemosensor was developed, the 2-bromo-N-(8-hydroxyquinolin-5-yl)acetamide ligand (1), **to sense** potentially **toxic species and high-value materials**. It has the following ^{1}H NMR signals obtained (δ $CDCl_3$, 300 MHz): 4.20 ppm (sl, 1H, 9-NH), 4.77 ppm (s, 2H, 10-CH_2), 7.49 ppm (d, 1H, 6-CH, 3J = 8.80 Hz), 7.83 ppm (dd, 1H, 3-CH, 3J = 6.42 Hz), 8.63 ppm (d, 1H, 7 CH, 3J = 8.99 Hz), 9.15 ppm (d, 1H, 4-CH, 3J = 8.99 Hz), 10.98 ppm (d, 1H, 2-CH, 3J = 7.15 Hz). The interaction with the fluoride ion was observed in UV-Vis spectroscopy analyses, where an isosbestic point was identified at 369 nm. An increase in the band at 457 nm was also observed, followed by a modification of the profile of this band. In the interaction with the copper ion, there was a hypsochromic shift of the 457 nm band to 429 nm, which resulted in a change in the color of the solution from yellow to colorless. Otherwise, an isosbestic point was observed for cobalt ion at 377 nm, a hypsochromic shift from 457 nm to 435 nm, and two new bands at 589 nm and 681 nm have arisen. The interaction with cobalt ions could be detected with the naked eye as the solution gradually turned green during titration. For this ligand (1), see the scheme below (Scheme 1); preliminary results indicate its potential as a colorimetric chemosensor.



Scheme 1: Photos of the results of the ligand **1** interaction with Cu^{2+} and Co^{2+} ions.

[1] ZIMMERMANN-DIMER, Lizandra Maria; MACHADO, Vanderlei Gageiro. Quimiossensores cromogênicos e fluorogênicos para a detecção de analitos aniônicos. Química Nova, v. 31, p. 2134-2146, 2008.

Agradecimentos/Acknowledgments

This work was carried out with the support of the Coordination for the Improvement of Higher Education Personnel – Brazil (CAPES) – Financing Code 001

Área: INO

Exploring the Biological Profiles of Silver(I) Complexes: $[Ag(L)(PPh_3)_2]^+$ and $[Ag(L)_2]^+$ Featuring Semicarbazones and Triphenylphosphine Ligands.

Vitor Y. G. Almeida (PG),[1*] Victoria C. R. Colmenares (PG),[1] Josias S. Rocha (PG),[1] Débora P. Felix (IC),[1] Gabriela P. Oliveira (PQ),[1] Mauro A. Lima (PQ),[1] Renan L. Farias (PQ),[2] Renan D. Zanetti (PQ),[2] Adelino V. G. Netto (PQ),[2] Carolina R. Zambom (PG),[3] Saulo S. Garrido (PQ),[3] and Fillipe V. Rocha (PQ),[1]

victoriacrc@estudante.ufscar,br; vyga_vitao@hotmail.com

[1]Chemistry Department, UFSCAR; [2]Department of Analytical Chemistry, Physicochemical and Inorganic Chemistry, Institute of Chemistry, UNESP; [3]Department of Biochemistry and Organic Chemistry. Institute of Chemistry, UNESP.

Palavras Chave: *Design New Silver (I) Complexes, DNA Interactions, Cytotoxicity and Antibacterial Activity.*

Highlights

The BBA complex exhibits higher selectivity for prostate cancer, as indicated by SI values for prostate cell lines. Interestingly, DNA is ruled out as a primary cytotoxic target due to imperceptible interactions between DNA and the complexes in the methods employed. This research offers concise insights into the ligand-driven biological profiles of silver(I) complexes, emphasizing their potential in targeted cancer therapies.

Abstract

The synthesized complexes underwent comprehensive characterization employing various techniques, including NMR (1H, 13C-{1H}, 31P), IR, UV-vis, molar conductivity, and CHN elemental analysis. The 1HNMR analysis of complex (3) revealed a resemblance to its free ligand, implying minimal changes in the electronic configuration of the d10 central ion upon coordination. A distinct feature was the superimposed signals for vinyl hydrogens (H7 and H8), potentially indicating chelated coordination with the silver ion. The 31PNMR spectra of compounds 2 and 4 displayed broad peaks at 9.01 ppm and 9.48 ppm, respectively, confirming the coordination of the phosphine group. Molar conductivity measurements suggested the stability of 1:1 cationic complex in dimethyl sulfoxide. Infrared (IR) analysis showcased shifts in C=N and C=O stretches, indicating the possible coordination of the ligand semicarbazone to silver(I) through nitrogen and oxygen donor atoms. Cell viability assays (MTT) were conducted on breast tumor cells (MDA-MB-231 and MCF-7) and both tumor and non-tumor prostate cells (PNT2 and DU-145). Intriguingly, complexes containing triphenylphosphine ligands (BAP and CAP) exhibited heightened inhibitory action compared to bisquelates. The BBA complex displayed the highest selectivity index (SI), particularly with an SI value (IC50[PNT2]/IC50[DU-145]) for prostate cells (IS = 3.13). Furthermore, the antibacterial evaluation demonstrated CAP's potent inhibition (above 70%) against Gram-positive and Gram-negative bacteria and its promising potential as an antimicrobial agent. This multifaceted exploration delves into the structural intricacies and highlights the diverse and promising biological activities of the synthesized silver(I) complexes. DNA interaction assays provided insight into the therapeutic mechanisms, suggesting weak or absent interactions and pointing towards alternative targets.

Acknowledgments

CNPq 401681/2023-8. CNPq 140870/2021-0. Fapesp 2022/02876-0

Área: INO

Exploring the combination of Ru/DMSO/quinolones as new metallopharmaceuticals

Pedro H.S. Marcon (PG),[1] Alzir A. Batista (PQ),[2] Javier A. Ellena (PQ),[3] João H.A. Neto (PQ).[1]*

pedromarcon@usp.br; joaohonorato@iq.usp.br

[1]Institute of Chemistry, USP; [2]Chemistry Department, UFScar; [3]Institute of Physics of São Carlos, USP.

Keywords: *ruthenium, quinolones, biomolecules interaction, DNA, HSA.*

Highlights

Structure elucidation of new ruthenium(II)-dmso complexes with quinolone based ligands and their interactions with vital biological molecular targets.

Resumo/Abstract

The application of coordination compounds as a class of antitumoral molecules is well known and established as a scientific fact, commercially feasible, oncological successful drugs and ruthenium-based complexes are amongst the most distinguished classes of bioactive inorganic molecules. On that matter, ruthenium complexes that bear DMSO as ligands demonstrate interesting anticancer properties[1]. Another well-established class of compounds are the quinolones, the first synthetic antibacterial drugs introduced into the market and are still in clinical and veterinary use, but only recently being discovered as human topoisomerase inhibitors[2], and its ruthenium complexes demonstrated diverse chemical and biological profiles[3], thus being dragged under the drug repositioning umbrella which summarizes the interest of this work. Here we report the synthesis, characterization and interactions with HSA and DNA of three new ruthenium(II)-dmso complexes with quinolone antibacterials nalidixic acid, oxolinic acid and ciprofloxacin as ligands, prepared from the precursor *fac*-[$RuCl_2$(dmso-S)$_3$(dmso-O)] (Scheme 1.). All complexes follow the general formula *fac*-[RuCl(dmso-S)$_3$(*O-O*)] (Figure 1), are neutral and were characterized via FTIR spectroscopy, ^{1}H and ^{13}C NMR, elemental analysis, mass spectrometry, UV-Vis spectroscopy and single crystal x-ray diffraction. The quinolones act as bidentate ligands through the pyridone and carboxylato oxygen atoms, carrying one negative charge, a chlorido ligand with the second negative charge balances out the positive charge on the metal center, and to complete the coordination sphere, there are three S-bonded dimethylsulfoxide molecules in a facial geometry comprising the structure's distorted octahedral geometry. Another structural factor that is common between the complexes is that the planar portion of ligands aren't on the same plane as the ruthenium(II) center, suggesting the lack of resonance of the new rings formed with the rest of the molecule. Preliminary assays on the interaction of the complexes with target biomolecules such as DNA and HSA are being conducted, as well as *in vitro* cytotoxic essays against tumor cell lines to establish the compounds' IC_{50} values and discussion will be shown.

Scheme 1. General synthetic route to obtain the complexes.

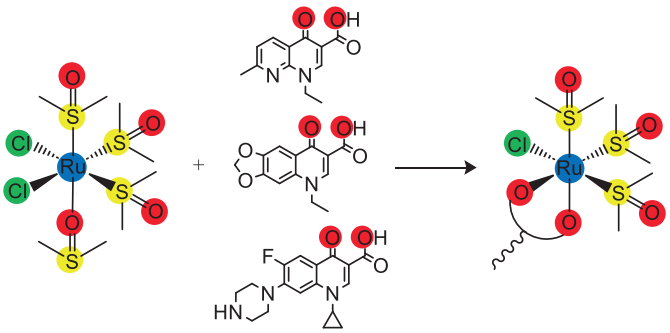
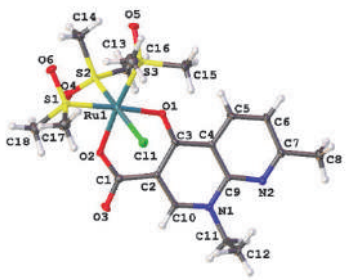


Figure 1. Crystal structure of [RuCl(dmso)$_3$(nal)].



[1]*ALESSIO, E.; et al. Inorganic Chemistry. Vol. 27, n. 23, p. 4099-4106, 1998.* DOI: 10.1021/ic00296a006

[2]*BISACCHI, G. S.; et al. Current Medicinal Chemistry. Vol. 23, n. 6, p. 520-577, 2016.* DOI: 10.2174/0929867323666151223095839

[3]*KLJUN, J.; et al. Inorganic Chemistry. V. 52, n. 15, p. 9039-9052, 2013.* DOI: 10.1021/ic401220x

Agradecimentos/Acknowledgments

The authors acknowledge the funding agencies CNPq and FAPESP, the institutes IQUSP and IFSC-USP.

Área: CAT

Fe-PHI Single-Atom Catalyst: as Photocatalyst for Biomass Conversion

Danielly Tamires da Silva Costa (PG),[1]* Mariana Baptista Marques (IC),[1] Ivo Freitas Teixeira (PQ).[1]

***danielly9@estudante.ufscar.br.**

[1]*Departamento de Química, UFSCAR.*

Palavras Chave: *Carbon nitrides, Biomass, Photocatalysis, Single atom catalysts (SACs).*

Highlights

1. Carbon nitrides catalyze green reactions for eco-friendly plastics; 2. Innovative use of GC-MS in synthesizing methyl furanoate; 3. Transforming furfural to methyl furanoate: sustainable plastic precursor; 4. Carbon nitrides drive selective chemical synthesis for eco-plastics;

Resumo/Abstract

The growing concern about greenhouse gas emissions is driving the search for sustainable solutions, with an emphasis on biomass as an alternative to replace fossil fuels. However, there is still a need to develop efficient biomass conversion processes. Herein, we investigated the oxidative esterification reaction of furfural (scheme 1), a substance derived from lignocellulosic biomass. As photocatalyst for this reaction we employed a single-atom catalysts (SAC) produced by exchanging the Na^+ cations of sodium poly(heptazine imide) (Na-PHI) by Fe^{3+}.[1] This method enabled the sustainable production of methyl furanoate, a precursor to the sustainable polymer PEF, a potential substitute for PET.

Scheme 1. Furfural oxidative esterification reaction

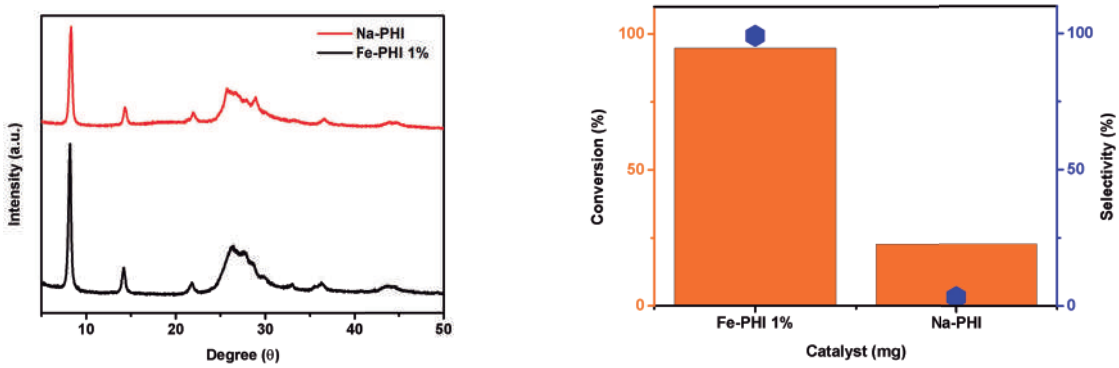


Fig. 1: a) XRD diffractogram of spectra for Na-PHI and Fe-PHI; b) Conversion and selectivity related to Furfural. Reactions conditions: Substrate (25 uL), Catalyst (25mg), Solvent (2mL - MeOH), O_2 (2 bar), 410nm 50W lamp, room temperature, cylindrical quartz reactor.

In Figure 1(a), the X-ray Diffraction (XRD) pattern related to the Na-PHI and Fe-PHI structures is shown, maintaining high crystallinity even after the cation exchange. Advanced characterizations (i.e. EXAFS and AC-STEM-HAADF) revealed that iron sites stabilize in the PHI structure as single-atoms.[2] After conducting oxidative esterification tests of furfural under different conditions and analyzing the reaction mixture by GC-MS, the conversion and selectivity for methyl furanoate were determined (Figure 1(b). Under optimal reaction conditions, a 90% conversion with 100% selectivity for the ester was achieved. These results underscore the promising perspective of carbon nitrides in photocatalytic processes for biomass conversion.

(1) da Silva, M. A. R.; Silva, I. F.; Xue, Q.; Lo, B. T. W.; Tarakina, N. V.; Nunes, B. N.; Adler, P.; Sahoo, S. K.; Bahnemann, D. W.; López-Salas, N.;
(2) da Silva, M. A. R.; Tarakina, N. V.; Filho, J. B. G.; Cunha, C. S.; Rocha, G. F. S. R.; Diab, G. A. A.; Ando, R. A.; Savateev, O.; Agirrezabal-Telleria, I.; Silva, I. F.

Agradecimentos/Acknowledgments

UFSCar and FAPESP.

Área: INO

Fotodegradação do corante rodamina B utilizando o híbrido $H_2T4SPP@TiO_2$.

Vinícius Ludgero da Silva de Oliveira (IC)[1], Alessandra Nayra Silva Batista (PG)[1], Marcelo Machado Viana (PQ)[1], Dayse Carvalho da Silva Martins (PQ)[1*].

viniciusludgeroufmg@gmail.com; *daysequimica@ufmg.br

[1]*Departamento de Química,ICEx, UFMG.*
Palavras Chave:*Porfirinas, Contaminante, Fotocatálise, Inibidores.*

Highlights

Photodegradation of Rhodamine B dye using the $H_2T4SPP@TiO_2$ hybrid. $H_2T4SPP@TiO_2$ hybrid was used to photodegrade the rhodamine B dye and the most efficient system was determined. The possible reactive species generated in the reaction system were identified by tests with inhibitors.

Resumo

Os corantes utilizados em indústrias têxteis tornaram-se um grande problema para a sociedade por conta da sua toxicidade. Diante disso, métodos químicos para a degradação de tais substâncias começaram a ser estudados com a finalidade de resolver essa questão. Óxidos metálicos semicondutores mostram-se eficientes no processo de degradação de corantes, porém, sua utilização fica limitada à faixa de comprimento de onda absorvida pelo óxido (band gap). Uma alternativa para superar essa limitação é combinar o óxido de interesse com uma molécula que amplie a faixa de trabalho em termos de energia absorvida, transicionando da região do UV (comum para a maioria dos óxidos) para a região do visível. No trabalho apresentado, foi utilizado o dióxido de titânio comercial (TiO_2-P25) como fotocatalisador e uma porfirina (H_2T4SPP^{4-}) como fotossensibilizador. Para o híbrido produzido, testou-se sua capacidade fotocatalítica, na degradação do corante rodamina B, quando irradiado com luz UVC e visível (400 a 700 nm) (Figura 1).

No gráfico da degradação do corante com o TiO_2-P25 (Figura 1a), observa-se que o uso da radiação UV levou ao sistema mais eficiente, conforme esperado uma vez que o material possui um band gap de 3,33 eV, sendo ativado sob radiação UV. O híbrido $H_2T4SPP@TiO_2$ foi testado (Figura 1b) e apresentou menor capacidade catalítica do que o material de partida sob luz UV provavelmente devido à elevação do band gap do híbrido para 3,40 eV. Acredita-se que o aumento do band gap pode estar associado à formação de múltiplas camadas do agente usado como ponte entre o TiO_2 e a porfirina ((3-aminopropil)trietoxisilano, APTES), como comprovado por meio de análises por microscopia eletrônica de transmissão de alta resolução. No sistema irradiado com luz visível, o padrão de degradação permaneceu praticamente o mesmo para ambos os materiais, indicando que a transferência de elétrons da porfirina para o TiO_2 não foi possível, provavelmente devido à presença da multicamada de APTES. Com isso, idealmente, a eficiência do sistema estaria diretamente relacionada com a quantidade de camadas do agente de acoplamento. A fim de se identificar as possíveis espécies reativas geradas no meio de reação, experimentos utilizando-se inibidores de radicais foram realizados. Azida de sódio, manitol, benzoquinona, ácido ascórbico e ácido 4,5-dihidroxi-1,3-benzenodissulfônico foram usados como inibidores para oxigênio singleto ($^1O_2$), radical hidroxila (·OH), radical oxigênio singleto ($\cdot^1O_2$) e superóxido (O^{2-}). Observou-se uma redução na fotodegradação da Rodamina B nos sistemas empregados esses inibidores, demonstrando a participação das espécies citadas na reação de degradação desse corante pelo híbrido $H_2T4SPP@TiO_2$.

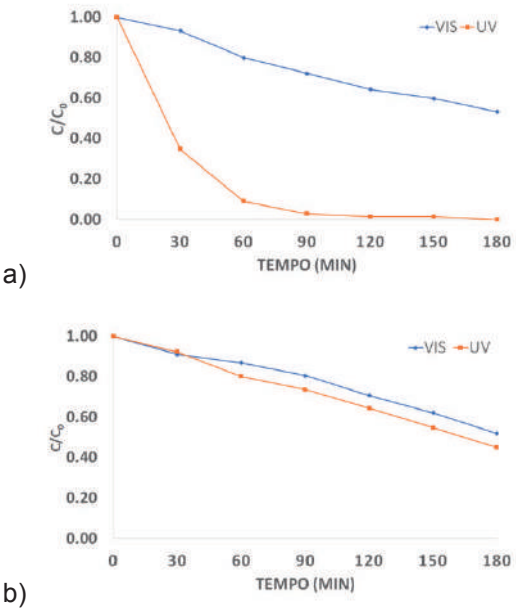


Figura 1. Degradação fotocatalítica da rodamina B para os catalisadores (a) TiO_2, (b) $H_2T4SPP@TiO_2$.

Agradecimentos

CAPES, CNPq, FAPEMIG, FINEP, INCT-CiMOL, PRPq/UFMG.

Referencias: 1) Stepanova, A. et al. 2023. DOI: 10.1021/acsomega.3c05890; 2) Ahmed, M.A. et al. 2017. DOI:10.1016/j.jphotobiol.2017.09.016; 3) Liu, W. et al. 2023. DOI: 10.1016/j.cej.2023.143161.

Área: INO

From disposal to light emission: Luminescent polymeric film through the recycling of disposable cups doped with Eu^{3+} for applications in OLEDs.

Levy R.S Bispo (IC)[1]*, Andrei Marcelino Sá Pires Silva (PG)[2,3], Michely S. Piropo (IC)[1], Jorge F. S. de Menezes (PQ)[1,2,3,4] .

levytheo9@gmail.com

[1]Universidade Federal do Recôncavo da Bahia UFRB, Centro de formação de professores CFP; [2]Programa de Pós-graduação em Química-Departamento de Ciências Exatas e Tecnológicas UESC; [3]INCITE-Nanotecnologia, Universidade Estadual de Feira de Santana UEFS; [4]INCT-Energia e Meio Ambiente, Universidade Federal da Bahia UFBA.

Keywords: *OLED, Luminescent, Complexes, Europium, Recycling, Materials.*

Highlights

This study aimed to align with the Sustainable Development Goals (SDGs) by developing a potential candidate for application in the emissive layers of red light in OLEDs using recyclable material obtained from disposable plastic cups combined with the $[Eu(TTA)_3.(H_2O)_2]$ complex.

Abstract

Currently, the production challenges of new organic light-emitting diode (OLED) devices underscore the importance of developing environmentally friendly innovations with future prospects to minimize ecological footprint aligned with the Sustainable Development Goals (SDGs). This study focused on the optical properties, photoluminescent parameters, and colorimetric characteristics of luminescents films produced from polystyrene (PS) obtained disposable plastic cups doped with the 1% $[Eu(TTA)_3.(H_2O)_2]$ complex, deposited using the casting method. A comparison between the complex and the luminescent polymeric film (LPF) in Table 1 revealed an increase in intrinsic quantum efficiency and decay time, along with a reduction in non-radiative transition rate, without significant changes in color coordinates. This system proves to be a potential candidate for application in the emissive layers of red light in OLEDs of the low cust .

Table 1 – Photoluminescent and colorimetric parameters of the complex and luminescent polymeric film.

Complexe	t(ms)	$A_{rad}(s^{-1})$	$A_{nrad}(s^{-1})$	$A_{tot}(s^{-1})$	η(%)	$\Omega_2(x10^{-20})$	$\Omega_4(x10^{-20})$	CIE (x, y coordinates)
$[Eu(TTA)_3.(H_2O)_2]$	0,25	980	2904	3884	25,23	27.53	7.25	0.65, 0.33
$[Eu(TTA)_3.(H_2O)_2]$1% in PS	0,35	873	1651	2524	34,59	24.34	6.56	0.66, 0.33

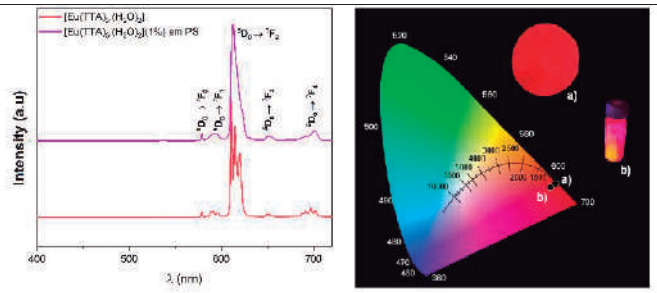


Figure 1: Spectrum of emission from both systems obtained at 298K (λ_{exc}=368nm) and respective chromaticity diagram with photo register.

[1] THEJOKALYANI, N.; DHOBLE, S. J. Importance of eco-friendly OLED lighting. In: **Defect and Diffusion Forum**. Trans Tech Publications Ltd, 2014. p. 1-27.

Acknowledgments

We are greatful to CNPq, FAPESB, INCITE Nanotechnology, and INCT-CNPq/Energy and Environment for the support and scholarships granted.

Área: INO

Heterogenization of Mn(III) 2-, and 4-*N*-alkylpyridylporphyrin-based catalysts on silica gel

Isaque A. A. Feitosa (IC),[1] Welida T. Alves-Silva (PG),[1] Victor Hugo A. Pinto (PQ),[1] Jacqueline C. Bueno-Janice (PQ),[1,2] Júlio S. Rebouças (PQ)[1]*

iaaf@academico.ufpb.br; jsreboucas@quimica.ufpb.br

[1]*Departamento de Química, UFPB;* [2]*Departamento de Biofísica e Radiobiologia, UFPE.*

Keywords: *Metalloporphyrins, Mn porphyrins, Porphyrins, Biomimetic catalysts, Silica gel.*

Highlights

Cationic Mn(III) porphyrins were electrostatically anchored on chromatographic silica gel. Immobilizations were quantitative and all materials were stable against leaching irrespective of MnP isomer or alkyl side-chain.

Resumo/Abstract

The rational design of Mn(III) *N*-alkylpyridylporphyrin-based catalysts (MnPs) as mimics of cytochromes P450 enzymes for the oxyfunctionalization of inert C-H bonds under mild biological conditions has inspired different research teams. These systems have been greatly studied under homogeneous conditions and show excellent results for the oxidative catalysis of different model substrates. Heterogenization of these compounds on inorganic matrices has yielded promising oxidation catalysts by limiting oxidative destruction of the porphyrin macrocycle often seen under homogeneous conditions, improved reaction yields and selectivities, as well as the possibility of easier recovery and recycle of the catalyst/material [1,2]. The use of silica gel as inorganic support in these materials has been driven by its affordability, abundance, chemical and mechanical resistance, and active surface of easy modification; the negative surface characteristic of commercial, chromatographic-grade silica gel has been explored recently as an effective means to electrostatically immobilize pentacationic Mn(III) complexes derived of 2- and 4-*N*-methylpyridylporphyrins (MnTM-X-PyP^{5+}; X = 2 or 4) [2]; the resulting SiO_2/MnTM-X-PyP^{5+} materials were highly efficient and recyclable catalysts for PhIO-oxidation of cyclic and linear alkanes with chemoselectivity for alcohols. Herein, we revisited the preparation of SiO_2/MnTM-X-PyP^{5+} and expanded the study to include the heterogenization of the lipophilic MnP analogues based on Mn(III) 2-, and 4-*N*-n-hexylpyridylporphyins to yield SiO_2/MnTnHex-X-PyP^{5+} (X = 2 or 4) materials. The immobilization reactions of MnP onto SiO_2 were carried out under small scale by suspending SiO_2 in a MnP aqueous solution at room temperature in a shaking incubator; for each MnP, 5 different concentrations were tested, resulting in a total of 20 materials with MnP loadings ranging from 0.1 to 5 μmol g^{-1}. In all cases the immobilization was essentially quantitative. Furthermore, all attempts to leach the heterogenized MnP from the SiO_2 surface using extractions with water (at room or high temperature) and washings with organic solvents (MeOH, EtOH, $CHCl_3$, and MeCN) were unsuccessful, showing a high stability of the immobilized MnP against leaching. It is worth noting that regardless of the MnP isomer or the nature of the *N*-alkyl side-chain, all MnPs were strongly anchored onto the silica surface, which is in direct contrast with the data on a more lipophilic silica of chloropropyl-functionalized surface (Sil-Cl, data not shown). Thus, the ready preparation and non-leaching characteristics of SiO_2/MnTalkyl-X-PyP^{5+} (X = 2 or 4; alkyl = Me or nHex) solids make them promising materials to be investigated as potential MnP-based P450 catalysts.

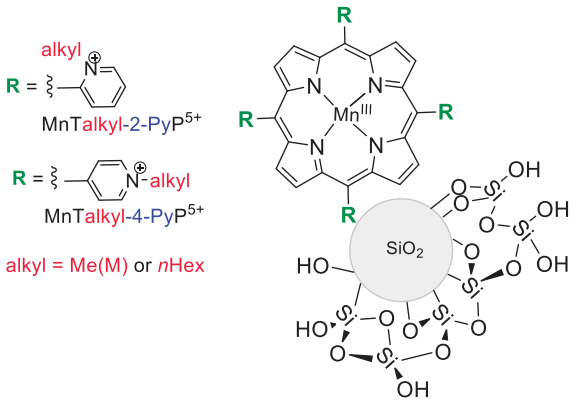


Figure 1. Representation of *N*-alkylpyridylporphyrins immobilized on SiO_2 (MnTalkyl-X-PyP^{5+}; X = 2 or 4; alkyl = Me or *n*Hex)

[1] Nakagaki, S.; Ferreira, G. K. B.; Marçal, A. L.; Ciuffi, K. J.; *Current Org. Synth.*, **2014**, *11*, 67.
[2] Pinto, V. H. A.; Falcão, N. K. S.; Silva, B. M.; Fonseca, M. G.; Rebouças, J. S.; *Dalton Trans.*, **2020**, *49*, 16404.

Agradecimentos/Acknowledgments

CNPq, CAPES, FINEP, FACEPE, UFPB, INCT-CiMol.

Immobilization of human Cofilin-1 protein on a 3-mercaptopropionic acid monolayer on Gold

***Rayssa Gabrielly Freitas Monteiro (IC)**, **Luiz Henrique da Costa Souza (PG), Ana Claudia Silva Gondim (PG), Eduardo Henrique Silva de Sousa (PG), Izaura Nogueira Cirino Diógenes (PG).**

monteirorayssa20@alu.ufc.br

Laboratório de Bioinorgânica, Departamento de Química Orgânica e Inorgânica, Centro de Ciências, Universidade Federal do Ceará

Keywords: sulfur molecule; surface plasmon resonance; cofilin-1 protein

Highlights

- Cofilin protein was successfully immobilized on a SAM of 3-mercaptopropionic acid on gold
- Thickness and surface coverage of the immobilized protein were determined by surface plasmon resonance

Abstract

Recent research suggests that the oxidation of cysteine residues (Cys 39, 80, 139, and 147) in the human Cofilin-1 protein (CFL-1) influences its physiological function and may lead to the formation of polymeric aggregates of alpha-synuclein known as Lewy bodies, a characteristic aspect of Parkinson's disease. Aiming at determining the oxidation level of CFL-1 through surface plasmon resonance (SPR), this work presents the results related to the first step of the project which is the immobilization of this protein on a self-assembled monolayer (SAM) of 3-mercaptopropionic acid (MPA) on gold though covalent interaction. The modified gold electrode was characterized by cyclic voltammetry, electrochemical impedance spectroscopy, and SPR through which the variation of the SPR angle directly gives the amount of adsorbed substances. Upon activation of the MPA SAM with N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC) and N-hydroxysulphosuccinimide (NHS), the CFL-1 protein was immobilized leading to a SPR angle variation of 224.4 mθ (Figure 1). SPR data obtained at two different wavelengths were analyzed by using the Layer Solver software (Bionavis) giving a thickness of 1.53 nm for the protein-formed film. Applying the results to the Feijter model yielded a surface coverage of 12.09 ± 1.72 ng cm^{-2} for the CFL-1-modified surface. The following step of the study includes the determination of the cysteine concentration on surface for evaluating the CFL-1 oxidation state.

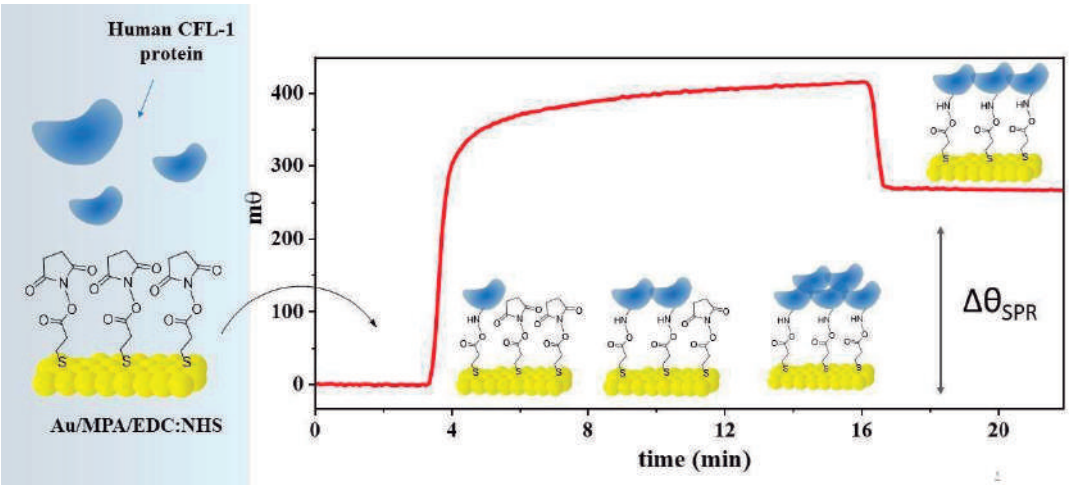


Figure 1 - Sensorgram of CFL-1 protein immobilization leading to a variation of the SPR angle (Δθ).

Acknowledgments

This work was financially supported by CAPES (PROEX 23038.000509/2020-82), FINEP (CV.01.22.0174.00), FUNCAP, and CNPq (311274/2020-0; 309010/2021-7)

Área: INO

Immobilization of isomeric, water-soluble Mn(III) *N*-alkylpyridylporphyrins onto chloropropyl-functionalized silica gel (Sil-Cl)

Welida T. Alves-Silva (PG),[1] Isaque A. A. Feitosa (IC),[1] Victor H. A. Pinto (PQ),[1] Jacqueline C. Bueno-Janice (PQ),[1,2] Júlio S. Rebouças (PQ)[1]*.

welidatamires14@gmail.com; jsreboucas@quimica.ufpb.br

[1]*Departamento de Química, UFPB;* [2]*Departamento de Biofísica e Radiobiologia, UFPE*

Keywords: *Mn porphyrin, Silica gel, Immobilization, Chloropropyl silica gel, Heterogenized MnP, Porphyrin.*

Highlights

Heterogenization of Mn(III) 2- or 4-*N*-alkylpyridylporphyrins on chloropropyl-functionalized silica gel was influenced by *N*-pyridyl isomer and very much depend on the lipophilicity of MnP, exerted by the *N*-alkyl side-chains.

Resumo/Abstract

Mn(III) porphyrins (MnPs) are good biomimetic models of oxidation enzymes that upon heterogenization onto inorganic matrices give rise to robust catalysts of ease recovery and reuse [1,2]. Mn(III) *N*-methylpyridylporphyrin derivatives have been electrostatically immobilized on unmodified silica gel (SiO_2) or covalently anchored on chloropropyl-functionalized silica (Sil-Cl) [2]. The catalytic activity of these materials indicated a slightly better alcohol selectivity using the Sil-Cl systems *vs*. non-functionalized SiO_2 ones [2]. Electrostatic immobilization of cationic MnPs on Sil-Cl seems a natural complimentary study exploring a support with hydrophobic surface and a straightforward heterogenization route, which may lead to selective catalysts. The objectives of the current study included the investigation of the immobilization of a series of MnPs of varied lipophilicity on the lipophilic, functionalized silica Sil-Cl. Thus, Mn(III) 2- and 4-*N*-alkylpyridylporphyrins, MnTalkyl-X-PyP^{5+} (X = 2 or 4; alkyl = methyl or *n*-hexyl), were used to prepare the materials Sil-Cl/MnTM-X -PyP^{5+}(X = 2 or 4) and Sil-Cl/MnTnHex-X-PyP^{5+}(X = 2 or 4). The impact of both the nature of the MnP isomer and the lipophilicity of MnP on the electrostatic interactions between MnP and Sil-Cl was investigated by evaluating heterogenization parameters such as MnP loading and immobilization yield. The immobilization reactions were carried out under small-scale conditions by mixing Sil-Cl with 0.01 to 0.5 mmol L^{-1} MnP aqueous solutions at room temperature followed by washings with water and various organic solvents, resulting in a total of 20 Sil-Cl/MnTalkyl-X-PyP^{5+} materials. MnP loadings and immobilization yields were determined indicating that saturation of the Sil-Cl surface with MnP was achieved in the MnTM-X-PyP^{5+} (X = 2 or 4) cases. The materials were stable against extraction by organic solvents, except for the Sil-Cl/MnTnHex-4-PyPCl$_5$ system that was slightly leached (< 5%) with MeOH washing. The Sil-Cl loading capacity and overall stability of the Sil-Cl/MnTalkyl-X-PyP^{5+} materials against leaching were remarkably dependent on both the nature of the *N*-alkyl side-chain and the temperature of immobilization/washings, but of little dependence on the nature of the isomer. These results are in direct contrast to studies on non-functionalized SiO_2 (methyl data in [2], *n*-hexyl data not shown). From a catalysis point of view, these materials may be promising biomimetic P450 catalysts in organic solvents; their use in aqueous conditions may be potentially compromised by unwanted Mn leaching, particularly in the methyl systems, *i.e.* Sil-Cl/MnTM-X -PyP^{5+}(X = 2 or 4).

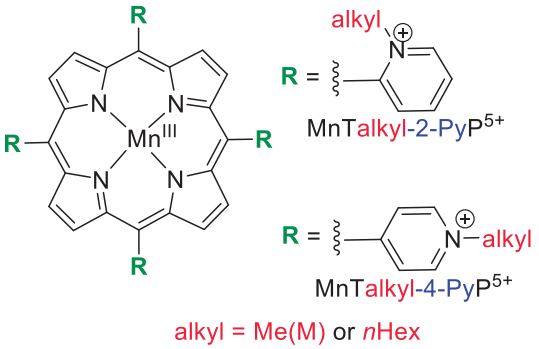


Figure 1. Representation of *N*-alkylpyridylporphyrins (MnTalkyl-X-PyP^{5+}; X = 2 or 4; alkyl = Me or *n*Hex)

[1] Nakagaki, S.; Ferreira, G. K.B.; Marcal, A. L.; Ciuffi, K. J.; *Current Organic Synthesis*. **2014**, *11*, 67.
[2] Pinto, V.H.A.; Falcão, N.K.S.M.; Mariz-Silva, B.; Fonseca, M.G.; Rebouças, J.S.; *Dalton Trans*. **2020**, *49*, 16404.

Agradecimentos/Acknowledgments

CNPq, CAPES, FINEP, FACEPE, UFPB, INCT-CiMol

Área: INO

Improving the photostability of Eu(III) luminescent complexes with imides and acylated sulfonamides ligands

Jéssika C. Lima (PG),[1] Ivani Malvestiti (PQ),[2] Ricardo L. Longo (PQ),[2] Nunes,R.R.[2]

jessika.lima@ufpe.br; ivani.malvestiti@ufpe.br, ricardo.longo@ufpe.br, rodolfonnunes@gmail.com.

[1]*Departamento de Química Fundamental, Universidade Federal de Pernambuco, Recife, PE, Brazil.*

Key words: *photostability, luminescent complexes, lanthanides, imides, acylated sulfonamides.*

Highlights

New Eu(III) complexes with imides and acylated sulfonamides were synthesized by mechanochemistry using an Ika Turrax device. The results suggest that imides are promising ligands to achieve higher photostability for these luminescent complexes.

Abstract

Complexes with lanthanides are of great interest due to their wide range of applications, such as: luminescent devices, catalysts, molecular thermometers, contrasts agents, etc. The nature of the ligands is relevant to their properties, namely, processability, luminescence brightness, thermostability, and photostability. An important factor of chelate complexes with Eu(III) and other ions is their low photostability, which can limit some applications. In this context is important to evaluate new ligands aiming at improving the photostability of the complexes, especially with Eu(III). In this work, Eu(III) complexes with imides and acylated sulfonamides were synthesized via mechanochemistry and their luminescent properties and photostability were evaluated. All reactions were performed in an Ika Ultra Turrax using 0.4 mmol of $EuCl_3{\cdot}6H_2O$, 1.2 mmol of ligand,1.2 mmol of NaOH and 25 µL of water for one hour at room temperature. Afterwards, an auxiliary ligand (0.4 mmol of phenanthroline) was added, and the mixture milled for another 30 minutes. All complexes exhibited luminescence when irradiated with UV radiation at wavelengths of 254 nm and 365 nm. For the Eu(III) complex with *N*-benzoylbenzamide, no decrease in the intensity of the luminescence was observed over a period of 5 hours, as illustrated in Figure 1. For the complex with *N*-benzoylbenzamide and phenanthroline, the luminescence intensity reduces 22% during the same period. However, the Eu(III) complex with *N*-tosylbenzamide and phenantroline showed a reduction of 52% after 5 hours of exposure to UV radiation.

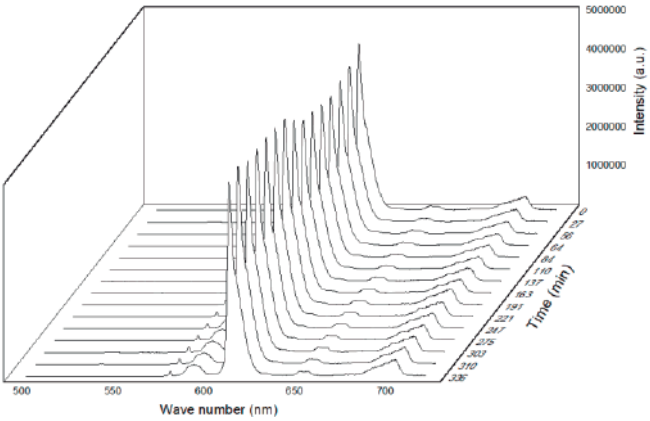


Figure 1- Luminescence intensity of the Eu(III) complex with the ligand N-benzoylbenzamide with the exposure to UV radiation.

These results highlight the potential of imides as ligands for the synthesis of photostable Eu(III) complexes and use of the Turrax in a greener mechanical synthesis of complexes.

References

ABERGEL, Rebecca J.; KOZIMOR, Stosh A. Innovative f-element chelating strategies. Inorganic Chemistry, v. 59, n. 1, p. 4-7, 2020.

ZHENG, Wei et al. Dramatic improvement in photostability of luminescent Eu (III) complexes with tetraphenylimidodiphosphinate ligand. Journal of luminescence, v. 146, p. 544-549, 2014.

Acknowledgments

FACEPE, CNPq, CAPES, and UFPE

Área: INO

Influência do haleto nos estudos espectroscópicos de complexos de Zn^{2+} da família $[Zn(bmimapy)X]^+$

Matheus C. Pessanha (PG)*, Alvicler Magalhães (PQ) e Marciela Scarpellini (PQ)

matheuscp@pos.iq.ufrj.br

Laboratório de Desenvolvimento de Compostos Bioinorgânicos (LDCB), Instituto de Química, Universidade Federal do Rio de Janeiro

Palavras-Chave: *Bioinorgânica, Química de Coordenação, Zinco, Espectroscopia, RMN*

Highlights

The halide influence in spectroscopic studies of $[Zn(bmimapy)X]^+$ complexes. Mimetics of β-lactamases Zn^{2+} complexes using a polimidazole ligand and different halides. Spectroscopic and X-ray diffractometry technics to elucidate structural features of complexes of Zn^{2+}.

Resumo/Abstract

As β-lactamases de classe B são enzimas produzidas por microrganismos e hidrolisam β-lactamas, que são constituintes de boa parte dos antibióticos. Assim, estão envolvidas no mecanismo de resistência a antibióticos β-lactâmicos. Uma das formas de intervir neste processo seria pela inibição das β-lactamases pela abstração do Zn^{2+}, seu cofator. Partindo desta premissa, nosso grupo ambiciona a obtenção de complexos de Zn^{2+} com moléculas orgânicas imidazólicas, que são versáteis e excelentes quelantes. Neste trabalho, são estudados os complexos de fórmula $[Zn(bmimapy)X]PF_6$, onde bmimapy=*N,N*-bis((1-metil-1H-imidazol-2-il)metil)-2-(piridin-2-il)etanamina e X= Cl^- (**C1**) ou I^- (**C2**). Nos espectros de IV foram atribuídas as seguintes bandas: νZn-N (amina) em 522 cm^{-1} para ambos; νP-F em 835 / 557 cm^{-1} para ambos; δC-H (aromático) em 775 cm^{-1} com Cl^-, 767 cm^{-1} com I^-; νC-N (amina) em 1284 cm^{-1} com Cl^-, região de 1276 a 1288 cm^{-1} com I^-; νC=N/C=C (anel) de 1606 a 1448 cm^{-1} para ambos; νC-H (alifático) de 3112 a 2935 cm^{-1} com Cl^-, de 2858 a 3122 cm^{-1} com I^-; νC-H (anel) de 3135 a 3112 cm^{-1} com Cl^-, de 3124 a 3170 cm^{-1} com I^-. Nos espectros de UV pode-se identificar que o **C1** apresenta uma banda em 264 nm (ε=20,2 $Lmol^{-1}cm^{-1}$), enquanto o **C2** apresenta duas bandas, em 250 e 265nm (ε=5,8 e 6,4 $Lmol^{-1}cm^{-1}$, respectivamente). As três bandas são de transferência de carga intraligante. Atribui-se o desdobramento da banda no **C2** ao seu maior raio atômico que tende a distorcer o ligante quelante. Nos espectros de massas (ESI+), a maior diferença deve-se à ausência do pico referente à espécie $[Zn(bmimapy)]^{2+}$ para **C1** indicando a manutenção do Cl^- coordenado nas condições de análise. Para **C2**, o pico da espécie $[Zn(bmimapy)]^{2+}$ é observado em m/z = 187,06 (100%). Os demais picos para **C1** são $[Zn(bmimapy)Cl]^+$ - 2 H^+ com m/z = 409,09 (100%) e [bmimapy] + H^+, com m/z = 311, 20 (4%). Para o complexo **C2** tem-se [bmimapy] + H^+ com m/z = 311,20 (25%), [Zn(bmimapy)I] - H^+ com m/z = 501,02 (60%). Os espectros de RMN ^1H (500,13MHz) foram obtidos com 64k pontos, AQ 3,28s, em solução de MeOD, (16,7 mg/mL) em sonda BBFO. Os FIDs foram processados utilizando zero filling, resolução digital a 0,16Hz/pt. As atribuições para o **C1**: δ 9,11 ppm (1H, dd, J= 7,40 Hz, J= 1,35 Hz), 8,05 ppm (1H, dt, J= 7,75 Hz, J= 7,40 Hz, J= 1,78 Hz); 7,58 ppm (1H, ddd, J= 7,75 Hz, J= 7,90 Hz, J= 1,35 Hz); 7,52 ppm (1H, dt, J= 7,90 Hz, J= 1,78 Hz); 7,29 ppm (2H, d, J= 1,55 Hz); 7,27 ppm (2H, d, J= 1,55 Hz); 4,17 ppm (4H, s); 3,69 ppm (6H, s); 3,34 ppm (2H, m, J= 5,53 Hz, J= 2,53 Hz); 2,90 ppm (2H, m, J= 5,41 Hz, J= 2,59 Hz); para o complexo **C2**: d 9,02 ppm (1H, dd, J= 7,40 Hz, J= 1,78 Hz, 1,48 Hz); 8,03 ppm (1H, ddd, J= 7,78 Hz , J= 1,78 Hz, J= 7.40 Hz); 7,57 ppm (1H, ddd, J= 1,48 Hz, J= 7.90 Hz, J= 7,78 Hz); 7,51 ppm (1H, dd, J= 7,90 Hz, 1,78 Hz); 7,37 ppm (2H, d, J= 1,55 Hz); 7,27 ppm (2H, d, J= 1,60Hz), 4,10 ppm (4H, s); 3,68 ppm (6H, s); 3,33 (2H, m, J= 5,74 Hz, J= 2,70 Hz), 2,88 (2H, m, J= 5,74 Hz, J = 2,70 Hz). As diferenças entre os espectros são fundamentadas no maior raio iônico do iodeto, que propicia o acoplamento espacial com certos hidrogênios. Os padrões dos difratograma de raios X de pó obtidos para ambos os complexos em forma de pó são completamente diferentes, sugerindo que o empacotamento dos compostos é distinto. Para o complexo $[Zn(bmimapy)Cl]PF_6$ foi obtido o DRX de monocristal, cujo resultado confirma que este assume a geometria bipirâmide de trigonal.

Agradecimentos/Acknowledgments

Ao CNPq, Capes e Faperj pelo fomento e ao Programa de Pós-Graduação em Química - UFRJ.

Área: INO

Influence of synthesis parameters on the luminescent properties of KGd_2F_7 fluoride matrix doped with Eu^{3+} ions

Paulo V. B. de Simone* **(IC),[1] Andreza C. S. Silva (PQ),[1] Hermi F. Brito** (PQ)[1]**

***pbrancacio@usp.br**, ****hefbrito@iq.usp.br**

[1]*Departamento de Química Fundamental, Instituto de Química - USP*

Palavras Chave: *Fluoretos de terra rara, nanopartículas, parâmetros de síntese*

Highlights

This work investigates the influence that synthesis paremeters have on the KGd_2F_7 matrix doped with Eu^{3+} ions. Our XRD analysis demonstrated the influence of the time between synthesis and washing of the particles on their size, showing how the synthesis parameters can influence the morphology of the particles, and, consequently, their optical properties.

Abstract

Rare earth fluorides have been recently well studied for their useful characteristics [1], such as their unique optical properties that arise from the electronic structure of the rare earth ions, thermostability, biocompatibility, and color tunability, including materials that present upconverting luminescence [1]. However, in order to refine and perfect all those properties, the synthesis of the materials must be well-studied and understood. With that in mind, this work aims to study the synthesis of rare earth fluorides, with emphasis on the KRE_2F_7 matrix (RE: Eu^{3+}, Gd^{3+}), through the modified coprecipitation method [2]. This method involves the mixture of rare earth acetates with sources of potassium (KOH) and fluoride (KF) where the solvent consists of a mixture of octadecene, oleic acid, and oleylamine. This mixture is then heated up to 120°C to yield the rare earth oleates. With the formed oleate complexes, the temperature is then raised to 300°C to start the formation of the particles, which are then separated through centrifugation and washed with ethanol and cyclohexane solvents. The prepared materials were characterised by different techniques, such as XRD, SEM, and TEM. Their photoluminescent properties were investigated from the excitation and emission spectra. To understand the synthesis, various parameters, such as temperature, solvents, and preparation time were varied. Our preliminary results show that the particle size increases with the time that it takes for the particles to be washed and that no difference was noted by both increasing and decreasing the cooling times after the step at 300°C.

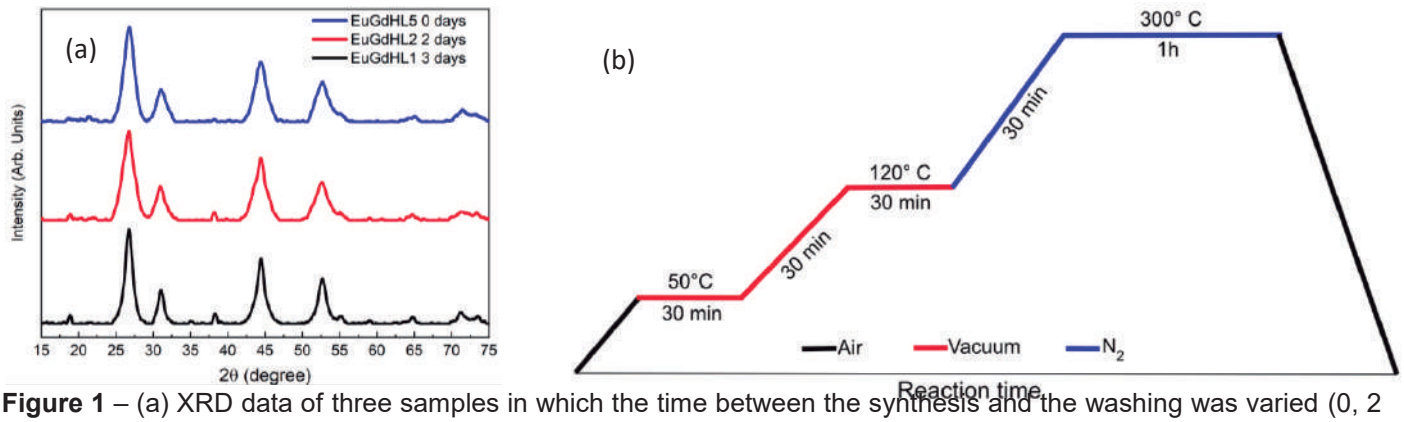


Figure 1 – (a) XRD data of three samples in which the time between the synthesis and the washing was varied (0, 2 and 3 days). (b) Scheme of the synthesis, with the temperatures and duration of each ramp and plateau.

Acknowledgments

P.V.B. de Simone is grateful to CNPq for the "Iniciação Científica" grant (133030/2023-7). This work was developed under the scope of FAPESP thematic project 2021/08111-2. H.F. Brito is grateful to CNPq for the "1A Produtividade" fellowship (Grant 308872/2022-3).

[1] Pedraza, F. J.; Avalos, J. C.; Yust, B.G; Tsin, A.; Sardar, D. K. *Nanotechnology*, v. 27, n. 38, (2016).
[2] Wang, F., Deng, R. & Liu, X. Nat Protoc 9, 1634–1644 (2014).

Área: INO

Insights into Water Oxidation Catalysts: Characterizing Prussian Blue Analogs Using Synchrotron Light at the IPÊ Beamline of Sirius

Rafael L. Germscheidt (PQ),[1] Tulio R C Roch (PG),[2] Juliano A. Bonacin (PQ).[1]*

jbonacin@unicamp.br

[1]*Departamento de Química Inorgânica – Universidade Estadual de Campinas*
[2] *Brazilian Synchrotron Light Laboratory*

Palavras Chave: *Synchrotron Radiation; X-ray Photoelectron Spectroscopy (XPS), X-ray absorption spectroscopy (XAS), Prussian Blue; water oxidation, hydrogen production*

Highlights

- Use of synchrotron radiation to characterize catalysts for water oxidation
- Determination of the oxidation state of the catalysts
- Characterization of the metals on the surface of the materials

Resumo/Abstract

Synchrotron light sources offer unparalleled advantages for chemistry research, providing high-intensity, tunable, and polarized beams across a wide spectral range, from infrared to UV and X-rays. These capabilities, combined with exceptional energy resolution and collaborative facilities, allow researchers to conduct non-destructive studies with high spatial resolution and chemical sensitivity, advancing our understanding of complex chemical phenomena and materials. In this work, we report the characterization of inorganic catalysts such as Prussian blue analogues (PBA) using the IPE beamline of the Sirius light source at the Brazilian Synchrotron Light Laboratory (LNLS). The IPE beamline specializes in X-ray Absorption Spectroscopy (XAS), X-ray Photoelectron Spectroscopy (XPS), and Resonant Inelastic X-ray Scattering (RIXS) within the soft X-ray spectrum (0.1 – 2 keV). These techniques enable the analysis of chemical composition and electronic structure of inorganic catalysts. Here we present the use of XAS and XPS to probe the composition and the nature of unconventional structural defects by analyzing PBA-based catalysts here named Traditional PBA (FeFe), Activated PBA (FeFe – with structural cyanide defects), CoFePBA and Activated CoFePBA (with structural cyanide defects). The elemental composition observed in the films with and without cyanide defects using the XPS analysis reinforces the persistence of an unchanged structure, even after the introduction of structural vacancies. The comparison of Fe L-edge XAS for Traditional PBA and Activated PBA unveils variations in the oxidation state, with Activated PBA exhibiting a predominance of Fe^{2+} and mixed valence between Fe^{2+}/Fe^{3+} in Traditional PBA. Similarly, the comparison of Fe L-edge spectra between CoFePBA and Activated CoFePBA indicates the predominance of Fe^{3+} upon the introduction of defects, evidenced by the near disappearance of absorption peaks assigned to Fe^{2+} in the activated catalyst. Notably, materials with defects show a distinct energy shift of approximately 0.3 eV of the absorption edge indicating changes in the local chemical environment assigned to unconventional CN− vacancies. A comparison among the spectra of the catalysts is presented in Figure 1. In conclusion, the unique chemical sensitivity of soft X-ray spectroscopy offers a compelling avenue for unraveling the intricacies of defect chemistry in earth-abundant 3d transition metal catalysts employed in recent catalysis and energy conversion studies. This study underscores the potential of soft X-ray spectroscopy as a robust tool for inorganic chemists seeking deeper insights into catalyst behavior.

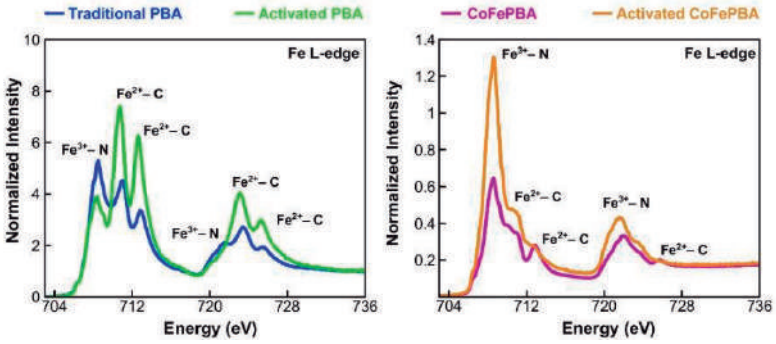


Figure 1. Comparison among the Fe L-edge XAS spectra of studied catalysts

Agradecimentos/Acknowledgments

CAPES: Finance Code 001; CNPq: 308203/2021-6; FAPESP: grant# 2017/11986-5 and 2021/05976-2

Área: INO
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Interactions of selenite anion with Al(III) ion on the surface of fine decomposed peat.

Bruna P. Szpoganicz (PG),[1] Bruno Szpoganicz (PQ),[1]

belabruna@yahoo.com; bruno.s@ufsc.br

[1]*Departamento de Química, UFSC;*

Palavras Chave : *(Peat, Titration, Selenite, Equilibrium constants).*

Highlights

The association of selenite with the Al(III) ion adsorbed in fine decomposed peat (FDP) was studied and the equilibrium constants determined. The major species detected as a function of pH is a protonated selenite coordinated to the metal ion.

Resumo/Abstract

Peat is an organic material that is formed in wetlands in acidic conditions in swamps and mangroves. These conditions favor the growth of mosses. Selenite is one of the most stable forms of selenium, being essential for living organisms. The interaction of selenite ion with fine decomposed peat (FDP) enables an arrangement involving the protonated selenite ion on the peat surface. This arrangement has the oxygenated chelating groups interacting with Al(III) ion, which interacts with the selenite in a supramolecular arrangement. The equilibrium constants were determined by potentiometric titration with the help of BEST7 program (MARTELL & MOTEKAITIS, 1992) and the species distribution shows that Al(III) is coordinated with the chelating groups present in the peat surface (SZPOGANICZ et al. 2024). In this study it appears coordinated with a phthalic group, a hydroxil group and a protonated selenite anion. The Al(III) ion coordinated with catechol and salicylic group also interact with selenite. At pH values higher than 10 selenite ion leaves the supramolecular arrangement and appears free in solution.

Referências/References

(1) MARTELL, A. E.; MOTEKAITIS, R. J**; Determination and use of Stability Constants,** 2ª ed. New York: VCH Publishers , 1992, p. 1-212.
(2) SZPOGANICZ, B. P.; PROBST, L. F.; COSTA, T. G.; MEURER, L.; SZPOGANICZ, B.; Chemistry of Inorganic. Materials, **2024**, v.2, 1-9.

Agradecimentos/Acknowledgments

The authors thanks CNPQ and UFSC.

Área: INO

Investigação da Cinética de Oxidação/Hidrólise do 4-Nitrofenil-β-D-glucopiranosídeo mediada por complexos de Zinco(II) e Manganês(II)

Marcos Aurélio da Silva Francisco (PG), Camilla Maria Barros da Silva (IC), Caroline Martins da Costa (PG), Roberto B. Faria(PQ) e Marciela Scarpellini[1](PQ)

marcosaur.sf@gmail.com; marcosaur.sf@gmail.com

Laboratório de Desenvolvimento de Compostos Bioinorgânicos (LDCB), Instituto de Química, Universidade Federal do Rio de Janeiro

Palavras Chave: catalysis, LPMOs, model complexes, bioinorganic.

Highlights

Investigation of oxidation/hydrolysis reaction parameters of 4-nitrophenyl-β-D-glucopyranoside mediated by zinc(II) and manganese(II) complexes. Synthesis of tetracoordinated zinc(II) and manganese(II) coordination compounds. Kinetic studies of the oxidation/hydrolysis of 4-nitrophenyl-β-D-glucopyranoside mediated by the complexes.

Resumo/Abstract

Um dos grandes desafios científicos da atualidade é o estabelecimento de matrizes energéticas e cadeias de produção de insumos químicos sustentáveis. Para este fim, o uso de matérias primas advindas de biomassa, como lignocelulose e quitina, é uma alternativa viável considerando a abundância destas fontes e os ODS 30. No entanto, estas duas fontes são polissacarídeos complexos, de difícil hidrólise, e, portanto, sua utilização em bioprocessos industriais para a obtenção de seus monômeros exige o emprego de misturas de enzimas e possui um alto custo. As enzimas conhecidas como LPMO (*lytic polysaccharide monoxigenases*) são capazes de auxiliar no desdobramento destas matérias primas em suas unidades monoméricas, diminuindo o custo dos processos. Estas enzimas possuem o íon Cu^{2+} como cofator, coordenado com duas histidinas e um triptofano. Assim, complexos modelos para a atividade catalítica das LPMOs utilizam o íon Cu^{2+} e ligantes que possuem similaridade à histidina em um arranjo "*histidine brace*". O objetivo deste trabalho é explorar o papel de complexos tetraédricos de Cu^{2+} e Zn^{2+} na reação de oxidação e consequente degradação do substrato modelo 4-nitrofenil-β-D-glucopiranosídeo. Os complexos $[M(L)_2](ClO_4)_2$ (M = Mn^{2+}, Zn^{2+}) foram obtidos pela reação do ligante L (4-(1-metil-1H-imidazol-2-il)-5-((1-metil-1H-imidazol-2-il)metil)-4,5,6,7-tetra-hidro-1H-imidazo[4,5-c]piridina) com o perclorato do metal (2:1), em metanol. Os complexos foram caracterizados por DRX, IV, UV, ESI-MS e RMN. Os dados cinéticos foram obtidos acompanhando-se a formação do produto *p*-nitrofenolato em 400 nm, em tampão carbonato (pH 10), empregando-se substrato ($1,5 \times 10^{-1}$ a $6,0 \times 10^{-1}$ mM), H_2O_2 (0,6 mM), trietilamina (0,6 mM) na presença dos complexos ($1,5 \times 10^{-3}$ mM). Os dados obtidos sem a presença dos complexos foram utilizados para descontar qualquer efeito de autodegradação do substrato. Os gráficos de V_0 ($M^{-1}s^{-1}$) *versus* [substrato] (mM) evidenciaram que ambos os complexos inibem a reação, enquanto que os sais dos metais promovem uma ligeira catálise. Este processo de inibição pode ser explicado pela coordenação do metal com o produto da reação, *p*-nitrofenolato, de forma monodentada com o oxigênio do grupo fenolato ou com o grupo nitro de forma bidentada.

Agradecimentos/Acknowledgments

Agradecemos ao CNPq, à CAPES e à Faperj pelo fomento e à PGQu-UFRJ.

Área: INO

Investigating Au(I)-NHC 2-thiol-thiazolines or 2-thiol-pyrimidine derivatives' Interaction with Cysteine and their Biological Relevance

Gustavo Clauss Rodrigues (PG)[1]*, Igor Santos Oliveira (PG)[1], Camilla Abbehausen (PQ)[1].

gustavoclaussr@gmail.com

[1]*Institute of Chemistry, UNICAMP*

Palavras Chave: *Computational, Gold(I) complexes, Thione Ligands, Metallodrugs, Antileishmanial.*

Highlights

Gold(I)-NHC show metallodrug potential. N-R group influences chemistry, as does the ligand trans to NHC. Our recent study explored ligand exchange of [Au(IMes)Cl] (IMes = [1,3-bis(2,4,6-trimethylphenyl)-2H-imidazol-2-ylidene]) with N-acetyl-L-cysteine (NAC), revealing a slow reaction. Currently, we investigate four thione donor ligands with biological relevance.

Resumo/Abstract

Our research has been studying Gold(I)(NHC) for antileishmaniasis and antiviral activity. N-R group modification in Au(NHC)Cl adjusts activity based on drug lipophilicity. [Au(IMes)Cl] excels in leishmanicidal activity due to balanced lipophilicity and stability. Ligand exchange with N-acetyl-L-cysteine (NAC) unveils compound reactivity, studied via ^{1}H NMR and *in silico* methods.[1-2] Thiol donors, like in the drug auranofin, enhance bioavailability. The study scrutinizes ligand exchange in [Au(I)(IMes)L] with L as thiazolidines and 2-thiol-pyrimidine derivatives: 2(3*H*)-benzothiazolethione (Sbtz), 2-thiazolidinethione (Stzn), 2(1*H*)-pyrimidinethione (Spym) and 4(1*H*)-pyrimidinone (2-tu) (Figure 1).

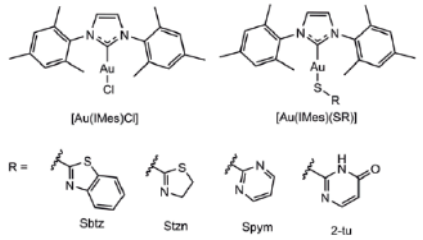


Figure 1. Structures of [Au(IMes)Cl] and [Au(IMes)(SR)].

The best *in vitro* results are the following: [Au(IMes)(Stzn)] and [Au(IMes)(2-tu)] showed IC_{50} values of 1.93 and 2.03 μmol·L^{-1}, respectively, against leishmania promastigotes. [Au(IMes)(Sbtz)] and [Au(IMes)(2-tu)] inhibited 95.5% and 93.8% of ZIKV viral replication, at 2 μM.

Ligand exchange reaction of [Au(IMes)L] was studied by ^{1}H NMR in DMSO-d6 with time and analyzing the Bound NAC % (Figure 2). The exchange is rapid, preventing kinetic evaluation. Thermodynamically, thiol derivatives favor exchange over chloride.

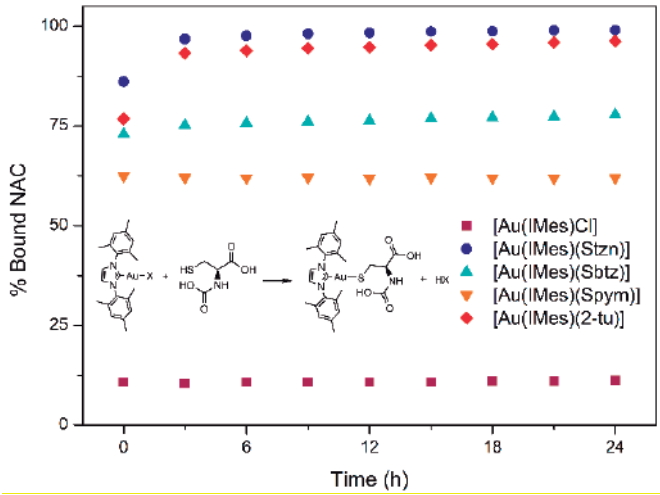


Figure 2. Bound NAC (%) by reaction time (h) with Au(I)-NHC.

DFT calculations illuminate the reaction, revealing dependence on ligand tautomeric forms and proton transfer in solution. Table 1 depicts Gibbs Free Energy changes, considering two tautomeric forms.

Table 1. Calculated ΔG (kJ/mol) for each reaction.

Complex	Thiol form	Thione form
[Au(IMes)(Spym)	17.6	6.0
[Au(IMes)(Sbtz)]	24.1	-15,5
[Au(IMes)(2-tu)]	27.0	-21.7
[Au(IMes)(Stzn)]	25.7	-30.7
[Au(IMes)Cl]	59.5	

Analysis favors the thione form, aligning with ^{1}H NMR findings. Future studies will delve into reaction kinetics, exploring potential pathways for proton transfer from free NAC to the thione ligand.

REFERENCES

[1] Rosa, L. B.; Galuppo, C.; Lima, R. L. A.; Fontes, J. V.; Siqueira, F. S.; Júdice, W. A. S.; Abbehausen, C.; Miguel, D. C. Journal of Inorganic Biochemistry 2022.
[2] Rodrigues, G. C.; Barrionuevo, M. V. F.; San-Miguel, M. A.; Abbehausen, C. New Journal of Chemistry 2024.

Agradecimentos/Acknowledgments

FAPESP 2022/02618-0 and 2023/12657-6, CNPq 404668/2021-6 for financial support and CENAPAD-SP project#638 for computer time.

Área: INO

In vitro antiproliferative activity of silver(I) complexes with trifluoromethyluracil isomers over squamous carcinoma cells

Gabriele de M. Pereira (PG)[1], Fernando R. G. Bergamini (PQ)[2], Kaio E. Buglio (PG)[3], Julia H. Bormio Nunes (PQ)[4], Daniele D. Affonso (PG)[5], Ana Lucia T. G. Ruiz (PQ)[3], João E. Carvalho (PQ)[3], Carmen S. P. Lima (PQ)[5] and Pedro P. Corbi (PQ)[1] *

g266005@dac.unicamp.com.br; ppcorbi@unicamp.br

[1]Institute of Chemistry-UNICAMP; [2]Institute of Chemistry-UFU; [3]Faculty of Pharmaceutical Sciences-UNICAMP; [4]Institute of Inorganic Chemistry- University of Vienna; [5]Department of Anesthesiology, Oncology and Radiology-UNICAMP.

Keywords: 5-(Trifluoromethyl)uracil, 6-(Trifluoromethyl)uracil, Silver(I), Antiproliferative agents.

Highlights

- Silver(I) complexes with trifluoromethyluracil isomers are presented.
- The complexes inhibited the proliferation of squamous carcinoma cell lines *in vitro*.

Abstract

With a higher incidence among men, head and neck cancers represent the eighth most common type of cancer in Brazil [1]. Therapies include surgery, radiotherapy and chemotherapy. However, the intended effects of chemotherapy are limited by adverse effects, systemic toxicity, and drug resistance [2]. One strategy for developing new chemotherapeutic agents is the combination of the anti-proliferative activities of metals with bioactive ligands, such as nucleoside analogues [3]. The present work describes the preparation and the studies on the anti-proliferative activity of silver(I) complexes with 5 and 6-trifluoromethyluracil (Figure 1) against tongue squamous carcinoma cell lines.

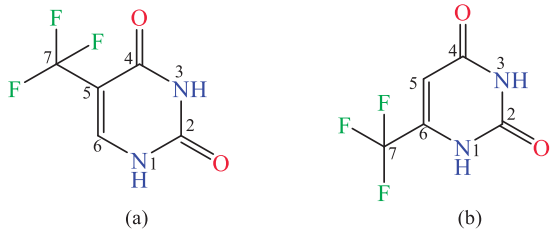


Figure 1. Structural formulas of (a) 5-(trifluoromethyl)uracil and (b) 6-(trifluoromethyl)uracil.

The silver complexes with 5-(trifluoromethyl)uracil (Ag-5TFMU) and 6-(trifluoromethyl)uracil (Ag-6TFMU) were prepared as recently described by our group [3,4]. The complexes were prepared by an equimolar reaction between either of the nucleosides and silver nitrate aqueous solutions at room temperature, and further collected by filtration and dried. Minimal formulas for Ag-5TFMU and Ag-6TFMU were determined as $AgC_5H_2F_3N_2O_2$ and $Ag_2C_5HF_3N_2O_2$, respectively, by elemental analysis. The anti-proliferative activity of the complexes were evaluated over tongue squamous carcinoma cell lines SCC-4 and SCC-15 and an immortalized human keratinocytes HaCaT (Table 1).

Table 1. Total growth inhibition values (TGI, μmol L^{-1}) for the complexes on cell growth of squamous carcinoma cell lines.

Cell lines	5FTMU	Ag-5TFMU	6TFMU	Ag-6TFMU	$AgNO_3$	5-FU	CisPt
SCC-4	>250	10.9 ± 3.4	>250	16.9 ± 1.8	39.4 ± 13.8	>250	202.4 ± 1.8
SCC-15	>250	26.0 ± 11.8	>250	20.2 ± 6.3	23.4 ± 9.5	>250	252.1 ± 45.1
HaCaT	>250	15.7 ± 5.5	>250	18.3 ± 7.6	68.0 ± 37.6	>250	71.8 ± 32.2

Both Ag-5TFMU and Ag-6TFMU showed a similar antiproliferative profile, with SCC-4 cells being slightly more sensitive than SCC-15 cells. Preliminary biophysical assays suggested that Ag-5TFMU can interact with DNA by intercalation, while a weak intercalation effect was observed for Ag-6TFMU.

References

[1] https://www.inca.gov.br/sites/ufu.sti.inca.local/files//media/document//estimativa-2023.pdf.
[2] MANIKKATH, J. et al. Nanomedicine, v.18, n. 27, p. 2061-2080, 2023.
[3] PEREIRA, G. M. et al. Journal of Fluorine Chemistry, v. 266, p. 110096, 2023.
[4] PEREIRA G. M. Preliminary *in vitro* antiproliferative assays over human tumor cells of a new silver(I) complex with 6-(trifluoromethyl)uracil. In: XIII Reunión Científica de Bioinorgánica BioGranada, Granada, Spain. June 5-7, 2023. Poster P-16.

Acknowledgments

The authors thank to CAPES, FAPESP (Grant #2021/10265-8, Cancer Theranostics Innovation Center, CancerThera), FAEPEX, FAPEMIG (APQ-01613–21), CNPq (Grant #309800/2021-8) and the FWF (ESPRIT74).

Área: INO

Kinetic Investigation of the Interaction between $[PdCl_2(C^2,N\text{-dmba})]_2$ and L-Cysteine

Maria Isabella Zachi Soares (PG),*[1] Wladimir Pereira Duarte Badaró (PG)[1] Adelino Vieira de Godoy Netto (PQ)[1],José Clayston Melo Pereira (PQ)[1].

zachi.soares@unesp.br

[1]São Paulo State University (UNESP), Department of Analytical, Physical-Chemical and Inorganic Chemistry, Institute of Chemistry, Araraquara, Brazil

Keywords: *complex, cancer, Palladium,L-cysteine, kinetic.*

Highlights

The promising activity of Palladium(II) compounds pose stability challenges. Investigation of interaction between L-cysteine and Palladium complexes aiming to enhance bioactivity with minimal side effects.

Abstract

Although cisplatin-based complexes have been the mainstay of chemotherapy for decades, their clinical application faces several challenges.[1] Toxicity, solubility, cytotoxicity, and resistance limit the effectiveness and use of these compounds.[1] To overcome these barriers, scientific research is dedicated to the development of new metal complexes with potential anticancer activity.[2] These new agents may present higher selectivity, lower toxicity, and better antitumor activity. Among them, Pd(II) complexes stand out, which according to the literature are more reactive and faster for ligand exchange when compared to Pt(II) complexes.[3] The lability of this complex can be an obstacle in the use of these complexes, since this can affect the activity of the complex.[4] For this, the use of chelating ligands is an alternative to reduce the lability of the complex without affecting its stability.[4] Although Pd(II) complexes containing chelating ligands are more stable than their analogs with monodentate ligands, they may not remain inert to attack by sulfur-donating molecules, such as L-cysteine or glutathione, the latter being found in high concentrations in the biological system.[5,6] These biomolecules tend to have a high affinity for Pt(II) complexes and Pd(II) complexes, which form metal-sulfur bonds before these compounds reach DNA or the target. Thus, the understanding of [Pd(dmba)]-type complexes in tumor cells has been studied in the last decade. [7,8] Therefore, the aim of this study is to investigate the reactions between sulfur-donating molecules and Pd(II) compounds and the relationship with their bioactivity. We hope that will contribute to the understanding of the activity of these complexes, such as their lability, release in biological medium and their relationship with resistance.To this end, we studied the kinetics between palladium complexes of the type $[PdCl_2(C^2,N\text{-dmba})]_2$ and the molecule L-cysteine using UV-Vis. The kinetic measurements were investigated by monitoring the changes in absorbance at a wavelength of 325nm. The observed pseudo-first order rate constants (k_{obs}) were determined from plots of $\ln(A_\infty - A_t)$ versus time. The specific rate constants, k_1 and k_{-1}, were calculated from $k_{obs} = k_1[Cys] + k_{-1}$, and the second-order specific rate constants were calculated according to the equilibrium equations for the respective reactions. The kinetics of the experiment followed the pseudo-first order method, which means that the L-cysteine present in the reaction medium was in excess, and the effective variation of [Cys] was small during the experiment. We identified that, since it is a binuclear complex, the reaction in DMSO occurs with the breaking of the complex forming a mononuclear complex and the coordination of DMSO $[Pd(C^2,N\text{-dmba})(DMSO)]$. The first step, with K_1= 8.2E-5 ± 1.9E-5 mol L^{-1} s^{-1}, is determined by the reaction of the complex with cysteine and the release of a Cl^-. The second step of the reaction occurs with the second cysteine coordinating to the intermediate complex $[Pd(C^2,N\text{-dmba})(DMSO)(cysteine)]$ replacing the DMSO ligand and forming the final complex $[Pd(C^2,N\text{-dmba})(Cysteine)_2]$. This last step has K_1=6.7E-5 ± 2.2E-6 mol L^{-1} s^{-1}.

Acknowledgments

I would like to thank CAPES, FAPESP and CNPq for funding the equipment. I would like to thank my research group (ChemCoBio) for their support and teachings throughout the realization of this work.

[1]. *Peng, K., Liang, B. B., Liu, W.*, & Mao, Z. W. (2021). Coordination Chemistry Reviews, 449, 214210.
[2]. Souza, M. L.; Roveda, A. C.; Pereira, J. C. M.; Franco, D. W.; Coord. Chem. Rev. 2016, 306, 615
[3]. Moro, A. C.; Mauro, A. E.; Godoy Netto, A. V.; Ananias, S. R.; Quilles, M. B.; Carlos, I. Z.; Pavan, F. R.; Leite, C. Q.; Hörner, M.; Eur. J. Med. Chem. 2009, 44, 4611
[5]. Pereira, J. C. M.; Souza, M. L.; Franco, D. W.; Eur. J. Inorg. Chem.2015, 2015, 1005.
[6]. Souza, W. A.; Ramos, L. M. S.; de Almeida, A. M.; Tezuka, D. Y.; Lopes, C. D.; Moreira, M. B.; Zanetti, R. D.; Godoy Netto, A. V.; Ferreira, F. B.; de Oliveira, R. J.; Guedes, G. P.; de Albergue, S.; Silva, J. R. L.; Pereira-Maia, E. C.; Resende, J. A. L. C.; de Almeida, M. V.; Guerrra, W.; J. Inorg. Biochem. 2022, 237, 111993. [Crossref]
[7]. Mukherjee, S.; Reddy, B. V. P.; Mitra, I.; Saha, R. N.; Bose, K. J. C.; Reddy, D. S.; Linert, W.; Moi, S. C.; RSC Adv. 2015, 5, 76987.]
[8]. Zanetti, R. D.; da Cunha, G. A.; Moreira, M. B.; Farias, R. L.; de Souza, R. F.; de Godoy, P. R. D. V.; Brassesco, M. S.; Rocha, F. V.; Lima, M. A.; Mauro, A. E.; Godoy Netto, A. V.; Polyhedron 2023, 229, 116.

Área: INO

(*E*) and (*Z*) isomers of a new nicotine-inspired *N*-acylhydrazone: synthesis, characterization, stability, log P and interactions with copper(II)

Alessandra Carvalho (PG),[1] Daphne S. Cukierman (PQ),[2] Nicolás A. Rey (PQ).[1]*

dcukierman.uerj@gmail.com; nicoarey@puc-rio.br

[1]*Departamento de Química, PUC-Rio;* [2]*Departamento de Química Geral e Inorgânica, UERJ*

Palavras Chave: *N-acylhydrazones, Copper(II), Aggregopathies, Isomers, Nicotinic acid hydrazide.*

Highlights

We report the (*E*) and (*Z*) isomers of a new nicotinic *N*-acylhydrazonic metallophore. (*E*)-X1NIC transforms into the (*Z*) isomer at high temperatures and is a stronger Cu^{2+} ligand with log K = 5.82 ± 0.16.

Resumo/Abstract

Type 2 diabetes *mellitus* (T2DM) can be considered an aggregopathy due to the pathological aggregation of the islet amyloid polypeptide (IAPP) that occurs in the extracellular space of islets.[1] Since the binding of copper(II) by IAPP leads to the formation of toxic oligomeric species,[2] we designed a new hydrazonic metallophore, with moderate affinity for this metal ion, with the ultimate goal of restoring metal homeostasis and disrupting abnormal metal-protein interactions. The ligand **X1NIC**, namely 1-methyl-1H-imidazole-2-carboxaldehyde nicotinoyl hydrazone, was designed based on the structure of nicotine, which has functional receptors in the pancreatic islets and beta cells,[3] with the goal of attaining greater bioavailability and a better pharmacokinetic profile. At first, a mixture of geometric stereoisomers was obtained during the synthesis, which directed the study to compare these isomers and how they both interact with copper(II). The next step was to prepare the isomers individually: **(*E*)-X1NIC** was synthesized in the presence of HCl, after 4 hours in reflux, and a hydrochloride was obtained. **(*Z*)-X1NIC**, on the other hand, was separated after 24 hours at reflux, in the absence of acid. Both compounds were structurally characterized by NMR, IR and MP. The octanol-water partition coefficient (log P) values were experimentally determined respectively as 0.62 ± 0.01 and 0.87 ± 0.02 for the (*E*) and the (*Z*) isomers. Both hydrazones are stable towards hydrolysis in buffered medium (pH = 7.4) at room temperature. However, a ^{1}H NMR study demonstrated the clear transformation of **(*E*)-X1NIC** into **(*Z*)-X1NIC** with increasing temperature. The same did not occur starting from the (*Z*) isomer, which confirms that this is the thermodynamic product. The apparent ligand-metal affinity was determined using the method of continuous variations through UV-Vis, with log *K* values of 5.82 ± 0.16 for the tridentate (*E*) isomer and 5.04 ± 0.04 for the bidentate (*Z*) isomer. A substoichiometric ^{1}H NMR experiment allowed the identification of the anchoring sites for each ligand. 1D ^{1}H and 2D ^{1}Hx^{1}H TOCSY NMR and cyclic voltammetry experiments will be the subject of a future report on the interactions of **(*E*)-X1NIC** and **(*Z*)-X1NIC** with the copper(II)-IAPP system.

References:
[1] Pilkington *et al.*, Scientific Reports, 2016, 6, 21274.
[2] Yu *et al.*, Chemical Communications, 2010, 46(37), 6909–6911.
[3] Yoshikawa *et al.*, Metabolism, 2005, 54(2), 247-254.

Agradecimentos/Acknowledgments

CAPES, CNPq and FAPERJ.

Área: INO

[^{68}Ga]Gallium radiolabeled ultrasmall paramagnetic nanoparticles as multimodal diagnostic imaging contrast.

Thomas V. Balzarini (IC),[1,2] Rodrigo K. Kawassaki (PQ),[2,3] Robson R. Guimarães(PQ),[2,4] Koiti Araki (PQ),[2] Fabio L.N. Marques (PQ),[1*]

thomas.balzarini@usp.br; fabio.marques@fm.usp.br

[1]Departamento de Radiologia e Oncologia (LIM 43), Faculdade de Medicina, USP; [2]Departamento de Química Fundamental, Instituto de Química, USP; [3]Departmento de Farmacologia, Instituto de Ciências Biomédicas, USP; [4]Spiron Tecnologia Ltda.

Keywords: *Radioisotope, Gallium-68; Nanoparticles, Radiolabeling, Diagnostic agent.*

Highlights

This work evaluated the radiolabeling of ultrasmall paramagnetic nanoparticles (UPN) with [^{68}Ga]Ga^{3+} to produce a novel nanomaterial to be applied as a potential PET/MRI bimodal diagnostic agent.

Abstract

Introduction: Imaging techniques are powerful tools for diagnosing diseases. Computed tomography (CT) and magnetic resonance (MR) are powerful techniques for anatomical images. In contrast, radioisotope imaging, such as positron emission tomography (PET), provides functional information about the cellular metabolism of a patient's tissues. The development of compounds that can be used for CT or MR contrast associated with radiation emitting radioisotopes can drastically improve diagnostics, simultaneously giving morphological and metabolic information. This work evaluated the radiolabeling of ultrasmall paramagnetic nanoparticles (UPN) with [^{68}Ga]Ga^{3+} to produce a novel nanomaterial to be applied as a potential PET/MRI bimodal diagnostic agent.

Material and methods: UPN was produced by a method previously reported by our group(1). [^{68}Ga]GaCl$_3$ was eluted from a ^{68}Ge/^{68}Ga generator, concentrated in a cation exchange resin (Strata® X-C) and reformulated in NaAcO 0.2 M pH 4 solution. The reaction conditions were evaluated in a solution containing 2 mg of UPN and 0.5 to 2 mCi of the radioisotope, under pH 4 and 7, temperature of 21 °C and 100 °C, and time of 10 and 30 min(2). The radiolabeling stability was assessed in citrate buffer, and the interaction with protein was checked by incubation with human serum albumin (HSA) at 37 °C. The results were analyzed using paper chromatography or TLC-SG, measured by autoradiographic image or in a gamma counter.

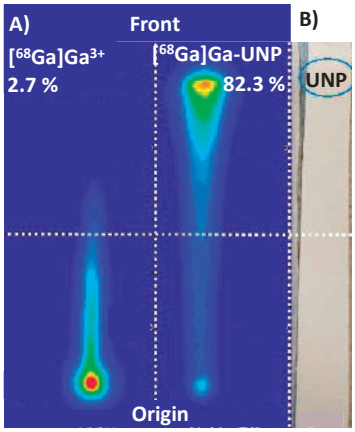


Figure 1. A) Radiochromatograms of the [^{68}Ga]Ga^{3+} and [^{68}Ga]Ga-UNP B) Chromatogram of the UNP

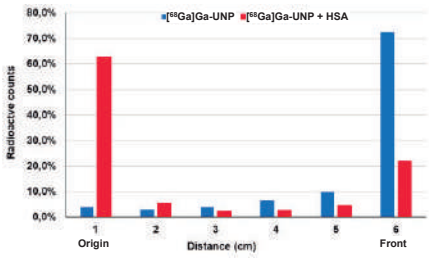


Figure 2. Radiochromatograms of the [^{68}Ga]Ga-UNP and [^{68}Ga]Ga-UNP + HSA

Results: The analysis demonstrated the migration of [^{68}Ga]Ga-UPN to the front of the chromatographic system (Figure 1), and the best radiolabeling condition was achieved at pH 4, 100 °C, and 30 min of incubation, given a radiochemical yield around 85 %. In the presence of HSA, both radioactive and chemical analyses demonstrated an interaction of HSA with UPN, moving the retention profile of the UPN from the front to the origin of the chromatographic systems. In addition, HSA exerts a protective effect against transchelation by citrate (Figura 2).

Conclusion: UPN can be adequately radiolabeled by direct interaction with the [^{68}Ga]Ga^{3+} ion, and the radiolabeled nanoparticles interact with albumin, in a form to be determined yet, promoting a protective effect against citrate transchelation.

1- Araki, K.; Guimarães, R.R.; *et al.* Nano Letters 2023 23 (12), 5497-5505
2- Karageorgou, M-A.; et al. Contrast Media Mol Imaging, Article ID 6951240, 13 pages (2017)

Acknowledgments

FAPESP (grants #2019/02151-2, #2018/21489-1, #2018/14375-0, #2018/13877-1), CNPq (442599/2019-6, 303137/2016-9, 401581/2016-0), CAPES (88881.465527/2019-01, 33002010191PO).

Área: INO

Luminescence spectroscopy to elucidate site selection of manganese in doped akermanite structure.

Juliana de Macedo Tavares (PG),[1] Alessandro B. S. Garcia (PG),[1] Ana M. Pires (PQ),[1,2] Airton G. Bispo Junior (PQ),[3] Marian Rosaly Davolos (PQ).[1]*

juliana.m.tavares@unesp.br; marian.davolos@unesp.br.

[1]São Paulo State University (Unesp), Institute of Chemistry, Araraquara; [2]São Paulo State University (Unesp), School of Technology and Sciences, Presidente Prudente; [3]University of Campinas (UNICAMP), Institute of Chemistry, Campinas.

Keywords: *$Ca_2MgSi_2O_7$, Manganese (II), XRD, Photoluminescence.*

Highlights

$Ca_2MgSi_2O_7$ doped with Mn^{2+} was synthesized by solid-state reaction. The product shows two emissions resulting from the activator substituting two different sites. Emission can be modulated depending on the concentration of Mn^{2+}.

Abstract

The host matrix, $Ca_2MgSi_2O_7$, a member of the melilite group, is tetragonal with space group $P\bar{4}2_1m$. It presents at ambient conditions five different sites: a tetrahedral site for Si^{4+}, another tetrahedral site for Mg^{2+}, and three non-equivalent sites for Ca^{2+} with coordination numbers between 6 and 8 when exhibits its incommensurate phase.[1,2] Because of its ionic radius, Mn^{2+} can only substitute for Mg^{2+} and Ca^{2+} sites (Table 1). The activator shows spin-forbidden *d-d* transitions, being the $^4T_1 \rightarrow {}^6A_1$ transition the dominant one in its emission when subjected to weak crystal field strength. The emitting $^4T_1$ level has its energy decreased as the strength of the crystal field increases. The Mn^{2+} doped compounds were synthesized through the solid-state reaction with $CaCO_3$, MgO, $MnCO_3$, and SiO_2. The mixture of the precursors was heated at 1350ºC for 8 hours. Mixing and heating twice under the same conditions showed a reduction of spurious phases in the final product. On the photoluminescence of the $Ca_2(Mg_{1-x}Mn_x)Si_2O_7$ compounds were observed two emission bands from two different sites and increasing the concentration of Mn^{2+} resulted in a more intense emission for the band with the greater wavelength (or from the stronger crystal field site) and a weaker intensity for the other one. The luminescence of the products with 2.5 at% shows only one band in the deep-red region (Figure 1). It is believed that the stronger crystal field is the antiprismatic Ca^{2+} site, and the weaker is the tetrahedral Mg^{2+} site or two non-equivalent Ca^{2+} sites. Comparing the X-ray diffraction profile of the synthesized products after the first heat treatment, spurious phases rich in calcium form less when considering that Mn^{2+} substitutes for Ca^{2+} than for Mg^{2+}, Figure 2. These results indicate that Mn^{2+}, contrary to the stated,[4] preferably occupies Ca^{2+} sites.

C.N.	Ionic Radius [3] / Å		Difference / %
	Host matrix	Mn^{2+}	
4	Si^{4+} | 0.26	0.66	153
4	Mg^{2+} | 0.57	0.66	15.8
6	Ca^{2+} | 1.00	0.83	17.0
7	Ca^{2+} | 1.06	0.90	15.1
8	Ca^{2+} | 1.12	0.96	14.3

Table 1 – difference in ionic radius of cations in $Ca_2MgSi_2O_7$ and Mn^{2+}

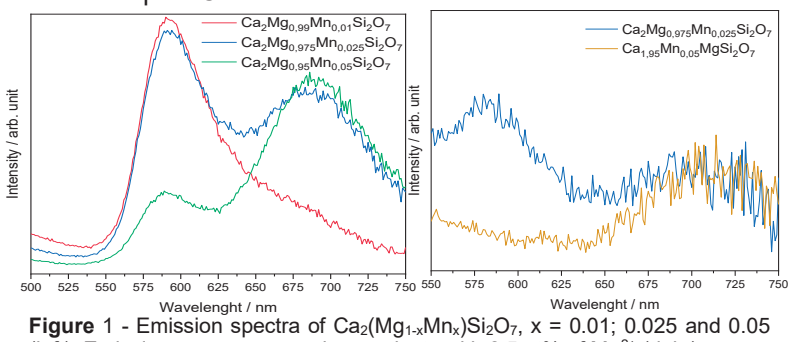


Figure 1 - Emission spectra of $Ca_2(Mg_{1-x}Mn_x)Si_2O_7$, x = 0.01; 0.025 and 0.05 (left). Emission spectra comparing products with 2.5 at% of Mn^{2+} (right).

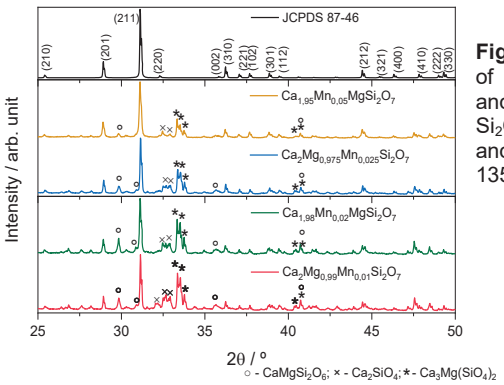


Figure 2 – XRD pattern of $Ca_2(Mg_{1-x}Mn_x)Si_2O_7$ and of $(Ca_{2-2x}Mn_{2x})MgSi_2O_7$, x = 0.01; 0.025 and 0.05, after 8h at 1350ºC.

Acknowledgments

CAPES (Proc. nº 88887.940705/2024-00), FAPESP (Proc. nº 2023/04576-6 e proc. nº 2020/02614-0), CNPq (Proc. nº 317610/2021-0)

References: [1] **Canadian Mineralogist**, v. 24, n. 3, p. 425-434, sep. 1986. [2] **American Mineralogist**, v. 94, p. 704-709, 2009. [3] **Acta Crystallographica Section A**, v. 32, n. 5, p. 751-767, Sep. 1976. [4] **Applied Physics Letters**, v. 90, n. 16, p. 161901, Apr. 2007.

Área: __INO__

Luminescent properties of n-(2-aminoethyl)-1,8-naphthalimide used as a chemosensor

Keryn H. V. Souza (PG),[1*] Izilda A. Bagatin (PQ).[1]

Keryn.hapul@unifesp.br

[1]*Instituto De Ciências Ambientais, Químicas E Farmacêuticas–ICAQF–UNIFESP–Diadema–SP*
Laboratório de Química de Calixarenos, Espectroscopia Molecular e Catálise - LQCEMC

Keywords: Naphthalimides, Sensor, Chemosensor, Luminescence

Highlights

Development of a chemosensor using naphthalimides.

The interaction of n-(2-aminoethyl)-1,8-naphthylimide with fluoride ions and benzene analysis.

Resumo/Abstract

Optical chemosensors are devices capable of transmitting a measurable signal when they come into contact with a particular analyte. These interactions can be analyzed using UV-Vis electronic spectroscopy, fluorescence spectroscopy, FTIR, and Raman [1]. Different molecules can be used for this purpose. In this study, we used naphthalimides, organic molecules that have luminescent properties, with efficient stability in their excited state, and which can have their properties altered by changing their organic substituent groups [2, 3].

Then, the naphthalimide molecule n-(2-aminoethyl)-1,8-naphthalimide was used as the chromophore ligand, which was synthesized using the reagents 1,8-naphthalic anhydride and ethylenediamine, resulting in a white solid. ^{1}H NMR (δ $CDCl_3$, 300 MHz), ppm: 8.64 ppm (dd, CH,^{3}J = 1.03 Hz), 8.25 (dd, CH,^{3}J = 1.03 Hz) and 7.78 (dd, CH,^{3}J = 7.83 Hz) showing the hydrogens of the conjugated rings, and at 4.31 (t, CH_2,^{3}J = 6.6 Hz), 3.09 (t, CH_2,^{3}J = 6.67Hz), 2.76 (s, NH_2). FTIR depicted the bands at ν(CH-Ar) 3051 cm^{-1}, ν(C=O) 1698 cm^{-1}, ν(CH-Ar) 783 cm^{-1}, ν(CH_2-N) 1491 cm^{-1}, ν(CH_2-Ass) 2922 cm^{-1}, ν(CH_2-Sim) 2850 cm^{-1}, ν(NH_2) 3309 cm^{-1}. The luminescence spectrum shows emission bands at λ_{em}345nm, with a preliminary quantum yield of 2.05%. The limit of detection (LOD) of the ligand concerning F^- is $7.6x10^{-5}$ mol dm^{-3}. The limit of detection (LOD) of the ligand about benzene is $1.58x10^{-4}$ mol dm^{-3}.

References:

[1]K. Kavallieratos, J. M. Rosenberg, W. Z. Chen, and T. Ren, J Am Chem Soc, vol. 127,no. 18, pp. 6514–6515, May 2005, doi: 10.1021/ja050296e.[2] S. Kagatikar, D. Sunil. J Mater Sci 57, 2022, 105–139.[3] I. A. Bagatin, A. T. Cruz, H. E. Toma, M. Politi, Journal of Inclusion Phenomena and Macrocyclic Chemistry 52(3-4), 2005. p.189. DOI:10.1007/s10847-004-6385-2

Agradecimentos/Acknowledgments

This work was carried out with the support of the Coordination for the Improvement of Higher Education Personnel – Brazil (CAPES) - Financing Code 001.

Área: INO

Mixed-sandwich organometallics as potential molecular spin qubits

Sarita Wisbeck (PG),[1] Andrea L. Sorrentino (PG),[3] Luana C. de Camargo (PG),[1] Ronny R. Ribeiro (PQ),[1] Francielli S. Santana (PQ),[1] Mario Chiesa (PQ),[2] Giulia Serrano (PQ),[3] Matteo Briganti (PQ),[3] Jaísa F. Soares (PQ),[1]* Roberta Sessoli (PQ).[3]*

jaisa.soares@ufpr.br; roberta.sessoli@unifi.it

[1]Departamento de Química, UFPR, Brazil; [2]Dipartimento di Chimica, Università di Torino, UNITO, Italia; [3] Dipartimento di Chimica, Università di Firenze, UNIFI, Italia

Keywords: *molecular qubits, organometallic, sandwich complexes, coherence time, ab-initio calculations, surface deposition*

Highlights

- Sublimable S=1/2 systems with remarkable spin coherence properties.
- Accessible d_{z^2} magnetic orbital for interaction with conductive substrates.
- Good candidates for acting as molecular qubits and quantum sensors.

Abstract

Quantum computing, the new computational frontier based on the quantum bit (qubit), is expected not only to improve on computational performance but to solve problems unsolvable with the current classical framework. An electron-spin-based qubit is a quantum-mechanical system of two states that can be brought into coherent superposition by pulses of electromagnetic radiation such as those employed in pulsed EPR. Our research group is interested in organometallic sandwich complexes as versatile molecular systems for magnetic molecule manipulation and spin detection experiments on metallic surfaces.[1] We have already demonstrated that the mixed-sandwich complex [CpTi^{III}(cot)], (η^8-cyclooctatetraene)(η^5-cyclopentadienyl)titanium, reaches a remarkable coherence time of 34 microseconds at 4.5 K.[2] We have also investigated the structural and chemical properties of a [CpTi(cot)] monolayer on Au(111) by experimental methods (STM and XPS) and computational protocols.[3]

Our current interest lies in additional S=1/2 organometallic molecules based on vanadium(IV) and titanium(III) such as [CpV^{IV}(cht)] (cht = cycloheptatrienyl), [V^{IV}(cot)$_2$] and [Flu^{III}Ti(cot)] (Flu = fluorenyl). In the latter (Figure 1), the higher molecular weight and larger pentahapto ligand led to *(i)* better control of deposition kinetics under ultrahigh vacuum, *(ii)* only one molecular orientation on Au(111), and *(iii)* preservation of the +III oxidation state, when compared to [CpTi(cot)]. Spin-lattice (T_1) and spin-spin (T_2) relaxation times we measured for [CpTi(cot)], [CpV(cht)], [V(cot)$_2$] and [FluTi(cot)] by pulsed EPR in toluene-d_8 are comparable, in the same concentration and temperature, to those reported for the record T_2 complex,[4] [V^{IV}(C$_8$S$_8$)$_3$]$^{2-}$, when the latter is dissolved in the same solvent. Such features make these sandwich compounds exciting models for studying electron spin relaxation and addressing individual magnetic molecules on surfaces.

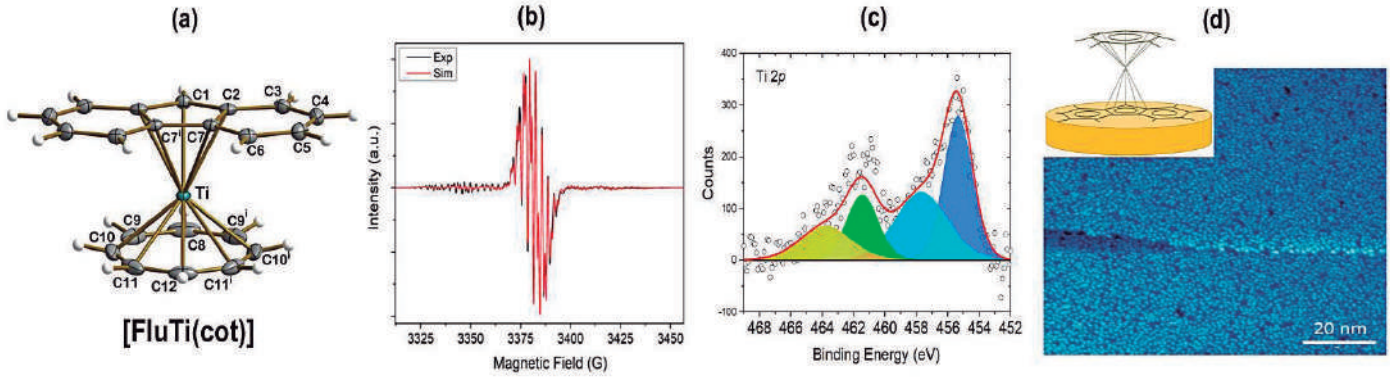


Figure 1. (a) The [FluTi(cot)] molecule; (b) CW-EPR spectrum in toluene solution, 298 K; (c) XPS core-level spectrum (Ti 2p region) of [FluTi(cot)] on Au(111); (d) STM image of a [FluTi(cot)]@Au layer, I_t = 10 pA, V_b= − 2.3 V.

Acknowledgments

UFPR, CNPq, PROEX and PrInt/Capes, Italian MIUR, Fondazione Cassa di Risparmio di Firenze, EU Commission.

[1] Czap, G. *et al. Science* 2019, **364**, 670; Verlhac, B. *et al. Science* 2019, **366**, 623; [2] Camargo, L. C. *et al. Angew. Chem. Int. Ed.* 2021, **60**, 2588; [3] Briganti, M. *et al. Nano Lett.* 2022, **22**, 8626; [4] Zadrozny, J. M. *et al. ACS Cent. Sci.* 2015, **1**, 488.

Área: INO

Modified electrodes containing hemicucurbit[6]uril for anion sensing

Débora M. Onusik (IC),[1] Renato S. Cicolani (PG),[1] Gregóire J. F. Demets (PQ).[1]

deboraonusik@usp.br; greg@usp.br.

[1]*Departamento de Química, FFCLRP-USP.*

Keywords: *hemicucurbit[6]uril, anion sensing, modified electrodes.*

Highlights

We have produced and characterized hemicucurbit[6]uril films on FTO and ITO electrodes. The morphology of the modified electrodes and their electrochemical behaviour were investigated, and we aim to apply those materials in anion sensing.

Abstract

Hemicucurbit[6]uril (hmCB[6]) is an urea-based macrocycle that forms stable caviplexes with anions. [1] The synthesis of hmCB[6] is quite simple: N,N'-ethyleneurea, formaldehyde and hydrochloric acid are mixed at room temperature and after 30 minutes the macrocycle is obtained as a white solid. [2] Since hmCB[6] is a non-expensive and easy-to-obtain compound, we decided to produce modified electrodes for anion sensing, especially fluorine in potable water. Atomic Force Microscopy (AFM) analyses showed that the film morphology depends on the electrode surface; the films on ITO were uneven with some fractures, while the one on FTO were quite regular. Zero-current galvanostatic measurements evidenced that hmCB[6] films were loosely adsorbed on both kinds of electrodes, since they were leashed away during the first 30 minutes analyses. The interactions between the macrocycles and the electrodes seems too weak. To overcome this issue, we have employed PVC as a binder, ensuring adhesion. The hmCB[6] films on FTO and ITO electrodes were obtained by dropping fixed amounts of a mixture containing tetrahydrofuran (THF), poly-vinyl chloride (PVC) and the macrocycle. This time, we produced stable films that are sensitive to the presence of the anion. Potentiometric measurements in H_2O/NH_4PF_6 0.1M show reversible potential drops during successive additions of F^- ions (10, 20, 30, 40, 50, 60, 70 and 100 µL/0.1M), indicating that the electrodes are sensitive to presence of the ion, and that this ion does not get stuck in the macrocycle's cavities, as expected for Cl^- for example. Reproducibility is still low and we believe that the sensing procedure could be enhanced by another electrochemical technique as square wave coulometry for example. These experiments are in progress at this moment.

[1] R. S. Cicolani and G. J. F. Demets. The bambus[n]uril family. Quim. Nova, 41(8):912–919, 2018.

[2] Y. Miyahara, K. Goto, M. Oka, and T. Inazu. Remarkably facile ring-size control in macrocyclization: Synthesis of hemicucurbit[6]uril and hemicucurbit[12]uril. Angew. Chem. Int. Ed. Engl., 43(38):5019–5022, 2004.

[3] G. J. F. Demets, B. V. S. Schneider, H. D. Correia, R.R. Goncalves, T.M. Nobre, and M.E.D. Zaniquelli. A technique to produce thin cucurbit[6]uril films. J. Nanosci. Nanotechnol., 8:432–435, 2008.

Acknowledgments

We acknowledge FAPESP grant number 2023/04770-7 and CNPq grant number 315063/2021-8.

Área: _____INO_____

Molecular modeling of [VO(L1–4)(R)] complexes (R = bipyridine, phenanthroline): DFT study of antioxidant activity, DNA binding and evaluation of electron-donating and -withdrawing substituent groups

Talis U. Silva (PQ),[1*] Everton T. Silva (PQ),[2] Camilo H. S. Lima (PQ),[1] Sérgio P. Machado (PQ).[1]

talisus2506@gmail.com; sergiopm@iq.ufrj.br

[1]*Instituto de Química, UFRJ;* [2]*Instituto Federal do Rio de Janeiro (Campus Duque de Caxias)*

Keywords: *DFT, Vanadium complexes, Molecular orbitals, Antioxidant activity, DNA interactions.*

Highlights

- DFT calculations of [VO(L^{1-4})(R)] complexes.
- L correlated to antioxidant activity and R to DNA binding.
- An electron-donation substituent in L^2 should increase both properties in C5-6.

Abstract

A density functional theory (DFT) study of eight oxovanadium complexes (C1–4,[1] C5–6,[2] and C7–8,[3] **Fig. 1**) [VO($L^{1–4}$)(R)] (R = bipyridine, phenanthroline; $L^{1–4}$ = ligands derived from dithiocarbamate) was done.

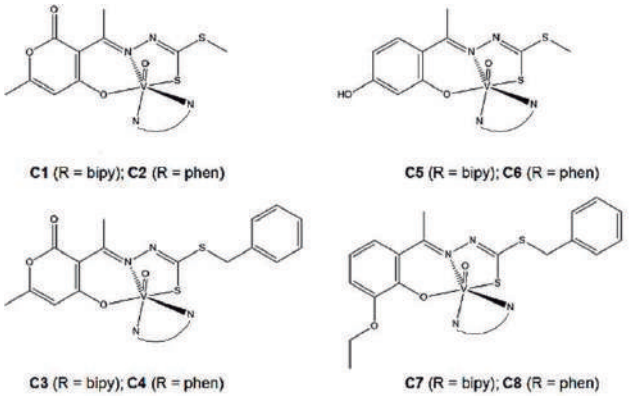


Fig 1. The general structure of the complexes

The molecular orbital analysis of the complexes (**Table 1**) revealed that the contribution of L in the SOMO correlated with the experimental antioxidant activity (IC_{50}), and the contribution of R in the LUMO correlated with the experimental complex-DNA interaction ($K_{b\ DNA}$). Adding an electron-donating substituent group (such as $–NH_2$) in the C5–6 structures should enhance these complexes' antioxidant and DNA interaction activities.

Table 1. Contribution of VO, L, and R fragments (bipy/phen) in molecular frontier orbitals (SOMO and LUMO) compared with experimental antioxidant activity (IC_{50})[1] and DNA binding ($K_{b\ DNA}$)[1-3].

	Ref.	$\%L_{SOMO}$	IC_{50} (μM)	$\%R_{LUMO}$	$K_{b\ DNA}$ (M^{-1})
C1	1	78.237	47	58.324	8.16×10^4
C2		75.954	60	59.008	1.20×10^4
C3		82.017	40	56.759	2.29×10^4
C4		77.431	59	57.964	5.47×10^4
C5	2	76.329	–	70.157	4.31×10^5
C6		75.213	–	69.646	4.96×10^5
C7	3	79.386	–	46.371	7.12×10^4
C8		80.198	–	46.631	6.5×10^4

References

[1] Sarhan et al. Appl. Organomet. Chem., 33 (2) (2019), doi: 10.1002/aoc.4655.

[2] El-Afify et al. Appl. Organomet. Chem., 35 (2) (2021), doi: 10.1002/aoc.6082.

[3] G. Sahu, et al. J. Inorg. Biochem., 233 (2022), doi: 10.1016/j.jinorgbio.2022.111844.

Acknowledgments

The authors are grateful to Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES); to Fundação Carlos Chagas Filho de Amparo à Pesquisa do Estado do Rio de Janeiro (FAPERJ) and Conselho Nacional de Desenvolvimento Científico (CNPq).

Área: INO

Nanocrystalline niobium oxide obtained via microwave promising for application in photocatalysis

Iury Horran Pereira Castro (IC),[1] Maikon Rangel Alves Alexandre (IC),[1] Osvaldo Previato Neto (IC),[1] Cleiton Policarpo Martins (PG),[1] Osmando Ferreira Lopes (PQ),[1] Renata Cristina de Lima (PQ)[1*]

castro.iury@ufu.br; rclima@ufu.br

[1]*Instituto de Química, Universidade Federal de Uberlândia (UFU).*

Keywords: *Niobium oxide, Nanoparticles, Semiconductor, Photocatalytic properties.*

Highlights

- The effect of synthesis conditions on the structure of $Nb2O_5$.
- Development of photocatalysts for hydrogen production.
- Niobium oxide as a potential in the photodegradation of pollutants.

Resumo/Abstract

Niobium Oxide (Nb_2O_5) is a semiconductor with a band gap energy of 3.4 eV, with high stability and which has a wide range of technological applications, such as in solar cells, batteries and photodegradation of organic pollutants.[1] Furthermore, this oxide has been evaluated as a catalyst for the water-splitting process, presenting promising results for the production of Hydrogen, which contributes to obtaining alternative and sustainable sources of fuel for energy generation.[2] The photocatalytic capacity of Nb_2O_5 is dependent on the oxide structure, which is a direct consequence of the heat treatment that the starting material is subjected to obtain the final product. In conventional synthesis methods, temperatures above 1000 ºC are necessary to obtain the material in the desired crystalline phase, while via microwave heating it is possible to control the size, morphology and crystallinity of the particles from low synthesis temperatures.[3] The growth in global energy demand in recent years, together with industrial and urban pollutant emissions, has emerged as one of the most latent problems for humanity as a species in the future. With this in mind, it is necessary to study the production of materials capable of reducing such threats, assisting in the production of alternative fuels for energy generation and pollutant degradation. In this work, Nb_2O_5 materials were prepared using microwave-assisted hydrothermal method providing a low energy demand to obtain the samples. Niobium ammoniacal oxalate ($NH_4[NbO(C_2O_4)_2(H_2O)].nH_2O$) and hydrogen peroxide (H_2O_2) were used as precursors and the synthesis was carried out at a constant temperature of 140 ºC for 32 minutes. Both Nb_2O_5 samples obtained, the as-prepared material and the washed material with distilled water and ethanol, were characterized by X-ray diffraction (XRD), Raman spectroscopy and field emission gun-scanning electron microscopy (FEG-SEM). The X-ray diffractograms of both materials confirmed the formation of the crystalline niobium oxide of interest in its orthorhombic structure according to the Joint Committee on Powder Diffraction Standards (JCPDS 27-1003). Raman spectra showed the characteristic Nb−O peaks related to orthorhombic structure as observed by DRX. FEG-SEM images revealed the nanoparticles formation with an average size of 50 nm. The Nb_2O_5 samples showed improved results in the photocatalytic degradation of organic toxic pollutants when compared to the oxide obtained via conventional hydrothermal method. Experiments to evaluate the performance of these materials for the production of hydrogen gas and degradation of pollutants via photochemistry are being investigated.

[1]Mohan, H. *et al.* PdS Coupled Nb_2O_5 superstructure for photocatalytic overall water splitting. *ChemCatChem* 15, 202201212, 2023.

[2]Asencios, Y. J. O. *et al.* Photodegradation of organic pollutants in seawater and hydrogen production via methanol photoreforming with hydrated niobium pentoxide catalysts. *Sustainable Chemistry* 3, 172, 2022.

[3]Ücker, C. L. *et al.* Photocatalytic degradation of rhodamine B using Nb_2O_5 synthesized with different niobium precursors: factorial design of experiments. *Ceramics International* 47, 20570, 2021.

Agradecimentos/Acknowledgments

The authors are grateful to Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES), Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq, grant #310290/2020-1) and Fundação de Amparo à Pesquisa do Estado de Minas Gerais (FAPEMIG, grant #APQ-01661-22) for the financial support.

New Silver(I) Complex Based on Thiocarbamoyl-naphthylpyrazoline-1,3,5-Trisubstituted Ligand.

Gleison A. Casagrande (PQ),[1] Natali L. Faganello (PG),[1] João P. C. Nascimento (PG),[1] Yasmin L. Santos (IC),[2] Clara A. Da Silva (IC),[2] Lucas Pizzuti (PQ),[2] Davi F. *Back (PQ).*[3]

gleison.casagrande@ufms.br

[1]Department of Chemistry, UFMS; [2]Department of Chemistry, UFGD,[3] Department of Chemistry, UFSM.

Keywords: Pyrazoline, spectroscopy, crystal structure.

Highlights

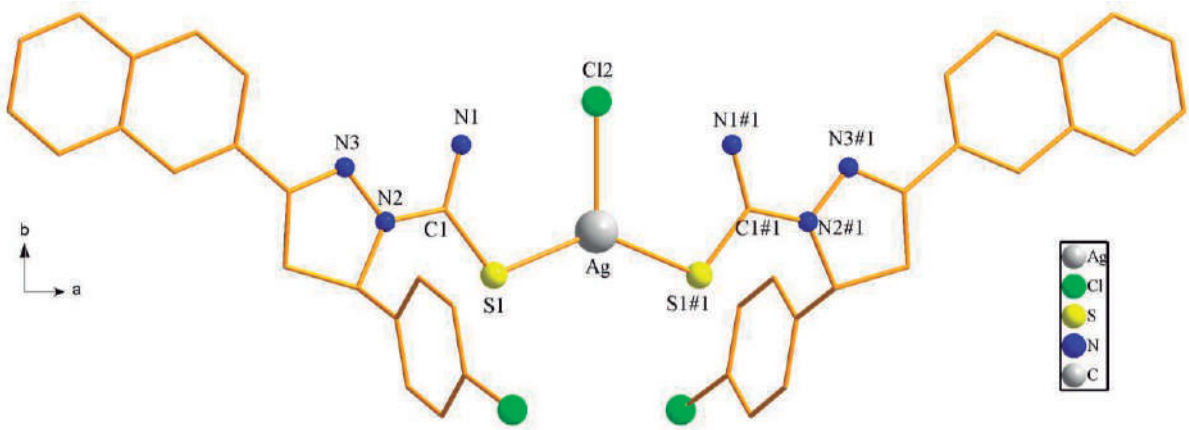
A new Ag^{I} complex was synthesized and characterized. X-ray studies revealed an approximately trigonal geometry around the Ag^{I} atom. Complete characterization also involved IR, UV-Vis and NMR spectroscopic analyses.

Resumo/Abstract

Pyrazoline compounds have been presented with broad pharmacological potential as anticancer, antitumor, and antioxidant activities. The metalation of biologically active ligands is a strategy to enhance their biological activities and broaden their applications in other areas such as materials chemistry and medicinal chemistry. Thus, the synthesis and characterization of new silver(I) complex with pyrazoline ligand is the focus of this work.

X-ray diffraction studies revealed (Figure 1) a molecular structure of silver (I) as a complex belonging to the monoclinic system and space group C12/c1, with two molecules of the pyrazolinic ligand coordinated in a monodentate way through the atom of sulfur to the metallic center of silver (I) which completes its sphere of coordination with a chlorine atom of the silver chloride salt. Analysis of the bond angles S(1)-Ag-S(1)#1 138.64(5) and S(1)-Ag-Cl(2) 110.68(2) show an approximately trigonal geometry for the complex.

Figure 1. Projection of the asymmetric unit of the complex. For clarity, the hydrogen atoms, DMSO solvate, have been omitted.



The infrared vibrational spectroscopy data obtained for the complex shows the main bands found in the free ligand. The section attributed to the thiocarbonyl group (v(C=S)) that appears in the region of 1388 cm^{-1} in the free ligand was shifted to a lower wave number of 1341 cm^{-1} in the complex, which may be related to coordination via the atom of sulfur to the silver metallic center (I).

The study of molecular absorption in the UV-Vis region shows similarity in the spectra of the ligand and the complex. After coordination, a hyperchromic effect is observed in the spectrum of the complex. The main absorption band observed in the complex spectrum is attributed to LMCT-type electronic transitions.

The 13C NMR data of the complex when compared to the ligand show a smaller chemical shift in the signal corresponding to the thiocarbonyl carbon atom (C=S), indicating greater shielding of this atom. It is suggested that this behavior may be related to the coordination of the ligand to the silver metal center (I). The silver (I) complex has been used in anticancer biological assays. the silver compound proved to be the most active in the three tumor lines, with IC50 in the order of 2 μM. Much more active than the free ligand, which presented an IC50 against the MDA-MB-231 strain of around 39μM and 4T1 8μM. The complex synthesized in this work demonstrated good results in luminescence analyses, making it possible to be used in future bioimaging analyses.

Agradecimentos/Acknowledgments

We thank the Chemistry Institute at UFMS, CAPES, and CNPQ.
We also thank FUNDECT/MS - Grant: 30/2022, SIAFEM: 32268, Process: 71/033.044/2022.

Área: INO

Nitrosyl ruthenium-based X-ray photoactivated compounds: A combination of PDT, chemotherapy and radiotherapy

Beatriz Correia Petry (IC), Juliana Cristina Biazzotto (PQ), Roberto Santana da Silva (PQ)*

beatrizcorreia@usp.br; silva@usp.br

Biomolecular Sciences Department, FCFRP.

Keywords: *Nitrosyl ruthenium, X-ray, PDT, Chemotherapy, Radiotherapy.*

Highlights

Ruthenium compounds as agents to expand the frontiers of the use of light radiation to treat cancer.

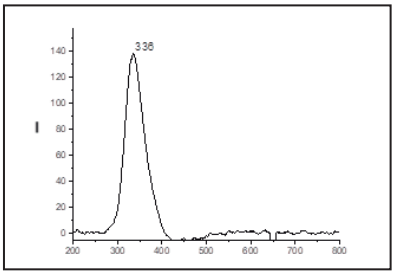
Resumo/Abstract

Photodynamic therapy (PDT) is a clinical process involving the use of sensitizer, oxygen and light irradiation. Unfortunately, there are limitations for the use of light irradiation in therapy. Furthermore, many therapies, such as radiotherapy, have a low penetration capacity into human tissue when compared to other types of ionizing radiation. To address this issue, we have been developing X-ray induced photodynamic therapy (X-PDT) using metal-based compounds. Essentially, strong luminescence of compounds activated by X-ray as an energy source may induce energy transfer process to a receptor producing cytotoxic molecules. In addition to breaking the shallow tissue penetration dogma, our studies aim to expand the use of combination therapy (X-PDT) for cancer treatment. As primer goals of this process, we have synthesized compounds, which show strong luminescence by X-ray excitation (Table 1).

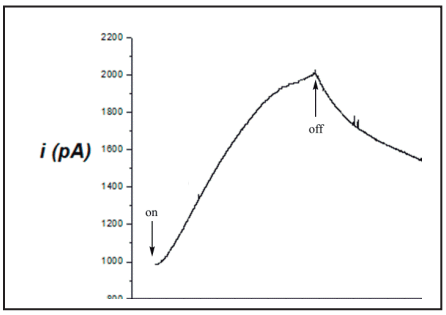
Table1: Emission under excitation with light and X-ray.

Compound	Fluorescence λ_{em} (nm)	Radioemission λ_{em} (nm)
$CuI(PPh_3)_3$	546	512
$CuCN(PPh_3)_3$	475	505
$CuI(3\text{-picoline})(PPh_3)_2$	468	493
$CuSCN(4\text{-picoline})(PPh_3)_2$	485	504
Sylgard	336	339

Figure 1: Emission after X-ray excitation of Sylgard polymer.



The X-ray energy transfer process is observed in one of the experiment where a polymer containing copper complex was mixed with $[Ru(bpy)_2Cl(NO)](PF_6)_2$,which release nitric oxide (NO) in very large amount when submitted to X-ray irradiation (Scheme 1; Figure 2).



X-

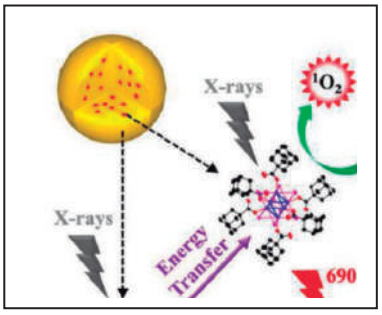


Figure 2: A) NO measurement during ray excitation of sylgard polymer embedded with nitrosyl ruthenium complex. B) Scheme 1: Energy transfer induced by X-ray excitation.

Therefore, given the ability of nitric oxide to be an active biological agent and induce the phenomenon of apoptosis (programmed cell death), a compound containing this molecule in its structure will be evaluated in its capacity of induce cytotoxicity in cancer cells by X-ray excitation. From this perspective, X-PDT can be viewed as a unique radiosensitizing method that can act synergistically with radiotherapy.

Agradecimentos/Acknowledgments

FAPESP, CAPES and CNPq.

Área: INO

Novel di- and polynuclear lanthanide ion compounds containing 2-acyl-1,3-indandionate ligands as luminescence sensitizers

Adrihellen L. Gouveia (IC),[1] Ashely A. S. S. de Jesus (IC),[1] Ercules E.S. Teotonio (PQ),[1] Joaldo G. Arruda (PG),[1] Paulo R.S. Santos (PG).[1] Israel F. Costa (PQ),[2] Wagner M. Faustino (PQ),[1] Maria Claudia F. C. Felinto (PQ),[3] Ercules E.S. Teotonio (PQ),[1] Hermi F. Brito (PQ)[2]

adrihellen.lopes@academico.ufpb.br

[1]Departament of Chemistry, Federal University of Paraiba; João Pessoa-PB, Brazil; [2]Institute of Chemistry, University of São Paulo (USP), São Paulo–SP, Brazil; [3]Nuclear and Energy Research Institute–IPEN/CNEN, São Paulo–SP, Brazil

Key words: *Trivalent europium, luminescence, indandionates.*

Highlights

Novel classes of Eu3+ -indandionate complexes with the ligand 1,2-bis(diphenylphosphine)ethane oxide (dppeO2) were synthesized and their luminescent properties investigated.

Resumo/Abstract

This present work reports the synthesis, characterization and study of the luminescent properties of Eu^{3+} ion compounds containing ligands derived from 2-acetyl-1,3-indandionate, such as 2-benzoyl-1,3-indandionate (bind), 2 -(4-methylphenyl)-1,3-indandionate (mbind) and 2-isovaleryl-1,3-indandionate (isovind), in which the ligand 1,2-bis(diphenylphosphine)ethane oxide ($dppeO_2$) acts as a bridging ligand. The complexes were synthesized by the direct reaction in ethanolic solution of the precursor compounds [Ln(indadionate)$_3$(H_2O)$_2$] and the $dppeO_2$ ligand. The obtained materials were characterized using absorption spectroscopy in the infrared region and thermogravimetric analysis (TGA) techniques. The absorption spectra of the complexes suggested that the coordination of the indandionate and bis(diphenylphosphinoxides) ligands occurs through the oxygen atoms of the C=O and P=O groups, respectively (Figure 1a). Thermal analysis data (TGA/DTA) indicate that the synthesized compounds present high thermal stabilities up to approximately 350°C, indicating the absence of water molecules coordinated to the metal ion(Figure 1b). The spectroscopic properties of the complexes were investigated from emission spectral data recorded at room temperature. When compared to the precursor complexes, the complexes containing the $dppeO_2$ ligand exhibit high emission intensities in the red region, corroborating the thermal analysis data for the replacement of water molecules by the neutral ligand. These data suggest that the prepared materials have great potential to act as light-converting molecular systems.

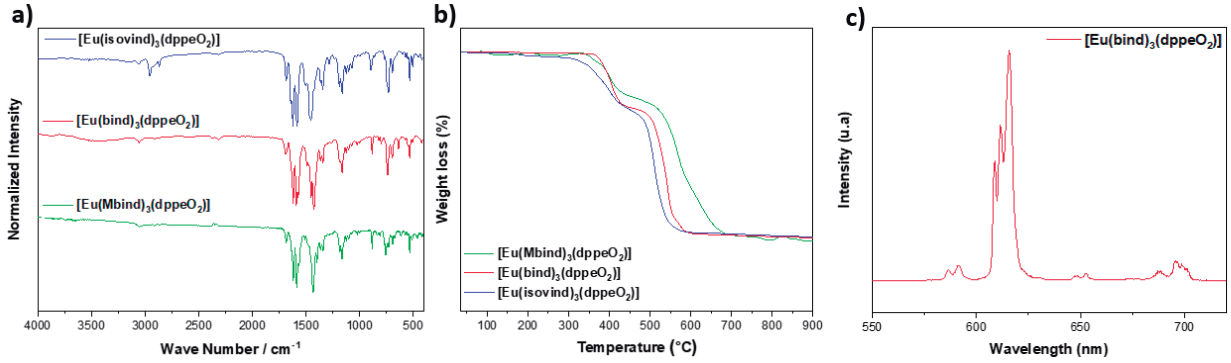


Figure 1 (a) Absorption spectra in the infrared region of the complexes. (b) TG curves of compounds recorded in synthetic air atmosphere (c) Complex emission spectra. The emission spectrum of the [Eu(bind)$_3$($dppeO_2$)] is presented as representative one.

Acknowledgments

This work was supported by CNPq, FAPESP, FINEP, CAPES and UFPB

[1] FUKUDA, Y. *et al.* (2002) *J. Chem. Soc., Dalton Trans*, pp. 527–533.
[2] Miranda, Y. C. *et al.* (2015) *European Journal of Inorganic Chemistry*, 2015(18), pp. 3019–3027.

Área: INO

Novel lanthanide complexes as platform for ligand-to-metal charge transfer of low energies

Ashley A. S. S. Jesus (IC),[1]* Adrihellen L. Gouveia (IC),[1] Paulo R. S. Santos (PG),[1] Joaldo G. Arruda (PG),[1] Israel F. Costa (PQ),[2] Wagner M. Faustino (PQ),[1] Maria Claudia F. C. Felinto (PQ),[3] Ercules E.S. Teotonio (PQ),[1] Hermi F. Brito (PQ)[2]

ashleypb12@gmail.com

[1]Department of Chemistry, Federal University of Paraíba, João Pessoa–PB, Brazil; [2]Institute of Chemistry, University of São Paulo (USP), São Paulo–SP, Brazil; [3]Nuclear and Energy Research Institute–IPEN/CNEN, São Paulo–SP, Brazil

Keywords: Lanthanides, β-diketone, Terpyridine, Luminescence, Charge transfer.

Highlights

Synthesis, characterization and investigation of the luminescence quenching processes via ligand-to-metal charge transfer in lanthanide ion coordination compounds.

Abstract

Coordination compounds of trivalent lanthanide ions (Ln^{3+}) are an important field of research due to their unique spectroscopic properties. Generally, these compounds exhibit high emission intensities with characteristic colors, reflecting the energy structure of the lanthanide ion when it is coordinated by luminescence-sensitizing ligands. However, the presence of non-radiative channels such as multiphonon relaxation and low-energy ligand-to-metal charge transfer (LMCT) states can contribute to the luminescence quenching processes. Despite advances in the investigation of the nature of LMCT states, the main structural factors that contribute to these deactivating processes are not well understood in the literature yet. In this context, the present work reports the synthesis, characterization and studies of the luminescent properties of new trivalent lanthanide ion compounds (Ln^{3+}: Eu^{3+} and Gd^{3+}) containing 2,2′,6′,2″-terpyridine (terpy) and β-dicetonate ligands, where β-dic: acethylacetonate (acac), dibenzoylmethanate (dpm) and benzoylacetonate (bzac), presenting the [Ln(β-dic)$(NO_3)_2$(terpy)] general formula. Particularly, this study is focused on a class of compounds that present LMCT states of low energies. The synthesized complexes were characterized using infrared absorption spectroscopy (FT-IR), thermogravimetric analysis (TGA), diffuse reflectance and luminescence spectroscopy techniques. The characterization data for [Ln(dpm)$(NO_3)_2$(terpy)] are presented as representative ones (Figures 1a and 1b). The FT-IR spectrum of this complex suggests that ligands are coordinated to the metal ion via oxygen atoms. Interestingly, the diffuse reflectance spectrum for the [Eu(dpm)$(NO_3)_2$(terpy)] complex (Figure 1b) shows a broad band in the longer wavelength spectral region that may be assigned to a ligand-LMCT state. Similar behavior has been observed for analogous complexes with different diketonate ligands. This finding suggests that the luminescence quenching via LMCT state is quite efficient in these compounds. Consequently, all investigated complexes exhibited very low luminescence intensities, which make them good candidates for further understanding the role of the LMCT state in lanthanide ion compounds.

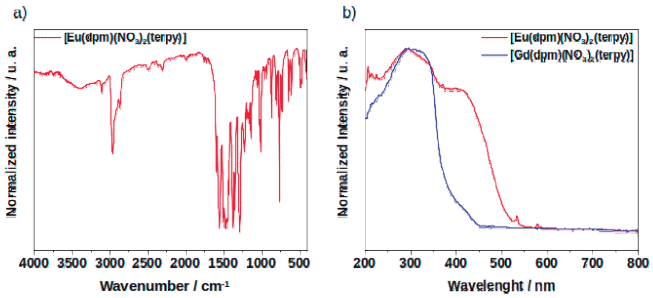


Figure 1. (a) Absorption spectra in the infrared region (b) Reflectance spectra of the complexes in the solid state.

Acknowledgments

This work was supported by CNPq, FAPESP, FINEP, CAPES and UFPB

[1] FUKUDA, Y. *et al*. (2002) *J. Chem. Soc., Dalton Trans*, pp. 527–533.
[2] MIRANDA, Y. C. *et al*. (2015) *European Journal of Inorganic Chemistry*, 2015(18), pp. 3019–3027.

Área: INO

Novel silver(I) complexes of 3-(aminomethyl)-2-hydroxy-1,4-naphthoquinone Mannich bases: synthesis and characterization

Vinícius Alkay Targino dos Reis Bispo (IC),[1] Gustavo Bezerra da Silva (PQ).[1]*

gusbezerra@ufrrj.br

[1]*Instituto de Química, Universidade Federal Rural do Rio de Janeiro (UFRRJ), BR-465, Km 7 – Seropédica, RJ, CEP 23897-000.*

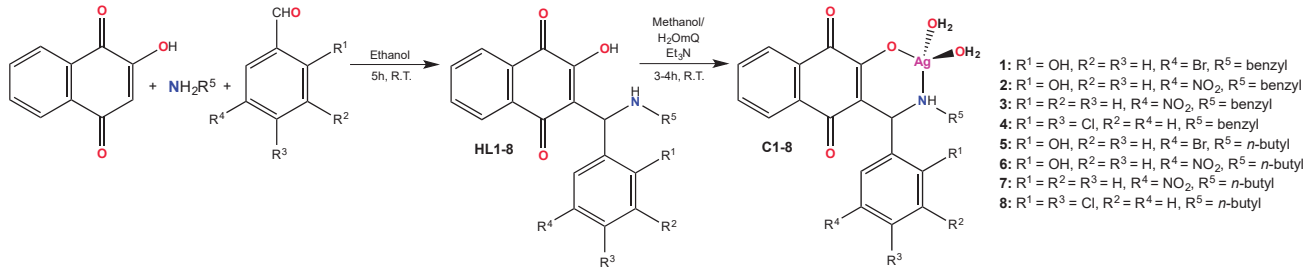
Keywords: *Naphthoquinone, Silver(I) complexes, Mannich bases.*

Highlights

Synthesis and characterization of silver(I) complexes of 3-(aminomethyl)-2-hydroxy-1,4-naphthoquione derivatives with well-known pharmacological potential.

Resumo/Abstract

To the best of our knowledge, silver(I) complexes are widely known by their bactericide and cytotoxic activities.[1] A judicious strategy to improve their biological activity is the molecular hybridization. In this scope, the complexation of 3-(aminomethyl)-2-hydroxy-1,4-naphthoquinone Mannich bases to silver(I) is promising due to their wide range of pharmacological potential.[2,3] Therefore, this work aimed the synthesis and characterization of novel silver(I) complexes (**C1-8**) with naphthoquinone Mannich bases (**HL1-8**, Scheme 1).



Scheme 1. *Naphthoquinone Mannich bases* **HL1-8** *and their silver(I) complexes* **C1-8**.

A series of Mannich bases of 3-((*R*^{1}-*R*^{4}-phenyl)(*R*^{5}-amino)methyl)-2-hydroxy-1,4-naphthoquinone was synthesized upon condensation reaction of 2-hydroxy-1,4-naphthoquinone and their respective *R*^{1}-*R*^{4}-benzaldehydes and *R*^{5}-amines, at room temperature. Products were obtained as orange solids, without further purification (yields: 80-95%).[3] Finally, the complexation reactions were investigated in a proportion 1:1 of ligands **HL1-8** and silver(I) nitrate in the presence of trimethylamine in order to deprotonate the 2-hydroxynaphthoquinonic ring. The complexes **C1-8** were obtained as reddish-orange solids (yields: 50-85%). All compounds were characterized by analytical (m.p. and elemental analysis) and spectroscopic (IR, ^{1}H NMR and ^{1}H X ^{1}H COSY) methods. IR data have shown that νN–H of naphthoquinones in complexes were clearly observed at ν = 3200-3100 cm^{-1}, while in ligands, these bands were not observed, possibly due to the broad band of νO–H. ^{1}H NMR spectra data have also shown the expected peaks for ligands, although a slight shift of the peaks were observed in complexes. Also, an appearance of a peak at δ = 5,70-5,50 ppm was attributed to the hydrogen of amine, upon coordination.

In summary, eight novel 3-(aminomethyl)-2-hydroxy-1,4-naphthoquinone silver(I)-based complexes were obtained. The proposed structures are [Ag(**L1-8**)(solvents)$_2$], in which ligands coordinate through deprotonated naphthoquinone and amine moieties to silver(I). Fully characterization and pharmacological assays are underway.

[1] Condé, C. A. S. R. et al *J. Inorg. Biochem.* **2023**, 246, 112303. [2] Olyaei, A. et al *RSC Adv.* **2020**, 10, 30265. [3] da Silva, G. B. et al *Bioorg. Med. Chem. Lett.* **2016**, 26, 3537.

Agradecimentos/Acknowledgments

Central Analítica at PPGQ-UFRRJ and Prof. Maurício Lanznaster (GQI-UFF) for donations of reagents/solvents.

Área: INO

One-pot sequential reaction for CO_2 fixation catalyzed by metalloporphyrin-layered hydroxide salt solid

Everton Henrique dos Santos (PG), Adriana Duarte Dalla Costa (IC), Eduardo Mariano Iwaya (PG), Shirley Nakagaki (PQ)

everhs1@gmail.com; shirleyn@ufpr.br

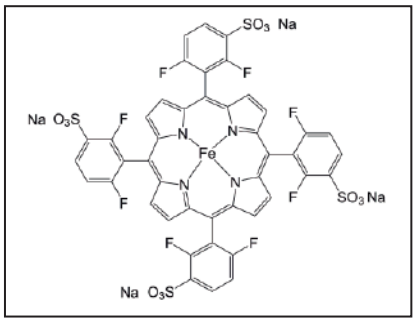
Laboratório de Bioinorgânica e Catálise, - Departamento de Química - Universidade Federal do Paraná, - CP 19032, fax: +55-41-33613186, CEP 81531-980, Curitiba, PR, Brasil.

Palavras Chave: Metalloporphyrin, Heterogeneous Catalysis, Sequential Reaction, CO_2 fixation, Layered Solids.

Highlights

Investigation of a layered hydroxide salt containing metalloporphyrin as a multifunctional catalyst for CO_2 cyclic addition reaction to an olefin.

Resumo/Abstract



To achieve the sustainable development goals (SDG), proposed as an alternative to overcome global warming concerns and to provide better conditions for future generations, it is necessary to propose different mechanisms aiming for more efficient routes to obtain the essential chemical products, and catalysis plays a key role on it [1]. For instance, systems based on metalloporphyrin (MP) as catalysts are usually reported as efficient and highly selective towards a scope of reactions [2]. Nevertheless, such reactions commonly take place in homogeneous single chemical reactions. Therefore, to improve the MPs' robustness and usability, giving the catalyst more possible reuse cycles, heterogeneous MP-based solids are proposed since the observed issues in homogeneous reactions are avoided [3], bringing up protection against bimolecular reactions and easy catalyst recovery. Besides, the preparation of catalytic solids based on MPs and different supports can also create new properties to the resulted catalyst *e.g.* acid and base catalytic sites, making them potential multifunctional catalysts, turning interesting their investigation in various and even in sequential reactions involving different mechanisms [4]. Here, we report the preparation and investigation of a multifunctional catalyst based on zinc hydroxide nitrate salt containing the MP **[Fe(TDFSPP)]** (Figure) immobilized over its surface in a promising one-pot sequential auto Tandem reaction of styrene epoxidation followed by carbonic gas C-C cross-coupling reaction with styrene oxide leading to impressive conversion values for the desired cyclic carbonate, under mild conditions of temperature and pressure. The prepared catalytic solid was characterized using powder XRD, TEM, FTIR, SEM, ICP-OES, and TGA techniques. The reactions when analyzed using gas chromatography and 1H NMR indicated conversion results up to 35% for the optimized condition.

[1] P.T. Anastas, J.C. Warner, Green Chemistry: Theory and Practice, 1st ed. Oxford University Press, Oxford, England, 1998.
[2] D. Dolphin, T.G. Traylor, L.Y. Xie, Acc. Chem. Res. 30 (1997) 251.
[3] G.S. Machado, G.G.C. Arízaga, F. Wypych, S. Nakagaki, J. Catal. 274 (2010) 130-141.
[4] E. H. Santos, C. Carvalho, C. M. Terzi, S. Nakagaki, Molecules, 23 (2018) 2796.

Agradecimentos/Acknowledgments

UFPR CME UFPR CAPES CNPq FUNDAÇÃO ARAUCÁRIA CIMOL

Área: INO

Oxidação do etilbenzeno catalisada por metaloporfirinas de Sn, Zn, Cu e Mn.

Lucas Ismael Passos* **(IC)** [1], **Caio Rodrigo Leao Souto (IC)** [1], **Dayse Carvalho da Silva Martins (PQ)**[1].

***lucasismaelpassos@ufmg.br; daysequimica@ufmg.br**

[1]*Departamento de Química, ICEx, UFMG.*

Palavras Chave: Catálise, Oxidantes, Acetofenona, 1-Feniletanol.

Highlights

Ethylbenzene oxidation catalyzed by Sn, Zn, Cu, and Mn metalloporphyrins. Metalloporphyrins were studied as catalysts for the oxidation of ethylbenzene. The selectivity for forming acetophenone was achieved using Mn(TPP)Cl, under excess oxidant.

Resumo

O etilbenzeno é utilizado na indústria química como intermediário do monômero de estireno, aplicado na fabricação de materiais sintéticos com propriedades manipuláveis. Além disso, é adicionado como aditivo em combustíveis de motores de veículos e máquinas. Nessa conjuntura, o presente trabalho consistiu no estudo do potencial catalítico de metaloporfirinas derivadas da H_2TPP (Sn, Zn, Cu e Mn) na reação de oxidação do etilbenzeno para a obtenção de acetofenona e 1-feniletanol, compostos de maior valor agregado para o setor de perfumaria e aromatizantes alimentícios.

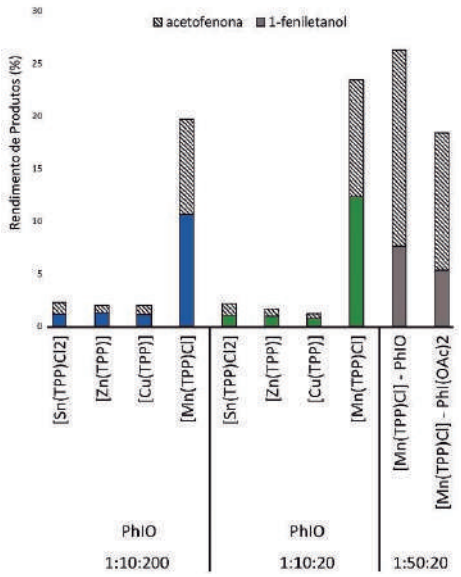


Figura 1. Oxidação de etilbenzeno catalisada por metaloporfirinas derivadas da H_2TPP.

A oxidação do substrato foi monitorada por CG-FID e a análise do grau de destruição do catalisador ao final da reação foi realizada por espectroscopia eletrônica de absorção na região do UV-Vis. Nas reações foram utilizados como oxidantes: iodosilbenzeno (PhIO), Oxone® e iodobenzeno diacetato, $PhI(OAc)_2$. As proporções molares utilizadas referem-se à catalisador:oxidante:substrato.

Ao se utilizar Oxone® não foi identificada a oxidação do etilbenzeno e a formação dos produtos de interesse e, por isso, este oxidante não continuou a ser utilizado nos estudos. Comparando-se os desempenhos das porfirinas (Figura 1) na primeira condição utilizada (1:10:200), empregando-se PhIO, a [Mn(TPP)Cl] demonstrou maior capacidade oxidativa. A mudança da relação molar, tornando a proporção oxidante:substrato menor (1:10:20), levou a um pequeno aumento no rendimento dos produtos nas reações contento a porfirina de manganês, porém os valores de rendimentos dos produtos para os demais catalisadores porfirínicos não sofreram alteração significativa. Propôs-se, então, uma nova condição com excesso de oxidante (1:50:20), que foi estudada somente para a porfirina de manganês, a qual apresentou melhores resultados nos ensaios anteriores. Utilizou-se, também, o $PhI(OAc)_2$, nesta condição de excesso de oxidante, e se observou menor rendimento para os produtos se comparado ao sistema com iodosilbenzeno (incluindo as demais proporções verificadas). Ressalta-se que, sob a condição de excesso de oxidante (1:50:20), as reações de oxidação de etilbenzeno mostraram maior seletividade para formação de acetofenona em contraste com os sistemas com excesso de substrato (1:10:200 e 1:10:20).

Ao se analisar as reações por espectroscopia UV-Vis, constatou-se a degradação integral da porfirina [Mn(TPP)Cl] nos sistemas com proporção 1:50:20, enquanto nas demais reações observou-se a presença de catalisador ao termino das reações. Nesta condição, o catalisador porfirínico de manganês serviu como substrato, sofrendo processos de degradação. Dessa forma, considera-se importante realizar novos estudos com porfirinas que sejam mais resistentes ao processo oxidativo e possam conduzir, também, a uma maior formação dos produtos de interesse, além de se estudar o mecanismo de reação para formação dos produtos obtidos que justifique a diferença de seletividade para as diferentes relações molares catalisador:oxidante:substrato.

Agradecimentos

CAPES, CNPq, FAPEMIG, FINEP, INCT-CiMOL, PRPq/UFMG.

1) Li, X. et al. 2007. DOI:10.1016/j.cclet.2007.06.019. 2) Yang, Y. et al. 2017. DOI: 10.1016/j.jorganchem.2017.10.034. 3) IARC Monographs on the Evaluation of Carcinogenic Risks to Humans Volume 77. Disponível em: <https://publications.iarc.fr/Book-And-Report-Series/Iarc-Monographs-On-The-Identification-Of-Carcinogenic-Hazards-To-Humans/Some-Industrial-Chemicals-2000>. Acesso em: 02 fev 2024.

Área: INO

Pearson governs the activity in M^{III}-NNN$(X)_3$ catalysts for CO_2 cycloaddition reaction with epoxides.

Gabriel M. Santos (IC)[1], Álvaro F.A. da Mata (PG)[2], Rafael P. das Chagas (PQ)[2], Jorge L.S. Milani (PQ)[1]
gabrielmoreira.gm325@gmail.com
[1]Departamento de Química, UFJF; [2]Departamento de Química, UFG

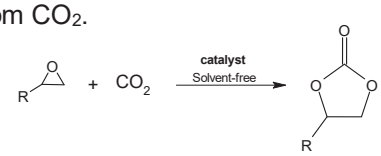
Keywords: *Group 13 complexes, CO_2, Cyclic carbonates, Cycloaddition reaction.*

Highlights

Gallium(III) and Indium(III) complexes bearing different halogens as high active, bifunctional catalysts for CO_2 cycloaddition reaction with epoxides in mild conditions.

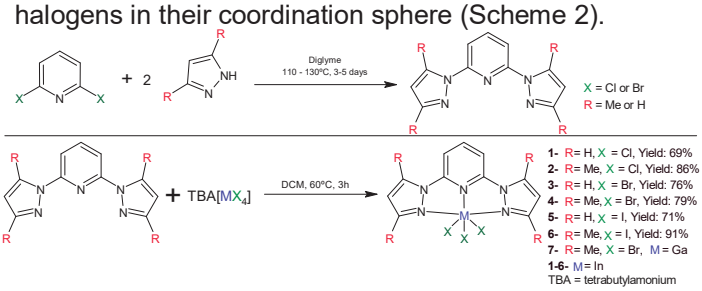
Resumo/Abstract

In the last years, anthropological emissions of greenhouse gases, especially carbon dioxide, has reached record levels in history, resulting in fast global warming and severe climate changes. Therefore, the use of CO_2, which is stable, abundant, non-flammable and non-toxic as a starting material in chemical transformations is highly desirable. In this sense, the CO_2 cycloaddition reaction with epoxides (Scheme 1) producing cyclic carbonates emerge as an useful protocol to achieve highly desirable products from CO_2.



Scheme 1. CO_2 cycloaddition reaction.

Then, we report the synthesis, characterization and catalytic studies of seven complexes containing group-13 metals bearing bis-pyrazolilpyridine ligand and different halogens in their coordination sphere (Scheme 2).



Scheme 2. Synthesis of the ligands and the complexes

First, the In^0 and Ga^0 was treated with HX (X = Cl, Br or I) and then, neutralized using tetrabutylammonium hydroxide to obtain pure crystals of $[TBA][MX_4]$ adducts. The In and Ga compunds was dissolved in methanol with the ligand to obtain the complexes **1-7** in good to excellent yields (69-90%); they were characterized by ^{1}H, IR and X-ray diffraction (complex 1).

Next, the complexes **1-6** were evaluated as catalysts in CO_2 cycloaddition reaction using styrene oxide (SO) as standard epoxide. The data showed the strong influence of halogens in catalytic conversion following the order Cl < Br < I, which is attached to coordination ability of halogens with hard In(III) ion. Softer ligands as iodide and bromide are able to exchange with epoxides easier than Cl analogues. The epoxide coordination is the first step of reaction and then, the free X^- open the epoxide ring. If, the bond In—X is strong, the epoxide is not activated and the reaction does not proceed (X = Cl). As summary, the iodide complexes **5** and **6** have performed the highest conversions, achieving >99% in 12 hours.

Table 1. Conversions and parameters of the cycloaddition reactions performed.

Complex	Conversion in 8h (%)[a]	TOF in 8h (h^{-1})[b]	Conversion in 12h (%)[a]	TOF in 8h (h^{-1})[b]
1	3	0.4	5	0.4
2	3	0.3	5	0.4
3	47	6	95	8
4	64	8	97	8
5	95	12	>99	8
6	98	12	>99	8

Reactions conditios: 0,0625 mmol catalyst (1 mol%), styrene oxide (SO) (6,25 mmol), Temperature = 90°C. [a] Conversions determined on basis of ^{1}H NMR and confirming by GC-MS. [b] Turnover frequency (mol of carbonate produced/mol catalyst . h).

Also, to evaluate the catalytic performance in ambient conditions, a reaction was conducted at 35 ºC, under 1 bar of CO_2 using 5 mol% of **6**, achieving conversions up to 68% in 8 h and remarkable 98% in 24 h.

Based on outstanding conversion even at 35 °C, kinetic study is being carried out in order to obtain the thermodynamic parameters ($\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$) and the activation energy with gallium and indium complexes.

In summary, it was synthesized 7 new complexes from two bis-pyrazolilpyridine ligands using $[TBA][MX_4]$, where M = In or Ga and X = Cl, Br or I in excellent yields. Also, they have presented high conversion when softer iodide was the X ligand, which correlates well with Pearson´s concept.

Next, the Ga and Al complexes will be synthesized and characterized to apply them as catalysts and corelate their conversions with their thermodynamic parameters.

Agradecimentos/Acknowledgments

CNPq, FAPEMIG

Área: INO
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Photocatalytic Reduction of Nitrobenzene Using Bimetallic AuPd Nanoparticles Supported on Layered Double Hydroxide

Gabriel Francisco Souza da Silva (IC),[1] Luiz Phelipe De S. Tomaso (PG),[2] Luiz Fernando B. Malta (PQ),[2] Jaqueline D. Senra (PQ).[1]*
gabriel.2409francisco.ss@gmail.com; jaqueline.senra@uerj.br

[1]Departamento de Química Geral e Inorgânica, IQ-UERJ; [2]Departamento de Química Inorgânica, IQ-UERJ.
Keywords: Palladium, Gold, Aniline, Localized Surface Plasmon Resonance, Lamellar Double Hydroxides.

Highlights

Bimetallic AuPd nanoparticles supported on Cu/Al LDH showed high photocatalytic activity in reducing nitrobenzene under mild conditions.

Resumo/Abstract

Layered double hydroxides (LDHs) are anionic clays, similar to hydrotalcite structure ($[Mg_6Al_2(OH)_{16}]CO_3{\cdot}4H_2O$), which have positively charged layers, due to the presence of unbalanced metallic cations in their structure. LDHs have been applied in a number of relevant base-catalyzed processes. However, their use in combination with moderate to strong reductants can lead to the colapse of the structure. On the other hand, the formation of LDH composites with metal NPs can stabilize and tune the catalytic selectivity. In this work, we propose the synthesis of bimetallic nanoparticles (AuPd) supported on Cu/Al LDH and their catalytic application in the reduction of nitrobenzene with NaBH4, as a model. Firstly, bimetallic AuPd nanoparticles were produced using the modified citrate method [1] and, then, supported on previously prepared Cu/Al LDH. Analysis by SEM-FEG of the bimetallic nanoparticles supported on LDH indicated an average size around 18.47 nm. In addition, the obtained mass percentage of AuPd in LDH was 1%.

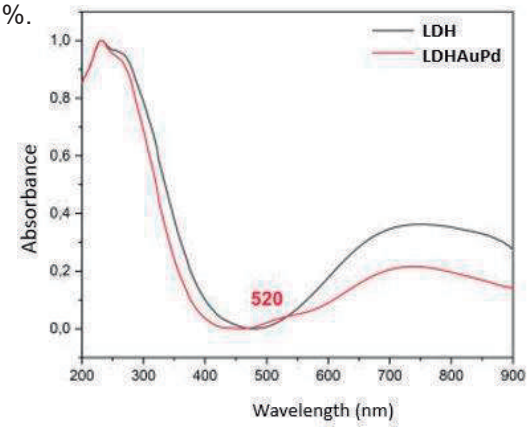


Figure 1: Electronic spectra in the UV-Vis region of LDH and LDHAuPd.

Since supporting gold and palladium nanoparticles in LDH increase their photoability by localized surface plasmon resonance (520 nm, figure 1), analysis by UV-Vis spectroscopy were carried out. Nicely, the characteristic absorption of LDH at 230 nm (metal-band charge transfer) and 700 nm (d-d transition) did not have significant change, which indicated the preservation of the LDH structure.

The second step of the work focused on the reduction of nitrobenzene (NB) to aniline (AN). The main results are showed in Table 1. AuPd LDH-supported showed high photocatalytic activity (99% yield), even under low metal load (1 mol%), compared to the reaction in the absence of catalyst (Table 1, entry 2). The best condition was under ambient light, in aqueous medium, 60°C, 5 eq. NaBH4 and 0.5 mol% AuPd (Table 1, entry 4). The synthetic scope is underway.

Entry	Reaction	Time (min)	Solvent	Yields (%)
1	HDL AuPd (1 mol%)	90	Water	99,30
2	Control	180	Water	17,74
3	HDL AuPd (1 mol%)	180	DMF	97,67
4	HDL AuPd (0,5 mol%)	180	Water	99,40

Table 1: AuPd LDH-supported catalyzed nitrobenzene reduction.

[1] J. Kimling et al. J. Phys. Chem. B 2006, 110, 15700-15707.
[2] SOUZA, A. P. N. et al. ChemistryOpen 2022, 11 (12), e202200177.

Agradecimentos/Acknowledgments

We acknowledge CNPq, FAPERJ and CAPES for funding and NANOFAB-UERJ for SEM-FEG analyses.

Área: INO

Photoinduced CO-Release Studies of Ruthenium(II) α-diimine complexes

Juliana Paula da Silva (PQ),[1] Matheus Allen Pestana da Silva (PG),[1] Adailton João Bortoluzzi (PQ),[1] Márcio Peres de Araujo (PQ),[2]

j.p.silva@ufsc.br

[1] Chemistry Department, UFSC; [2] Chemistry Department, UFPR

Palavras Chave: *ruthenium, carbonyl, α-diimines, photorelease.*

Highlights

New class of ruthenium II complexes with *p*-substituted alpha diimines.
Blue light induced carbon monoxide release.
Solution chemistry of alpha diimines ruthenium complexes.
Study of electronic structure by DFT analyses.

Resumo/Abstract

Carbon monoxide performs some physiological actions related to its endogenous production that occurs in the body during normal digestion of the heme enzyme. Recently, studies have shown that carbon monoxide release in the body, under controlled conditions, can have beneficial applications such as anti-inflammatory action or induction of apoptosis in tumor cells. In this sense, the development of PhotoCORMs (photoinduced CO released molecules) has been focus of studies aiming to obtain complexes that are capable to promote CO photorelease in the visible region. In this sense, the present work shows the synthesis of ruthenium carbonyl complexes with α-diimine ligands and its application as PhotoCORMs. Ruthenium carbonyl complexes obtained have been characterized using spectroscopic techniques that confirm the formation of the expected product. ^{1}H NMR, UV-Vis and FTIR analyzes show that the electronic properties of the complexes are sensitive to the variation in the R substituent of the α-diimine ligand, which may allow modulation of the wavelength related to CO photorelease in future tests. Solution chemistry of the complexes and CO photorelease were investigated by FTIR analysis in solution. DFT calculations were performed in order to understand the electronic and structural properties of such complexes.

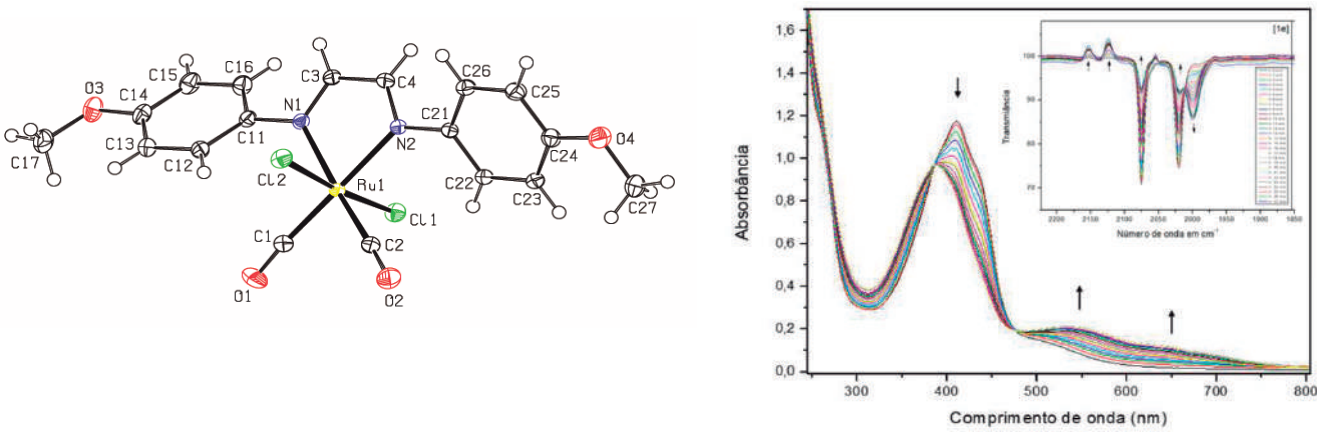


Figura 1. ORTEP view of ruthenium carbonyl complex with general formula [$RuCl_2(CO)_2$(MeO-DAB)] (left) and UV-Vis and FTIR spectra of carbon monoxide release under blue light (right).

Agradecimentos/Acknowledgments

CAPES, CNPq, PPGQ-UFSC and PPGQ-UFPR.

Área: INO

Polyurethane sponges bearing cucurbituril adsorb Cr(III) and Pb(II) ions from contaminated water samples

Lilian R. R. Souza (PQ)*[1], Renato S. Cicolani (PG)[1], Bruno E. S. de Freitas (PG)[1], Giovana L. Floriano (IC)[1], Maycon L. de Oliveira (PG)[1], Antonio G. S. de Oliveira Filho (PQ)[1], Márcia A. M. S. da Veiga (PQ)[1], Gregoire J.-F. Demets (PQ)[1]

lilianrosa@usp.br

[1]*Departamento de Química, FFCLRP-USP*

Palavras Chave: *Cucurbit[6]uril, Cucurbit[8]uril, Sponges, Water remediation, Toxic metals, Adsorption*

Highlights

Langmuir adsorption model fit Cr in CB[6] and Pb in CB[6] and CB[8]. Sponges with CBs decreased Cr in tannery effluent sample up to 42%. CB[6] and CB[8] show potential for adsorbing metals in water.

Resumo/Abstract

Cucurbiturils (CBs) can be employed as promising options for remediating water contaminated with toxic metals since they provide ion-dipole stabilization and hydrogen bonding with the CB portals due to the presence of carboxyl oxygen atoms. The adsorption of metals was initially investigated by semiempirical computational calculations which suggest that CB[6] and CB[8] stabilize the Pb^{2+} ion by ion-dipole interactions while the $[Cr(OH)(H_2O)_5]^{2+}$ ion are stabilized by hydrogen bonds. The CBs were synthesized (Bardelang et al. 2007) and were added to a sponge prepared by method proposed by Silva et al. 2014, and to investigate their efficiency in remediation, adsorption test was performed. The decrease in concentrations of Pb^{2+} and Cr^{3+} ions were respectively 80 and 33.7% for CB[6] and 31.2 and 72.2% for CB[8], as depicted in Figure 1, which indicates high adsorption of these metals in CBs and high remediation efficiency. The adsorption tests showed that the Langmuir isotherm described the adsorption of both metals in CB[6] and Pb in CB[8], achieving high values of Q_0 for Pb in CB[6] and CB[8] (approximately 30 mg L^{-1}); while Cr with CB[8] followed the Dubinin–Radushkevich isotherm model.

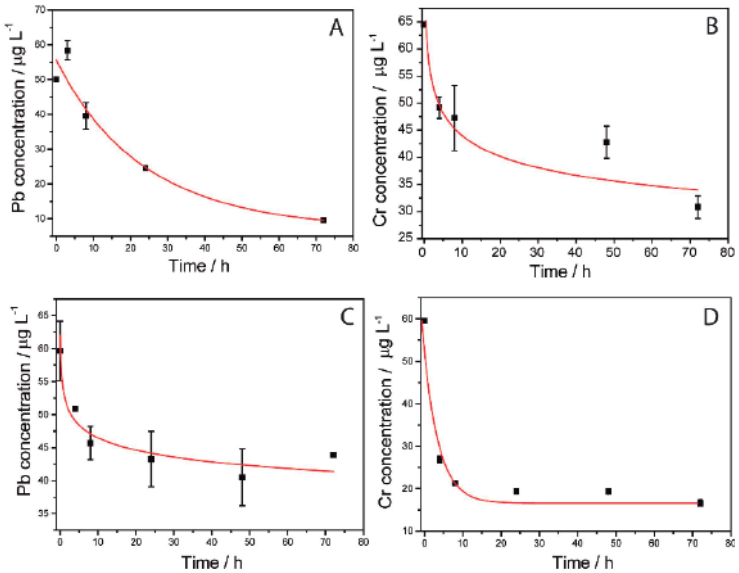


Figure 1. Contact time optimization for (A) Pb solution with CB[6], (B) Cr solution with CB[6], (C) Pb solution with CB[8], and (D) Cr solution with CB[8] (n=3).

The sponges with CB[8] and CB[6] showed efficiency in decrease the concentration of Pb and Cr in complex matrices such as tannery effluent samples (about 42% of decrease) indicating that this material has great potential for adsorption of these toxic metals and remediate contaminated water and effluent samples.

References: Bardelang D, et. al. (2007). Cryst Eng Comm 9:973–975. Silva FCS, et. al. (2014). RSC Adv 4:58796–58799.

Agradecimentos/Acknowledgments

The authors thank to CNPq (158644/2019-0, 315063/2021-8, and 309.909/2018-0), FAPESP (2017/19595-5), PRP-USP PIPAE (2021.1.10424.1.9) for financial support, and Francouro for supplying the tannery effluent samples.

Área: INO

Porfirina imobilizada em nanopartículas de TiO_2 modificadas com silano utilizada como fotocalisador para a degradação do azul de metileno

Ana Flávia Silva Reis (PG),[1]Marcelo Machado Viana (PQ),[1] Dayse Carvalho da Silva Martins (PQ).[1*]

anasreis.ar@gmail.com; *daysequimica@ufmg.br

[1]*Departamento de Química, ICEx/UFMG.*

Palavras Chave: *Dióxido de titânio, Fotocatálise, Luz branca, Azul de metileno*

Highlights

Porphyrin immobilized on silane-modified TiO_2 nanoparticles used as photocatalysts for the degradation of methylene blue. The catalytic activity of a TiO_2 material modified with a porphyrin was verified under visible light. The hybrid material was the most efficient catalyst, degrading 32% of the methylene blue.

Resumo/Abstract

O dióxido de titânio, TiO_2, é um semicondutor amplamente utilizado como fotocatalisador desde meados do século XX devido a seu baixo custo, alta estabilidade química e atoxicidade (1). Em função de seu *bandgap* de 3,2 eV, em reações de fotocatálise é necessário utilizar radiação ultravioleta que, além de mais energética, equivale à menor fração fornecida pela radiação solar, tornando-se necessário o uso de fontes artificiais de radiação. Visando a utilização de radiação menos energética, muitos estudos propõem a modificação superficial deste óxido por meio do uso de fotossensibilizadores, moléculas que absorvem energia na região visível do espectro eletromagnético, como corantes e moléculas aromáticas, com destaque para compostos porfirínicos (2,3).

Neste trabalho, foi proposta a modificação da superfície do TiO_2 comercial (P25, Degussa) utilizando-se o (3-aminopropil)trietoxisilano (APTES), que funciona como uma ponte entre as moléculas de porfirina e a superfície do TiO_2, e a imobilização da porfirina base livre 5,10,15,20-tetraquis(4-carboxifenil)porfirina (H_2T4CPP) ao TiO_2 funcionalizado. Para verificar a atividade catalítica e a influência da presença do silano no material proposto, utilizaram-se o TiO_2 comercial (com e sem APTES) e o híbrido $H_2T4CPP@TiO_2$ (do TiO_2 com e sem APTES) como fotocatalisadores na degradação do azul de metileno (AM) utilizando-se luz na região do visível (400-700 nm).

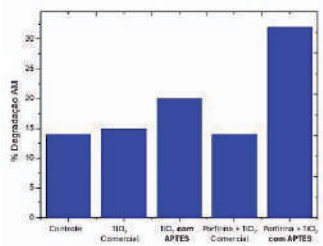


Figura 1 - Reações de degradação do AM com adição de Oxone®. Sistema controle na ausência de catalisador. Relação em quantidade de substância 1:10:100 para catalisador:substrato:oxidante.

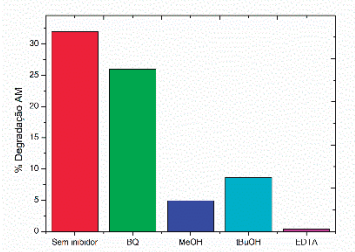


Figura 2 - Reações de degradação do AM benzoquinona (BQ), metanol (MeOH), terc-butanol (tBuOH) e EDTA utilizando o material $H_2T4CPP@TiO_2$ com o APTES como catalisador.

Na ausência de oxidante, a degradação do AM variou entre 1 e 11%, sendo o maior valor obtido utilizando-se como catalisador o híbrido $H_2T4CPP@TiO_2$ (com o APTES). Propôs-se, então, a utilização de Oxone® como oxidante nas reações (Figura 1).

Os materiais contendo o silano apresentaram menor taxa de adsorção do AM, com uma diferença de aproximadamente 30% de AM adsorvido, em comparação com os materiais sem o silano, provavelmente em função da menor área de contato do TiO_2. Além disso, após 210 minutos de irradiação, esses materiais apresentaram maior atividade catalítica com 20% de degradação do AM para o TiO_2 funcionalizado e 32% para $H_2T4CPP@TiO_2$ (com o APTES).

Por meio de ensaios adicionando-se benzoquinona, terc-butanol, metanol e EDTA, inibidores de $O_2^{\bullet-}$, $\bullet OH$ e $SO_4^{\bullet-}$, $\bullet OH$, h^+, respectivamente, ao meio de reação utilizando-se $H_2T4CPP@TiO_2$ com o APTES como catalisador (Figura 2) acredita-se que sem a formação de h^+ (responsável pelas reações oxidativas) não ocorre a degradação do AM. Pode-se, portanto, supor que o mecanismo principal associado à degradação do AM e utilizando-se o catalisador porfirínico com o APTES ocorre devido à formação do par elétron-buraco (e^- e h^+) na superfície do catalisador, sendo dependente da não recombinação e^-/h^+ para que as reações oxidativas ocorram.

A partir os resultados obtidos, embora preliminares, é possível propor que o híbrido $H_2T4CPP@TiO_2$ modificado com silano possui potencial de utilização como fotocatalisador para a degradação de azul de metileno e de outros contaminantes emergentes.

Agradecimentos/Acknowledgments

CAPES, CNPq, FAPEMIG, FINEP, INCT-Cimol, PRPq/UFMG.

Referências: 1) SCHNEIDER, J. et al. 2014. DOI: 10.1021/cr5001892; 2) MANIVANNAN, R. et al. 2021. DOI: 10.1016/j.colsurfa.2020.125601; 3) WANG, H. et al. 2014. DOI: 10.1016/j.materresbull.2014.06.017.

Área: INO

Porfirinas como fotossensibilizadores na terapia fotodinâmica: uma alternativa contra um câncer de mama agressivo

Pedro Fonseca Pinheiro (IC),[1] Larissa Pereira Bento (IC),[2] Nathany Isabelly Dias Vieira (PG),[1] Gilson DeFreitas-Silva (PQ),[1] Elaine Maria de Souza Fagundes (PQ),[2] Dayse Carvalho da Silva Martins (PQ)[1]*

pedrofp.ufmg@gmail.com; *daysequimica@ufmg.br

[1]Departamento de Química, ICEx/UFMG; [2]Departamento de Fisiologia e Biofísica, ICB/UFMG.

Palavras Chave: *Metaloporfirinas, Ensaio clonogênico, Tumor, Luz*

Highlights

Porphyrins as photosensitizers in photodynamic therapy: an alternative against an aggressive breast cancer. The potential use of a porphyrin and its zinc complex as photosensitizers was investigated. Breast cancer cells were successfully killed by the association of the porphyrins and visible light.

Resumo

O câncer é a maior causa de óbitos no âmbito global, especialmente o câncer de mama, que é o quinto tipo mais letal da doença[1]. Dentre as variações do câncer de mama, destaca-se o triplo-negativo, que apresenta como tratamento principal a quimioterapia, que é citotóxica para células saudáveis, e nem sempre eficaz[2]. Uma alternativa interessante para o tratamento de diversos tipos de câncer que vem sendo explorada atualmente é conhecida como terapia fotodinâmica (TFD), a qual consiste no uso de um fotossensibilizador que, irradiado com luz, provoca a formação de espécies reativas e a consequente morte das células cancerosas. Dessa forma, a TFD destaca-se como uma possibilidade de tratamento minimamente invasivo e direcionado para o câncer de mama triplo negativo.

Neste trabalho, investigou-se o uso da porfirina base livre 5,10,15,20-tetraquis(*N*-etil-piridinio-3-il)porfirina (H_2P) e seus complexos de Zn^{2+} (ZnP), Cu^{2+} (CuP) e Mn^{3+} (MnP) como possíveis fotossensibilizadores para o uso em TFD contra a linhagem de células de câncer de mama triplo-negativa MDA-MB-231. Para tanto, realizou-se uma triagem *in vitro* com os compostos, que consistiu em avaliar a viabilidade das células de câncer não irradiadas e irradiadas com luz verde (519 nm) por 30 minutos (Figura 1). Observa-se que a H_2P e a ZnP foram eficazes em inibir a proliferação celular abaixo de 50% quando irradiadas e, por isso, continuaram como foco do presente estudo.

Determinou-se, para H_2P e ZnP, a concentração inibitória de 50% do crescimento (CI_{50}) das células de câncer e verificou-se que os compostos mostraram-se mais citotóxicos em baixas concentrações (<0,3μM) quando irradiados, em comparação com os sistemas não irradiados (Figura 2).

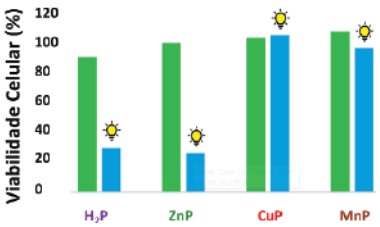


Figura 1- Resultados da triagem para sistemas irradiados (30 min, luz verde, 4,5 mW cm^{-2} e 8,1 J cm^{-2}) e não irradiados com luz.

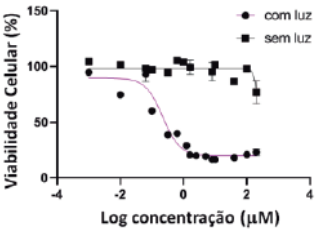


Figura 2- CI_{50} para a ZnP, em sistemas irradiados (30 min, luz verde, 4,5 mW cm^{-2} e 8,1 J cm^{-2}) e não irradiados com luz. Os resultados para a H_2P serão apresentados no evento.

O ensaio clonogênico, que permite avaliar a eficácia dos compostos em bloquear metástases, foi realizado e, pelos resultados preliminares, sugere-se que os compostos são eficazes na redução da sobrevivência clonogênica na presença de luz. Ensaios de avaliação do ciclo celular indicam que a apoptose não é o mecanismo de morte celular decorrente da ação dos compostos.

A partir dos resultados, comprova-se o potencial dos compostos porfirínicos para o uso como fotossensibilizadores na TFD contra células agressivas de câncer de mama.

Agradecimentos

CAPES, CNPq, FAPEMIG, FINEP, INCT-CiMOL, PRPq/UFMG.

Referências: 1) Garrido, G. et al. 2024. DOI:10.1016/j.ijbiomac.2023.127692; 2) Abramson, V. et al. 2015. DOI: 10.1002/cncr.28914; 3) Fiebig, H. H., et al. 2004. DOI:10.1016/j.ejca.2004.01.009.

Área: INO

Predicting the standard reduction potential of Ru(III) complexes with nitrogen ligands

Fernanda G. da Silva (PG),[1] Diego F. S. Paschoal (PQ)[1]*

diegopaschoal01@gmail.com

[1]*Núcleo de Química Teórica e Computacional de Macaé, Polo Ajuda, Instituto Multidisciplinar de Química, Centro Multidisciplinar UFRJ-Macaé, Universidade Federal do Rio de Janeiro, Macaé, RJ, Brazil.*

Keywords: *Cancer, Ru(III) complexes, DFT, basis sets, solvent effects, relativistic effects.*

Highlights

The role of the DFT functional, basis sets, dispersion, relativistic and solvent effects were assessed.

The protocol PWP-D3BJ/Stuttgart-RSC/def2-SVP/SMD presented the best description of the ε^0.

Abstract

Cancer stands ais one of the primary public health challenges globally. Despite the efficacy of platinum complexes in cancer chemotherapy, these compounds exhibit significant toxicity and resistance in biological environments. As an alternative, ruthenium (Ru) complexes have demonstrated promising antitumor activity and reduced toxicity compared to platinum compounds. Research indicates that the reduction of Ru(III/II) complexes plays a crucial role in the mechanism of action of these complexes [1]. The present study presents the construction of a computational protocol for predicting the reduction potential (ε^0) of Ru(III) complexes with nitrogen ligands. The Ru(III) → Ru(II) reduction reactions of a set of three Ru complexes, $[Ru^{III/II}(NH_3)_6]^{3+/2+}$, $[Ru^{III/II}(en)_3]^{3+/2+}$, and $[Ru^{III/II}(bipy)_3]^{3+/2+}$, which present experimental data from $\varepsilon^0_{Ru^{III/II}}$ available in the literature. All calculations were carried out in ORCA 5.0.4 program. Computational protocols at the Functional-DFT/def2-SVP/def2-SVP//SMD level, considering 36 different DFT functionals, were evaluated. The calculated results show that the property is very sensitive to the functional used and that the results obtained with the PWP functional present the best description when the three complexes are considered, mean relative deviation (MRD) of 20.4%. The role of the Ru basis sets (RUBS) and relativistic effects were also evaluated considering 15 different RUBS, six of which were effective core potentials (ECP), four nonrelativistic all-electron basis sets and five *quasi*-relativistic all-electron basis sets. The calculated results indicate that ε^0 is also very sensitive to the RUBS used, with the ECP Stuttgart-RSC presenting the best description of the reduction potential when the three complexes are considered, MRD of only 17.4%. Subsequently, the ligand basis sets (LBS) were also evaluated. Only basis sets with VDZP and AVDZP characters were considered, aiming for a low computational cost. The calculated values showed that the inclusion of diffuse functions (AVDZP) does not play a fundamental role in the description of ε^0. The LBS def2-SVP had the lowest MRD (17.4%), therefore, the PWP/Stuttgart-RSC/def2-SVP//SMD protocol was selected. Finally, the effects of the solvent on geometry (SMD) and dispersion (D3BJ) were considered. The ε^0 values obtained in this way resulted in a MRD of only 9.1%, indicating that the PWP-D3BJ/Stuttgart-RSC/def2-SVP/SMD protocol presents a better description than the reference protocol in the literature, MRD of 51% [2], making it an excellent alternative for the redox study of Ru(III/II) complexes with nitrogen ligands.

[1] Lee, S. W.; Kim, C. Y.; Nam, T.-G. *Drug Des. Devel. Ther.* **14**, 5375-5392 (2020).

[2] Rulísek, L. *J. Phys. Chem. A* **117**, 16871-16877 (2013).

Acknowledgments

The authors would like to thank the Brazilian agency FAPERJ (E-26/201.336/2022 – BOLSA and E-26/210.070/2022 – DCTR) and CAPES (Finance Code 001) for the financial support.

Área: INO

Preparação de sólidos catalíticos empregando metaloporfirinas imobilizadas em Hidróxidos Duplos Lamelares Trimetálicos de diferentes composições

Gabriela Oro (PG), Renaldo M. da Silva Junior (PG), João F. Stival (PG), Everton H. Santos (PG), Vitor V. S. Machado (PG), Adriana D. Dalla Costa (IC), Fernando Wypych (PQ), Shirley Nakagaki (PQ)*

gaabrielaoro@gmail.com; shirleyn@ufpr.br

Grupo de Bioinôrganica e Catálise, Departamento de Química, Universidade Federal do Paraná, UFPR.

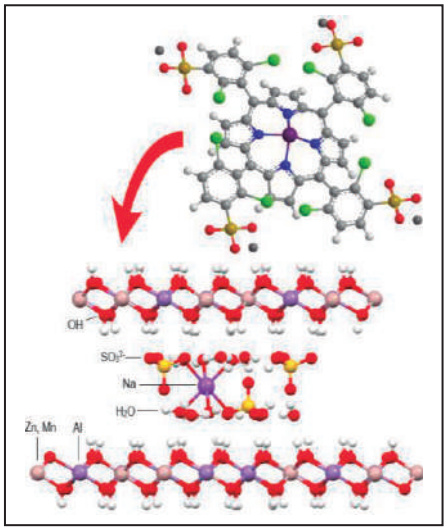
Palavras Chave: *porfirinas, compostos lamelares, HDL, catálise heterogênea.*

Highlights

Synthesis of metalloporphyrin and layered compounds to prepare solids for heterogeneous catalysis.

Immobilization of metalloporphyrins in trimetallic layered double hydroxide solids with different compositions.

Resumo/Abstract



As metaloporfirinas (MP) têm sido vastamente estudadas como catalisadores demonstrando alta eficiência e seletividade em um grande número de reações químicas tais como as de oxidação de alcanos e olefinas, as de acoplamento C-C, as de geração de hidrogênio, as de oxigenação por meio do uso de oxigênio singleto, dentre outras [1]. Mais recentemente as MP quando imobilizadas em diferentes suportes têm sido estudadas como catalisadores em processos heterogêneos apresentando excelentes resultados catalíticos. Suportes muito empregado para a imobilização de MP são os Hidróxidos Duplos Lamelares (HDL) que conferem ao catalisador a possibilidade de recuperação para posterior reuso, diminuição da formação de espécies não ativas na catalise como por exemplo dímeros além de evitarem reações de autodegradação da espécie catalítica. Os HDL de diferentes composições são compostos de lamelas com carga residual positiva formadas por ligações covalentes entre hidroxilas e metais, em geral, bi e trivalentes ao longo de duas dimensões, empilhadas na direção basal por interações fracas como as de van der Waals; apresentando potencial como suportes de MP aniônicas para aplicação em reações catalíticas em meio heterogêneo, podendo atuar como modulador de seletividade [2]. Neste trabalho descrevemos a preparação de sólidos catalíticos baseados na metaloporfirina tetra aniônica [5,10,15,20-tetrakis(2,6-dicloro-3-sulfonatofenilporfirinato)mangânes(III)] imobilizada em HDLs de composição trimetálica $[Zn_{6-x}Mn_xAl_3(OH)_{18}][(SO_4)_2Na]$ onde x = 0, 1, 3, 5 e 6 (Figura). Os sólidos de HDL foram preparados pelo método da co-precipitação em pH crescente [3] e caracterizados por difração de raios X de pó (DRX), absorção atômica (ICP), espectroscopia vibracional no infravermelho (FTIR) e eletrônica na região do UV-Vis e microscopia eletrônica de varredura e transmissão (MEV, TEM); confirmando a obtenção dos sólidos preparados nas composições químicas desejadas. Os sólidos foram utilizados na imobilização da metaloporfirina [2] sendo caracterizados por UV-Vis. Os sólidos preparados serão investigados como catalisadores em reações de hidroxilação de alcanos, epoxidação de olefinas e formação de carbonatos cíclicos a partir da reação de epóxidos como CO_2 sob condições controladas e já previamente investigadas no grupo.

[1] D. Dolphin, T.G. Traylor, L.Y. Xie, Acc. Chem. Res., 30 (1997) 251.
[2] K. C. M. Westrup, R. M. Silva Jr., K. M. Mantovani, L. Bach, J. F. Stival, P. G. P. Zamora, F. Wypych, G. S. Machado, S. Nakagaki App. Catal. A: Gen. 602 (2020) 117708.
[3] A. R. Sotiles, V. V. S, Machado, F. Wypych, Inorg. Chem. Commun. 146 (2022) 110180.

Agradecimentos/Acknowledgments

CNPq UFPR CAPES CIMOL

Área: INO

Preparação e caracterização de suportes baseados em alumina mesoporosa para a imobilização de catalisadores metaloporfirínicos.

Emanuelly O. Oliveira (IC), Everton H. dos Santos (PG), João F. Stival (PG), Shirley Nakagaki (PQ)*

orbeli@ufpr.br; shirleyn@ufpr.br

Grupo de Bioinôrganica e Catálise, Departamento de Química, Universidade Federal do Paraná, UFPR.

Palavras-Chave: Porfirina, Alumina, mesoporos, *catálise.*

Highlights

Here we report the preparation and characterization of mesoporous aluminum oxide with different phases such as amorphous and γ-alumina using sol-gel process aiming the obtention of solids with distinct textural and morphological properties for immobilization of metaloporphyrins.

Resumo/Abstract

A demanda por catalisadores eficientes e seletivos, a exemplo dos catalisadores de reações de oxidação de diferentes substratos orgânicos tais como alcanos a álcoois e de alquenos a epóxido tem levado a intensa pesquisa acadêmica e industrial na área [1,2]. As metaloporfirinas (MP), apresentam excelente desempenho catalítico nessa classe de reações [2]. Esses compostos podem ser aplicados em sistemas catalíticos homogêneos, sendo a eficiência catalítica dependente da solubilidade das espécies no meio de reação bem como da estabilidade estrutural do composto a processos de desativação e degradação. Como alternativa a catalise homogênea, a catalise heterogênea empregando estes compostos imobilizados ou heterogenizados em diferentes suportes ou estruturas (MOFs, COFs, etc), se apresenta como excelente alternativa além de proporcionar a possibilidade de recuperação e de reuso. O emprego de catalisadores resultantes de imobilização ou heterogenização pode também conferir ao sólido propriedades morfológicas e/ou texturais além de conferir ao sólido catalítico novos sítios de reação (Lewis/Brønsted-Lowry) interessantes a catalise [1]; resultante em um sólido catalítico mais eficiente, seletivo e em alguns casos, multifuncional [3]. Dentre as possibilidades de sólidos que podem ser investigados como catalisadores e/ou suporte de espécies catalíticas, o óxido de alumínio (alumina) vem se destacando devido à sua abundância na natureza, alta estabilidade química e, em alguns casos, baixo custo para sua obtenção [3,4]. A alumina pode ser obtida em diferentes fases, texturas e morfologias, sendo uma alternativa no uso como suporte de espécies catalíticas. Neste trabalho, é descrita a obtenção e caracterização de sólidos de alumina mesoporosa, a partir da reação de isopropóxido de alumínio, surfactantes e ácidos para o direcionamento da textura e empregando o processo sol-gel [5]. Diferentes sólidos foram preparados modificando-se condições de reações tais como reagentes direcionadores de estrutura, temperatura, tempo de reação e envelhecimento, dentre outras. Os sólidos foram caracterizados por espectroscopia vibracional na região do infravermelho, difratometria de raios X de pó, microscopia eletrônica de varredura e de transmissão e análise textural por adsorção e dessorção de nitrogênio, mostrando resultados superiores a 30%. O sólido calcinado a temperatura de 400 °C foi utilizado como sonda para a imobilização de espécies catiônicas (corante alaranjado de metila) mostrando alta capacidade de adsorção de cargas positivas sendo, portanto, adequado a imobilização de espécies metaloporfirínicas catiônicas. Sendo assim A imobilização de uma metaloporfirina tetracatiônica foi realizada apresentando resultados muito promissores.

[1] M. Saltarelli, E. H. Faria, K. J. Ciuffi, E. J. Nassar, R. Trujillano, V. Rives, M. A. Vicente. Mol. Catal. 462 (2019) 114.
[2] G. M. Ucoski, V. H. A. Pinto, G. DeFreitas-Silva, J. S. Rebouças, R. M. da Silva Jr, I. Mazzaro, F. S. Nunes, S. Nakagaki. Microporous Mesoporous Mater. 265 (2018) 84.
[3] R. M. da Silva Jr., E. H. Santos, S. Nakagaki. Mol. Catal. 541 (2023) 113080.
[4] A. Pearson. Activated. Kirk-Othmer Encyclopedia of Chemical Technology. 2 (2003) 391.
[5] Q. Yuan, A. Yin, C. Luo, L. Sun, Y. Zhang, W. Duan, H. Liu, C. Yan. J. Am. Chem. Soc.130 (2008) 3465.

Agradecimentos/Acknowledgments

CNPq UFPR CAPES CIMOL

Área:INO

Ru(II)/2-mercapto-4(3H)quinazolinone complexes: cytotoxicity against skin cancer cell lines and mechanism of action

Nádija Natalice Paixão da Silva (PG)[1*], Marcos V. Palmeira-Mello (PQ)[1], Matheus R. S. de Melo (PG)[2], Carlos A. F. Moraes (PG)[1], João Honorato A. Neto (PQ)[3], Denise C. Tavares (PQ)[2], Katia M. Oliveira (PQ)[4], Fillipe V. Rocha (PQ)[1], Alzir A. Batista (PQ)[1]

nadijasilva.nn@gmail.com; nadijasilva.nn@gmail.com

[1]Departamento de Química, UFSCar; [2]Universidade de Franca (UNIFRAN); [3]Universidade de São Paulo (USP); [4]Universidade de Brasília (UnB)

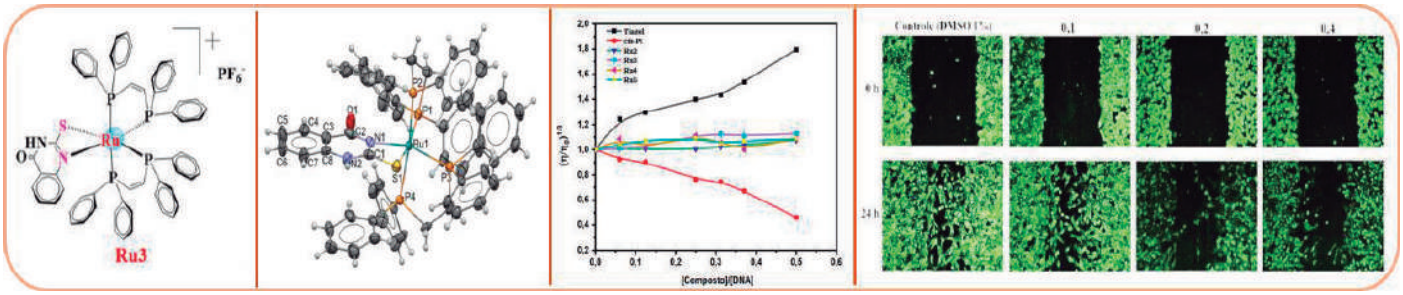
Keywords: skin cancer, ruthenium complexes, 2-mercapto-4(3H)-quinazolinone

Highlights

New Ru(II) complexes were studied against several cancer cells. Morphological, clonogenic, and wound healing assays were performed. Ru3 interacts with DNA via minor grooves and electrostatic contacts.

Abstract

Skin cancer is the most common type of cancer worldwide, and chemotherapy is a strategy indicated in advanced stages of the disease.[1] Ruthenium complexes are emerging as an alternative to overcome the toxicity observed in platinum-based complexes. Herein, this study aimed to synthesize Ru(II) complexes and investigate them as possible anticancer agents. Five complexes (**Ru1–Ru5**) containing the ligand 2-mercapto-4(3H)quinazolinone (H2mq) were synthesized and characterized. The cyclic voltammetry in CH_2Cl_2 indicated *quasi*-reversible process related to Ru^{II}/Ru^{III}, and the molar conductance data indicates that the electrolytes are 1:1,[2] which was confirmed by the presence of a band at 835-845 cm^{-1} in IR spectra, which indicates the presence of PF_6 counter ion. The purity of these compounds was verified by elemental microanalysis, and the structure was confirmed by XRD. An interaction study with DNA was carried out, and it was found that the complexes interact through the minor grooves and possibly electrostatic interactions occur due to the positive charge of the compounds. The nature of the interactionwas assessed using viscosity, circular dichroism, competition fluorescence assay and agarose gel electrophoresis. The cytotoxicity of the complexes was evaluated on human (A-375) and murine (B16-F10) melanoma cell lines and non-tumor human keratinocytes (HaCat) using the XTT colorimetric assay. The results indicated better performance for the **Ru3** complex, which was selected for further experiments. This complex inhibited the formation of colonies in the HaCat and A-375 cells with a more pronounced effect on the A-375 line and modified its morphology after 24 hours at concentrations above the IC_{50} values. Furthermore, in the Wound Healing test, **Ru3** inhibited cell migration at concentrations of 0.2 and 0.4 μM.



[1] NCI - National Cancer Institute. Skin cancer (including melanoma) - Patient version. Disponível em: < https://www.cancer.gov/types/skin>. Acesso em: February 16.

[2] POELHSITZ, G. V. Nitrosilo Complexos de Rutênio com Ligantes Bifosfínicos: Espectroscopia, Eletroquímica, Estudo de Reatividade e Liberação de NO. São Carlos, Programa de Pós-Graduação em Química - UFSCar, 2005. Tese de Doutorado, 284 p.

Acknowledgments

CNPq (processes 302844/2022-8, 130556/2021-1, 141476/2023-0 and 401681/2023-3), CAPES, FAPESP (processes 2023/02475-8, 2021/01787-0 and 2022/02876-0).

Área: INO

Ruthenium-terpyridine based complex with anthracene ligands and bioactive species.

Victor H. S. Lima (IC), Geângela de F. S. Oliveira (PG), Francisca M. S. de Alencar (PG), Idalina M. M. de Carvalho (PQ).

victorhsombra@alu.ufc.br; idalina@dqoi.ufc.br

Grupo de Bioinorgânica, Departamento de Química Orgânica e Inorgânica, Universidade Federal do Ceará (UFC)

Palavras Chave: *Ruthenium complex, anthracene, oxygen singlet.*

Highlights

- Anthracenyl-bipyridine coordinated to ruthenium(II) show ROS photogeneration.
- Ruthenium(II) terpyridine with anthracene ligands and bioactive species

Resumo/Abstract

The polypyridyl complexes of Ru(II) have been developed as potential therapeutic agents. The objective of this work is to synthesize the complex $[Ru(phtpy)(bpyanth)(L)]^{2+}$, where phtpy = (4'-phenyl-2,2':6',2''-terpyridine), mbpy-anth = (4'-methyl-N-(anthracen-2-yl)-[2,2'bipyridine]-4-carboxamide), and L = bioactive molecule as NO. The choice of the anthracene ligand is due to its low-energy intraligand triplet state, ^{3}IL. This allows the complex to undergo energy transfer processes with molecular oxygen, thereby producing singlet oxygen species. These singlet oxygen species are known to be highly reactive and can be utilized in various applications, including photocatalysis and photodynamic therapy. On the other hand, the third ligand in the coordination sphere, the bioactive species, could be dissociated via light irradiation. Therefore, the complex could potentially be studied in applications involving controlled photodissociation of bioactive species or generation of reactive oxygen species. To obtain such a complex, different synthetic steps were planned: firstly, the ligands phtpy and bpy-anth were synthesized, and then the starting complex $[Ru(phtpy)(bpy\text{-}anth)Cl]^{2+}$ was prepared. These compounds were characterized by cyclic voltammetry, NMR ^{1}H, IV and UV-visible absorption spectroscopy. The absorption UV-Vis spectrum of $[Ru(phtpy)(bpy\text{-}anth)Cl]^{2+}$ shows the $\pi\pi^*$ transitions relative to tpy and bpy ligands in the UV region along with the vibronic absorption profile in the range of 350-400 nm typical of the anthracene. In the lower energy of the spectrum, it is observed the absorption arising from metal-to-ligand $Ru(d\pi)\rightarrow L(\pi^*)$ charge transfer (MLCT) involving bpy or tpy as π^* acceptor orbitals. The stretching of the amide bond is observed at 1643 cm^{-1} in the IR spectrum and the half-wave potential of Ru(III)/Ru(II) redox pair was around 1.0V vs Ag/AgCl. The results point out that the desired complex was obtained. The next stage of the work involves adding NO molecule to the complex, as well as studying its photoreactivity.

Agradecimentos/Acknowledgments

CAPES, FUNCAP, CNPq.

Área: INO

SÍNTESE DE UM NOVO NITROSILO COMPLEXO DE RUTÊNIO HIDROSSOLÚVEL COM POTENCIAL FARMACOLÓGICO

Francisco Vitor da Silva Leite (IC)[1*], Walysson Gomes Pereira (PG)[1], Eduardo Henrique Silva de Sousa (PQ)[1], Luiz Gonzaga de França Lopes (PQ)[1].

vitor.leite@alu.ufc.br; lopeslu@dqoi.ufc.br

[1]*Laboratório de Bioinorgânica, Departamento de Química Orgânica e Inorgânica, Universidade Federal do Ceará, 60455-760 Fortaleza – CE, Brasil*

Palavras Chave: Complexos de rutênio, Óxido nítrico, Potenciais vasodilatadores.

Highlights

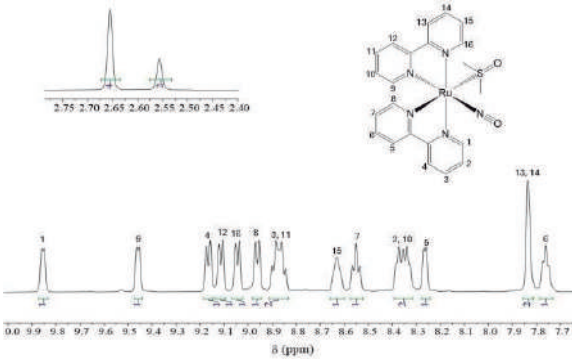
Synthesis of a Novel Water-Soluble Ruthenium Nitrosyl Complex with Pharmacological Potential.

A novel ruthenium complex, FOR08S, synthesized and characterized using spectroscopic and voltammetric techniques. Studies confirm RuNO predominance at physiological pH.

Resumo/Abstract

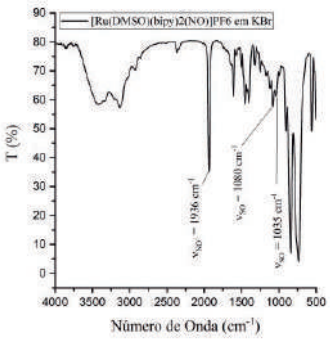
O NO é uma molécula que possui importantes funções biológicas, mas sua produção endógena pode ser comprometida em condições patológicas, exigindo a reposição. Neste estudo se idealizou um novo complexo de rutênio doador de NO, denominado $[Ru(DMSO)(bipy)_2(NO)]PF_6$. A caracterização por RMN de ^1H e COSY revelou sinais para 16 hidrogênios piridínicos e 6 hidrogênios do ligante DMSO coordenado. A coordenação de NO^+ é confirmada por FTIR (ν_{NO} = 1936 cm^{-1}). A voltametria cíclica revelou um par redox ($E_{1/2}$ = 0,175 V) atribuído ao processo NO^+/NO^0, suprimido após a adição de NaN_3, sugerindo que após a redução de NO^+ a NO^0, este último é liberado da esfera de coordenação do metal. O espectro de UV-Vís em água apresentou absorções com máximos em 297 ($\varepsilon = 5{,}64\times10^3$ L mol^{-1} cm^{-1}) e 332 nm ($\varepsilon = 2{,}67\times10^3$ L mol^{-1} cm^{-1}). Titulação espectrofotométrica indicou um pH de conversão nitrosil/nitro de 9,05. Estudos adicionais futuros visarão compreender a reatividade do complexo e seu potencial farmacológico.

Figura 1. RMN ^1H do complexo metálico.



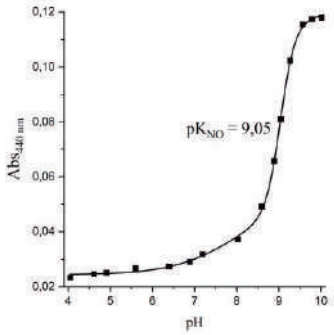
Fonte: Dos autores.

Figura 2. FTIR em pastilha de KBr.



Fonte: Dos autores.

Figura 3. pH de conversão.



Fonte: Dos autores.

Agradecimentos/Acknowledgments

Aos órgãos de fomento CNPQ, CAPES, FUNCAP e FINEP pela concessão da bolsa e financiamento do projeto. Ao Cenauremn pela disponibilização do equipamento de Ressonância Magnética Nuclear.

Área: INO
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Síntese e caracterização de complexos de ferro (II) com ligantes tiossemicarbazonas e tiadiazóis

Bruno Eduardo Rodrigues Dos Santos (IC),[1] Julia Caroline Silva (IC),[1] José Clayston Melo Pereira (PQ).[1]*

ber.santos@unesp.br; josé.clayston@unesp.br

[1]*Departamento de físico-química, química analítica e química inorgânica, Universidade Estadual Paulista "Júlio de Mesquita Filho" UNESP,*
Instituto de Química, Araraquara, Estado de São Paulo, Brasil
Palavras Chave: *Complexos de ferro II, tiossemicarbazonas, tiadiazóis, anticâncer, vanilina, piridina*

Highlights

Synthesis and characterization of iron II complexes with thiosemicarbazone and thiadiazole ligands and study of anticancer activity; synthesis of iron II complexes with organic ligands; study of the anticancer potential of iron II complexes; organic ligands derived from 2-pyridine-carboxaldehyde.

Resumo/Abstract

O tratamento do câncer conta com drogas como a cisplatina ou 5-fluoracil, entretanto possuem efeitos colaterais fortes e baixa seletividade às células alvos [1-3]. Dessa forma, foi proposto a síntese de complexos de ferro II com ligantes tiossemicarbazonas (TSC) e tiadiazol (TD) com grupo funcional piridina, para um estudo dos possíveis efeitos contra células cancerígenas e a caracterização por meio de técnicas tais como espectroscopia vibracional na região do infravermelho, espectroscopia eletrônica na região do UV-vis e espectrometria de massas. A síntese do complexo ferro II com tiossemicarbazona consiste numa proporção molar 1 mmol de tetrafluorborato de ferro II para 2 mmol de TSC em solvente metanol, dissolvendo os reagentes, misturando e deixando a solução repousar até a formação de precipitado. Após a precipitação, o composto é recolhido e lavado com uma mistura de hexano e éter etílico. O espectro de massas do complexo ferro com tiossemicarbazona derivada da piridina com radicais R1 e R2 = H (Figura 1) apresenta um pico de m/z igual a 414,2. Assim, com os cálculos das massas molares das possibilidades, a hipótese mais provável com o resultado é a formação de um complexo [Fe^{II}(TSC)(TD)]. Os dados obtidos do espectro vibracional na região indicam picos referentes às aminas primárias na região de 3500 a 3300 cm^{-1}. As aminas secundárias possuem uma pico fraco (compostos alifáticos) na faixa de 3000 cm^{-1} para vibrações de estiramento. O estiramento da ligação C-N apresenta um pico na faixa de 1350 a 1000 cm^{-1}. Ligações duplas entre carbonos de anel aromático apresentam picos entre 1600 a 1475 cm^{-1}. No espectro de IV da tiossemicarbazona todos os picos e bandas anteriormente citados estão presentes. O complexo com TSC com radicais R1 = H e R2 = Etil apresentou um pico de m/z igual a 470,29 em seu espectro de massas. A espécie mais provável é [$Fe^{III}(TSC)_2$] com valor estimado de 470,39 $g.mol^{-1}$. As bandas em torno de 330 nm dos espectros eletrônicos dos complexos também indicam a presença do ligante na esfera de coordenação.

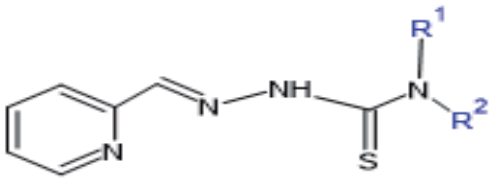


Figura 1: estrutura da tiossmicarbazona derivada da piridina, R1 = H, R2 CH_2-CH_3 ou H

1 – Introdução.In: INCA.Estimativa 2023 | incidência de câncer no Brasil. Rio de Janeiro: INCA, 2022, introdução, p.29-31. Disponível em: https://www.inca.gov.br/sites/ufu.sti.inca.local/files/media/document/estimativa-2023.pdf. Acesso em: 16 fev. 2024. 2 - FERLAY, J. et al. Cancer statistics for the year 2020: an overview. International Journal of Cancer, New York, Apr. 2021. DOI 10.1002/ijc.33588.

Agradecimentos/Acknowledgments

Agradecimentos a UNESP pela infraestrutura, a FAPESP pela parceria e amparo ao projeto e ao grupo de pesquisa.

Área: INO

Síntese e caracterização de Porfirazinas de Zinco (II) e ensaios de interação com biomoléculas

Matheus J. Silva (IC), Gustavo W. Streit (PG), Gilson DeFreitas-Silva (PQ), Thiago T. Tasso (PQ).

matheusjose0815@gmail.com; thiago@qui.ufmg.br

Departamento de Química, ICEX, UFMG.

Palavras-Chave: *Porfirazinas, ADN, Anfifilicidade, Câncer.*

Highlights

Synthesis and characterization of Zinc Porphyrazines (II) and interaction assays with biomolecules. Two Zinc(II) porphyrazines were synthesized and characterized. Porphyrazines showed high solubility in water. Amphiphilicity of macrocycles coud be turned to favor interaction with biomolecules.

Resumo/Abstract

O câncer é um grupo de doenças com grande incidência na sociedade e que reduz significativamente a expectativa de vida de milhares de pessoas no mundo todo, tendo como característica o crescimento celular desordenado, podendo invadir outros tecidos e se espalhar pelo corpo.[1] Alguns macrociclos, como as porfirazinas, que são compostos tetrapirrólicos que contêm átomos de nitrogênio na posição meso, possuem potencial como fármacos para o tratamento do câncer.[2] Neste trabalho, teve-se por objetivo sintetizar e caracterizar duas porfirazinas e seus complexos com zinco (II), além de realizar ensaios de interação desses compostos com biomoléculas, com o intuito de analisar a afinidade desses macrociclos com alvos biológicos. Foram sintetizadas porfirazinas catiônicas de zinco (II) com os substituintes 3-etilpiridil (ZnEtPz) e 3-hexilpiridil (ZnHexPz), cujas estruturas são mostradas na Figura 1. O propósito em sintetizar essas moléculas com diferentes cadeias carbônicas baseia-se em tentar modular a anfifilicidade dos compostos e analisar o efeito sobre a eficiência de interação com os alvos.

Após a síntese, essas porfirazinas de zinco (II) foram caracterizadas por ressonância magnética nuclear de hidrogênio (RMN ^{1}H), espectroscopia de absorção na região ultravioleta e visível, análise elementar e termogravimétrica. A partir do espectro de RMN ^{1}H foi possível observar a completa etilação e hexilação dos grupos piridil dos macrociclos, além disso pôde-se inferir que o tosilato formado durante a síntese foi completamente removido. Por meio do UV-vis verificou-se que esses compostos possuem alta solubilidade em água e que em solvente aquoso esses macrociclos apresentaram bandas intensas de absorção na região do vermelho e na região do azul. Segundo as análises elementar e térmica esses compostos exibiram, respectivamente entre 12 e 20 e entre 6 e 18 águas de hidratação em sua estrutura, sendo que elas foram consideradas para o cálculo dos valores de absorptividade molar.[3]

Constatou-se que as porfirazinas com o grupo hexil apresentam uma solubilidade diferente das etiladas, sendo que as primeiras se tornaram mais lipofílicas quando comparadas com as últimas. A solubilidade desses macrociclos aumentou em solventes orgânicos menos polares, fazendo com que a anfifilicidade seja maior, o que pode facilitar a interação com as biomoléculas. Logo, devido à essa alta solubilidade das porfirazinas catiônicas de zinco (II) tanto em água, quanto em solventes orgânicos pouco polares, estão sendo realizados também experimentos de interação desses compostos com ADN e com a albumina, a fim de compreender os possíveis alvos desses fotossensibilizadores nas células tumorais.

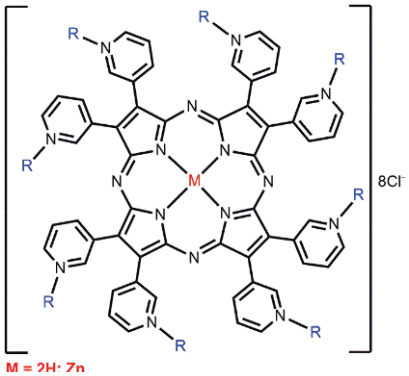


Figura 1 – Estrutura das Porfirazinas.

Agradecimentos/Acknowledgments

FAPEMIG, CNPq, CAPES, FINEP, PRPq/UFMG.

[1] World Health Organization, 21 de setembro, 2021, Disponível em: <https://www.who.int/news-room/fact-sheets/detail/cancer>. Acesso em: 20 de Janeiro de 2024;

[2] FUCHTER, M. J., et al, Porphyrazines: Designer Macrocycles by Peripheral Substituent Change, Australian Journal of Chemistry, vol. 61, p. 235–255, 2008.

[3] SCISCIONE, F. et al. Octakis(2-pyridyl)porphyrazine and Its Neutral Metal Derivatives: UV−Visible Spectral, Electrochemical, and Photoactivity Studies, Inorganic Chemistry, vol. 56, p. 5813−5826, 2017.

Área: INO

Síntese e caracterização do novo complexo de európio com ligante $C_7H_6N_4OBr$, derivado de tetrazol

Lucas Gabriel da Silva Andrade (IC)[1], Simone R. Silva (PQ)[1] simone.rodrigues@ufrr.com

[1]*Departamento de Química, UFRR*

Palavras Chaves: európio, tetrazol, síntese, caracterização.

Highlights

Synthesis and characterization of the new europium complex with ligand $C_7H_6N_4OBr$, derived from tetrazole

The complex exhibits unique properties, confirmed by electrical conductivity and thermogravimetric analyses, highlighting its successful synthesis and therapeutic potential.

Resumo/Abstract

Os elementos de terras-raras, especialmente íons lantanídeos como o európio, estão sendo destacados na medicina devido às suas propriedades multifacetadas [1]. Eles mostram, quando associados a moléculas orgânicas, potencial no tratamento do câncer e combate a diversas infecções [2]. O európio, em particular, destaca-se por sua biocompatibilidade, baixa toxicidade e aplicações em antibióticos e terapia anticâncer, incluindo agentes de contraste para ressonância magnética. Neste estudo, um complexo $EuC_{17}H_{25}N_9Br_2O_5Cl$ foi sintetizado e caracterizado. Testes de solubilidade indicaram sua dissolução em vários solventes. A temperatura de fusão/decomposição foi avaliada, e análises espectroscópicas, incluindo infravermelho e UV-Vis, confirmaram a ligação metal-ligante. Análises termogravimétricas e elementares apoiaram a fórmula proposta. A microscopia petrográfica indicou a formação de cristais. Este complexo apresenta propriedades distintas do ligante, e análises de condutividade elétrica e termogravimétricas confirmaram sua estrutura. Novas pesquisas devem ser conduzidas para analisar as propriedades químicas do composto, bem como para avaliar seu potencial terapêutico.

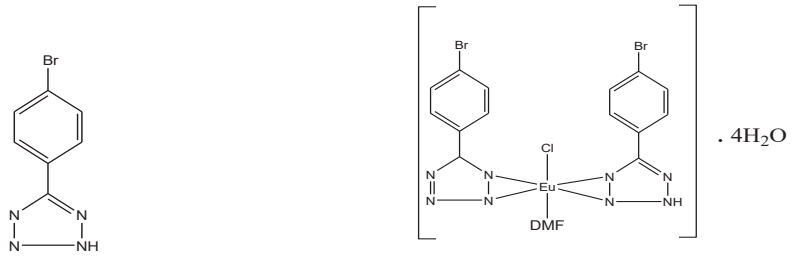


Figura 1 – Esquerda - Estrutura do ligante tetrazol; Direita- Fórmula proposta para o complexo $EuC_{17}H_{25}N_9Br_2O_5Cl$

[1] BALARAM,V. Geoscience Frontiers, volume 10, Edição 4, páginas 1285-1303, 2019.
[2] SADLER, A. W. E; HOGAN, L; FRASER, B; RENDINA, L. M. EJNMMI Radiopharmacy and Chemistry, volume 7, n° 21, 2022.

Agradecimentos/Acknowledgments

Universidade Federal de Roraima, ao Conselho Nacional de Desenvolvimento Científico e Tecnológico e ao Laboratório de Bioinorgânica da UFRR.

Área: INO

Solvatochromic effect of a new polypyridyl-naphtalimide rhenium(I) complex

Luis G. A. do Nascimento (PG),[1] Pedro H. O. Santiago (PQ)[2], Javier A. Ellena (PQ)[2], André S. Polo (PQ)[3] and Sofia Nikolaou (PQ)[1]

luis_nascimento@usp.br

[1]Department of Chemistry, LABiQSC[2] – Laboratório de Atividade Biológica e Química Supramolecular de Complexos de Coordenação, FFCLRP-USP; [2]Institute of Physics of São Carlos, USP; [3]Center for Natural and Human Sciences, UFABC

Keywords: *Naphthalimide, polypyridyl rhenium, solvatochromism*

Highlights

The *fac*-[Re(CO)$_3$(phen)(py-NI)]PF$_6$ complex was synthesized and fully characterized. Its solvatochromism was evaluated using the Kamlet-Taft and Catalán models of multiparametric analysis.

Abstract

Naphthalimides (NI) are organic dyes with a planar and aromatic structure that have caught the researcher's attention due to their stacking and photophysical properties.[1] Rhenium(I) polypyridyl compounds ([Re(CO)$_3$(NN)(L)]^n, NN and L = N-heterocyclic bi- and monodentate ligands, respectively; n = complex charge) are interesting chromophores because the coordination of the NN ligand allows the existence of emissive charge transfer states generated by an effective intersystem-crossing.[2] This work aims to modulate the electronic properties of the complex [Re(CO)$_3$(phen)(py-NI)]PF$_6$ (**1**) (phen = 1,10-phenanthroline; py-NI = N-(4-pyridyl)-1,8-naphthalimide) and to probe it by investigating the solvatochromic effect of different solvents on the py-NI intraligand (IL) and metal-to-ligand charge transfer (MLCT) electronic transitions. The new molecule was fully characterized (UV-vis, CH$_3$CN, $\lambda_{max,abs}$ (nm)/logε(L mol^{-1} cm^{-1}): 230 / 4.7; 275 / 4.3; 333 / 4.2; $\lambda_{max,em}$ (CH$_3$CN) = 548 nm; IR (KBr) ν/cm^{-1}: 2038, 1940, 1713, 1640, 840, 560; ^{1}H NMR (400 MHz, CD$_3$CN) δ(ppm): 9.64; 8.88; 8.50; 8.48; 8.39; 8.22; 8.15; 7.81; 7.31; HRMS (ESI) m/z 725.010 [M$^+$]). The electronic and emission spectra of **1**, collected in 13 different solvents (Figure 1), showed hypsochromic shifts (IL) and bathochromic shifts (MLCT), revealing solvatochromic effects. The multiparametric regression showed that, for the IL absorption band (superimposed with the MLCT), the parameters that most contributed were β (solvent basicity Kamlet-Taft parameter, 39%) and SP (solvent polarizability Catalán parameter, 37%), consistent with the polarizability of the py-NI large π–cloud, and no changing in the dipolar moment of the unsubstituted py-NI during the transition.[4] On the other hand, for the MLCT emission, the parameters that most contributed were β (60%) and SdP (solvent polarity Catalán parameter 50%), showing that the dipolar moment established in the Re^I-phen excited state (due to the π-receptor character of the ligand) is stabilized by more polar and basic solvents, agreeing with the redshift observed.

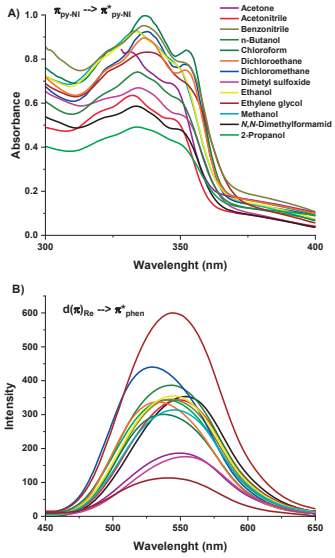


Figure 1. Absorption (A) and emission (B) spectra of **1** in different solvents

[1] S. Saha and A. Samanta, Journal of Physical Chemistry A, 2002, 106, 4763–4771. [2] A. S. Polo, M. K. Itokazu and N. Y. Murakami Iha, J Photochem Photobiol A Chem, 2006, 181, 73–78. [3] E. E. Langdon-Jones, C. F. Williams, A. J. Hayes, D. Lloyd, S. J. Coles, P. N. Horton, L. M. Groves and S. J. A. Pope, Eur J Inorg Chem, 2017, 2017, 5279–5287. [4] D. B. G. Mateus, A. P. L. B., S. S. Souza, G. J-F. Demets, S. Nikolaou, Spectrochim Acta Part A, 2023, 292, 122420.

Acknowledgments

CNPq, FAPESP, and CAPES for funding this project.

Spin Crossover Cobalt(II) and Iron(II) Molecular Nanomagnets with pH-Switchable Properties

Francielly F. Faria (PG),[1]* Renato Rabelo (PQ),[1] Meiry Edvirges Alvarenga (PQ),[1] Felipe T. Martins (PQ),[1] Danielle Cangussu (PQ).[1]

francielly_faria@@discente.ufg.br

1 Instituto de Química, UFG;

Palavras Chave: *Coordination Chemistry, Spin Crossover, Single-Molecule Magnet.*

Highlights

Synthesis and characterization of novel isostructural cobalt(II) and iron(II) complexes with spin crossover and single-molecule magnet behaviours potentially switchable with pH stimuli.

Resumo/Abstract

A Química de coordenação é uma ferramenta que possibilita a síntese de novas moléculas com propriedades de interesse para aplicações em Nanociência e Nanotecnologia. Nesse sentido, moléculas spin crossover (SCO) e single-molecule magnet (SMM) são as menores unidades que possuem potencial para serem empregadas em dispositivos eletrônicos e spintrônicos devido a suas propriedades finamente moduláveis através de fatores internos (estrutura eletrônica) ou externos (estímulos físicos ou químicos). Neste trabalho, apresentamos a síntese de dois complexos do tipo SCO/SMM de cobalto(II) e ferro(II), respectivamente **1** e **2**, com ligante do tipo Base de Schiff substituído com grupos ácido benzoico. A elucidação de suas estruturas cristalinas através da técnica de difração de raios X em monocristal (Figura 1) revelou que **1** e **2** são isoestruturais e que os grupos ácido carboxílico se encontram parcialmente desprotonados, denotando a sensibilidade destes complexos ao pH do meio. Portanto, **1** e **2** constituem exemplos de complexos multiestáveis em que suas propriedades magnéticas SCO e SMM podem ser moduláveis pelo grau de protonação do ligante, oferecendo possibilidades fascinantes como dispositivos magnéticos multifuncionais e de resposta múltipla para a spintrônica molecular.

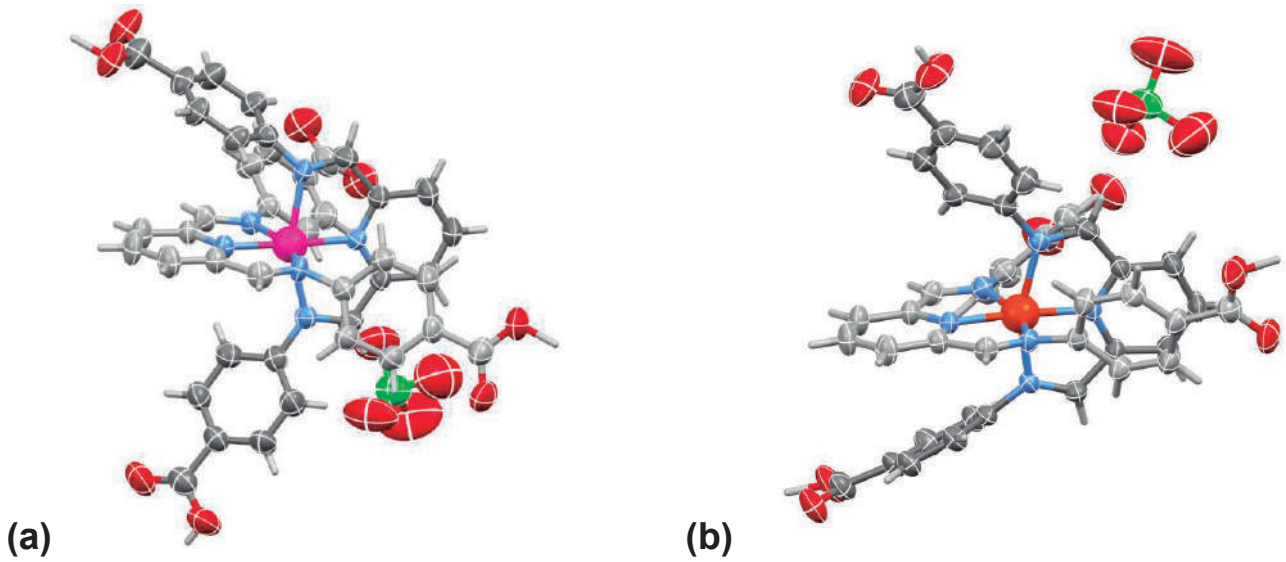


Figure 1. Vista persperctiva da estrutura molecular de **1** (a) e **2** (b) juntamente com seus respectivos contraíons perclorato. Os esqueletos dos ligantes foram representados em diferentes tons de cinza enquanto moléculas de dimetilformamida foram ocultadas para maior clareza. Átomos de não-hidrogênio e hidrogênio foram representados como elipsóides com 50% de probabilidade e bastões de tamanho arbitrário, respectivamente.

Agradecimentos/Acknowledgments

CNPq, CAPES, UFG.

;Área: ___INO____

Square-planar complexes containing functionalized vanillin thiosemicarbazones: synthesis, cytotoxicity, and DNA binding studies.

Danielle C.O. Mascaro (IC),[1*] Ana M.R. Polez (PG),[1] Wladimir P.D. Badaró (PG),[1] Adelino V.G. Netto (PQ),[1].

danielle.mascaro@unesp.br; adelino.netto@unesp.br

[1]Departamento de Química Analítica, Físico-química e Inorgânica, Instituto de Química de Araraquara, UNESP

Palavras-Chave: câncer de mama, complexos, citotoxicidade.

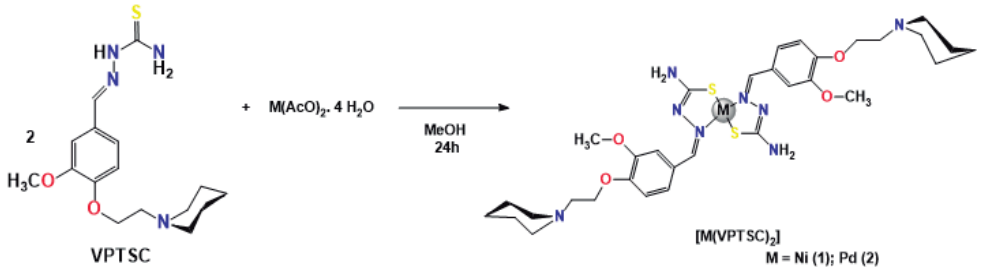
Highlights

Complexes of the type $[M(VPTSC)_2]$ (M= Ni (II), Pd(II)) were synthesized and characterized.

$[Ni(VPTSC)_2]$ is less toxic than cisplatin towards MCF-10A and did not intercalate into ctDNA

Abstract

Breast cancer (CM) is the most common cancer between women in the world. Breast tumors present different behavior and responses to available therapeutic treatments. Considering the complexity of this battle, there is an urgent need to discover new molecules to increase the arsenal of chemotherapeutic drugs. Thiosemicarbazones and their metal derivatives have been attracting interest because of their promising effects against tumor cells, especially those from breast cells. Recently, our group described the action of complexes containing the ligand 3-methoxy-4-[2(piperidine-1-yl)ethoxy]benzaldehyde thiosemicarbazone (VPTSC) against some CM cell lines, being observed values IC_{50} below 10 µM for the triple-negative MDA-MB-231 tumour cells [1]. This work has motivated us to study the antiproliferative effects of other metal derivatives of VPTSC. In this work we describe the synthesis of two complexes with the formula $[M(VPTSC)_2]$ {M = Ni(II); Pd(II)} and the study of their cytotoxic effects against MDA-MB-231 and MCF-10A (a non-tumour cell line). The synthesis of complex **1** and **2** involves the reaction between the VPTSC ligand [1] and the metal salt, in a 2:1 proportion respectively (Scheme 1).



Complex 1 was obtained as a brown crystalline solid. The IR spectrum **1** shows the typical VPTSC bands coordinated in 1608 (δNH + νC=N) and 810 cm^{1}(νCS) and the absence of the νNH hydrazine band, suggesting N,S chelating coordination.

The ^{1}H NMR spectrum showed a single set of signals, indicating the presence of only one species in solution. Furthermore, the anionic N,S coordination of VPTSC was revealed by the absence of the signal referring to the hydrazinic NH (~11 ppm). The other signals and their respective integrals agree with the proposed structure: ^{1}H NMR (ppm): 8.07 (s, 1H); 7.49 (al, 1H); 7.23 (s, 1H); 6.98 (m, 3H); 4.09 (t, 2H); 2.64 (t, 2H); 2.41 (al, 4H); 1.48 (m, 4H); 1.36 (al, 2H). Studies of the behaviour of the complexes in DMSO-d_6 solution (0;24 and 48h) suggest that their structures remained unchanged over the 48h interval. Preliminary results from in vitro cell viability test show that complex **1** (IC_{50}: 46.08 ± 5.53 µM) and cisplatin (IC_{50}: 43.85 ± 2.4 µM) exert the same effect against the MDA-MB-231 cells. However, complex **1** is considerably less toxic (> 100 µM) than cisplatin (28.81 ± 5.84 µM) towards the non-tumor MCF-10A cells. Initial results from spectrophotometric titration suggested that **1** did not intercalate into DNA.

References

[1] D. E. S. Silva et al. Silver(I) complexes of 3-methoxy-4-hydroxybenzaldehyde thiosemicarbazones and triphenylphosphine: structural, cytotoxicity, and apoptotic studies, Dalton Trans., 2020,49, 16474-16487.

Acknowledgments

The authors thanks to FAPESP (2022/14041-0 e 2023/12153-8), CNPq, CAPES/PROEX – Finance code 001 for financial supporting.

Área: INO

Square planar complexes featuring thiosemicarbazone ligands: Synthesis, characterization, cytotoxicity assessment, and exploration of their interaction with biomacromolecules.

Ludimila T. P. Silva (PG),[1,2*] Tamara Teixeira (PG),[1] George B. S. Pereira (PG),[1] Gabriela P. de Oliveira (PQ),[1] Mauro A. Lima (PQ),[1] João H. de A. Neto (PQ),[3] Renan L. de Farias (PQ),[4] Marcelle A. Vieira (PG),[5] Amos O. Akimyemi (PG),[6] Nailton M. N. Júnior (PQ),[5] Adelino V. G. Netto (PQ),[4] Fillipe V. Rocha (PQ).[1*]

tamara.teixeira.296@gmail.com; ludimilapaes@hotmail.com; fillipe@ufscar.br;

[1]Departamento de Química, UFSCAR; [2]Instituto Federal de Educação, ciência e Tecnologia Baiano, Campus Guanambi; [3]Departamento de Química Fundamental USP-SP; [4]Departamento de Química Geral e Inorgânica, Instituto de Química de Araraquara UNESP; [5]Departamento de Bioquímica e Química Orgânica, Instituto de Química de Araraquara UNESP; [6]Department of Toxicology and Canecr Biology, University of Kentucky.

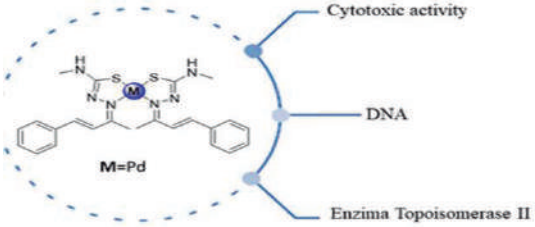
Palavras Chave: *ct-DNA, topoisomerase, cytotoxicity, thiosemicarbazone, palladium(II).*

Highlights

Eight recently developed palladium complexes displayed a distorted square planar geometry. The importance of subtle modifications in ligands was investigated to enhance cytotoxic activity. Comprehensive investigations into compound interactions with DNA and topoisomerase IIα.

Abstract

Cancer is one of the world's leading causes of death, and many researchers are looking for new ways to treat it. Chemotherapy is often used in cancer treatment, employing cytotoxic agents that may have different mechanisms of action. Complexes containing thiosemicarbazones have been extensively studied in developing candidates for new metallodrugs. Thus, this study reports the synthesis and characterization of eight new palladium complexes containing thiosemicarbazone ligands derived from chalcones and benzalketones. Several techniques characterized the compounds. Crystallography was successful for five complexes and two ligands, allowing X-ray diffraction analysis. DNA interaction assays using agarose gel electrophoresis and UV-Vis titration revealed no DNA interaction or inhibition of topoisomerase IIα enzyme activity. However, these compounds exhibited potent cytotoxic effects (IC_{50}) against breast tumor (MCF-7) and prostate (DU-145) cell lines as well as non-tumor prostate (PNT2) cell lines. These results highlight the importance of structural variations in achieving cytotoxic effects and provide insights into the design of bioactive compounds.



IC_{50} ($\mu mol \cdot L^{-1}$ ± Standard error)			
Compound	DU-145	MCF-7	PNT2
$[Pd(BT\text{-}H)_2]$	0.22 ± 0.02	0.41 ± 0.10	0.83 ± 0.02
$[Pd(BT\text{-}M)_2]$	0.97 ± 0.04	0.56 ± 0.06	0.39 ± 0.07
$[Pd(BT\text{-}E)_2]$	4.49 ± 0.19	0.91 ± 0.06	1.09 ± 0.04
$[Pd(CT\text{-}H)_2]$	3.17 ± 0.09	0.907 ± 0.078	1.01 ± 0.13
Cisplatin	15.00 ± 1.40	8.64 ± 0.8	11.74 ± 1.20

CHABNER, B. A. Drug Shortages — A Critical Challenge for the Generic-Drug Market. **New England Journal of Medicine**, v. 365, n. 23, p. 2147–2149, 2011.
PAPROCKA, R. et al. Latest developments in metal complexes as anticancer agents. **Coordination Chemistry Reviews**, v. 452, p. 214307, 2022.
ROCHA, Fillipe V. et al. Computational studies, design and synthesis of Pd (II)-based complexes: Allosteric inhibitors of the Human Topoisomerase-IIα. **Journal of Inorganic Biochemistry**, v. 199, p. 110725, 2019.

Acknowledgments

CNPq 401681/2023-8, CAPES and FAPESP 2022/02876-0.

Área: INO

Structural and Spectroscopic Properties of Lanthanide Coordination Polymer (Ln-CPs) with N-phthaloylglycinates and N-(2-carboxybenzoyl)glycinate

Israel F. Costa (PQ),[1*] Joaldo G. Arruda (PG),[2] Iana Vitória S. Oliveira (IC),[2] Tássio Max A. Martins (IC),[2] Iran F. da Silva (PG),[2] Wagner M. Faustino (PQ),[2] José R. Sabino (PQ),[3] Albano N. Carneiro Neto (PQ),[4] Hermi F. Brito (PQ),[1] Rômulo A. Ando (PQ),[1] Ercules E.S. Teotonio.[2]

israelfc@iq.usp.br;

[1]Department of Fundamental Chemistry, Institute of Chemistry, University of Sao Paulo (USP), São Paulo–SP, Brazil. [2]Department of Chemistry, Federal University of Paraíba, João Pessoa–PB, Brazil; [3]Instituto de Física - Universidade Federal de Goiás-Goiânia-GO, Brazil. [4]Physics Department and CICECO, University of Aveiro, Aveiro, Portugal.

Keywords: Lanthanide, Luminescence, Energy Transfer, N-phthaloylglycinate, Phenanthroline.

Highlights

New structure of the Ln^{3+}-(N-phthaloylglycinate) coordination polymer and mixed Eu –Tb compounds with efficient ligand to lanthanide (Ligand → Ln^{3+}) and terbium → europium energy transfers.

Resumo/Abstract

Coordination polymers (CPs) designed by lanthanide (Ln^{3+}) ions and organic ligands have attracted great interest for different applications in areas such as tunable luminescence, thermometry, chemical sensing, catalysis, and X-ray scintillator. Herein, structural and spectroscopic properties of the Ln^{3+} coordination polymers (Ln-CPs) have been synthesized with N-(2-carboxybenzoyl)glycinate (cbgly) and N-phthaloylglycinate (phtgly), $\{[Tb(phthgly)_3(H2O)_x]\cdot xH_2O\}_\infty$ and $\{[Eu(phthgly)(cbgly)(H_2O)_2](H_2O)\}_\infty$ CPs as well as those mixed $[Tb_{1-x}Eu_x(phthgly)(cbgly)(H_2O)_2](H_2O)\}_\infty$ (x = 0.25, 0.50 and 0.75) are discussed. Structural data revealed that the shortest distances between Ln^{3+} ions in these CPs are find between 4.0 and 5.3 Å (Figure 1a). Based on the PL spectra of the Ln-CPs, we can suggest that the ligand absorption via $S_0 \rightarrow S_1$ transitions produces intense luminescence from the Tb^{3+} (CP1 and CP2) and Eu^{3+} (CP6) material respectively (Figure 1b). Additionally, in the mixed system $Tb_{1-x}Eu_x$ – CPs, x = 0.25, 0.50 and 0.75 (CP3-CP5), as can be observed in the photoluminescence (Figure 1c) and X-ray excited optical luminescence (XEOL) (Figure 1d) spectra of the mixed Tb-Eu coordination polymer, the intensities of the bands arising to the $^5D_0 \rightarrow {}^7F_J$ (Eu^{3+}) are significantly higher than those ones from $^5D_4 \rightarrow {}^7F_J$ (Tb^{3+}) transitions even at low concentration of the "dopant" ion. This behavior can be explained by the high efficiency in the energy transfer from Tb^{3+} to Eu^{3+} ion. The $Tb^{3+} \rightarrow Eu^{3+}$ energy transfer process was also investigated from the luminescence decay curves, the lifetime value for $^5D_4$ level for Tb-CPs (τ = 1.177 ms) decreases deeply to 0.134 ms for x = 0.25 in (CP3), indicating a very efficient luminescence quenching of the Tb^{3+} ion by the Eu^{3+} ions close to emitting metal. In this way, the transfer efficiency $Tb^{3+} \rightarrow Eu^{3+}$ of $\eta_{ET} \approx 90\%$ were determined.

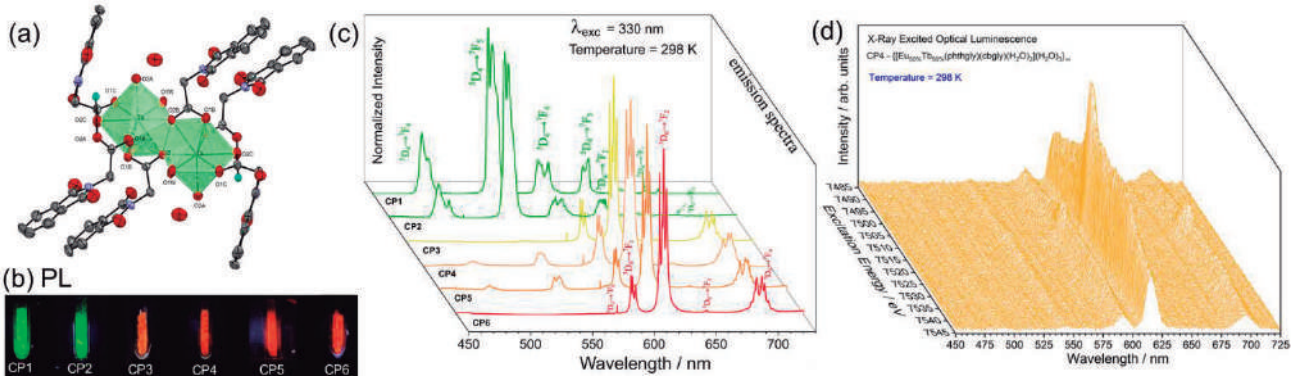


Figura 1. a) Structure of the Tb^{3+} coordination polymer CP-1. b) Photographs of the CP1 to CP6 (under 330 nm UV light) compounds, c) PL spectra of de CP1 to CP6 at 300 K, and XEOL spectra of the $[Tb_{0.5}Eu_{0.5}(phthgly)(cbgly)(H2O)_2](H_2O)\}_\infty$ at 300 K.

Reference

[1] Arteaga, Ana, Lulich, Alice, Nyman, May, Surbella, Robert G. CrystEngComm, 2023,25, 4496-4502.

Agradecimentos/Acknowledgments

This work was supported by FAPESP, CNPQ and CAPES.

Área: _____INO_____

Structure determination and *In vivo* anti-melanoma evaluation of cinnamic acid fluorine Ru(II) complex

Caio Cesar Candido (PG)[1*], Leticia H. Parreira (PG)[2], Michele O. Carvalho (PG)[2], Hanna K. A. Batistão (PG)[2], Luiz F. Ramos (IC)[2], Isabella B. Reis (IC)[2], Camila B. Pinto (PQ)[3], Marília I. F. Barbosa (PQ)[1], Javier A. Ellena (PQ)[3], Pollyanna F. de Oliveira (PQ)[2*], Antônio C. Doriguetto (PQ)[1*]

caiocandido95@hotmail.com; pollyanna.oliveira@unifal-mg.edu.br; antonio.doriguetto@unifal-mg.edu.br

[1]Instituto de Química, UNIFAL-MG; [2]Laboratório de Genética Humana, ICN, UNIFAL-MG; [3] Instituto de Física de São Carlos, USP

Palavras Chave: *Ruthenium complex, cinnamic acid derivative, fluorine, melanoma.*

Highlights

In vivo evaluation of ruthenium(II) cinnamic acid derivative complex. Anti-melanoma potential with tumor size reduction characteristic. Structure determination by single-crystal X-ray analysis. Ruthenium complex of the type [Ru(L)(bipy)(dppb)]PF_6 where: L = 4-trifluoromethyl cinnamic acid, dppb = 1,4-bis(diphenylphosphino)butane, and bipy = 2,2′-bipyridine

Resumo/Abstract

Ruthenium compounds are known to be potential drug candidates, especially for antitumor purposes [1]. We have recently reported the synthesis, characterization, and *in vitro* cytotoxic studies of ruthenium(II) complexes containing cinnamic acid derivatives as ligands against melanoma cell lines [2]. The studies demonstrated positive results in inhibiting cell proliferation, invasion, and migration in melanoma cell lines at very low concentrations, in highlight, the complex that contains 4-trifluoromethyl cinnamic acid [2]. So, *in vivo* evaluation of the anti-melanoma potential of cinnamic acid fluorine derivative ruthenium(II) complex were evaluated. The antitumor activity of the complex in the murine syngeneic model of metastatic melanoma B16F10 cells were inoculated into black male C57BL/6 mice and the animals were treated for five consecutive days with different doses of complex [2.5; 5 and 10 mg/kg body weight (b.w.), subcutaneously (s.c)] and a cisplatin (CDDP 7 mg/kg b.w. s.c.) group was included. We demonstrated that the obtained complex reduces tumor size (Figure 1) and toxicity assessment was performed by monitoring the animals' body weight, water consumption, and creatinine. The previous results provide preliminary anti-melanoma potential with tumor size reduction characteristics.

In addition, this complex has the structure determination by the single-crystal X-ray analysis to contribute to the structural characterization of this promising class of complexes (Figure 2).

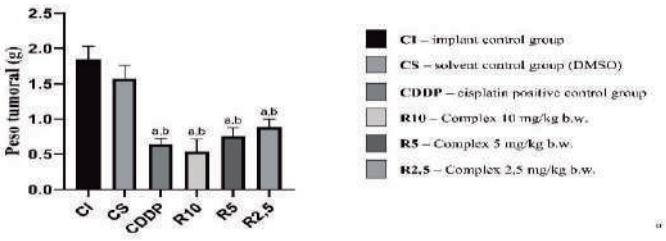


Fig. 1. Tumor weight (g) different control group

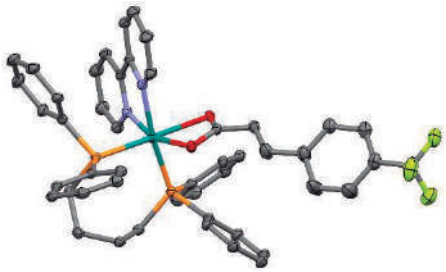


Fig. 2. Crystal structure of the complex

[1] S. Thota, *et al.*, J. Med. Chem., 61 (2018) 5805-5821

[2] A. A. Negreti, *et al.*, New J. Chem., 46 (2022) 3325-3337

Agradecimentos/Acknowledgments

The authors are grateful for the financial support from CAPES (Finance code 001 and research fellowships), CNPq, FINEP (CT-INFRA), UNIFAL-MG, and FAPEMIG.

Área: INO

Studies on the nitric oxide and nitroxyl modifications of human cofillin-1

Pedro A. Landim (IC),[1] Wellinson G. Guimarães (PQ),[1] Luiz Henrique da Costa Souza (PG),[1] Celso S. Nagano (PQ),[2] Rômulo F. Carneiro (PQ),[2] Ana C. S. Gondim (PQ),[1,3] Eduardo H. S. Sousa (PQ)[1].

pedro.a.landim@gmail.com; eduardohss@dqoi.ufc.br

[1]Grupo de Bioinorgânica, Departamento de Química Orgânica e Inorgânica, Universidade Federal do Ceará (UFC); [2]Laboratório de Biotecnologia Marinha, Departamento de Engenharia de Pesca, Universidade Federal do Ceará (UFC); [3]Universidade da Integração Internacional da Lusofonia Afro-Brasileira (Unilab)

Palavras Chave: *Cofillin-1; Nitric oxide; Nitroxyl; Neurodegenerative disease.*

Highlights

Cofillin-1 has been implicated in Parkinson's disease. Their cysteines are associated to this process. Nitric oxide and nitroxyl can modify these cysteines. Circular dichroism, SEC and mass spectrometry studies validated this reaction.

Abstract

Cofillin-1 (COF1) is a protein commonly involved in the regulation of actin including cytoskeletal formation. Other new biological roles have been unveiled including in apoptosis regulation triggered by oxidative processes. These events promote the formation of intramolecular disulfide bridges with its four cysteine residues (C39, C80, C139 e C147, shown in red). Currently, this protein has also been associated to the development of neurodegenerative diseases (e.g., Parkinson's), which might be mediated by the oxidation of the cysteine residues as well. Considering the key role of these residues and the capacity of nitric oxide (NO) and nitroxyl (HNO) to modify them, our lab carried out some studies to shed light on these potential reactions involving these species, including the use of metallonitrosyl compounds. Nitric oxide can react under aerobic conditions with thiols, where cysteine can originate nitrosothiol species (-SNO) that might even decay to disulfide bridge in specific cases. Nitroxyl is a well-known efficient cysteine reactive agent originating mainly sulfinamide group (-$SONH_2$). In this work, we expressed and isolated non-tagged recombinant COF1 in *E. coli* using chromatographic procedures (cationic exchange and size exclusion resins). This protein was sequenced and its intact molecular mass measured, which were consistent with full-length human COF1. A series of studies were carried out by measuring the molecular mass of this protein under distinct treatment with NO or HNO. Interestingly, NO was seen to modify at least one cysteine residue originating a nitrosothiol group (ΔMW = 28 Da). This was further validated by following a treatment with ascorbic acid/Cu^{2+} that decomposes nitrosothiol group, where a molecular mass corresponding to nitrosothiol-COF1 modification disappeared given rise to its full-length molecular mass of COF1 (MW = 18,370 Da). Nitroxyl seemed to be even more efficient in modifying cysteines of COF1, where no signal of the starting reduced COF1 was noticed. On the other hand, there was a match with a molecular mass corresponding to two thiols of cysteines converted into sulfinamide (ΔMW = 63 Da). By treating this sample with ascorbic acid/Cu^{2+} that molecular mass did not change discarding any nitrosothiol species. Circular dichroism measurements were done where changes in the secondary structure were noticed upon treatment with NO and HNO. Size-exclusion chromatography showed native reduced cofilin run as a monomeric species while oxidized was found as a dimer. Treatment with NO or HNO did not alter its oligomeric state, suggesting these modifications did not originate similar conformation as seen with oxidation. Overall, these results support cysteine modifications of COF1 can be achieved and may lead to distinct conformational states. Since NO is a well-known neurotransmitter, it is important to further looking into the biological effects of NO donors in the fate of COF1 or even if HNO donors could have some beneficial role as well.

Acknowledgments

Prof. Dr Fábio Klamt (UFRGS), CAPES, FUNCAP, CNPq and Finep.

Área: INO

Study of biochar properties derived from the pyrolysis of residual acerola biomass

Luiz F. Veridiano C. da Silva (IC),[1*] Ivoneide de Carvalho L. Barros (PQ),[1] Flávia Christiane G. de M. B. Silva (PQ),[1] José Geraldo A. Pacheco (PQ),[2] Lhorenzo Morandi (IC),[1] Sebastião B. M. Júnior (IC),[1] Rômulo P. de Almeida (IC).[2]

Luizfelipeveridiano1@gmail.com

Department of Chemistry, UFRPE[1] Department of Chemistry, UFPE[2]

Keywords: *Biochar, Pyrolysis; Residual biomass*

Highlights

Synthesis of biochar from the pyrolysis of residual acerola biomass. The biochar produced can serve as activated carbon for adsorption or heterogeneous catalysis

Resumo/Abstract

Brazil is a major agricultural producer, and consequently, uses large quantities of fruit in the industry, thus generating a big amount of solid waste from fruits seeds. This residue has no market value nor proper disposal. In order to overcome this problem and reuse this waste, the production of biochar through a fast pyrolysis process is viable. Therefore, residual biomass from acerola seeds was subjected to a pyrolysis process conducted at temperatures between 500 to 600 °C to produce biochar. physicochemical properties of the biochar were analyzed using thermal analysis (TG/dTG) and X-ray diffraction (XRD). In the TG/dTG curves, it was possible to observe three mass loss events. The first event occurs between 50 and 150ºC, related to the humidity of the sample, the second, between 200 and 380ºC, is associated with volatile materials, cellulose and hemicellulose and the third event, between 400 and 800ºC, corresponds to the decomposition of lignin and the remaining residues [1]. Moisture content of 1.34%, ash content of 8.5%, volatile material content of 9.87%, and fixed carbon content of 80.29% were obtained, typical of a solid material subjected to pyrolysis. XRD data showed reflections at 2θ = 20, indicating that the material is predominantly amorphous, which is characteristic of biochar. The reflections observed at 2θ = 30 and 2θ = 40 are related to the graphitic structure (Cgraphite) of the biochar [2]. The results corroborate that the solid material obtained from fast pyrolysis is a biochar, and it enables various applications, especially as activated carbon, which can be used as an adsorbent or heterogeneous catalyst.

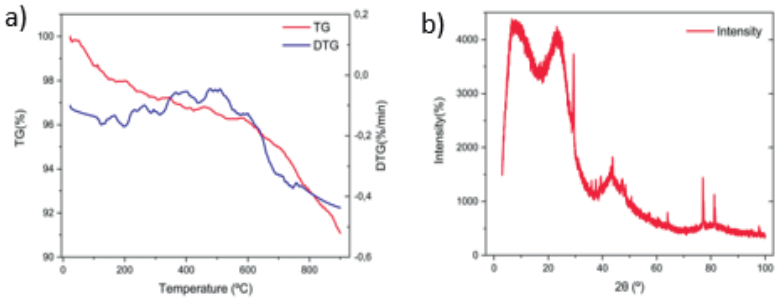


Figure 1: Thermal analysis (TG/dTG) (a) and X-ray diffraction (b) of acerola biochar.

[1] MISHRA, R. K.; MOHANTY, K. Pyrolysis kinetics and thermal behavior of waste sawdust biomass using thermogravimetric analysis. **Bioresource Technology**, v. 251, p. 63–74, mar. 2018.

[2] OLEKSII TOMIN; MARYAM ROZA YAZDANI. Production and characterization of porous magnetic biochar: before and after phosphate adsorption insights. **Journal of Porous Materials**, v. 29, n. 3, p. 849–859, 1 mar. 2022.

Agradecimentos/Acknowledgments

We are grateful to UFRPE, LAQUIMAT, UFPE and LATECLIM.

Área: INO

Study of the structural and spectroscopic properties of Cu(I) and Ag(I) isothiocyanate complexes containing neutral ligands

Ana Luiza C. Januário (IC),[1*] Jayr Henrique Marin (PG),[1] Leandro R. Marques (PQ),[1] Lucca Blois (PG),[1] João H. Araujo Neto (PQ),[1] Romulo A. Ando (PQ),[1] and Israel F. Costa (PQ),[1].

analuizajan@usp.br;

[1]Department of Fundamental Chemistry, Institute of Chemistry, University of Sao Paulo (USP), São Paulo–SP, Brazil.

Keywords: Cu(I), Ag(I), Spectroscopy, LMCT, isothiocyanate, Phenanthroline.

Highlights

Cu(I) and Ag(I) complexes with luminescence in wide range of the visible spectrum. Structural influence on luminescence properties.

Resumo/Abstract

Coordination compounds containing Cu(I) and Ag(I) are among the most studied in the field of luminescent materials. One of the most interesting features, which has attracted attention to these compounds, is the possibility of emitting different colors in the visible region (blue to red) [1]. In this way, one of the main challenges is the preparation of compounds that present thermal and photophysical stability and high emission quantum yield, mainly for application in luminescent devices [2]. Herein, we synthesized, characterized and studied the photophysical properties of coordination compounds based on Cu(I) and Ag(I), containing isothiocyanate (NCS^-) as an anionic ligand, also nitrogenous neutral ligands (LN) and triphenylphosphine (PPh_3), with the general formula [M(NCS)(LN)(PPh_3)] in which M: Cu(I) or Ag(I) and LN: pyridine, 2,2'-bipyridine, 1,10-phenanthroline, 5-nitro-1,10-phenanthroline and 1,10-phenanthroline-5,6-dione. Furthermore, in this work we investigate the influence of these different neutral ligands coordinated to the metal center on the metal–ligand charge transfer (MLCT) state. The FTIR, Raman spectra (Figure 1a), TGA/DTA, elemental analysis, diffuse reflectance (UV-vis), and emission were carried out, indicating the formation of the complexes. Thus, the thermal stability of the compounds was analyzed by TGA/DTA, the onset of decomposition varied within a range of 150-200ºC. According to UVvis absorption spectra by diffuse reflectance the M^I(NCS)(phen)(PPh_3) shows an absorption range from 200 to 600nm, the Cu(I) complex presenting low LMCT states (Figure 1b). The Cu(I) and Ag(I) complexes presented distinct characteristics regarding the emitting properties, displaying red and yellow color emission, as presented in Figure 1c.

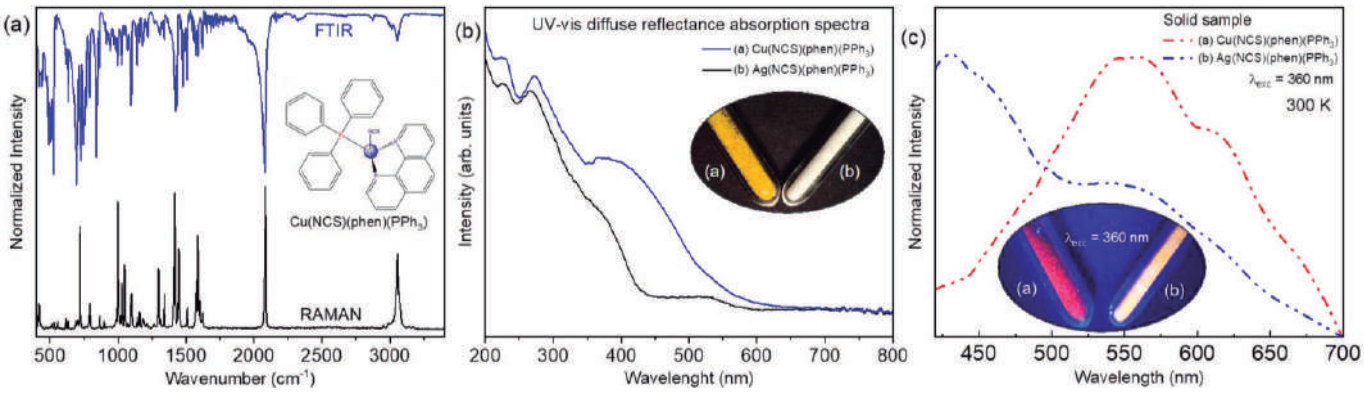


Figura 1. a) Infrared and Raman spectra of the Cu^I(NCS)(phen)(PPh_3), b) UV-vis diffuse reflectance spectra and inserted photographs (under daylight) of the Cu^I(NCS)(phen)(PPh_3) and Ag^I(NCS)(phen)(PPh_3), and c) Emission spectra and photographs (under 360 nm UV light) of the Cu^I(NCS)(phen)(PPh_3) and Ag^I(NCS)(phen)(PPh_3) complexes at 300 K.

Reference

[1] C. Bizzarri, E. Spuling, D.M. Knoll, D. Volz, S. Bräse, Coord. Chem. Rev. 470 (2022) 214700.
[2] M.J. Leitl, F.R. Küchle, H.A. Mayer, L. Wesemann, H. Yersin, J. Phys. Chem. A. 117 (2013) 11823–11836.

Agradecimentos/Acknowledgments

This work was supported by CNPQ, FAPESP and CAPES.

Synthesis and Characterization of a Copper(II) Complex with Salicylhydrazide

Pedro H. O. Santiago (PQ),[1*] Javier Ellena (PQ).[1]

pedrophs.santiago@gmail.com

[1]*Instituto de Física de São Carlos, Universidade de São Paulo.*

Palavras Chave: Hydrazide, Copper(II), Crystallography

Highlights

A pentacoordinate copper(II) complex with a hydrazide ligand was synthesized and characterized by single crystal X-ray diffraction technique, FTIR and UV-Vis spectroscopies, and Hirshfeld surface analysis.

Abstract

Metal complexes based on hydrazide ligands have attracted great interest in the last years due to their interesting biological properties, including antitumor, trypanocidal and antimicrobial activity.[1–3] In this work, we describe the characterization of the new copper(II) complex $[Cu(NO_3)(Salhyd)(bipy)]NO_3$ with the ligand salicylhydrazide (Salhyd), aiming to obtain a bioactive coordination compound.

The X-ray diffraction analysis and the spectroscopic techniques revealed the formation of a mononuclear complex, which is composed of one $[Cu(NO_3)(Salhyd)(bipy)]^+$ cation and one nitrate (Figure 1a), with the pentacoordinate copper(II) center attached to the Salhyd and bipy neutral ligands, and to one nitrate. The analysis of the Hirshfeld surface (Figure 1b) shows the presence of non-covalent intermolecular interactions in the crystal structure of the complex, which organizes the ions in a two-dimensional network. The energy partitioning indicates that the stabilization of the crystal lattice is mainly from the Coulomb component, with contribution of 38% for the stabilizing energy.

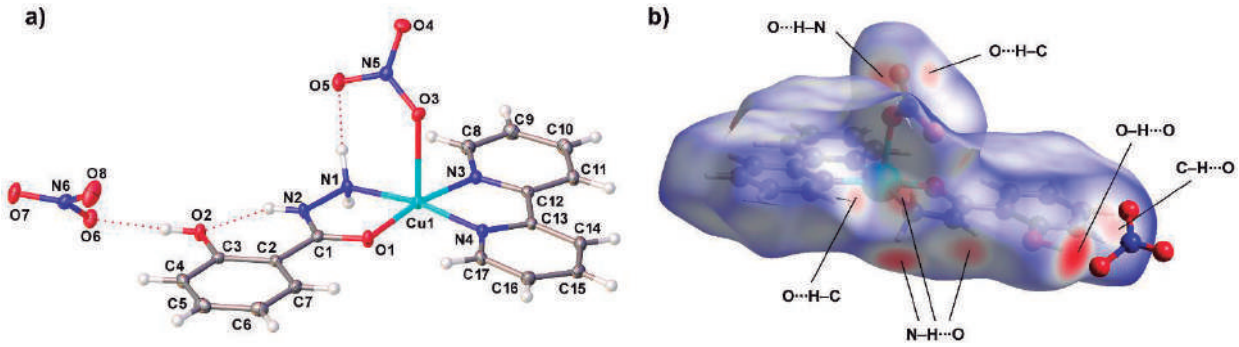


Figure 1. ORTEP type illustration of $[Cu(NO_3)(Salhyd)(bipy)]NO_3$, with thermal ellipsoids represented at 50% of probability (a), and Hirshfeld surface mapped with d_{norm}(b).

1 - Paixão, D. A. et al.; Inorg. Biochem. 2017, 172, 138.

2 - Paixão, D. A. et al.; J. Saudi Chem. Soc. 2018, 22, 809.

3 - Mohanraj, M. et al.; Appl. Organomet. Chem. 2017, 31, e3582.

Acknowledgments

The authors are grateful for the support from FAPESP (2017/15850-0 and 2021/10066-5) and IFSC-USP.

Área: INO

Synthesis and characterization of Mn(II) complexes bearing phenanthroline derivatives as ligands: citotoxicity evaluation.

Roberto S. Silva (PG),[1]* Débora V. Silva (IC),[2] Cid Pereira (PQ),[3] Celisnolia M. Leite (PQ),[1] Alzir A. Batista (PQ),[1] Mário S. Schultz (PQ).[2]

mss060@gmail.com; s.silvaroberto1@gmail.com

[1]Departamento de Química, UFSCar; [2]Instituto de Biodiversidade e Sustentabilidade, UFRJ-Macaé; [3]Instituto Multidisciplinar de Química, Centro Multidisciplinar UFRJ-Macaé

Keywords: *Manganese(II) complexes, phenanthroline derivatives, cytotoxicity.*

Highlights

Four manganese complexes were synthesized and characterized. The complexes showed good cytotoxicity against several cancer cell lines. Complex $[Mn(Ona)_2Cl_2]$ was highly cytotoxic against the human breast tumors (MCF7 and MDA-MB-231), and lung tumors (A549) cell lines.

Resumo/Abstract

Several applications have been proposed for newly synthesized manganese complexes, with biological activities being the most explored properties.[1] Structural modification caused by coordination with metal ions is a growing and emerging strategy in recent years. [2] Several complexes containing N-N-heterocyclic ligands have been reported to have anti-inflammatory [3] anti-cancer [4] and antifungal [5] activity. In this work, Mn(II) complexes containing the ligands 1,10-phenanthroline (Phen), 1,10-phenanthrolin-5-amine (5N), 1,10-phenanthroline-5,6-dione (Ona) e 5,6-Epoxy-5,6-dihydro-[1,10]phenanthroline (Epoxi) were synthesized. The complexes obtained, $[Mn(Phen)_2Cl_2]$ (1), $[Mn(Ona)_2Cl_2]$ (2), $[Mn(Epoxi)_2Cl_2]$ (3), $[Mn(5N)_2Cl_2]$ (4) were characterized by elemental analysis, electronic spectroscopy, FTIR, molar conductivity, magnetic susceptibility, cyclic voltammetry and electron paramagnetic resonance, confirming the proposed structures. The cytotoxicity of the complexes and free ligands were evaluated against human breast tumors (MCF7 and MDA-MB-231), lung tumors (A549), and nontumor cells (MCF-10A and MRC-5), and the results are shown in Table 1. In general, the complexes showed improvement in their cytotoxic activity, when compared to their respective free ligands. The results constitute important initial aspects to be considered to promote new studies involving anticancer activity and Mn(II) complexes.

Table 1. *In vitro* cytotoxic activity of ligands, complexes and cisplatin against MCF7, MDA-MB-231, A549 neoplastic cell lines and MCF 10A, MRC-5 non-neoplastic cell lines, after 48h of incubation.

Compounds	Cytotoxicity, IC_{50} (μM)							
	MCF7	MCF 10A	SI[a]	MDA-MB-231	SI[b]	A549	MRC-5	SI[c]
Phen	> 50	> 50	-	> 50	-	> 50	> 50	-
Ona	5.63 ± 1.25	5.02 ± 0.53	0.89	6.97 ± 3.08	0,72	10.54 ± 0.98	7.05 ± 2.68	0,67
Epoxi	> 50	> 50	-	> 50	-	> 50	27.98 ± 0.92	-
5N	> 50	13.12 ± 2.42	-	19.73 ± 8.88	-	> 50	1.98 ± 0.10	-
(1)	> 50	> 50	-	> 50	-	> 50	5.75 ± 0.24	-
(2)	1.21 ± 0.10	4.44 ± 0.45	3.67	0.89 ± 0.15	4.99	1.49 ± 0.57	0.93 ± 0.13	0,62
(3)	38.49 ± 5.60	25.20 ± 2.93	0.65	12.72 ± 1.97	2.00	27.77 ± 8.35	5.63 ± 0.28	0,20
(4)	> 50	7.33 ± 0.53	-	2.14 ± 0.16	3.43	18.07 ± 7.99	0.72 ± 0.10	0,04
Cisplatin	8.91 ± 2.60	23.90 ± 0.70	2.68	12.44 ± 0.20	9.80	14.40 ± 1.40	29.09 ± 0.78	2,02

[a]IC_{50} (MCF 10A)/ IC_{50} (MCF7); [b]IC_{50} (MCF 10A)/ IC_{50} (MDA-MB-231); [c]IC_{50} (MRC-5)/ IC_{50} (A549)

[1] B. Ali and M. A. Iqbal. *ChemistrySelect*, 2, 4,1586-1604. [2] E. N. da Silva Júnior *et al.*. *Eur J Med Chem*, 179, 863-915. [3] J. Vančo, Z. Trávníček, J. Hošek, and P. Suchý. *PLoS One*, 12, 7, e0181822. [4] R. A. De Grandis *et al. Bioorg Chem*, 85, 455-468. [5] I. Kani, Ö. Atlier, and K. Güven. *Journal of Chemical Sciences*, 128, 4, 523-536.

Agradecimentos/Acknowledgments

FAPESP, FAPERJ, CNPq, UFSCar and UFRJ

Area: INO

Synthesis and characterization of nitrosyl ruthenium complex containing Thiosemicarbazone derived from Cinnamaldehyde.

Lara M. Gracindo (IC),[1] Douglas Scarabello (PG)[2], Maria Isabella Zachi Soares (PG)[1], José C. M. Pereira (PQ)[1]

lara.gracindo@unesp.br;

[1]*Department of Analytical, Physical-Chemistry, and Inorganic Chemistry, São Paulo State University (Unesp), Institute of Chemistry, Araraquara, Brazil.*
[2]*Department of Engineering, Physics, and Mathematics, São Paulo State University (Unesp), Institute of Chemistry, Araraquara, Brazil.*

Keywords: Cancer, Ruthenium, Complex, Thiosemicarbazone.

Highlights

Synthesis and characterization of nitrosyl ruthenium complex containing Thiosemicarbazone derived from Cinnamaldehyde. Ruthenium complex with NO and thiosemicarbazone promises selective cancer treatment. Successful synthesis of $[Ru(Cl_3)(NO)(TSC)].2H_2O$; Spectroscopic and thermogravimetric analyses provided valuable insights and revealed crucial properties. Future experiments will explore NO release and inhibitory efficacy in cancer cells.

Abstract

Ruthenium complex has been studied for cancer treatment due to its potential to reduce side effects compared to conventional and widely used treatments. A Ruthenium complex with nitric oxide and thiosemicarbazone as ligands may be more selective for tumor cells, enhancing therapeutic efficacy and reducing toxicity to healthy cells[3]. This complex was synthesized by adding 4-Methyl-3-thiosemicarbazone (TSC) to methanol containing $RuCl_3.6H_2O$; after stirring, $NOBF_4$ was added to precipitate the complex. The complexes and ligands were characterized using Fourier-transform infrared (FT-IR) vibrational absorption spectroscopy in the infrared region with Fourier transform, UV-Vis electronic absorption spectroscopy, and thermogravimetric analysis (TG/DTG). In the FT-IR, the presence of sharp bands at 1882 cm^{-1} was observed, which may be attributed to the vibration of the N=O molecule, indicating that NO appears as a linear positive ion[4]. Regarding TSC, the band attributed to the vibration of the C=S bond, which originally appeared around 840 cm^{-1} in free ligands, disappeared after the formation of the complexes. This suggests the possibility of coordination through the deprotonated sulfur atom. Absorptions due to the vibration of the C=N molecule are observed in the range of 1614 cm^{-1}, with a shift of about 10 cm^{-1} compared to the free ligand[4]. This change indicates the coordination of the nitrogen atom in the azomethine group with the metal atom. The electronic absorption spectra showed bands in the regions of 293, 392, and 400 nm. The low-energy bands were attributed to metal-ligand charge transfer (MLCT) transitions, while the high-energy bands were associated with intra-ligand charge transfer transitions[1]. Furthermore, calculations performed by TG allowed proposing a composition for the complex, namely $[Ru^{II}Cl_3(NO)(TSC)].2H_2O$, with an error between the total weight losses determined by experimental analysis and the calculated weight for RuO_2 not exceeding 1.2% for this chemical formula[2]. Regarding the loss of mass related to hydration water, the error found between the experimental mass and the calculated mass was 2.52%. Therefore, the synthesis and characterization of the complex $[Ru^{II}Cl_3(NO)(TSC)].2H_2O$ have been studied. As a perspective, experiments involving photochemical tests are anticipated to verify the release of NO. Additionally, IC50 tests will be conducted to assess the inhibitory efficacy on cancer cells of the synthesized material.

Acknowledgments

I thank CAPES, FAPESP, and CNPq for funding the equipment. I express gratitude to the LATIG group for the TG and to my research group for the support and teachings throughout the entire completion of this work.

[1]KUMAR, A. *et al*. **Polyhedron**, v. 52, p. 837–843, 22 mar. 2013.
[2]MATIKOVÁ-MAĽAROVÁ, M.; NOVOTNÁ, R.; TRÁVNÍČEK, Z. **Journal of Molecular Structure**, v. 977, n. 1–3, p. 203–209, 10 ago. 2010.
[3]MEDICI, S. *et al*. **Coordination Chemistry Reviews**, v. 284, p. 329–350, 2015.
[4]MUTHUSAMY, G. *et al*. **Phosphorus, Sulfur and Silicon and the Related Elements**, v. 184, n. 8, p. 2115–2124, ago. 2009.

Area: INO

Synthesis and characterization of the novel carbonyl trinuclear ruthenium acetate [Ru3O(CH3COO)6(THIQ)2(CO)]

Thuany G. Toledo (IC),[1*] Nathan C. Fernandes (IC), [1] Sofia Nikolaou (PQ).[1] thuanygalli@usp.br

[1]*Departamento de Química da Faculdade de Filosofia, Ciências e Letras de Ribeirão Preto – Universidade de São Paulo*

Keywords:*(Carbon monoxide, Ruthenium).*

Highlights

A novel carbonyl trinuclear ruthenium acetate, aiming its application as a CORM, was synthesized and characterized by using spectroscopic techniques such as ^{1}H-NMR, FTIR and electronic absorption (UV-vis).

Resumo/Abstract

Since Rosenberg's discovery about the antitumor activity of cisplatin in the 1960s, studies about the development of new pharmaceuticals based on other metals, such as ruthenium, have increased. There is a growing interest in molecules that can release carbon monoxide in a controlled manner in biological environments, due to its properties such as heme degradation and its properties at low concentrations including cytoprotection, anti-inflammatory, anti-apoptotic and anti- proliferative effects.[1] This has led to the study of the class known as CORMs (CO-Releasing Molecules). Trinuclear ruthenium acetates, complexes with the general formula $[Ru_3O(CH_3COO)_6(L)_2(CO)]^0$ (L = N-heterocyclic ligands), have been the subject of investigation as complexes capable of releasing CO in a controlled way, being sensitive to light and, mainly, redox stimuli.[2] Both the biological properties and the influence of peripheral ligands on the structure of these carbonyl complexes are areas of study for CORMs. Aiming to expand the biological applications of this class of complexes, this study involves the synthesis and characterization of the novel carbonyl trinuclear ruthenium acetate $[Ru_3O(CH_3COO)_6(THIQ)_2(CO)]$, THIQ = 5,6,7,8-tetrahydroisoquinoline (**1**). The THIQ ligand was chosen because of the *in vitro* antitumor and antiparasitic activities against the Chagas' disease parasite observed for the analogue $[Ru_3O(CH_3COO)_6(THIQ)_3]PF_6$.[3] For the synthesis of the complex (Figure 1), literature procedures were adapted.[4] After purification by column chromatography in neutral alumina, it was obtained a 20.5% yield. For the characterization, it was used cyclic voltammetry and spectroscopic techniques such as FTIR, electronic absorption (UV-vis) and ^{1}H-NMR. From the UV-vis spectra the extinction coefficients were 4310 $M^{-1}cm^{-1}$ at 591 nm (intra-cluster transition) and 5260 $M^{-1}cm^{-1}$ at 340 nm (cluster-to-ligand charge transfer transition) in dichloromethane solution. The FTIR spectrum (KBr pellets) shows the vibrations of alkane (νC-H) and alkene (δ_{ip}(=C-H)), besides the symmetric (ν_sCOO) and asymmetric (ν_{as}COO) stretching bands of the carboxyl group from the acetate bridges. In addition, it can be observed peaks assigned to the bond vibrations C=N, C-N (aromatic), C=C and the most intense band is assigned to the C≡O stretching at 1937 cm^{-1}. This frequency is lower than the value observed for free CO, showing the effect of the π-backbonding between the Ru(II) ion and the CO ligand.[5] In the ^{1}H-NMR spectrum, collected in $CDCl_3$, it is possible to see a diagnostic profile of the asymmetric cluster (point group C_{2v}), leading to different chemical shift values for the methyl hydrogens of the acetate bridges: 12 hydrogen nuclei of the acetates in between the THIQ and CO ligands (2,09 ppm, singlet) and the other 6 assigned to the methyl group of the acetate in between two THIQ ligands (1,81 ppm, singlet). Using the COSY correlation spectrum, it was possible to assign the chemical shifts of the THIQ ligand as well (Figure 2). Finally, the voltammograms for the complex **1** showed the multi-electronic profile typical of the $[Ru_3O]$ core, displaying three pair of waves ascribed to the reversible redox processes $E_{1/2}$ = -1,04 V ($[Ru_3O]^{0/-1}$); +0,56 V ($[Ru_3O]^{+1/0}$); +1,32 V ($[Ru_3O]^{+2/+1}$); V vs. Ag/AgCl in CH_2Cl_2). The next step of this work will study the CO release through the reaction with the H_2O_2 oxidant agent.

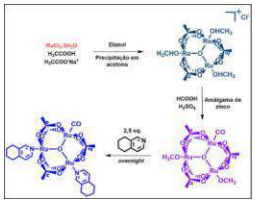


Figure 1. Synthesis scheme of complex **1**

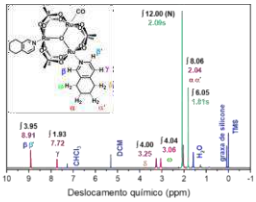


Figure 2. ^{1}H-NMR spectrum of **1** in $CDCl_3$

[1] S. W. Ryter, L. E. Otterbein, *BioEssays* **2004**, *26*, 270. [2] S. Nikolaou, L. G. A. do Nascimento, A. D. P. Alexiou, *Coord Chem Rev* **2023**, *494*, 215341. [3] B. Possato, Z. A. Carneiro, S. de Albuquerque, S. Nikolaou, *J Inorg Biochem* **2017**, *176*, 156. [4] H. E. Toma, K. Araki, A. D. P. Alexiou, S. Nikolaou, S. Dovidauskas, *Coord Chem Rev* **2001**, 187. [4] M. B. Moreira, C. F. N. Da Silva, R. B. P. Pesci, V. M. Deflon, S. Nikolaou, *Dalton Trans* **2016**, *45*, 16799. [5] Z. Teixeira, S. P. Vasconcellos, L. Koike, G. H. M. Dias, *Quim Nova* **2007**, *30*, 494.

Agradecimentos/Acknowledgments

FAPESP CAPES CNPq

Laboratório de Atividade Biológica e Química Supramolecular de Compostos de Coordenação

Área: INO

Synthesis and structural characterization of an organometallic Ru(II)*p*-Cymene with β-diketonate as ligand.

Maria Eduarda Arruda (IC),[1] Roberta Rocha Macêdo (PG),[1] Marcos E. G. do Carmo (PG),[1] Antonio O. T. Patrocinio (PQ),[1]Gustavo Von Poelhsitz (PQ).[1*]

Maria.arruda@ufu.br; gustavopoelhsitz@ufu.br

[1]Instituto de Química, UFU

Palavras Chave: *Ru(II) complex, p-Cymene, β-diketonate.*

Highlights

A Ru(II) complex containing *p*-cymene and *β*-diketonate as ligand was successfully synthesized and characterized. This type of complex has potential cytotoxic action against cells derived from human tumors.

Abstract

The complexes based on Ru(II) have been investigated due to the their chemistry versatility and strong potential in the pharmacological field as immunoregulator agent, antibacterial, antifungal, antitumor among others.[1] In this work the synthesis and structural characterization of the [Ru(BNT)(η^6-*p*-cim)Cl] complex were conducted, aiming *in vitro* studies of cytotoxic activity against tumoral cells. The [Ru(BNT)(η^6-*p*-cim)Cl] complex was synthesized as following: [$RuCl_2$(η^6-*p*-Cymene]$_2$ dimer (8.16 mmol), 4,4,4-Trifluoro-1-(2-naphthyl)-1,3-butanedione (BNT) (3.95 mmol) and triethylamine (1.80 mmol) were refluxed in methanol for 4 h. The mixture was then cooled to room temperature, filtered and washed with water as similar synthetic routes described by Jensen et al. 1998 and Hanif et al. 2014.[2,3] Yield: 52%. Anal. Calc. for $C_{24}H_{22}RuO_2ClF_3$: C: 53.73%; H: 4.14%. Found: C: 54.73%; H: 4.35%. ^{1}H NMR (($CDCl_3$) 400 MHz, δ/ppm): 1.4 (2d, 6H); 2.33 (s, 3H); 3.00 (h, 1H); 5.39 (dd, 2H); 5.67 (dd, 2H); 6.4 (s, 1H); 7.56 (m, 2H); 7.86 (dd, 2H); 7.94 (dd, 2H); 8.4 (s,1H). MS: *m/z* calcd. 501.512; found 501.0655. The ^{1}H NMR shows chemical shifts between 1 and 9 ppm that agree well with the expected for the hydrogen atoms of the coordinated ligands. Such signals are downshield shift in relation to those observed for the free ligands due to the interaction with the Ru(II), the most remarkable signal is a singlet from the *β*-diketonate hydrogen at 6.4 ppm and signals from the *p*-Cymene (1.4 – 6.0 ppm). Additionally, the elemental analysis was also performed to quantify the percentage of C and H which was found in concordance with the expected values for the proposed structure of the complex. The mass spectrometry showed an *m/z* equivalent to the complex without the chloride ligand, [Ru(BNT)(η^6-*p*-cim)]$^+$, as expected for this type of analysis. FTIR spectra were performed for both [$RuCl_2$(η^6-*p*-Cymene]$_2$ dimer and [Ru(BNT)(η^6-*p*-cim)Cl] complex, indicating the absence of the coordination bond between the Ru(II) and Cl^- (expected νRu-Cl at 259 cm^{-1}), evidencing that it was broken to produce the final complex. Finally, we can conclude that the synthesis of the [Ru(BNT)(η^6-*p*-cim)Cl] complex was successfully realized as evidenced by ^{1}H NMR, mass spectrometry, elemental analysis and FTIR. As a future perspective this synthesized complex will be investigated regarding its cytotoxic activity for alveolar basal epithelial cells human adenocarcinomas (A549) and human bronchial epithelial cells (BEAS-2B).

---

[1]KOSTOVA, I. Current Medicinal Chemistry, v.13, n.09, p.1085–1107, 2006.

[2]JENSEN, S. Journal of Organometallic Chemistry, v.556, p.151–158, 1998.

[3]HANIF, M. Molecules, v.19, p.8080-8092.

Acknowledgments

The authors are thankful to the Fundação de Amparo à Pesquisa (FAPEMIG-APQ-0182021), Conselho Nacional de Desenvolvimento Científico (CNPq - 311424-2021-0) and Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES).

Área: _____INO_____

Synthesis, Characterization and Biological Studies on new Palladium*(II)* compounds containing orthometallated Methyl Ester of *L*-Phenylalanine

Wladimir P. D. Badaró (PG),[1*] Bárbara R. S. Feitoza (PG),[1] Gabriela P. Oliveira (PG),[2] Mauro A. Lima (PG),[2] Fillipe V. Rocha (PQ),[2] Javier A. Ellena (PQ),[3] Mariete B. Moreira (PQ),[4] José C. M. Pereira (PQ),[1] Eduardo T. de Almeida (PQ),[5] Adelino V. G. Netto (PQ),[1*]
wladimir.badaro@unesp.br; adelino.netto@unesp.br;
[1]Institute of Chemistry Araraquara, UNESP; [2]Chemistry Department, UFSCar; [3]Institute of Physics São Carlos, USP; [4]State University of Maringá, UEM; Institute of Chemistry Alfenas, UNIFAL-MG.
Keywords: Cancer, palladium*(II)*, *L*-phenylalanine, DNA, HSA, cytotoxicity and XRD.

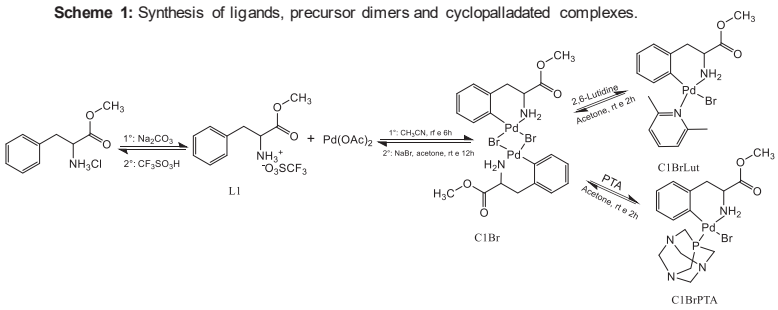
Highlights

New palladium*(II)* compounds orthometallated with methyl ester *L*-phenylalanine are more cytotoxic than cisplatin for breast and ovarian cancer cells with moderate interaction with DNA and HSA.

Abstract

According to the WHO, Cancer is the second leading cause of death in the world. In 2020, 10 million deaths were recorded worldwide due to this condition. In Brazil, INCA reported that there were 232,000 deaths from neoplasms in 2021. In addition, it is estimated that there will be 704,000 new cases of cancer in the country in 2023. Thus, the search for new anti-tumor substances has focused on overcoming the limitations of the drugs currently in use. In particular, metal complexes naturally appear as very promising candidates because they are capable of acting on multiple targets. Among them, palladium*(II)* complexes have attracted interest not only due to their structural similarity with platinum*(II)* compounds, but also their *in vitro* and *in vivo* cytotoxic action against various types of tumor cells. The introduction of biological-type ligands in the molecular structure of Pd(II) compounds may offer exciting possibilities, and can exert an important role in decreasing the toxicity.

Scheme 1: Synthesis of ligands, precursor dimers and cyclopalladated complexes.



In this sense, the aim of this work is to synthesize new complexes with the formula [PdCl(C^2,*N*-phal)(L)] {C^2,*N*-phal = cyclometallated methyl ester of *L*-phenylalanine; L = 2,6-lutidine (C1BrLut), 1,3,5-Triaza-7-phosphaadamantane (C1BrPTA)}. The synthesized compounds (scheme 1) were characterized by elemental analysis (CHN), infrared vibrational spectrometry (IR), ^{1}H and ^{13}C nuclear magnetic resonance (NMR), mass spectrometry (MS) and X-ray diffraction (XRD). The characterization analyses showed that the products agree with the structural proposal of this work. Results from *in vitro* cell viability tests against the tumor cell lines A2780 (ovary), MDA-MB-231 (breast) and A549 (lung) and the non-tumor cell lines MCF-10A (breast) and MRC-5 (lung) indicated that the C1BrLut compound was not only active against the breast and ovary tumor cell lines, but also showed low toxicity against the non-tumor cell lines (table 1). Interaction studies with the biomolecules Human Serum Albumin (HSA) and DNA revealed considerable affinity for HSA, but moderate interaction with DNA (table 1).

Table 1: Results of inhibitory concentration (IC50) and interaction with DNA and HSA.

	IC_{50} (μM)			kb ctDNA		HSA		
Cell lines	C1BrLut	C1BrPTA	Cisplatin	C1BrLut	C1BrPTA		C1BrLut	C1BrPTA
MCF-10A	>50	>50	52.43 ± 2.32			$Kb_{298/(310)}$	3.89x104 (4.89x103)	9.03x104 (2.09x104)
MDA-MB-231	6.04 ± 0.40	30.26 ± 0.87	33.14 ± 0.36			$\Delta G_{298/(310)}$	-25.75 (-21.89 kJ.mol-1)	28.27 (-25.60 kJ.mol-1)
A2780cis[a]/ A2780[b]	9.13 ± 0.25[a]	9.37 ± 1.07[b]	25.09 ± 0.89	1.50x104	1.94x104	ΔH°	-92.12 kJ	-93.65 kJ
MRC-5	>50	>50	21.62 ± 0.8			ΔS°	-226.5 J.(mol.K)-1	-213.3 J.(mol.K)-1
A549	>50	>50	13.01 ± 0.47			$Ksv_{298/(310)}$	6.83x104 (6.70x104)	1.88x103 (1.93x103)

The results indicated that these compounds are interesting, since they demonstrated to be equally or more active than cisplatin against the tumor cell lines tested and less toxic against non-tumor cell lines as well.

1- INSTITUTO NACIONAL DE CÂNCER (Brasil). Estatísticas de câncer. Disponível em: https://www.gov.br/inca/pt-br/assuntos/cancer/numeros. Acessado em: 25 de janeiro de 2024;
2- VICENTE, José; SAURA-LLAMAS, Isabel; OLIVA-MADRID, María-José; GARCÍA-LÓPEZ, José-Antonio; BAUTISTA, Delia. v. 30, n. 17, p. 4624-4631, 28 jul. 2011;
3- Zanetti, R. D., da Cunha, G. A., Moreira, M. B., Farias, R. L., de Souza, R. F. F., de Godoy, P. R. D. V., Brassesco, M. S., Rocha, F. v., Lima, M. A., Mauro, A. E., &Netto, A. V. G. (2022).. Polyhedron, 229, 116185.

Acknowledgments

CNPq, CAPES (Finance Code 001), FAPESP (2022/14041-0)

Área: INO

Synthesis, characterization and in vitro anticancer activity of copper(II) compounds

Enzo Imparato (IC)[1]*, Antonio Carlos Massabni (PQ) , José Clayston M. Pereira (PQ)[1]

enzo.imparato@unesp.br; jose.clayston@unesp.br

[1]*São Paulo State University (Unesp), Department of Analytical, Physical-Chemical and Inorganic Chemistry, Institute of Chemistry, Araraquara, Brazil*

Palavras Chave: *Copper, Complex, Metionine, Thiosemicarbazone, anticâncer, Picolinic acid*

Highlights

Antitumor activity of copper complex; characterization of copper complex; Development of compounds containing thiosemicabazone;

Resumo/Abstract

Os complexos metálicos são uma alternativa promissora para o tratamento do câncer, como visto nos resultados da cisplatina, porém tem seu uso limitado devido sua toxicidade relevante. Sendo assim, outros metais começaram a ser usados para formar compostos com potencial antitumoral, tais como complexos de cobre. Nesta pesquisa foram sintetizados complexos de cobre usando como ligante os compostos, metionina, ácido picolinico, tiossemicarbazona e tiadiazol. Esses novos complexos serão testados com relação suas atividades citotóxicas usando linhagens celulares humanas MCF7 (ATCC – HTB-22, carcinoma de mama) e linhagem humana normal (ATCC – PCS-201-012, fibroblasto de pele). Primeiramente foi feita a síntese para se obter o complexo de cobre com metionina [$Cu(met)_2$], que será usado futuramente como precursor, e foi obtido um precipitado azul e brilhante. O espectro vibracional na região do infravermelho do produto da síntese apresentou estiramentos referente ao grupo amina nas regiões de 3301 cm^{-1}, 3246 cm^{-1} e 1621 cm^{-1} e estiramentos referentes ao grupo carboxila nas regiões de 1568 cm^{-1} e 1403 cm^{-1}, os dois grupos estão presentes no aminoácido utilizado como ligante e ao serem comparados com os dados de Wagner e Baran (2002). Também foi feita a síntese do complexo de cobre com ácido picolinico e metionina [$Cu(pic)(met)_2$] e foi obtido um produto azul que aparenta ser um cristal. O espectro IV indicou a presença de bandas de absorção atribuídas ao ácido picolínico, enquanto as bandas referentes a metionina não foram observadas no espectro, possivelmente devido à menor quantidade adicionada ao fazer a reação ou por ocultação, devido bandas do ácido picolínico na região de 1646 cm^{-1}, que condizem com a literatura (Pavia *et al*. (2012) e Zurowska *et al*. (2003). O espectro de massas apresentou diversos sinais, entre os quais citamos o sinal em 308 m/z que corresponde a massa do complexo de cobre com dois ligantes de ácido picolínico. Sinais mais elevados, de 800m/z e 1107 m/z, podem ser atribuídos a dímeros, trímeros ou polímeros do complexo. Essa polimerização já foi descrita na literatura por Nayak *et al*. (2022), sendo formada pela coordenação de dois picolinatos no íon cobre, e cada picolinato está ligado a dois íons metálicos. A condutimetria foi feita baseada na massa molar de 308 $g.mol^{-1}$ em etanol e foi obtido o valor de 0,78 $S.cm^2.mol^{-1}$. De acordo com a literatura de Geary (1970) é característico de um composto neutro. O composto será enviado para análise de DRX para confirmação da estrutura cristalina e obtenção de informações mais detalhadas sobre sua estrutura molecular.

GEARY, William J. The use of conductivity measurements in organic solvents for the characterisation of coordination compounds. **Coordination Chemistry Reviews**, v. 7, n. 1, p. 81-122, 1971.

NAYAK, Bharat *et al*. 1D copper (II) based coordination polymer/PANI composite fabrication for enhanced photocatalytic activity. **Journal of Photochemistry and Photobiology A: Chemistry**, v. 427, p. 113803, 2022.

PAVIA, Donald *et al*. **Introdução à Espectroscopia.** 4. ed. São Paulo: Cengage Learning, 2012.

WAGNER, Claudia C.; BARAN, Enrique J. Vibrational spectra of bis (L-methioninato) copper (II). **Acta Farmacéutica Bonaerense**, v. 21, n. 4, p. 287-290, 2002.

ŻUROWSKA, Bogumiła *et al*. Synthesis, spectroscopic and magnetostructural evidence for the formation of Cu (II) complexes of pyridyl-2-carboxylate (2-pca) and quinolyl-2-carboxylate (2-qca) as a result of a novel oxidative P-dealkylation reaction of diethyl 2-pyridylmethylphosphonate (2-pmpe) and diethyl 2-quinolylmethylphosphonate (2-qmpe) ligands. **Inorganica chimica acta**, v. 357, n. 3, p. 755-763, 2004.

Agradecimentos/Acknowledgments

Agradeço à FAPESP pelo apoio e financiamento. Agradeço ao grupo LACAQUE pela espectrometria de massas e ao meu grupo de pesquisa pelo apoio e ensinamentos durante toda a realização deste trabalho.

Área: INO

Synthesis, characterization and leishmanicidal activity of ruthenium(II)-dppm complexes containing β-diketonates

Roberta R. Macêdo (PG),[1] Mônica S. Costa (PG),[2] Kelly A. G. Yoneyama (PQ),[2] Gustavo V. Poelhsitz (PQ)[1*]

roberta.rocha.macedo@educacao.mg.gov.br; gustavopoelhsitz@ufu.br

[1]Instituto de Química, Universidade Federal de Uberlândia; [2]Instituto de Biotecnologia, Universidade Federal de Uberlândia

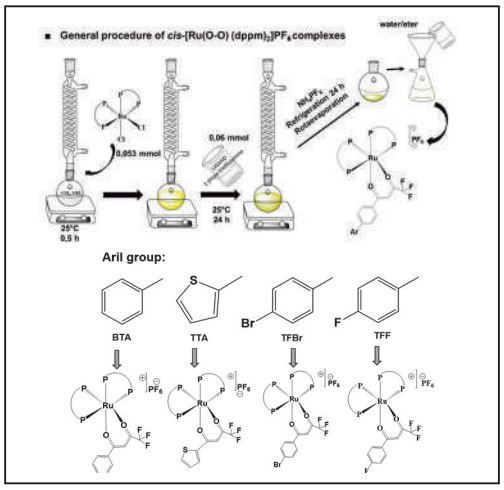
Palavras Chave: *Ruthenium(II), Dppm, Leishmaniosis, β-diketonate*

Highlights

A new series of ruthenium(II) complexes with dppm and β-diketonates were synthesized and fully characterized.
In vitro cytotoxicity against *Leishmania L. amazonensis* was evaluated.

Abstract

According to the World Health Organization (WHO), leishmaniasis is a disease that causes many risks to public health, being classified in the category of Neglected Tropical Diseases[1], whose treatment basically involves the use of pentavalent antimonial agents. However, the available therapeutic alternatives displayed adverse effects, limited efficiency and parasite resistance. Given this fact, there is a need searching novel strategies that involve the development of potential drugs that can replace such treatments. Within this perspective, ruthenium(II)-based compounds have been extensively studied for the promising results exhibited not only for the metallic center[2], but also for the species that form its coordination sphere, such as phosphinic and β-diketonates ligands utilized in this work, which showed promising bioactivity, according to the literature[3,4]. This work describes the synthesis, characterization and *in vitro* leishmanicidal activity of new ruthenium(II) complexes with general formula *cis*-[Ru(O-O)(dppm)$_2$]PF$_6$, where dppm = 1,1´-*bis*(diphenylphosphine)methane and O-O corresponds to the chelating β-diketonate: 1,3-butanedione-1-phenyl-4,4,4-trifluoro (BTA), 2-thenoyltrifluoroacetone (TTA), 1,3 -butanedione -1-(4-bromophenyl)-4,4,4-trifluoro (TFBr) and 1,3-butanedione-1-(4-fluorophenyl)-4,4,4-trifluoro (TFF) as showed in the scheme. The empirical formulas and purity of the new complexes were suggested by elemental analysis (CHN). FTIR spectroscopy presents the typical vibrational modes of biphosphine and the presence of β–diketonate was confirmed by the C-O stretching mode (carbonyl) in the range 1600-1700 cm^{-1}). The absence of Ru-Cl vibrational modes close to 280 cm^{-1} also helps to confirm the formation of the new complexes. In the ^{1}H NMR spectra the chelation of the β-diketonate ligands was confirmed by the singlet close to 6.0 ppm attributed to methylenic hydrogen. In the ^{31}P NMR spectra the ddd pattern typical of systems with four non-equivalents phosphorus was observed besides the presence of a septet signal at -144.3 ppm from the PF$_6^-$ counterion. Single crystals of *cis*-[Ru(bta)(dppm)$_2$]PF$_6$, suitable for structure determination, were obtained. Structural data confirmed the proposed structure for this series of complexes with *cis* positioned dppm and chelating β–diketonate ligands. *In vitro* viability assays against the *Leishmania (L.) amazonensis* species were performed for new complexes, precursor and free ligands. It was found that all complexes were active with IC$_{50}$ values ranging from 24.7 µM and 3.9 µM depending of the β-diketonate ligand. These values are comparable to that observed for second-choice compounds currently used in the treatment of leishmaniasis, which makes the ruthenium synthesized complexes promising leishmanicidal agents.



1. WHO. Leishmaniasis. 2024. World Health Organization (WHO). Available in: https://www.who.int/health-topics/leishmaniasis#tab=tab_1
2. SARNIGUET, C. *et al.* Water-soluble ruthenium complexes bearing activity against protozoan parasites. Biological Trace Element Research, v. 159(1-3), p. 379–392, 2014. https://doi.org/10.1007/s12011-014-9964-0
3. GOMES, D. *et al.* Synthetic derivatives of durcumin and their activity against *Leishmania amazonensis*. Arzneimittelforschung, v. 52(2), p. 120−124, 2002a.
4. RODRIGUEZ-BARZANO, A. *et al.* Synthesis and anticancer activity evaluation of η^5-C$_5$(CH$_3$)$_4$R ruthenium complexes bearing chelating diphosphine ligands. Dalton Transactions, v. 44, n. 7, p. 3265-3270, 2015. https://doi.org/10.1039/C4DT02748E

Acknowledgments

FAPEMIG (APQ-01820-21), CNPq (311424-2021-0) and CAPES for financial support.

Área: INO
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Synthesis of a mimetic of the enzyme polysaccharide lytic monooxygenase (LPMO) to catalyse the polysaccharide hydrolysis reaction.

Larissa Moreno (IC) e Caterina G. C. M. Netto (PQ)*.

larissamoreno@estudante.ufscar.br; caterina@ufscar.br

Departamento de Química, UFSCar

Palavras Chave: *LPMO, polysaccharides, biomimetics, copper complexes, energy, oxidation.*

Highlights

- Synthesis of an LPMO mimetic using copper complexes coordinated to three nitrogens;
- Analysis of their catalytic activity for efficiency in polysaccharide hydrolysis reactions.

Resumo/Abstract

In this work, a mimetic of the LPMO enzyme was synthesised in order to study the catalytic activity of this complex to be applied in the segregation of polysaccharides for the production of non-polluting energy derived from biomass through oxidative hydrolysis reactions. LPMO is a mononuclear copper enzyme coordinated to the terminal histidine residue and a second histidine residue; its comparison with the synthesised mimetic is shown in figure 1.

The project was divided into four organic synthesis steps to obtain the ligand and a coordination synthesis. The ligand was obtained from L-proline, which was esterified to obtain the product (1). An alkylation reaction of (1) with 2-bromo-methyl-pyridine produced compound (2), which was hydrolysed in a basic medium to obtain compound (3). From (3) and the use of esterified anthranilic acid we were able to obtain the ligand (LH), which we coordinated to the copper ion to obtain the [CuL] complex. The complex was characterised by high-resolution mass spectrometry, EPR, microanalysis, electrochemistry and absorption in the UV-Vis region. In the latter analysis, a non-linearity of the bands was observed in relation to the concentration of the complex in solution, as can be seen in figure 2. This is due to the possibility of the formation of polymers between them, as in figure 3.

After characterisation, catalytic activity tests were carried out using colorimetric methods, using p-nitrophenyl-β-d-glucopyranoside and H2O2 as substrates. The efficiency of the catalytic activity of the complex as an LPMO mimetic was observed as the concentration of H2O2 on the substrate increased. This activity can be analysed in figure 4.

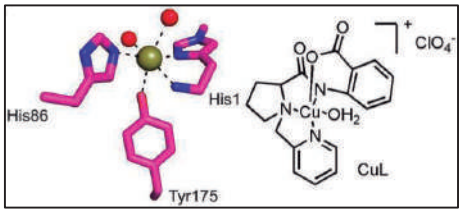


Figure 1.

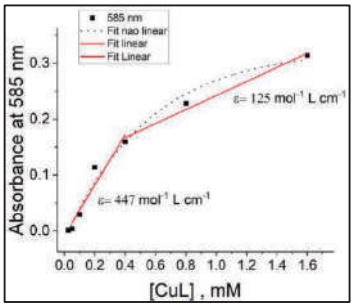


Figure 2.

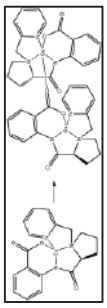


Figure 3.

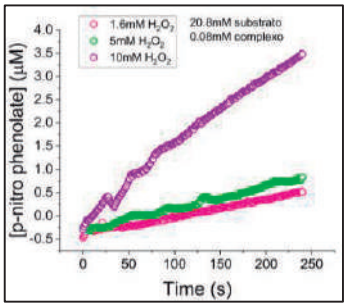


Figure 4.

It is concluded that the synthesised complex can be used as an LPMO mimetic.

Agradecimentos/Acknowledgments

We thank CNPq (142364/2023-1) and FAPESP (23/09722-0) for the financial support.

Área: INO

Synthesis of a new water-soluble tricationic Zn(II) porphyrin of interest for Antimicrobial Photodynamic Therapy (aPDT)

José F. Sarmento-Neto (PQ),[1] Maria Eduarda L. Oliveira (PG),[1] Jacqueline C. Bueno-Janice (PQ),[2] Clarissa G. C. Maia (PQ)[1], Dayse C. S. Martins (PQ)[3], Adriana Fontes (PQ),[2] Júlio S. Rebouças (PQ)[1]*

ferreira.system@gmail.com; jsreboucas@quimica.ufpb.br

[1]*Departamento de Química, UFPB;* [2]*Departamento de Biofísica e Radiobiologia, UFPE*; [3]Departamento de Química, UFMG.

Keywords: Zn(II) porphyrin, Porphyrins, Photosensitizers, Antimicrobial Photodynamic Therapy, Photodynamic Inactivation.

Highlights

Synthesis and characterization of a water-soluble A_3B-type Zn(II) porphyrin containing 2-*N*-methylpyridinium (A) and *O*-methylvanillin (B) moieties inspired by potent Zn(II) 2-*N*-alkylpyridylporphyrin-based photosensitizers.

Resumo/Abstract

Water-soluble Zn(II) porphyrins (ZnPs) derived from A_4-type 2-*N*-alkylpyridylporphyrins, ZnTalkyl-2-PyP^{4+} (alkyl = Me to *n*Hex), have been widely explored as promising photosensitizers (PSs) in Photodynamic Therapy (PDT) and Photodynamic Inactivation (PDI). ZnTalkyl-2-PyP^{4+}-based PS *in vivo* efficiency in PDT/PDI is associated not only with the good photophysical/photochemical properties of ZnPs but with also their positive charges that result in good solubility in biological fluids and facilitate interactions with cell membranes. Additionally, tailored PS lipophilicity is achieved by modulation of the pyridyl-moiety alkyl side-chain yielding improved cell uptake [1,2]. Inspired in these A_4-type ZnPs, a new tricationic ZnP was designed by replacing one 2-*N*-pyridinium group by a *O*-methylvanillin group, resulting in a A_3B-type Zn(II) porphyrin, ZnMVanTriM-2-PyP^{3+} (**Fig. 1**). The synthesis of ZnMVanTriM-2-PyP^{3+} was achieved by a three-step route: i) neutral free-base porphyrin synthesis **(1)** via condensation of pyrrole, 2-pyridinecarboxaldehyde and veratraldehyde (*O*-methylvanillin) in acetic acid as solvent/catalyst. ii) *N*-methylation of 2-pyridyl groups with methyl tosylate, resulting in the tricationic free-base porphyrin (**2**), and iii) Zn(II) metallation with Zn(II) acetate to yield ZnMVanTriM-2-PyP^{3+}. All free-bases and ZnP were characterized by UV-vis, Luminescence, and ^{1}H NMR spectroscopies, ESI-MS, and TLC-SiO_2. All characterization data were compared with those of the corresponding A_4-type analogues. UV-vis spectra were characteristic of either free base porphyrins (**1** and **2**) or metalloporphyrins (ZnP). ^{1}H NMR spectra showed the expected aromatic-*H* signals for porphyrins of A_3B-type symmetry along with methyl signals from vanillin and/or pyridinium moieties. N*H* pyrrole signal at δ –2.9 present in the free-bases was absent in ZnP, consistent with Zn(II) metallation. ESI-MS data showed the expected molecular ions. TLC-SiO_2 data for ZnMVanTriM-2-PyP^{3+} suggested that this ZnP may have similar lipophilicity to the potent, bioavailable PS Zn(II) *meso*-tetrakis(*N*-*n*-butylpyridinium-2-yl)porphyrin (ZnT*n*Bu-2-PyP^{4+}) [3]; the n-octanol/water partition coefficient (log Pow) was measured and confirmed the higher lipophilicity of ZnMVanTriM-2-PyP^{3+}. Overall, the data suggests that this fluorescent tricationic ZnP is a promising PS for antimicrobial PDT or PDI.

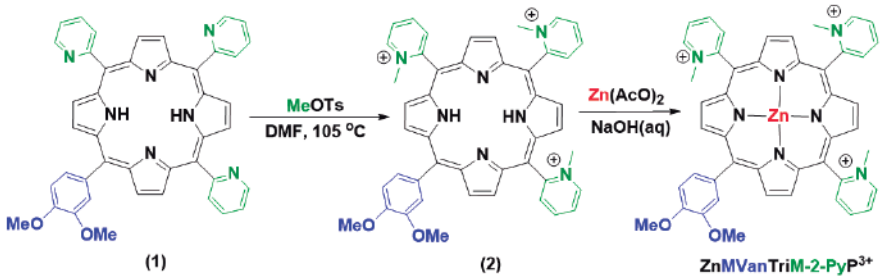


Figure 1. Schematic synthetic route for preparation of ZnTMVanTriM-2-PyP^{3+}.

[1] Souza, T.H.S.; Sarmento-Neto, J.F.; Souza, S.O.; Raposo, B.L.; Silva, B.P.; Borges, C.P.F.; Santos, B.S.; Cabral Filho, P.E.C.; Rebouças, J.S.; Fontes, A.; *J. Photochem. Photobiol. C: Photochem. Rev.*, **2021**, 49: 100454.
[2] Moghnie, S.; Tovmasyan, A.; Craik, J.; Batinić-Haberle, I.; Benov, L.; *Photochem. Photobiol. Sci.*, **2017**, 16: 1709.
[3] Thomas, M.; Craik, J.D.; Tovmasyan, A.; Batinić-Haberle, I.; Benov, L.;, *Future Microbiol.*, **2015**, 10: 709.
[4] Odeh, A.M.; Craik, J.D.; Ezzeddine, R.; Tovmasyan, A.; Batinić-Haberle, I.; Benov, L.; *PLoS One*, **2014**, 9: e108238.

Agradecimentos/Acknowledgments

CNPq, CAPES, FINEP, FACEPE, UFPB, INCT-CiMol.

Área: INO

Synthesis of Ruthenium Complex Incorporated in a Zinc Metal-Organic Framework as a Drug Delivery System

Alexandre L. Fernandes (IC),[1*] Marina P. Abuçafy (PQ),[2] Thales R. de Moura (PQ),[2] Sidney J. L. Ribeiro (PQ),[2] Luiz G. F. Lopes (PQ).[1]

alexchem02@alu.ufc.br;

[1]Departamento de Química Orgânica e Inorgânica, UFC; [2]Departamento de Química Analítica, Físico-Química e Inorgânica, UNESP.

Key Words: *Anticancer, NO, MOF, NO_2^-, NO^+, Ruthenium*

Highlights

Ruthenium complex incorporated into MOFs. Metal-Organic framework as a complex delivery system. Ruthenium complex as antitumoral active molecule.

Resumo/Abstract

NO-releasing species have been studied as possible platforms for cancer treatment. Depending on concentration, nitric oxide might inhibit cancer cell proliferation and angiogenesis in a tumour. NO antitumour effects might be a consequence of its reactivity towards specific cystein residues and might also be associated with NO and HNO interconversion. The compound cis-$[Ru(bpy)_2(SO_3)NO]PF_6$ is a NO donor, and has shown promising results as a possible drug for Chagas' disease, exhibiting trypanocide and antiproliferation activity. This complex originates from the anion cis$[Ru(bpy)_2(SO_3)NO_2]^-$ that converts to the cation cis-$[Ru(bpy)_2(SO_3)NO]^+$ in acid media. The aim of this work was to synthetize the complex $Na[Ru(bpy)_2(SO_3)NO_2]$ and study its incorporation into a Metal-Organic Framework (MOF) ZIF-8, using the one-pot method. We intend for this synergism between systems to result in the sustained release of the complex at a physiologically relevant concentration over extended periods. The complex cis-$Na[Ru(bpy)_2(SO_3)NO_2]$ was synthetized through 1 hour reflux of the precursor cis-$[Ru(bpy)_2Cl_2]$, previously synthetized by the research group, with Na_2SO_3 in a 1:1 ethanol/water mixture. Then, $NaNO_2$ was added, and reflux was kept for 2 hours and NaI solution was added for precipitation. The obtained solid was characterized through FTIR and UV-vis spectroscopy. The complex incorporation into a MOF was realized during ZIF-8 synthesis. For that purpose, saturated solution of the complex was prepared in methanol. In the same solution, $Zn(NO_3)_2.6H_2O$ was added and kept in agitation. Subsequently, a solution of the ligand, 2-MeIm, was added dropwise, and the reacting mixture was stirred for 1 hour at room temperature. In this way, it is expected that the MOF structure grows around the complex, forming a core-shell structure. ZIF-8 was characterized through FTIR spectroscopy, XRD and Scanning Electron Microscopy confirming the MOF structure. In the complex UV-vis spectrum in water, characteristic absorption bands were observed in 242 nm, 284 nm and 401 nm, in alignment with literature. In UV-vis spectrum in acetonitrile, the band in 401 nm suffered a shift towards a higher wavelenght region, which indicates it is a metal-ligand charge transfer band (MLCT), as the literature states. In FTIR spectrum, signs in 1340 $cm^{-1}$and 1290 cm^{-1} were assigned to N-O bond symmetric and assymetric stretching in the ligand NO_2^-, respectively. In ZIF-8 FTIR spectrum in KBr pellet, signs in 1580 cm^{-1} and 422 cm^{-1} were assigned to C=N and Zn-N bonds stretching, respectively. X-ray diffraction studies showed that the observed pattern of the ZIF-8 nanocrystals confirmed that the MOF maintained the structural integrity because of the high dregree correspondence between the patterns of diffraction at specific two-theta values (7.3°, 10.42 °, 12.7 °, 18.0 °), which were observed both in pure ZIF-8 and in cis-$Na[Ru(bpy)_2(SO_3)NO_2]$@ZIF-8. The incorporation of the complex to ZIF-8 was monitored through UV-vis spectroscopy. Drug loading content was 0.030 g g^{-1}, and encapsulation efficiency was 45.06%, showing the ability to incorporate an interesting amount of the complex. Cis-$Na[Ru(bpy)_2(SO_3)NO_2]$@ZIF-8 is being characterized to confirm the structural integrity of MOF after drug-occluded. The drug doxorubicin will be loaded in the MOF pores to optimize antitumor treatment and act in synergy with the complex. Complex releasing assays for cis-$Na[Ru(bpy)_2(SO_3)NO_2]$@ZIF-8 in PBS showed that, in 10 h, 13.70% of the complex was released at pH 7.4 and at least 17.50% of the complex was released at pH 5.0, showing the ability to release a greater amount of the complex in acid media. Cell viability assays are being conducted.

Agradecimentos/Acknowledgments

Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP): Processo 2023/13840-9. Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq).

Área: ____INO_____

Antioxidant capacity of biomass-derived carbon dots against mercury compound-induced oxidative stress in erythrocyte cells

Joyce Souza Nascimento (IC), [1] **Anna Paula de Lima Araujo (IC)**, [1] **Ivy Santos Soares (PG)**, [1] **Livia Elias da Silva (IC)**,[1] **Cintya D' Angeles do Espirito Santo Barbosa (PQ)** [1], **Sheila Oliveira de Souza (PG)**[1], **Ana Catarina Rezende Leite (PQ)**[1]

joyce.nascimento@iqb.ufal.br

[1] *Instituto de Química e Biotecnologia (IQB)*

Palavras Chave: *Fluorescência, carbon dots, antioxidante, Eritrócitos, Estresse oxidativo.*

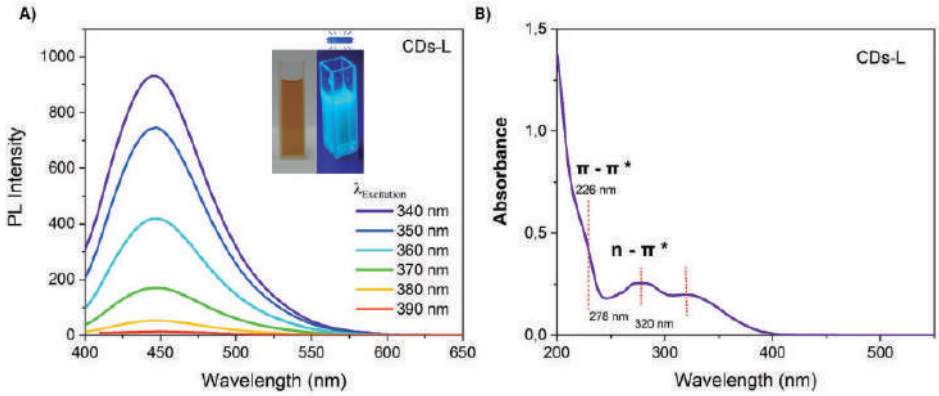
Highlights

Carbon dots derived from lemon bagasse;
Carbon dots efficient in capturing reactive oxygen species;
CDs-L reduced oxidative stress in human erythrocyte cells.

Resumo/Abstract

Os *carbon dots* (CDs) são nanopartículas luminescentes que vem despertando o interesse em diversas áreas, incluindo a biológica devido às características como emissão de luz sintonizável, baixa toxicidade, fotoestabilidade, biocompatibilidade etc.[1] Nesse sentido, o presente trabalho visa à síntese de CDs via micro-ondas a partir do extrato do bagaço de limão (CDs-L) e aplicação como agente antioxidante na redução de estresse oxidativo em células de eritrócitos humanos. Eritrócitos humanos foram submetidos a estresse oxidativo induzido pelo cloreto de mercúrio, com o CDs-L sendo empregado como agente antioxidante. As análises demonstraram que o CDs-L exibe emissão independente do comprimento onda de excitação (λ_{exc}), com máximo de fluorescência no azul em 450 nm (λ_{exc}= 340 nm) (Fig 1 a).[2] Além disto, o CDs-L apresentou grupos de superfície característicos das moléculas precursoras (O-H, N-H, CH_3, C=O, C=C, C-O) e absorções referentes às transições π-π* do núcleo grafítico e n-π* dos defeitos de superfície (Fig. 1. c). O CDs-L apresenta uma viabilidade celular superior a 80 % em células de HFF-1 para concentrações até 1000 µg/mL^{-1}, e capacidade antioxidante validada frente ao radical $^{\bullet}O_2^-$, ácido hipocloroso (HOCl) e pelo método DPPH. Ensaios preliminares demonstraram redução da espécie reativa de oxigênio, peróxido de hidrogênio, em eritrócitos humanos com ação do CDs-L. Por fim, essa pesquisa destaca o potencial do CDs-L como agente antioxidante visando seu uso no âmbito da medicina e da biotecnologia.

Fig. 1. a) Espectro de fotoluminescência e Suspensão aquosa do CDs (CDs-L) sem luz uv e com Luz Uv B) UV-vis



1. Meng, W. *et al.* **Energy e environmental materials**. doi:10.1002/2.12038, 2023.
2. Da silva. *et al.* **Frontiersin.org**. doi: 10.3389/frcrb.2023.1300811, 2023

Agradecimentos/Acknowledgments

UFAL IQB LUMIAM Finep CAPES CNPq

Área: INO

Theoretical and spectroscopic study of an europium(III) complex containing the zwitterionic form of 4-picolinic acid as antenna ligand

Ana Carolina C. do Nascimento (PG),[1] Esther S. Areas (PQ),[1] Glaucio B. Ferreira (PQ),[1] Fabio S. Miranda (PQ),[1] Guilherme P. Guedes (PQ),[1*]
anacellis@id.uff.br; guilherme_guedes@id.uff.br

[1]*Universidade Federal Fluminense, Instituto de Química, Departamento de Química Inorgânica*

Keywords: *europium, antenna ligand, semiempirical methods, TD-DFT, spectroscopy, UV-visible.*

Highlights

The absorption and luminescence properties of an europium(III) complex with an antenna were investigated with semiempirical and TD-DFT methods. The energy transfer rates were calculated in order to understand the role of 4-picolinc acid as antenna ligand.

Abstract

Lanthanide(III) complexes are widely studied due to their possible optical applications.[1] Although the emission of lanthanide ions is usually of low intensity, it can be intensified when coordinated to antenna ligands, which transfer energy to the lanthanide excited levels.[2] In this work, the spectroscopic properties on the UV-visible region of a mononuclear europium(III) complex with the zwietterionic form of 4-picolinic acid as antenna ligand[3] (Eu(4pic)) were studied through theoretical methods and compared to experimental data in order to evaluate the ligand's ability to sensitize the lanthanide ion.

Initially, one molecular unit of the crystal structure solved by single-crystal X-ray diffraction afforded the initial coordinates to the calculations, and only the hydrogen atoms' positions were optimized in the PBE/def2-TZVP level. Then, theoretical (TD-DFT) UV-visible absorption spectra were calculated with ten different hybrid and double-hybrid functionals (B3LYP, PBE0, CAM-B3LYP, ωB97X-D3, ωB88PP86, ωPBEPP86, SCS-B2GP-PLYP, SCS-PBE-QIDH, SCS-ωB88PP86 and SCS-ωPBEPP86) and the SARC2-DKH-QZVP basis set for the lanthanide ions and def2-TZVP for all ligand atoms, in order to compare the results with the experimental solid-state absorption spectrum, comparing the methodologies employed. All DFT calculations were performed in the ORCA 5.0.3 software. **Figure 1** shows the experimental and calculated spectra along with the calculated oscillator strengths at the SCS-PBE-QIDH level. The preliminary results show that the f-f forbidden transitions are not well modelled by TD-DFT methods.

In addition, based on the coordinates of the crystal structure and the experimental emission spectrum, the energy transfer rates from the singlet and triplet states of the ligand, as well as theoretical Judd-Ofelt parameters and radiative and non-radiative decay rates were calculated with the semiempirical method INDO/S, also on ORCA 5.0.3 software, considering the lanthanide ion a point charge of +3*e*. Those calculations were also performed considering the ethanol solvent effects with COSMO method; the coordinates were obtained from a geometry optimization in solution with the RM1 model implemented in the MOPAC 2019 software (**Figure 2**). **Table 1** presents the experimental and theoretical intensity parameters. Afterwards, the energy transfer rates, radiative and radiative and non-radiative decay rates and quantum efficiency will be calculated and compared to experimental values, to allow an increasing understanding of the energy transfer process occurring in this coordination compound.

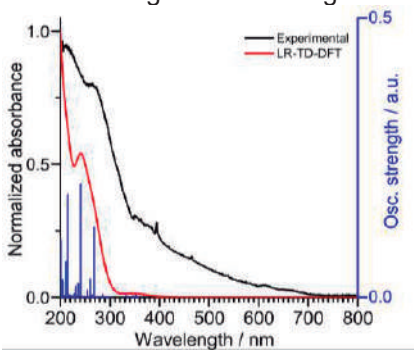


Fig. 1. Theoretical and experimental UV-visible absorption spectra calculated with functional SCS-PBE-QIDH.

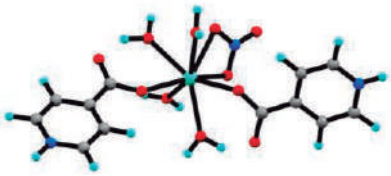


Fig. 2. Optimized structure with RM1 model and ethanol solvent effects included with the COSMO method. Green: Eu; Red: O; Blue: N; Gray: C; Light-blue: H.

Table 1. Experimental and theoretical Judd-Ofelt intensity parameters for compound Eu(4pic).

Intensity parameter	Solid	Solution
Experimental		
Ω_2 / 10^{-20} cm^{-2}	5.095	6.456
Ω_4 / 10^{-20} cm^{-2}	6.856	5.975
Theoretical		
Ω_2 / 10^{-20} cm^{-2}	5.09	7.34
Ω_4 / 10^{-20} cm^{-2}	6.86	4.84

[1] MONTEIRO, J. H. S. K. et al. *Journal of Luminescence*, **2022**, 245, 118768.
[2] SINGH, A. K. *Coordination Chemistry Reviews*, **2022**, 455, 214365.
[3] AREAS, E. S. et al. *Journal of the Brazilian Chemical Society*, **2023**, e-20230160.

Acknowledgments

CNPq, FAPERJ, CAPES, NACAD-UFRJ, LQC-UFF, LDRX-UFF and LAME-UFF.

Área: INO
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

The potential of alginate as a controlled release system for iron and complexes for symbiodinium cultivation

Gabriel R. M. Moreira (PG)[1*], Aline P. de Oliveira (PQ)[1], Cassiana S. Nomura (PQ)[1], Breno P. Espósito (PQ)[1]
gabrielrmmoreira@usp.br
[1] *Department of Fundamental Chemistry, USP*

Keywords: bleaching, alginate, iron

Highlights

Alginate beads were developed for the controlled release of iron, aiming applications in microalgae cultivation.

Resumo/Abstract

Corals are invertebrates that, for the most part, live in symbiosis with single-celled algae known as symbiodinium. They provide most of the nutrients for the animal, in exchange for protection and continuous exposure to light. The symbiosis is disturbed by environmental stressors and anthropogenic activity, leading to coral bleaching events (the disruption of the coral-symbiodinium symbiosis). Among various nutrients, iron (Fe) plays a crucial role in enhancing symbiodinium production. However, administering simple salts of this metal in marine environments can be detrimental as they disperse rapidly and may be assimilated by competing organisms. Therefore, the controlled release of well-defined chemical species of iron is required. In this work, we developed alginate (Alg) -based beads crosslinked with Ca^{2+} or Sr^{2+} that included either free Fe or its complexes with histidine and deferoxamine (FeHis and FeDFO, respectively). FTIR-ATR spectra of lyophilized beads (Fig 1a) show interactions between alginate and Fe, evidenced by the shift of bands from 3233 cm^{-1} to 3293 cm^{-1} and from 1084 cm^{-1} to 1585 cm^{-1}, corresponding to -OH and –COOH stretches, respectively. DSC measurements showed the shift of the melting temperature from 93 °C to 115 °C after Fe load. TGA (Fig 1b) reveals significant mass losses up to 200 °C, indicative of solvent release. Polymer bond degradation occurs at 280 °C and 290 °C for Alg and FeAlg, respectively. Elemental analyses (C/H/Fe, %) of Alg is 20.03/5.56/non detected, 16.05/4.95/1.15 for FeAlg. When comparing the crosslinkers, no significant differences are observed in FTIR, TGA, and elemental determinations. However, a higher release of Fe after 24 h is noted with Ca^{2+}. FeDFO is more easily released (Fig 1c), regardless of the crosslinker, while FeHis exhibits intermediate release, also independent of the crosslinker. In contrast, Fe dispersed in alginate shows a smaller release for both crosslinkers. The release of Fe can be controlled by the proper choice of ligands and crosslinkers. Studies with symbiodinians are currently underway.

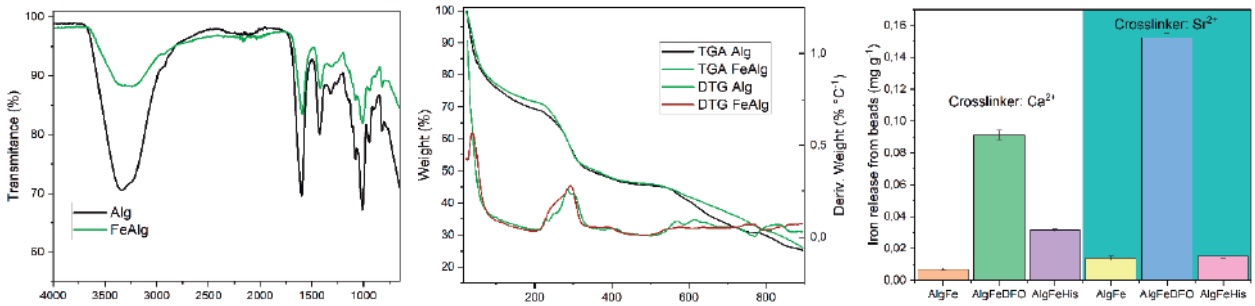


Figure 1: (a) FTIR-ATR spectra of Alg and FeAlg; (b) TGA and DTG curves of Alg and FeAlg; (c) Iron release after 24 h in artificial seawater

Acknowledgments

Prof. Dr. Rômulo Ando and Mr Ahmed Páez (ATR-FTIR measurements), Prof. Dr. Maria Teresa Machini and Dr. Cleber Liria (lyophilization), CNPq and FAPESP (financial support).

Área: INO

Towards the improvement of slow relaxation of magnetization and luminescence thermometry in multifunctional Dy^{III} single-molecule magnets

Airton G. Bispo-Jr (PQ),[1,2] Laurence Yeh (PG),[2] Dylan Errulat (PG),[2] Diogo A. Gálico (PQ),[2] Muralee Murugesu (PQ).[2]* Fernando A. Sigoli (PQ)[1*]

agbj@unicamp.br; * fsigoli@unicamp.br *; m.murugesu@uottawa.ca**

[1] *Department of Inorganic Chemistry, Institute of Chemistry, University of Campinas, Campinas 13083-970, Brazil.*
[2] *Department of Chemistry and Biomolecular Sciences, University of Ottawa, Ottawa, Ontario K1N 6N5, Canada.*

Keywords: Lanthanides, Single-Molecule Magnets, Luminescence Thermometry, X-ray, Rare-earths.

Highlights

- Single-molecule magnets (SMMs) as candidates for ultra-compact information storage devices;
- Lanthanide ions at the forefront of the state-of-the-art SMMs;
- Luminescence thermometry for the self-monitoring of the slow relaxation of magnetization.

Abstract

SMMs display potential applications in high-density data storage devices, molecular spintronics, and quantum computing devices.[1] With plentiful SMMs being investigated, Dy^{III} coordination compounds stand out due to the Dy^{III} unquenched angular moment in the $^6H_{15/2}$ ground state, strong spin−orbital coupling, and an unparalleled uniaxial anisotropy.[1] In these complexes, the temperature at the molecular level is of paramount importance, which can be monitored by luminescence thermometry.[2] However, boosting the combined SMM and luminescence performances still remains as an open challenge. That is because to maximize the effective barrier (U_{eff}) of Dy^{III} SMM, the target is usually to design systems with high pseudo-symmetries of the Dy^{III} polyhedron. Conversely, the luminescence thermometry based on Stark sublevels could be enhanced by distorted pseudo-symmetries of the Dy^{III} polyhedron. To work around such issue, herein, we discuss how the clever design of the luminescent $[Dy(acac)_3bpm]$ ($acac^-$ = acetylacetonate, bpm = 2,2'-bipyrimidine) monomer helps to understand how the symmetry and bond distances of the Dy^{III} polyhedron can play synergistically to boost the U_{eff} of Dy^{III} β-diketonate complexes.[3] By taking advantage of the ligand-to-Dy^{III} energy transfer, the complex shows luminescence thermometry with thermal sensitivity of 0.2 – 0.7% K^{-1} within the SMM operation range. The $[Dy(acac)_3bpm]$ complex operates as a zero-field SMM with U_{eff} = 309 K. The value is among the largest reported so far for mononuclear Dy^{III} β-diketone complexes as well as for Dy^{III} SMMs operating as luminescent temperature probes. These features come from the slightly-distorted D_{4d} pseudo-symmetry displayed by the Dy^{III} polyhedron that enables a considerable separation of the Kramers doublets arising from the Dy^{III} $^6H_{15/2}$ ground state. Moreover, bpm also induces long Dy – N bonds in $[Dy(acac)_3bpm]$ that should contribute to decrease the transverse crystal field terms and enhance the U_{eff}. It is noteworthy that from the synthetic point of view, this complex is also an attractive building block for extended polynuclear structures due to the "open coordination pocket" on bpm. Therefore, the lessons learned from this study help understand how the clever molecular design combined to the electronic nature of ligands can play synergistically to enhance the magnetic and luminescence performance of multifunctional Dy^{III} β-diketonate SMMs.

[1] K. L. M. Harriman, D. Errulat, M. Murugesu, *Trends Chem.*, 2019, **1**, 425.
[2] D. Errulat, R. Marin, D. A. Gálico, K. L. M. Harriman, A. Pialat, B. Gabidullin, F. Iikawa, O. D. D. Couto-Jr., J. O. Moilanen, E. Hemmer, F. A. Sigoli, M. Murugesu, *ACS Cent. Sci.*, 2019, **5**, 1187.
[3] A. G. Bispo-Jr, L. Yeh, D. Errulat, D. A. Gálico, Fernando Aparecido Sigoli, M. Murugesu, *Chem. Commun.*, 2023, **59**, 8723.

Acknowledgments

INCT/INOMAT (CNPq 465452/2014-0 and FAPESP 50906-9/2014), FAPESP (2021/06326-1, 2021/09755-0, 2019/23763-6, and 2020/02614-0), CAPES, University of Ottawa, the Canadian Foundation for Innovation (CFI), and the Natural Sciences and Engineering Research Council of Canada (NSERC).

Área: INO

Unusually strong ligand field splitting observed in an anionic Eu^{3+} *tetrakis* (β-diketonate) complex with a small organic counterion

Lucca Blois (PG),[1*] Israel F. Costa (PQ),[1] João Honorato (PQ),[1] Albano N. Carneiro Neto (PQ),[2] Oscar L Malta (PQ),[3] and Hermi F. Brito (PQ)[1]**

***blois@iq.usp.br; **hefbrito@iq.usp.br**

[1]Departamento de Química Fundamental, Instituto de Química, Universidade de São Paulo; [2] Physics Department and CICECO – Aveiro Institute of Materials, University of Aveiro; [3]Departamento de Química Fundamental, Universidade Federal de Pernambuco

Palavras Chave: Lantanídeos, Luminescência, Teoria do Campo Ligante

Highlights

An unusually strong ligand field splitting was observed for a special Eu^{3+} complex with a small organic counterion. single-crystal structure for the complex was obtained and when Ligand Field (LF) Theory is applied to such structure the experimental large splitting is reproduced. Analogous complex with a larger cation was also prepared and no such large splitting was observed. Single-crystal X-ray diffraction was obtained, and LF calculations were also performed.

Abstract

Lanthanide complexes (and specially the β-diketonates) are wildly investigated due to their remarkable photophysical properties and every year new and interesting complexes are studied [1]. In this context, we have prepared a new *tetrakis* anionic europium (III) complex with the 2-thenoyltrifluoroacetone ligand (well known to yield highly luminescent Eu^{3+} complexes) containing the small 1-ethyl-3-methylimidazolium counterion, C_2mim[Eu(tta)$_4$]. This complex was characterized by elemental analysis and mass spectrometry. The luminescence spectrum of the complex in the solid state (**Figure 1a**) showed an unusually high ligand field splitting of 293 cm^{-1} in the $^5D_0 \rightarrow {}^7F_1$ transition. Single-crystal X-ray diffraction data (**Figure 1b**) were obtained, and Ligand Field (LF) Theory calculations (Simple Overlap Model [2]) performed on the experimental geometry showed good results in reproducing the observed splitting. Our hypothesis is that small substituents allow for a shorter cation-anion distance that leads to more distortions in the first coordination sphere, leading to high B_q^2 parameters ($B_0^2 = 660$ and $B_2^2 = 673$ cm^{-1}) and thus to a larger LF splitting. The analogous complex prepared with a bulkier cation 1-butyl-3-methylimidazolium, C_4mim[Eu(tta)$_4$], showed no anomaly in the ligand field effect, thus supporting our initial hypothesis. Single-crystal X-ray diffraction data were obtained, and theoretical ligand field calculations were also performed for the C_4mim complex.

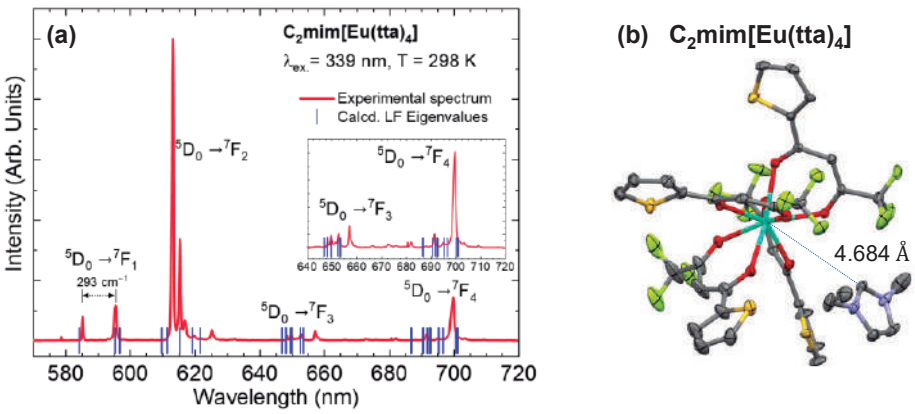


Figure 1: (a) Crystal structure of the C_2mim[Eu(tta)$_4$] complex drawn at 50% probability and (b) Emission spectrum of the solid recorded at room temperature (red line) and SOM ligand field theory eigenvalues (blue markers)

Acknowledgments

L. Blois thanks FAPESP for the PhD grant (2020/16795-6). This work was developed under the scope of FAPESP thematic project 2021/08111-2. The authors also thank CAPES for the support to PPG-Química from IQ-USP and to CNPq for the funding. H.F. Brito is grateful to CNPq for the 1A "Produtividade" fellowship (Grant 308872/2022-3).

[1] I.F. Costa; L. Blois; T.B. Paolini; I.P. Assunção *et al*; *Coordination Chemistry Reviews*, 502, 215590 (2024)
[2] O.L. Malta, *Chemical Physics Letters*, 88, 353–356 (1982).

Área: INO

Uso de catalisadores baseados em metaloporfirinas e sólidos lamelares para a reação de adição de CO_2 à epóxidos

Adriana D. Dalla Costa (IC), Everton H. Santos (PG), Eduardo M. Iwaya (PG),Shirley Nakagaki (PQ)*

adriana.duarte@ufpr.br; shirleyn@ufpr.br

Grupo de Bioinôrganica e Catálise, Departamento de Química, Universidade Federal do Paraná, UFPR.

Palavras Chave: Porfirina, Catálise, adição de CO_2, sólidos lamelares.

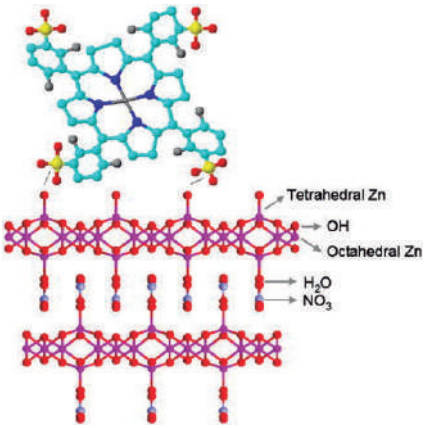
Highlights

Use of catalysts based on metalloporphyrins and layered solids for the CO_2 addition reaction to epoxides.

Immobilization of metalloporphyrin in layered zinc hydroxy nitrate for the CO_2 addition reaction to styrene oxide.

Resumo/Abstract

Catalisadores que sejam versáteis, eficientes e multifuncionais vêm se tornando cada vez mais necessários, principalmente quando se pensa no atual cenário de aquecimento global, sendo a emissão de CO_2 um dos principais agravantes. Pensando no aproveitamento de CO_2, uma reação interessante é a sua adição à epóxidos [1]. Esta reação vem sendo cada vez mais estudada uma vez que os carbonatos produzidos podem ser utilizados como matéria-prima para diferentes tipos de aplicações. Entretanto, a rota tradicional de produção dos carbonatos cíclicos geralmente é conduzida a pressões e temperaturas relativamente altas na presença de catalisadores, em alguns casos, considerados tóxicos [2]. Portanto, propor rotas alternativas, envolvendo o uso de catalisadores mais eficientes, se faz necessária. As metaloporfirinas (MP) são catalisadores extremamente versáteis para uma gama de reações. As MP são compostos macrocíclicos tetrapirrólicos, insaturados e altamente conjugados. As MP podem ser utilizadas como catalisadores em reações de oxidação e redução, sendo eficientes em meio homogêneo [3]. Todavia, em meio homogêneo, dependendo da MP e das condições de reação, podem sofrer reações secundárias, como as interações bimoleculares e auto degradação oxidativa, levando a inativação ou destruição da espécie catalítica ativa. Como alternativa, a heterogenização de MP pela sua imobilização em suportes inorgânicos tem sido muito explorada visando obter um sólido catalítico mais robusto para processos heterogêneos, além de possibilitar o fácil reuso do catalisador [4]. Um exemplo de suporte para a imobilização das MP são os compostos lamelares como, por exemplo, o hidroxinitrato de zinco (HNZ), sendo esse formado pelo empilhamento de unidades bidimensionais (lamelas) conectadas umas às outras por forças fracas, como de van der Waals ou interações eletrostáticas (Figura). Neste trabalho, um catalisador multifuncional baseado em uma metaloporfirina (Cloreto de [5,10,15,20-Tetrakis(2,6-dicloro-3-sulfonatofenilporfirinato)ferro(III)] de sódio), imobilizada em HNZ foi preparado e sua atividade catalítica avaliada na reação de adição de CO_2 a um epóxido, levando a resultados promissores.



[1] N. Thonemann, Energia Aplicada, 263 (2020) 114599.

[2] D. Niu, Z. Wu, L. Zhang, R. Dub, H. Xu, X. Zhang, Chinese Journal of Catalysis, 37 (2016) 1076-1080.

[3] G. S. Machado, G. M. Ucoski, O. J. Lima, K. J. Ciuffi, F. Wypych, S. Nakagaki, Appl. Catal. A 460-461 (2013) 124-131.

[4] G.S. Machado, G.G.C. Arízaga, F. Wypych, S. Nakagaki, J. Catal. 274 (2010) 130.

Agradecimentos/Acknowledgments

CNPq UFPR

Área: INO

Zeolite-Imidazole Frameworks with Nd^{3+} Ions: Synthesis, Characterization, and Its Potential Use as a Drug Delivery Platform for Leishmaniasis Treatment

Angela Assis[a] (IC)[1], Daniel Reis Moraes (IC)[1], Kleyton Ritomar Monteiro da Silva[a] (PG)[1], Uéslen Rocha Silva (PQ)[2], Cintya D' Angeles do Espírito Santo Barbos[a] (PQ)[1] e Rodrigo da Silva Viana (PQ)[3].

angela.assis@iqb.ufal.br

[1]Institute of Chemistry and Biotechnology, UFAL; [2]Institute of Physics,UFAL; [3]Technology Center, UFAL.

Keywords: *Metal-Organic Frameworks; Neodymium, Luminescence.*

Highlights

- Incorporation process of Nd^{3+} ions did not promote significant changes in the crystalline structure of the materials.
- Detailed study of the photoluminescence was conducted.
- Initial drug loading assays were performed using $KSb(OH)_6$.

Abstract

Zeolitic Imidazole Frameworks-8 (ZIF-8) represent a class of highly porous coordination compounds known for Its potential as a platform for loading and releasing bioactive molecules [1,2]. Incorporating luminescent lanthanide ions, such as Nd^{3+}, into ZIF-8 expands its applications, including drug detection and elucidating action pathways in vitro and in vivo [3]. This work focuses on synthesizing and characterizing ZIF-8 incorporated with Nd^{3+} ions (ZIF-8:Ndx%). Additionally, we explore its potential as an advanced material for loading $KSb(OH)_6$ as a potential leishmanicidal agent. ZIF-8:Ndx% were synthesized using room temperature crystallization, involving a combination of Zn^{2+} and Nd^{3+} ions with the 2-methylimidazole ligand. For $KSb(OH)_6$ adsorption, the protocol described by Horcajada *et al.* [4]. was used. X-ray diffraction analysis for ZIF-8:Ndx% confirmed no significant alterations in the original crystal structure post-synthesis. Photoluminescence results revealed characteristic transitions of Nd^{3+} ion: $^4F_{3/2} \rightarrow {}^4I_{9/2,11/2,13/2}$ in the emission spectrum. Furthermore, analyses of the loaded material, ZIF-8:x%-$KSb(OH)_6$, indicated efficient adsorption, as evidenced by the presence of both ZIF-8 and the drug.

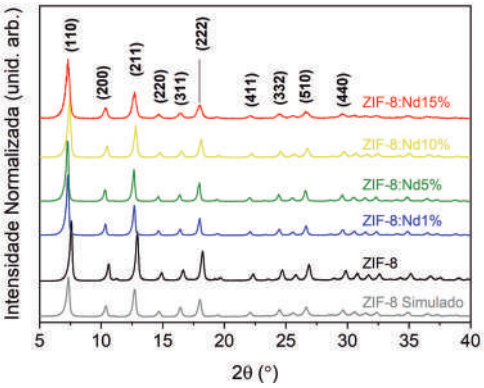


Figure 1: X-ray diffraction for ZIF-8, ZIF-8:Nd: (1%, 5%,10% e 15%) and ZIF-8 simulated data obtained from the literature.

References:
[1] Journal of Materials Chemistry A, 2, 40,16811-16831, 2014.
[2] Optical Materials, 111,110581, 2021.
[3] Coordination Chemistry Reviews, 381, 104–134, 2019
[4] Nature materials, v. 9, n. 2, p. 172-178, 2010

Acknowledgments

UFAL LUMIAM TecNano IQB CAPES CNPq PPGQB PGMateriais

MAT

Química de Materiais

Sociedade Brasileira de Química

Area: MAT

ACRYLATES AND METHACRYLATES COPOLYMERS AS ANTIFREEZE ADDITIVES FOR BIOFUELS

Gabriel S.P. Souza (IC),[1] Amanda G.F. Villain (IC),[1] Lucas Nakashima (IC-M),[1] Mayara Powrosnek (PG),[1] Aline S. Muniz (PQ),[1] Valéria G. Costa (PQ),[2] Angelo R.S. Oliveira (PQ),[1] Maria Aparecida F. César-Oliveira (PQ).[1]*

mafco@ufpr.br

[1]Departamento de Química – LEQUIPE, UFPR; [2]Divisão de Materiais – LAMAP, INT

Keywords: *Biofuel, Biodiesel, Cold Flow, Antifreeze Additives, Acrylic Copolymers, Pour Point.*

Highlights

Development of antifreeze polymeric additives allows the use of low-quality residual oils and fats to produce high-quality biofuels throughout the national territory.

Abstract

The growing need for the use and production of fuels needs to be combined with the concern with the preservation of the environment and the reduction of pollutant emissions. In this sense, despite recent advances in the development of new biofuels, biodiesel is still an excellent alternative to petrodiesel. However, despite the large number of advantages that biodiesel presents, some disadvantages are known, such as the tendency to solidify with the reduction of the ambient temperature. The properties of biodiesel are directly related to the chemical composition of the raw material that gave rise to it. Low value-added oils and fats, including residues and rejects from the food industry and other productive segments, have been studied to diversify the raw material and lower production costs. In many cases, a high content of saturated esters is observed, which promotes the solidification of biodiesel even at moderate temperatures (around 10 to 15ºC, for example). The problem is aggravated in the winter periods when much of the country, especially the southern region, faces much lower temperatures, making it difficult to widely use biodiesel, in addition to the restrictions imposed on production and transportation processes. Consequently, studies are increasingly needed to improve the cold flow properties of biodiesel from different raw materials through the development of additives capable of reducing the solidification temperature of biofuels, making crystallization occur only at temperatures much lower than those observed anywhere in Brazil. The cold flow properties of biofuels can be monitored mainly by determining the Cloud Point (CP), Cold Filter Plugging Point (CFPP) and the Pour Point (PP).

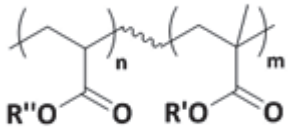


Fig.1 – Acrylate and alkyl methacrylate copolymers

Eighteen different acrylic-methacrylic copolymers were synthesized by polymerization in toluene solution, via free radicals initiated by benzoyl peroxide, through the combination of dodecyl acrylate (DDA), octadecyl methacrylate (ODMA), dodecyl methacrylate (DDMA) and octadecyl acrylate (ODA), in different molar compositions. DDA-ODMA copolymers (Fig.1: R"= C_{12}; R'= C18) were obtained at yields of 50-75%. ODA–DDMA copolymers (Fig.1: R"= C_{18}; R'= C_{12}) were obtained at yields of 55-90%.

All copolymers were characterized by FTIR and ^{1}H and ^{13}C NMR and evaluated as reducing soybean biodiesel (B100) CP and PP (CP= 11ºC; PP= 9ºC) and B13 blend with S10 diesel (13% soybean biodiesel + 87% S10 diesel; CP= -7ºC; PP= -9ºC). Significant reductions in PP values were obtained with only 1000 ppm of several of the synthesized additives, especially the copolymers that presented high levels of dodecyl methacrylate, such as PDDMA-ODA 80/20 that reduced the PP of B13 to -16ºC and PDDMA-ODA 90/10 that reduced the PP of B13 to -21ºC. The determination of the structure-performance relationship of copolymers as antifreeze additives of these biofuels contributes to the development of additives that allow the use of low-value, residual feedstocks in the production of quality biofuels.

References: MUNIZ, A.S. *et al.* Energy & Fuels v.34, p.5907-16, 2020; FERRAZ, F.A. *et al.* J. Polym. Sci., Part A: Polym. Chem. v.56, p.1039-45, 2018.

Acknowledgments/Acknowledgmentsts

UFPR LQUIP BioDiesel MINISTÉRIO DA CIÊNCIA, TECNOLOGIA, INOVAÇÕES E COMUNICAÇÕES BRASIL FINEP CNPq INSTITUTO NACIONAL DE TECNOLOGIA INT Laboratório RMN

Área: MAT

Acrylic biomaterials fast curing in ambient temperature for cranioplasty applications

Matheus A. Coelho (PG),[1] Marcos L. Dias (PQ),[1] Alexandre M. Rossi (PQ),[2]

Matheus.alves@ima.ufrj.br;

[1]*Instituto de Macromoléculas Professora Eloisa Mano (IMA-UFRJ);* [2]*Centro Brasileiro de Pesquisas Físicas (CBPF)*

keywords: *PMMA; Amine; Cranioplasty; biomaterials.*

Highlights

New lower toxicity aromatic, aliphatic and heterocyclic tertiary amines were Investigated as co-initiators in low temperature free radical polymerizations in different concentrations, showing increase in the reaction rate with concentration increase.

Resumo/Abstract

Cranioplasty is a surgical procedure whose purpose is to repair and reconstruct bone defects in the skull, caused by severe head trauma, through a permanent prosthesis. Currently one of the most used materials for this purpose is poly(methyl methacrylate) (PMMA). The main advantage of PMMA-based prostheses includes the ability to be molded and prefabricated to the shape of the cranial defect intraoperatively. Bone cement is obtained from the free radical polymerization of methyl methacrylate (MMA), using the benzoyl peroxide (BPO)/tertiary amine initiation system. The standard tertiary amine used is *N,N*-dimethyl-p-toluidine (DMT). Studies indicate that DMT produces cytotoxicity, a fact that encourages the scientific community to discover more biocompatible amines. Thus, the objective of this work was to investigate the efficiency of different tertiary amines: aliphatic, heterocyclic, and aromatic in polymerizations at ambient temperature in comparison with the standard tertiary amine. The influence of the concentration of tertiary amine and the molar mass of PMMA on the reaction kinetics in polymerizations at room temperature for the synthesis of bone cements applied to cranioplasty was also investigated. All experiments were conducted at ambient temperature, using different concentrations of tertiary amines. The studies found that the concentration of tertiary amine interferes with the speed of the reaction. The higher the concentration of tertiary amine in the reaction system, the faster the reaction, indicating the influence of tertiary amine on the reaction rate. It was also possible to observe that the higher the concentration of tertiary amine, the lower the glass transition temperature (tg) of the material. The percentage of residual monomer during the reaction was monitored using FTIR. All aliphatic and heterocyclic amines studied showed only a slight increase in temperature immediately in the first minute of reaction, followed by a decrease until reaching room temperature, not being able to initiate the proposed polymerization system. Polymerization reactions with aromatic amines are the most efficient. The new organic amine proved to be a promising substitute for the standard amine used in acrylic bone cement polymerization systems, as it presents a lower exothermic peak, reaching around 50 °C. In terms of molar mass, the lower the molar mass of the polymer, the faster the reaction occurs.

Amine (%)	$Temp_{(peak)}$ (°C)	Time (min.)	Tg (°C)	M_w (g/mol)
0,75	70	9	104,3	130.000
1,50	75	8	101,7	96.500
3,75	81	3	96,3	93.000

Table1. Peak temperature, glass transition and molar mass of acrylic bone cement at different concentrations amine.

References:

[1] ASCHILIAS, D. S.; SIDERIDOU, I. D. Study of the effect two BPO/amine initiation systems on the free-radical polymerization of mma. Macromolecules, v.37, p. 4254–4265, 2007.

Agradecimentos/Acknowledgments

The authors would like to thank CnPQ for the support.

Área: MAT – Química de Materiais

Advanced Structural Characterization of Luminescent Halide Perovskites Nanostructures through Transmission and Cryo-Electron Microscopy

Olavo Fiamencini Verruma* **(PG),[1,2] Ana Flávia Nogueira (PQ),[2] João Batista Souza Junior (PQ)[1,2]**

olavo.verruma@lnnano.cnpem.br

[1]National Center for Energy and Materials Research (CNPEM) - National Nanotechnology Laboratory (LNNano);
[2]State University of Campinas (UNICAMP) - Institute of Chemistry (IQ).
Keywords: Nanomaterials, Structural Characterization of Nanomaterials, Quantum Dots, Perovskites, Luminescence.

Highlights

Nanostructured perovskites, also known as perovskite quantum dots, exhibit controlled optical properties and high quantum fluorescence yield. Advanced electron microscopy techniques provide crucial data for nanomaterial characterization, identifying structural defects to enhance the efficiency of optoelectronic devices.

Resumo/Abstract

Semiconductor materials play a crucial role in our society due to their significant economic, technological, and social impact. These materials are integral to the functioning of everyday electronic devices such as TVs, cell phones, computers, and various other electronic components[1]. Perovskite nanostructures, also known as perovskite quantum dots, which hold immense promise for advancing optoelectronic devices. Achieving high quantum fluorescence yield and precise control over optical properties is paramount for optimizing semiconductor usage in such devices. To attain perovskites with tailored optical properties, especially in the blue spectrum, meticulous control over the morphology, chemistry, and structure of nanoparticles is imperative[2]. This necessitates the utilization of statistically accurate and representative structural characterization techniques capable of pinpointing atomic-level defects within the produced systems. Advanced techniques like Transmission Electron Microscopy (TEM) offer invaluable insights into both the morphology and structural correlations of nanomaterials[3]. However, challenges arise due to the interaction of certain perovskite components with the electron beam, leading to structural decomposition. Consequently, there's a scarcity of advanced TEM studies on perovskites documented in the literature, largely due to the difficulties in mitigating electron beam-induced damage. In this work, novel methods for sample preparation and data collection will be explored, including low-dose imaging and serial image acquisition akin to Cryo-EM processes. These approaches aim to furnish critical information for identifying structural defects that hamper device efficiency and can be rectified through innovative synthesis methods and ligand exchanges. The overarching goal is to conduct advanced characterization of perovskite-type nanostructured systems, thereby yielding samples with reduced defects and enhanced photoluminescence emission. Such advancements hold promise for future applications in perovskite light-emitting diodes (PeLEDs), paving the way for more efficient and sustainable optoelectronic devices.

[1] Jena, A. K., Kulkarni, A. & Miyasaka, T. Halide Perovskite Photovoltaics: Background, Status, and Future Prospects. *Chem Rev* **119**, 3036–3103 (2019);
[2] Chen, D. & Chen, X. Luminescent perovskite quantum dots: synthesis, microstructures, optical properties, and applications. *J Mater Chem C Mater* **7**, 1413–1446 (2019);
[3] Park, J. *et al.* 3D structure of individual nanocrystals in solution by electron microscopy. *Science (1979)* **349**, 290–295 (2015).

Agradecimentos/Acknowledgments

FAPESP, CNPq, CAPES, IQ-UNICAMP, CNPEM.

Área: MAT

Amphiphilic main-chain poly(fullerene xylene)s

Eleftheria Batagianni[1] (PG), Jessyka C. Bittencourt[1,2] (PG), Vitor Fernandes Moreno[1,3] (PG), Deuber L. Silva Agostini[2] (PQ), Patricia Targon Campana[5] (PQ), Clarissa Olivati[2] (PQ), Luiz Carlos da Silva Filho[3] (PQ), Carlos F. O. Graeff[3] (PQ), Didier Bégué[1] (PQ), Roger C. Hiorns[1,3*] (PQ)

roger-clive.hiorns@cnrs.fr

[1] CNRS/Univ Pau & Pays Adour, Institut des Science Analytiques et Physico-Chimie pour l'Environnement et les Materiaux, Pau, France;
[2] Faculdade de Ciências e Tecnologia, UNESP Presidente Prudente-SP, Brazil;
[3] Departamento de Química, Faculdade de Ciências, UNESP Bauru-SP, Brazil;
[4] Departamento de Física, Faculdade de Ciências, UNESP Bauru-SP, Brazil;
[5] EACH-USP, School of Arts, Sciences and Humanities, University of São Paulo, 03828000, São Paulo, SP, Brazil

Highlights

This presentation introduces poly(fullerene)s. It reviews the various methods of making them, and then looks at new methods that make possible the preparation of amphiphilic copolymers that might be of use for both solar cells and antibacterial applications alike.

Resumo/Abstract

Main-chain fullerene-based polymers are still relatively rare. However, because they combine the properties of fullerene, such as exceptional electron acceptance capability and semiconductivity, with those of polymers such as good solubility and excellent film-forming characteristics, they are gaining particular interest for their use as interlayers in photovoltaics and organic electronics. They exhibit many of the properties of fullerenes, combined with the ability to be formed as a regular thin film. For examples, recent work has demonstrated their use as interlayers in perovskite solar cells to give efficiencies around 23% and good stabilities[1], and that they might find use in ammonia sensors [2].

The methodology used to make these polymers can impact extremely heavily on its final physico-chemical properties. Therefore in this work, by way of introduction, we review the different known methods of preparing main-chain poly(fullerene)s and how those methods can modify the polymer's behaviour in application [3-6]. We further look to new methods for reacting with the chain-ends of these materials to expand their properties, especially by combining them with poly(ethylene glycol) to give amphiphilic materials. It is expected that these new materials might be of interest for 'green' processing of interlayers and drug delivery systems.

References

[1] *J. Yin, X. Shi, L Wang, H. Yan, S Chen, Angew. Chem. Int. Ed.* **2022,** *61,* e202210610.
[2] A. V. Santos Simõis, L. K. Martins Roncaselli, V. J. Rodrigues de Oliveira, M. E. Rocha Santos Medina, H. H. Ramanitra, M. Stephen, D. L. Silva Agostini, R. C. Hiorns, C. de Almeida Olivati, **2021**, *24*(1), *Materials Research*, https://doi.org/10.1590/1980-5373-MR-2021-0435
[3] M. Stephen, H. H. Ramanitra, H. Santos Silva, S. A. Dowland, D. Bégué, G. Juška, G. E. Morse, A. Distler, R. C. Hiorns, *Chem. Comm.*, **2016**, *52*, 61070.
[4] H. Santos Silva, H. H. Ramanitra, B. A. Bregadiolli, A. Tournebize, D. Bégué, S. Dowland, C. Lartigau-Dagron, C. F. O. Graeff, A. Distler, H. Peisert, T. Chassé, R. C. Hiorns, *J. Polym. Sci., Pt B, Polym. Phys.,* **2019**, *57*, 1434.
[5] L. Roncaselli, E. da Silva, M. Braunger, H. Ramanitra, M. Stephen, L. Citolino, J. Fernandes, A. Simõis, C. J. Constantino, D. Agostini, D. Bégué, R. Hiorns, C. Olivati, *Physical Chemistry Chemical Physics*, **2022**, *24*, 12442.
[6] R. C. Hiorns, E. Cloutet, E. Ibarboure, L. Vignau, N. Lemaitre, S. Guillerez, C. Absalon, H. Cramail, *Macromolecules*, **2009**, *42*, 3549.

Agradecimentos/Acknowledgments

This work is indebted to: Campus France Eiffel 2021 968030F; CAPES-PrInt 8887.893208/2023-00; European Union Seventh Framework Program (FP7) under grant agreement ESTABLIS no. 290022; and grant 2023/12686-6 of the São Paulo Research Foundation (FAPESP).

Área: MAT

Bentonite@chitosan@gelatin nanocomposites as adsorbents for toxic metals

Eduardo M. Camboim (IC)[1*], Susiely S. Tomas (PG)[1], Lucilane G. Oliveira (PG)[1], Maria G. Fonseca (PQ)[1]

eduardomcamboim@gmail.com

[1]*Núcleo de Pesquisas e Extensão - Laboratório de Combustíveis e Materiais, Universidade Federal da Paraíba, 58059-970, João Pessoa, PB.*

Keywords: *Bentonite, Chitosan, Gelatin, Bionanocomposites, Copper(II).*

Highlights

- Bionanocomposites were obtained via intercalation of chitosan and gelatin into montmomorillonite;
- The modification of the clay mineral was confirmed by structural, morphological, and thermal techniques;
- The biocomposites presented different Cu(II) adsorption capacities dependent on experimental conditions.

Resumo/Abstract

Toxic metal cations, like copper (II), are substances associated with the contamination of aquatic environments, and the increase in their intake requires the development of new techniques for water cleaning. In this sense, a promising strategy is the use of natural or chemically modified clay minerals, such as montmorillonite, as adsorbents for the metal's removal from water[1]. The use of polysaccharides and/or proteins as modifiers of montmorillonite originates inorganic-organic hybrid materials[2], which may improve the adsorption capabilities of the clay mineral. Herein, sodium bentonite (Na^+-Bent) and chitosan hybrids (Na^+-Bent@CS) with a proportion of 100% of the clay's cationic exchange capacity were synthesized, and then modified with different gelatin (GEL) amount of 10 and 20%wt in relation to the total mass of Na^+-Bent@CS to form Na^+-Bent@CS@GEL10 and Na^+-Bent@CS@GEL20 hybrids, respectively. The solids were characterized by X-ray diffractometry (XRD), infrared spectroscopy (FT-IR), thermogravimetry and field emission scanning electron microscopy, whose results indicated the formation of the intercalation hybrids in the evaluated conditions as indicated by the XRD patterns (Fig. 1). FT-IR was useful to confirm the presence of the biopolymer and protein in the Na^+-Bent. For Na^+-Bent, characteristic bands occurred at 3638, which was assigned to the -OH structural stretching of the octahedral sheet (M-OH, M = Al^{III}, Mg^{II}), and at 3443 cm^{-1} to -OH stretching of water and silanol[1]. OH deformation of the interlayer water occurred at 1641 cm^{-1}. Si-O antisymmetric and symmetrical stretchings occurred at 1117 and 1045 cm^{-1}. Al-Al-OH and Al-Mg-OH deformations occurred at 915 and 850 cm^{-1}, respectively. While Si-O-Al and Si-O-Si deformation bands were observed at 521 and 466 cm^{-1}, respectively. For hybrids, spectra presented typical bands associated to -CH anti symmetrical and symmetrical stretchings at 2940 and 2890 cm^{-1} as well CH_2 and -CH_3 deformation at ~1380 cm^{-1}. Absorption of the -NH_2 group was observed in the region of 1527–1550 cm^{-1}. Hybrids demonstrated different adsorption capacities in pH (3, 4, 5, and 6), adsorbent mass (50, 75, 100, and 125 mg), contact time (1, 2, 3, and 4 h) and initial copper (II) concentrations (10^{-3} to 10^{-2} mol L^{-1}). Na^+-Bent@CS hybrid exhibited the highest adsorption performance at pH 6, with a saturation at 0.005 mol L^{-1}, after a 3 h, 125 mg of the adsorbent, resulting in 0.85 mmol of Cu(II) removed per gram of solid. Proposed bionanocomposites were successfully obtained, and Cu(II) removal was improved by using the hybrids.

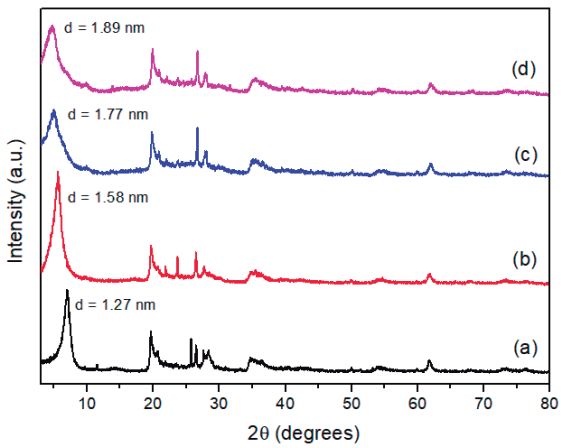


Fig. 1. XRD patterns for (a) Na^+-Bent, (b) Na^+-Bent@CS, (c) Na^+-Bent@CS@GEL10, and (d)Na^+-Bent@CS@GEL20

[1]Nunes Filho, F. G; Silva Filho, E. C; Osajima, J. A; de Melo Alves, A. P; Fonseca, M. G. Appl Clay Sci. 239 (2023) 106952;

[2]da Silva, J. C. S; França, D. B; Rodrigues, F; Oliveira, D. M; Trigueiro, P; Silva Filho, E. C; Fonseca, M. G. Colloids Surf. A 609 (2021) 125584.

Agradecimentos/Acknowledgments

The authors acknowledge CNPq for financial support in the form of a research fellowship awarded to M.G. Fonseca (Grant 310921-2017-1) and L.G. Oliveira (Grant 164081/2022-4), Paraíba State Research Foundation (FAPESQ/PB) grant 2021/ 3094, and Brazilian agencies MCTIC/CNPq (Grant 406973/2022-9) through INCT/ Polysaccharides (National Technology-Science Institute for Polysaccharides).

Área: MAT

BixMyOz bismuth composites (M = V, Ti, Nb) dispersed in ZSM-5 zeolite with potential photocatalytic application

João Pedro S. Alves (IC),[1*] Letícia S. Novais (IC),[1] Luciana A. Silva,[1,2] Raildo Alves Fiuza Junior (PQ),[1,2] Mauricio Brandão dos Santos (PQ),[1,2] Artur J. S. Mascarenhas (PQ),[1,2] Fernanda T. Cruz (PQ)[1,2]

alvesj@ufba.br; fernandateixeira@ufba.br

[1] *Laboratory of Catalysis and Materials - LABCAT, DQGI, IQ, Ondina Campus, Federal University of da Bahia, Salvador-BA, Brazil*
[2] *Multitasking Laboratory, Interdisciplinary Center for Energy and Environment – CIENAM, Ondina Campus, Federal University of Bahia, Salvador - BA, Brasil.*

Keywords: *bismuth composites, heterogeneous photocatalysis, zeolite, H-ZSM-5.*

Highlights

Bi composites with Ti, V, and Nb were synthesized by wet impregnation on H-ZSM-5.
The dispersion of oxides in H-ZSM-5 led to a decrease in the particle size of the oxides and of the band gap values.

Abstract

Heterogeneous photocatalysis is a chemical process of great interest for the degradation of pollutants, such as dyes and pharmaceuticals in aqueous media. The preparation of broad-spectrum photocatalysts is of great importance, given the need for semiconductor materials with thermal and mechanical stability, low toxicity for various applications. In the present work, composites were prepared by wet impregnation containing 5% of metals (V, Ti and Nb) and 5% of Bi dispersed in ZSM-5. The materials were named as BiV/H-ZSM-5, BiTi/H-ZSM-5, and BiNb/H-ZSM-5. The obtained composites were calcined and characterized by XRD, TG/DTG, FTIR, DRS, SEM, and textural analysis. The synthesized H-ZSM-5 presents good crystallinity and pure phase compared to the International Zeolite Association (IZA) standard. The materials impregnated with BiV (Fig. 1A) and BiNb (Fig. 1B) did not show characteristic peaks of the oxides, suggesting that $BiVO_4$ and Bi_3NbO_7 are finely dispersed in the crystalline structure of H-ZSM-5. In BiTi (Fig. 1C), peaks suggesting a mixture of orthorhombic TiO_2 phase (ICSD 075179) and monoclinic Ti_3O_5 phase (ICSD 015894) were observed, along with peak broadening indicating the influence of Ti-O on the external surface and channels of the zeolite structure. The band gap values (Eg) obtained by the Tauc method are 2.88 eV (BiV/H-ZSM-5); 3,12 eV (BiTi/H-ZSM-5), and 4.20 eV (BiNb/H-ZSM-5), respectively. The BiV/H-ZSM-5 and BiNb/H-ZSM-5 composites showed a higher Eg than the respective oxides reported in the literature, suggesting a smaller particle size and, consequently, a greater dispersion on the zeolite surface. Only the BiTi/H-ZSM-5 composite showed Eg lower than TiO_2 (3.2 eV), suggesting the penetration of the particles in the micropores.It is worth noting that the band gap energy (Eg) is an important factor for analysis in materials intended for photocatalysis. Composites with a lower Eg value require less energy for electronic transitions. The materials prepared in this work favor application in various regions of the UV/visible spectrum, making them potential candidates for pollutant degradation.

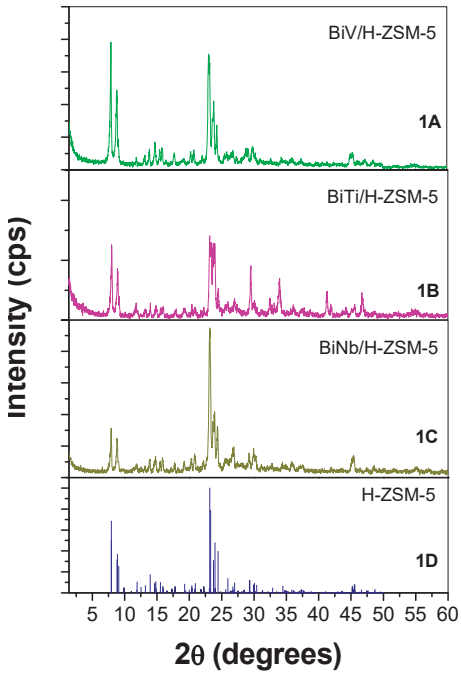


Figure 1: XRD of the synthesized composites

Acknowledgments

To PROPCI - PRPPG/UFBA 007/2022– JOVEMPESQ UFBA for granting the scholarship and to FINEP ref. 0057/21.

Área: MAT
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Blendas de polipirrol com polímeros derivados de celulose visando a regeneração de tecidos nervosos

Mariana Silva Lopes (IC) [1]*, Clodoaldo Junior Aires Duarte (IC)[1], Naiton Martins da Silva (PG)[1],Samuel Oliveira Lima (IC)[1], Fernando Henrique Cristovan (PQ).

lopes.mariana@discente.ufj.edu.br; fhcristovan@gmail.com

[1]*Instituto de ciências exatas e tecnológicas, UFJ.*

Palavras Chave:*(Blendas,Celulose,Polímeros,Polipirrol).*

Highlights

Polypyrrole blends with cellulose-derived polymers aiming at the regeneration of nervous tissues

The nervous system is the most complex and important system present in humans and other living beings. Its main component is nervous tissue, which works in communication through nerve synapses, of which the spinal cord is the center. An injury to this tissue has severe consequences for humans, which leads to a worsening of their quality of life. In this sense, the search for new materials for the development of new therapies for injuries to nervous tissue is necessary. Blends prepared with conductive polymers and biocompatible polymers are candidates for this type of treatment, as they can mimic nervous tissue. Thus, in this work, blends of polypyrrole (PPy) with cellulose acetate phthalate (CAP) were prepared, where PPy has the role of electrically conducting the material, and CAP has the role of being the polymeric matrix. The material was processed in the form of a film and characterized by Fourier Transform Infrared spectroscopy (FTIR) and electronic spectroscopy in the UV-Vis region.

Resumo/Abstract

O sistema nervoso é o sistema mais complexo e importante presente no ser humano e em outros seres vivos. Seu principal componente é o tecido nervoso, o qual trabalha em comunicação por sinapses nervosas, no qual a medula espinhal é o centro. Uma lesão nesse tecido traz consequências severas ao ser humano, como a perda dos movimentos dos membros, o que leva a falta de locomoção, perda de fala, dentre outros. Nesse sentido, os polímeros condutores e polímeros biocompatíveis podem desempenhar um papel fundamental na busca de novos materiais que possam ser utilizados em terapias para regeneração do tecido lesionado, pode-se citar o polipirrol (PPy) e o acetato ftalato de celulose (CAP) que podem ser misturados para formar blendas que têm capacidade de serem processadas para utilização no tratamento. Neste estudo, foi utilizado como matéria prima do CAP a celulose extraída do algodão, a qual passou por uma reação de acetilação com ácido acético, anidrido acético e ácido sulfúrico, resultando no triacetato de celulose (TAC) que em seguida foi reduzido para o diacetato de celulose (DAC). O acetato ftalato de celulose foi obtido a partir da mistura de ácido acético, ácido sulfúrico e anidrido ftálico e o DAC, resultando em uma reação de ftaloização e substituindo assim, os grupos hidroxilas por grupos ftalil, dessa forma tem-se a formação de um éster derivado de celulose misto. Já o polipirrol foi sintetizado a partir do pirrol, dopado com DBSA, o qual visa a melhoria da solubilidade do PPy em solventes orgânicos, como o clorofórmio. As blendas de PPy e CAP foram processadas na forma de filmes e os materiais foram caracterizadas por espectroscopia de FTIR e UV-Vis. Os espectros de FTIR apresentaram as absorções características do CAP, mostrando que ftaloização do diacetato de celulose foi realizada com sucesso. Já o espectro de FTIR do PPy apresentou que o polímero condutor foi sintetizado sem a abertura do anel de pirrol. Já o espectro das blendas não apresentou o surgimento de novas bandas, o que sugere que há apenas a interação física entre os materiais. O espectro de UVVis do CAP mostra uma banda de absorção abaixo de 300 nm, o espectro do PPy mostra uma banda larga na região do visível proveniente da formação de polarons. Nos espectros das blendas de PPy/CAP pode ser observado a absorção do polipirrol, isto é importante uma vez que este será implantado em Danio Rerio (*Zebra Fish*) para auxiliar na regeneração da medula espinhal do animal e esta banda poderá ser utilizada para a observação do material no ambiente biológico.

Agradecimentos/Acknowledgments

Os autores agradecem a FAPEG (processo: 202310267001409), CAPES, INCT-CIMOL (processo: 406804/2022-2) pelo financiamento do projeto.

Área: MAT

Cadmium oxyorthossilicate synthesis by a Sol-Gel method

Elena Iraê A.H.P.Santos (PG),*[1] **Flavio M. Vichi(PQ)**,[1]

elena.santos@usp.br;fmvichi@iq.usp.br [1]*Instituto de Química, Universidade de São Paulo, Av. Prof. Lineu Prestes, 748,* Bloco 3T, Sala 325,05508-900 São Paulo-SP, Brazil

Palavras Chave: *Cadmiun oxyorthosilicate, Sol-Gel, Inorganic synthesis*

Highlights

Cadmium oxyorthosilicate, Cd_3SiO_5 synthesis was viable using a sol-gel route

Resumo/Abstract

Cadmium silicates are a group of materials of great interest due to its stability and the possibility of tailoring phosphors.[1] While cadmium metasilicate ($CdSiO_3$) is well described in the literature and orthosilicate (Cd_2SiO_4) is being explored in some studies, the same does not happen with oxyorthosilicate due to difficulties in obtaining it pure.[2] A sol-gel route, using Cadmium Acetate and Tetraetylorthosilicate (TEOS) as precursors in a stoichiometric proportion of 2:1, obtained cadmium oxyorthosilicate.The solution was subjected to constant stirring for 2 h at 80 ºC. The Gels dried and underwent calcination at 800ºC for 4h. Different pH conditions were applied.

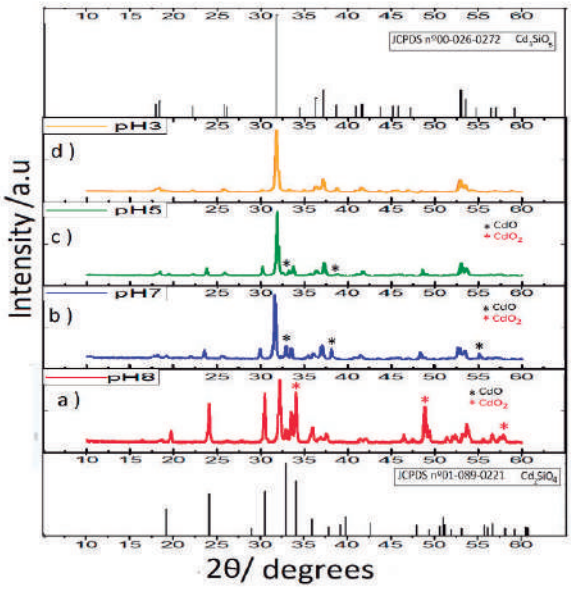


Figure 1. DRX of samples obtained by sol-gel

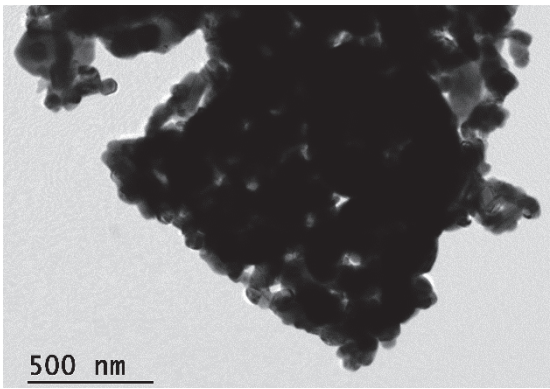


Figure 2.TEM image of Cd_3SiO_5 sample

The use of pH 3 and calcination at 800ºC resulted in the Cadmium Oxyorthosilicate compound Cd_3SiO_5, identified by x-ray diffraction (XRD). The use of pH 8, on the other hand, increases the formation of the Cd_2SiO_4 phase. Transmission electronic microscopy (TEM) images shows the formation of aggregates.

Reference

1. Rojas-Hernandez, R. E.; Rubio-Marcos, F.; Rodriguez, M. Á.; Fernandez, J. F. ; *Renew. Sust. Energ. Rev.* **2018**, *81*, 2759.

2. Glasser,L.S.D.; Glasser,F.P.; *Inorg. Chem.* **1964**, *3*,1228.

Agradecimentos/Acknowledgments

Acknowledgments to the Brazilian agencies CAPES, CNPq and FAPESP for the financial support.

Área: MAT

Carbon Nitride as potential metal-free active component on sunscreen: A study on SPF determination

Izadora R. S. Menezes[1]* (PG), Mariana de Barros Souza[1] (IC), Ivo Freitas Teixeira[1] (PQ).

menezes.irs@gmai.com

[1]*Departamento de Química, UFSCAR*

Palavras-Chave: *SPF in vitro, Physical sunscreen, Semiconductor.*

Highlights

The SPF of TiO_2, ZnO, Na-PHI and H-PHI was determined by *in vitro* UV-Vis method. According to the results, carbon nitride offers comparable sun protection to conventional materials and sunscreens.

Abstract

Sunscreen is an essential product in contemporary life once it prevents short- and long-term skin damage, as well as other complications such as skin cancer. The active components in sunscreens must absorb, reflect, or scatter UV rays (λ = 100 to 400 nm).[1] Carbon nitride, a class of polymeric semiconductors of chemical representation C_3N_4, also absorbs light below 400 nm as TiO_2 and ZnO, typical inorganic materials used as active components in sunscreens. Therefore, it is a positively metal-free alternative for sunscreen formulation. Through the thermal condensation of melamine in sodium chloride one crystalline form of carbon nitrides can be obtained, i.e. poly(heptazine) imide (PHI). This synthesis yields Na-PHI, which Na^+ cations can be easily exchanged for H^+ by adding HCl, resulting in protonated poly(heptazine imide) (H-PHI). In this work we aim to determine the SPF of a Na-PHI and H-PHI simple sunscreen formulation by *in vitro* diffuse reflectance UV-Vis spectroscopy method, comparing to TiO_2, ZnO, and commercial sunscreens to evaluate the potential of carbon nitride as active ingredient.

The Sun Protection Factor (SPF) is more accurately determined by *in vivo* testing, but due to the cost and ethical concerns, *in vitro* methods were established. For the SPF determination, we mixed (magnetic stirring) 2% ww^{-1} of the active ingredient (TiO_2, ZnO, Na-PHI and H-PHI 2 M) in a commercial moisturizer cream. Then we applied them to the Teflon sample plates at a concentration of 24 $mgcm^{-2}$, pressing the quartz plate for spreading. We measured the total transmittance using a UV-Vis spectrophotometer with an integrating sphere for diffuse reflectance, and we calculated the SPF according to the reference method.[2,3]

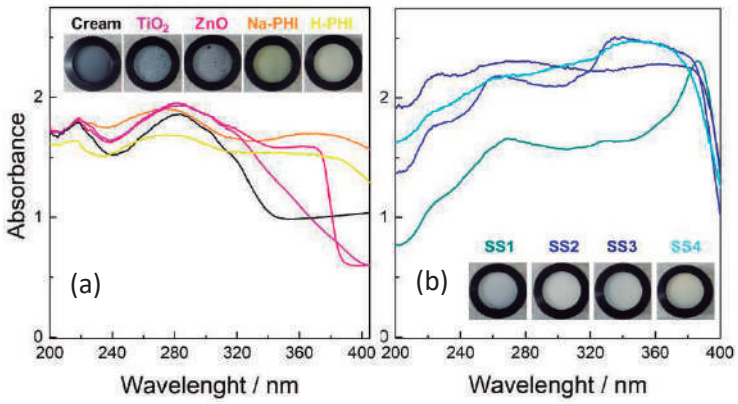


Figure 1: UV-Vis absorbance spectra of a) inorganic active compounds and b) commercial sunscreens.

$$FPS = CF^*\sum EE_{(\lambda)}{}^*I_{(\lambda)}{}^*Abs_{(\lambda)}$$

CF: Correction Factor = 10
EE: Erythemal Efficiency
I: Solar intensity
Abs: Absorbance

EE*I : 290 nm = 0.015
300 nm = 0.2874
310 nm = 0.1864
320 nm = 0.018

Table 1: SPF calculated by *in vitro* UV-Vis *spectroscopy* method

	SPF
Cream	15
TiO_2	16
ZnO	17
Na-PHI	17
H-PHI	16
SS1 – 50	16
SS2 – 60	23
SS3 – 70	23
SS4 - 70	24

The SPF results of commercial sunscreens do not match the label SPF, indicating the *in vitro* method is not completely adequate, as discussed previously in the literature.[4] However, comparing the results of Na-PHI and H-PHI 2M to the usuals active compounds, we concluded that the carbon nitride has similar activity, pointing out as a potential new active material for sunscreens. Nevertheless, we must further explore methods for determining SPF and other important parameters, as well different formulations for testing.

References: [1] Trends in Analytical Chemistry (2022), 157: 116724(1-19). [2] Photochemistry and Photobiology (1979), 29(3): 559-566. [3] Rev Ciênc Farm Básica Apl. (2011), 32(1): 27-34. [4] Skin Pharmacol Physiol (2010), 23: 201-212.

Acknowledgments

UFSCar, Fapesp and CNPq.

Área: MAT_____
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Carboxymethylcellulose and alginate-based biofilms: Composition and properties

Raimunda N. de S. Oliveira (IC),[1] Fernando C. Damasceno (PQ)[2].

raimundaoliveir277@gmail.com; fernando.damasceno@univasf.edu.br.

[1]*Licenciatura em Química, UNIVASF;* [2]*Colegiado de Licenciatura em Química,UNIVASF.*

Palavras Chave: *Biofilms, Carboxymethylcellulose, Alginate, Wound dressings.*

Highlights

Synthesis of eco-friendly CMC/ALG biofilms using glycerol as plasticizer.
Wate-soluble biofilms.
Polymerization of CMC and ALG confirmed by FTIR.
CMC/ALG biofilms has potential for wound dressings.

Resumo/Abstract

Plastic materials find extensive applications in diverse sectors such as construction, biomedical, hygiene, food and beverage industries. Although versatile, plastic materials rely on non-renewable resources, leading to enduring environmental impacts when improperly disposed. Aiming to reduce these environmental impacts, many studies have been carried out to develop biodegradable plastic materials from renewable sources, at low cost and with properties similar to non-biodegradable plastics. Biopolymers has shown great potential as substitute to petroleum-based polymers for most different applications spanning from biomedical to food packaging.Among various biopolymers, polysaccharideshave shown great potential to develop plastic biofilms with chemical and mechanical properties suitable for food packaging and biomedical applications. In this studybiofilms were synthesized by solution casting method using carboxymethylcellulose (CMC) and alginate (ALG) as matrix and glycerol (GLY)as the plasticizer. The main goal was to investigate the influence of composition on the properties of these biofilms and evaluate possible applications. Biofilms with different ratios of carboxymethylcellulose and alginate were synthesizedand characterized using FTIR spectroscopy.

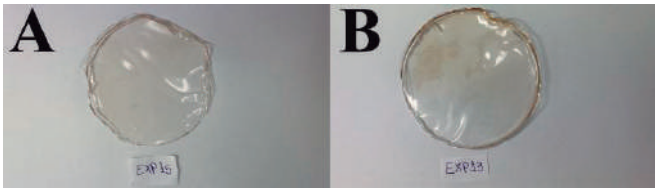


Figure 1: Two samples of biofilms used in the study. Biofilm A (3g CMC; 5mL GLY). Biofilms (3g of ALG; 5mL GLY).

Solubility and moisture content of biofilms were performed to assess the suitability of these biofilms for specific applications. The results shows that all biofilms were readily soluble in water, rendering then unsuitable for food packaging but potentially valuable asdissolvable wound dressings. The moisture content, measured by gravimetric method, revealed to be highly dependent on composition. Samples containing more glycerol are more flexible and has higher moisture content. The FTIR shows typical bands for -OH; C – H; C = O and C – O stretching vibrations, confirming the polymerization of CMC and ALG. To date, the findingssuggest that CMC/ALG-based biofilms are potential candidates for wound dressing. Future investigations will include the measurement of mechanical properties and the assessment of the antibacterial activity of biofilms containing plant extractsaiming to determine their potential in preventing microbial proliferation.

Agradecimentos/Acknowledgments

Victória Laysna dos Anjos for FTIR acquisition.

UNIVASF
UNIVERSIDADE FEDERAL DO VALE DO SÃO FRANCISCO

Área: MAT
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Catalytic performance of the nickel Prussian-blue with cyanide vacancy in water oxidation reaction under mild conditions

Nycolas S. Galdino* **(PG),[1] Juliano A. Bonacin (PQ),[1]**

n256959@dac.unicamp.br; jbonacin@unicamp,

[1]*Departamento de Química, IQ-UNICAMP*

Palavras Chave: *Nickel Prussian blue analogues, Electrocatalysts, Defects engenieering, Water oxidation reaction.*

Highlights

Enhancing catalytic oxygen production in water oxidation reaction under mild conditions using engineering defects in nickel prussian blue analogues catalysts

Resumo/Abstract

Intensifying research on sustainable energy aims to shift from finite fossil fuels, which cause environmental harm, to renewable energy sources. Current water electrolysis relies on costly noble metals catalysts (e.g., Ru, Pt, and Ir), prompting a search for earth-abundant elements catalysts (e.g., Fe, Co, Ni, and Cu). Despite the effectiveness of Prussian blue analogues (PBA) towards electrocatalysis, their limited active sites drive defect engineering efforts for enhanced catalytic performance. Our focus is on synthesizing nickel Prussian blue analogues (Ni-FePB) via electrodeposition, introducing cyanide vacancies (CN-vac) in their structure (Ni-FePB$_{(CN\text{-}vac)}$) to activate and improve electrocatalytic activity for oxygen production in water oxidation reaction (WOR) under mild conditions (pH ≅ 7). Both films (Ni-FePB and Ni-FePB$_{(CN\text{-}vac)}$) had their catalytic activity evaluated towards WOR. The films were characterized by Raman spectroscopy, and the cyanide band (νCN^-) characteristic fingerprint of the materials was found (see figure 1A). Furthermore, the results showed a bathochromic effect, shifting the cyanide band to a lower energy from 2120/2176 cm-1 to 2059/2147 cm-1 for Ni-FePB and Ni-FePB$_{(CN\text{-}vac)}$, respectively, indicating the creation of vacancies in the activated film. During the linear sweep voltammetry (LSV) studies for both films in 0.5 M KNO_3, the O_2 evolution starts na onset potential 200 mV earlier (see figure 1B) for Ni-FePB$_{(CN\text{-}vac)}$ film (841 mV E vs. RHE) compared to Ni-FePB film (1061 mV E vs. RHE). To quantify the O_2 produced during catalysis, a four-electrode cell system was used, and the results showed that Ni-FePB$_{(CN\text{-}vac)}$ film produced around 3 times more O2 than Ni-FePB film (137.4 µmol and 40.6 µmol, respectively). Moreover, Electrochemical EIS showed that the catalysts with vacancy defects present lower R_{ct} compared to the normal material, with values of 78.3 Ω and 252 Ω for Ni-FePB$_{(CN\text{-}vac)}$ and Ni-FePB in 0.1 M KNO_3 under 1.7 V conditions. Other electrochemical results, such as CV, Tafel slope, K_{obs}, and ECSA, have been used to confirm that the produced activated material exhibits faster kinetics when defects are created in the structure.

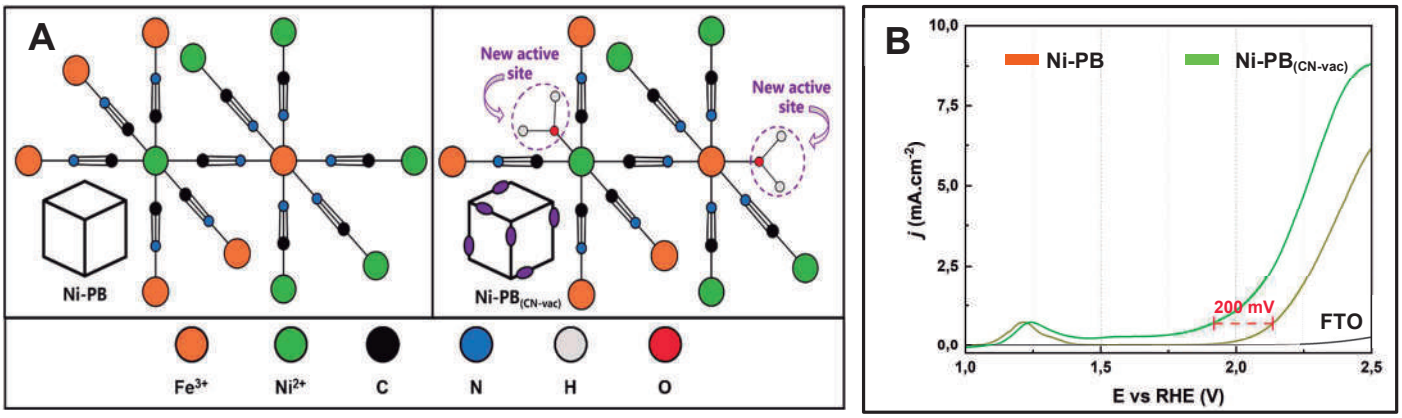


Figure 1: Schematic structure for Ni-PB and Ni-PB$_{(CN\text{-}vac)}$ catalysts (A); Linear sweep voltametry (LSV) of FTO in gray line, Ni-PB in brown line and Ni-PB$_{(CN\text{-}vac)}$ in green line in 0.5 M KNO_3 (B).

Acknowledgments

UNICAMP IQ Instituto de Química FAPESP CNPq CAPES CINE CENTER FOR INNOVATION ON NEW ENERGIES

Sociedade Brasileira de Química

Área: Química de Materiais - MAT

Characterization of Fe_3O_4 nanoparticles incorporated with soybean oil biopolymer by cooprecipitation

Luis Fernando R. C. Lemes (PG),[1] Aroldo Geraldo Magdalena (PQ),[1] Maria Laura Ferreira Della Costa (PG),[1] Fernanda Kelly Alves de Souza (PG).[1]

luis.lemes@unesp.br; luis.lemes@unesp.br

[1]*Universidade Estadual Paulista (Faculdade de Ciências de Bauru)*

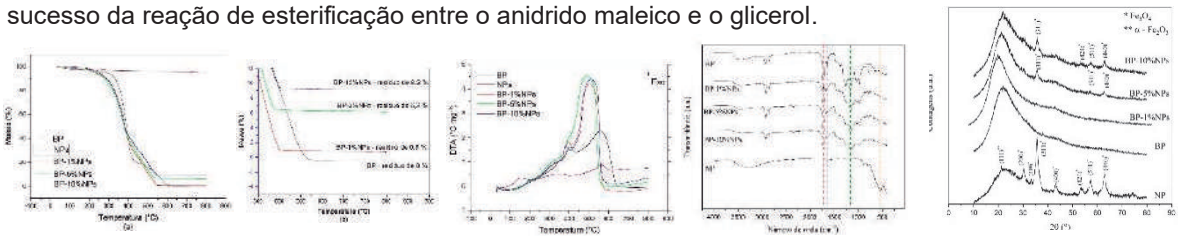
Palavras Chave: (*Análise térmica, Fe_3O_4, Nanocompósitos).*

Highlights

The present work studied the characterization of magnetic nanoparticles and magnetic nanocomposites based on iron oxide functionalized with soybean oil-based biopolymer, (BPLMR).

Resumo/Abstract

O presente trabalho evidência a caracterização do nanocompósito de Fe3O4 com o polímero a base de óleo de soja, onde foi realizadas as seguintes caracterizações, DRX, FTIR e Análise térmica (TG-DTA). As primeiras figuras apresentam as curvas termogravimétricas para as amostras estudadas, onde é possível ver que os materiais possuem dois eventos térmicos e desidratação. Esses eventos em questão são exotérmicos, como é possível visualizar pelo DTA, no qual devem estar relacionados com a decomposição seguida da oxidação da matéria orgânica Alarcon et al. Os resíduos são basicamente óxidos inorgânicos, no nosso caso, estão relacionados com as nanopartículas de óxido de ferro incorporadas durante a síntese. Os dados obtidos dos resíduos são bastante similares aos valores incorporados durante a síntese, indicando que as composições nominais e reais são similares. Quando se analisa os dados do DRX, eles sugerem que as nanopartículas estão incorporadas na matriz polimérica e que os ensaios de análise térmica comprovam a estequiometria inicial. Já no FTIR foi possível obter informações precisas a respeito dos grupos funcionais e quais as possíveis interações entre o polímero e as nanopartículas de Fe3O4, onde foi possível ver o estiramento da função éster formado entre o glicerol e o anidrido maleico, estiramento C=C presente no óleo vegetal, estiramento de C-C(C=O)-O dos ésteres de ácidos -insaturados o que mostra o sucesso da reação de esterificação entre o anidrido maleico e o glicerol.



Agradecimentos/Acknowledgments

CNPQ, UNIVESP, CAPES.

Area: MAT

CHEMICAL RECYCLING OF PMMA ARTIFACTS FOR THE PRODUCTION OF METHACRYLIC COPOLYMERS

Isadora de Souza (IC),[1] Gabriel S.P. de Souza (IC),[1] Celso K. Hardoin Jr. (IC-M),[1] Amanda G.F. Villain (IC),[1] Mayara Powrosnek (PG),[1] Aline S. Muniz (PQ),[1] Valéria G. Costa (PQ),[2] Angelo R.S. Oliveira (PQ),[1] Maria Aparecida F. César-Oliveira (PQ).[1]*

valeria.costa@int.gov.br; mafco@ufpr.br

[1]Departamento de Química – LEQUIPE, UFPR; [2]Divisão de Materiais – LAMAP, INT

Key words: *Poly(methyl methacrylate), Chemical Recycling, Post-use PMMA Artifacts, Methacrylic Copolymers, Alkaline Hydrolysis, Methacrylic Acid.*

Highlights

Methacrylic acid copolymers can be obtained from the controlled hydrolysis of post-use PMMA artifacts and give rise to copolymeric esters of varied composition, properties and applications.

Abstract

Acrylic and methacrylic copolymers can be obtained by copolymerization and by chemical modification of preformed polymers. Acrylic polymers, obtained from propenoic acid and its various esters, can be produced from renewable sources. Multi-step synthetic routes can transform glycerol into propenoic acid (acrylic acid) and, subsequently, multiple derivatives. Vegetable oils (triacylglycerols) are sources of glycerol, which can also be obtained as a co-product of biodiesel production, made from virgin and waste oils and fats. Unlike acrylics, methacrylic monomers are not obtained as easily from renewable sources. It is essentially obtained from oil refining. This characteristic encourages us to study the chemical recycling of industrial waste and post-use artifacts of poly(methyl methacrylate) – PMMA, with a proposal for a noble destination for plastic waste, contributing to the mission of environmental protection. Copolymers containing repetitive carboxylic acid units are used as thickeners in the cosmetics, pharmaceutical, cleaning products industry, among others, and can be used in the composition of different well-known products in the consumer market. Poly(methyl methacrylate-co-methacrylic acid) copolymers – PMMA-MAA – can be produced from the partial hydrolysis of PMMA, in a process of chemical recycling of both burrs and rejects from the artifact molding industry, as well as the production of corrective lenses and even post-use artifacts, such as the materials used in illuminated signs. The high molar mass of PMMA used in these applications is a limiting factor for chemical recycling, as it hinders the regularity of the sequencing of repetitive units, consequently affecting the properties of the resulting copolymer. PMMA-MAA of different compositions can be used as a final product, but also as a raw material to produce other copolymer esters or terpolymers, by esterification of acid units, which can be used, for example, as additives for biofuels. The scarcity of scientific studies involving the hydrolysis of PMMA inspired the study of different experimental conditions on the composition of copolymers. The performance of different hydroxyl bases (NaOH, KOH, LiOH, $Ca(OH)_2$, $Mg(OH)_2$) was studied in the hydrolysis of PMMA from a post-use lighted sign plate compared to commercial PMMA (Aldrich). The PMMA samples were crushed in a knife mill, dissolved in hot isopropanol, added with an equimolar amount of base, and then water was added so that the reaction could be processed for 24 hours. The PMMA-MAA copolymers were characterized by FTIR, ^{1}H- and ^{13}C NMR spectroscopy and the content of methacrylic acid units in the copolymers was quantified by neutralization volumetry. Submitted to the same experimental conditions, post-use PMMA presented results comparable to those obtained with virgin PMMA (Aldrich), but the use of NaOH and KOH produced much higher degrees of hydrolysis than those provided by the other bases. The use of LiOH and $Mg(OH)_2$ provided hydrolysis degrees of 1.2-1.6 mol% and for $Ca(OH)_2$ the result was around 3.2 mol%. Under the hydrolysis conditions described the use of NaOH and KOH promoted 11 mol% and 12 mol% of hydrolysis, respectively. The different levels of MAA achieved were already sufficient to modify the properties of the products in comparison to the original PMMA.

Reference: MUNIZ, A.S. Master's Thesis. PPGQ. Federal University of Paraná. 2012; CÉSAR-OLIVEIRA, M.A.F. *et al.* Polymers: Science and Technology. v.4, p.156-62. 1999.

Acknowledgments/Acknowledgmentsts

Área: MAT

Circularly polarized upconversion emission on lanthanide-doped $NaGdF_4$ nanoparticles

Nagyla A. Oliveira (PG),[1] Isabela M. S. Diogenis[1] (PG), Sergio Fernando N.Coelho[1] (PG), Fernando A. Sigoli (PQ).[1]*

n234905@dac.unicamp.com; fsigoli@unicamp.br

[1]*Instituto de Química, UNICAMP*

Palavras-Chave: *UC-CP, Functionalization, Core@shell*

Highlights

Circularly polarized upconversion emission (UC-CP) and high dissymmetry factor on non-functionalized or functionalized with chiral ligand $hfbc^-$ core@shell $NaGdF_4$ nanoparticles.

Resumo/Abstract

The Circularly Polarized Luminescence (CPL) has become an important research area due the huge possible applications of chiral luminescent materials, mainly photoelectronic devices. These materials, among other methods, can be obtained from the association with chiral structures, which can induce chirality to some materials resulting in peculiar photophysical properties. [1,2,3]

This study presents some aspects and results about UC-CP properties of core@shell nanoparticles (NP) $NaGd_{0,5}Tm_{0,01}Yb_{0,49}F_4$@$NaGd_{0,85}Eu_{0,15}F_4$ oleate-functionalized (NP-capped), (+)-3-heptafluorobutyryl camphorate-($hfbc^-$) functionalized (NP-hfbc) and oleate-functionalized with hfbc-nonfunctionalized (NP-capped + hfbc). The thermal decomposition method was used to obtain the NPs on the hexagonal (β) crystalline structure as confirmed by XRD analysis. The surface of NPs was analyzed by FTIR spectroscopy that shows the absence of bands from oleic acid on the nonfunctionalized NPs and the β-diketonate bands, from $hfbc^-$ ligand, confirming the functionalization. The spectroscopic analyses were obtained using PDMS films with 10% (w/w) of NPs. The Eu(III) electronic transitions $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$, about 595 nm and 612 nm, respectively, were monitored in upconversion PL spectra, using a 980 nm laser, indicating the energy migration upconversion (EMU) energy transfer mechanism. The CPL analyses indicate a variation in the preferential circularly polarized emission, depending on the nanoparticles functionalization. Table 1 shows the dissymmetry factor (g_{lum}) values. For the oleate-functionalized with hfbc-nonfunctionalized NPs (NP- capped + hfbc) -PDMS membrane, the g_{Lum} value is negative for the $^5D_0 \rightarrow {}^7F_1$ and positive for $^5D_0 \rightarrow {}^7F_2$ transitions. These variations can indicate a modification of the coordination sites of Eu(III) due the chiral ligand, amplifying the dissymmetry emission according to the increasing interaction strength with $hfbc^-$. In g_{Lum} terms, we can see this influence mainly from the $^5D_0 \rightarrow {}^7F_1$ transition, because it is partially allowed by magnetic dipole and forced electric dipoles in specific group points. That and forced electric dipole, is essential to obtain high values of luminescent dissymmetry. The results obtained suggest the possibility to obtain high dissymmetry factor values (g_{lum}) for UC-CP emission, making them promising for futures applications in optical-electronic devices.

Table 1: Dissymmetry factor values (g_{lum}) of PDMS films having NPs β-$NaGd_{0,5}Tm_{0,01}Yb_{0,49}F_4$@$NaGd_{0,85}Eu_{0,15}F_4$ and $hfbc^-$ ligand.

	***g_{Lum}* Values** ***Eu(III)* transitions**	
PDMS Films	**$^5D_0 \rightarrow {}^7F_1$**	**$^5D_0 \rightarrow {}^7F_2$**
NP-hfbc	-0.38	-0.04
NP-capped + hfbc	-0.24	+0.08
NP-capped	+0.00008	+0.16

Agradecimentos/Acknowledgments

The authors are grateful to CNPq, FAPESP, CAPES, CNPEM, LNNANO and INOMAT.

[1] [1] D. P. Sebastiano and D.B. Lorenzo, Inorg. Chem. **51,** 12007-12014 (2012).
[2] Han, D., Li, C., Jiang, C., Jin, X., Wang, X., Chen, R., Cheng, J., Duan, P., *Aggregate,* 2022, 3, e148.
[3] Xiaoning Li, Yujun Xie,* and Zhen Li*. , Adv. Photonics Res. 2020, 2000136

Área: MAT

Computational fluid dynamics: the influence of different clay minerals structures in heat release rate of intumescent formulation composites

Ana Lucia S. Ventapane (PG),[1]* Simone P. S. Ribeiro (PQ),[1].

analuciaventapane@pos.iq.ufrj.br

[1]*Instituto de Química, UFRJ*

Palavras Chave: *Computational Fluid Dynamics (CFD)*, *Fire Dynamics Simulator (FDS)*, *Clay Minerals*, *Synergistic Agent*, *Intumescent Formulation*, *Flame Retardant*.

Highlights

Computational fluid dynamics was used to investigate the fire effect of different clay minerals such as mica, kaolinite and feldspar in intumescent formulation composites using its heat release rate.

Resumo/Abstract

Heat release rate (HRR) is an important parameter to evaluate the risks of fire in polymeric materials. To reduce the HRR, intumescent formulation, a type of flame retardant, forms a char layer preventing the heat and mass transfer. Furthermore, the incorporation of clay minerals increases intumescent formulation flame retardant properties promoting a synergistic effect. In previous work, different clay minerals such as mica, kaolinite (Kaol) and K-Feldspar (K-Fsp) on intumescent formulation composed by ammonium polyphosphate (APP) and pentaerythritol (PER) formulations in poly (ethylene-co-butyl acrylate) (EBA-30) was investigated. Mica presented the most positive effect in reducing HRR. The present work aims to evaluate, through computational fluid dynamics using Fire Dynamics Simulator software the fire behaviour of clay minerals in APP/PER systems in EBA-30 composites. The fire behavior and ambient temperature were evaluated at peak of heat release rate, i.e., the maximum flammability of pure EBA-30 (200 s). Table 1 shows the fire animations and room temperature at 200 seconds.

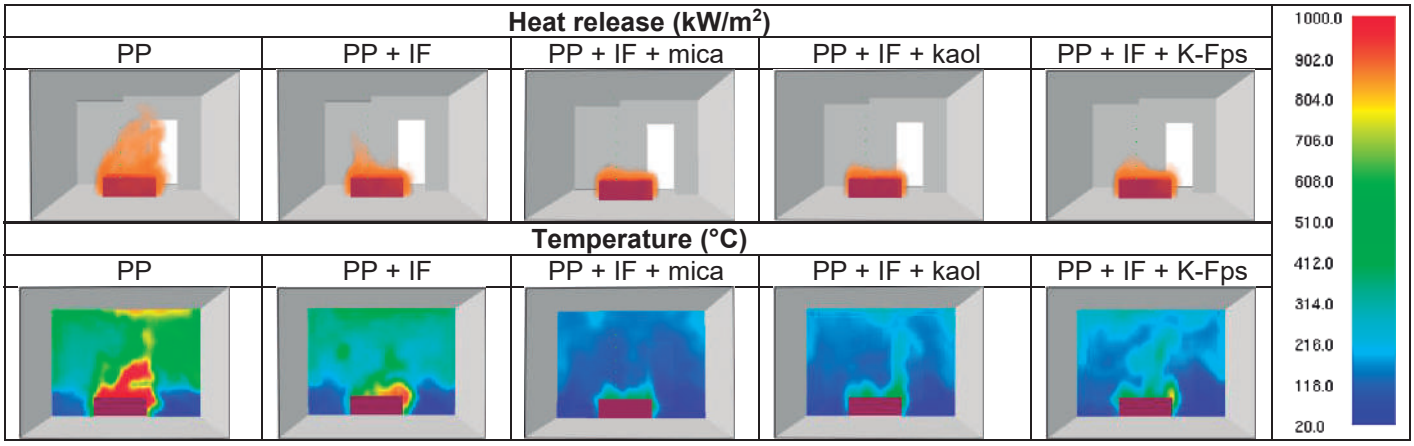


Table 1 – Fire animation and room temperature at 200 seconds

The composite with mica which has similar structure with montmorillonite, a well-established clay in literature, lead greater reduction of heat release and room temperature at 200 s which can improve more safety scape on a fire scenario. Mica can catalyze more efficiently the reaction between APP and PER, precursors of char, but all clay improved the thermal stability and enhanced the flame-retardant properties.

[1] RIBEIRO, S. P. S.; *et al*. Effect of clay minerals structure on the polymer flame retardancy intumescent process. Applied Clay Science, v. 161, p. 301-309, 2018.

Agradecimentos/Acknowledgments

The author wishes to thank CAPES program for the support.

Área: MAT

Designing Nanoarchitectures: A liquid-liquid interfacial route to obtain nanocomposites of hBN, graphene and silver nanoparticles

Maria Karolina Ramos (PG)[1], George Bepete (PG)[2], David Emanuel Sanchez (PG)[2], Alex Sredenschek (PG)[2], Mauricio Terrones (PQ)[2], Aldo José Gorgatti Zarbin (PQ)[1]

mariakarolina@ufpr.br; aldozarbin@ufpr.br;

[1]Departament of Chemistry, Federal University of Paraná (UFPR); [2]Departament of Physics, Pennsylvania State University - USA

Keywords: Hexagonal Boron Nitride, Graphene, Silver Nanoparticles, Nanoarchitectonics, Liquid-liquid Interfacial Route

Highlights

The use of liquid-liquid interfacial route (LLIR) to fabricate thin films comprising two or three components, involving hexagonal boron nitride (hBN), graphene (Gr), and silver nanoparticles (AgNPs).

Resumo/Abstract

Two-dimensional hexagonal boron nitride (2D-hBN), isomorphic with graphene (Gr), stands out due to its distinctive optoelectric properties, coupled with mechanical robustness, thermal stability, and chemical inertness. Recognized as a highly promising material, 2D-hBN holds potential for integration with other 2D materials like Gr and transition metal dichalcogenides, paving the way for the next generation of microelectronics and various technologies. Despite being inherently insulating, 2D-hBN exhibits adaptability through strategies such as doping, substitution, functionalization, and hybridization, rendering it an exceptionally versatile category of functional materials across a wide spectrum of applications.[1] This study focused on obtaining stable dispersions of hBN and Gr by employing intercalation with metallic potassium, followed by chemical exfoliation in suitable solvents.[2] Subsequently, a methodology developed by our research group, the liquid-liquid interfacial route (LLIR),[3] proved instrumental in producing thin films of nanocomposites comprising two or three components.[4] Thin films of hBN/Gr and hBN/Gr with embedded metallic silver nanoparticles (AgNPs) were fabricated using LLIR and characterized through UV-Vis, XRD, SEM, EDS, Raman, and HRTEM. UV-Vis spectra of hBN exhibited a band at 208 nm, corresponding to the transition from the valence band to the conduction band, while Gr displayed a band at 273 nm, indicative of the π-π* transition. Nanocomposites with varying proportions of hBN/Gr showcased bands at 221 nm for the hBN/Gr 1:0.5 film and 250 nm for the hBN/Gr 0.5:1 film, signaling the formation of distinct composites. The introduction of AgNPs into the nanocomposites induced changes in the hBN band-gap, revealing bands at 230 nm and a silver plasmon band at 480 nm. The resulting thin films exhibited diverse colors, with hBN appearing white, Gr appearing black, and hBN/Gr combinations displaying shades of light and dark gray. Nanocomposites with silver nanoparticles took on an orange hue due to the incorporation of NPs into the 2D material structure. Raman spectra unveiled the D, G, D', and 2D bands of Gr at positions 1344, 1579, 1610, and 2713 cm^{-1}, respectively, corresponding to structural defects (D and D'), the structural organization of graphene (G), and the E_{2g} mode (2D). The hBN spectra featured a band at 1366 cm^{-1} attributed to the E_{2g} mode of the B–N bond. Analysis of the nanocomposites revealed bands from both materials, with a shift of the D band to 1340 cm^{-1} and the D' band to 1620 cm^{-1} in the Gr bands, indicating alterations in the defect regions with the incorporation of hBN into the structure. Morphologically, large sheets of Gr (600 to 800 nm) were observed on a well-structured film of small hBN sheets (100 to 200 nm), while spherical AgNPs, with an average size of 6 nm, were evident in both structures. The study conclusively demonstrated the efficacy of LLIR in forming two- and three-component nanoarchitectures in the form of thin films.

References: [1]ZHANG, Kailiang et al. *Journal of Materials Chemistry C*, v. 5, n. 46, p. 11992-12022, 2017. [2]YANG, Ruijie et al. *Nature Synthesis*, v. 2, n. 2, p. 101-118, 2023. [3]ZARBIN, Aldo JG. *Materials Horizons*, v. 8, n. 5, p. 1409-1432, 2021. [4]RAMOS, Maria K. et al. *Materials Horizons*, v. 10, n. 12, p. 5521-5537, 2023.

Agradecimentos/Acknowledgments

CAPES/PRINT, CNPq, INCT-Nanocarbon and INCT-NanoVida.

Área: MAT

Detection of psychoactive N,N-dimethytriptamine alkaloid based on SERS using Au nanostars in flexible inkjet-printing paper substrates

Edison Huertas Montoya (PG)[1], Lucas M. F. Oliveira (PG)[1], Anerise de Barros (PQ)[1], Fernando A. Sigoli (PQ),[1] Paola A. Caro (PG)[2], Alexandre L. Oliveira (PQ)[2], Italo O. Mazali (PQ)

edisonqca@gmail.com; mazali@unicamp.br

[1] *Universidade Estadual de Campinas, Instituto de Química, Laboratório de Materiais Funcionais, Campinas, SP, Brazil.*
[2] *Universidade Estadual de Campinas, Instituto de Biologia, Laboratório de Regeneração nervosa, Campinas, SP, Brazil.*

Keywords: *SERS, Paper-based sensor, Inkjet-printing, Plasmonic nanoparticles, N,N-dimethyltryptamine detection.*

Highlights

Preparation of novel low-cost inkjet-printed paper substrates based on gold nanostars as high-performance SERS sensors for detection of N,N-dimethyltryptamine drug at ultra-low concentrations.

Resumo/Abstract

N,N-dimethyltryptamine (DMT) is a natural compound commonly present in South American biota such as *Mimosa tenuiflora*, typical of the semi-arid areas of Brazil.[1] There is a growing interest in the therapeutic potential of DMT due to recent clinical data showing the improvement of cognitive deficits associated with some neurological diseases such as depression and Alzheimer.[2] Therefore, the development of analytical methodology for the monitoring of the appropriate dosage of DMT for the treatment of patients is essential. In this context, inkjet printing paper sensors using gold nanostars were fabricated and evaluated through the Surface-Enhanced Raman Scattering (SERS) technique. The substrate performance was optimized using violet crystal, showing great reproducibility among measures. The optimal number of printing cycles was established as 1 for a [Au°] = 27 mM, which is an excellent result in comparison to traditional inkjet-printed substrates that require higher nanoparticle concentrations and several printings to achieve a reproducible SERS signal. Finally, the inkjet-printed substrate was applied to the SERS detection of DMT, allowing its detection up to the nanomolar range. The SERS analyses between 10^{-3} and 10^{-10} mol L^{-1} reveal a high sensitivity of the sensors, with a silhouette coefficient of 0.84 obtained by PCA statistical projections. **(1)** Araujo, I. *et al. Rev. Bras. Farmacogn.* 905–911 (2022). **(2)** Dunlap, L. E. *et al. Pharmacol Rev* **162**, 264–355 (2022).

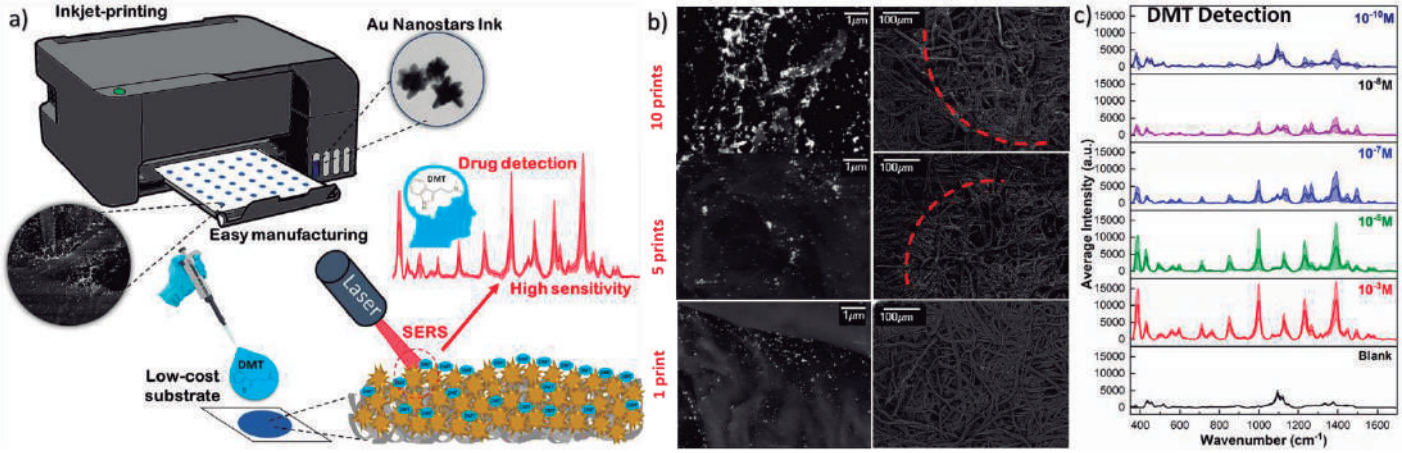


Figure 1. a) Graphical Abstract of this work, **b)** SEM images of the inkjet-printed paper substrates, and **c)** SERS spectra of DMT on the Au NSs substrate at different concentrations.

Agradecimentos/Acknowledgments

UNICAMP, Instituto de Química, Laboratório de Materiais Funcionais, EMMU, FAPESP, CNPq, CAPES, LNNano, Inomat

Área: MAT

Development and characterization of copper metal-organic frameworks using different organic linkers

Ana Carolina R. Felix (PG),[1] Geórgia C. Labuto (PQ),[1] Christiane de Arruda Rodrigues (PQ).[2]*

ana.felix@unifesp.br; christiane.arruda@unifesp.br*

[1]*Departamento de Química, UNIFESP;* [2]*Departamento de Engenharia Química, UNIFESP.*

Palavras Chave: *Metal-Organic Frameworks, Copper, Synthesis, Organic linkers, Characterization.*

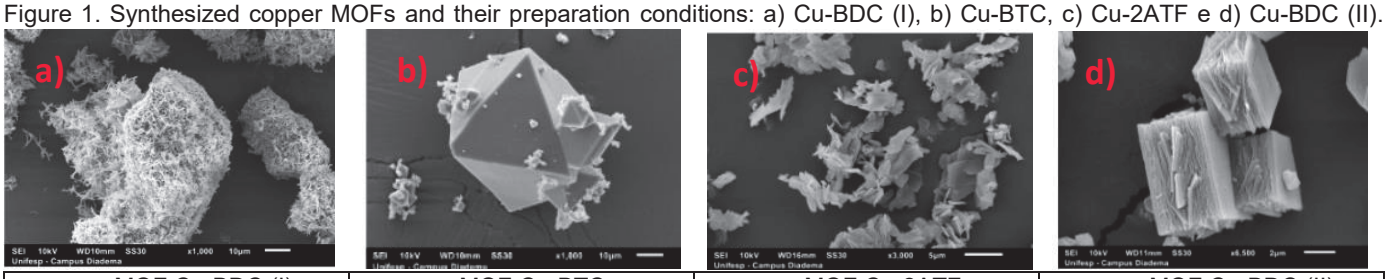
Highlights

Synthesis of MOFs using different acids as organic ligands and copper as a metal cluster. Characterization of the synthesized materials and comparison of their physicochemical properties.

Resumo/Abstract

Metal organic frameworks (MOFs) are compounds made of porous materials in which a coordination network between a metal cluster and organic ligands has potentially empty cavities. This class of material is relatively new, but has enormous importance due to its range of applications in a wide variety of areas. MOFs have specific characteristics such as permanent microporosity, high crystallinity, low density, high surface area values, and good physical and chemical stability. The stability of the MOFs in water is a current challenge to be applied in the aqueous system. In addition to these characteristics, it is possible to use different strategies for synthesizing and functionalizing this type of material to apply it in various areas**.** Among the most common techniques are solvothermal, hydrothermal, sonochemical, electrochemical and microwave-assisted synthesis. This work aims to synthesize copper MOFs (Cu-MOFs) stable in an aqueous solution via the solvothermal method to apply in adsorption and photocatalytic processes. To reach this objective, three parameters of the syntheses were investigated: organic ligands (terephthalic, trimesic and 2-aminoterephthalic acids), drying time (12 to 22h) and solvent (ethanol, water, dimethylformamide (DMF) and acetic acid). To characterize the Cu-MOFs the following techniques were used: powder X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FT-IR), Thermogravimetric Analysis (TG/DTA), specific surface area calculation (BET) and water stability test. The synthesized MOFs presented structural differences, as shown in Figure 1, such as needle, planar and octahedral structures. For spectra analyses, the bands obtained for all MOFs indicated the binding of copper to the organic linkers. Thermogravimetric curves indicated the stability of the Cu-MOFs at approximately 250ºC and 300ºC. High surface area values were obtained for all Cu-MOFs synthesized. The MOF Cu-BTC was chosen for application in photocatalysis due to the highest yield, largest surface area, best synthesis conditions, high stability in water and well defined structure.

Figure 1. Synthesized copper MOFs and their preparation conditions: a) Cu-BDC (I), b) Cu-BTC, c) Cu-2ATF e d) Cu-BDC (II).



MOF Cu-BDC (I)	MOF Cu-BTC	MOF Cu-2ATF	MOF Cu-BDC (II)
Organic Ligand: terephtalic acid; Drying Time: 12h; Solvents: DMF, H_2O, ethanol	Organic Ligand: trimesic acid; Drying Time: 18h; Solvents: DMF, H_2O, ethanol	Organic Ligand: 2-aminoterephtalic acid; Drying Time: 22h; Solvents: DMF, acetic acid	Organic Ligand: terephtalic acid; Drying Time: 22h; Solvent: DMF

Agradecimentos/Acknowledgments

UNIFESP, CAPES, CEMU Diadema, LENCA e LabInScience, FAPESP (2020/12263-0, 2020/14419-7,2022/08358-0).

Área: MAT_____

Development of Hybrid Microfibers Based on Graphene Derivatives and Carbon Nanotubes

Marcos Rocha D. Silva (IC)[1*], Milena Avancini (PG)[1,2], Matheus C. Dias (PG)[1,2], Camila M. Maroneze (PQ)[1,2], Cecilia de Carvalho C. Silva[1,2] (PQ).

marcosrochadiniz@hotmail.com;cecilia.silva@mackenzie.br

[1]School of Engineering, Mackenzie Presbyterian University, UPM; [2]MackGraphe – Mackenzie Institute for Research in Graphene and Nanotechnologies, Mackenzie Presbyterian Institute.

Palavras-Chave: *Graphene Oxide, Graphene Fiber, Carbon Nanotubes, Wet Spinning*

Highlights

Preparation and characterization of hybrid microfibers based on graphene oxide nanosheets and carbon nanotubes aiming the development of electrical sensors.

Resumo/Abstract

Since graphene was discovered in 2004, it has attracted the attention of many researchers due to its outstanding electrical, thermal, and optical properties. Based on that, graphene and its derivatives, like graphene oxide (GO) and reduced graphene oxide (rGO), have been touted as a candidate for the development of microfibers due to their superior properties concerning conventional carbon fibers [1]. Previously, we reported the development of graphene derivative microfibers with controlled and homogeneous shapes and tunable diameters, fabricated exploring the 3 dimensional (3D) hydrodynamic focusing concept on a microfluidic device [2]. However, there still is some room related to the improvement of the mechanical properties of neat graphene derivatives microfibers. One interesting approach consists of using molecular-like materials that can act as a bridge between the GO nanosheets, improving the binding between them. In this way, we address an optimization study of incorporating carbon nanotubes (CNTs) on GO dispersion, aiming to prepare graphene derivative fibers with superior mechanical properties. The GO sheets were obtained by Hummer´s method [3] and characterized by Raman spectroscopy. We investigate the effect of mild oxidation of single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs), aiming to obtain stable aqueous dispersion. For this, we performed the procedure described by Rosca et al [4], followed by the sonication in ultrasound tip and ultrasound bath at a frequency of 24 Hz and power of 280 W in 0.5 cycles for one hour and twenty minutes. It was possible to obtain stable CNTs dispersion by the low insertion of oxygen functional groups. It was evaluated the effect of the incorporation of SWCNTs ox. and MWCNTs ox. 1 mg/mL in the GO dispersion (5 mg/mL) pointing to the preparation of GO microfibers, using a CTAB solution (0.05% m/v) as a coagulant agent, and a GO dispersion with a flow rate of 4 $mL.min^{-1}$. Based on our preliminary results, the incorporation of CNTs on the GO dispersion allowed the formation of GO fibers with mechanical resistance to the drawing process used in the wet-spinning technique. We obtained GO fibers longer than 5 cm. We demonstrated a systematic study of the fabrication of hybrid CNTs ox - GO fibers by wet-spinning. Ongoing experiments have been performed to evaluate the alignment between the GO nanosheets and CNTs ox and the employment of the hybrid carbon nanofibers as electrical yarns.

Agradecimentos/Acknowledgments

Fapesp, Mackpesquisa, INCT NanoVida, CNPq, and FINEP.

References

1 – XU, Z.; GAO; C. Graphene Fiber: A New Trend in Carbon Fibers. Materials Today, v. 18, N.9, p. 480-492, 2015.
2- ROCHA, J. F. et al. Graphene oxide fibers by microfluidics assembly: A strategy for structural and dimensional control. **Nanoscale**, v. 13, n. 14, p. 6752–6758, 14 abr. 2021.
3- HUMMERS, W. S.; OFFEMAN, R. E. Preparation of Graphitic Oxide. Journal of the American Chemical Society, v. 80, N. 6, p. 1339, 1958.
4- Rosca, I. D., Watari, F., Uo, M. & Akasaka, T. Oxidation of multiwalled carbon nanotubes by nitric acid. Carbon N. Y. 43, 3124–3131 (2005).

Área: MAT

Development of new organoselenium derivatives containing 1H-Tetrazol nucleus as efficient anticorrosive agents

Victor H. M. Costa (IC)[1], Pâmella S. Cordeiro (PG)[1], Vinicius M. dos Santos (PG)[2], Caio M. Fernandes (PG)[2], Joel S. Reis (PQ)[1], Eduardo A. Ponzio (PQ)[2] and Vanessa Nascimento (PQ)[1]

vhmenezescosta@id.uff.br, nascimentovanessa@id.uff.br

[1] *Laboratório SupraSelen, Universidade Federal Fluminense, Niterói, RJ, Brasil*
[2] *LAMUFF, Department of Chemistry, Fluminense Federal University*

Keywords: Organoselenium, Tetrazole, Corrosion

Highlights

Based on a series of 8 synthesized selenocompounds containing the tetrazole nucleus, this work shows successful studies on the application of these molecules against corrosion phenomenon.

Resumo/Abstract

Corrosion consists in the spontaneous degradation of metallic materials due to their interaction with the environment[1]. One of the main methods of protecting metal alloys is the application of organic corrosion inhibitors[1]. Compounds containing heteroatoms (N, O and S) and π electrons have been described for their ability to increase adsorbent properties on the metal surface due to the donation of electron pairs to empty d orbitals of metal surface atoms, forming protective layers[1]. In this way, organoselenium compounds emerge as a promising alternative due to the characteristic of increasing the strength of the bond between the organic molecule and the metal surface, forming a protective layer. Thus, the objective of this work was to synthesize and evaluate the anticorrosive potential of organoselenium derivatives in order to compare the effect of the tetrazole nucleus with its precursor "CN". Therefore, **1a-d** (SeCN) and **2a-d** (Se-Tetrazole) compounds were synthesized.[3]. The Weight Loss Study (WLS)[4] was the preliminary test chosen to obtain the first indications that organic molecules could be applied as anticorrosive agents. The results obtained on 1020 carbon steel in an acidic environment (1M HCl) are shown in Figure 1 by the highest anticorrosive rate value achieved by each compound. Thus, it can be observed that aliphatic derivatives presented the greatest potential for prevention, however, at a concentration 2x higher than aromatic derivatives. Therefore, aromatic derivatives presented the best results, as they reach high values under low concentration. and the presence of the tetrazolic nucleus increased the anticorrosive activity of the derivatives. Furthermore, electrochemical tests have shown that these molecules act by reducing cathodic and anodic currents, increasing the polarization resistance of carbon steel and protecting it against corrosion. Figure 2 exemplifies the polarization curve for compound **2a** which was the best result.

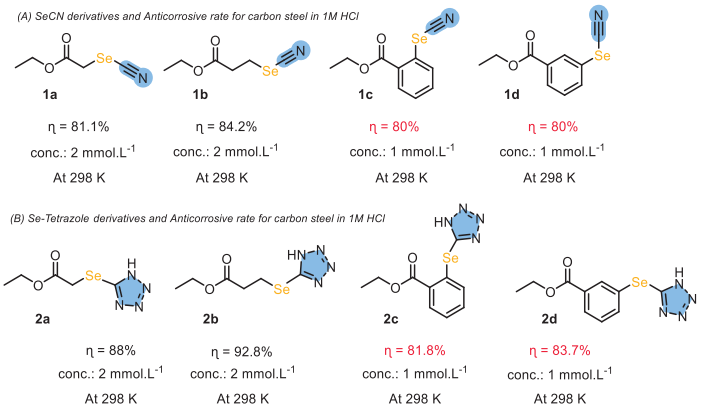


Figure 1. Structures of anticorrosive derivatives.

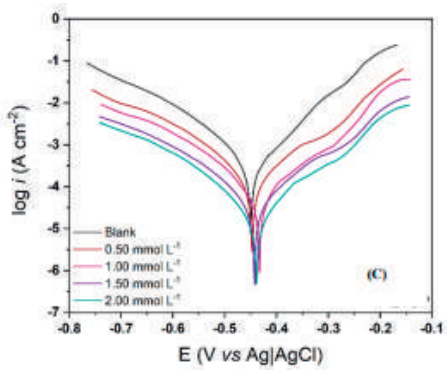


Figure 2. Polarization curves for selenocompound 2a in steel carbon in HCl 1 mol.L^{-1} at 298K

Agradecimentos/Acknowledgments

CAPES, FAPERJ, UFF

[1] Fernades. C. M. et al; *J. Mol. Liq.*, **2023**, 375, 12199. [2] Abd El-Lateef H. M. et al; *J. Tai. Inst. of Chem. Eng.,* **2022**, *133*, 9360. [3] Leal, J. G. et al; *New Journal of Chemistry*. **2017**, 41, 5875 [3] Clarembeau, M. et al. *Tetrahedron*. **1985**, 41 (21), 4793–4812. [4] DE SAMPAIO, M. T. G. et al; *J. Bio- and Tribo-Corrosion*, **2021,** v. 7, n. 1, p. 14.

Área: MAT

Development of SBA-15:CeNi nanocomposites: The influence of the synthetic method on metal dispersibility and oxygen vacancy formation.

Danilo Waismann Losito (PG),[1*] Tereza S. Martins (PQ).[1]

d.losito@unifesp.br

[1]*Departamento de Química, Instituto de Ciências Ambientais, Químicas e Farmacêuticas, UNIFESP, São Paulo, SP, Brasil;*

Palavras Chave: *Nanocomposites, Oxygen vacancy, Ceria-Nickel Solid solution, Direct synthesis, Post synthesis.*

Highlights

Comparison between the properties of the nanocomposites prepared by Direct Synthesis and Post Synthesis. The direct synthesis method results in metallic nanoparticles on the external surface of SBA-15, while the post-synthesis method retains these nanoparticles within the SBA-15 mesoporous. The formation of CeO_2 structure dopped with nickel is influenced by the synthesis method, providing different concentrations of oxygen vacancies, extremally important for the adsorption and catalysis of CO_2.

Resumo/Abstract

Cerium-Nickel oxide-based nanocomposites are very promising for use in environmental technologies due to their catalytic behavior and unique structural, textural, and morphological properties. The development of nanocomposites containing CeO_2 and SBA-15 as support for metals such as nickel (Ni) has been investigated to provide promising materials to be applied as adsorbents and catalysts for pollutant molecules. The presence of CeO_2 improves catalytic activity through the dispersion of Ni in the mesoporous of SBA-15, avoiding agglomeration and providing better metal-support interaction. Moreover, SBA-15 increases the stability of the inorganic species, preventing its early deactivation. To study the preparation of materials with these characteristics, CeO_2 and NiO provided by nitrate precursor salts were incorporated intoSBA-15 using different methods known as direct synthesis and post-synthesis to check the influence of synthetic rote in their structural, textural, and morphological properties. The Small-angle X-ray scattering (SAXS) curves showed that all nanocomposites have a 2D hexagonal mesostructured porous (p6mm space group) with a narrow pore size distribution similar to that of SBA-15. X-ray powder diffraction (XRD) analysis revealed the crystalline cubic fluorite-type and halite-type of space group Fm3m structure of CeO_2 and NiO respectively. Raman spectroscopy shows the doping of ceria structure, through nickel particles forming a solid solution and providing oxygen vacancies. Scanning electron microscopy (SEM) images evidenced the different morphology and particle size of the materials prepared. Comparatively, this work highlights the enhanced properties for nanocomposites prepared by post-synthesis, with better dispersion of CM and consequent better metal-support interaction, using ceria and nickel nanoparticles.

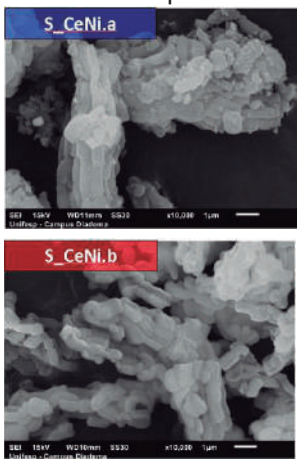


Figure 1 SEM images for the nanocomposites S_CeNi.a and S_CeNi.b .

Legend for the samples names

S = SBA-15 - **CeNi** = CeO_2 and NiO in 10% of molar ratio (M/Si)
a= direct synthesis **b**= post synthesis

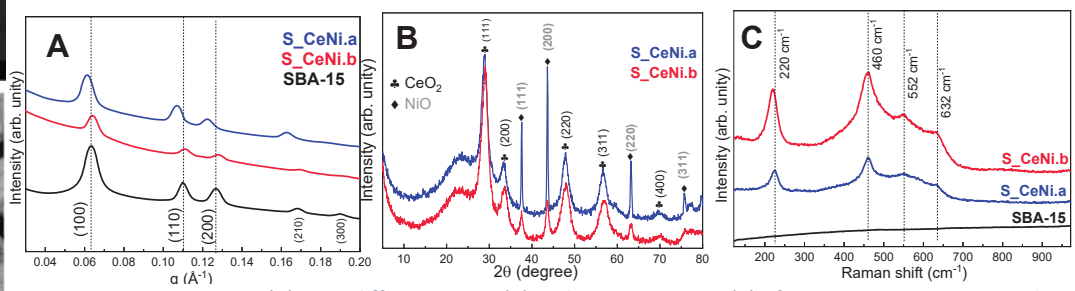


Figure 2 SAXS curves (A), XRD diffractograms (B) and Raman spectra (C) of nanocomposites prepared.

Agradecimentos/Acknowledgments

Gratitude to CAPES (Grant No. 88887.807767/2023-00), INCT/INEO, and FAPESP for financial support. Special thanks to Prof. Dr. Marcia C. A. Fantini, Prof. Dr. Cristiano L.P. Oliveira, Mr. Tarsis M. Germano, and Mr. Antonio Carlos F. da Silveira from the USP Institute of Physics for their assistance with SAXS and XRD equipment. Thanks for Prof. Paula S. H. Ferreira from Unifesp Diadema for the availability of the FTIR equipment. We also acknowledge support from CaPGPQ-UNIFESP Diadema for SEM and Raman analyses. Appreciation to Prof. Dr. Norberto S. Gonçalves for Raman analysis support.

Área: _____MAT_____
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Development of Zika virus detection method using an immunosensor and dynamic light scattering

Carolina B.P. Ligiero (PQ),[1] Claudio C. Cirne (PQ),[2] Izabel Paixão (PQ),[2] Célia M. Ronconi (PQ)*[1]

cligiero@id.uff.br; cmronconi@id.uff.br

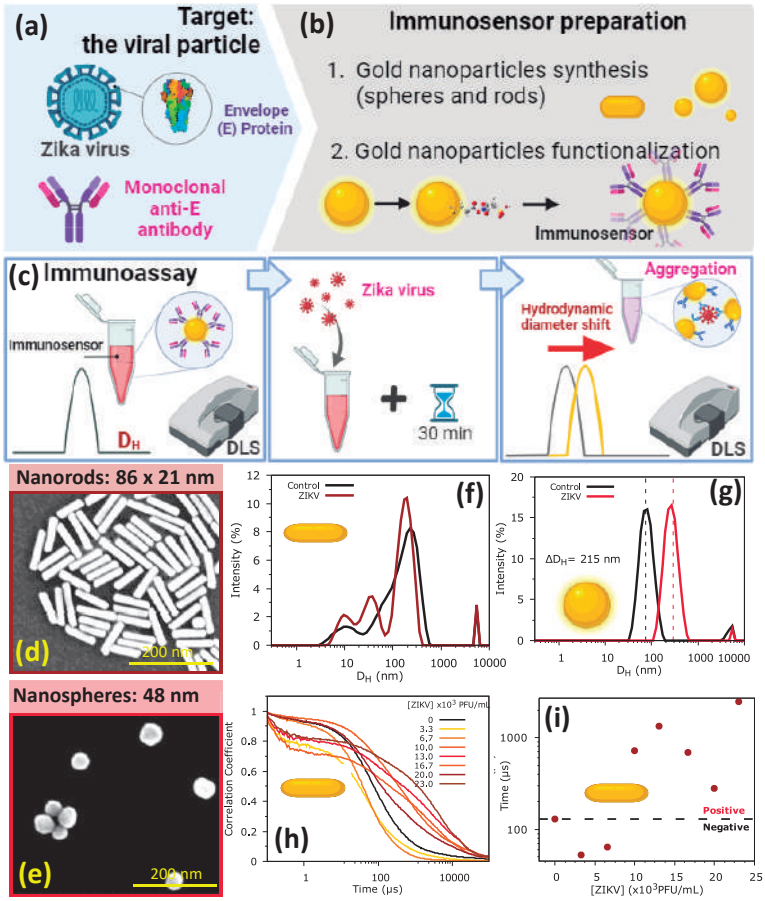
[1]Departamento de Química Inorgânica, Universidade Federal Fluminense, Campus do Valonguinho, Outeiro de São João Batista, s/n, 24020-141, Niterói, RJ, Brasil; [2]Departamento de Biologia, Campus do Gragoatá, rua Prof. Marcos Waldemar F. Reis,, Niterói, RJ, 24210-201 Niterói, RJ, Brasil

Key words: *Gold Nanoparticles, Zika Virus, Dynamic Light Scattering, Immunoassay*

Highlights

Zika virus fast detection. The test is an immunoassay based on antibody-gold nanoparticles with different morphologies. Zika virus is traced by changes in the Dynamic Light Scattering (DLS) response.

Abstract



Zika (ZIKV) is a pathogenic arbovirus from the *Flavivirus genus.* In the 2015 Brazilian epidemic outbreak, the association of ZIKV contamination and microcephaly in newborns was well established.[1] Due to severe neurological complications attributed to Zika infection, the development of fast and selective tests is an important task.[2] Due to the relevance on the earliest detection to disease management, selective detection of the viral particle was chosen as target **(a)**. To achieve a new rapid test for ZIKV, we synthesized gold nanospheres and nanorods. Next, we functionalize the nanoparticles to covalently couple monoclonal anti-envelope antibodies on their surfaces **(b, d, e)**.[3,4] Then, we analyze the modulation on the DLS response in the presence of the ZIKV particles in an immunoassay **(b)**. The immunosensors of both morphologies provides positive shifts of the hydrodynamic diameter (D_H) in the presence of ZIKV by DLS **(f, g)**, indicating aggregation induced by the formation of an immune complex.

When DLS correlogram was used as the response tracer **(h)**, we got a detection limit of 10×10^3 PFU/mL **(i)**, a useful detection range. The results are being optimized to be validated.

References
[1] Schuler-Faccini, L *et al. Morb. Mortal. Wkly.* **2016**, *65*, 59.
[2] Santos, C.C.C. *et. al Arch. Biomed. Eng. Biotechnol.* **2019**, *1*, 1.
[3] Ligiero, C.B.P. *et al. Mater. Today Chem.* **2022**, *25*, 100924.
[4] Silva, P.B. *et al. Talanta.* **2022**, *243*, 123355.

Acknowledgments

FAPERJ SEI-260003/006613/2022 LAMATE INMETRO

Área: MAT

Direct population in the triplet states using $NaREF_4$:Yb functionalized with 3,5-dibromobenzoate for obtaining luminescent temperature probes

Sergio F. N. Coelho (PG),[1*] Airton G. Bispo-Jr (PQ)[1], Nagyla A. Oliveira (PG)[1], Italo O. Mazali (PQ)[1], Fernando A. Sigoli (PQ)[1]

Sergio.fern@hotmail.com;

[1]*Institute of Chemistry, University of Campinas, Campinas, Brazil*

Palavras Chave: *Nanoparticles, Triplet State, Antenna Effect, Luminescence*

Highlights

Direct population of 3,5-dibromobenzoate ligand triplet states in Yb^{III} -doped $NaGdF_4$:Yb^{III} nanoparticles leading to Yb^{III} NIR emission due to ligand-to-Yb^{III} non-radiative energy transfer on the nanoparticle surface.

Resumo/Abstract

Fluorides, especially $NaREF_4$ (RE= Rare Earth) are an excellent matrix for luminescent lanthanide ions. They have low phonon energy (~400 cm^{-1}), are photochemically stable, are synthesized with controlled particle sizes and morphologies and can be easily surface-functionalized. Some organic ligands such as 3,5-dibromobenzoate (3,5-bbza$^-$) ligand may functionalize these nanoparticles surface improving the light absorption at UV-Vis region and, therefore, the emission by the well-known antenna effect. The use of this ligand introduces a new excitation pathway in ligand-nanoparticle hybrid systems using direct excitation from singlet to triplet states ($S_0 \rightarrow T_n$). This strategy can lead to some advantages such as a decrease in the excitation energy when compared to the energy used in the $S_0 \rightarrow S_n$ transition, minimization of energy losses in energy transfer processes such as internal conversion and intersystem crossing. In this work, it is demonstrated the direct population of triplet states through spin-forbidden $S_0 \rightarrow T_n$ transitions in Yb^{III}-doped $NaGdF_4$ nanoparticles functionalized with the 3,5-bbza$^-$ ligand coordinated to the Ln^{III} centers onto the particle surface, leading to the typical Yb^{III} emission within the NIR window. The $NaGd_{0.80}F_4$:$Yb_{0.20}$ nanoparticles have been synthesized by thermal decomposition method. The surface modified-free nanoparticle was prepared by acid washing and then its surface was functionalized by adding the 3,5-dibromobenzoate ligand (3,5-bbza$^-$). The NPs were characterized by XRD, FTIR, DRS and PL. Herein, this possibility is discussed for hybrid systems based on spheroidal $NaGdF_4$:Yb^{III} nanoparticles (average diameter of 7.8 nm) functionalized on the surface with 3,5-dibromobenzoate (3,5-bbza$^-$) coordinated to Ln^{III} ions. The triplet states of 3,5-bbza$^-$ are directly populated upon excitation at 368 nm or 430 nm, followed by energy transfer to Yb^{III} that emits within the NIR spectral region. On the other hand, the ligand singlet states are populated at 300 nm. Taking advantage of the intensity ratio of the emission spectrum collected upon $S_0 \rightarrow T_n$ (368 nm or 430 nm) and $S_0 \rightarrow S_n$ (300 nm) excitation, and two conditions were used to define the thermometric parameter by considering the emission spectra collected upon the S→T excitation at 368 nm ($\Delta_{368/300} = I_{368/I300}$) or at 430 nm ($\Delta_{430/300} = I_{430/I300}$). And with that, the luminescence thermometry was performed for the hybrid system, which displays maximum relative thermal sensitivity of 0.58% K^{-1} at 77 K for both intensity ratio. Therefore, the $S_0 \rightarrow T_n$ transitions observed in the $NaGdF_4$:Yb^{III} nanoparticles functionalized with 3,5-bbza$^-$ enable visible-shifted excitation bands and luminescence thermometry, which are interesting features aiming application in cell imaging and temperature probing, respectively.

Agradecimentos/Acknowledgments

INOMAT, FAPESP, CNPq and Capes

Área: MAT

Direct synthesis bismuth compounds [BiMO]-HZSM-5 (M = V, Ti, Nb) in ZSM-5 zeolite aiming materials with photocatalytic properties

João Pedro S. Alves (IC),[1,*] Letícia S. Novais (IC),[1] Luciana A. Silva (PQ),[1,2] Raildo A. F. Júnior (PQ),[1,2] Mauricio B. dos Santos (PQ),[1,2] Artur J. S. Mascarenhas (PQ),[1,2] Fernanda T. Cruz (PQ)[1,2]

*** alvesj@ufba.br; fernandateixeira@ufba.br**

[1] Laboratory of Catalysis and Materials - LABCAT, DQGI, IQ, Ondina Campus, Federal University of da Bahia, Salvador-BA, Brazil
[2] Multitasking Laboratory, Interdisciplinary Center for Energy and Environment – CIENAM, Ondina Campus, Federal University of Bahia, Salvador - BA, Brasil.

Palavras Chaves*:* heterogeneous photocatalysis, pollutants, H-ZSM-5, quantum confinement, *bandgap*.

Highlight

- Insertion of BiMOx (M = Ti, V, or Nb) during the hydrothermal synthesis of ZSM-5 zeolite.
- Segregated phases of mixed oxides are not observed.
- The BiMOx nanoclusters promote interesting electronic properties for photocatalysis.

Abstract

The development of materials with potential applications in photocatalysis is necessary given the current environmental scenario of aqueous effluent pollution. One of the most commonly used advanced oxidative processes (AOPs) for pollutant removal is heterogeneous photocatalysis. The process involves irradiating photons onto the semiconductor, which, through electronic transitions from the valence band to the conduction band, generates the electron/hole pair, acting as redox sites to degrade the target molecule. Zeolites have high surface area and are good adsorbents but lack significant optical and electronic properties. However, the insertion of metals into the zeolitic structure can promote interesting optical characteristics as well as redox sites available for use in photocatalytic systems. In this study, composites with 5% of each metal (Bi, V; Bi, Ti; and Bi, Nb) were prepared in ZSM-5 by adding them to the synthesis gel, following a synthesis methodology adapted from the International Zeolite Association - IZA. After preparation, the materials were calcined and named [BiVO]-HZSM-5, [BiTiO]-HZSM-5, and [BiNbO]-HZSM-5. The obtained composites were characterized by XRD, TG/DTG, FTIR, DRS, SEM, and textural analysis. The pure and crystalline H-ZSM-5 exhibited peaks compatible with the crystallographic pattern of zeolite ZSM-5 (MFI topology) IZA. The synthesized composites (Fig. 1) showed a similar profile to ZSM-5, an interesting zeolitic structure. The absence of characteristic oxide peaks in XRD suggests that they must be inserted into the zeolitic structure (Ti, V) and/or finely dispersed in the channels and external surface (Bi, Nb). The band gap (Eg) value calculated by the Tauc method for the materials [BiVO]-HZSM-5, [BiTiO]-HZSM-5, and [BiNbO]-HZSM-5 are 4.23, 4.06, and 3.23 eV, respectively. The quantum confinement effect suggests that the shift of the absorption edge is inversely proportional to the particle size; thus, high Eg values are related to smaller particles that can be modulated and applied in photocatalysis. Therefore, the synthesized composites exhibit photocatalytic properties of great interest for application in the ultraviolet region, as indicated by Eg.

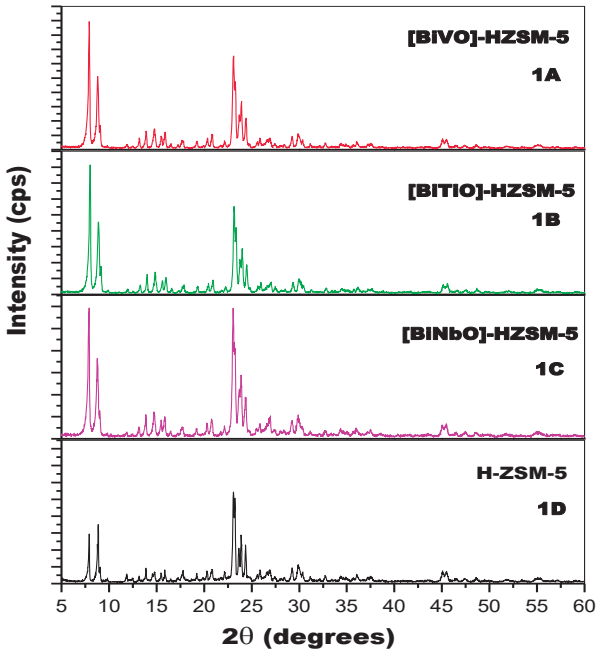


Figura 1: DRX dos materiais

Acknowledgments

To PROPCI - PRPPG/UFBA 007/2022– JOVEMPESQ UFBA for granting the scholarship and to FINEP ref. 0057/21.

Área: QM

Donor–acceptor 1–donor–acceptor 2 terpolymers with tunable properties based on a fluorene donor.

Harison J. Toledo (IC)[1], Leonardo V. Cunha (IC)[1], Paula C. Rodrigues (PQ)[1*]

paulac@utfpr.edu.br

[1]Chemistry and Biology Department, UTFPR.

Palavras Chave: *Conjugated polymers, Diketopyrrolopyrrole, Benzothiadiazole, D-A copolymers, Optoelectronic devices.*

Highlights

Compared with conventional D-A copolymers, the D-A_1-D-A_2 terpolymer approach is a promising strategy to tune the light absorption and emission profiles of materials applied in optoelectronic devices.

Resumo/Abstract

The donor−acceptor (D−A) approach, with alternating electron-rich (donor, D) and electron-deficient (acceptor, A) units along the conjugated polymer backbone, is an effective method to control the optical and electrochemical properties of the conjugated copolymers. One strategy to develop alternative D-A polymers is to synthesize random terpolymers by incorporating a third component (such as an acceptor unit) to form a Donor-Acceptor 1-Donor-Acceptor 2 (D-A_1-D-A_2) chain. Compared to the conventional binary D–A copolymers, random terpolymers have been proven as an effective and alternative method to control the optoelectronic properties, such as energy level, absorption spectrum, and aggregation, by controlling the proportion of the Acceptor 2 component. In this work, two conventional D−A copolymer and a random terpolymer D-A_1-D-A_2 composed of fluorene (D), benzothiadiazole (A_1), and thiophene-diketopyrrolopyrrole-thiophene (A_2) as a building block have been designed, synthesized, and analyzed in terms of optical and electrochemical properties. The D-A_1, D-A_2, and D-A_1-D-A_2 (with the D:A_1:A_2 molar ratio equal to 1.0:0.75:0.25) systems were synthesized using Suzuki cross-coupling reaction. The chemical structure of the copolymers was determined by NMR and FTIR. The copolymers displayed a dual-band absorption profile in their optical features, a phenomenon often reported in the literature. The electronic spectra of the binary D–A copolymers showed an intermolecular charge transfer band (ICT) in 445 and 650 nm, for the D-A_1 and D-A_2, respectively. Incorporating 25% of electron-withdrawing diketopyrrolopyrrole derivative (A_2) into the D-A_1 backbone, the D-A_1-D-A_2 random terpolymer presented a small blue shift in the ICT bands. This suggests that the absorption spectral ranges of the terpolymers could be adjusted by controlling the molar ratio of the A_1 and A_2 units, which act as moderate and strong accepting units, respectively. Regarding the photoluminescence properties, two distinct spectral features are observed in the emission spectra of the D-A_1-D-A_2 terpolymer upon excitation at 320 nm: (i) the green charge transfer emission (535 nm) from the D-A_1 unity and (ii) the red charge transfer emission (658 nm, with a shoulder at 720 nm) from the D-A_2 segments. Furthermore, initial findings indicate that the redox potentials of the D-A_1-D-A_2 structures can be effectively adjusted by incorporating varying proportions of the A_2 moiety into the polymer chain. This demonstrates that terpolymer synthesis is a simple yet effective strategy for tuning the optical and electrochemical properties of conjugated polymers in optoelectronic devices.

Agradecimentos/Acknowledgments

The authors acknowledge the National Institute of Organic Electronics (INEO), CNPq, and Araucaria Foundation.

Área: MAT

Dynamic Light Scattering detection of Zika virus NS1 protein based on monoclonal antibody functionalized AuNPs

Dayenny L. D. Leite (PG),[1] Isabela A. A. Bessa (PG),[1] Carolina B. P. Ligiero (PQ),[1] Célia M. Ronconi (PQ).[1]*

dayennylouise@id.uff.br; cmronconi@id.uff.br

[1]*Departamento de Química Inorgânica, Universidade Federal Fluminense, Campus do Valonguinho, Outeiro de São João Batista, s/n, 24020-141, Niterói, RJ, Brasil;*

Key words: *Zika virus detection, dynamic light scattering, gold nanoparticles, NS1 protein.*

Highlights

The development of an immunoassay-based selective biosensor for detection of ZIKV NS1 protein using dynamic light scattering is described

Abstract

Dengue, chikungunya and Zika virus are a few pathogens transmitted by the vector *Aedes aegypti* that constantly threats Brazil and other tropical regions around the world.[1] The absence of proper tests and the similar symptoms caused by these arboviruses make the clinical diagnoses inaccurate and the treatment less specific. Therefore, the development of new detection methods that differentiate these diseases arises to facilitate the diagnostic and guide a better treatment. Herein, we developed a nanobiosensor based on gold nanoparticles (AuNPs) for detection of NS1 protein of zika virus (ZIKV) through Dynamic Light Scattering (DLS). The 130 nm AuNPs were synthesized with the seeded-growth method and had their size measured by transmission electron microscopy (TEM). Then, the particles were functionalized with a monoclonal anti-ZIKV NS1 protein antibody using the crosslinker 3,3′-dithiobis(sulfosuccinimidylpropionate) (DTSSP), yielding the biosensor.[2] In the presence of saline phosphate buffer (PBS) (control), the nanobiosensors were destabilized due to the high ionic strength of the medium, leading to an increase in the hydrodynamic diameter (D_H) and a polydisperse profile in DLS analysis. However, in the presence of ZIKV NS1 protein, the D_H remains unchanged, monodisperse and with an average size of 150 nm (Figure 1(a)). These studies suggested that the antigen-antibodies interactions were able to stabilize the system, forming a passivation layer around the AuNP surface, resulting in a monodisperse medium. The detection limit was calculated by varying the protein NS1 concentration and analyzing the changes in D_H, which was 5.13 µg/mL (Figure 1(b)). To verify if the proposed nanobiosensors were specific to ZIKV NS1 protein, the same test was performed, using the NS1 protein of dengue virus (DENV2) and Spike protein from SARS-CoV-2. Interestingly, none of these proteins were able to stabilize the nanobiosensor, indicating that the only the specific interaction with ZIKV NS1 protein prevented the salt induced agglomeration (Figure 1(c)). These results suggests that the nanobiosensor can potentially be used as a detection method. Further tests to improve the limit detection are undergoing.

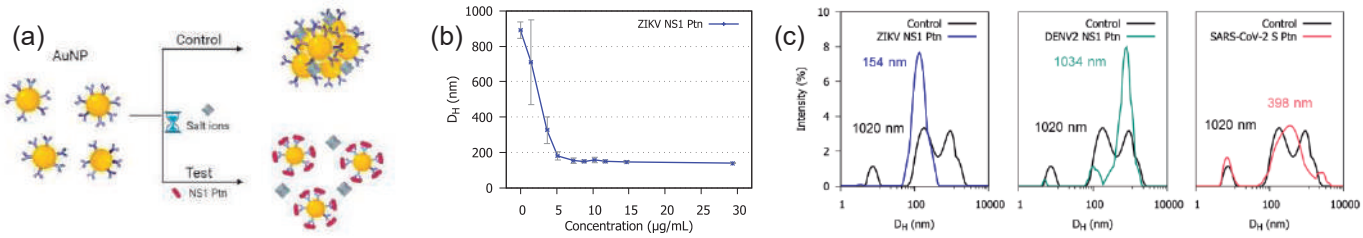


Figure 1. (a) Scheme of the working test; (b) Immunoassay varying the ZIKV NS1 protein concentration; (c) Selective tests with ZIKV NS1 protein, DENV2 NS1 protein and SARS-CoV-2 Spike protein.

Acknowledgments

UFF, CNPq, CAPES, FAPERJ, LAMATE-UFF, INMETRO, LECC-UFRJ

[1] Laporta, G. Z.; Potter, A. M.; Oliveira, J. F. A.; Bourke, B. P.; Pecor, D. B.; Linton, Y.-M. *Insects* **2023**, *14*, 49.
[2] Ligiero, C. B. P.; Fernandes, T. S.; D'Amato, D. L.; Gaspar, F. V.; Duarte, P. S.; Strauch, M. A.; Fonseca, J. G.; Meirelles, L. G. R.; da Silva, P. B.; Azevedo, R. B.; Martins, G. A. S.; Archanjo, B. S.; Buarque, C. D.; Machado, G.; Percebom, A. M. e Ronconi, C. M. *Mater. Today Chem.* **2022**, *25*, 100924.

Área: MAT

Efeito dos agentes de ligações cruzadas em imunossensores na detecção da proteína espícula do vírus SARS-CoV-2

Camille C. De Mello (PG),[1] Carolina B. P. Ligiéro (PQ), Célia M. Ronconi (PQ).[1]*

camillemello@id.uff.br; cmronconi@id.uff.br

[1] *Departamento de Química Inorgânica, Universidade Federal Fluminense, Campus do Valonguinho,* Outeiro de São João Batista, s/n, 24020-141, Niterói, RJ, Brasil

Palavras Chave: *Imunossensores, Nanopartículas de ouro, Espalhamento dinâmico de luz, Funcionalização, Proteína espícula.*

Highlights

Effect of cross-linking agents in immunosensors on the detection of the spike protein of the SARS-CoV-2 virus. Synthesis of immunosensors based on gold nanoparticles with bifunctional thiol/carboxylate cross-linkers for antibody coupling. The spike protein was detected by dynamic light scattering (DLS).

Resumo

Devido à recente pandemia de COVID-19, fez-se necessário investir no desenvolvimento de testes de detecção do vírus SARS-CoV-2.[1] O presente trabalho visa a obtenção de novos testes de antígeno para a detecção da proteína espícula (Ptn S). Os sensores (AuNPs-pAb) usados foram obtidos através do recobrimento de nanopartículas de ouro (AuNPs) com anticorpos policlonais (pAb).[2] Para isso, foi feita a funcionalização da superfície das AuNPs testando três agentes de ligações cruzadas: o ácido 11-mercaptoundecanóico (MUA), o ácido 6-mercaptohexanóico (MHA) e o ácido 3-mercaptopropiônico (MPA), com espaçadores de 11, 6 e 3 carbonos, respectivamente (Fig. 1a). A técnica escolhida para a detecção da Ptn S foi a de espalhamento dinâmico de luz (DLS). Partindo de AuNPs de 56 nm (Fig. 1b), foram notadas mudanças no diâmetro hidrodinâmico (D_H) durante a síntese dos AuNPs-pAb (Fig. 1c). Ao avaliar os sensores para o reconhecimento da Ptn S em diferentes concentrações do antígeno, nota-se que o bioconjugado com espaçador mais longo forneceu uma resposta mais promissora (Fig. 1d). O sensor preparado com MUA foi aquele que mostrou uma maior estabilidade, e além disso, os imunoensaios mostraram uma maior capacidade para o reconhecimento da Ptn S, resultando em maiores deslocamentos (maior ΔD_H) e um limite de detecção (LD) menor.

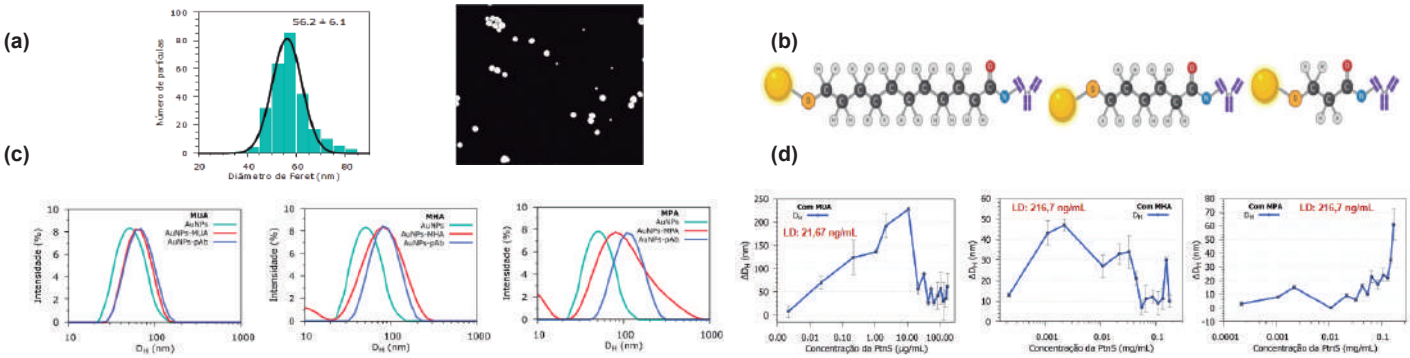


Fig. 1: (a) Agentes de ligação cruzada; (b) Caracterização das AuNPS; (c) Mudanças no D_H (DLS) durante as etapas de bioconjugação; (d) Curvas de concentração da Ptn S obtidas nos imunoensaios por DLS.

[1] Ligiero, C.B.P. *et al.* Influence of particle size on the SARS-CoV-2 spike protein detection. *Mat. Tod. Chem.*, v. 25, 2022.

[2] Silva, P. B. *et al*. Detection of SARS-CoV-2 virus via dynamic light scattering using antibody-gold nanoparticle bioconjugates against viral spike protein. *Talanta*, v. 243, 2022.

Agradecimentos

CAPES, PPGQ, UFF.

Área: MAT

Effect of synthesis parameters on the plasmonic properties of gold and platinum-based bimetallic nanoparticles (Au@PtNPs)

Franccesca Fornasier (PG),[1] Sthefany Faber Passos (IC),[1] Guilherme Conceição Concas (PG),[2] Liying Liu (PQ),[3] Yutao Xing (PQ),[4] Tommaso Del Rosso (PQ),[2] Ana Maria Percebom (PQ).[1]*

franc_ces_ca@hotmail.com; apercebom@puc-rio.br

[1]Department of Chemistry, Pontifical Catholic University of Rio de Janeiro, PUC-Rio; [2]Department of Physics, Pontifical Catholic University of Rio de Janeiro, PUC-Rio; [3]Centro Brasileiro de Pesquisas Físicas, CBPF; [4]Laboratório de Microscopia Eletrônica de Alta Resolução, Centro de Caracterização Avançada para Indústria de Petróleo (LaMAR/CAIPE), Universidade Federal Fluminense, UFF.

Keywords: *Core-shell, plasmon resonance, materials chemistry, nanotechnology*

Highlight

Controlling the synthesis parameters allows tailoring the optical properties of Au@PtNPs

Abstract

The deposition of metals such as platinum on the surface of spherical gold nanoparticles (AuNPs) makes it possible to improve the optical properties of AuNPs through the synergism of the two metals.[1] However, to achieve these new properties, it is necessary to control key synthesis parameters. As a strategy, the use of the two-step synthesis route allows the formation of bimetallic gold and platinum nanoparticles (Au@PtNPs) with powerful optical properties, which can be directed to various scientific and technological applications.[2] In this study, different sizes of spherical gold cores (7, 25 and 32 nm), Pt/Au molar ratios (0.33, 0.5, 1.0, 2.0, 3.0), using $H_2PtCl_6.6H_2O$ as platinum precursor and synthesis time (1, 4 and 6 h) were parameters selected to understand their effects on the morphology and plasmonic properties of Au@PtNPs. The samples were characterized by DLS, Zeta Potential, TEM and Spectroscopy. The results obtained were systematically correlated to understand the influence of each selected synthesis parameter. The variation of the platinum precursor influenced the growth of denser layers of platinum nanoparticles (PtNPs) as the Pt/Au molar ratio increased, and this directly reflected the morphology and plasmonic properties (Figure 1A), as well as stability of Au@PtNPs. All syntheses were carried out at 30 °C without the use of surfactants and interestingly, after 4 h of synthesis no major changes in plasmonic properties were observed (Figure 1B). By varying the size of the gold core and fixing the 2.0 Pt/Au molar ratio, it was possible to control the shift of the plasmonic resonance band of the Au@PtNPs to longer wavelengths (Figure 1C). With the systematically correlated results, it was possible to understand the role of each synthesis parameter in the formation of Au@PtNPs, controlling and adapting the optical properties that are fundamental in various applications, such as photothermal treatment.

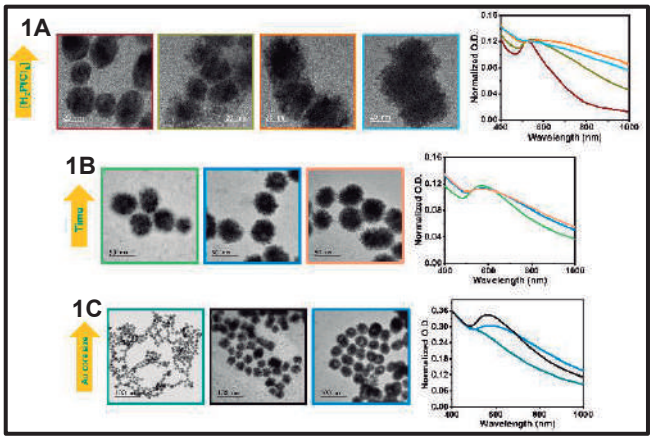


Figure 1. (a) TEM images of Au@PtNPs with [H_2PtCl_6] variation and plasmonic effect, (b) TEM images of Au@PtNPs with variation of synthesis time and plasmonic effect and, (c) TEM images of Au@PtNPs with variarion of core size and plasmonic effect.

References:
1. FU, Qiangqiang et al. Versatile barometer biosensor based on Au@Pt core/shell nanoparticle probe. **ACS sensors**, v. 2, n. 6, p. 789-795, 2017.
2. GAO, Zhuangqiang et al. Platinum-decorated gold nanoparticles with dual functionalities for ultrasensitive colorimetric in vitro diagnostics. **Nano Letters**, v. 17, n. 9, p. 5572-5579, 2017.

Acknowledgments

We thank: CNPq, FAPERJ, and CAPES for financial support; LNNano for the use of TEM; CAPLH for the use of the DLS instrument; LSQN: for kindly providing part of the 25 nm AuNPs used as core.

Área: MAT

Effect of thermal treatment on ZnO-derived zinc-metal-organic framework for detecting volatile organic compounds

Henrique S. Gropelo (PG),[1]* Reinaldo S. Theodoro (PG),[1] Diogo P. Volanti (PQ).[1]*

henrique.gropelo@unesp.br; diogo.volanti@unesp.br

[1] *Laboratory of Materials for Sustainability (LabMatSus), São Paulo State University (UNESP), Rua Cristóvão Colombo 2265, São José do Rio Preto 15054-000, Brazil*

Keywords: *MOF-5, Microwave-assisted solvothermal, Thermal processing, Gas sensor, ZnO, VOCs*

Highlights

Effects of crystallite size on ZnO sensors to enhance the rapid and selective detection of volatile organic compounds. Synthesis of MOF-5 using a microwave-assisted solvothermal method.

Abstract

This research aims to test ZnO, an n-type semiconductor metal oxide derived from metal-organic frameworks (MOF), as a sensor for volatile organic compounds (VOCs) and assess the effects of different ZnO crystallite sizes on sensor performance. MOF-5 is the precursor of zinc oxides and was synthesized using the modified microwave-assisted solvothermal method (MAS), following the methodology described by WANG [1]. The synthesis was carried out by mixing 12 mmol of $Zn(NO_3)_2.6H_2O$ and 4 mmol of terephthalic acid (H_2BDC), dissolved in 60 mL of DMF. The solution was transferred to a hydrothermal microwave reactor and maintained at 150 °C for 2 hours. After the synthesis of MOF-5, it underwent heat treatment at different calcination temperatures (450 to 800 °C) to obtain ZnO with various crystallite sizes, as illustrated in Figure 1. It is worth noting that temperature is the primary factor influencing microstructural characteristics [2]. Following this logic, 0.5 g of MOF-5 was calcined under six different temperature conditions: 400, 450, 500, 550, 600, and 800 °C for 2 hours, with a pre-treatment at 150 °C for 2 hours and a heating rate of 5 °C/min. This process resulted in the following samples: ZnO-400, ZnO-450, ZnO-550, ZnO-600, and ZnO-800. The thermogravimetric analysis (TGA) of MOF-5 and the samples' X-ray diffractometry (XRD) data indicated the complete formation of ZnO at temperatures above 450 °C. High calcination temperatures (600 and 800 °C) resulted in diffractograms with narrow peaks. The peaks in the diffractograms of the ZnO nanoparticles align with the characteristic indexing peaks (JCPDS no. 79-205). The sizes of the crystallites were determined by applying the Debye-Scherrer equation based on the diffractograms, revealing an increase in crystallite size with the rise in calcination temperature. Specifically, ZnO-450 exhibited a size of 17.8 nm, ZnO-550 (21.9 nm), and ZnO-800 (34.3 nm). It is essential to highlight that the present research described here is in development, and the performance analyses of ZnO sensors are in the testing phase. During this stage, the ZnO sensors will undergo testing for the following VOCs (acetone, 2-butanone, benzene, toluene, m-xylene, and 1-pentanol). The change in the resistivity of the material will be analyzed in the presence of VOCs (100 ppm) under different environmental conditions of temperature (200 to 450 °C) and relative humidity (from dry to 90% RH). Additionally, the research aims to determine the detection range of the sensors about VOCs (1 to 500 ppm), stability, and selectivity. The ZnO-600 sample showed the best response (562) for 100ppm of 1-pentanol at 350 °C in a dry atmosphere. References: [1] Y. Wang, S. Ge, W. Cheng, Z. Hu, Q. Shao, X. Wang, J. Lin, M. Dong, J. Wang and Z. Guo, *Langmuir*, 2020, **36**, 9658–9667. [2] Y. He, L. Zhong, X. Wang, J. He, L. Wang, C. Zhong, M. Liu, Y. Zhao, X. Lai, J. Bi and D. Gao, *Electrochim. Acta*, 2021, **367**, 137435.

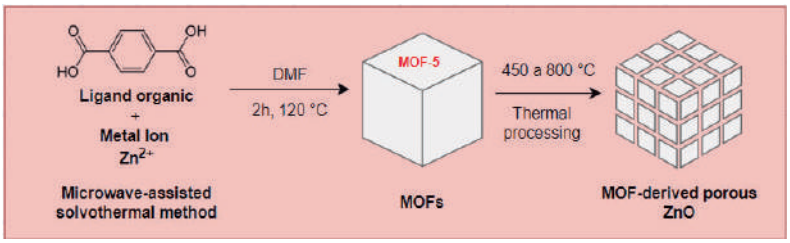


Figure 1: Synthesis of MOF-5 and obtaining ZnO sensors.

Acknowledgments

Fapesp (2020/06421-1), CNPq (311453/2021-0), CAPES, PROPG & PROPe-Unesp, PROAP/CAPES - PPG-Química Unesp SJRP and Laboratório de Sucroquímica e Química Analítica (LSQA).

Área: MAT

Electrokinetic and electroanalytical studies of nicotine electrooxidation promoted by reduced graphene oxide/silver-copper-mixed hexacyanoferrate

Pedro H. S. Borges (PG),[1]* **Edson Nossol (PQ).**[1]

pedroborges@ufu.br

[1]*Instituto de Química, Universidade Federal de Uberlândia, Uberlândia, MG, Brasil*

Palavras Chave: *Graphene, Prussian blue, Nanocomposite, Sensor, Nicotine, Tobacco*

Highlights

The copper-silver-mixed hexacyanoferrate/reduced graphene oxide novel nanocomposite showed synergistic effect towards the electrooxidation of nicotine and its viability as sensor was evaluated.

Resumo/Abstract

Nicotine (NIC) is an alkaloid found in tobacco leaves and it is strongly addictive. Cigars and cigarettes are the most commonly consumed tobacco-based products. It is known that the habit of smoking tobacco, and consequently consuming NIC, is very harmful for human health, triggering strokes, cancer, and heart, lung, and brain diseases.[1] Therefore, it is essential that this substance be sensitively and selectively monitored in tobacco products. So, the present work demonstrates a route of synthesis of a novel nanocomposite for NIC sensing purposes.

The preparation of a reduced graphene oxide/silver-copper-mixed hexacyanoferrate (rGO/AgCuHCF) nanocomposite is firstly reported by this work. The electrochemical synthesis of the material was optimized for the electrooxidation of NIC studying the molar fractions of Ag (X_{Ag}) and Cu (X_{Cu}), and the pH value of the ferricyanide solution (pH_{HCF}) used to form the metal hexacyanoferrate species. Those two parameters were evaluated through a 2^2-factorial design of the experiments, resulting better sensitivity when X_{Ag} = 0.75 and pH_{HCF} = 7.0.

Typical signals in Raman and infrared spectroscopies confirmed the coexistence of rGO and AgCuHCF in the composition of the nanomaterial, attesting a successful preparation method. Cyclic voltammetry (CV) in a neutral KNO_3 solution for 100 cycles showed that the presence of rGO drastically improves the electrochemical stability of the AgCuHCF material. The electrochemical oxidation of NIC promoted by the rGO/AgCuHCF nanocomposite showed higher signal in neutral pH and it involves the irreversible extraction of one proton and one electron. Other electrochemical tests revealed that the enhanced signal promoted by the material is due to synergistic interactions between rGO and AgCuHCF components.

Electroanalytical evaluation of the rGO/AgCuHCF modified electrode was performed by chronoamperometry assisted by a batch injection analysis (BIA) cell. The cell parameters were previously optimized. The injections of increasing concentrations of NIC showed good linear correlation in two ranges: 5.0 – 100.0 (R^2 = 0.998) and 100.0 – 2000.0 μmol L^{-1} (R^2 = 0.997). The method returned a satisfactory limit of detection (LOD) of 1.62 μmol L^{-1} and good responses towards repeatability, reproducibility, selectivity, and stability tests, demonstrating the viability of rGO/AgCuHCF for NIC determination in commercial samples.

[1] Rajendran, J., Reshetilov, A. N., & Sundramoorthy, A. K. (2021) Materials Advances, 2(10), 3336-3345.

Agradecimentos/Acknowledgments

The authors thank to GQMIN, UFU, GMIT, CNPq, CAPES, FAPEMIG, and INCT Nanocarbon.

Área: MAT
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Electrostatic Charging in 3D Printing: Manufacturing Quasi-Electrets

Milton A. F. Neto (IC),[1] Thiago A. L. Burgo (PQ) [1]*.

milton.faria@unesp.brmail.com; thiago.burgo@unesp.br

[1]*Departamento de Química e Ciências Ambientais, Instituto de Biociências, Letras e Ciências Exatas, Universidade Estadual Paulista "Júlio de Mesquita Filho" (Unesp), Campus de S. J. do Rio Preto*

Palavras Chave: *3D printing, electrostatics, electrets, energy harvesting, Kelvin probes, charge dissipation.*

Highlights

We 3D-printed an object in an electric field, showcasing a remarkably stable electrostatic potential with the potential to revolutionize electret production.

Resumo/Abstract

Considering all the mechanisms whereby materials become electrified, we posed a simple question: should objects printed in 3D accumulate charge?
The ubiquitous nature of electrostatic charges finds its roots in many sources. Objects created through the fused deposition modeling (FDM) process in 3D printers undergo a range of electrostatic charging phenomena, from friction to phase change. Indeed, 3D-printed objects, even with a few polymer layers, accumulate charges exceeding thousands of volts. This oversight in considering their electrical properties is crucial, especially in electronics for miniaturized components where electric field gradients must not exceed a few volts.
Apart from noting the spontaneous charge accumulation in polymers, our group's expertise in dielectric electrostatic charging guided the development of straightforward protocols for 3D printing electrets. An electret is a dielectric material that has a quasi-permanent electric charge. Electrets find applications in various technologies, including microphones, sensors, and other electronic devices, where a stable electric charge is needed for proper functioning.
Here, two copper tapes were applied atop the glass substrate and linked to a ±200 V DC power source, where the printing of an acrylonitrile butadiene styrene (ABS) square object between the copper wires was done. We have used non-contact Kelvin electrodes connected to electrostatic voltmeters (Trek, 320C) to monitor charge build-up and dissipation. The result is a homogeneous negative charged ABS material with a very slow potential dissipation. This quasi-electret is the result of trapped charges within the electric field that is facilitated during the melting/solidification process of the polymer. Water adsorption mediate charge buildup on polarized glass surfaces and this negative charge can be transferred to the polymer during the 3D printing process.
The production of electrets using a 3D print machine represents a breakthrough with far-reaching implications for many technologies. Energy harvesting and sensor devices relying on charged materials for input and/or feedback systems stand to benefit significantly from this easily constructed electret. We believe that even the fundamental, long-standing, and persistent questions of electrostatics, such as the nature of charge carriers, could be addressed through 3D printing.

Agradecimentos/Acknowledgments

This work is supported by Brazilian agencies MCTIC/CNPq (465452/2014-0) and FAPESP (2014/50906-9) through INCT/INOMAT (National Institute for Complex Functional Materials).

Área: MAT

Endodontic sealer: effects of N-acetylcysteine and Hydroxyapatite

Ermelinda Silvana Junckes (PG),[1] Marcia Margarete Meier (PQ)[1]
ermelindasilvana@gmail.com; marcia.meier@udesc.br.

[1]*Departamento de Química, UDESC/CCT*

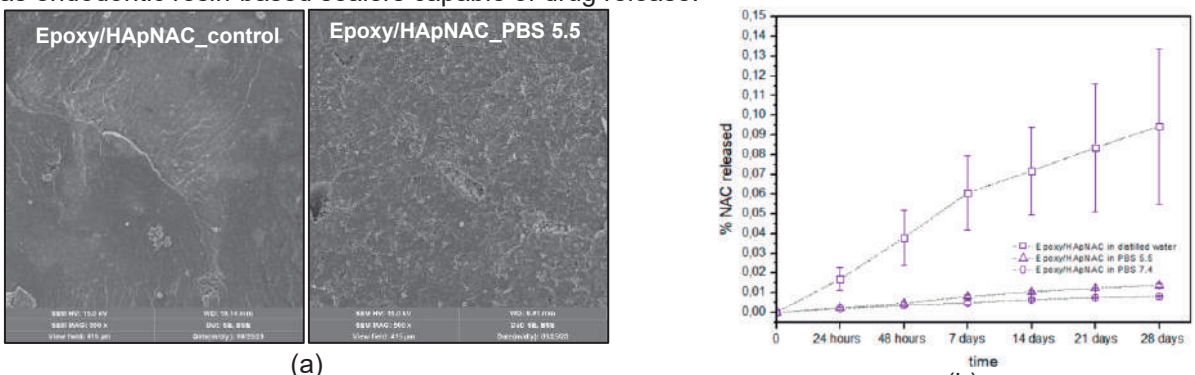
Palavras-Chave: endodontic sealer, hydroxyapatite, epoxy resin, n-acetylcysteine, solubility.

Highlights

Hydroxyapatite particles, with and without adsorbed N-acetylcysteine (NAC), were incorporated into a resin-based experimental endodontic sealer. This work evaluated Ca^{2+} and NAC release, pH media changes, and weight loss.

Resumo/Abstract

Among the currently available endodontic sealers, those made of epoxy resin present excellent root canal sealing capability, however, their bioactivity is minimal [1]. Although sealers based on silicates and calcium hydroxides are bioactive, their sealing properties are limited by their high solubility [2]. Therefore, this work aimed to produce and evaluate an endodontic sealer with properties of both categories of sealers. Due to its antibacterial properties, N-acetyl-cysteine (NAC) was chosen to provide bioactivity [3] and hydroxyapatite (HAp) due to its solubility in different pH values. NAC molecules were adsorbed on hydroxyapatite surface nanoparticles (HApNAC). Nanocomposites were prepared by dispersing HAp, NAC, and/or HApNAC into monomers to form epoxy composites via chemical polymerization. Solubility and sorption assays were performed by immersion composite specimens in distilled water and phosphate-buffered saline media at pH=5.5 and pH=7.4, for 28 days. Ca^{2+}, NAC release and pH media changes were measured. In the Epoxy/NAC group NAC was almost completely released during the assay, in all media, which increased the sealer solubility, causing pH decrease after 24 hours of immersion in all media solutions. Figure 1 indicates that NAC release for Epoxy/HApNAC reached 49 μmol. L^{-1} (0,09% m/m) NAC in distilled water after 28 days, which is theoretically adequate to promote antioxidant action according to the literature [4]. The Epoxy/HApNAC group presented similar behavior to the commercial sealer [5]. There was a release of up to 3.2 mg/L of Ca^{2+} ion, which was higher than that of commercial epoxy sealers but lower than that of bioceramic ones [6]. The Epoxy/HApNAC group showed properties closer to the gold standard, AH Plus, such as compressive strength (55 MPa) weight loss (solubility), and the ability to release NAC when in contact with aqueous fluid. In conclusion, Epoxy/HApNAC composites are a promising material for use as endodontic resin-based sealers capable of drug release.



(a) (b)

Figure 1. (a) SEM images of surface fracture and (b) release profile of NAC from Epoxy/HApNAC composite.

References:

[1] KOMABAYASHY, T. et al. *Dental Materials Journal*, 5, 2020. 703-720.
[2] SAAVEDRA, F. M. et al. *International Endodontic Journal*, 55, 2022. 772-783.
[3] ABDULRAB, S. et al. BMC Oral Health, 22, n. 1, 2022. 398(1-12).
[4] YANG, Y. et al. *Dental Materials*, v. 33, n. 4, p. 418-426, 2017.
[5] DE MORAES, T. G. et al. *Polymers*, 14, 2022. 729 (1-11).
[6] CANDEIRO, G. T. D. M. et al. *Journal of Endodontics*, 38, n. 6, 06 Abril 2012. 842-845.

Agradecimentos/Acknowledgments

This project was financed by Conselho Nacional de Desenvolvimento Científico e Tecnológico – CNPQ, Fundação de Amparo à Pesquisa e Inovação do Estado de Santa Catarina – FAPESC. The authors thank colleagues and fellow scientists from Universidade do Estado de Santa Catarina – UDESC, Centro Universitário do Maranhão – CEUMA, and Universidade Federal do Maranhão – UFMA for their support.

Enhancing sensitivity: SERS sensors on flexible inkjet printing paper utilizing Ag nanoprism ink

Lucas F. Oliveira (PG),[1*] Anerise B. Riul (PQ),[1] Edison H. Montoya (PG),[1] Fernando A. Sigoli (PQ),[1] Italo O. Mazali (PQ).[1]

***l230040@dac.unicamp.com; mazali@unicamp.br**

[1] *Universidade Estadual de Campinas, Instituto de Química, Laboratório de Materiais Funcionais, Campinas, SP, Brazil.*

Keywords: silver, n*anoprism, inkjet printing, SERS, cellulosic materials.*

Highlights

Silver nanoprisms ink for the inkjet printing of paper-based SERS substrates, a study on the effect of the number of printing cycles in the SERS activity of an organic molecule.

Abstract

Raman Spectroscopy is a powerful technique for the identification and quantification of analytes. However, most molecules of biological and environmental interest have a weak Raman signal. Therefore, the use of Surface-Enhanced Raman Spectroscopy (SERS) allows for highly sensitive and specific analysis. In this regard, the development of new substrates production procedures that are portable, reproducible, user-friendly, and decrease the time of analysis and the detection limits of analytical methods is in great demand, to broaden the applications of SERS. In such manner, inkjet printing is a promising method as it facilitates large-scale and automated production by way of depositing an ink composed of metallic nanoparticles onto paper. Furthermore, local production of the substrate combined with portable instruments eases in situ analysis. Thus, the aim of this work is the manufacture and evaluation of silver triangular nanoprisms (AgNPrs) inkjet printed paper-based SERS substrates. It was assessed two methods for AgNPrs synthesis, one seeded grown and the other plasmon-mediated. UV-VIS spectroscopy and scanning electron microscopy characterizations showed that the plasmon-mediated method led to AgNPrs more stable and with sharper edges. The extinction spectra of the obtained colloidal suspension is marked by an intense plasmonic excitation band centered around 600 nm, and two smaller bands around 340 nm and 430 nm. The electron micrographs of the AgNPrs presented homogeneous nanoparticles with an average size of 65 nm (as depicted in Figure 1).

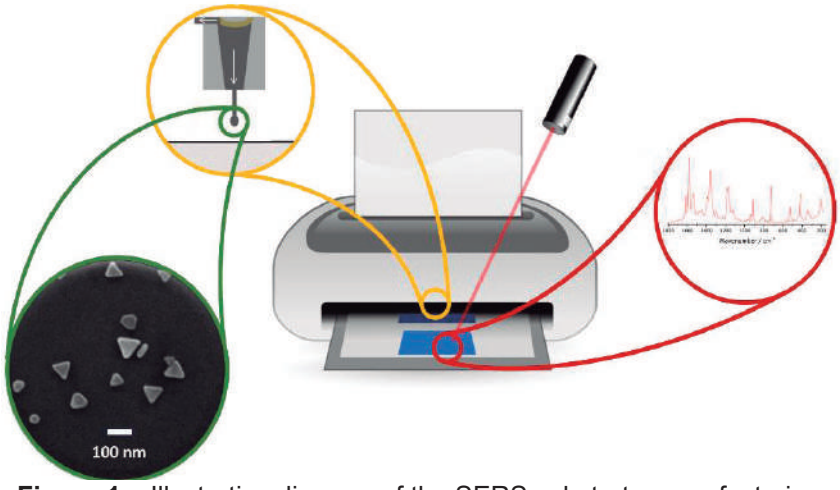


Figure 1 – Illustrative diagram of the SERS substrate manufacturing process. Insert: Micrograph of silver nanoprisms.

Due to its low fluorescence intensity, chromatographic paper was selected for the printing process using a commercial printer. Then, the SERS spectra of crystal violet (CV) in different concentrations (10^{-3} to 10^{-6} mol·L^{-1}) were acquired to evaluate the performance of the substrates when varying the number of printing cycles (1, 3, and 5). To decide on the best substrate, the number of printing cycles was balanced against the SERS intensity, the reproducibility of measurements, and the detection limit. The use of CV as a model molecule is justified for the optimization of the manufacturing process of the substrate developed so a more interesting analyte can be evaluated.

Acknowledgments

UNICAMP · Instituto de Química · Laboratório de Materiais Funcionais · EMMU · FAPESP · CNPq · CAPES · LNNano · Inomat

Área: MAT
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Evaluation of the influence of different deposition techniques on the formation of transparent conductive silver nanowire films

Stefany R. Saraiva (IC),[1*] Barbara P. G. Silva (PQ),[1] Crystian W. C. da Silva (PG),[1] Larissa Otubo (PQ).[1]

[*]stefany.r@ipen.br

[1]*Instituto de Pesquisas Energéticas e Nucleares, IPEN.*

Key words: *Transparent Conductive Films; Silver Nanowires; Deposition techniques.*

Highlights

Production of transparent conductive silver nanowires (AgNW) films using different deposition techniques.
Assessment of homogeneity and transmittance of AgNW transparent conductive films.

Resumo/Abstract

Transparent conductive films (TCFs) are components of optoelectronic devices, characterized by high transparency and conductivity, being used in various applications, such as displays, solar cells, etc. The most used material in TCFs is ITO (indium tin oxide), with transmittance greater than 90% and low sheet resistance, but it is expensive, its production is harmful to the environment, and, in addition, it is a rigid and fragile, that is, it cannot be used on flexible screens. For the new generation of TCFs, the use of nanomaterials, such as silver nanowires, has been gaining prominence due to their characteristics of flexibility, high conductivity and mechanical resistance, therefore, they can be used in flexible screens [1]. In transparent conductive silver nanowires films production, different deposition techniques can be used, such as dip-coating, drop-casting and spray-casting, which consist of immersing the substrate in a dispersion containing the conductive material, dropping the material dispersed and spraying the dispersion onto the substrate, respectively [2]. Therefore, in this work TCFs containing silver nanowires on flexible substrate using different deposition techniques were produced, aiming to obtain total coverage, greater homogeneity and high transmittance of the films. Afterwards, the films were evaluated and characterized by SEM, UV-VIS and XRD. In the XRD analysis, it was possible to observe reflections referring to the planes (111) and (200) characteristic of Ag-FCC. In the SEM and UV-VIS analyses, it was possible to verify that the films produced with the drop-casting technique showed a greater amount of deposited material, however, with lower transmittance, reaching 83% transmittance at 550 nm for 1 deposited layer. However, the dip-coating and spray-casting techniques were the most homogeneous and presented the highest transmittance, with respectively 92% and 90% at 550nm. According to the results obtained, the techniques that most favor homogeneity and transmittance are dip-coating and spray-casting.

References

[1] He, L.; Tjong S. C. Nanostructured transparent conductive films: Fabrication, characterization and applications, v. 109, p. 1-101, 2016. https://doi.org/10.1016/j.mser.2016.08.002

[2] Kumar, A. et al. Silver Nanowire Synthesis and Strategies for Fabricating Transparent Conducting Electrodes. Nanomaterials, v. 11, nº 693, p. 1-50, 2021. https://doi.org/10.3390/nano11030693

Agradecimentos/Acknowledgments

The author thanks the financial support from CNPq (143546/2023-6) and support from the Center for Lasers and Applications' Multiuser Facility and Laboratório de Microscopia e Microanálise at IPEN-CNEN/SP.

Área: MAT

Exploring shaped-induced enhanced Raman scattering (SIERS) in silicon V-shaped microchannels for atrazine herbicide detection without metallic nanostructures

Deysiane A. L. dos Santos (PG)[1], Anerise de Barros (PQ)[1], Fernando A. Sigoli (PQ)[1], Italo O. Mazali (PQ)[1]

deyseals@gmail.com; mazali@unicamp.br

[1] *Universidade Estadual de Campinas, Instituto de Química, Laboratório de Materiais Funcionais, Campinas, SP, Brazil.*

keywords: SIERS, Microchannels, Atrazine detection.

Highlights

V-shaped silicon microchannels for the detection of the herbicide atrazine in low concentrations. Investigation of the SIERS effect.

Abstract

Recently, silicon (Si) substrates with cavities covered by gold (Au) or silver (Ag) metallic film have been studied to verify the electromagnetic field contribution generated at the edges of the cavities to intensify the Raman signal, contributing to better sensitivity of SERS substrates[1]. A recently published work in our group demonstrates that, in the absence of the metallic film (Au or Ag) and metallic colloidal nanostructures, the enhancement of the Raman signal also occurs due to the V-shaped microchannel formed in the Si substrate. We attribute this effect to scattering Shape-induced Raman (SIERS), whose contribution to the increase in Raman intensity is given by constructive interference patterns of the electric field generated in the cavity[2]. Based on that, we investigated how the Si-V microchannel substrates act in the Raman signal enhancement even in the absence of metallic nanoparticles to atrazine molecule detection. The V-shaped microchannels were obtained through the microfabrication etching process and characterized by confocal microscopy (Figure 1 (a,b)) and scanning electron microscopy (SEM). For this, we used different atrazine solution concentrations from dropping an aliquot of 10 µL onto the Si-V substrate. Speciffically, the Si-V substrate should be positioned at a 5° inclination to improve the deposition by capillarity, which was allowed to dry at room temperature (~25°C). This process was repeated three more times, totaling 40 µL of atrazine solution. For comparison purposes, the same procedure was performed for the flat Si substrate. The efficiency of the substrates was then evaluated using Raman spectroscopy, enabling enhancement of the Raman signal for the atrazine molecule at a concentration of 10^{-8} mol L^{-1}. It is noted in Figure 2 that in addition to the better spectral definition, a greater intensity of the spectrum is observed for atrazine deposited on the Si-V substrate (Figure 1 (c)) compared to flat Si (Figure (d)). Thus, from a practical point of view, Si-V substrates are very promising for commercial application, with reusability being their main advantage.

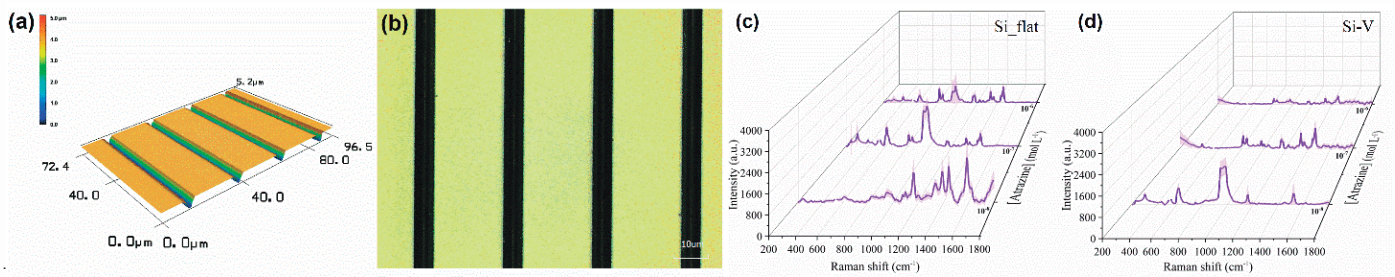


Figure 1. (a,b) Three-dimensional and two-dimensional confocal images obtained during monitoring of the corrosion process in microfabrication; Raman spectra of atrazine at different concentrations deposited on (c) flat Si and (d) Si-V.

Acknowledgments

UNICAMP · Instituto de Química · Laboratório de Materiais Funcionais · EMMU · FAPESP · CNPq · CAPES · LNNano · Inomat

[1] Li, N.; Feng, L.; Teng, F.; Lu, N. Fabrication of Plasmonic Cavity Arrays for SERS Analysis. *Nanotechnology* **2017**, *28*, No. 185301.

[2] Bär, J.; de Barros, A.; Camargo, D. H. S.; Pereira, M. P.; Merces, L.; Shimizu, F. M.; Sigoli, F. A.; Bufon, C. C. B.; Mazali, I. O.; *ACS Applied Materials and Interface* **2021**, 13, 36482-36491.

Área: MAT

Fabrication of Mesoporous Silica Containing Amino Groups and Glycerol as Potential CO_2 adsorbents

Leonardo Oliveira Osta (IC),[1] Thiago Custódio dos Santos (PQ).[1*]

leonardo.osta@gradu.iq.ufrj.br; thiagocustodio@iq.ufrj.br

[1]*Instituto de Química, Universidade Federal do Rio de Janeiro. Av. Athos da Silveira Ramos, 149, CT, Cid. Univ., 21941-909, Rio de Janeiro, RJ, Brasil*

Palavras-Chave/Keywords: *carbon dioxide; mesoporous sílica; MCM-41; CO_2 capture*

Highlights

Functionalized MCM-41 with both amino and hydroxyl groups as a potential adsorbent for CO_2 capture.

Potential adsorbents containing basic organic groups for CO_2 capture with low-cost energy.

Resumo/Abstract

CO_2 emissions into the atmosphere have increased due to human activities, which include thermoelectric power plants, industry, livestock, and vehicles as the main source of CO_2 release. The large CO_2 concentration in the atmosphere has resulted in the escalation of global warming. In that manner, it is imperative to stop the increase of CO_2 concentration in the atmosphere. At room temperature and atmospheric pressure, it is demonstrated by literature that MCM-41 silica functionalized with amino groups is a potential material for CO_2 capture due to reaction among CO_2 and amino groups originating carbamate species.[1] A main drawback in this method is due to high temperature necessary for CO_2 desorption (> 100 °C) and the reutilization of the solids. One strategy consists in preparing MCM-41 modified with both amino and hydroxyl groups. The amino group is a higher basic group than hydroxyl and can interact with the proton of OH (RHN···H-OR) allowing the oxygen atom to attack the CO_2 molecule.[2] This reaction produces organic carbonate, which degrades at lower temperatures (> 60 °C) than carbamate. Herein, our objective is to prepare MCM-41 functionalized with primary amino group (MCM-41-NH_2), followed by impregnation of MCM-41-NH_2 with glycerol (Gly) to originate MCM-41-NH_2@Gly(X) as the potential adsorbents for CO_2 capture. The materials MCM-41-NH_2@Gly(X) were prepared with 5, 10 and 20% of Gly and named MCM-41-NH_2@Gly(5), MCM-41-NH_2@Gly(10), MCM-41-NH_2@Gly(20), respectively. Different amounts of Gly were used to evaluate the physical and chemical properties of MCM-41-NH_2@Gly(X) materials. Tetraethyl orthosilicate (TEOS) was used as a silica precursor and (3-aminopropyl)triethoxysilane (APTES), as an amine source. These compounds were added to a cetyltrimethylammonium bromide (CTAB) suspension and maintained under stirring for 24 h, at room temperature. The reactions were filtered to yield white solids, which were refluxed in ethanolic solutions of ammonium chloride, filtered, and washed with ethanol and deionized water. N_2 isotherms shows that the materials present type IV curves typical of mesoporous material. The surface areas were 83.0, 75.8 and 9.3 m^2/g for MCM-41-NH_2@Gly(5), MCM-41-NH_2@Gly(10) and MCM-41-NH_2@Gly(20), respectively, indicating that the increase in the Gly impregnation results in the decrease of specific surface areas. The same absorption bands were observed for all MCM-41-NH_2@Gly(X) materials, being 1060 and 800 cm^{-1} attributed to Si-O-Si bonds, a broad absorption band at 3400 cm^{-1} is related to O-H, N-H and hydrogen bonds, indicating the presence of water molecules. For all materials, TGA curves exhibit a weight loss below 100 °C related to water evaporation. A weight loss of 12% observed in the range of 120 – 180 °C for MCM-41-NH_2 is attributed to decomposition of TEOS, which confirms the MCM-41 functionalization. For all MCM-41-NH_2@Gly(X) materials, XRD pattern shows peaks at $2\theta(°)$ = 2.15; 3.65 and 4.20 related to the reflection planes (100), (110) and (200), confirming that MCM-41-type materials were obtained. In conclusion, N_2 isotherms and XRD patterns showed that the mesoporous materials were obtained, as well as infrared spectroscopy and thermogravimetric analyses confirm the presence of organic groups. These characterizations indicate that the syntheses of MCM-41-NH_2@Gly(X) were successful. In the next stages, CO_2 adsorption experiments will be performed to obtain adsorption capacities and solid-gas interactions.

Agradecimentos/Acknowledgments

I would like to thank LaMaP(UFRJ), RECAT(UFF), LAMATE(UFF) and PIBIC(UFRJ).

1. DOS SANTOS, T. C., BOURRELLY, S., LLEWELLYN, P. L, CARNEIRO, J. W. M., RONCONI, C. M. Adsorption of CO_2 on amine-functionalised MCM-41: experimental and theoretical studies. **Phys. Chem. Chem. Phys.**, n. 17, p. 11095-11102, 2015.
2. DOS SANTOS, T. C., LAGE, M. R., DA SILVA, A. F. M., FERNANDES, T. S., CARNEIRO, J. W. M., RONCONI, C. M. Supramolecular dimers drive the reaction between CO_2 and alkanolamines towards carbonate formation. **Journal Of CO2 Utilization**, n. 61, p. 102054, 2022.

Área: MAT

Fast release of paracetamol using electrospun non-woven of PVP/VA: a morphological analysis and characterization by FTIR

Vanessa Rong Jen Chang (PG)[1*], Josiane Caetano (PQ)[1], Douglas Cardoso Dragunski (PQ)[1].

vanessajen@hotmail.com

[1] Center for Engineering and Exact Sciences, State University of Western Paraná – UNIOESTE, Street: Guaíra, 3141 CEP - 85903-000 - Toledo-PR-Brazil

Keywords: *Drug, Polymer, Microfiber, Fast solubilization.*

Highlights

- It was possible to perform electrospinning of PVP/VA containing 10% w/w paracetamol.
- With the addition of paracetamol to non-woven fabric, the diameter of the microfibers increases.
- Through FTIR analysis, possible intermolecular interactions between paracetamol and PVP/VA were demonstrated.
- The average conductivity of PVP/VA0 and PVP/VA10 showed a small difference of 0.1 µm.

Resumo/Abstract

The project under development seeks to improve the fast release drug administration system, aiming for rapid solubilization of the drug in the mouth, without the need to swallow or chew. The main focus is to develop a non-woven fabric (they are misaligned and disorganized fibers, unlike fabric), using the electrospinning technique, to promote the fast release of the drug paracetamol (PCM) inserted into polymer nanofibers of poly(1-vinylpyrrolidone-co-vinyl-acetate) (PVP/VA). The choice of PCM is due to its low solubility in water. To date, PVP/VA fibers with 10% (w/w) PCM (PVP/VA10) and pure PVP/VA fibers[1] (PVP/VA0) have been produced, analyzed by optical microscopy (OM) and Fourier Transform Infrared Spectroscopy (FTIR), revealing morphological changes and intermolecular interactions between the drug and the polymer. The electrospinning technique allowed the obtaining of PVP/VA fibers without and with 10% PCM, revealing significant differences in the morphology and diameter of the fibers. In PVP/VA0[1], it presents more homogeneous, smooth characteristics and without the presence of *beads* (imperfections), to which the average fiber diameter obtained (1.45 ± 0.23) µm.[1] The PVP/VA10 fibers have the presence of *beads* and obtained a diameter (2.25 ± 0.14) µm, that is, 0.8 µm in diameter (Figure 1), difference between the two non-woven fabrics, indicating the influence of the drug on the structure of the microfibers. FTIR analysis demonstrated possible intermolecular interactions between paracetamol and PVP/VA. Because through Figures 2 and PVP/VA0 data[1] it is possible to observe changes in the characteristic peaks of C—H (2500 to 3000 cm^{-1}) and in the region of digital printing (1700 to 500 cm^{-1}). The average differential conductivity between PVP/VA0 and PVP/VA10 is 0.01 µS, without much significant difference (Table 1). Indicating that for this amount of paracetamol there was no significant difference in ionic conductivity. Therefore, there is a need for more samples with higher concentrations of PCM, to confirm the decrease in conductivity while increasing the drug concentration.

Figure 1: Microfibers obtained by OM and frequency histogram.

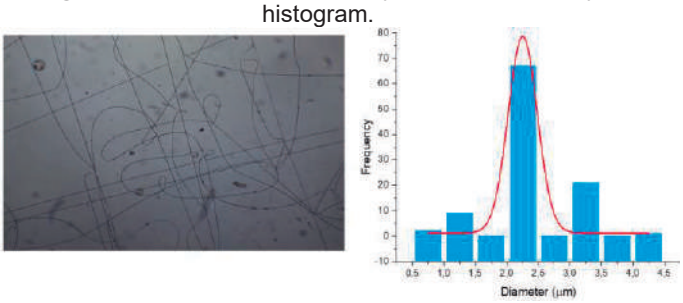
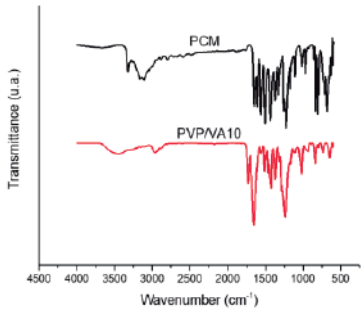


Table 1: Results obtained for the diameter and conductivity of PVP/VA0[1] and PVP/VA10

Microfibers	Diameter (µm)	Conductivity (µS)
PVP/VA0	1.45 ±0.23	2.69 ± 0.17
PVP/AV10	7.47 ± 0.18	2.68 ± 0.17

Figure 2: FTIR of PCM and PVP/VA10



Reference:

1. Martins, L.M. *et al. Poly (1-vinylpyrrolidone-co-vinyl-acetate)-based electrospun dissolvable nanofibrous film for quercetin administration*. Elsevier, Process Biochemistry. **2022,** 122, 8-15.

Agradecimento/Acknowledgments

We would like to thank all collaborators and supporters who contributed to the development of this project. We thank UNIOESTE, and the financial support CAPES, CNPQ and Fudação Araucária.

Área: MAT

Fotossensibilizadores azínicos do tipo D-π-A para fotoclivagem da água: síntese e estudos teóricos preliminares

Alan I. Ribeiro (IC),[1] Amanda R. P. Costa (PG),[1] Pedro N. Batalha (PQ).[1*]

alanimperatori@id.uff.br; pedrobatalha@id.uff.br

[1]*Departamento de Química Orgânica, Universidade Federal Fluminense*

Palavras Chave: *Photosensitizers. Organic Dyes. Water Splitting. Artificial Photosynthesis. Molecular Hydrogen*.

Highlights

Azinic D-π-A type photosensitizers for photocleavage of water: synthesis and preliminary theoretical studies. In this work, new push-pull organic photosensitizers were synthesized, applicable to photocatalytic processes to produce molecular hydrogen.

Resumo/Abstract

Os combustíveis fósseis permanecem sendo a principal fonte de energia utilizada em todo o mundo, apesar de estarem associados a um alto impacto ambiental. A diminuição das descobertas de novas fontes de petróleo, a crescente demanda energética e o apelo mundial pela minimização das mudanças climáticas ocasionadas por ação antrópica tornam urgente a busca por fontes de energia sustentáveis.[1] Nesse cenário, uma alternativa promissora para o futuro do setor energético mundial é a produção de hidrogênio molecular por meio do processo de clivagem fotocatalítica da água.[2,3] Com isso, o presente trabalho propõe a síntese, caracterização estrutural e avaliação teórica preliminar das propriedades eletrônicas de uma nova série de fotossensibilizadores orgânicos do tipo *push-pull* (**1a-c**), aplicáveis a processos fotocatalíticos para a produção de hidrogênio molecular. Os rendimentos reacionais obtidos variaram de 11 a 49%. O estudo teórico das propriedades eletrônicas dos corantes sintetizados foi realizado, fazendo-se uso do método da Teoria do Funcional da Densidade no nível CAM-B3LYP/6-31G*, utilizando a água como solvente implícito. As geometrias dos orbitais moleculares de fronteira confirmam a separação de cargas após fotoexcitação eletrônica, e os *gaps* HOMO-LUMO calculados das substâncias estão na faixa de 2,95 eV a 3,25 eV. Esses dados teóricos indicam que tais fotossensibilizadores obedecem aos requisitos estruturais para promover a injeção de elétrons na banda de condução do semicondutor e fotocatalisador, além de poderem ser regenerados após o processo de foto-oxidação. Ademais, a geometria otimizada dos fotossensibilizadores demonstrou um desvio da coplanaridade esperada entre as porções estruturais destes corantes. Assim, como perspectiva, pretende-se explorar a realização de modificações estruturais nestas substâncias que levem ao aumento de sua coplanaridade e, consequentemente, à potencialização de seu perfil fotossensibilizador.

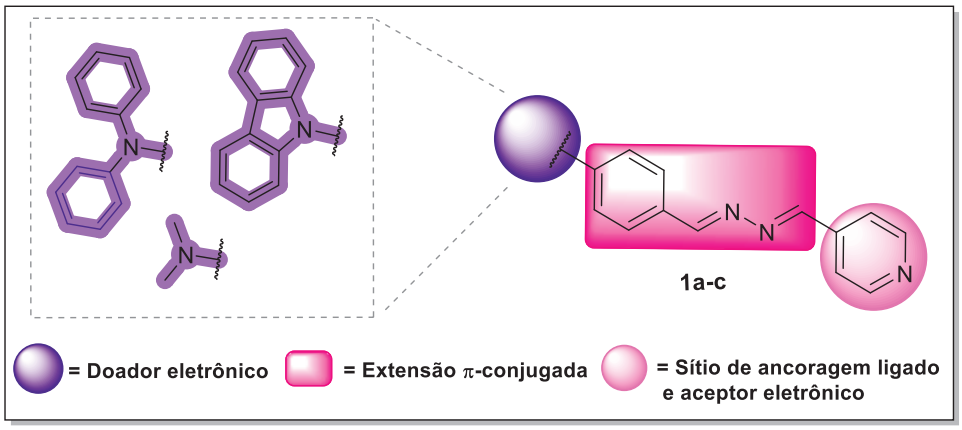


Figura 1. Fotossensibilizadores do tipo **1** planejados.

Agradecimentos/Acknowledgments

CNPq, FAPERJ, PPGQ-UFF, PROAP-UFF, CNPq - PIBIC, CAPES (Finance Code 001).

[1] TASHIE-LEWIS, B. C.; NNABUIFE, S. G., Chemical Engineering Journal Advances, **2021**, 8, 100172.
[2] WATANABE, M. *et al.*, Journal of Materials Chemistry A, **2014**, 2 (32), 12952–12961.
[3] YOUNGBLOOD, W. J. *et. al.*, Accounts of Chemical Research, **2009**, 42 (12), 1966-1973.

Área: MAT

Harvesting Hope: Avocado Seed Hydrochars for Sustainable Methylene Blue Reduction in Wastewater

Rogério S. Maniezzo (IC) [1,2*], Maria Eduarda V. Perciliano (IC)[3], Hugo H. C. Lima (PQ)[1,2], Francielle Sato (PQ)[4], Andrelson W. Rinaldi (PQ)[1,2]

rsmaniezzo@gmail.com; awrinaldi@uem.br

[1]Rinaldi Research Group, UEM; [2]Marili Hidrocarvões Ativados; [3]Departamento de Biologia, UEM; [4]Departamento de Física, UEM

Palavras Chave:*Hydrochar, Adsorption, Dye, Avocado, Environmenal.*

Highlights

GREEN INNOVATION FROM AVOCADO WASTE.
HYDROCHAR MARVELS.
ADSORTION OF METHYLENE BLUE.
SURFACE AREA *vs.*ADSORPTION BATTLE

Resumo/Abstract

In 2022, Brazil produced 338,238 tons of avocado (Persea americana), according to IBGE data. The avocado pit has the potential to be used in various applications, including the production of flours and biosorbents. The objective of this study was to transform the avocado pit into a modified hydrochar for use in the adsorption of methylene blue dye in effluents.

To achieve this goal, the hydrocarbonization process (HTC) was conducted at a temperature of 463 K for 12 and 24 h to obtain the hydrochar. Subsequently, a chemical activation was carried out using NaOH under two conditions: with heating at 463 K for 12 h and without heating for 12 h. After this modification, the materials were washed with water until reaching pH 7.0 and dried in an oven. The hydrochars were named AVC-12 h and AVC-24 h (hydrochars modified with NaOH without heating) and AVCH-12 h and AVCH-24 h (hydrochars modified with heating).

The hydrochars were characterized through N_2 physisorption, scanning electron microscopy, FTIR-ATR, Raman spectroscopy, zero point charge pH, and Boehm titration. The surface areas of the hydrocarbons were 24.44 m^2g^{-1} (AVC-12 h), 8.43 m^2g^{-1} (AVCH-12 h), 33.71 m^2g^{-1} (AVC-24 h), and 15.95 m^2g^{-1} (AVCH-24 h). The Langmuir model, presented in Table 1, better describes the materials. It is observed that hydrochars with a larger surface area exhibited a lower amount of adsorbed dye. For example, the AVCH-12 h hydrochars, with a surface area of 8.43 m^2g^{-1}, adsorbed 309.24 mgg^{-1}, while the other coal, AVC-12 h, with a surface area of 24.44 m^2g^{-1}, adsorbed only 179.62 mgg^{-1}. The same pattern was observed with the 24 hours hydrochars. Those activated without heating showed a higher surface area but a lower amount of adsorbed dye, whereas the hydrochars activated with heating exhibited a smaller surface area compared to the former but a higher adsorption capacity. This indicates that the activation process with heating provides a material with significant adsorption capacity.

Table 1: Kinetic parameters of pseudo first and second order and Elovich for activated carbons.

Parameters	Samples			
	AVC-12 h	AVC-24 h	AVCH-12 h	AVCH-24 h
$Q_{t,exp}$ (mgg^{-1})	179.62	148.62	309.24	380.73
Pseudo-First Order				
q_e (mgg^{-1})	167.71	134.52	285.27	352.91
k_1 (min^{-1})	$1.05E^{-02}$	$1.66E^{-02}$	$1.981E^{-02}$	$5.01E^{-03}$
R^2	0.9607	0.8904	0.88379	0.9568
Pseudo-Second Order				
q_e (mgg^{-1})	182.67	143.67	301.53	409.2
k_2($mingmg^{-1}$)	$8.04E^{-05}$	$1.72E^{-04}$	$1.034E^{-04}$	$1.47E^{-05}$
R^2	0.9909	0.9537	0.9455	0.9825
Elovich				
α(gmg^{-1} min^{-2})	10.58	17.07	57.27	8.10
β(gmg^{-1} min^{-1})	0.034	0.047	0.024	0.014
R^2	0.9889	0.9912	0.9797	0.9822

In this way, it is worth noting, that the activated hydrochars produced from avocado pits using the NaOH impregnation activation method with heating proved to be effective and promising.

Agradecimentos/Acknowledgments

CNPQ, CAPES, Fundação Araucária, COMCAP and Universidade Estadual de Maringá - UEM.

Área: MAT
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

High Energy Radiation Converting Luminescent Materials

Gustavo C. Portes (PG),[1]* Lucas C.V. Rodrigues (PQ).[1]

gustavo.portes@usp.br;*

[1]*Fundamental Chemistry Department, Institute of Chemistry of the University of São Paulo*

Palavras Chave: *Converters, Films, Luminescence, Solar cells, Ultraviolet Vacuum, X-Rays.*

Highlights

High energy radiation converting luminescent materials. Synthesis and characterization of luminescent nanoparticles. Material application in films. Application of the films on satellite solar cells.

Resumo/Abstract

Solar cells are known to have a decreasing in efficiency with growing temperature, [1] so it is necessary to dissipate the heat. Usually the cell can dissipate the heat through the atmosphere or with liquid coolants, but solar cells coupled to satellites has more difficulty releasing this heat, because they are constantly receiving high-energy radiation from the sun and it can't transfer the heat to the environment because it is in vacuum.

Luminescent materials are able to efficiently convert high energy photons into lower energy photons, by doing so, it is able to convert most of the energy irradiated in visible light, which can be used by the solar cell, dispersing the energy without increasing the temperature of the material. Inorganic compounds were chosen for this work since they show better photo-stability than compound than presents organic parts. [2] By using films containing luminescent materials, this work aims to reduce the excess non-usable energy that is irradiated to the solar cell by converting this high-energy radiation to visible light through downconversion, which is an inherent effect of the material to absorb one higher-energy photon and release two lower-energy photons.

The GdF_3 doped with Eu^{3+} was synthetized through the coprecipitation method [3] with different rates of europium in order to determine the ideal percentage of Eu^{3+} as dopant for maximum conversion of energy while avoid the effects of quenching. By using NH_4F as source of fluoride, it was possible to synthesize the material in its orthorhombic form, which presents excitation bands around 250 nm and have a strong the emission around 590 nm referent to the Eu^{3+} transition $^5D_0 \rightarrow {}^7F_1$. This Eu^{3+} transition can be used to convert the excess energy into visible light, this way it can help reduce the solar cell temperature and possibly increase the usable energy getting to the cell.

The $GdF_3:Eu^{3+}$ is a material capable of downconversion and its efficiency will be compared with other materials that are able to do downconversion, like $LiGdF_4:Eu^{3+}$ and $BaF_2:Eu^{3+},Gd^{3+}$, and it will be compared with scintillators like $SrCl_2:Ce^{3+}$ and $Ba_3La(PO_4)_3:Ce^{3+}$, in order to select the best film to be used in solar cells, with the possibility of using multiple films to cover a greater range of wavelength.

[1] Bensalem, S., Chegaar, M., & Aillerie, M. (2013). Solar cells electrical behavior under thermal gradient. *Energy Procedia*, *36*, 1249–1254. https://doi.org/10.1016/j.egypro.2013.07.141

[2] Grzyb, T., & Lis, S. (2009). Photoluminescent properties of LaF3:Eu3+ and GdF3:Eu3+ nanoparticles prepared by co-precipitation method. *Journal of Rare Earths*, *27*(4), 588–592. https://doi.org/10.1016/S1002-0721(08)60294-X

[3] Zhang, X., Hayakawa, T., Nogami, M., & Ishikawa, Y. (2011). Variation in Eu3+ luminescence properties of GdF 3:Eu3+ nanophosphors depending on matrix GdF3 polytype. *Journal of Alloys and Compounds*, *509*(5), 2076–2080. https://doi.org/10.1016/j.jallcom.2010.10.143

Agradecimentos/Acknowledgments

To CAPES process: 88887.825181/2023-00

Área: MAT

How Carbon Black Morphology Influences Hydrogen Production from 3D-Printed Electrodes

Mateus Veras Pereira (PG),[1] **Naile Vacilotto Neumsteir (IC),[1] Juliano Alves Bonacin (PQ)[1]**

m265987@dac.unicamp.br; jbonacin@unicamp.br

[1]*Institute of Chemistry, University of Campinas - UNICAMP*

Keywords: *Carbon Black, 3D Printing, Hydrogen Production*, *Energy Conversion.*

Highlights

Innovating with 3D printing for decentralized hydrogen generation.
CBMAX22 forms granules, while CB72R exhibits dispersed aggregates.
CB72R's better dispersion enhances 3D-printed electrode in hydrogen production.

Abstract

The increasing energy demand, the depletion of conventional energy sources, and environmental concerns have led to an energy crisis in recent times. To overcome this challenge, innovative and economically viable approaches have been sought, such as the use of 3D printing for decentralized hydrogen generation.[1] In this study, we explored the application of two types of carbon black as conductive additives in the manufacturing of filaments for 3D electrodes for later use in hydrogen production through water electrolysis. Two types of carbon black, VULCAN® XCMAX™ 22 (CBMAX22) and VULCAN® XC72R (CB72R), were chosen because of their conductive properties and commercial availability. To obtain the filament, the precursor materials (PLA e Carbon black) were solubilized in a reflux system under constant temperature, then recrystallized, and the resulting solid was dried and processed through extrusion.[2] The produced filaments were used for 3D printing of the electrodes. The prepared materials were characterized by scanning electron microscopy (SEM), thermal analysis, and electrochemical techniques. Subsequently, the hydrogen production efficiency of the 3D printed electrodes was assessed. According to the SEM images (Figure 1a and b) related to the carbon blacks, it is possible to observe that both exhibit primary particles with spherical geometry. However, the aggregates formed from these primary particles revealed distinct organizational patterns in the samples. Therefore, we observed that CBMAX22 formed granules with aggregated carbon black particles (Figure 1a). Meanwhile, CB72R has aggregates in which the primary particles are much more dispersed than CBMAX22 (Figure 1b). The 3D printed electrodes using the filament prepared with CB72R demonstrated superior hydrogen production performance (Figure 1c) compared to the electrodes printed with CBMAX22 filament, producing 10.08 and 6.93 µmol min^{-1}, respectively. This suggests that the formation of more compact granules in CBMAX22 may lead to a reduced available surface area for electrochemical reactions, compromising the overall performance when dispersed in a polymer matrix (PLA). In contrast, it is believed that CB72R's primary particles exhibit better dispersion in the polymer matrix, favoring a larger contact area and promoting enhanced hydrogen production performance, as shown in Figure 1c. Therefore, we can infer that the morphology of the investigated carbon black plays a crucial role in the effectiveness of 3D-printed electrodes when utilized in hydrogen production.

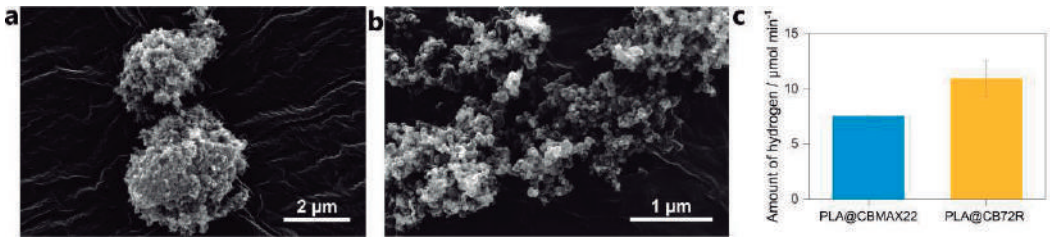


Figure 1. SEM images were obtained for Carbon Black: (a) CBMAX22 and (b) CB72R. (c) Amount of hydrogen produced by each electrode.

(1) Silva, M. B.; Germscheidt, R. L.; Pereira, M. V.; Bonacin, J. A. 3D Printing Electrodes for Energy Conversion. **2023**.
(2) Stefano, J. S.; Guterres e Silva, L. R.; Rocha, R. G.; Brazaca, L. C.; Richter, E. M.; Abarza Muñoz, R. A.; Janegitz, B. C. New Conductive Filament Ready-to-Use for 3D-Printing Electrochemical (Bio)Sensors: Towards the Detection of SARS-CoV-2. *Analytica Chimica Acta* **2022**, *1191*, 339372.

Acknowledgments

UNICAMP · IQ Instituto de Química · Bonacin Research Group · CNPq · CAPES · FAPESP grant# 2020/14769-8; 2017/11986-5 · FAEPEX grant#40056-23

Área: MAT

Imaging and quantification - the power of Raman Spectroscopy for high-performance characterization of the chemical composition of oxidized graphene (GO) and reduced graphene oxide (rGO)

Renato D. Matosinhos* (PQ)[1], Luiza De Lazari (PQ)[1], Pablo R. S. Lima (IC)[1], Pedro A. e Silva (IC)[1], Matheus H. C. Braga (IC)[1], Marcos Pimenta (PQ)[1], Hállen D. R. Calado (PQ)[1,2].

renato.matosinhos@ctnano.org* , hallendaniel@yahoo.com.br

[1] Centro de Tecnologia em nanomateriais e grafeno (CTNano/UFMG); [2] Departamento de Química da UFMG

Key-words: *Raman Spectroscopy, graphene, Metrology, Quality Control*

Highlights

Spectral maps obtained by high-performance Raman spectroscopy are a powerful tool for determining the chemical composition of graphene oxide.

Resumo/Abstract

Carbon nanomaterials have revolutionized the field of materials science in recent years. The processing, modification, and customization of these materials demands efficient tools for characterizing of the composition[1]. Obtaining images or maps using high-performance Raman spectroscopy allows you to explore the molecular morphology of carbon materials [2] and obtain precise information about the chemical composition of the sample[3]. The CTNano/UFMG characterization front has explored the versatility of this technique to establish metrological criteria for the characterization of carbon nanomaterials. Freeze-dried GO and rGO samples were investigated using a Witec spectrometer, laser λ = 457 nm, 50X objective, and 1mW power. Different points in the sample space were evaluated allowing interpretations of electronic and phonon dispersion. Initially, the Raman spectra of each sample were obtained (Fig. 1A) where the peaks are associated with the D and G bands. From the Raman spectral images, a quantitative analysis of the chemical composition was carried out, identifying the presence of Carbon (C) and Oxygen (O) in the respective proportions of 68.8% and 31.2% for the GO samples, in addition to evaluate the heterogeneity of the sample (Fig. 2). Figure 1 B and C indicate, respectively, the spectra generated by Figure 2, where the blue color is associated with C and the red color with O. The thermogravimetric curve (TG) and its derivative (DTG) indicate a degree of functionalization close to 35% (Fig. 3) and precisely corroborates the quantification obtained by Raman spectroscopy. Similar interpretations were obtained for the rGO samples. The results of this study confirm the efficiency of the technique for quantifying the chemical composition, homogeneity, and quality control of GO and rGO samples.

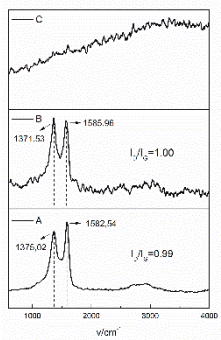


Figure 1 – Raman spectrum for GO sample

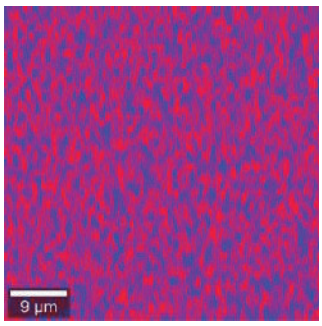


Figure 2 – Raman map for GO sample

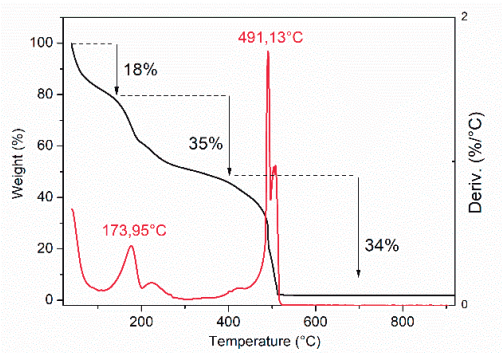


Figure 3 – TG/DTG curves for GO sample

1. Malard LM, Pimenta MA, Dresselhaus G, and Dresselhaus MS. Raman spectroscopy in graphene. *Phys Rep* Elsevier B.V.; **473**:51–87 (2009).
2. González-garcía D, et al. A Raman spectroscopic tool to estimate chemical composition of natural volcanic glasses. *Chem Geol* Elsevier; **556**:119819 (2020).
3. Shafer-peltier KE et al.. Model-Based Biological Raman Spectral Imaging. **137**:125–137 (2002).

Agradecimentos/Acknowledgments

CTNANO UFMG · INCT Nanomateriais de Carbono · CNPq

IMMOBILIZATION OF CELLULASES ON NANOMAGNETIC SCAFFOLDS FOR BIOMASS DECOMPOSITION

Mariana Martinussi de Godoy (IC), [1] **Caterina Gruenwaldt Cunha Marques Netto (PQ)** [1].

marianamartinussi@estudante.ufscar.br; caterina@ufscar.br

[1]*Departamento de Química, UFSCar.*

Keywords: Cellulase, Enzymatic immobilization, Magnetic nanoparticles, Biocatalysis.

Highlights

Unveiling new opportunities: enhancing cellulase stability for biomass conversion with magnetite nanoparticles

Abstract

Cellulases are enzymes that play a crucial role in the degradation of cellulose, a macromolecule found in the plant cell wall. Comprising glucose chains connected by hydrogen bonds, cellulose undergoes hydrolysis into reducing sugars through the action of these enzymes. Consequently, cellulases have various significant applications, particularly in paper manufacturing and waste treatment. Unfortunately, their low stability in response to environmental variations poses challenges for large-scale applications, necessitating optimization efforts. Thus, the immobilization of cellulases on solid supports, both organic and inorganic, emerges as a promising alternative. This approach aims to enhance stability and reduce contamination of the final product, enabling easy separation from the reaction medium. Magnetic supports, in particular, stand out as they allow rapid and efficient enzyme recovery through an external magnetic field, in addition to being cost-effective and easily synthesized. In this study, magnetite nanoparticles were synthesized through the co-precipitation of Fe^{2+} and Fe^{3+} ions in an alkaline medium. These nanoparticles were coated with Tetraethyl Orthosilicate (TEOS) and functionalized with (3-Aminopropyl)triethoxysilane (APTS) to immobilize the enzymes. This immobilization seeks to depolymerize biomass, converting it into high-value-added products. The samples were subjected to characterization by Fourier-transform infrared spectroscopy (FT-IR), yielding the following results. It is possible to observe the presence of stretching bands of Si-O near 900 cm^{-1}, as well as at 800 cm^{-1}, corresponding to Si-C stretching, Si-O-H bending, and Si-O stretching, confirming the coating with TEOS. Additionally, stretching bands of C-H can be noted at 3000-2800 cm^{-1}.

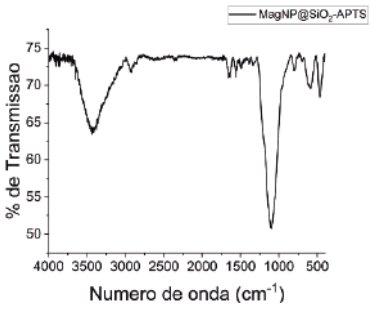


Figure 1. Infrared spectrum of silanized and functionalized nanoparticles

Acknowledgments

This work was funded by FAPESP (23/09722-0)

Área: MAT

Improving micronutrient solubilization using bioactive composites with acidifying microorganisms: Implications for fertilizer granule coating.

Vinícius F. Majaron (PQ) [1], Ricardo Bortoletto-Santos* (PQ) [2], Rodrigo Klaic (PQ) [3], Denise Bevilaqua (PQ) [2], Sidney J.L. Ribeiro (PQ)[4], Cristiane S. Farinas (PQ) [5], Caue Ribeiro (PQ)[5], Wagner L. Polito (PQ)[1].

vinicius.f.majaron@gmail.com

[1]Instituto de Química de São Carlos (USP), [2]Universidade de Ribeirão Preto (UNAERP), [3]Departamento de Química (UFSCar); [4]Instituto de Química (UNESP); [5] Laboratório Nacional de Nanotecnologia para o Agronegócio (Embrapa Instrumentação).

Keywords: *Acidithiobacillus thiooxidans; Aspergillus niger; Fertilizer; Micronutrients; Starch.*

Highlights

The innovative system can ensure the supply of multiple nutrients to plants by using low reactivity sources through a more environmentally-friendly management; The synergy between the nutrients and microorganisms incorporated in the coating resulted in system acidification and increased availability of micronutrients.

Abstract

Fertilization is essential to provide suitable conditions for plant development and crop productivity, but the environmental cost of fertilizers is a drawback for achieving a sustainable agriculture. A potential alternative is the use of unprocessed (raw) nutrient sources such as mineral oxides (ZnO, MnO, CuO) as fertilizers. However, these low reactive sources are not readily available to plants. Here, we developed a bioactive coating material containing microorganisms that allowed different nutrients to be made available from unprocessed nutrient sources. For that, the coating material composed of maize starch, mineral oxides (ZnO, MnO, CuO), and a microbial source (*Aspergillus niger* or *Aciditiobacillus thiooxidans*) was applied on monoammonium phosphate (MAP) granules, as a model fertilizer. Our results revealed that the bioactive coating did not affect the phosphorus (P) release, since it did not impose a physical barrier. However, the acidifying capacity of both microorganisms significantly enhanced the oxide solubilization. The presence of *Aspergillus niger* or *Aciditiobacillus thiooxidans* promoted local acidification, as well as the bioactive coating material with *Aspergillus niger* reached Cu, Zn and Mn solubilization up to 10.9, 14.6 and 34.3% in 42 days of soil incubation. This phenomenon suggested that the organic acids produced by *Aspergillus niger* chelate the cations, reducing precipitation and, therefore, increasing their solubilization. This innovative system can effectively supply nutrients to plants using cheap and low reactivity nutrient sources with the advantage that it can be co-applied on currently used fertilizer granules in a single delivery, making easier the adoption by producers.

Acknowledgments

The authors are thankful for the financial support given by FAPESP (São Paulo State Research Foundation, grant#2016/10636-8, #2017/18673-2, #2018/10448-2, and #2020/03259-9), CAPES (Coordination for the Improvement of Higher Education Personne, CAPES-Embrapa Program), CNPq (Brazilian National Council for Scientific and Technological Development), SISNANO/MCTI, FINEP, and Embrapa AgroNano research network.

Área: MAT
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Inducing molecular orientation in solution processed thin films of fluorene-bithiophene-based copolymer: photoemission and photoabsorption studies

Cássia F. C. Pereira[1] (PG), Bruno G. A. L. Borges[1] (PQ), Cleber Marchiori[2] (PQ), Maria Luiza M. Rocco (PQ)[1*]

luiza@iq.ufrj.br

[1]*Institute of Chemistry, UFRJ;* [2]*Departament of Engineering and Physics, Karlstad University, Karlstad, Sweden.*

Palavras Chave: *Organic photovoltaics, Semiconductors, XPS, NEXAFS, Core-hole clock method.*

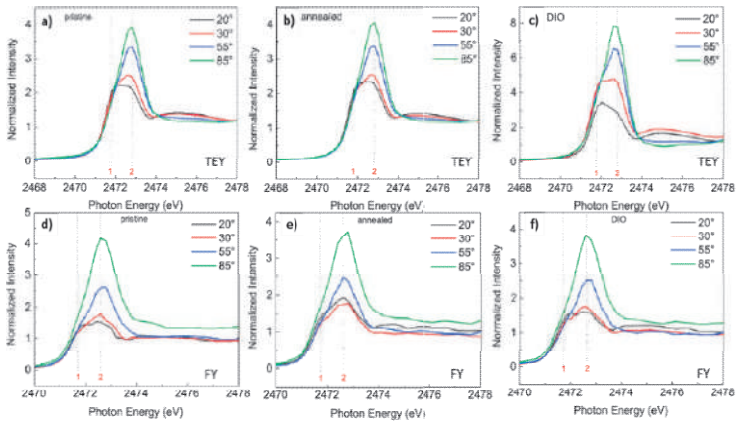
Highlights

NEXAFS measurements show an increased orientation of the conjugated backbone for F8T2 films processed with DIO. Enhancement in the charge transfer process was also observed via Resonant Auger spectra.

Resumo/Abstract

Fluorene-based copolymers are highly attractive organic semiconducting materials thanks to their well-known synthetic route, and chemical and thermal stability. Moreover, many optoelectronic properties of devices based on conjugated copolymers depend on the final morphology, reached after thin film fabrication[1].To understand the factors that influence the morphology of thin films based on conjugated polymers, we investigated the electronic structure and morphology of thin films of the poly(9,9-dioctyl-fluorenyl-*co*-bithiophene) (F8T2) copolymer in its pristine form, as well as samples processed with the solvent additive 1,8-diiodooctane (DIO) and thermally annealed.

Figure 1. Angle-resolved S K-edge NEXAFS spectra of F8T2: a-d) pristine; b-e) annealed and c-f) DIO additive.



Measurements carried out using angle-resolved S K-edge NEXAFS (near-edge X-ray absorption fine structure) in total electron yield (TEY) and fluorescence yield (FY) detection modes showed two main transitions at the S1s NEXAFS spectra, S 1s → π* and S 1s → σ* (S-C), respectively at 2471.7 eV and 2472.6 eV (Fig. 1). Additionally, the observed dichroism pointed to a face-on orientation of the conjugated backbone, which is significantly increased for F8T2 films processed with DIO.

We analyzed Resonant Auger decay spectra via the Core-Hole Clock (CHC) method, an elementally-sensitive synchrotron-based approach that utilizes the core-hole lifetime of core levels as an internal reference clock[2]. Enhancement in the charge transfer process was observed for thermally annealed films and samples processed with DIO, indicating an increase in film ordering. We also attested the presence of the thiophene unit in the samples through X-ray photoelectron spectroscopy, where some of its sulfur atoms were shown to have been positively polarized for the F8T2 films.

REFERÊNCIAS

1. Pereira C. F. C. et al (2024). *Inducing molecular orientation in solution processed thin films of fluorine-bithiophene-based copolymer: thermal annealing vs solvent additive* [paper submitted for publication].

2. Arantes C.; Borges B. G. A. L. et al (2013). *Femtosecond Electron Delocalization in Poly(thiophene) Probed by Resonant Auger Spectroscopy*. *J. Phys. Chem. C.* 117(16):8208-8213.

Agradecimentos/Acknowledgments

This work was partially supported by LNLS – National Synchrotron Light Laboratory, Brazil. The authors acknowledge the financial support from CNPq (308930/2019-3), CAPES, CT-INFRA FINEP and FAPERJ (E-26/202.623/2019).

Área:
MAT
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

INFLUENCE OF ALUMINUM ION CONCENTRATION ON THE PREPARATION OF GADOLINIUM ALUMINATE VIA SOL–GEL

João V.G. Faria (PG)[1*], Lauany M.Z. Pontes (PG)[1], Lucas A. Rocha(PQ)[1], Eduardo J. Nassar (PQ)[1].

queromineorg@hotmail.com

[1]*Universidade de Franca, Av. Dr. Armando Salles Oliveira, 201 Pp. Universitário, CEP 14404-600, Franca, SP, Brasil*

Keywords: sol-gel, non-hydrolytic, GAG, photovoltaic cell, upconversion, cancer

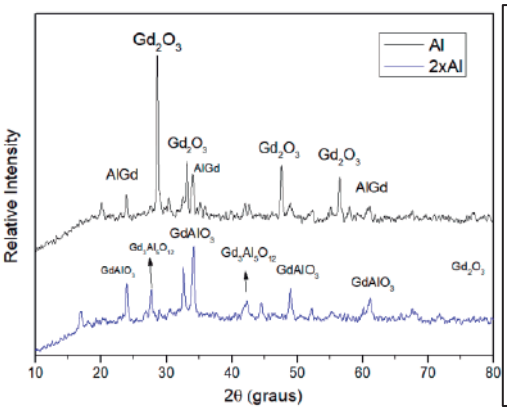
Highlights

INFLUENCE OF ALUMINIUM ION CONCENTRATION ON THE PREPARATION OF GADOLINIUM ALUMINATE VIA SOL-GEL. Alumina-based matrixes are excellent candidates for application as luminophores, we studied how the aluminum ion concentration affects Eu3+, Er3+, and Yb3+ doped gadolinium aluminate.

Resumo/Abstract

We aimed to study how the Al^{3+} concentration affects formation of the $Gd_3Al_5O_{12}$ (GAG) phase doped with optically active ions prepared by the non-hydrolytic sol-gel route. The synthesis precursors were $AlCl_3$, $GdCl_3$, $EuCl_3$, $ErCl_3$, and $YbCl_3$, employed at 5:3:1:1:1 molar ratio, respectively, for the as-prepared sample and at 10:3:1:1:1, respectively, for the sample containing twice the aluminum concentration. The salts were dissolved in ethanol and kept in a closed system under argon atmosphere at 110 ºC for 4 h, followed by resting for 24 h.

Figure 1: X-ray diffractogram of different concentrations of aluminum



The GAG crystalline phase displays properties that allow it to be used in the technological and medical areas. Its doping with Eu3+, Yb3+, and Er3+ intensifies its spectroscopic properties, with a view to its application in voltaic cells and cancer therapy. To obtain the desired phase, we synthesized two samples by using different ratios of the AlCl3 precursor. Additionally, we thermally treated the samples 1000 ºC for 4 h. The X-ray diffractograms (Figure 1) indicated that a mixture of the GdAlO3 and

The emission spectra displayed peaks typical of Eu^{3+} excited in the ultraviolet region. Broad bands indicated that more than one Eu^{3+} crystallographic site existed in the sample. Moreover, the excitation spectra exhibited peaks due to Gd^{3+}. A study of energy up-conversion under 980-nm laser revealed the typical Er^{3+} peaks in the regions of 550 and 650 nm, in the red and green region of the electromagnetic spectrum, respectively. FTIR analyses showed bands in the metal–oxygen bond region, at 700 cm^{-1}, attributed to Al-Gd, Al-O, and Gd-O bonds. Therefore, the aluminum ion concentration directly affects phase formation.

Agradecimentos/Acknowledgments

FAPESP, CAPES and CNPq

Área: MAT_____

Influence of Bi_2MoO_6 Synthesis Method on ZSM-5 Photocatalytic Properties

Letícia S. Novais (IC),[1*] João P. S. Alves (IC),[1] Luciana Almeida Silva (PQ),[1,] Raildo Alves Fiuza Junior (PQ),[1,2] Mauricio Brandão dos Santos (PQ),[1,2] Artur José Santos Mascarenhas (PQ),[1,2] Fernanda Teixeira Cruz (PQ)[1,2]

leticia.novais@ufba.br; fernandateixeira@ufba.br

[1]*Laboratório de Catálise e Materiais-LABCAT, DQGI, IQ, Campus Ondina, UFBA, Salvador-BA, Brasil*
[2]*Laboratório Multitarefas, Centro interdisciplinar de Energia e Meio Ambiente-CIENAM, Campus Ondina, UFBA, Salvador-BA, Brasil*

Keywords: ZSM-5, Bismuth Molybdate, Band gap, Photocatalysis

Highlights

The dispersion of the semiconductor Bi_2MoO_6 in H-ZSM-5, whether by wet impregnation or direct hydrothermal synthesis.
Nanometric materials that allow adjustment of the band gap for photocatalysis.

.Resumo/Abstract

Heterogeneous photocatalysis has been growing due to its potential applications that span across various sectors, including the degradation of medications, dyes, and pesticides. Bulk photocatalysts exhibit rapid recombination of electron-hole pairs (e-/h+), which reduces the efficiency of the photocatalytic system. Thus, in order to reduce the e-/h+ recombination rate, semiconductors have been dispersed on various supports, among which zeolites stand out due to their high surface area, adsorption properties, shape selectivity, and good thermal and chemical stability. In this work, bulk λ-Bi_2MoO_6 was synthesized and dispersed in H-ZSM-5 using different methods: direct hydrothermal synthesis ([Bi_2MoO_6]-HZSM-5) and wet impregnation (Bi_2MoO_6/HZSM-5), both at a 5% content. The materials were calcined at 550°C and characterized by XRD, TG/DTG, FTIR, DRS, SEM, and textural analysis. In the X-ray diffraction pattern, Figure 1.a, the obtaining of the λ-Bi_2MoO_3 phase with orthorhombic symmetry is observed, according to the Inorganic Crystal Structure Database (ICSD 037251). Figure 1b presents the characteristic profile of zeolite ZSM-5, according to the International Zeolite Association (IZA) standard. Samples [Bi_2MoO_6]/HZSM-5 and Bi_2MoO_6/HZSM-5, Figures 1c and 1d, respectively, present characteristic peaks of H-ZSM-5, with the impregnated material showing a peak related to Bi_2MoO_6 (28,28°), while the material synthesized directly does not present characteristic peaks, suggesting that the composite is finely dispersed in the zeolitic structure. Evaluating the lattice parameters of the crystalline planes located in: (151), (303), and (133) of the MFI topology in the composites, a decrease in crystallinity in Bi_2MoO_6/HZSM-5 compared to pure zeolite is observed. This suggests the presence of λ-Bi_2MoO_6 phase dispersed on ZSM-5. The material obtained by direct synthesis ([Bi_2MoO_6]-HZSM-5) did not show this alteration. This analysis is consistent with the DRS, as λ-Bi_2MoO_6 exhibited a band gap of 2,48 eV, resulting from the electronic transition between the valence and conduction bands in the formation of semiconductor heterojunctions. In the impregnated material, Bi_2MoO_6/HZSM-5, there was an increase in the band gap energy of Ebg= 2,85 eV, suggesting a decrease in particle size, which can be explained by quantum confinement, considering the size and dispersion present on the surface of the crystalline structures, resulting in an increase in the interval between the conduction and valence bands. In the material [Bi_2MoO_6]-HZSM-5, the band gap increased significantly to Ebg= 3,51 eV, which is consistent with a subnanometric particle size of Bi_2MoO_6 in the channels and cavities of zeolite HZSM-5. The SEM images of the materials present morphologies as reported in the literature, making it possible to identify the presence of Bi_2MoO_6 on the surface of the impregnated zeolite, while it was not identified in the synthesized one. The FTIR spectra indicated the characteristic vibrational bands of H-ZSM-5, as well as Bi_2MoO_6 in the composites. Thus, materials were synthesized by two methods, obtaining distinct particle sizes of Bi_2MoO_6, as well as variation in the band gap, allowing the application of photocatalysts at different wavelengths for the photodegradation of pollutants in aqueous media.

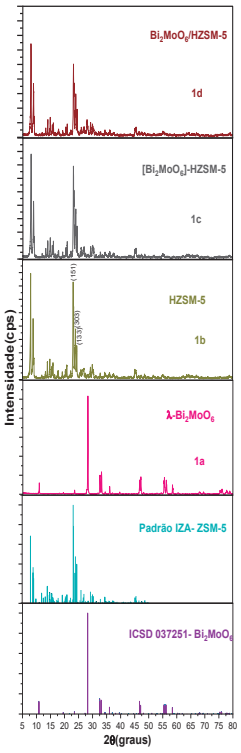


Figure 1. XRD of the materials synthesized with Bi_2MoO_6.

Agradecimentos/Acknowledgments

I thank PIBIC-UFBA for the scholarship granted and FINEP reference 0057/21.

Área: MAT
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Influence of CNFs on monoammonium phosphate fertilizer spray-drying encapsulation

Gabriela Bueno de Godoy (PG),[1] Roselena Faez (PG).[1*]

gabrielagodoy@usp.br; faez@ufscar.br.

[1]*Laboratório de Materiais Poliméricos e Biossorventes, DCNME; Universidade Federal de São Carlos, Araras, SP, Brasil;* [2]*Universidade de São Paulo – Faculdade de Zootecnia e Engenharia de Alimentos (FZEA), Pirassununga, SP, Brasil de Química*

Keywords: *Cellulose nanofibrils; Enhanced Efficiency Fertilizers; Microspheres; Spray Dryer.*

Highlights

The microspheres obtained from 1% CNFs dried in the atomizer resulted in higher yield; CNFs (1 and 2% wt%) present similar results in structural, thermal, and morphological characterization.

Abstract

The continuous search for intensification and improvement of agricultural production has brought demand for technologies that boost the sector, developing ecologically correct inputs with low cost and high output. Enhanced efficiency fertilizers (EEFs) meet the need to increase agricultural productivity. Developing these fertilizers requires preparing fertilizer microparticles coated with a biopolymer that allows the material to release nutrients in a prolonged manner. This work produced microspheres from solutions of monoammonium phosphate fertilizer (MAP, $NH_4H_2PO_4$) and cellulose nanofibrils (CNFs, donated by Suzano Papel e Celulose S.A., Brazil). Drying solutions were prepared by first homogenizing CNFs (1 and 2 wt.%) with MAP (27.6 wt.%) in a total volume of 200 mL for each concentration for 24 h. Then, the dispersions were treated in Turrax (IKA) for 15 min at 12,000 rpm. Finally, the solutions were dried by spraying (Mini Spray-Dryer BUCHI B-290) using a 2-fluid atomizing nozzle with an inlet temperature of 180ºC, 100% aspiration rate, and 20% pump. The microspheres were characterized in terms of structure (FTIR, XRD), thermal (TGA and DSC), and morphological (SEM) (DSC). CNF concentration (1 and 2% wt.%) exhibited minimal impact on microsphere yield (29 and 26%, respectively). However, the observed results fell short of expectations, potentially due to the initial degradation of MAP at 210°C. MAP has a narrow working window since it melts at 197°C, degrades at 210°C, and plays a crucial role in microsphere formation. The MAP diffraction patterns covered the CNFs one; therefore, the degrees of crystallinity were not obtained through XRD analysis. CNF concentration affected the thermal properties of the materials. The 2 wt.% CNF exhibited higher weight loss and lower decomposition temperature than 1 wt.%. The earlier decomposition is attributed to NH_3 (g) formation during burning, and the gas can interact with available CNFs. As the amount of CNFs increases, more gas can be consumed, leading to higher weight loss. The DSC results align with TGA. Both samples display an initial endothermic melting peak around 180°C, rising until roughly 200°C. Within this temperature range, the degradation process also begins. Subsequently, at 210°C, distinct endothermic peaks emerge, reflecting the contribution of CNFs and impurities. The 2 wt.% CNF sample required less heat to reach these peaks. Despite minimal variation in overall properties, the lower yield suggests that spray drying parameters influence CNF concentration more than within this range. Thermal analysis reveals that 1 wt.% CNF inclusion enhances material thermal capacity, expanding its operational window to withstand higher temperatures than theoretical values for the pure material and observed behavior of the 2 wt.% CNF sample. Future work will focus on optimizing spray drying parameters to improve yield and further explore the potential of 1 wt.% CNFs in enhancing thermal stability and nutrient release characteristics. This study lays the groundwork for developing EEFs with biopolymer coatings, paving the way for a more sustainable approach to agricultural intensification.

Acknowledgments

FZEA USP Ciência e inovação da fazenda à mesa
PPG EnCiMat USP
LAB-MPB Laboratório de Materiais Poliméricos e Biossorventes
ufscar
CAPES
FAPESP

Área: MAT

Interfacing reduced graphene oxide with cationic pillar[5]arene as new drug plataform to treatment of neurological diseases

Isabela A. A. Bessa (PG),[1] Natália C. Gomes-da-Silva (PG),[2,3] Fernanda D. Marques (PQ),[4] Bráulio S. Archanjo (PQ),[4] Maria Luiza M. Rocco (PQ),[6] Thiago C. dos Santos (PQ),[6] Ralph Santos-Oliveira (PQ),[2,3] Célia M. Ronconi (PQ)[1]

isabelabessa@id.uff.br; cmronconi@id.uff.br

[1]Departamento de Química Inorgânica, UFF; [2]Nuclear Engineering Institute; [3]Laboratory of Radiopharmacy and Nanoradiopharmaceuticals, UERJ; [4]Divisão de Metrologia de Materiais, Inmetro;

Keywords: *reduced graphene oxide, pillar[5]arene, doxorubicin, biodistribution, pharmacokinetics.*

Highlights

The biodistribution of technecium-99m labeled reduced graphene oxide functionalized with cationic pillar[5]arene showed > 9% uptake by the brain, demonstrating that rGO-$NMe_3P[5]A^+$-DOX was able to cross the blood–brain barrier

Abstract

Graphene-based materials (GBMs) have been investigated in nanomedicine owing to their high surface areas, high drug loading capacities and photothermal effects.[1] By interfacing GBMs with biocompatible molecules, such as polymers and macrocycles, it is possible to improve their biocompatibility and cell penetrance. Therefore, in this work we interfaced quaternary ammonium pillar[5]arene on reduced graphene oxide (rGO-$NMe_3P[5]A^+$) surface through noncovalent interactions.[2] Both GBMs and pillar[5]arene have unique properties that, when combined, can lead to novel and versatile materials. Herein, the functionalization with $NMe_3P[5]A^+$ resulted in a device with a positive surface charge (+28 mV), which is desirable property for interacting with biological systems [3]. Doxorubicin (DOX) was loaded onto rGO-$NMe_3P[5]A^+$, forming rGO-$NMe_3P[5]A^+$-DOX and used as a model drug. The in vivo biodistribution was evaluated by radiolabeling rGO-$NMe_3P[5]A^+$-DOX with technetium-99m (^{99m}Tc). Almost 10% of injected material was found in rats' brain, indicating that ^{99m}Tc-labeled rGO-$NMe_3P[5]A^+$-DOX was able to cross the blood–brain barrier (BBB). Additionally, biochemical analysis showed a small alteration in liver and pancreas enzyme (alanine aminotransferase and amylase) levels, indicating a transient functional alteration. These results suggest that ^{99m}Tc-labeled rGO-$NMe_3P[5]A^+$-DOX presents as a potential strategy for theragnostic agent for neurological disorders. Thus, the drugs temozolomide and taurine will be further loaded onto rGO-$NMe_3P[5]A^+$ and the effects in vivo will be evaluated towards brain cancer and Alzheimer's diseases.

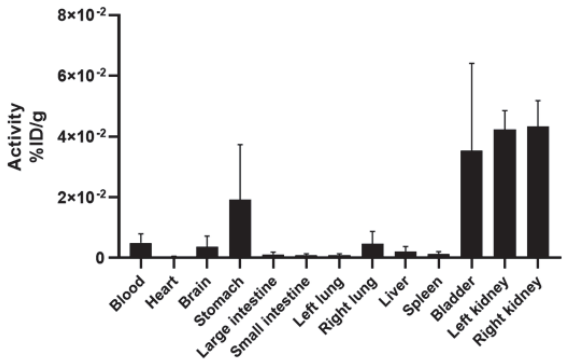


Figure 1. Biodistribution of ^{99m}Tc-labeled rGO-$NMe_3P[5]A^+$-DOX in healthy Wistar rats.

Acknowledgments

UFF, CNPq, CAPES, FAPERJ, PPGQ-UFF, LQSN, LAME, LAMATE

[1] VITORINO, L. S. et al. **Colloids Surf B**, v. 209, p. 112169, 2022.
[2] SANTOS, E. C. S. et al. **J Mater Chem B**, v. 8, p. 703, 2020.
[3] CHEN, Y. et al. **Nanoscale**, v. 15, p. 9348, 2023.

Área: _____
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

INVESTIGATING THE ROLE OF CHOLESTEROL IN DPPC MONOLAYERS ON PROTEIN INTERACTIONS RELATED TO SARS-COV-2

Priscila S. Ferreira (PG), Barbara B. Gerbelli (PQ), Ana. C. H. Castro-Kochi (PQ), Fabiola L. Castro (PG), Wendel A. Alves (PQ).

priscila.sabbag@ufabc.edu.br

Centro de Ciências Naturais e Humanas, Universidade Federal do ABC, Av. dos Estados, 5001, Santo André - SP 09210-580.

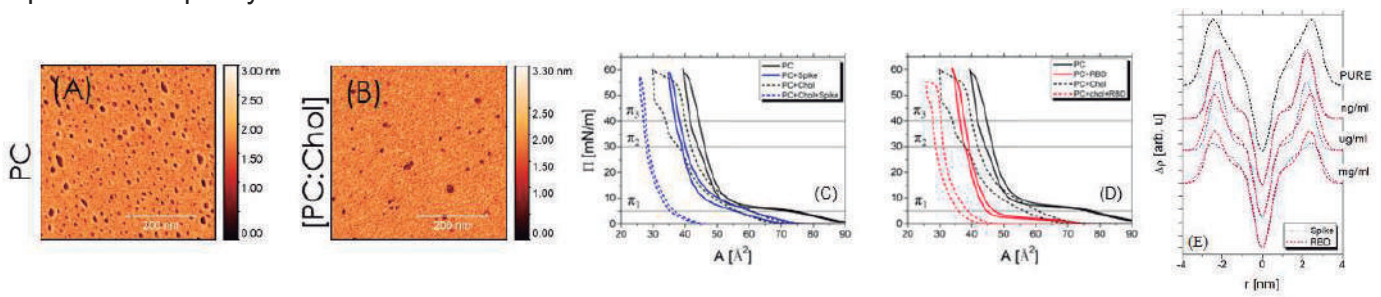
Keywords: *Dipalmitoylphosphatidylcholine (DPPC), SARS-CoV-2, Lipid Membranes, Cholesterol Dynamics, Monolayer Systems, Atomic Force Microscopy (AFM).*

Highlights

Investigation of the structural modifications resulting from cholesterol incorporation into lipid membranes and the mechanisms involved, as well as how this amount of cholesterol can influence protein adhesion, such as that of Spike and RBD proteins. Observations indicate that cholesterol acts as a lipid raft, influencing membrane incorporation. Additionally, the study explored the mechanism of protein entry into the model membrane.

Abstract

Cholesterol is an essential sterol in cell membranes that regulates the organization and fluidity of biological membranes. This biomolecule has been identified as one of the critical factors in the internalization process of various viruses in the human body. Therefore, understanding these viral mechanisms is crucial for a deeper comprehension of viral pathogenicity in the search for effective therapeutic approaches against viral diseases. The biochemical and biophysical processes related to these diseases are highly complex; thus, studying model systems capable of mimicking the interaction between lipid membranes modeled with cholesterol and proteins is fundamental. Recent studies have shown that patients infected by SARS-CoV-2 exhibit high cholesterol levels in their bodies. In this work, we propose to study the structural and elastic changes in lipid systems, both bi- and tridimensional, composed of dipalmitoyl phosphatidylcholine (DPPC) with varying amounts of cholesterol, in the presence and absence of Spike proteins and the receptor-binding domain (RBD). To characterize these systems, we used techniques such as Langmuir trough, atomic force microscopy (AFM), small-angle X-ray scattering (SAXS), and electrochemical methods. We observed that cholesterol in DPPC monolayers promotes local alterations, inducing the formation of more rigid membrane regions. The results of this work led us to conclude that cholesterol-rich lipid membranes increase the investigation of proteins in the membrane, mainly the Spike protein. With the interpretation of all results obtained in this work, it was possible to propose a structural model of the membrane in the presence of cholesterol and the interaction with Spike and RBD proteins. The behavior of the adsorption isotherm and SAXS data demonstrated that the presence of cholesterol in the membrane plays a crucial role in facilitating the allocation of SARS-CoV-2 proteins in lipid systems.



Acknowledgments

This work was supported by FAPESP (grant number 2017/02317-2), CNPq (grant number 304389/2019-6), and the National Institute of Science and Technology in Bioanalytics (FAPESP grant number 2014/50867-3 and CNPq grant number 65389/2014-7). B.B.G. acknowledges the FAPESP fellowship (project numbers 2018/05888-3, 2020/02192-8).

Área: MAT

Investigation of new quinoline photoinitiators in UDMA photopolymerization

Vitor Fernandes Moreno* **(PG),[1] Ilana Sganzerla Rosário (PG),[1] Bruno Hori Barboza (PG)[2], Augusto Batagin-Neto (PQ),[3] Luiz Carlos Da Silva Filho (PQ)[1]**

*e-mail: **vitor.moreno@unesp.br**

[1]*Department of Chemistry, São Paulo State University (UNESP), School of Sciences, 17033-360, Bauru, São Paulo, Brazil*
[2]*School of Sciences, POSMAT, São Paulo State University (UNESP), 17033-360, Bauru, São Paulo, Brazil*
[3]*Department of Science and Technology, São Paulo State University (UNESP), Institute of Science and Engineering, 18409-010, Itapeva, São Paulo, Brazil*

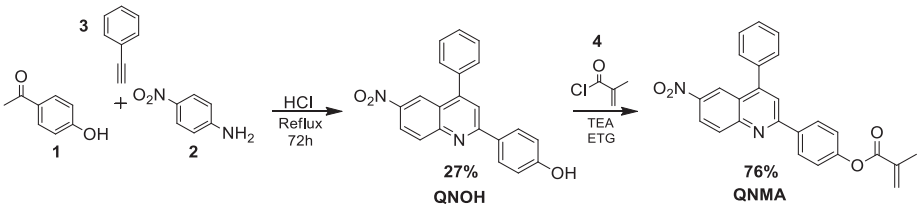
Keywords: quinoline derivatives, photopolymerization, photoinitiator, luminescent polymers, dental restorations

Highlights

Fast and efficient polymerizations. Production of fluorescent polymers from a monomer used in dental restorations. Photopolymerization that can be carried out both under blue and UV light irradiation. Type II photoinitiators, alternatives to camphorquinone.

Abstract

This work sought the synthesis and application of two quinoline derivatives (Scheme 1) capable of acting as photoinitiators (PI's) in the photopolymerization reaction of urethane dimethacrylate monomer (UDMA) (Figure 1a) which is widely used in the composition of dental restoration resins.[1,2] Among the objectives, we verified the effect promoted by the different quinoline compounds including one of them having a methacrylate group like the monomer, which showed promise when reaching more than 60% of conversion degree, result similar to camphorquinone that is used in several composite resins currently.[2] The polymerization times also drew attention, being between 40 and 60 s, and by means of a photolysis investigation we observed the formation of radical species from the first second to the exposure of the PI's to the light (Figure 1b). The obtained materials present fluorescence and good thermal properties, which may be interesting for application in the dental field. Some computational calculations helped to understand the photoinitiating system between PI's and the ethyl-4-(dimethylamino)benzoate (coinitiator).



Scheme 1. Synthesis of quinoline derivatives

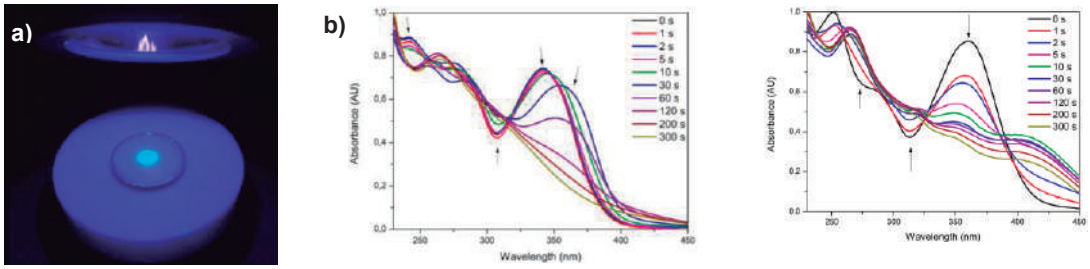


Figure 1. a) Photopolymerization of UDMA using quinolinic PI's, b) Photolysis behavior of QNOH and QNMA PI's.

[1]. Moszner, et al., *Angew. Makromol. Chem*. 1999, 265 (1), 31–35.
[2]. Fouassier, J. P.; Lalevée, *J. Photoinitiators for Polymer Synthesis*; John Wiley & Sons, 2013.

Acknowledgments

The authors would like to thank CAPES (88882.330148/2019-01), CNPq (303141/2021-2), FAPESP (2018/14506-7), and PROPe-UNESP for their financial support.

Área: _____MAT_____
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Mailable films with up converting and persistent properties

Elaine Andrade de Mattos(PG),[1] Pedro Caus (IC),[1] Lucas Carvalho Veloso Rodrigues (PQ).[1]*

elaine.mattos@usp.br

[1]Departamento de Química Fundamental, Instituto de Química, Universidade de São Paulo

Palavras Chave: up conversion, persistent luminescence, cellulose films, mailable film.

Highlights

This composite aims to study radiative energy transfer between the up-conversion and persistent luminescence. The use of hydroxy propyl methylcellulose (HPMC) film endeavors to achieve proximity between UCNps and in order to facilitate the radiative transfer of energy. This kind of smart material can help increase the applicability of IR emitting phosphorus, once the composite can be excited at 980 nm and emit at 700nm, both being in the biological window.[1]

Resumo/Abstract

In this study, two luminescent materials were combined in a cellulose ether polymer, HPMC, to create a mailable film that preserved the luminescent materials optical properties. The first is a core-shell structure, YF_3@YF_3:Yb^{3+}, Er^{3+} (UCNps) that presents up-conversion when excited with an IR (980 nm) laser, emitting both in 550 nm and 660 nm. The second is a persistent luminescent material $Zn_{1,3}Ga_{1,4}Sn_{0,3}O_4$: Cr^{3+}(PLM), that presents two interesting excitation bands, one in the blue-violet region (400 – 450 nm) and other in the green region of the visible spectra (500-600 nm) and emits light in 700 to 800 nm. That means that the HPMC composite can emit light when excited throughout the uv-vis and near-IR spectra. The composites were synthesized by a drop casting process, where the HPMC was first dissolved in water;

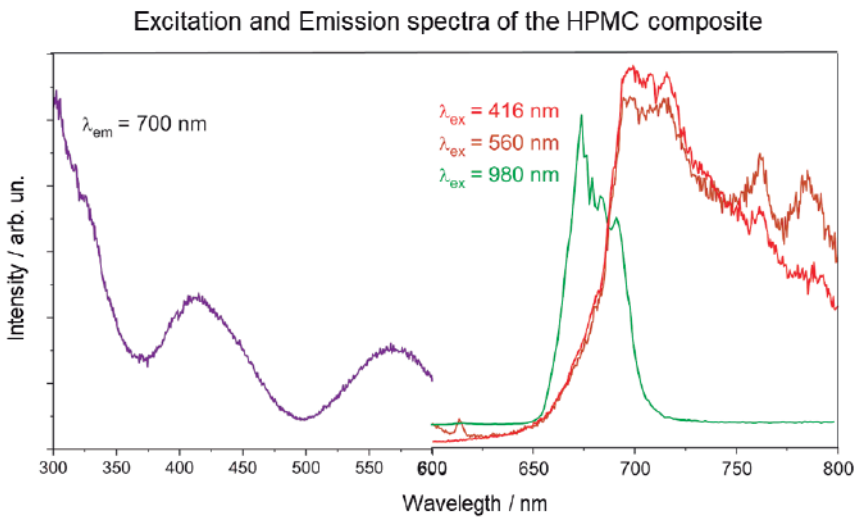


Figure 1: Excitation and emission spectra for the HPMC/UC+PL film

then the luminescent materials were then added the solution and homogenized This suspension was poured into silicon molds and put to dry overnight at 80 °C.
Figure 1 shows that the characteristic excitation and emission profiles of both luminescent compounds can be seen even after the casting process, the emission band of Cr^{3+} in this matrix can be seen with excitation in 415 nm and 560 nm. The excitation in 560 nm presents a partial spectral alignment with the emission of the UCNps in 550 nm. This shows the potential of the combination of these luminescent materials in a smart IR (980 nm) to IR (800 nm) up conversion composite.

In the case of a radiative energy transfer from the green emission of YF_3@YF_3:Yb^{3+},Er^{3+} in 550 nm to the excitation band of the $ZnSnGaO_3$: Cr^{3+} in 575 nm, no emission in the 700 nm was seen when the material was excited with 980 nm laser, therefore the radiative energy transfer can not be observed in the film.

Agradecimentos/Acknowledgments

Acknowledgments: CNpq, FAPESP and CAPES.

Referências

(1) Kamimura, M. Recent Progress of Near-Infrared Fluorescence in vivo Bioimaging in the Second and Third Biological Window. ANAL. SCI. 37, 691–697 (2021). https://doi.org/10.2116/analsci.20SCR11

Área: MAT

Metal oxide heterostructures for acetone sensor devices

Douglas Scarabello (PG)[1], Rafael Aparecido da Silva (PG)[1], Anderson A. Felix (PQ)[1], Marcelo Ornaghi Orlandi (PQ)[1]

douglas.scarabello@unesp.br

[1]*Departamento de Física, Engenharia e Matemática, Universidade Estadual Paulista (Unesp), Instituto de Química, Araraquara, Brasil*

Keywords: Acetone, diabetes mellitus, molybdenum oxide, yttrium oxide, sensor devices.

Highlights

The acetone in the breath is a promising biomarker for the non-invasive diagnosis of diabetes mellitus.
The synthesis of a material sensitive to acetone aims to mitigate the drawbacks of conventional methods.
The study of molybdenum oxide, with yttrium oxide, revealed morphological changes that affect sensor sensitivity.

Abstract

Acetone is considered a non-invasive biomarker of diabetes mellitus. Its concentration in the breath of non-diabetic individuals ranges from 300 to 900 ppb (DISKIN; ŠPANĚL; SMITH, 2003); however, for diabetics, the concentration is higher than 1710 ppb (DENG et al., 2004). According to the International Diabetes Federation (IDF), this disease affects 537 million people worldwide. Currently, checking of this disease is performed using blood samples with glucose meters. Despite the efficiency of these methods, the blood sample withdrawal makes this technique intrusive, painful, and inconvenient (RISBY; TITTEL, 2010). Therefore, due to the potential of diagnoses from the quantification of acetone in the breath, the goal of this work is to synthesize a chemical compound sensitive to the presence of acetone to reduce the damage caused by conventional analysis methods. The material studied in this work is molybdenum oxide, synthesized by the hydrothermal method and decorated with different amounts of yttrium oxide, using the Pechini method. Scanning electron microscopy showed that pure molybdenum oxide has a plate-like morphology, and the addition of the Pecchini solution to the material, followed by calcination up to 500°C, alters the morphology with the presence of nanospheres on the plates. From high-resolution transmission electron microscopy analysis, it was possible to find the interplanar distances of the plates and nanospheres. These distances, together with electron diffraction, were used to name the materials present. From the Tauc plot of the pseudo-absorbance curves as a function of energy (eV) of the different films, it was figured out that the optical band gap of the decorated materials has values close to 3.4 eV, with a different of 0.2 eV compared to the molybdenum oxide film. The phases of the materials present in the film were found by Raman spectroscopy and X-ray diffraction (XRD). Due to the limits related to the quantities of the second added material, Raman did not show significant changes with alterations in the amounts of the yttrium oxide, while XRD showed changes both in the appearance of new peaks related to the cubic structure of yttrium oxide and small shifts related to the peaks of the orthorhombic structure of molybdenum oxide. Films of the characterized materials were prepared on alumina substrates coated with interdigitated platinum electrodes (Pt finger arrays of 300 µm spaced 300 µm apart), and the electrical resistance of the sensors was checked by varying environmental conditions, both in relation to diverse types of gases and their concentration and the temperature of the system. Therefore, this work presented the study of materials little studied in the literature, as well as their applications for sensor devices. With the advancement of tests, it may be concluded whether the material has potential for the manufacture of diabetes mellitus sensor devices.

Acknowledgements

I would like to thank CAPES, FAPESP, FINEP, and CNPq for funding the equipment, and UNESP for the research scholarship. My gratitude goes to my research group for their support and insights throughout the completion of this work.

DENG, C. et al. Determination of acetone in human breath by gas chromatography–mass spectrometry and solid-phase microextraction with on-fiber derivatization. Journal of Chromatography B, v. 810, n. 2, p. 269–275, 2004.
DISKIN, A. M.; ŠPANĚL, P.; SMITH, D. Time variation of ammonia, acetone, isoprene and ethanol in breath: a quantitative SIFT-MS study over 30 days. Physiological measurement, v. 24, n. 1, p. 107, 2003.
RISBY, T. H.; TITTEL, F. K. Current status of midinfrared quantum and interband cascade lasers for clinical breath analysis. Optical engineering, v. 49, n. 11, p. 111123, 2010.

Área: MAT

Metrological evaluation of interaction between biomolecules and graphene quantum dots produced from urea and citric acid.

Rocio Soto-Chochocca (PG),[1*] Renan Lira de Farias (PQ),[2] Marlin Pedrozo-Peñafiel (PQ),[3] Luis Miguel Gutierrez-Beleño (PQ)[4], Ricardo Q. Aucelio (PQ),[1]

aucelior@puc-rio.br; rsotojah22@gmail.com

[1] *Post-graduate Program in Metrology, PósMQI; Pontifical Catholic University of Rio de Janeiro (PUC-Rio), RJ, Brazil.*
[2]*Department of Chemistry, Pontifical Catholic University of Rio de Janeiro (PUC- Rio), Rio de Janeiro, RJ, Brazil.*

Palavras Chave: *Graphene quantum dots(GQDs), Urea, Biomolecule interactions, Photoluminescence, Stability over time).*

Highlights

Luminescent graphene quantum dots were produced from urea/citric acid. Stability in size and surface charge was found. Consistent biomolecular affinity with HSA and *ct*DNA was found up to 28 days after preparation.

Resumo/Abstract

Graphene quantum dots are highly promising in biological applications due to their photoluminescence and small size to be diffused inside cells. This research investigated the interaction of the nanomaterial (GQDs-U), produced with urea and citric acid, with two model biomolecules: Human serum albumin (HSA) and *calf thymus* DNA (ctDNA). The temporal study was made in two replicates in intervals within 28 days (672 h) after producing of the GQDs aqueous dispersion. The GQDs were characterized by spectroscopic techniques and their concentration expressed in terms of total carbon content in aqueous dispersion. GQDs-U have showed stability in average hydrodynamic diameter (around 12 nm) surface charge (–7 mV). Assays revealed that progressive increases in GQDs concentration led to quenching in HSA fluorescence (emission band between 293-443 nm). The temporal profiles of the interaction constant (K_i) between GQDs-urea and HSA oscillated in the first 48 h, fluctuating towards stability up to the evaluated time of 672 h. Quenching mechanism is mixed but prevailing the dynamic type. This temporal kinetic profile suggests mutual conformational rearrangements of biomolecules/GQDs for geometric optimization of intermolecular interactions before reaching thermodynamic equilibrium. Interaction with DNA was monitored by spectrophotometric titration (200 to 400 nm range) revealing bio-interaction between GQDs-U with apparent binding constants varying slightly (K_{bap} from 1.3×10^5 to 1.6×10^5 L mol^{-1}), denoting a weak interaction guided by hydrophobic and electrostatic forces. Additionally, an ethidium bromide (BET) competition assay was conducted to verify if the GQDs-U can bind to DNA, forming a stable interaction. The binary mixture BET-DNA revealed that GQDs-U do not act as intercalators but may alter the secondary structure of DNA, possibly through non-covalent interactions via the groove, disrupting some BET-DNA interaction complexes. Statistical tests, confirm the consistency of results with 95% confidence, demonstrating the reproducibility of interactions with HSA and DNA along the period of study. The stability of quantification parameters over time suggests the viability of GQDs as analytical probes even after long periods of bio-conjugation. Finally, this study presents metrological sound foundations for the safe application of GQDs in biomedical technologies, expanding the understanding of the intricate time-structure-activity relationship in these ultrasensitive systems.

Agradecimentos/Acknowledgments

CNPq, FAPEJ, CAPES, VRAC-PUC-Rio

Área: MAT

Microfluidic SERS devices for selective molecule detection

Cleber S. Torres (PG),[1*] Anerise de Barros (PQ),[1] Varlei Rodrigues (PQ),[2] Fernando A. Sigoli (PQ),[1] Italo O. Mazali (PQ).[1]

*cstorres20@gmail.com, mazali@unicamp.br

[1] *Universidade Estadual de Campinas, Instituto de Química, Laboratório de Materiais Funcionais, Campinas, SP, Brazil.*
[1] *Universidade Estadual de Campinas, Instituto de Física "Gleb Wataghin", Campinas, Brazil.*

Keywords : N*anoparticle, Gold, Silver, SERS, microfluidic.*

Highlights

- 3D printing microchannels in double Y design.
- SERS sensors based on Au and Ag nanoparticles junctions.
- Selective detection of Fluorescein 5 isothiocyanate and crystal violet.

Abstract

Strategies of development SERS sensors have been extensively performed in order to achieve more efficient platforms, with high sensitivity and selective detection. In this sense, the development of SERS platforms with selectivity is a great challenge to make the tool more attractive from an analytical point of view. Based on that, we are developing SERS platforms using a microfluidic system for the simultaneous deposition of silver and gold nanoparticles (AgNPs and AuNPs). For this, 3D printing microchannels in double Y-shaped (Figure 1(a)) and two peristaltic pumps are used to deposit both nanostructures. Transmission electron microscopy (Figure 1(b, c)) results show that the effective synthesis was obtained with sizes closed in order to minimize differences in the hot spot regions created by the nanoparticles. Additionally, the zeta potential are also close, -22.1 and -17.1 mW for AuNPs and AgNPs, respectively. The UV-VIS extinction spectra for AuNPs and AgNPs displayed the maximum absorbance band at 520 and 407 nm, respectively. The laser wavelength (532, 633, 785 nm) for SERS analysis was evaluated for each nanoparticles type in order to achieve the better performance of the sensor. For this, we used crystal violet (CV) and fluorescein-5-isothiocyanate (FITC) to investigate the selective and simultaneous detection of both molecules by AuNPs and AgNPs. Briefly, the CV and FITC displayed a different interaction with nanoparticles which leading to changes in the spectral profile. Specifically, the CV molecule when interacting electrostatically with negative nanoparticles has parallel adsorption, while the FITC molecule has a chemisorb interaction with perpendicular adsorption. Previous results of the SERS spectra for the individual detection of both molecules for the two metallic nanostructures show different spectral profiles as expected (Figure 1(d)). Based on these results, we started the investigation by the region substrate with simultaneous AuNPs and AgNPs deposited for molecules in order to achieve the selective detection based on the recognition by the spectral profile.

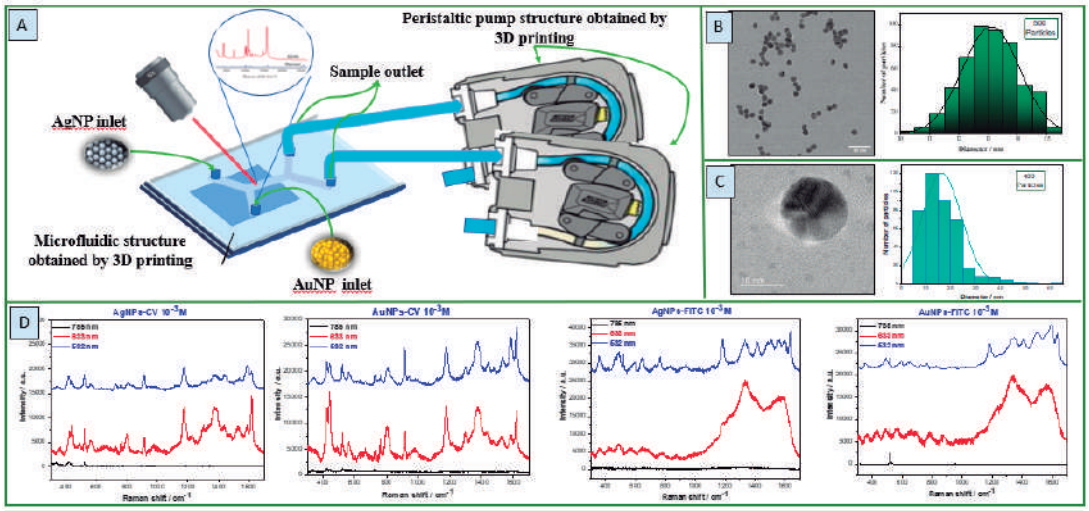


Figure 1 – a) deposition system with microfluidic structures (b-c) AuNPs and AgNPs characterization, (d) SERS spectrum of the violet crystal molecule and fluorescein-5-isothiocyanate.

Acknowledgments

UNICAMP, Instituto de Química, Laboratório de Materiais Funcionais, EMMU, FAPESP, CNPq, CAPES, LNNano, Inomat

Área: MAT

Molybdenum disulfide and polyaniline nanocomposite thin films prepared by liquid-liquid interfacial route (LLIR): Synthesis, Characterization and electrochemical studies

João Victor Gonçalves (IC)[1], Amanda F. Pereira (PG)[1], Aldo J. G. Zarbin (PQ).[1]*

joao.victorzg06@gmail.com; aldozarbin@ufpr.br

[1]*Departamento de Química, UFPR*

Palavras Chave: *Nanomaterials,Molybdenum Disulfide,Conducting Polymers, Electrochemistry.*

Highlights

Investigation of the preparation process and properties of MoS_2/PAni nanocomposite thin films by LLIR, and their potential application in eco-friendly and sustainable electronic/optoelectronic devices.

Resumo/Abstract

Given the rapid development and evolution of technology over the past decades, the demand for materials to be employed in the construction of electronic devices has risen massively, which spiked interest in the development of new, more sustainable and readily available materials, to supply such demand. Molybdenum disulfide (MoS_2) is an example of a material that has been heavily studied due to its natural abundance, low toxicity and promissing optical and electrical properties[1]. Alongside, conjugated conducting polymers, such as Polyaniline (PAni), have been investigated for similar applications, since this class of materials also presents desirable characteristics for the development of eco-friendly and sustainable electronic devices[2]. Therefore, this work deals with the preparation of thin films of MoS_2/PAni nanocomposites in a toluene/aqueous acid solution interface, via liquid-liquid interfacial route (LLIR)[3], and a study of the effects provided by varying reaction conditions, such as precursors amount and pH of the aqueous phase. These films were characterized by UV-Vis Spectroscopy, X-ray Diffractometry (XRD), Scanning Electron Microscopy (SEM), Fourier-Transform Infrared Spectroscopic (FTIR), Raman Spectroscopy, and their electrochemical behavior was also investigated by various techniques. Results show that each reactional condition generates slightly different films. Visually, films prepared at lower pH values seem thicker and more intense in color, despite still being transparent. UV-Vis spectra show that films synthesized at higher pHs present lower quantities of delocalized polarons, which indicates lower doping of the polymer, and this also happens with the decrease of the monomer quantity. FTIR and Raman spectra don't seem to indicate significant changes when the monomer quantity is varied, though it becomes evident through these analyses that higher pHs generate a more planar polymer. Electron Microscopy analyses show that variation of monomer quantity also didn't give rise to much difference regarding morphology of the films, while pH changes did. The morphology of films obtained at lower pHs are comprised of islands of polymer covered in MoS_2; In contrast, higher pHs generate a more spread-out polymer base, with regions of concentrated MoS_2 flakes. Initial electrochemical studies reveal that decreasing the amount of monomer increases the electrochemical stability of the emeraldine Salt (ES) form of PAni, and that the presence of the MoS_2 elevates the composite's conductivity. The effect of pH is also evident in the electrochemical behaviors, where higher pHs result in less conducting films, where the ES form is generally less stable, and the presence of the MoS_2 appears to modify the composite's electrochemical behavior to a smaller degree, probably due to it being more isolated in these cases, as remarked in the SEM analyses. Possible applications of these composites in electronic/optoelectronic devices are under investigation.

[1] Mak, K. F.; Lee, C.; Hone, J.; Shan, J.; Heinz, T. F. Phys. Rev. Lett. **105** (2010).

[2] A. Malinauskas, J. Malinauskiene, A. Ramanavicius. Nanotechnology, **16** (2005).

[3] ZARBIN, Aldo J. G. Materials Horizons, **8**, 1409-1432 (2021).

Agradecimentos/Acknowledgments

UFPR, CNPq, CAPES, INCT Nanocarbono, INCT Nanovida, CME-UFPR, GQM-UFPR.

Área: MAT

Multi-walled carbon nanotubes decorated with Prussian Blue for pesticide electrochemical sensor.

Thiago S. D. Almeida (PG),[1] Luiz H. Marcolino Jr. (PQ),[1] Marcio F. Bergamini (PQ),[1] Elisa S. Orth (PQ),[1] Aldo J. G. Zarbin (PQ) ,[1]*

thiagolmeida1@ufpr.br; aldozarbin@ufpr.br*

[1]Departamento de Química, UFPR;

Thin film, sensors, pesticide, Prussian blue, carbon nanotubes.

Highlights

The formation of carbon nanotube films decorated with different amounts of Prussian blue. The films were characterized and will be used as a non-enzymatic electrochemical sensor for pesticide detection

Resumo/Abstract

Seeking to ensure the control and appropriate use of agricultural pesticides, many countries and organizations limit the maximum amount of waste in different matrices. In this sense, new materials and the development of reliable techniques for the quantification and detection of different pesticides present in different matrices becomes of great importance and urgency. Several methods have been developed to determine these chemical compounds, including: high-performance liquid chromatography, gas chromatography and mass spectrometry, among others. These techniques have some characteristics such as low detection limits and high sensitivity, but they present high cost, long sample preparation process and longer analysis time. The electrochemical method is highlighted, as it presents advantages: (i) simplicity; (ii) low cost of instruments; (iii) quick responses; (iv) portability. [1] In this sense, the search for materials capable of detecting pesticides by electrochemical method has been growing. This work explores the use of a nanocomposites between carbon nanotubes (CNT) and Prussian blue (AP) as active component in electrochemical sensor. CNT films were previously prepared on ITO to carry out the electrosynthesis of Prussian blue nanocubes on the CNT walls. This was obtained through the heterogeneous reaction between the ferricyanide ions in solution and the iron species present in the CNT film. Different amounts of AP electrodeposition were carried out using cyclic voltammetry (50,100 and 150 cycles). The compounds were characterized by UV-Vis, Raman, SEM and electrochemistry. The nanocomposites exhibited an interaction between AP and CNTs, promoting greater stability and improving redox properties. It is noted that the formation of AP on CNT occurs up to 100 cycles without the formation of AP aggregation. With 150 cycles, the formation of AP agglomerates on CNT is noted. The formation of composites formed by Prussian blue and carbon nanotubes promotes both electrochemical stability and improved conductivity, [2] enabling investigate the activity of this material against pesticide detection.

[1] Li, Shumin, et al. Analytical Methods 8.27 (2016): 5435-5440.

[2] Husmann, Samantha, and Aldo JG Zarbin. Chemistry–A European Journal 22.19 (2016): 6643-6653.

Agradecimentos/Acknowledgments

UFPR, FINEP, CNPq, CAPES, INCT Nanocarbono, INCT NanoVida.

Área: MAT

Nanoarchitecting 2D materials by demand: 1T-MoS_2 interfacial functionalization with micro-organic pollutants.

Ariane Schmidt (PG),[1] Hussain A. Al Nasser (PQ),[2] Robert A. W. Dryfe (PQ),[2] Aldo J. G. Zarbin (PQ)[1*].

arianeschmidt@ufpr.br; aldozarbin@ufpr.br

[1]Department of Chemistry, Federal University of Paraná (UFPR), 81531-980 Curitiba, Paraná, Brazil; [2]Department of Chemistry, and Henry Royce Institute for Advanced Materials, University of Manchester, Manchester M13 9PL, United Kingdom.

Keywords: *2D Materials, Functionalization, Liquid-Liquid Interfacial Route, Nanoarchitecture, Ion transfer.*

Highlights

The phase engineering combined with the liquid-liquid interfacial route paves the way for the functionalization of MoS_2 with three organic dye pollutants, changing their ion transfer properties.

Abstract

After the graphene ascension, molybdenum disulfide (MoS_2) is one of the 2D materials most studied, with Mo and S atoms covalently bonding in the plane and van der Waals interactions between the layers. MoS_2 is a promising 2D material due to its layer-dependent band gap in the 2H phase and metallic behaviour in the 1T phase, which has many applications in electronics, energy storage, sensors, and catalysis. Nevertheless, advancements in 2D materials depend highly on their preparation, especially for developing materials by demand. In this context, this work aims to nanoarchitect materials using phase engineering and interfacial functionalization through the liquid-liquid interfacial route (LLIR) developed by our group. For this, the electrochemical exfoliation and phase conversion of 2H MoS_2 leads to a stable dispersion of 1T MoS_2, which is substantial for the functionalization step. The interfacial functionalization (IF) occurred with three dyes: methylene blue, neutral red, and crystal violet, all of them known for being a pollutant in residual water, Figure 1. The presence of the dye proved crucial for MoS_2-functionalized thin film formation by the LLIR, being the first clue of the interaction between the components. The complete characterization of the films by UV-Vis, Raman, XPS, and SEM confirms the successful functionalization, in which 0.01 mmol L^{-1} is the optimal dye concentration. The proposed mechanism of IF is the electrostatic interaction and charge transfer from 1T-MoS_2 to the dyes, corroborated by spectroscopy measurements. The ion transfer properties of the MoS_2-functionalized membranes at the interface between two immiscible electrolyte solutions disclose the influence of the dye in the transfer of Na^+, $(CH_3)_4N^+$, and PF_6^- compared to non-functionalized MoS_2 and bare interface, facilitating the transfer of cations over anions, assigned to the synergism of negative charge of MoS_2 with the π cloud of the dyes. Overall, this study displays the potential of the LLIR to nanoarchitect thin films by demand, contribute to the circular economy, and modulate the materials' properties, aiming at a targeted application.

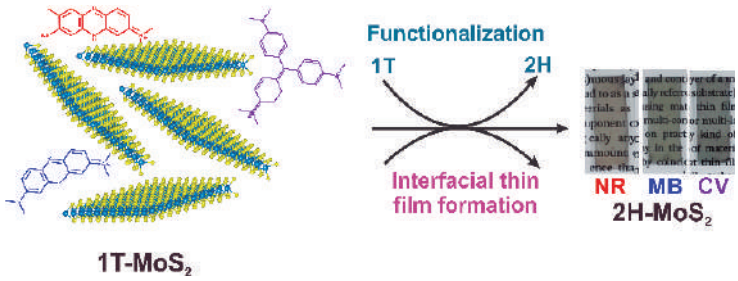


Figure 1. Scheme of interfacial thin film formation and functionalization of MoS_2 with the dyes.

Agradecimentos/Acknowledgments

CAPES, CAPES-PRInt, CNPq, INCT-Nanocarbono, INCT-NanoVida, and EPSRC-UK for financial support.

Nanobastões de ouro como biossensores para detecção de antígenos virais por Espalhamento Dinâmico de Luz (DLS)

Ana Beatriz C. Souza (IC)[1], Carolina B. P. Ligiero (PQ)[1]*, Célia M. Ronconi (PQ)[1]*

ab_costa@id.uff.br; cmronconi@id.uff.br

[1]*Departamento de Química Inorgânica, Universidade Federal Fluminense, Campus do Valonguinho, Outeiro de São João Batista, s/n, 24020-141, Niterói, RJ, Brasil.*

Palavras Chave: *Nanobastões de ouro, Espalhamento dinâmico de luz, SARS-CoV-2*

Highlights

Gold nanorods as biosensors for viral antigen detection using dynamic light scattering (DLS) was employed. Decay time in the correlogram was used as a tracer to understand antibody coupled gold nanorods agglomeration in an immunoassay.

Resumo

Em razão da pandemia de COVID-19, nosso grupo de pesquisa deu início, em 2020, ao desenvolvimento de biossensores para detecção da proteína S presente na superfície da partícula viral através do DLS[1,2]. Nanobastões (AuNRs) de ouro apresentam elevada sensibilidade óptica, podendo ser um sistema interessante, mas pouco explorado na literatura para a detecção de moléculas biológicas por meio de DLS. AuNRs com razão de aspecto 1.8 foram sintetizados (Figura 1-A).[3] Em seguida, foi feita a substituição do brometo de cetiltrimetilamônio por citrato de sódio. A bioconjugação dos anticorpos anti-proteína S foi realizada por meio do agente de ligação cruzada 3,3'-ditiobis(sulfosuccinimidil propionato). A análise por DLS dos AuNRs é diferente das nanoesferas; o movimento Browniano típico dos nanobastões resulta em dois decaimentos no correlograma, que são convertidos em dois picos de diâmetro hidrodinâmico (D_H) (Figura 1-B e C). Imunoensaios com a proteína S mostraram que os tempos de decaimento do sinal de autocorrelação dependem da concentração do antígeno, indicando agregação induzida pela presença do antígeno (Figura 1-D e E).

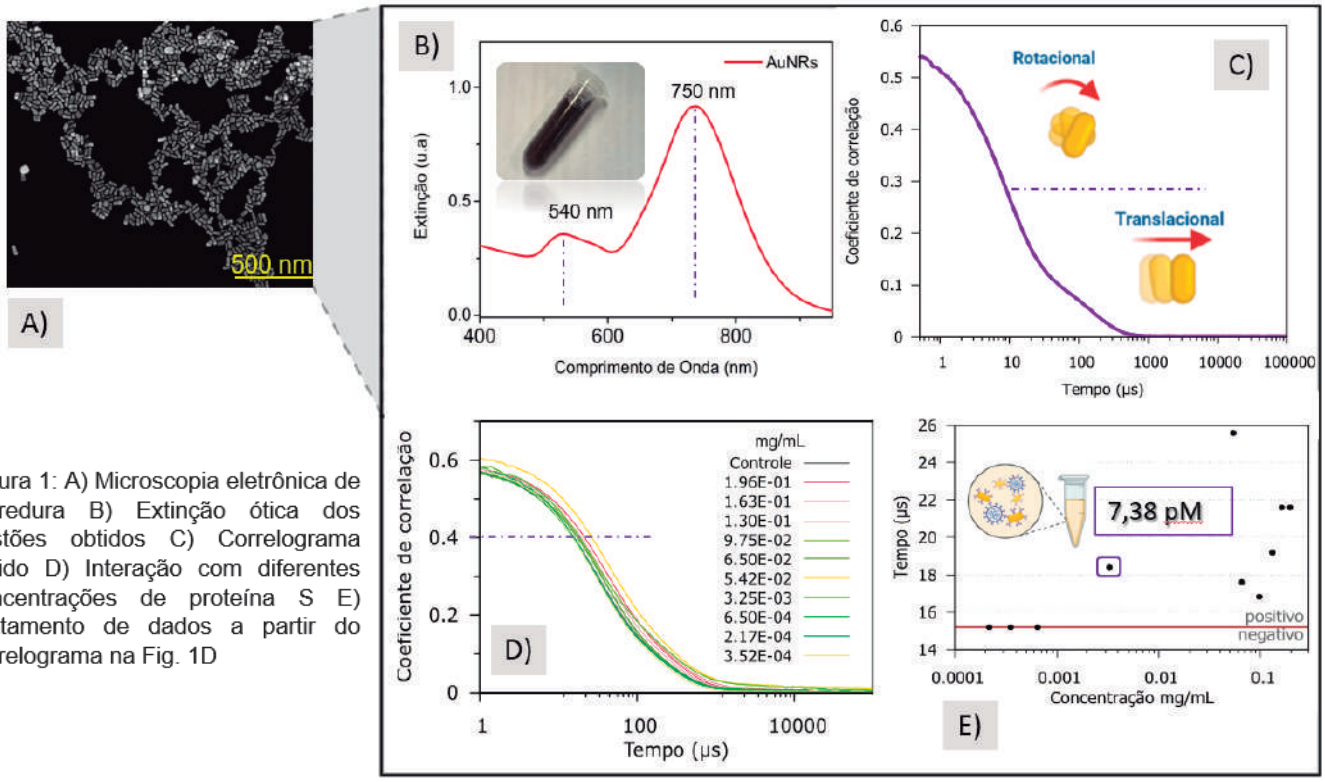


Figura 1: A) Microscopia eletrônica de varredura B) Extinção ótica dos bastões obtidos C) Correlograma obtido D) Interação com diferentes concentrações de proteína S E) Tratamento de dados a partir do correlograma na Fig. 1D

Para aumentar a sensibilidade do método, um modelo matemático está sendo desenvolvido com base nos correlogramas. O Limite de Detecção alcançado foi de 7,38 pM, indicando a formação de agregados de nanobastões de ouro devido à formação de um complexo imune pela interação dos anticorpos com a proteína S.

Agradecimentos

UFF, CNPq, CAPES, FAPERJ, LQSN, LAME, LAMATE, Instituto Vital Brasil e LECC-Coppe/UFRJ

[1] LIGIERO, C. S. *et al.* Mater. Today Chem. 2022, 25, 100924.
[2] SILVA, P. B. *et al.* Talanta. 2022, 243, 123355.
[3] NIKOOBAKHT, B., et al. Mater. 2003, 15, 1957.

Área: MAT

Nanocomposite films based on carbon materials and bismuth hexacyanoferrate for application in energy storage.

Diego Alves Peixoto (PG),[1] Renata Cristina de Lima (PQ),[1] Edson Nossol (PQ)[1]

diego93.alves@gmail.com

[1]*Chemistry Institute, UFU.*

Keywords: *Bismuth hexacyanoferrate, Carbon nanotubes, Reduced graphene oxide, Energy storage devices.*

Highlights

The materials were obtained by the liquid-liquid interfacial method. The BiHCF/rGO film showed the best result in charge/discharge tests, with a specific capacity of 154 mAh g^{-1} at 300 mA g^{-1}.

Resumo/Abstract

Metallic hexacyanoferrates has attracted much attention as promising material for energy storage devices due to their high redox potential, non-toxicity, low cost of raw materials, and open crystalline structure. Furthermore, the addition of carbon materials to hexacyanoferrates provides an improvement in the stability of the electrochemical cycle of these materials in neutral and basic media. Here, the electrochemical performance and electronic structure information of bismuth hexacyanoferrate (BiHCF) were studied in aqueous K-ion batteries. The BiHCF/rGO (reduce graphene oxide) and BiHCF/CNTs (carbon nanotubes) nanocomposite films were synthesized by the liquid-liquid interfacial method. The prepared materials were characterized by Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDS). The FTIR spectra of the nanocomposite films showed bands corresponding to BiHCF, attributed to the vibrational modes υ(OH), υ(CN), δ(HOH), υ(FeC), and δ(FeCN). The vibrational modes υ(CN), υ(FeC), and δ(FeCN) which are related to the octahedral unit $[Fe(CN)_6]$, while the vibrational modes υ(OH) and δ(HOH) are related to crystallized water. It is also possible to observe in the spectrum a vibrational absorption band corresponding to rGO, attributed to the C=O stretching. The Raman spectra showed the D and G bands, characteristic of carbon materials, located at 1343 and 1585 cm^{-1}, respectively. The bands associated with BiHCF can be observed at wavenumber values below 600 cm^{-1}, and in the region between 2030 and 2100 cm^{-1}. The bands observed at lower wavenumbers are related to stretching of the cyano group in Fe^{II}-CN octahedral coordination compounds, while the two bands at higher wavenumbers are characteristic of stretching of the cyano group coordinated to Fe^{II} and Fe^{III}. The SEM images revealed that the BiHCF nanoparticles exhibited a prism-like morphology. These particles are covered by rGO sheets and carbon nanotubes. The electrochemical behavior of the nanocomposite films was characterized by cyclic voltammetry. The voltammograms showed a faradaic current response with peaks associated with the Fe^{II}/Fe^{III} redox process. Based on the cyclic voltammetry and galvanostatic charge/discharge results, the BiHCF/rGO nanocomposite film exhibited a specific capacity of 154 mAh g^{-1} at a current density of 300 mA g^{-1}. This performance presented may be associated with the rapid intercalation of K^+ ions. The rGO sheets play a fundamental role in the performance of the nanocomposite film since the presence of carbon materials provides an increase in the conductivity of the hexacyanoferrate. The physical characteristics and electrochemical properties presented by the BiHCF/rGO nanocomposite film suggest that the synthesized material is promising for the development of new lower-cost and safer energy storage devices compared to currently existing technologies.

Agradecimentos/Acknowledgments

UFU, CNPQ, CAPES, FAPEMIG, INCT Nanocarbono, and GMIT.

Área: MAT

Nanocomposites of GO, rGO and MoS_2 characterized by scanning probe microscopy in different acquisition modes

Amanda F. Pereira (PG),[1] Ariane Schmidt (PG),[1] Bernardo R. A. Neves (PQ),[2] Camilla K. B. Q. M. Oliveira (PQ),[3] Aldo J. G. Zarbin (PQ).[1]*

amanda.figueiredo@ufpr.br; aldozarbin@ufpr.br

[1]Chemistry Department, UFPR; [2]Physics Department, UFMG; [3]Physics Department, UFPR

Palavras Chave: *Graphene, Molybdenum Disulfide, Microscopy, SPM, AFM, PeakForce*

Highlights

The properties of nanocomposites can be investigated through different SPM modes (lateral force microscopy, phase contrast and PeakForce) that identify possible interactions between GO, rGO and MoS_2.

Abstract

Scanning probe microscopy (SPM) is a very versatile technique used in the characterization of nanomaterials that identifies changes in the interaction of the probe with the sample surface. This technique not only investigates the morphology, thickness and roughness of the sample, but also identifies the most different properties of the material.[1] In this work, different SPM modes were used to characterize nanocomposites containing graphene oxide (GO), reduced graphene oxide (rGO), and molybdenum disulfide (MoS_2) to study the different properties and the nature of the interaction between the individual components of these nanocomposites. The samples were prepared by the liquid-liquid interfacial route (LLIR) and deposited by film transfer on Si/SiO_2 substrates.[2] Characterizations were carried out in contact mode and dynamic mode, as well as, phase contrast microscopy, lateral force microscopy (LFM) and PeakForce Quantitative Nanomechanics to verify the properties of friction, deformation, adhesion, and stiffness. Different properties were observed in the films due to the presence of oxygenated functional groups (films containing GO), structural defects, edge effect and Puckering effect. Due to these factors, the GO film presented a stiffer (low adhesion and deformation) film, followed by rGO sample when analyzed by PeakForce. The presence of MoS_2 in these films also results in different interactions for each sample. The GO/MoS_2 sample showed an increase in adhesion and deformation strength resulting in a decrease in its stiffness when compared to the GO film. Meanwhile, the opposite was observed for the rGO/MoS_2 film, indicating that the interaction of MoS_2 in these films changes the final properties of the material. Through this study we can elucidate the possible interactions between GO, rGO and MoS_2 and which of these interactions can interfere with the properties of the material obtained.

1. SUN, Wei et al. Friction, **11**, 1-19, 2023.

2. ZARBIN, Aldo J. G. Materials Horizons, **8**, 1409-1432, 2021.

Agradecimentos/Acknowledgments

UFPR, CNPq, CAPES, INCT Nanocarbono, INCT NanoVida, CME-UFPR.

Área: MAT

Nanocomposites of MoS_2 and Au-NPs for hydrogen evolution reaction

Carla Requena Klimpovuz (PG),[1] Marcela Mohallem Oliveira (PQ),[2] Aldo José Gorgatti Zarbin (PQ)[1]*

carlaklimpovuz@ufpr.br; aldozarbin@ufpr.br

[1]Department of Chemistry, UFPR; [2]Academic Department of Chemistry and Biology, UTFPR.

Key Words*: Thin Films, Plasmon Band, Metal Nanoparticles, 2D Materials, Energy Production*

Highlights

Thin films of three-component nanocomposites of MoS_2, Au-NPs, and carbon used as catalysts for hydrogen production. Thin films obtained through spontaneous reaction and in a single step.

Abstract

Developing nanostructured catalysts by architecting composites between metal nanoparticles and two-dimensional materials is the aim of this work. We describe the production of thin films of three-component nanocomposites of molybdenum disulfide (MoS_2), gold nanoparticles (Au-NPs), and amorphous carbon for electrochemical hydrogen production. We obtained the nanocomposites in interfacial films form, using the liquid-liquid interfacial route, through a spontaneous reaction and in single step.[1] All nanocomposites were formed and processed in this two-phase system, containing water, toluene, and precursors – MoS_2 exfoliated in acetonitrile and $HAuCl_4$ aqueous solution – under ambient conditions. Different materials were obtained by varying the proportion between precursors and time of reaction. All samples were characterized by UV-Vis and Raman spectroscopy, XRD, SEM-EDS, HRTEM, and XPS. By varying those reaction parameters, nanocomposites with different spectroscopic and morphological properties were formed. The proportion between MoS_2 and metallic precursor proved to be an essential factor for preserving the structural characteristics of MoS_2 as well as for determining the catalytic efficiency of these materials for hydrogen evolution reaction (HER). Spectroscopic studies are being conducted to propose a mechanism for the formation of the three-component nanocomposites. The nanocomposites were applied as electrodes for HER and showed better efficiency than the pristine MoS_2. This indicates that the synergy between the three components modulates the properties of MoS_2 and gives rise to a good alternative of catalysts for hydrogen production.

[1] Zarbin, A. J. G. Mater. Horiz. 2021, v. 8, p. 1409.

Acknowledgments

CNPq, CAPES, INCT NanoVida, INCT Nanocarbono, LNNano-CNPEM, LAQUIS-UFRJ, and CME-UFPR.

Área: MAT

New Insights in Sulfur Dioxide Scavenging: Study of the Reversible Interaction Between Polyamines and Mixed Polyamines-Polyacrilic Acid Polimers with Sulfur Dioxide

John Alexander Alzate Castillo (PG), Paulo Sérgio Santos (PQ) and Gianluca Camillo Azzellini* gcazzell@iq.usp.br

Departamento de Química Fundamental – Instituto de Química - USP

Palavras Chave: *Sulfur Dioxide Scavenging Materials; Polyamines; Polyamine-Polyacrylic Acid Mixed Polymers*

Highlights

Polyamines (PPI Dendrimers and Hyperbranched PEI) and particularly their mixed polymers with Polyacrilic Acid show great and reversible uptake of SO_2 compared with other amine based materials

Resumo/Abstract

Sulfur dioxide (SO_2) is an important atmospheric pollutant, with serious implications for the occurrence of acid rain, human health problems and interference with the normal development of plants. Therefore, there is an urgent need to develop effective SO_2 capture systems. In the present study has been investigated the interaction of gaseous SO_2 and polyamines, namely: i) Polypropyleneimine Dendrimers (generations 1 $\rightarrow$ 3; PPI-G1; PPI-G2; PPI-G3) and ii) hyperbranched polyethyleneimine (PEIb); as well as the respective mixed polymers of these polyamines with polyacrylic acid (PAA@Polyamine). Unlike the interaction of monomeric amines that form molecular complexes with SO_2, polyamines generate bisulfite ($HO\text{-}SO_2^-$) and sulfite (SO_3^{-2}) by acid-base reactions between water strongly linked by hydrogen bonds to polyamines and SO_2, as unequivocally shown by Raman spectroscopy. Interestingly, TGA-MS studies show that upon heating the acid-base reaction is reversible and SO_2 is released. The SO_2 uptake capacity is presented in the Table:

Polyamine	SO_2 uptake (mmol/g)	PAA@Polyamine	SO_2 uptake (mmol/g)	Ratio
PPI-G1	3,35	PAA@PPI-G1	6,54	1,9
PPI-G2	4,55	PAA@PPI-G2	7,54	1,7
PPI-G3	4,82	PAA@PPI-G3	7,90	1,6
PEIb	6,12	PAA@PEIb	8,53	1,4

It can be clearly seen that the incorporation of polyamine into the mixed polymer significantly increases the incorporation of SO_2, especially in mixed polymers containing dendrimers (PAA@PPI-G1 / PAA@PPI-G2). In these cases, we have an increase of 1,9 and 1,7 times respectively for PAA@PPI-G1 and PAA@PPI-G2; and for PAA@PEIb the increase is comparatively smaller but still significant with an uptake increment of 40%.

The polyamines and particularly the mixed PAA@Polyamines show great incorporation of SO_2 compared with other recently reported materials such as silica-supported dendrimers [1], polystyrene polymers with diamines [2] or cross-linked tetramethylguanidine acrylate polymers [3] with absorption maxima of 4,68; 3,40 and 4,06 mmol/g of absorbent material respectively with similar SO_2 gas absorption experiments, therefore mixed polymers are promising platforms for reversible SO_2 uptake.

[1] A. Sayari *et al "Environ. Sci. Technol."* **48**, 2025 (2014);

[2] H. Lee *et al "ACS Sustain. Chem. Eng."* **4**, 2012 (2016);

[3] S. Zhu *et al. "Macromolecules"* **40**, 3388 (2007).

Agradecimentos/Acknowledgments

Fapesp and Capes

Área: MAT

Obtaining and comparing technical lignin microspheres through spray-drying for application in enhanced efficiency fertilizers (EEFs)

Sahmira Bianchi (PG),[1,2] Roselena Faez (PQ).[1]*

sahmirabianchi@usp.br; faez@ufscar.br

[1]Laboratório de Materiais Poliméricos e Biossorventes, Departamento de Ciências da Natureza, Matemática e Educação, Universidade Federal de São Carlos (UFSCar); [2]Faculdade de Zootecnia e Engenharia de Alimentos (FZEA), Universidade de São Paulo (USP)

Palavras Chave: *Agriculture, Biopolymer, Biomass, Microparticles*, *SDGs*

Highlights

Global food demand strains traditional agricultural practices due to unsustainable fertilizer use; biopolymer-based EEFs offer a promising sustainable solution; Spray-drying efficiently creates lignin microspheres; Microparticles from three lignins show promise for EEFs production.

Resumo/Abstract

As the global population soars, so too does our demand for food. Consequently, this food demand has fueled an unsustainable reliance on fertilizers in agriculture. Unfortunately, these fertilizers lose significant nutrients – meant to nourish crops – into the environment. The realization of sustainable food production, as outlined by the United Nations Sustainable Development Goals (SDGs) 2 and 12, necessitates a paradigm shift in agricultural practices. Enhanced efficiency fertilizers (EEFs) emerge as a potential solution, combining essential nutrients, typically salt, with a matrix that anchors and gradually releases the nutrients. Selecting a suitable matrix for EEFs demands sustainability and efficacy. Lignin, the Earth's most abundant renewable aromatic polymer and a byproduct of papermaking or bioethanol production, ticks all the boxes. However, burning as fuel releases several organic pollutants (Abbas et al. 2022). Therefore, repurposing lignin into EEFs offers a double purpose: reducing environmental waste and enhancing food security. The three-dimensional network structure, composed of phenolic and aliphatic hydroxyls, carboxyls, and methoxy groups, gives it hydrophobicity, which can help delay the nutrient release in EEFs. In addition, EEFs production relies on finding a method compatible with the materials used and the desired objectives. In this context, the spray-drying technique has some advantages: reproducible production of particles, flexibility of parameters, and variety of raw materials that can go through the process. This study sought to evaluate and compare the potential of microspheres obtained by spray drying Kraft lignin from two sources (KLI and KLII) and sodium lignosulfonate (SL) as a coating matrix in EEFs. Lignin preparation and drying parameters were studied to optimize microsphere yield and desired nutrient loading and release properties. The microspheres were structural, thermal, and morphologically characterized. Spray-drying proved remarkably efficient for lignin suspensions, requiring minimal magnetic (30 min) and mechanical (15 min) pre-treatment. Notably, all drying experiments delivered high yields, achieving better results with lower feed flow rates for Kraft lignins - from 58 to 68% yield. FTIR and XRD showed that spray-drying does not change the original structure of lignins, that KLS and KLA are structurally the same, and that sulfur trioxide groups are even present in the LSA sample. SEM images showed that LSA particles are more spherical and smaller than those of KLS/KLA after spray-drying. These first studies show that spray-dried KLS, KLA, and LSA are promising for coating nutrients in EEFs. LSA has even more desirable characteristics for this application (surface charges and formation of spherical particles).

References:

ABBAS, A. et al. Lignin-based controlled release fertilizers: A review. International Journal of Biological Macromolecules, v. 222, p. 1801–1817, dez. 2022.

Agradecimentos/Acknowledgments

LAB - MPB, ufscar, USP Universidade de São Paulo, CAPES, suzano, INEO, FAPESP

Área: MAT
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Obtaining nanocomposites by in situ polymerization of thiophene monomer in the presence of graphene oxide

Stefany R. Saraiva (IC),[1*] Everaldo C. Venancio (PQ).[1]

[*]stefany.rodrigues@ufabc.edu.br

[1]*Centro de Engenharia, Modelagem e Ciências Sociais Aplicadas, UFABC.*

Key words: *Nanocomposites; Polymerization; Thiophene; Graphene Oxide.*

Highlights

Synthesis and characterization of polythiophene in aqueous media by surfactant-assisted polymerization. Synthesis and characterization of polythiophene/graphene oxide nanocomposite.

Resumo/Abstract

Intrinsically conductive polymers (PIC) are of great interest from both a technological and theoretical point of view. In the particular case of polythiophene and its derivatives, these materials are applied in energy storage and conversion systems, photovoltaic solar cells, supercapacitors and in active cell phone and television screens (OLEDS), among others [1]. Nanocomposites of intrinsically conductive polymers containing Graphene oxide as a dispersed phase showed improvement in electrochemical characteristics when compared to pure PIC, and has been gaining a lot of scientific interest [2]. This work aimed to carry out the synthesis of polythiophene and polythiophene nanocomposite containing graphene oxide, in order to evaluate changes in morphology. The synthesis of polythiophene was carried out in aqueous media by polymerization assisted by surfactant, hexadecyltrimethylammonium bromide (CTAB), while the synthesis of the nanocomposites was carried out through in situ polymerization of the thiophene monomer in the presence of graphene oxide. The scanning electron microscopy (SEM) results showed that the polythiophene presented a morphology in the form of plates and the nanocomposites presented a morphology containing graphene oxide plates. The FTIR results showed the characteristic bands of polythiophene and graphene oxide, both in the polythiophene samples and in the nanocomposite samples are compatible with the materials.

[1] Mehmood, U.; Al-Ahmed, A.; Hussein, I.A. Review on recent advances in polythiophene based photovoltaic devices. **Renewable and Sustainable Energy Reviews**, v. 57, p.550-561, 2016. https://doi.org/10.1016/j.rser.2015.12.177

[2] Alabadi, A.; *et al*. Graphene oxide-polythiophene derivative hybrid nanosheet for enhancing performance of supercapacitor. **Journal of Power Sources**, v. 306, p. 241-247, 2016. https://doi.org/10.1016/j.jpowsour.2015.12.028

Agradecimentos/Acknowledgments

The author thanks the support from the Central Experimental Multiusuários at UFABC.

Área: MAT

Obtaining sustainable magnetic porous carbons from tannin biomass to remove emerging contaminants

Rubens Lucas de Freitas Filho* **(PG)** [1], **Lucas Coelho de Oliveira (IC)**[1], **Rayane Cristian Ferreira Silva (PQ)**[1], **Ana Paula de Carvalho Teixeira (PQ)** [1]

rubensfreitas@ufmg.br; anapct@ufmg.br

[1]*Departamento de Química, Instituto de Ciências Exatas (DQ-ICEX) - UFMG*

Palavras Chave: *Magnetic porous carbons, biomass, adsorption; emerging contaminants*

Highlights

Synthesis of magnetic porous carbon from tannin (biomass) for removal emerging contaminants (caffeine, paracetamol, and tenofovir disoproxil fumarate) from water.

Resumo/Abstract

In this work, sustainable magnetic porous carbons were synthesized using tannic acid (tannin), the surfactant Pluronic F127, and nickel acetate as a crosslinking agent, in different proportion.[1] The magnetic porous carbons (MPC) were prepared via the mechanochemical route.[1] The materials were characterized using elemental analysis (CHN), XRD (X-ray diffraction), TG (thermogravimetric analysis), SEM (scanning electron microscopy), Raman spectroscopy, TEM (transmission electron microscopy), and physisorption analysis (BET). It was observed that the amount of crosslinking agent used directly influences the type of porosity (isotherm profiles), textural parameters, and magnetism of the obtained porous carbons (Table 1, Figure 1). Through XRD, peaks corresponding to nickel carbide and metallic nickel phases were observed. The magnetic porous carbons were applied in the adsorption of emerging contaminants such as caffeine (CAF), paracetamol (PAR), and tenofovir disoproxil fumarate (TDF). The materials exhibited removal rates above 99% for caffeine, paracetamol, and tenofovir after 24 hours of contact. From the contact tests, the materials behaved as excellent adsorbents for the studied contaminants. Kinetic and adsorption isotherm studies will be conducted for the material showing the highest indication of mesoporosity and magnetism. The materials were named with the acronym MPC-x (where x refers the nickel contents varied between 0.5 - 2.2 mmol)

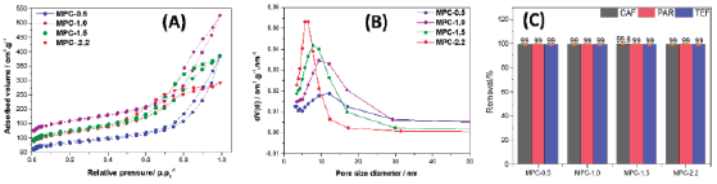
Table 1: Textural parameters from MPC synthetized.

Sample	S_{BET}/ $m^2.g^{-1}$	PSD/nm	V_{TOTAL}/ $cm^3.g^{-1}$	Ni content/%
MPC-0.5	294	12.2	0.595	7.5
MPC-1.0	578	9.4	0.816	13.9
MPC-1.5	441	7.7	0.599	17.1
MPC-2.2	427	5.6	0.453	21.1

Comentado [AT1]: Ei rubens, em algum lugar colocar o que significa as nomenclaturas e a diferença deles

Comentado [RF2R1]: adicionado

Figure 1: N_2 sorption isotherms for the synthesized magnetic carbon porous (a). Pore size distribution for the materials by BJH method (b), Contact tests from emerging contaminants (c).



References:

1 J. Zhao, W. Shan, P. Zhang and S. Dai, *Chem. Eng. J.*, 2020, **381**, 122579.

Agradecimentos/Acknowledgments

CNPQ, CAPES, UFMG Microscopy Center, FUNDEP, CTNano, Rota 2030, INCT Midas, Chemistry Department UFMG, and Laboratory LABPEMOL

Obtaining the stoichiometric composition of the crystalline phases in the devitrification process in porous germanophosphate glass ceramics

Caio C. de Lima (PG),[1] Italo O. Mazali (PQ).[1]

caiocarvalho796@gmail.com, mazali@unicamp.br

[1]Universidade Estadual de Campinas, Instituto de Química, Laboratório de Materiais Funcionais, Campinas, SP, Brazil.

Keywords: Glass, NASICON, porous materials, crystallization.

Highlights

NASICON-type materials were obtained from leaching crystalline phases of germanophosphate glass ceramics. The stoichiometric composition of the crystalline phases formed was obtained.

Abstract

Glass ceramics are materials obtained from the controlled crystallization of glassy materials. The existence of crystalline phases dispersed in glass allows the production of porous materials through leaching in an acidic environment, where the soluble phases produce pores, while the insoluble phases maintain the structure. Sodium superionic conductive materials (NASICON), which can be expressed as $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$ ($0 \leq x \leq 3$), are porous materials that stand out in applications related to solid-state lithium batteries, precisely because of their high density of energy combined with thermal and mechanical stability. In this context, the present work proposes to develop germanophosphate glass-ceramics from glass materials with the composition $6LiO_2$-$24GeO_2$-$39CaO$-$31P_2O_5$ (g-LGCP), and to investigate their potential for obtaining NASICON phases through leaching in an acidic médium, as well as the stoichiometric composition of the crystalline phases obtained through the devitrification process of the. For this, DTA analyzes of the g-LGCP powder were carried out, where two crystallization peaks were detected at 658 ºC and 750 ºC. Compact pieces of glassy materials were obtained by sintering g-LGCP powder at 625 ºC for 2 hours. From the compacted pieces, two groups of samples were separated (both referred to as gc-LGCP), the first being formed by pieces treated at 658 ºC for 12 hours; and the second, for pieces treated at 658 ºC for 12 hours and 750 ºC for another 12 hours. Spectroscopic and diffraction techniques were used to investigate the crystalline phases formed during devitrification, which allowed the identification of the de β-$Ca_2P_2O_7$, $Ca_3(PO_4)_2$, $LiGe_2(PO_4)_3$, $LiCaPO_4$ e GeP_2O_7 phases in the samples treated at 658 ºC, and additionally GeO_2 was detected in samples treated at 658/750 ºC. Samples of gc-LGCP subjected to the two heat treatments were immersed in solutions of 1 mol L^{-1} of HCl or H_3PO_4, and for each solution, temperatures of 25 ºC and 70 ºC were tested. NASICON $LiGe_2(PO_4)_3$ phases were detected in all samples treated at 25 ºC, in both acidic solutions, in addition to the solubilization of the β-$Ca_2P_2O_7$, $Ca_3(PO_4)_2$, GeP_2O_7 e $LiCaPO_4$ phases; in treatments at 750 ºC, there was complete leaching of the NASICON phase, leaving only GeO_2 in HCl, and GeO_2 and β-Ca_2P2O_7 in H_3PO_4. The micrographs obtained by SEM show the porous structures formed by the $LiGe_2(PO4)_3$ phase. From the crystalline phases formed, it was possible to provide a stoichimetric relationship of the glass devitrification process of the g-LGCP system, which is given by: $[6LiO_2\text{-}24GeO_2\text{-}39CaO\text{-}31P_2O_5]^{glass} \rightarrow 12LiGe_2(PO_4)_3 + 13Ca_3(PO_4)_2 \rightarrow (12\text{-}x)LiGe_2(PO_4)_3 + (13\text{-}x)Ca_3(PO_4)_2 + x\beta\text{-}Ca_2P_2O_7 + xGeO_2 + xLiCaPO_4 + xGeP_2O_7$, for ($0 \leq x \leq 12$).

Acknowledgments

UNICAMP LNNano LMM CAPES EMMU FAPESP CNPq Inomat

Área: MAT

Obtenção do híbrido $H_2T4SPP@TiO_2$ por meio da estratégia de ponte molecular com APTES e aplicação na fotodegradação da rodamina B.

Alessandra Nayra Silva Batista (PG)[1], Dayse Carvalho da Silva Martins (PQ)[1], Marcelo Machado Viana (PQ)*[1].

alenayra.silva@gmail.com; *marcelomachado@ufmg.br

[1]*Departamento de Química, Instituto de Ciência Exatas (ICEx), Universidade Federal de Minas Gerais (UFMG);*

Palavras Chave: *Fotocatálise heterogênea, dióxido de titânio, fotossensibilização.*

Highlights

Obtaining the $H_2T4SPP@TiO_2$ hybrid through the molecular bridge strategy with APTES and application in the photodegradation of rhodamine B.

The $H_2T4SPP@TiO_2$ hybrid was obtained through the molecular bridge strategy with APTES and was subsequently tested for the photodegradation of rhodamine B under UVC and visible light.

Resumo/Abstract

O dióxido de titânio (TiO_2) é um semicondutor (SC) amplamente utilizado em estudos envolvendo fotocatálise heterogênea, porém, devido ao seu amplo band gap (3,0–3,2 eV), a sua aplicação é restrita à região da radiação ultravioleta (100-400 nm), o que torna inviável o uso da luz solar. Diante disso, a fotossensibilização utilizando-se porfirinas é uma estratégia adotada a fim de aumentar a faixa de absorção do SC para a região do visível (400-750 nm). Entretanto, comumente observa-se uma baixa estabilidade do híbrido obtido, assim, a funcionalização superficial do SC com um agente de acoplamento, como os organossilanos, torna-se um caminho alternativo para aumento da estabilidade dos híbridos por meio da formação de uma "ponte molecular" entre a porfirina e o SC. Neste trabalho, o dióxido de titânio sintetizado por meio do método de precipitação a partir do tetracloreto de titânio, produzido pelo CTNano UFMG, foi funcionalizado com o agente de acoplamento 3-aminopropiltrietoxisilano (APTES) e, posteriormente, realizou-se a imobilização da porfirina H_2T4SPP^{4-}.

A inserção do APTES à superfície do TiO_2 foi confirmada pelas técnicas de infravermelho (IV), Raman, termogravimetria e por espectroscopia de raios X por energia dispersiva (EDS). O espectro de IV (Figura 1.a) do híbrido obtido apresentou bandas referentes às ligações Ti-O-Si, Si-O-Si e C-N, na região de 750-1300 cm^{-1}, que são indicativas da formação da ligação covalente entre o SC e o organossilano, bem como da ocorrência da sua polimerização horizontal. A imobilização da porfirina ao material funcionalizado foi confirmada pela espectroscopia UV-Vis de reflectância difusa, por Raman e pelo cálculo do *loading*. A absorção de luz na região do visível para o híbrido obtido foi confirmada pelo aparecimento das bandas de Soret (414 nm) e Q (500-600 nm) da porfirina no espectro de absorção de reflectância difusa (Figura 1.b), evidenciando a interação entre a porfirina e o semicondutor. Em seguida, o material de partida, funcionalizado com APTES (APTES-TiO_2) e o híbrido obtido ($H_2T4SPP@TiO_2$) foram testados na fotodegradação do corante rodamina B sob luz UVC e visível. Os resultados indicam que possivelmente a porfirina foi capaz de atuar como uma antena para o visível a partir da formação de uma heterojunção do tipo II com o óxido metálico. Foi observada a degradação de 23% e 27% da RhB após os testes fotocatalíticos com o híbrido de interesse sob luz UV e Visível, respectivamente (Figura 1.c).

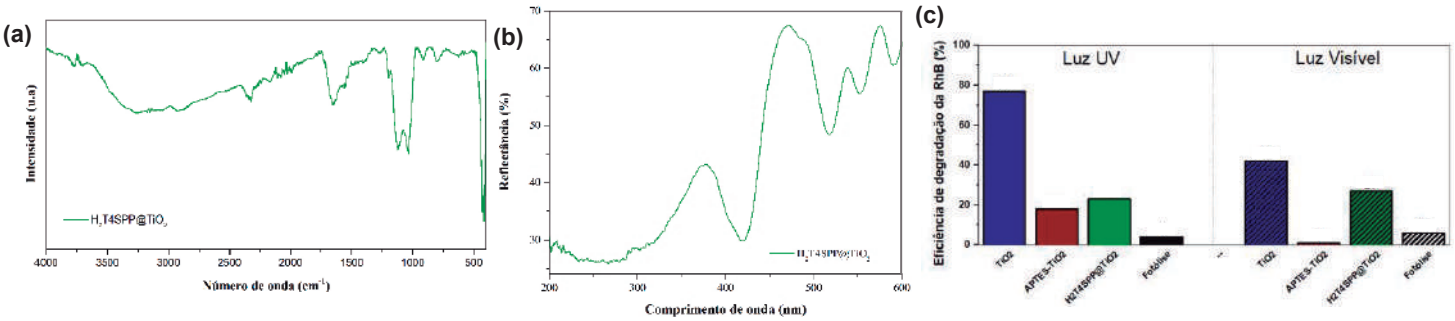


Figura 1. (a) espectro de infravermelho; **(b)** espectro de absorção de reflectância difusa na faixa de 200 a 800 nm para o híbrido obtido ($H_2T4SPP@TiO_2$) e **(c)** eficiência de degradação da RhB dos materiais estudados após os testes fotocatalíticos em luz UV e visível.

Referências: 1) Stepanova, A. et al. 2023. DOI: 10.1021/acsomega.3c05890; 2) Ahmed, M.A. et al. 2017. DOI:10.1016/j.jphotobiol.2017.09.016; 3) Zhang, Y. et al. 2022. DOI: https://doi.org/10.1016/j.cclet.2021.06.013

Agradecimentos/Acknowledgments

CAPES, CNPq, FAPEMIG, FINEP, INCT-CIMOL, LCPnano, CTNano UFMG, Centro de Microscopia UFMG.

Área: MAT

Oil-based polyurethane nanocomposites for application as a coating in the slow and controlled release of urea

Cassio L. Vellani (PG),[1] Vinícius F. Majaron (PG),[2] Wagner L. Polito (PQ),[2] Alberto Carlos Campos Bernardi (PQ),[3] Caue Ribeiro (PQ),[4] Ricardo Bortoletto-Santos* (PQ).[1]

ricbortolettosantos@hotmail.com

[1]Universidade de Ribeirão Preto (UNAERP); [2]Instituto de Química de São Carlos, USP; [3]Embrapa Pecuária Sudeste; [4] Laboratório Nacional de Nanotecnologia para o Agronegócio (Embrapa Instrumentação); [5].

Keywords: *Castor oil, polyurethane, urea, controlled release.*

Highlights

Small amounts of lamellar material are effective to control the N diffusion; Polyurethane-coated with lamellar material reduced the N2O emissions; PU-coatings modified with Montmorillonite can delay the N release from urea.

Abstract

Despite the indispensable use of agricultural fertilizers to achieve current levels of productivity, chemical nutrients have their effectiveness limited by problems such as NH_3 volatilization and soil immobilization. Urea is the main nitrogen source applied in agriculture and directly impacts agricultural productivity. However, it presents significant losses that reduce plants' nitrogen use efficiency (NUE) and promote greenhouse gas emissions, such as N_2O. The coating technology allows for an increase in the NUE, making the nutrient available gradually and uniformly. It is desirable that the formed polymer should have a homogeneous adhesive line on the granule surface and be able to control the diffusion of soluble nutrients through its structure, allowing the barrier to assume an active role and not just that of a physical obstacle, which release would occur by polymer fracture. Moreover, the permeation through a polymer can be significantly reduced by the presence of internal diffusional barriers such as finely dispersed nanoclays. Thus, we proposed a nanocomposite system based on castor oil-derived polyurethane (PU) and montmorillonite for controlling the release of urea by an ion-exchange mechanism. We tested the coated urea granules in Palisade grass (*Brachiaria brizantha*) and measured losses of N_2O and NH_3. The results showed that the combination between controlled release and nanoclay reduced the N_2O and NH_3 emissions. The release times were proportional to the contents of the cation-exchange materials, which exhibited specific correlations with the kind of nutrient released, confirming the diffusion barrier promoted by the PU coating structures. Moreover, the urea loss reduction significantly impacted plant development, increasing N use efficiency, dry mass production, and N uptake. Moreover, our results support the suitability of a coating system combining controlled release and nanoclay, aiming to better synchronize the nutrient with the plant and reduce environmental impacts.

Acknowledgments

The authors are thankful for the financial support given by FAPESP (São Paulo State Research Foundation), CAPES (Coordination for the Improvement of Higher Education Personne, CAPES-Embrapa Program), CNPq (Brazilian National Council for Scientific and Technological Development), SISNANO/MCTI, FINEP, and Embrapa AgroNano research network.

Área: MAT

On reduction of Ruthenium over layered double hydroxide mediated by hydroxypropylated cyclodextrin

Maria Eduarda A. Rocha (IC),[1*] Juliana C. A. Paiva (IC),[1] Luiz Phelipe Tomaso (PG),[1] Luiz F. B. Malta (PQ)[1]

rochamaria.e.a@gmail.com

[1]*Instituto de Química, UFRJ*

Palavras Chave: *Ruthenium, layered double hydroxides (LDHs), metal nanoparticles, hydrogenation, cyclodextrin.*

Highlights

- MgAl LDHs can be used as support for Ru nanoparticles
- RuNPs can be obtained from cyclodextrin/solvent mediated processes.
- LDHs supporting RuNPs can be used as catalysts for hydrogenation reactions

Resumo/Abstract

Layered double hydroxides (LDHs) are inorganic clays with cationic layers and anionic interlayers for charge stabilization. They can be a support for metal nanoparticles (MNPs) - in order to stabilize and avoid agglomeration -, which can be useful in catalysis since the area-to-volume ratio is enhanced. Particularly, the use of such composite catalyst to hydrogenation reactions is growing interest, mainly applying RuNPs [1,2]. In this study, MgAl LDHs were synthesized using the rising pH approach until 10 with NaOH 1M. To optimize the support of 1%wt Ru, a 2^2 factorial design was proposed being the parameters of the solvent (water or N,N-dimethylformamide) and the use or not of 2-hydroxypropyl-beta cyclodextrin. The responses to be evaluated were the crystallinity of support/NPs and the Ru oxidation state. The immobilizations of Ru were carried out at 80°C for 24h using $RuCl_3$. In XRD patterns there are no apparent peaks of Ru phase; however the LDH materials submitted to water were more crystalline. In contrast HPCD-containing materials were less crystalline, probably due to the stabilization effect induced by CDs. The FTIR spectra indicated higher CO_3^{2-}/NO_3^{1-} ratio for the composites obtained from water which may be related to their higher crystallinity. SEM-FEG and XPS characterization are underway.

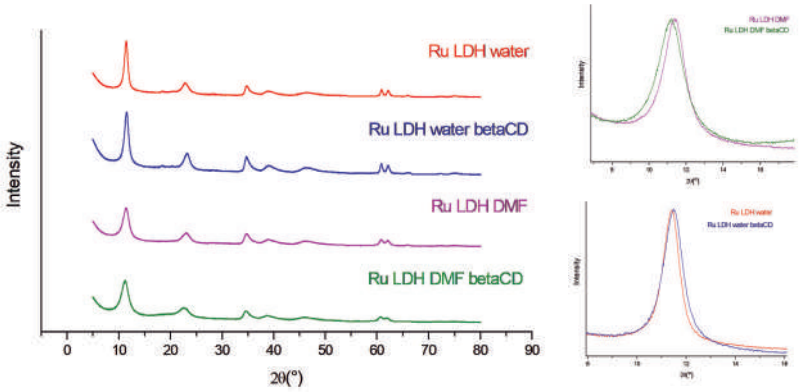


Fig 1: XRDs of Ru LDHs.

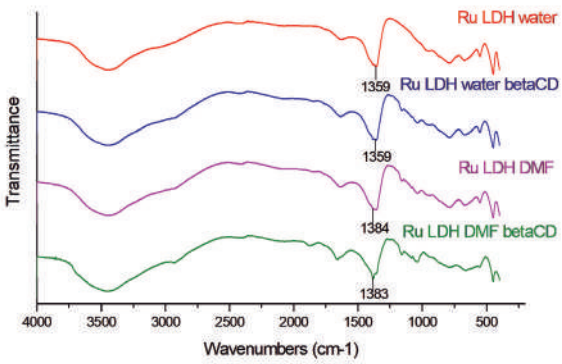


Fig 2: FTIR of Ru LDHs.

Agradecimentos/Acknowledgments

CAPES, FAPERJ e CNPq

[1] Neves, V. A., Modena, M. L., Bomfim, J. F., Aguilera, L. S., Roco, H. V., de Campos, J. B., Serra, J.D., Malta, L. F. B.. Applied Clay Science, 230, 106702, 2022.

[2] Liu, X., Shi, J., Bai, X., Wu, W.. Ultrasonics Sonochemistry 81, 105840, 2021.

Área: MAT

Otimizando o tamanho de nanopartículas de ouro para sensoriamento da proteína Spike do vírus SARS-CoV-2

Mariana C. Oliveira (PG),[1] Carolina B. P. Ligiero (PQ),[1] Dayenny L. D'Amato (PG),[1] Célia M. Ronconi (PQ).[1]*

marianacarvalhooliveira@id.uff.br; cmronconi@id.uff.br

[1]*Departamento de Química Inorgânica, Universidade Federal Fluminense, Campus do Valonguinho, Outeiro de São João Batista, s/n, 24020-141, Niterói, RJ, Brasil*

Palavras Chave: Nanopartículas de ouro, SARS-CoV-2, Imunoensaio, Biosenssores, Espalhamento de luz dinâmico.

Highlights

Optimization of the size of gold nanoparticles for sensing the Spike protein of the SARS-CoV-2 virus. Determination of the size of gold nanoparticles (135, 166 or 182 nm) which would be ideal for functionalization with IgG and detection of the SARS-CoV-2 S protein using the DLS technique.

Resumo/Abstract

O rastreamento de pacientes infectados é uma etapa crucial para controlar o avanço de viroses, porque ajuda a direcionar as estratégias de contenção e previne que ocorram grandes prejuízos para a saúde pública, como na pandemia de COVID-19. Desenvolver testes rápidos, baratos e eficientes é um trabalho recorrente na ciência, devido à capacidade de evolução dos vírus e suas consequências. Em publicação recente[1,2] de nosso grupo de pesquisa, foi utilizada a técnica de espalhamento dinâmico de luz (DLS) para verificar o aumento do diâmetro hidrodinâmico (ΔD_H) de nanopartículas de ouro (AuNPs) de até 130 nm funcionalizadas com anticorpos em presença da proteína Spike do SARS-CoV-2 (Figura 1a). O estudo demonstrou que além de boa sensibilidade e reprodutibilidade, maiores tamanhos de AuNPs proporcionaram maiores ΔD_H. No presente trabalho, AuNPs de 135, 166 e 182 nm são bioconjugadas para a determinação do tamanho limite que irá gerar o maior espalhamento de luz sem interferência do fenômeno de espalhamento múltiplo. Na primeira etapa, AuNPs de até 182 nm foram sintetizadas pelo método de crescimento semeado e caracterizadas por espectroscopia na região do UV-visível, microscopia eletrônica de varredura (MEV) e DLS (Figura 1b, c, d). A funcionalização foi realizada com anticorpo policlonal equino anti-S, e estudou-se a melhor concentração de reagente de ligação cruzada para a realização do imunoensaio. Resultados preliminares mostraram que os bioconjugados com AuNPs de 166 nm tiveram melhor performance nos imunoensaios, com média de ΔD_H maior que 10 nm para todas as concentrações de Ptn S utilizadas. Os próximos passos do projeto serão arquitetados para determinar o limite de detecção de cada biossensor e avaliar qual tamanho é mais vantajoso para a detecção do SARS-CoV-2.

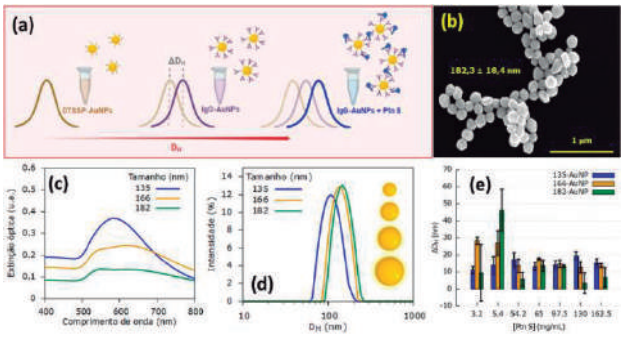


Figura 1: (a) Método de detecção da Ptn S, (b,c,d) caracterização das AuNPs e (e) resultados dos imunoensaios para diferentes AuNPs.

[1] LIGIERO, C.B.P.; FERNANDES, T.S.; D'AMATO, D.L.; GASPAR, F.V.; DUARTE, P.S.; STRAUCH, M.A.; FONSECA, J.G.; MEIRELLES, L.G.R.; SILVA, P.B.; AZEVEDO, R.B.; MARTINS, A.S.; ARCHANJO, B.S.; BUARQUE, C.D.; MACHADO, G.; PERCEBOM, G.M.; RONCONI, C.M., *Materials Today Chemistry,* **2022**, 25, 100924.

[2] SILVA, P.B.; SILVA, J.R.; RODRIGUES, M.C.; VIEIRA, J.A.; ANDRADE, I.A.; NAGATA, T.; SANTOS, A.S.; SILVA, S.W.; MODENA, J.P.; ANGELIM, M.K.C; SOUZA, G.F.; MURARO, S.P; BARROS, A.L.B.; MARTINS, G.A.S.; DIAS, F.R.; MACHADO, G.; FESSEL, M.R.; TAVASSI, A.M.C.; RONCONI, C.M.; GONÇALVES, D.; CURI, R.; OLIVEIRA, O.N.; AZEVEDO, R.B., *Talanta,* 2022, **243**, 123355.

Agradecimentos/Acknowledgments

FAPERJ, CNPq, PPGQ-UFF, LAMATE (UFF), INMETRO, LECC-UFRJ.

Área: Química de Materiais (MAT)

Persistent luminescence in doped Lu_2O_2S materials: structural analysis and optical investigation

Karina T. Fonseca (PG),[1] Nataly S. Santos (IC),[1] Fernando A. Garcia (PQ),[2] Lucas C.V. Rodrigues (PQ).[1]*

karina.fonseca@usp.br; lucascvr@iq.usp.br

[1]*Departament of Fundamental Chemistry, Institute of Chemistry, University of São Paulo;*
[2]*Departament of Applied Physics, Institute of Physics, University of São Paulo.*

Key words: *Persistent luminescence, Rare-earths, Lutetium, Oxysulfides, Photonic applications.*

Highlights

- Doped lutetium oxysulfides are versatile and highly efficient phosphors, with great thermal and chemical stability, and also of easy color tunability.

- Applications of Lu_2O_2S-based materials include X-rays scintillator screens, field emission displays, and advances in medical and industrial areas.

- The effect of doping on the structure and optical behavior of Lu_2O_2S materials was investigated through X-ray diffraction and spectroscopic techniques.

Resumo/Abstract

Rare earth oxysulfides (RE_2O_2S, RE^{3+}: Y, La, Gd, Lu) are suitable matrices for luminescent materials, which is due to their high thermal and chemical stability, low cost, and suitable sensitization of trivalent lanthanide ions, resulting in high luminescent efficiency [1]. Lutetium oxysulfide (Lu_2O_2S) has been widely investigated as the host material for three-dimensional plasma display panels, field emission displays and light-emitting diodes [2]. $Lu_2O_2S:Eu^{3+}$ is a persistent luminescent material in which Eu^{3+} efficiently emits red light, while $Lu_2O_2S:Ti^{3+/4+}$ presents a wide band in the orange region, related to titanium. The duration of these emissions after the irradiation removal can be increased by the insertion of Mg^{2+}, with the purpose of creating charge compensation defects and allowing energy storage in trap levels.

In this work, crystalline structure, optical absorptions, and persistent luminescence behavior of Lu_2O_2S, $Lu_2O_2S:Eu^{3+}$, $Lu_2O_2S:Ti^{3+/4+}$ and $Lu_2O_2S:Mg^{2+}$ were investigated. The effect of co-doping was also studied in $Lu_2O_2S:Eu^{3+},Ti^{3+/4+}$, $Lu_2O_2S:Eu^{3+},Mg^{2+}$, $Lu_2O_2S:Ti^{3+/4+},Mg^{2+}$ and $Lu_2O_2S:Eu^{3+},Ti^{3+/4+},Mg^{2+}$ materials.

Lu_2O_2S materials were obtained by a rapid and energy-saving microwave-assisted solid-state synthesis. Phase purity and crystal parameters were obtained through X-ray diffraction (XRD) with Rietveld refinements. The incorporation of Eu^{3+}, $Ti^{3+/4+}$ and Mg^{2+} ions in Lu_2O_2S host was evaluated, along with structural changes.

Optical absorptions were measured through diffuse reflectance spectroscopy (DRS), which also enabled the calculation of Lu_2O_2S band gap energy with Kubelka-Munk theory. Eu^{3+} 4f-4f transitions and ligand-to-metal charge transfer (LMCT) transitions were observed in the 200-700 nm region of the spectra. The presence of $O^{2-}/S^{2-} \rightarrow Eu^{3+}$ and/or $O^{2-}/S^{2-} \rightarrow Ti^{3+/4+}$ bands proved to be correlated with luminescence mechanism in these materials.

Photoluminescence spectroscopy studies and persistent luminescence measurements demonstrated the effect of the incorporation of activator ions (Eu^{3+} and/or $Ti^{3+/4+}$), as well as an optically inactive co-dopant (Mg^{2+}), into Lu_2O_2S structure. Emissions in the visible region, excited by UV or X-ray irradiation, and the high storage capability of these materials provide several applications in dosimetry, bioimaging and optoelectronic devices [1,2].

REFERENCES

[1] Machado, I. P, Teixeira, V. C., Pedroso, C. C. S., Brito, H. F., Rodrigues, L. C. V, *J. Alloys Compd.*, 2019, **777**, 638-645.

[2] Zhang, B. *et al, Cryst. Eng. Comm.*, 2017, **19**, 699–707.

Agradecimentos/Acknowledgments

The authors thank the financial support of São Paulo Research Foundation, Brazil (FAPESP, grants #2019/26689-1 (KTF), #2021/05603-1 (LCVR), and #2021/08111-2 (HFB)).

Área:Química de Materiais (MAT)

Persistent perovskite synthesized by microwave-assisted solid-state method.

Franciele F.S. Figueirêdo (PG),[1] Lucas C.V. Rodrigues (PQ).[2]

cyelle26@usp.br; lucascvr@iq.usp.br

Department of Fundamental Chemistry, Institute of Chemistry, University of São Paulo;

Keywords: Perovskite, Persistent luminescence, Solid state synthesis, Microwaves, IVCT.

Highlights

Calcium titanate perovskite synthesized in less than an hour in a domestic microwave exhibits phase purity and persistent luminescence in the red region when doped with Praseodymium.

Resumo/Abstract

The material produced was calcium titanate doped with praseodymium ($CaTiO_3$-Pr^{3+}) through solid-state synthesis using an adapted domestic microwave oven. The proposed method does not use flux for synthesis at low temperatures, but rather a microwave susceptor better known as charcoal. The material produced showed phase purity from 15 minutes at 700 W; its best result in terms of persistent luminescence was 45 minutes at 500 W.

The persistent luminescence mechanism is described as Intervalence charge transfer – IVCT, which consists of the excitation of the dopant ion to the conduction band of the matrix where the charge transfer from the dopant to the main ion occurs. The electrons from the photoredox process are trapped in traps generated by the dopant in the band gap and released with heat gain, returning to the conduction band and subsequently to the ground state, generating emission [1]. This process competes with the $^3P_0 \rightarrow {}^3H_4$ transition at 546 nm of the Pr^{3+} ion and as a result, its green emission is not observed [1,2,3].

When studying the variation of the dopant concentration, it was observed that the ideal concentration was 0.01% in mol, since at higher concentrations the intensity of persistence decreases proportionally. This occurs due to the cross-relaxation phenomenon observed mainly with dopants such as praseodymium, which when in excess, ends up favoring less energetic relaxation processes, disadvantaging the IVCT mechanism [1].

The persistence time under the best concentration and synthesis conditions was around 120 seconds, however, more accurate analyses are necessary to determine this value more precisely.

REFERENCES

[1] Perovskite Ceramics. Recent Advances And Emerging Applications. editor: Elsevier - Health Sciences Division, November of 2022.

[2] Philippe Boutinaud, Rachid Mahiou, Enrico Cavalli, Marco Bettinelli. Luminescence properties of Pr3+ in titanates and vanadates: Towards a criterion to predict 3P0 emission quenching. Chemical Physics Letters, Volume 418, Issues 1–3,2006.

[3] Philippe Boutinaud, Piotr Putaj, Rachid Mahiou, Enrico Cavalli, Adolfo Speghini & Marco Bettinelli (2007): Quenching of Lanthanide Emission by Intervalence Charge Transfer in Crystals Containing Closed Shell Transition Metal Ions, Spectroscopy Letters: An International Journal for Rapid Communication,40:2, 209-220

Agradecimentos/Acknowledgments

The authors thank the University of São Paulo and the Chemistry Institute for infrastructure and financial support.

Area: MAT

Phosphorylated Chitosan: Characterization and 3D Porous Network Assembly by Ionotropic Gelation and Chemical Crosslinking.

Celso A. Bertran (PQ),[1] Thalita M. Missano (PG).[1*]

bertran@unicamp.br; thalitamissano@gmail.com

[1]*Institute of Chemistry, UNICAMP.*

Keywords: *Biopolymers, Biomaterials, Phosphorylated Chitosan, Porous Network, Hydrogel.*

Highlights

- Phosphorylation of Chitosan;
- Combination of biofunctionality of biopolymer and calcium phosphate;
- 3D porous network forming by ionotropic gelation and chemical crosslinking.

Abstract

Chitosan is the only cationic polysaccharide found in nature derived from biomass, which has several biological properties. However, the solubility of chitosan is one of its main limitations, being insoluble at pH value above 6. Therefore, modification through phosphorylation is an alternative method to increase the water solubility and biological activity of the polysaccharide. In this work, the modification followed the method described by Nishi *et al.* where the phosphorylation occurred only in the hydroxyl groups of chitosan, due to protection of amino group, that was proved by NMR and FTIR. The phosphorylation of hydroxyl groups transforms it into a pH-responsive polymer with pKa 6.70 and 10.08 corresponding to the amino and phosphate groups, respectively, making it soluble at pH above 7 and partially soluble at pH below 2. In addition, its solubility is increased, making it possible to solubilize around 18% (m/m) of the material. The incorporation of phosphates groups into the chitosan structure allows the complexation with Ca^{2+} ions by ionotropic gelation and the free amino group present in chitosan allows the crosslinking of the polymeric chains results in a consistent gel (Figure 1a) that, after lyophilization, turns into foam (Figure 1b) with interconnected pores and thin walls (Figure 1c). Tests with fibroblast cells (NIH/3T3) indicate that the material is not cytotoxic and is suitable for biological use.

Figure 1:(a) Hydrogel of modified chitosan; (b) Lyophilized modified chitosan - foam; (c) SEM micrographs of modified chitosan foam.

Acknowledgments

CAPES, CNPQ, FAPESP 2021/11019-0; Biomembranes Laboratory - Institute of Biology – UNICAMP, Nano-Cell Interactions Lab - Institute of Biology – UNICAMP; FMILab – Functional Materials and Interfaces Laboratory; Institute of Chemistry – UNICAMP.

Área:
_____MAT_____
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Photocorrosion reaction of Cu_2WO_4 photoelectrode during the CO_2 conversion

Jéssica Costa Alvim (PG)[1], Rafael Vicente Alcides (PG)[1], Abner de Siervo (PQ)[2], Márcio Sangali (PG)[3], Rubens Caram Jr (PQ)[3], Pablo Sebastian Fernandez (PQ)[1], Claudia Longo (PQ)[1,*]

costaalvimjessica@gmail.com; clalongo@unicamp.br

[1]Physical Chemistry Department, Institute of Chemistry- UNICAMP; [2]Gleb Wataghin Institute of Physics - UNICAMP; [3]Mechanical Engineering Faculty – UNICAMP

Palavras Chave: CO_2 conversion, photoelectrochemical reaction, Cu_2WO_4 photocathode, photocorrosion mechanism

Highlights

Photoelectrochemical (PEC) reaction for solar fuels production
Oxides semiconductors promising materials as photocathodes
CO_2 reduction reaction (CO_2RR) promoted by Cu_2WO_4
Structural stability of Cu_2WO_4 was investigated under reaction conditions
Insights of Cu_2WO_4 photocorrosion reaction

Resumo/Abstract

Photoelectrochemical (PEC) CO_2 reduction reaction (CO_2RR) is a promising route to mitigate the CO_2 emissions and generate value-added chemicals through the conversion of photons energy into chemical energy. Although significant progress has been achieved in developing of oxides semiconductors to promote PEC-CO_2RR, the performance of these materials remains insufficient for commercial application. The little-studied p-type semiconductor Cu_2WO_4 has interesting properties to be used as a photocathode, such as narrow band-gap (1.98 eV), conduction band with energy enough to promote CO_2 conversion under irradiation and enhanced stability in comparison to Cu_2O binary oxide although it still not enough for practical application. The reasons for the Cu_2WO_4 instability under CO_2RR conditions is still unclear and should be investigated to provide strategies for increasing the long-term stability of Cu_2WO_4 electrodes for solar fuel production. This work reports the performance of gas diffusion electrodes (GDE) based on Cu_2WO_4 as well as the investigation of photocorrosion mechanism of copper(I) tungstate during the PEC-CO_2RR. The CO_2 conversion into ethanol promoted by GDE/Cu_2WO_4 can be related to the structural stability of semiconductor and reaction conditions. Moreover, in situ Raman spectroscopy measurement and X-ray Diffraction (XRD) analyses of Cu_2WO_4 photoelectrode corroborated with ICP-OES and XPS analyses, which suggest Cu_2O crystalline phase as product from Cu_2WO_4 degradation during the PEC-CO_2RR. Further studies are required to elucidate the origin of Cu_2WO_4 degradation, that is, if the electrochemical reaction or the photons absorption and charge carrier accumulation in the semiconductor are the main reasons for corrosion reaction of copper (I) tungstate.

Agradecimentos/Acknowledgments

The authors gratefully acknowledge support from CINE, FAPESP (Process 2021/05853-8), CNPEM, CNPq and CAPES.

Área:_MAT_____
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Photodegradation of methyl orange dye under sunlight using bimetallic AuPd nanoparticles supported on CuAl layered double hydroxide as catalyst

Luiz P. de S. Tomaso (PG),[1] Sébastien Noël (PQ),[2] Anne Ponchel (PQ),[2] Eric Monflier (PQ),[2] Jaqueline D. Senra (PQ),[3] Luiz F. B. Malta (PQ)[1]*

phelipe.tomaso@gmail.com; lfbmalta@iq.ufrj.br

[1]Instituto de Química, Universidade Federal do Rio de Janeiro, Rio de Janeiro – RJ, Brasil, CEP 21941-909; [2]Unité de Catalyse et Chimie du Solide (UCCS), Université d'Artois, CNRS, Centrale Lille, Univ. Lille, UMR 8181, 62300 Lens, France; [3]Instituto de Química, Universidade do Estado do Rio de Janeiro, Rio de Janeiro – RJ, Brasil, CEP 20550-900.

Palavras Chave: *Degradation, Dye removal, LSPR, LDH, Catalysis.*

Highlights

Degradation of dye using AuPd/LDH composite was investigated. Effect of sunlight and halogen lamp on degradation was studied. More than 93% dye degradation was achieved in 120 min under sun light.

Resumo/Abstract

Wastewater from textile industries, if improperly discharged, poses a threat to the environment. Additionally, specific dye classes can exhibit carcinogenic and/or mutagenic properties. CuAl LDH was synthesized using the coprecipitation method with a constant pH. AuPd nanoparticles were formed by reducing metal precursors in water through sodium citrate and cyclodextrin. The structure and chemical composition of the composites were characterized by vibrational spectroscopy in the infrared region, Xray powder diffraction (XRD), electron spectroscopy in the ultraviolet-visible region and scanning electron microscopy (SEM). The XRD diffractograms of the materials show the characteristic peaks of LDH. SEM micrographs revealed uniformly dispersed nanoparticles on the LDH surface, ranging in size from 18 to 40 nm. UV-Vis electronic spectra exhibited LDH's characteristic bands and the plasmonic resonance band of Au nanoparticles at approximately 520 nm. Photocatalytic tests, conducted in water at 40 ºC under sunlight, utilized methyl orange dye (0.5 mmol L^{-1}) and AuPd/LDH catalysts (0.5 g L^{-1}), achieving over 93% dye degradation in 120 minutes. In conclusion, the employed methodology successfully immobilized nanoparticles in LDH, and the synthesized materials demonstrated effective photocatalytic activity under natural sunlight exposure.

Agradecimentos/Acknowledgments

The authors wish to express their gratitude to the Laboratório Multiusuário de Nanofabricação e Caracterização de Nanomateriais (NANOFAB) for the SEM images and to the CAPES, CNPq and FAPERJ for the financial support.

Área: MAT
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Photo-resin based on cigarette filters as an efficient system to vitrimeric polymers

Caroline Gaglieri[1*] (PD), Rafael T. Alarcon[2] (PD), Gabriel I. dos Santos[1] (IC), Fernanda B. dos Santos[1] (IC), Gilbert Bannach (PQ)[1]

[1]São Paulo State University (Unesp), School of Sciences, Department of Chemistry, 17033-260, Bauru, SP, Brazil; [2]Universidade de São Paulo-USP, Instituto de Química de São Carlos, 13566-590, São Carlos, SP, Brazil.

Keywords: *photopolymerization; 3D printing; self-healing polymers;*

Highlights

New photo-resin using cigarette filters;
Application of cigarette filters from illegal cigarettes seized;
Self-healing polymers;

Resumo/Abstract

Several tons of illegal cigarettes are seized every year by the Brazilian Federal Revenue Office. In 2022 alone, the amount reached approximately 5.3 million tons.1 Most of these cigarettes are destroyed (incinerated); however, it is also of interest to develop new processes that can transform them into products with applications other than their original purpose. In this context, this study presents the application of a novel photo-resin obtained from cigarette filters. The synthesis process is under patent application (BR1020190249099). Polymerization is achieved under UV light and results in a white polymeric material within seconds. Furthermore, dyes can be incorporated into the photo-resin without affecting the polymerization time (Fig. 1a). The final polymer can be cut and subsequently joined by applying manual pressure after heating both parts at 50°C for 5 minutes (Figures 1b and 1c). The polymeric material exhibits thermal stability up to 143°C, as demonstrated by its TG/DTG-DTA curves (Figure 1d). This stability confirms that the joining process does not involve thermal degradation but rather leverages the material's self-healing properties. This promising new photo-resin shows potential for 3D printing applications, offering rapid UV-induced polymerization and resulting in a polymer with vitrimeric properties (further investigation is warranted).

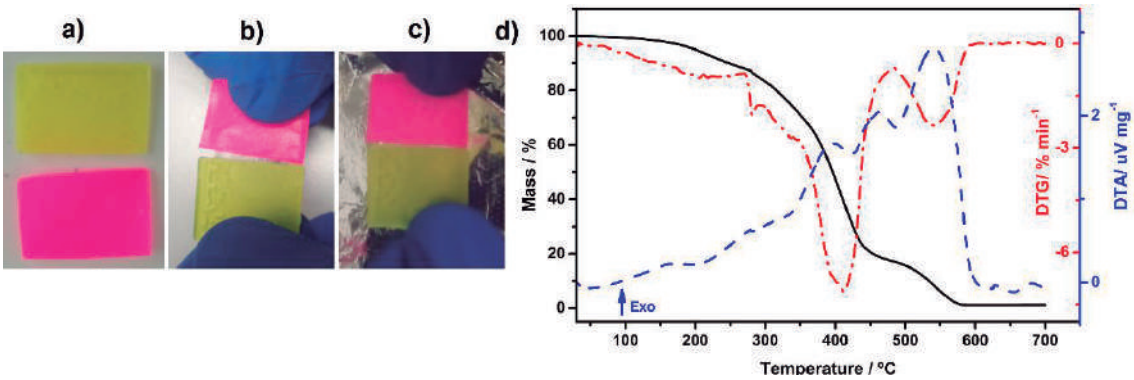


Figure 1- a) colorful polymers and) before heating and pressing, b) and c) after heating and pressing, and d) TG/DTG-DTA curves.

References:
[1]Receita Federal (Brazil). Available at: https://www.gov.br/receitafederal/pt-br/assuntos/noticias/2023/janeiro/receita-federal-destroi-mais-de-5-300-toneladas-de-cigarros-apreendidos Accessed Feb. 2024.

Agradecimentos/Acknowledgments

FAPESP: grants 2021/02152-9, 2021/14879-0, and 2022/03489-0; CNPq: grants 303247/2021-5 and 150233/2022-1.

Área: MAT

Polymerization of Brazil nut oil using different polytols as intercrosses

Fernanda B. dos Santos (IC),[1*] Caroline Gaglieri (PQ),[1] Gabriel I. dos Santos (IC),[1] Gilbert Bannach (PQ),[1]
fernanda-barreto.santos@unesp.br
[1]*Departamento de Química, Universidade Estadual Paulista Júlio Mesquita Filho – UNESP, Faculdade de Ciências,;*
Keywords: Vegetable oils; Polymerization; thiols; epoxy-thiol.

Highlights

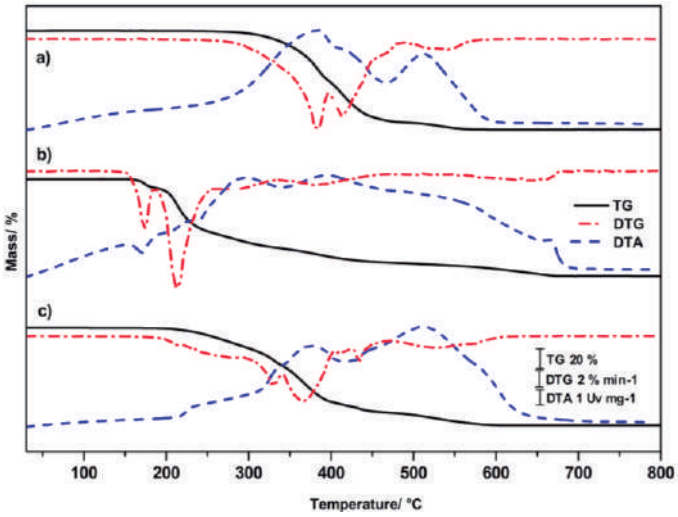
Polymerization of semi-drying vegetable oil by epoxy-thiol reaction using different polythiols.

Resumo/Abstract

Thousands of tons of plastic waste are generated annually, with the majority originating from non-renewable sources, taking centuries to decompose. In light of this, vegetable oils emerge as an eco-friendly alternative due to their versatility in structural modifications. Brazil nut oil is a semi-drying oil according to the iodine value (98.3 g of I_2 per 100g of the sample). Thus, this study aims to investigate the polymerization of Brazil nut oil (BNO) through the epoxy-thiol reaction using different polythiols as crosslinkers: 1,3,4-Thiadiazole-2,5-dithiol, and 3,6-dioxa-1,8-octanedithiol. Brazil nut oil was epoxidized (BNE), and its epoxy rings were quantified, resulting in 0.38 ± 0.01 moles of epoxy rings per 100 g of BNE. This monomer was reacted with polythiols and thermally cured. However, only the polymerization using 1,3,4-Thiadiazole-2,5-dithiol as a crosslinker was effective. This occurrence may be related to the reactivity between polythiols and the newly synthesized monomer.

The compound with thiol groups linked to the Thiadiazole ring has more acidic hydrogens, allowing for easier removal, thus forming a stronger base that reacts with the epoxy.[1,2] The polymer and raw materials were characterized by Simultaneous Differential Thermal Analysis, and TG/DTG-DTA curves are presented in Figure 1. It can be observed that the thermal stability of polymer was 167.9 °C, which was higher than the thiol (140.2 °C) and lower when compared to the thermal stability of the BNO (253,2 °C) and. This decreasing may be associated with residual thiol, as well as incomplete crosslinking between the monomers.

Figure 1: TG/DTG-DTA curves in a dry air atmosphere using a heating rate of 10 °C min-1 between 30-800 °C; (a) BNO; (b) 1,3,4-Thiadiazole-2,5-dithiol; and (c) polymer.



References:
1 KONURAY, Ali Osman *et al*. Latent curing of epoxy-thiol thermosets. **Polymer**, [S.L.], v. 116, p. 191-203, may 2017. Elsevier BV. http://dx.doi.org/10.1016/j.polymer.2017.03.064.

2 HU, Yang *et al*, 1,3,4-Thiadiazole: Synthesis, Reactions, and Applications in Medicinal, Agricultural, and Materials Chemistry, **Chemical Reviews**, v. 114, n. 10, p. 5572–5610, 2014.

Agradecimentos/Acknowledgments

Unesp rectory for the scientific initiation scholarship, as well as FAPESP (projects 2022/03489-0 and 2021/02152-9) and CNPq (projects 303247/2021-5 and 150233/2022-1)

Área: MAT

Polyvinylpyrrolidone (PVP) membrane in the release of salicylic acid (AS) for *Acne vulgaris*.

Diogo J. S. Silva (IC),[1]* Gabriel N. Fraga (PG),[1] Douglas C. Dragunski (PQ),[1] Josiane Caetano (PQ).[1]

caetanojosi@gmail.com; diogo.silva13@unioeste.br

[1]*Universidade Estadual do Oeste do Paraná, Rua da Faculdade, 645 – Toledo – PR – Brasil*

/Key Words: Polymer, Electrospinning, Non-woven Material.

Highlights

Salicylic acid built in the membrane has a quick release in polimeric materials highly soluble in aqueous media.

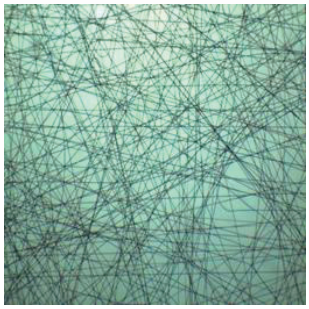
The adhesive properties of PVP in the nanostructured material allow transdermal drug release with ease.

Resumo

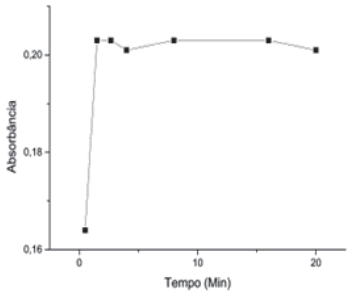
O ácido salicílico (AS) é um composto fenólico conhecido por inibir a germinação de plantas, mas também por suas propriedades cicatrizantes (KERBAUY, 2008). O PVP é um polímero atóxico, não iônico, inerte, biocompatível, estável a pH e temperatura e apresenta boa afinidade tanto com fármacos hidrofílicos quanto hidrofóbicos (KURAKULA, 2020). Portanto, um material nanoestruturado obtido por eletrofiação do polimero PVP em conjunto com o AS foi proposto para o tratamento da *Acne vulgar.*

Para a obtenção da membrana, inicialmente prparou-se uma solução polimérica contendo 8% de PVP e 1,5% de AS, nos solventes etanol e água (80:20). A solução foi agitada por 24 horas, colocada em uma seringa de vidro e eletrofiada usando os parâmetros: distância da agulha no coletor de 15 centímetros, vazão de 1,8 ml.h-1 e tensão de 18 quilovolts (kV). A umidade e a temperatura foram mantidas em aproximadamente 45% e 25ºC, respectivemente. Após a obtenção de uma boa fibra com a técnica, foram realizados experimentos de solubilidade e liberação do fármaco utilizando um tampão fosfato/hidróxido com pH 5,7. A quantificação do ácido salicílico liberado foi realizada por espectroscopia no ultravioleta visível (UV/Vis) no espectrofotômetro Shimadzu no comprimento de onda 295nm.

Na Figura 1A pode-se observar que a membrana não tecido obtida encontram-se com fios homogêneos e sem beads. Após a obtenção da membrana, realizou-se os testes de liberação do AS (Figura 1B), nota-se uma rápida e efetiva liberação. Isso ocorre devido à alta solubilidade do polímero em meio aquoso.



A



B

Figure 1: (A) Imagem da membrana de PVP/AS; (B) Gráfico da liberação do SA em tampão fosfato pH 5,7.

Desta forma, o material obtido é promissor para utilizar como adesivo para desinflamar, diminuir a vermelhidão e ajudar na cicatrização de espinhas.

REFERENCES:

1 KERBAUY, Gilberto Barbante. **Fisiologia Vegetal. 2. ed.** Rio de Janeiro: Editora Guanabara Koogan Ltda, 2008. 452 p.

2 Kurakula M, Rao KGSN. **Journal of Drug Delivery Science and Technology**, 2020.

Agradecimentos/Acknowledgments

Fundação araucária, CNPq e CAPES, GIPeFEA e UNIOESTE.

Área: *MAT*

Preparation, functionalization and characterization of graphene oxide for use in CO_2 capture materials

Rayanne Cristina da Silva Santos (PG)[1*], Patrícia Viana Rodrigues (PQ)[2], Márcio Soares de Moraes (IC)[2], Clarissa Perdomo Rodrigues (PQ)[2], Kátia Regina de Souza (PQ)[1].

rayanne.cristina@ime.eb.br; katia.souza@ime.eb.br

[1] *Seção de Ensino de Engenharia Química, Instituto Militar de Engenharia, 22290270 RJ, RJ, Brasil;*
[2] *Laboratório de Catálise, Divisão de Catálise, Biocatálise e Processos Químicos, Instituto Nacional de Tecnologia, 20081312 RJ, RJ, Brasil.*

Keywords: *Graphene oxide, CO_2 capture, Ethylenediamine.*

Highlights

The research investigates how ethylenediamine can influence the functionalization of graphene-based materials to capture the main gas that causes the greenhouse effect, carbon dioxide.

Resumo/Abstract

Nos últimos anos, as emissões de gases poluentes aumentaram significativamente e tornaram-se um dos desafios mais importantes da humanidade. O CO_2 é o principal gás antropogênico do efeito estufa, o principal responsável pelas alterações climáticas e, consequentemente, o que mais preocupa devido à velocidade com que é emitido a partir da combustão de combustíveis fósseis, incêndios florestais e processos industriais.

Diante disso, há uma constante busca por alternativas promissoras capazes de reduzir a concentração de CO_2 na atmosfera. Uma delas é a captura desse gás em superfícies sólidas. Portanto, encontrar novos sólidos que apresentem uma capacidade elevada de armazenamento de CO_2 é de importante interesse para toda a comunidade.

Um material que tem atraído grande atenção devido às suas interessantes propriedades físicas e química, é o grafeno. Ainda, recentemente, materiais à base de grafeno estão sendo utilizados como adsorvente na remediação ambiental. Se comparado com o método de absorção, o processo adsortivo é caracterizado por investimento menor, fácil operação, menos perda de adsorvente, sem corrosão no equipamento e sem poluição ambiental.

O óxido de grafeno (GO) é um derivado do grafeno e possui em sua estrutura grupos funcionais de oxigênio em seus planos basais e bordas, por esse motivo, a modificação da superfície desse derivado com aminas ou moléculas contendo amina ocorre facilmente através das reações de substituição nucleofílica correspondentes. Se as poliaminas se ligarem às suas camadas, as aminas residuais que não reagiram podem reagir com o CO_2 e ter potencial para capturá-lo. Portanto, neste trabalho foi realizada a síntese e funcionalização do óxido de grafeno, e avaliada sua captura de CO_2.

No que tange à síntese do GO, essa foi realizada pelo Método de Hummers modificado. Quanto à funcionalização, ela ocorreu sob refluxo a temperatura de 33°C. Para isso, adicionou-se 400 mg de GO e 200 mL de água destilada em um balão, previamente disperso em ultrassom por 30 minutos. Finalizado esse tempo, adicionou-se etilenodiamina (EDA) gota a gota ao balão, e a solução permaneceu sob agitação magnética por 4 horas. Posteriormente a isso, foi feito o procedimento de lavagem e secagem. É importante ressaltar que a funcionalização foi realizada com 0,1 e 0,5 mL de EDA, sendo as amostras denominadas GOEDA0,1/4H e GOEDA0,5/4H, respectivamente. Adicionalmente, foi obtida uma amostra de 16 horas, na qual usou-se 0,1 mL de EDA, sendo chamada de GOEDA0,1/16H.

De acordo com a caracterização realizada, a funcionalização foi alcançada com sucesso. A capacidade de adsorção de CO_2 foi avaliada por Dessorção a Temperatura Programa e os resultados foram os seguintes: 4,2 (GO); 3,4 (GOEDA0,1/4H); 2,5 (GOEDA0,1/16H) e 4,6 (GOEDA0,5/4H) $\mu mol.g^{-1}$. A modificação do grafeno com etilenodiamina não foi eficiente para a captura de CO_2, uma vez que as amostras após funcionalização apresentaram captura de CO_2 semelhante ao grafeno.

Agradecimentos/Acknowledgments

Este estudo foi financiado em parte pela Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - (CAPES) - Código Financeiro 001, FAPERJ (Projetos nos: E-26/210.022/2021 e E-26/211.062/2021), Instituto Nacional de Tecnologia (INT) e Instituto Militar de Engenharia (IME).

Área:MAT

(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Preparation of polymeric scaffolds processed by the Salt Leaching technique

Clodoaldo Junior Aires Duarte (IC), Naiton Martins da Silva (PG)[2], Fernando Henrique Cristovan (PQ)[1].

junior_aires@discente.ufj.edu.br; naitonmartins@estudante.ufscar.br; fhcristovan@ufj.edu.br

[1]*Departamento de Química, UFJ;* [2]*Departamento de Química UFSCar*

Palavras-Chave:*(Scaffolds, Salt Leaching, Poliuretana (PU) 66, Curcumina).*

Highlights

Polymeric scaffolds are objects of study due to their versatility and unique properties. These materials can be easily modulated to adjust density, malleability and porosity, characterized by highly porous three-dimensional structures. This architecture allows the retention of compounds for a later release that can be controlled. The scaffolds produced in this study were prepared using the Salt Leaching technique, where the material used was polyurethane (PU) 66. Using this technique, a material with a highly porous 3D conformation was obtained. This approach offers a controlled strategy to develop polymeric scaffolds with specific characteristics for biomedical applications in tissue engineering.

Resumo/Abstract

Os scaffolds poliméricos representam estruturas tridimensionais altamente porosas, cuja aplicação abrange diversos propósitos, desde suportar o crescimento de células e tecidos até possibilitar a liberação controlada de medicamentos. A diversidade de estruturas superficiais, funcionalidades e resistência mecânica tornam esses *scaffolds* recursos para aplicações biomédicas. É crucial observar que a biocompatibilidade e biodegradabilidade desses materiais podem variar consideravelmente, dependendo dos polímeros utilizados em sua fabricação. Desta forma, neste estudo forma preparados scaffolds de (PU)66 pela técnica de *Salt Leaching.* Assim o (PU)66 foi dissolvido em uma solução aquosa de ácido fosfórico a qual foi vertida em molde contendo o fosfato de potássio monobásico (sólido). Esta solução permeia os interstícios entre os cristais de sal à medida que se transforma em um polímero sólido. Após a solidificação completa, os cristais de sal são eliminados por dissolução com a água, que é usada para se retirar os cristais de sal da matriz polimérica. Visualmente, é possível identificar a formação de uma estrutura porosa 3Da na superfície do polímero após a secagem, o que foi posteriormente confirmada por microscopia ótica. O material foi caracterizado por espectroscopia de Infravermelho com transformada de Fourier (FTIR) que mostrou que a (PU)66 não sofreu nenhum processo de degradação durante o processamento confirmou sendo que foi observado a presença de bandas características associadas à PU (66). Os espectros de infravermelho apresentaram padrões distintos na faixa de 2940~2830 cm^{-1}, indicativos da presença de grupos metila e metileno. Na banda de 1473,35 cm^{-1} demostra a deformação do grupo angular de C-H alifático do grupo metileno e na banda 1370~1310 cm^{-1} atribuído a deformação angular de C-H alifático do grupo metila e com a junção de curcumina na sua confecção, apresentaram além das bandas PU(66) a banda 3510-3490 cm^{-1} característico de OH, no pico de 1643 cm^{-1} , um alongamento simétrico do anel aromático C=C, um pico aproximado de 1537 representando C=O, enquanto o pico obtido em 1275 cm^{-1} o pico de enol e na banda 934 cm^{-1} a vibração do benzoato , assim verificando a presença da curcumina como bioativo juntamente com a PU(PU) no scaffolds .Desta forma, pode-se constatar que a abordagem alcançou seus objetivos, sugerindo oportunidades para estudos mais aprofundados com o intuito de explorar seu potencial no transporte direcionado com a utilização de moléculas bioativas, uma perspectiva para futuras pesquisas neste campo específico.

Agradecimentos/Acknowledgments

Os autores agradecem a FAPEG (processo: 202310267001409), INCT-CIMOL (processo: 406804/2022-2) e CAPES pelo financiamento do projeto.

Área: MAT

Production of a dressing with Ecovio® nanofibers by electrospinning containing garlic wood essential oil for antimicrobial activity

Bruna A. Alexandre (PG),[1] Douglas C. Dragunski (PQ).[1]
bruna.alexandre1@unioeste.br; douglas.dragunski@unioeste.br
[1]*Programa de Pós-Graduação em Química, Unioeste*

Keywords: *Polymer, Scanning electron microscopic, Gallesia integrifólia.*

Highlights

- Garlic wood essential oil was inserted into Ecovio® for electrospinning;
- Scanning Electron Microscopy shows that the greater the polymer/oil interaction, the more beads are formed;
- The antimicrobial activities of nanofibers with essential oil indicated a decrease in microbial growth.

Abstract

The objective was to develop nanofibers from the incorporation of garlic wood essential oil extracted from the leaf, flower, and fruit, with the Ecovio® polymer in concentrations of 1%, 5%, and 10% in relation to the mass of the polymer using the technique electrospinning, thus enabling the production of dressings that aid in wound healing. Scanning electron microscopy and microbial analysis were used as characterization methods. SEM analysis (Figure 1) is used to examine material surfaces, mainly evaluating morphology. For oil extracted from leaves (Figure 1 A2-A4), the formation of more uniform fibers was observed at a concentration of 5.69%. For fruit and flower oils (Figure 1 A5 and A6), the diameters and quantities of beads formed are similar. This fact may be directly linked to the oil-polymer interaction, modifying important properties for electrospinning, such as viscosity and surface tension. Furthermore, the composition of the oil from different parts of the plant and, consequently, the interaction with the polymer can also be an important factor.

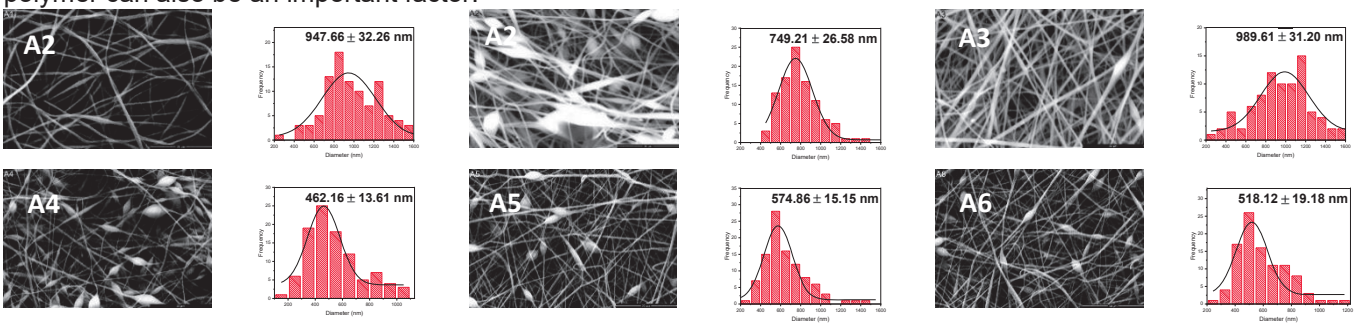


Figure 1. Scanning electron microscopy and average fiber diameter. A1 – PBAT/PLA; A2 – PBAT/PLA + 1.20% leaf; A3 – PBAT/PLA + 5.69% leaf; A4- PBAT/PLA + 9.73% leaf A5- PBAT/PLA + 4.72% fruit; A6- PBAT/PLA + 4.93% flower.

The antimicrobial activities of electrospun fibers were studied against Pseudomonas aeruginosa (PA) (Figure 2) and Candida albicans (CA) (Figure 3). The results for both are similar. Polymers with higher leaf oil concentrations (5.69% and 9.73%) considerably decreased microbial growth. Against PA, inhibition with floral oil (PA-8) had better results compared to fruit oil, while against CA, inhibition was promising with both oils (CA-6 and CA-7).

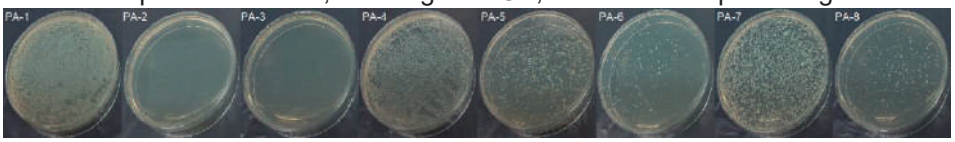


Figure 2. Antibacterial activity. PA-1 PBAT/PLA; PA-2 Chloramphenicol; PA-3 Gentamicin; PA-4 PBAT/PLA + 1.20% leaf; PA-5 PBAT/PLA + 5.69% leaf; PA-6 PBAT/PLA + 9.73% leaf; PA-7 PBAT/PLA + 4.72% fruit; PA-8 PBAT/PLA + 4.93% flower.

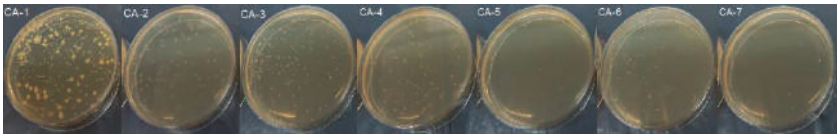


Figure 3. Antifungal behavior. CA-1 PBAT/PLA; CA-2 PBAT/PLA + amphotericin B; CA-3 chloramphenicol; CA-4 PBAT/PLA + 5.69% leaf; CA-5 PBAT/PLA + 9.73% leaf; CA-6 PBAT/PLA + 4.72% fruit; CA-7 PBAT/PLA + 4.93% flower.

In this way, the membranes obtained from the electrospinning technique with garlic wood essential oil can be used as a dressing, indicating a good surface and critical antimicrobial properties.

Acknowledgments

I thank CNPq, CAPES, and Fundação Araucária for the support provided.

Área: MAT

Recycling of electronic waste: borogermanate glasses containing rare earth ions for magneto-optical applications.

Ana Elisa Berno (IC)[1], Fábio José Caixeta (PQ)[1], Elias Paiva Neto (PQ)[2], Marcelo Nalin (PQ)[1], Sidney José Lima Ribeiro (PQ)[1], Douglas Faza Franco (PQ)[1*].

ae.berno@unesp.br

[1]Instituto de Química UNESP-Araraquara; [2]Departamento de Química UFSC

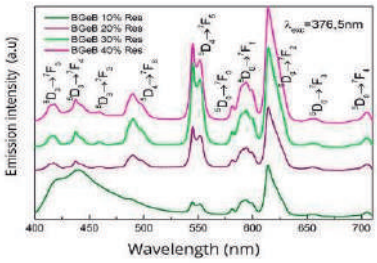
Keywords: *Glasses, Rare earth, electronic waste, Magneto-optical glasses*

Highlights

Borogermanate glasses containing residue from the recycling of electronic waste**,** mainly from fluorescent lamps were prepared. These materials have a great potential for magneto-optical applications.

Abstract

Magneto-optical (MO) glasses have attracted the attention of the scientific community in recent years due to the potential for developing MO sensors to detect magnetic fields and electrical currents from industrial equipaments. Borogermanate glasses enable the solubilization of high concentrations of rare earth (RE) ions [1]. It is important to highlight that the addition of RE ions in glass compositions strengthens the optical and MO properties of these materials. This work focuses on strategies that enable the extraction, recovery, and synthesis of advanced materials from the reuse of electronic waste. In this work, preliminary results of the synthesis and characterization of GeO_2-B_2O_3-Al_2O_3-Na_2O-BaO (BGeB) glasses containing different proportions (in %m/m) of residues obtained from fluorescent lamps, which include RE ions such as Eu^{3+} and Tb^{3+} will be presented. The preparation of borogermanate (BGeB-xRes) glasses containing x = 0.10, 20, 30 and 50% (in %m/m) of electronic residue were obtained from the conventional melt-quenching method at 1400 °C for 1 h. Subsequently, the molten liquids were cast in preheated steel molds below the glass transition temperature of the glasses (around 480 °C). After the cooling process, all samples were cut and polished to perform optical characterizations. All BGeB-xRes glasses were characterized for Differential Scanning Calorimetry (DSC), X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM) analysis, Photoluminescence (PL) and UV-Vis-NIR absorption spectroscopies. BGeB glasses are transparent and exhibit a greenish color. SEM analysiss of the samples show the absence of crystals or clusters. The XRD patterns confirmed the non-crystalline nature of all samples, while from the DSC curves it was possible to attribute the typical temperatures of a glass (Tg, Tx and Tp). The BGeB-xRes glasses exhibit a glass transition (Tg) temperature around 516 °C. The transmission spectra of BGeB-xRes glasses show an optical transmission window from 0.56 to approximately 2.6 µm. Figure 1 shows the emission spectra of BGeB glasses excited at ʎ = 376.5 nm.



The electronic transitions $^5D_0 \rightarrow {}^7F_2$ and $^5D_4 \rightarrow {}^7F_5$ presented at 615 and 550 nm are assigned to Eu^{3+} and Tb^{3+} ions, respectively. As conclusion, considering the importance of recycling electronic residue containing rare earth ions, highlighting the preliminary results of the use of these materials for the synthesis of glasses containing Eu^{3+} and Tb^{3+} with potential application in magneto-optics in the future.

Figure 1: Emission spectra of BGeB- x%Res glasses obtained from excitation at 376.5 nm.

References

[1] Franco, D.F. et al., Sci. Rep. 11**,** 9906 (2021).

Acknowledgments

I would like to express my gratitude to CNPQ (process number 407747/2022-2), to the IQCAr-Unesp, and the LAVIE and LAMF research groups, I would like to extend my thanks to my supervisors, Prof. Dr. Douglas F. Franco and Dr. Fábio J. Caixeta.

Área: MAT

Reduced graphene oxide covalently modified with β-cyclodextrin as a nanoplatform for application in chemo-photothermal therapy

Mikaelly O. B. de Sousa (PQ),[1] Célia M. Ronconi (PQ)[1]

mikaellysousa@id.uff.br; cmronconi@id.uff.br

[1]*Departamento de Química Inorgânica, Universidade Federal Fluminense, Campus do Valonguinho, Outeiro de São João Batista, s/n, 24020-141, Niterói, RJ, Brasil.*

Palavras Chave: *reduced graphene oxide, β-cyclodextrin, chemo-photothermal therapy.*

Highlights

Near infrared (NIR) absorbing rGO nanosheets modified with cyclodextrins for synergistic therapy based on photothermal therapy (PTT) and controlled drug delivery.

Abstract

PTT employing NIR laser has attracted interest in cancer and infectious diseases treatment due to its efficacy and few adverse reactions.[1] Carbon-based nanomaterials, such as graphene oxide (GO) and reduced graphene oxide (rGO) exhibit notable photothermal effects under NIR radiation,[2] along with good biocompatibility[3] and versatile surface area, making them promising drug carriers. The desired nanoplatform was prepared using GO as the starting material. After dispersing GO in Milli-Q water and subjecting it to a 2-hour exfoliation in an ultrasound bath, β-cyclodextrin (βCD) was incorporated into GO via covalent bonding, employing EDC and DMAP as coupling agents[4]. Following the esterification reaction; ascorbic acid (AA) served as an environmentally friendly reducing agent.

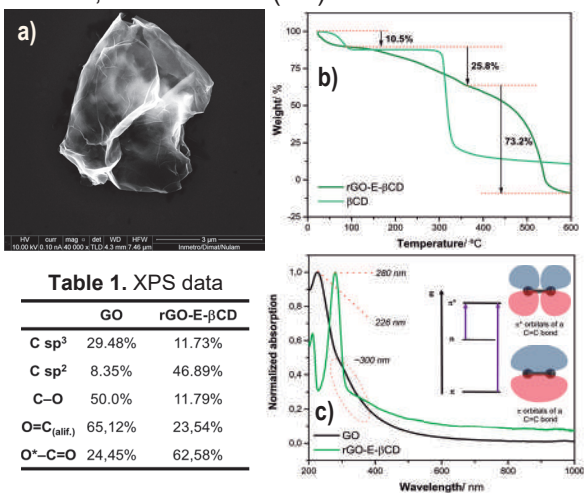


Table 1. XPS data

	GO	rGO-E-βCD
C sp³	29.48%	11.73%
C sp²	8.35%	46.89%
C–O	50.0%	11.79%
O=C$_{(alif.)}$	65,12%	23,54%
O*–C=O	24,45%	62,58%

Scanning electron microscopy (SEM) revealed typical morphology, displaying wrinkled and folded sheets with crumpled edges. FTIR spectrum (ATR) indicated material functionalization, supported by the appearance of bands associated with βCD. X-ray photoelectron spectroscopy (XPS) measurements were employed to characterize the surface functional groups of GO and **rGO-E-βCD**. In the survey analysis, there was an increase in the percentage of surface oxygen groups, with the C/O ratio rising from 1.9 to 3.5. The high-resolution O 1s spectra displayed an increase in the percentage of O*–C=O type bonds, strongly supporting the successful anchoring of βCD onto the GO plane. Thermogravimetric (TGA) curve exhibited three mass loss stages. The second stage, ranging from 95 to 360 ºC, corresponds to the decomposition of βCD, indicating potential functionalization of macrocycles at rGO sheet edges. Zeta potential analysis of the material afforded an average value of -36.38 ± 3.24 mV, being considered a stable dispersion in water.

Figure 1. a) SEM image of rGO-E-βCD; b) TGA of rGO-E-βCD and βCD; c) UV-Vis-NIR of GO and rGO-E-βCD**.**

UV-Vis-NIR absorption spectra were acquired for 0.1 mg mL^{-1} aqueous dispersions of GO and **rGO-E-βCD**. GO spectrum displayed one main peak at 226 nm attributed to the π–π* transitions of C–C/C=C bonds in sp^2 hybrid regions with a shoulder peak around 300 nm corresponding to the n–π* transitions of C=O bonds in sp^3 hybrid regions. Upon reduction, a bathochromic shift to 280 nm was observed alongside the disappearance of the 300 nm shoulder, indicating the restoration of the π-conjugation network. Notably, the new composite demonstrated a ninefold increase in NIR absorbance compared to GO. The nanosystem will be properly characterized by other relevant techniques and its photothermal efficiency will be evaluated. Loading experiments with temozolomide, a chemotherapy agent for brain cancer, are currently in progress.

---

[1]Wang, Y. *et. al. Bioact. Mater.*, **2022**, 14, 335; [2]Qi, K. *et. al. Biomed. Pharmacother.*, **2023**, 165, 115070; [3]Zhang, S. *et. al. Carbon*, **2011**, 49, 4040; [4]Einafshar, E. et al. *J. Polym. Environ.*, **2021**, 29, 3161.

Acknowledgments

CNPq FAPERJ PGQ LAME INMETRO

Área: _____MAT_____
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Renewable vitrimeric polymers based on rosin and vegetable oil derivatives

Caroline Gaglieri[1*] (PD), Rafael T. Alarcon[2] (PD), Gabriel I. dos Santos[1] (IC), Fernanda B. dos Santos[1] (IC), Gilbert Bannach (PQ)[1]

[1]São Paulo State University (Unesp), School of Sciences, Department of Chemistry, 17033-260, Bauru, SP, Brazil; [2]Universidade de São Paulo-USP, Instituto de Química de São Carlos, 13566-590, São Carlos, SP, Brazil.

Keywords: *rosin; self-healing; shape memory; renewable polymers.*

Highlights

Obtention of a renewable polymer derived from triglycerides and terpenoids; Recovery of thermosetting polymers by covalent adaptative networking by IR irradiation; Obtention of shape memory and self-healing polymers.

Resumo/Abstract

In 2022 the polymer production achieved 400.3 million tons, and most of them were derived from finite sources, and less than 10% were recycled, which is resulted from the exponential consumption these materials in several fields of society. Thus, it is clear the demand for greener polymers, such as those derived from biomass, which are organic molecules found abundantly in nature and that can be easily extracted at low cost, has great potential in the polymer field. Rosin, also known as rosin acids, is a biomass extracted in Brazil, and most of them are exported or destined for undervalued applications. The present work shows the polymer resulted from polymerization of maleinized grape seed oil (previously synthetized and characterized)[1] And a new rosin derivative (which synthesis is under patent process). They were mixed and then heated at 150 ºC for 48 h. The final polymer was thermal stable until 247.0 ºC, which was around 60 ºC higher than the rosin derivative (TG/DTG-DTA curves in Figure 1a). Moreover, the polymeric material maintained the final shape after twisted, and can be reshaped after cutting and exposure to infrared irradiation (740 nm) for 3 minutes (Figure 1b), which can be considered was a self-healing. These characteristics suggests that this material present shape memory and vitrimeric properties, which are properties of great interesting in the use and recovery of thermosetting in the present days.

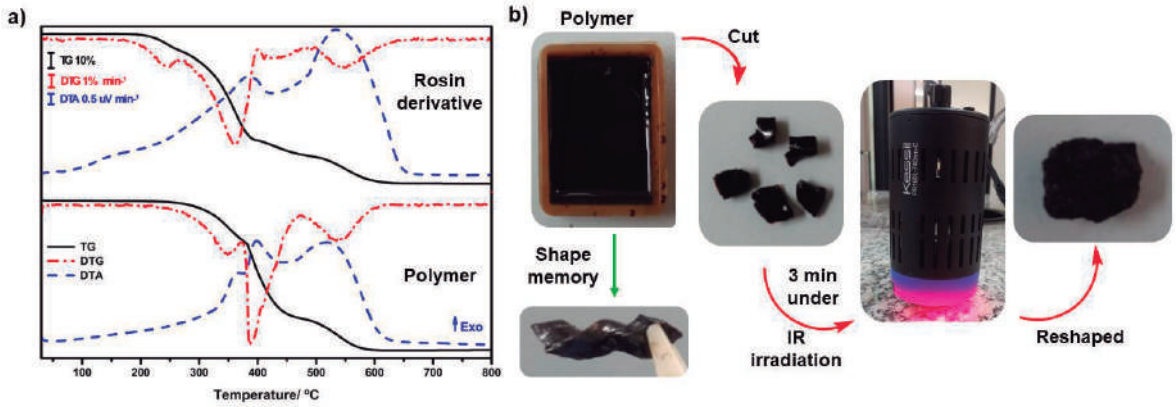


Figure 1- a) TG/DTG-DTA curves, and b) polymer reshaped, before and after cutting, under IR exposure, and then reshaped by self-healing.

References:
[1]Gaglieri, C.; *et al*. J. Braz. Chem. Soc. 2021, 11, 2120. DOI: 10.21577/0103-5053.20210104

Agradecimentos/Acknowledgments

CNPq: grants 303247/2021-5 and 150233/2022-1; FAPESP: grants 2021/02152-9, 2021/14879-0, and 2022/03489-0.

Área: MAT

rGO/Ni(OH)$_2$ nanocomposites: characterization and application as electrochemical glucose sensor

Lucas Grutzmacher (IC)[1], Carolina Ferreira de Matos Jauri (PQ)[2], Eduardo G.C. Neiva(PQ)[3*]

eneiva@furb.br

[1] *Coordenadoria Especial de Engenharia de Materiais, Universidade Federal de Santa Catarina (UFSC), CEP 89036-002, Blumenau, SC, Brasil;*

[2] *Departamento de Química, Universidade Federal de Santa Maria (UFSM), CEP 97105-900, Santa Maria, RS, Brasil*

[3] *Departamento de Química, Universidade Regional de Blumenau (FURB), CEP 89012900, Blumenau, SC, Brasil;*

Key words: *Reduced graphene oxide; Nickel hydroxide; Electrochemical sensor; Glucose.*

Highlights

Synthesis of rGO/Ni(OH)$_2$ nanocomposites;

Electrochemical characterization of rGO/Ni(OH)$_2$ nanocomposites;

Development of electrochemical sensor for glucose with low detection limit.

Abstract

Nanocomposites with varying rGO:Ni ratios were synthesized through autoclave, by the addition of nickel acetate in a dispersion of graphene oxide. The resulting material was determined to be rGO/NiO, and was investigated for its electrochemical properties, focusing on its application as a glucose sensor. The material was dispersed in water in a ultrasonic bath and films were deposited onto an FTO (fluorine doped tin oxide) support electrode and electrochemical characterizations were conducted in an aqueous alkaline solution (KOH 1.0 mol L^{-1}), employing an Ag/AgCl reference electrode and Pt counter electrode. A glucose sensor with a low detection limit was developed and validated via chronoamperometry, wich was preceeded by fifty cycles of cyclic voltammetry in a 0.0 – 0.6 V range for stabilization of the Ni(OH)$_2$ species. The rGO/Ni(OH)$_2$ sensor exhibited a glucose detection limit as low as 0.23 ± 0.12 μmol L^{-1} and quantification limit of 0.76 ± 0.42 μmol L^{-1}, for the nanocomposite synthesized with higher nickel acetate mass. A sample with lower nickel content presented a glucose detection limit of 0.68 ± 0.14 μmol L^{-1} and a quantification limit of 2.26 ± 0.47 μmol L^{-1}.

Acknowledgments

The authors are very thankful to the National Institute of Science and Technology Nanomaterials for Life (INCT-NanoVida) and National Institute of Science and Technology Carbon Nanomaterials (INCT-NanoCarbono) for financial support, to FURB for supporting the research with dedicated infrastructure, to CLAIMS for the equipaments and to professor Dr. Aldo J. G. Zarbin from Grupo de Química de Materiais (GQM-UFPR) for XRD and SEM characterizations.

Área: MAT

Síntese de Triacetato de Celulose (TAC) e Acetato-Ftalato de Celulose (CAP) utilizando como matéria prima a palha de milho.

Samuel Oliveira Lima (IC)[1*], Clodoaldo Junior Aires Duarte (IC)[1], Mariana Silva Lopes (IC)[1], Naiton Martins da Silva (PG)[1], Fernando Henrique Cristovan (PQ).

samuellima@discente.ufj.edu.br

[1]*Instituto de ciências exatas e tecnológicas, UFJ.*

Palavras Chave: *(Acetilação, Celulose, Polímero, Purificação, Síntese).*

Highlights

Synthesis of Cellulose Triacetate (TAC) and Cellulose Triacetate-Phthalate (PAC) using corn stover as raw material. With population growth, it becomes very difficult to preserve the environment, mainly due to the intrinsic relationship between market demand and the production of raw materials. This agreement between these two areas makes environmental preservation an even more distant issue, since the more it produces, the more agro-industrial waste is generated. Thus, there is a need to create alternatives for the possible purposes of these substrates, enabling a reversal of the existing critical scenario. With this in mind, this work aimed to use corn stover as a starting material for the production of polymers derived from cellulose.

Resumo/Abstract

Com o crescimento populacional, torna-se muito difícil a preservação do meio ambiente, principalmente pela intrínseca relação existente entre a demanda do mercado e a produção de matérias-primas. Essa concordância entre essas duas áreas, torna a preservação ambiental em uma questão ainda mais distante, uma vez que, quanto mais se produz, mais resíduos agroindustriais são gerados. Com isso, surge a necessidade da criação de alternativas, para possíveis fins destes substratos, possibilitando uma reversão do crítico cenário existente. Pensando nisso, este trabalho teve como objetivo utilizar a palha de milho como material de partida para a produção de polímeros derivados de celulose. A palha de milho foi purificada utilizando uma solução de $EtOH/HNO_3$ (80:20 v/v), logo após foi deixada em refluxo, a fim de obter a celulose purificada. Essa celulose obtida foi submetida a reação de acetilação (substituição dos grupos hidroxilas por grupos acetil) e também uma reação de ftaloização (substituição parcial das hidroxilas presentes no polímero acetato por grupos ftalil). Os polímeros triacetato de celulose (TAC) e acetato ftalato de celulose (CAP) foram analisados por métodos de titulação a fim de definir seus devidos gruas de acetilação (% GA), ftaloização (% GF) e substituição (GS). Foi utilizada a caracterização do polímero por Espectroscopia de Infravermelho por Transformada de Fourier (FTIR), com o intuito de validar a eficácia dos processos de síntese realizado. A purificação da palha de milho realizada alterou os aspectos físicos do material, onde foi possível observar o surgimento de uma coloração esbranquiçada, sendo característica da celulose. O TAC apresentou valores de GA e GS de 42,80% e 2,77, respectivamente, onde valores de GS entre 2,5 – 2,9 indicam que um polímero é tri-substituído. Já o CAP, por se tratar de um polímero derivado de celulose misto, foi necessário definir o GA e GS para o grupo acetil (GS_A) e GF e GS para o grupo ftalil (GS_F). Para o grupo ligante acetil foi encontrado um GA de 30,47% e GS_A de 1,63, já para o grupo ftalil o valor de GF foi de 34,09% e GS_F de 0,56. Observando os espectros obtidos pelo FTIR é possível identificar o aparecimento das bandas características aos materiais acetilados em 1750 cm^{-1}, 1374 cm^{-1}, 1240 cm^{-1}, 1160 cm^{-1} e bandas que são características de materiais ftalil substituídos em 1600 cm^{-1} e 744 cm^{-1}. Analisando todos os dados obtidos é possível concluir que os métodos adotados de purificação e de síntese dos derivados de celulose foram bem sucedidos e que o reaproveitamento da palha de milho para a produção de polímero é uma alternativa viável.

Agradecimentos/Acknowledgments

Os autores agradecem a FAPEG (processo: 202310267001409), CAPES, INCT-CIMOL (processo: 406804/2022-2) pelo financiamento do projeto.

Área: MAT

Síntese e caracterização Óptica de Pontos de Carbono contendo o íon metálico Zn^{2+}

Igor D. Campos (PG),[1] Leticia F. Magalhães (PG),[1] Luana C. de. O. Lima (PG),[1] Flávia S. Silva (PG),[1] Marco Antônio Schiavon (PQ)[*1]

igor.campos03@gmail.com; **schiavon@ufsj.edu.br**

[1]Grupo de Pesquisa em Química de Materiais, Departamento de Ciências Naturais, Campus Dom Bosco, Universidade Federal de São João del-Rei – UFSJ, São João del-Rei - MG.

Palavras-Chave: *Pontos de carbono, Síntese, Propriedades ópticas.*

Highlights

Synthesis and characterization of carbon dots containing the metal ion Zn^{2+}.

- Synthesis of carbon dots by the solvotermal method.
- Optimization of synthetic parameters.
- Study of optical properties of carbon dots containing the metal ion Zn^{2+}.
- Evaluate the effect of the metal ion incorporation on the structure of Carbon dots.
- Evaluate the concentration of ions Zn^{2+} on producing changes in the optical properties of Carbon Dots.

Resumo/Abstract

Os pontos de carbono (PCs) são nanopartículas de carbono, contendo em sua estrutura, majoritariamente, carbono, oxigênio, hidrogênio e nitrogênio, sendo o núcleo formado por carbonos do tipo sp^3 e sp^2 e a superfície contendo grupos funcionais[1]. Existem duas maneiras de sintetizar estes nanomateriais, via *top down* ou *botton up*. Na primeira, o material *bulk* de carbono é processado por meio da combustão, ablação a laser ou rotas eletroquímicas. Em contrapartida, o método *botton up*, consiste na utilização de precursores orgânicos em processos hidrotérmicos, solvotérmicos, pirolíticos e micro-ondas[2]. Apesar de muitos estudos na literatura na última década, ainda hoje, busca-se o aprimoramento das propriedades ópticas dos PCs, como o deslocamento da banda de absorção e de emissão ao longo da região visível do espectro eletromagnético, a intensificação da fluorescência e, consequentemente, o aumento do rendimento quântico de fotoluminescência (PLQY) do material, ampliando as possibilidades de aplicação. Dessa forma, a incorporação de íons metálicos nos PCs possibilita alterações que, em alguns casos, corresponde a melhora nas propriedades ópticas do material[3]. Neste trabalho foram sintetizados pontos de carbono pela técnica *botton up*, via método solvotérmico, o qual envolve o aquecimento de uma solução contendo precursores orgânicos em um recipiente selado sob alta pressão e temperatura. Para as sínteses dos PCs, utilizou-se o tolueno como solvente da reação, sob a temperatura de 180 ºC, variando-se os parâmetros de tempo de síntese (6, 9, 12 e 24 horas) e concentração do íon metálico Zn^{2+} (1, 3 e 6mmol). Avaliando-se as propriedades ópticas dos materiais obtidos, foi possível perceber que, a adição de zinco a estrutura, levou a um deslocamento batocrômico, no qual os PCs passaram a emitir na região de ~510 nm (amarelo), diferentemente da emissão tradicional na região azul dos PCs sem a presença dos íons metálicos. Além disso, obteve-se um aumento do rendimento quântico de fotoluminescência (PLQY) e do tempo de vida no estado excitado, sendo os melhores dados referente a amostra sintetizada em 12 horas com 3 mmol do íon dopante. Para tal amostra, o PLQY aumentou de 31,8% para 36,0% e o tempo de vida foi de 7,97 ns enquanto na ausência do Zn^{2+}, o tempo de vida médio foi de 6,79 ns. Estruturalmente os PCs apresentaram grupos funcionais compatíveis com as moléculas precursores, quando analisadas por infravermelho. Por meio da difração de raios X os PCs sintetizados apresentaram estrutura não-cristalina, mesmo na presença dos íons metálicos Zn^{2+}.

Referências:

[1] Asmaa, M.; El-Shafey *Synth.* **2021**, *10*, 134.
[2] Machado, E.; Vieira, O.; Ferrari, L.; Schiavon, A. *Rev. Virtual Quim.* **2015**, *7*, 1306.
[3] Tejwan, N.; Kumar, S.; Das, J. *Adv. Colloid Interface Sci.* **2020**, *275*, 102046.

Agradecimentos/Acknowledgments

Este trabalho foi apoiado pelo CNPq, CAPES, FINEP e FAPEMIG.

Área: MAT

Síntese e caracterização de Pontos Quânticos Gigantes de CdTe/CdS/ZnS

Thalita Cristina Teixeira (PG), Marco Antônio Schiavon (PQ)*.

thalita.teixeira50@gmail.com; schiavon@ufsj.edu.br

Grupo de Pesquisa em Química de Materiais, Departamento de Ciências Naturais, Campus Dom Bosco, Universidade Federal de São João del-Rei – UFSJ, São João del-Rei - MG.

Palavras-Chave: *Ponto Quântico Gigante, Síntese, Propriedades, Monocamadas.*

Highlights

Synthesis and characterization of Giant Quantum Dots of CdTe/CdS/ZnS

- Synthesis of CdTe quantum dots with three different sizes.
- Evaluate the effect of the formation of CdS forming shells (CdTe/CdS) and ZnS to generate GQDs.
- Study of optical and structural properties as a function of the number of layers of each shell.

Resumo/Abstract

Os pontos quânticos (PQs) são materiais semicondutores nanocristalinos coloidais que possuem tamanho de nanopartícula variando entre 2 e 15 nm[1], sendo este um fator determinante para as propriedades deste material, em que o efeito de confinamento quântico se destaca como o mais proeminente. Trata-se de uma área ativa na pesquisa científica atual, tendo sido laureada com o Prêmio Nobel de Química de 2023, a descoberta e síntese coloidal de PQs pelos pesquisadores Moungi G. Bawendi, Louis E. Brus e Aleksey Yekimov.[2] Os Pontos Quânticos Gigantes (PQG) são um tipo único de nanocristais semicondutores coloidais no sistema caroço-casca para os quais a casca é adicionada para ser especialmente espessa e livre de defeitos ao redor do caroço, geralmente, maior que 8 monocamadas, elevando assim os rendimentos quânticos de fotoluminescência.[3] Neste trabalho foram sintetizados PQs de sistema caroço/casca/casca de CdTe/CdS/ZnS, que correspondem a uma classe de pontos quânticos que consistem em um caroço (*core*) de telureto de cádmio (CdTe), envolto em uma casca (*shell*) de sulfeto de cádmio (CdS), seguido de uma nova casca externa de sulfeto de zinco (ZnS), nos quais as cascas foram crescidas pelo método de síntese SILAR (Sucessiva Reação e Adsorção de Camadas de Íons). As sínteses para obter esses PQs foram realizadas em meio aquoso, o que não requer alta temperatura, sendo esta uma rota de síntese rápida e simples. Foram estudadas suas propriedades em função do tamanho do caroço (CdTe), em que três tamanhos de nanocristais foram usados (2,64; 2,99 e 3,08 nm), e também do número de camadas de cada casca (1 a 5 monocamadas de cada semicondutor CdS e ZnS), preparadas pelo método SILAR. Com base nos resultados obtidos, foi observado que através da variação da espessura da casca dos PQGs, ocorre uma alteração nas propriedades ópticas e estruturais desses nanocristais. As bandas de absorção e emissão apresentaram deslocamentos para a região do vermelho no espectro, ou seja, foram deslocadas para maiores comprimentos de onda, o que indica o aumento no tamanho dos NCs à medida que mais monocamadas de CdS e/ou ZnS são crescidas sobre os PQs de CdTe. Neste caso, deslocamentos de ~ 10 nm foram obtidos entre cada monocamada depositada de CdS e ZnS. Assim, as propriedades ópticas e estruturais desses materiais foram alteradas com o aumento do tamanho, devido ao efeito de confinamento quântico, ampliando as possibilidades de aplicações do material em estudo. O deslocamento das bandas de emissão e a variação no tempo de vida do estado excitado serão discutidas em função do número de camadas da casca, bem como do tipo de semicondutor preparado.

Referências:
[1] Park, H.; Shin, D. J.; Yu, J. *J Chem Educ* **2021**, *98*, 703.
[2] Yu, K.; Schanze, K. S. *ACS Cent Sci* **2023**, *9*, 1989.
[3] Farahmandzadeh, F.; Molaei, M.; Alehdaghi, H.; Karimipour, M. *Applied Physics A* **2022**, *128*, 239.

Agradecimentos/Acknowledgments

Este trabalho foi apoiado pelo CNPq, CAPES, FINEP e FAPEMIG.

Área: MAT_____
)

Selective functionalization of graphene oxide for nanocatalysis: where does the catalytic synergism come from?

Bernardo M. Régnier (PG), André H. G. Martinez (PG), Aldo J. G. Zarbin (PQ), Elisa S. Orth (PQ)

bernardoregnier@gmail.com

Department of Chemistry, Universidade Federal do Paraná (UFPR) – Curitiba, PR, Brazil.

Palavras Chave: *Organophosphates*, *Basic catalysis, Nanocatalysis, Green chemistry, bioinspired catalysis.*

Highlights

Graphene oxide was modified with ethylenediamine via epoxide and carboxylic acid sites. They were studied in a reaction with organophosphates. It is proposed a bifunctional catalysis for its synergism

Resumo/Abstract

Organophosphates are a class of toxic compounds that comprise pesticides and chemical weapons. Nucleophilic catalysis is a promising approach for neutralizing these compounds. Herein, we selectively modified graphene oxide (GO) with ethylenediamine (EDA) via epoxy and carboxylic acid routes, therefore obtaining nanocatalysts with nucleophilic groups in the basal plane and another in the edge of GO sheet, respectively. Seeking to block the acid sites of GO, they were functionalized with ethanol. These materials were analyzed via thermogravimetric analysis (TGA), Fourier-transform infrared spectroscopy (FTIR) and potentiometric titration. The nanocatalysts were evaluated in the degradation reaction of diethyl 2,4-dinitrophenyl phosphate (DEDNPP), showing high rate enhancements in the order of 10^3 when compared to DEDNPP in water. The catalyst functionalized via epoxide sites showed the highest performance which was attributed to a bifunctional catalysis: neighboring carboxylate present in GO act as general base catalyst together with the terminal amine, which in turn becomes a better nucleophile towards the phosphorus center (Figure 1). Indeed, upon blocking the acid sites, the catalysis decreases significantly.

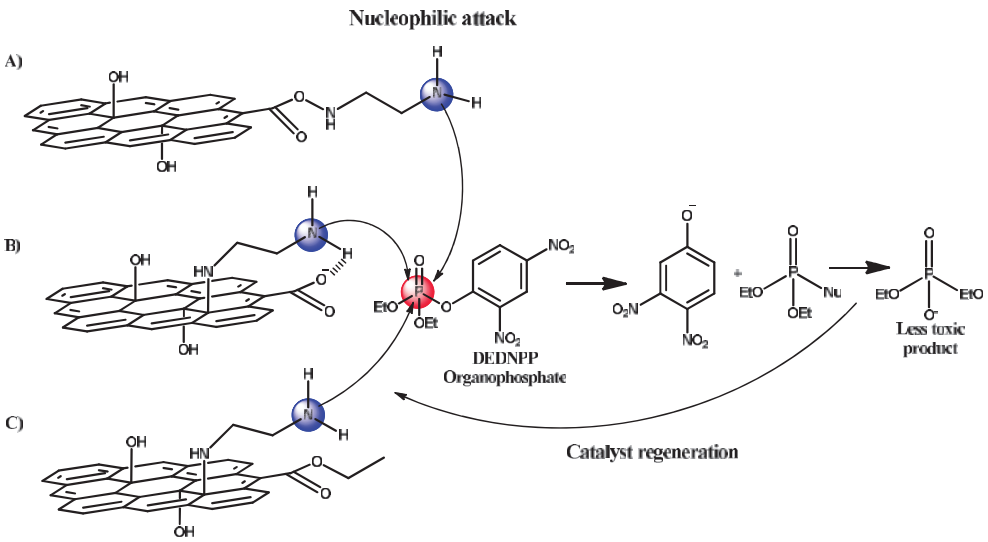


Figure 1) Nucleophilic attack of the modified GO with the nucleophilic group in the A) edge, B) on the basal plane and C) on the basal plane with the carboxylic acid blocked with etanol.

Agradecimentos/Acknowledgments

UFPR, CNPq, CAPES, L'Oréal-UNESCO-ABC, PhosAgro/UNESCO/IUPAC, National Institute of Science and Technology of Nanomaterials for Life (INCTNanovida) and National Institute of Science and Technology of Carbon Nanomaterials (INCTNanocarbon).

Área: MAT

Si_3N_4 SURFACE FUNCTIONALIZATION WITH GOLD NANOPARTICLES FOR BIOSENSING APPLICATIONS

Kevin S. B. Martins (PG) [1,2], Jessica E. S. Fonsaca (PQ)[1,2], Daniel Grasseschi (PQ)[3], Cecília de C. C. e Silva (PQ) [1,2] Christiano J. S. de Matos (PQ)[1,2]*

kevinboszko@hotmail.com; christiano.matos@mackenzie.br

[1]Engineering School, Mackenzie Presbyterian University, São Paulo, Brazil; [2]Mackenzie Institute for Advanced Research in Graphene and Nanotechnologies – MackGraphe, Mackenzie Presbyterian Institute, São Paulo, Brazil; [3]Rio de Janeiro Federal University, Rio de Janeiro, Brazil.

Key words: Aptamers, AuNP, Photonic biosensor, Plasmonic scattering, Silicon Waveguide.

Highlights

AuNPs were synthesized and functionalized with aptamers for SARS-CoV-2 detection. In parallel, AuNPs were evenly immobilized on treated Si_3N_4 surface.

Abstract

Photonic biosensors have emerged as promising diagnostic platforms due to their low detection limits, high sensitivity, and ease of integration into various analytical systems. They are based on optical responses resulting from the interaction of the analytes with the transducer. Silicon-photonic biosensors (usually constituted of Si_3N_4) are one of the most promising for clinical applications. They are based on optical-frequency waves confined in its core that are propagated along a longitudinal dimension. In this case, the guided modes display evanescent field, which is responsive to refractive index changes in the tested sample (Figure 1A). One way of enhancing their performance would be through the combination with gold nanoparticles (AuNPs), thus taking the advantage of their localized surface plasmon resonance (LSPR) phenomenon. In this sense, this work proposes integrating AuNPs onto waveguides to exploit their strong plasmonic light scattering behavior to develop a novel photonic biosensor for viral pathogens detection. Viruses in the sample will be detected due to the plasmonic scattering of light caused by the AuNP agglomeration induced by the pathogen. This will appear as bright spots on the image captured on an optical microscope coupled to a camera, positioned over the waveguide (Figure 1B). Here, we show preliminary steps towards the proposed sensor, consisting of two fronts: (i) synthesis of AuNPs and their functionalization with aptamers for the SARS-CoV-2 spike protein, and (ii) surface treatment of Si_3N_4 substrates to immobilize the AuNPs. Different sizes of NPs (12, 32 and 58 nm) were synthesized through the Turkevich method. To estimate the AuNP plasmonic behavior when agglomerated, aggregation tests were conducted by adding salt and monitoring the process via UV-Vis spectroscopy. 12 and 58 nm NPs showed the most interesting spectral changes. Then the AuNPs were functionalized with the aptamer. Changes in the suspension color from red to purple seem to indicate successful AuNP functionalization. For the immobilization of the AuNPs on Si_3N_4, the surface was oxidized and then treated with APTS, followed by the interaction with the AuNP suspension. This resulted in a homogeneous coverage of the surface with the AuNPs, as shown in the SEM image of Figure 1C. In conclusion, AuNPs were synthetized and functionalized with aptamers and the aimed substrate was successfully covered with AuNPs. This is an on-going work and next steps include the functionalization of Si_3N_4 waveguides and monitoring of the plasmonic scattering.

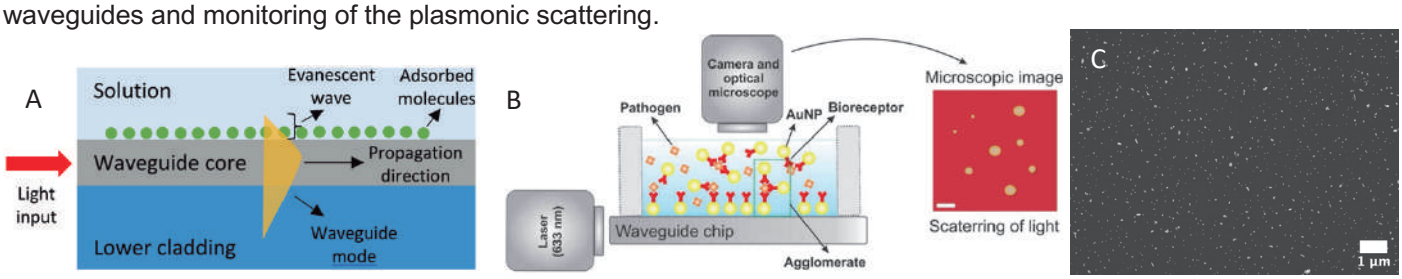


Figure 1 – A - Illustration of evanescent field interacting with the adsorbed molecules on the surface of the waveguide. B – Scheme of the detection method of virus in samples through the formation of agglomerates. C - SEM image of a Si_3N_4 with immobilized AuNPs.

Acknowledgments

Authors acknowledge FAPESP (#2020/13288-6), INCT of Carbon Nanomaterials, Mackenzie Presbyterian University, CNPq and CAPES.

Área: MAT

Starch based film with anthocyanin: biodegradation test, pH sensitivity and tensile test

Yasmin Fernandes de Almeida (TM),[1] Renan Ferreira Menegassi de Souza (PG),[2] Thalita Ferreira Menegassi de Souza (PQ),[1]*.

thalita.menegassi@ifsuldeminas.edu.br

[1] Instituto Federal de Educação, Ciência e Tecnologia do Sul de Minas, IFSULDEMINAS; [2] Centro de Ciências Naturais e Humanas, Universidade Federal do ABC, UFABC

Palavras Chave: *Amido, Antocianina, Filme, Biodegradação, pH, Propriedades mecânicas.*

Highlights

The end of biodegradation process was achieved in two months. Colour responses by pH changes and reduction in tensile strength were observed on the film with anthocyanin.

Resumo/Abstract

Neste trabalho, filmes biodegradáveis de amido de milho foram preparados pela técnica de *casting* empregando o glicerol, como plastificante, e a antocianina obtida do extrato de repolho roxo, como aditivo. Os filmes produzidos se apresentaram uniformes e transparentes, sendo que o filme de amido contendo a antocianina apresentou uma coloração roxa. A espessura média dos filmes variou de 0,117 a 0,130 mm. O resultado do ensaio de biodegradação dos filmes, após 2 meses, não apresentou resíduos comprovando a sua biodegradação. Em relação a estabilidade química, após 24 horas em contato com soluções, o filme de amido em meio ácido e meio neutro, se apresentaram, qualitativamente, mais resistentes comparado com o filme em meio básico. O filme de amido com antocianina em meio ácido adquiriu coloração rosa/vermelha, em meio neutro permaneceu roxo e em meio básico a coloração verde (Figura 1) e após 24 horas, ficaram qualitativamente mais frágeis. A tabela 1 apresenta os dados das propriedades mecânicas dos filmes produzidos. Os dados foram submetidos à análise de variância (ANOVA) e as médias comparadas pelo teste de Tukey a 5% de probabilidade ($p \leq 0,05$), empregando-se o software SISVAR.[1]

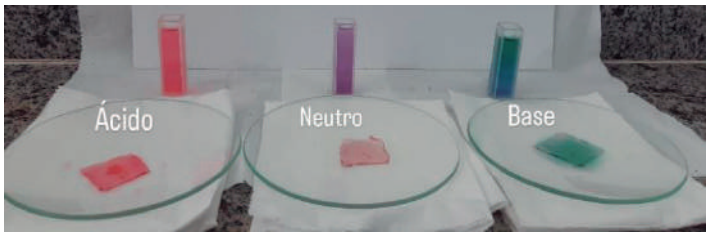


Figura 1. Amostras de filme de amido com antocianina em meio ácido, neutro e básico.

Tabela 1. Propriedades mecânicas dos filmes.

Amostra	Resistência à tração (MPa)	Deformação na ruptura (%)
Filme de amido	2.19713[a]	19.78879[a]
Filme de amido com antocianina	1.74310[b]	16.21035[a]

*Médias seguidas pela mesma letra não diferem entre si pelo teste de Tukey ($p \leq 0,05$).

Estatisticamente, a presença da antocianina não alterou significativamente a deformação na ruptura do filme e foi observada uma diminuição de 20% na resistência à tração indicando a redução desta propriedade mecânica. Este resultado indica que o filme contendo antocianina possui uma resistência menor a tração com o mesmo alongamento, ou seja, uma baixa resistência ao escoamento. Contudo, o corante agregou a propriedade funcional de mudança de coloração em relação ao pH o que pode ser interessante para embalagens inteligentes.

[1] FERREIRA, D. F. Sisvar: a computer analysis system to fixed effects split plot type designs. Revista Brasileira de Biometria, Lavras, MG, v. 37, n. 4, p. 529-535, 2019. Disponível em: http://www.biometria.ufla.br/index.php/BBJ/article/view/450. Acesso em: 14 de fev. de 2024.

Agradecimentos/Acknowledgments

Ao IFSULDEMINAS e a UFABC

Área: MAT
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Structural study of spinels in manganese doped zinc gallate ($ZnGa_2O_4$:Mn^{2+}) by electronic paramagnetic resonance (EPR)

Marcelo C. Portes (PQ),[1] Douglas L. Fritzen (PG),[1] Lucas C. V. Rodrigues (PQ),[1].

marcelo.portes@usp.br; lucascvr@iq.usp.br

[1]*Departamento de Química Fundamental, USP;*

Palavras Chave: *rare earth, epr, zinc gallate, structure, spinel.*

Highlights

EPR analysis of manganese doped zinc gallate using X band Bruker EMX equipment at room temperature. The manganese sites were investigated using Easyspin toolkit in a MATLAB environment to determine the possible formation of inverted spinel in the structure.

Resumo/Abstract

$ZnGa_2O_4$ (ZGO) matrix is a spinel-type compound. When we dope the matrix with Mn^{2+} we expect manganese to substitute primarily in the tetrahedral site of zinc (Zn^{2+}), but with the smaller possibility of also substituting in the octahedral site of gallium (Ga^{3+}), forming the so-called inverted spinel. To address this possibility the manganese dopped matrix was studied by Electronic Paramagnetic Resonance (EPR) to help identify if there were more than one type of manganese present on the system.

The EPR spectrum was obtained using a Bruker EMX X-Band 9.4Ghz equipment, at room temperature in solid state. Then the recorded spectrum was treated using a Easyspin toolkit in a MATLAB environment to obtain the spectrum parameters. Simultispin toolkit was also used to help narrow down the possibilities and adjust the fitting of the simulation. The results can be seen at Figure 1 below.

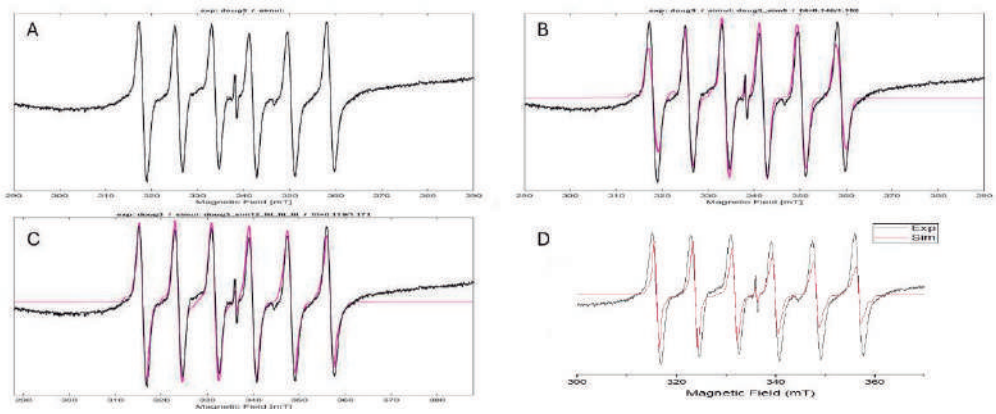


Figure 1. A) Raw spectrum of ZGO:Mn^{2+}, B) Simultispin simulation considering two Mn sites. C) Simultispin simulation considering one Mn site. D) Easyspin simulation considering one Mn site.

At first the inverted spinel hypothesis, with the Mn^{2+} substituting both Zn^{2+} and Ga^{3+}, showed a good fit, we can see on Figure 1B that peak correlation it is not the best for peak intensities. On Figure 1C the simulation was adjusted for one Mn site, considering a magnetic interaction between different electrons of the same Mn atom [1]. This adjustment was carried out to the Easyspin toolkit, Figure 1D, adding a zero-field tensor, D, that helped to field a better fitting for the simulation. Therefore, it was possible to attest that the inverted spinel did not form, with the Mn occupying only the Zn sites.

[1] J. Chem. Soc., Faraday Trans. 2, 1973,69, 1537-1541

Agradecimentos/Acknowledgments

To CNPq process: 151180/2022-9

Área:MAT

Sulfur quantum dots obtained by femtosecond laser ablation of elemental sulfur in water

Aldebarã Fausto Ferreira (PG)[1], Gabriela da Costa Carvalho (PG)[1], João Paulo Barbosa de Almeida (PG)[1] Vagner Bezerra dos Santos (PQ)[1], Walter Mendes de Azevedo (PQ)[1*]

Walter.azevedo@ufpe.br

[1]*Departamento de Química, C.C.E.N. UFPE*

Palavras Chave:*SQDOT, Fentosecond laser ablation, highly photoluminescence quantum yield.*

Highlights

New synthesis route for sulfur quantum dots, non conventional synthesis route for preparation of nanomaterials. Chemical synthesis using femtosecond laser ablation, High quantum yield sulfur quantum dots

Resumo/Abstract

Sulfur quantum dots (SQDs) have received great attention in recent years due to their unique chemical, optical and biocompatible properties [1]. However, the long reaction time, low photoluminescence quantum yield (PLQY) and very low S-to-SQDs conversion efficiency (less than 1%) have been reported to hinder real applications [1,2]. On the other hand, the laser ablation technique is a known physical methodology applied to obtain nanoparticles of many metals and oxides and to promote synthesis under unconventional conditions [3,4]. In this work, for the first time, a femtosecond laser was applied to synthesize SQDs. For this purpose, elemental sulfur powder (S) was ablated in an alkaline aqueous solution containing PEG-400 for 1 h. After that, the brownish transparent solution obtained was reacted with hydrogen peroxide solution in a ratio of 3:4. As a result, a transparent and highest cyan fluorescence emission was obtained with PLQY of 75%. The samples were analyzed by FTIR, Raman, TGA, XRD and luminescence measurements. Also, the digital imaging technique was applied to determine the concentration of Hg in environmental water.

References

[1] Gao, P., Huang, Z., Tan, J., Lv, G., Zhou, L. (2022). ACS Sustain. Chem. Eng., 10(14), 4634-4641.

[2] Shen, L., Wang, H., Liu, S., Bai, Z., Zhang, S., Zhang, X., Zhang, C. (2018). J. Am. Chem.Soc., 140(25), 7878-7884.

[3] S.E Silva, Freitas D. V, Navarro M. [a], de Azevedo W.M. Material today communication 2022, V 32, 104141

[4] Ferreira, A. F., Falcão, E. H. L., de Azevedo, W. M. (2023). Mater. Lett., 134365.

Agradecimentos/Acknowledgments

This work was supported by: CNPq, CAPES and FACEPE.

Área: MAT

Sustainable technology: heavy metal oxide glasses and glass-ceramics containing Eu^{3+} and Tb^{3+} ions recycled from fluorescent lamps.

João Pedro Costa Ruzene (IC),[1] Fábio J. Caixeta (PQ),[1] Elias P. F. Neto (PQ),[2] Marcelo Nalin (PQ),[1] Sidney J. L. Ribeiro (PQ),[1] Douglas Faza Franco (PQ),[1*].

j.ruzene@unesp.br

[1]*Instituto de Química, Unesp Araraquara;* [2]*Departamento de Química, UFSC.*

Keywords: *Glasses, Glass-ceramics, Recycling, Rare earth ions.*

Highlights

- Recycling of rare earth (RE) ions.
- Synthesis and characterization of heavy metal oxide glasses and glass-ceramics doped with Eu^{3+} and Tb^{3+} obtained from fluorescent lamps.

Abstract

Heavy metal oxide (HMO) glasses exhibit interesting properties, including broad transparency in the infrared region, high nonlinear optical coefficients and high refractive indices [1]. Additionally, HMO matrices have the potential to solubilize a high concentration of rare earth (RE) ions. The presence of high concentrations of RE ions provides these materials interesting optical and magneto-optical (MO) properties. In this work, preliminary results of the synthesis and characterization of $40PbO\text{-}20GeO_2\text{-}25Bi_2O_3\text{-}15Ga_2O_3$ (PGBG) glasses and glass-ceramics containing Eu^{3+} and Tb^{3+} from the recycling of fluorescent lamps will be presented. Electronic waste recycling emerges as a crucial factor in the production and recovery of RE ions, especially in Brazil. Glasses and glass-ceramics based on the PGBG-xResidues composition (where x_{res} = 0, 1, 10, 20, 30 and 60 %m/m) were synthesized by the conventional melt-quenching method. Initially, the precursors were weighed stoichiometrically and homogenized for subsequent melting in platinum crucibles at 1300°C for 40 minutes. After that, the glass compositions were rapidly cooled in preheated metal molds at 50 °C below the glass transition temperature of the materials (Tg ~ 350 °C). Subsequently, the PGBGglasses and glass-ceramics were characterized by Differential Scanning Calorimetry (DSC), X-ray Diffraction (XRD), Raman, UV-VIS-NIR and Photoluminescence (PL) Spectroscopies, Visual analysis of the PGBG samples showed the synthesis of transparent glasses and glass-ceramics. The DSC curves of the samples showed typical glass temperatures, such as glass transition (Tg) and onset of the crystallization process (Tx). The XRD pattern confirmed the non-crystalline nature of the PGBG0% sample, which allowed it to be classified as glass. The morphological characterizations of the PGBG1, 10, 20 and 30%Res samples obtained from optical microscopy indicated the presence of cubic crystals with an average size of 25 µm indicating the formation of PGBG glass-ceramics. According to the Raman spectrum profile, there is a decrease in the intensity of the vibrational modes attributed to the BiO_6 and Pb-O species, with bands centered at 185 and 260 cm^{-1}, respectively. Through Photoluminescence, the presence of bands attributed to the electronic transitions of Tb^{3+} and Eu^{3+} ions at 514 nm ($^5D_4 \rightarrow {}^7F_5$) and 615 nm ($^5D_0 \rightarrow {}^7F_2$), respectively, stands out. Qualitatively, based on the analysis of the emission intensities of both rare earth ions, there is a greater predominance of Eu^{3+} ions in relation to Tb^{3+} inserted in the PGBG glass network. From the PGBG glass matrix it was possible to synthesize glasses and glass-ceramics containing the rare earth ions Tb^{3+} and Eu^{3+} present in residues from fluorescent lamps. In summary, preliminary results showed the possibility of preparing transparent glass-ceramics with potential application in optics and magneto-optics.

[1] SOUZA, A. E. et al. Heavy metal oxide glass-ceramics containing luminescent gallium-garnets single crystals for photonic applications. Journal of Alloys and Compounds, v. 864, p. 158804, 25 maio 2021.

Agradecimentos/Acknowledgments

To CNPq (407747/2022-2), Unesp, tLAViE and LAMF research groups. Likewise, I would like to extend my thanks to my supervisors, Prof. Dr. Douglas F. Franco and Dr. Fábio J. Caixeta.

Synergy of Shaped-Induced Enhanced Raman Scattering to improve Surface-Enhanced Raman Scattering signal for Thiram molecule detection

Jaciara Bär (PG),[1] Anerise de Barros (PQ),[1] Flavio Makoto Shimizu (PQ),[2,3] Fernando Aparecido Sigoli (PQTC),[1] Carlos César Bof Bufon (PQ),[4] Italo Odone Mazali (PQ).[1]*

anerise@unicamp.br; mazali@unicamp.br

[1]Universidade Estadual de Campinas, Instituto de Química, Laboratório de Materiais Funcionais, SP, Brasil; [2] Universidade Estadual de Campinas, Instituto de Física Gleb Wataghin, Campinas, SP, Brasil; [3] Laboratório Nacional de Nanotecnologia – LNNano, Centro Nacional de Pesquisa em Energia e Materiais – CNPEM, Campinas SP, Brasil; [4]Instituto Presbiteriano Maxkenzi, São Paulo, SP, Brasil.

Palavras Chaves: *SIERS, SERS, Microchannels, Gold Nanorods, Thiram detection, IDMAP, Machine Learning*

Highlights

Synergy of Shaped-Induced Enhanced Raman Scattering to improve Surface-Enhanced Raman Scattering signal for Thiram molecule detection.

- Silicon V-shaped microchannels modified with gold nanorods;
- Thiram molecule in low concentration detection;
- Investigation of SIERS@SERS effect in different Si-V regions.

Abstract

Surface-enhanced Raman Scattering (SERS) is a powerful tool for detecting molecules in ultralow concentrations due to their ability to increase Raman signal by analyte molecules adsorbed on SERS-active substrate [1]. However, several strategies have been development to improve the SERS signal, among this, we development platforms which has been identified a new effect, called of Shaped-Induced Enhanced Raman Scattering (SIERS). The SIERS effect is attributed to the V-shaped microchannels on the Si surface, providing a distribution of Raman scattering high-intensity, i.e., the electric field intensification is caused by the constructive interference patterns of light irradiated from the V-shaped cavity [2]. Based on that, we explore the combined effect of SIERS and SERS for detecting thiram molecules. We fabricated V-shaped microchannels on a silicon (100) substrate through a standard lithography and etching process. The analysis of SIERS@SERS was performed for Si-V substrates modified with AuNRs with different thiram concentrations, 10^{-7} to 10^{-10} mol L^{-1}. The spectra were collected for different regions of the Si-V substrates, i.e., in the inside, edge, between (flat top), and far from Si-V (coffee-ring AuNRs aggregation) to assess the performance of Si-V microchannels obtained. The IDMAP statistical projection reveals a higher silhouette coefficient of 0.91 for the inside of Si-V, indicating a more excellent spectral reproducibility with closer relative intensities. The device platform used in this study stands out as a robust option for commercial sensors, demonstrating exceptional sensitivity in detecting a diverse range of molecules, even at low concentrations.

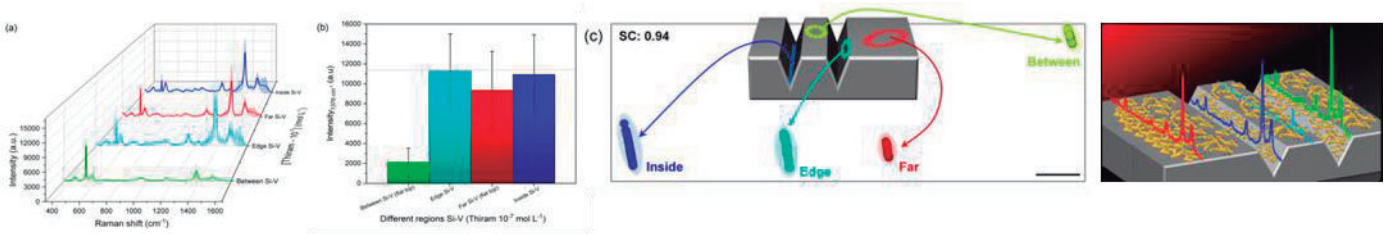


Figure 1. (a)SIERS@SERS spectra for thiram 10^{-7} mol L^{-1}in different regions of Si-V microchannels; (b) bar graphical of average intensity for the band at 1376 cm^{-1} comparison; (c) IDMAP projection of SIERS@SERS spectra (1100 – 1600 cm^{-1}) for thiram 10^{-7} mol L^{-1}, the black bar inset is only a guide to measure distances between data points. Schematic representation of SIERS@SERS signal in different regions of Si-V microchannels substrate.

Acknowledgments

INCT/INOMAT, UNICAMP-IQ, Laboratório Multiusuário de Espectroscopia Óptica Avançada (LMEOA), LNNano, CNPq, Capes, FAPESP (2022/02893-1)

[1] J. Langer, et al. Present and Future of Surface-Enhanced Raman Scattering, ACS Nano. 14 (2019) 28–117.
[2] J. Bär, et al. Silicon Microchannel-Driven Raman Scattering Enhancement to Improve Gold Nanorod Functions as a SERS Substrate toward Single-Molecule Detection, ACS Appl. Mater. Interf. 13 (2021) 36482-36491.

Área: MAT

Synthesis and application of quinoline derivate as photoiniciator in photopolymerization reactions

Ilana Sganzerla Rosário* **(PG),[1] Vitor Fernandes Moreno (PG),[1] Luiz Carlos Da Silva Filho (PQ)[1]**

*e-mail: **ilana.sganzerla@unesp.br**

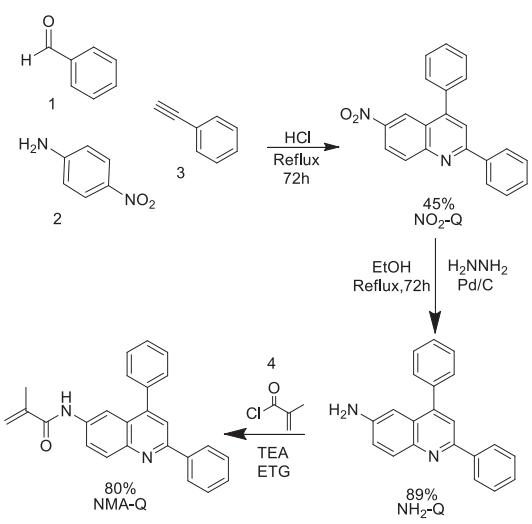
[1]Department of Chemistry, São Paulo State University (UNESP), School of Sciences, 17033-360, Bauru, São Paulo, Brazil
Keywords: quinoline derivatives, photopolymerization, photoinitiator, luminescent polymers, multicomponent reactions

Highlights

Fast and efficient photopolymerizations. Production of fluorescent polymers. Photopolymerization carried out under blue and UV light irradiation.

Abstract

In these work we related ours results about the synthesis, characterization and application of new quinoline derivative (Scheme 1) for actuation as Type II photoinitiator in the photopolymerization reaction of the monomer urethane dimethacrylate (UDMA), widely used in resin formulations for dental restoration. Methacrylated aminoquinoline (NMA-Q) was obtained in three steps with good yield, starting by Multicomponent reaction followed by reduction of nitro group and methacrylation of amino group. Photolysis analyzes of this derivative (NMA-Q) and synthetic intermediates (NO_2-Q and NH_2-Q) (Figure 1) show that the formation of reactive species occurs in the first second of exposure to light, providing clear evidence of the photosensitivity of these molecules. All synthesized quinoline derivatives were tested as photoinitiators in the UDMA photopolymerization reaction using a Kessyl lamp under 370 nm irradiation, and the polymers were obtained with a conversion rate of up to 49% in approximately 50 seconds. These results are very similar to those presented by camphorquinone, a commercial photoinitiator. It is worth mentioning that the polymers obtained have fluorescent characteristics (Figure 2), a characteristic that may be relevant for applications such as the dental field. The most recent results of this study were obtained from the thermal analysis of quinoline derivatives, which demonstrated thermal stability up to approximately 180ºC.



Scheme 1. Synthesis of quinoline derivatives

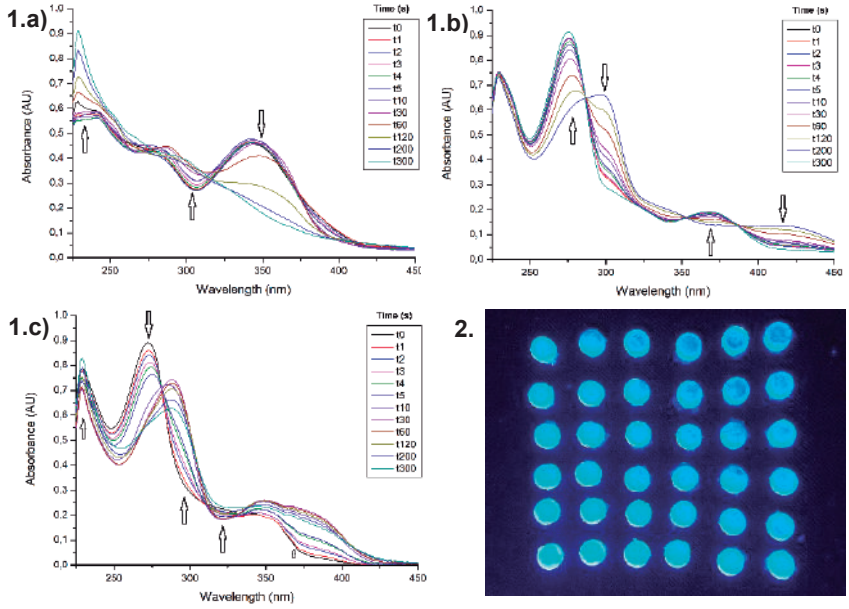


Figure 1. Photolysis behavior of a) NO_2-Q, b) NH_2-Q and c) NMA-Q.
Figure 2. Luminescent polymer of UDMA using quinolinic PI's

[1]. Moszner, N.; Völkel, T.; Fischer, U. K.; Klester, A.; Rheinberger, V., Angew. Makromol. Chem. 1999, 265 (1), 31–35.
[2]. Alarcon, R. T.; dos Santos, G. C.; de Oliveira, A. R.; da Silva-Filho, L. C.; Bannach, G., J. Appl. Polym. Sci. 2019, 136 (19), 47461.
[3]. Fouassier, J. P.; Lalevée, J. Photoinitiators for Polymer Synthesis; John Wiley & Sons, 2013

Acknowledgments

The authors would like to thank FAPESP (2018/09235-4 and 2018/14506-7), CAPES (88887.827622/2023-00), and Pró-Reitoria de Pesquisa da UNESP (PROPe-UNESP) for their financial support.

Área: MAT

Synthesis and characterization of α-MoO3 and polypyrrole composites

Arthur L. Santa Maria (PG)[1]*, Eryza G. de Castro (PQ).[1]

eryza.castro@gmail.com

[1]*Chemestry Departament, UNICENTRO*

Key Words: *Polypyrrole Molybdenum Oxide, Nanomaterials, Composite.*

Highlights

Polylyrrole and molybdenum oxide composites can be synthesized by direct polymerization in oxidative environment. This simple route process shows great particle dispersion in the polymetric matrix.

Resumo/Abstract

The molybdenum trioxide, α-MoO_3, was synthesized using MoS_2 as a precursor. This synthetic route consists of refluxing the precursor in oxidant media (HNO_3/H_2SO_4 aqueous solution) leading to α-MoO_3 with reduced size particles in nanobelt forms, high purity and strongly-preferred orientation. In sequence, the composite with polypyrrole was obtained by mixing the distilled pyrrole solved in hydrochloric acid, the ammonium persulfate (oxidizing agent) and the molybdenum oxide (10% m/m) in magnetic stirring for 24 hours. After that time the resulting material was centrifuged, washed, and dried at room temperature. The SEM images in A for the pure PPY and B for the composite show that the oxide is well integrated to the polymeric structure with good dispersion. The FTIR spectra in C presents the characteristic peaks for the PPY for both materials. The XRD in D shows the characteristic peaks for the α-MoO_3 in 23º ,25º and 27º overlapping the semicrystalline broad peak shown in the pure polymer. These peaks are in agreement with the α-MoO_3 diffraction pattern, indexed to the (110), (040) and (021) planes respectively. The composite and pure pyrrole also were characterized by EDS. The spectrum of pure pyrrole shows only peaks of the elements constituting the structure of this material, as well as some contaminants of the synthesis process. For the composite EDS spectrum, the elements present are the same, with the presence of the molybdenum. This data shows that the composite has good integration and dispersion of oxide, without changing the structure of the polymer, resulting in a promising new material for a wide range of applications.

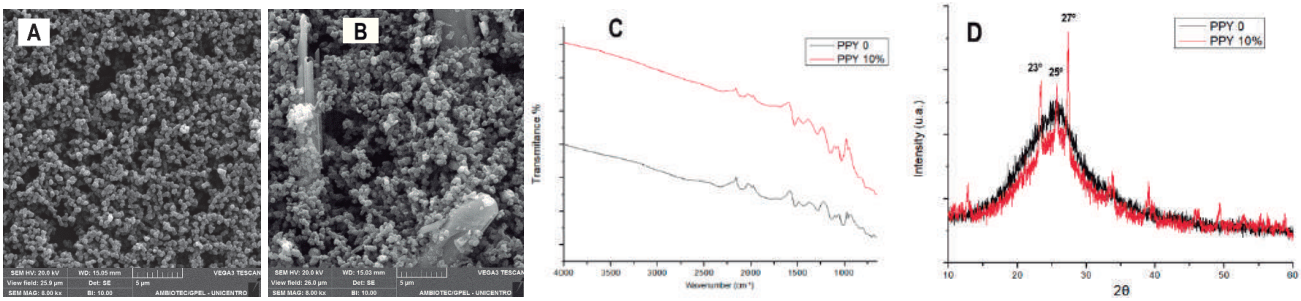


Figure 1: Pure PPY SEM (A), PPY/σ-MoO_3 composite SEM (B), FTIR Spectra (C) and XRD Diffractogram (D)

References:

1 - H. Sinaim, D. J. Ham, J. S. Lee, A. Phuruangrat, S. Thongtem, and T. Thongtem, "Free-polymer controlling morphology of a-MoO_3 nanobelts by a facile hydrothermal synthesis, their electrochemistry for hydrogen evolution reactions and optical properties," J. Alloys Compd., vol. 516, pp. 172–178, 2012.

2 - Bortoti, A.A.; Gavanski, A. de F.; Velazquez, Y.R.; Galli, A.; Castro, E.G. de Facile and low-cost oxidative conversion of MoS2 in α-MoO3: Synthesis, characterization and application. Journal of Solid State Chemistry, v. 252, n. May, p. 111–118, 2017.

Agradecimentos/Acknowledgments

UNICENTRO PARANÁ · QUÍMICA APLICADA · CAPES · Finep INOVAÇÃO E PESQUISA · FUNDAÇÃO ARAUCÁRIA

Área: MAT

Synthesis and characterization of cobalt hexacyanoferrate/carbon nanotubes/folic acid nanocomposites for breast cancer therapy.

Hellen C. Novais de Oliveira (PG),[1*] Patrícia Alves de Matos (PG),[1] Luciana Machado Bastos(PQ)[2] ,Tayana Mazin Tsubone (PQ),[1] Edson Nossol (PQ).[1]

hellen.oliveira@ufu.br;

[1]Instituto de Química, UFU; [2]Laboratório de Nanobiotecnologia Professor Dr Luiz Ricardo Goulart Filho, UFU.

Keywords: *metallic hexacyanoferrates, carbon materials, cancer therapy.*

Highlights

Cancer, a top cause of death, faces new hope with nanocomposites. Synthesis of cobalt hexacyanoferrate/carbon nanotubes/folic acid showed promising efficacy against breast cancer cells MDA-MB 231, presenting potential for innovative treatment.

Abstract

Breast cancer is the most commonly diagnosed cancer among women and is also the leading causes of female mortality[1]. Conventional treatments, such as radiation and chemotherapy, have limitations such as cytotoxicity and drug resistance to multiple drugs. In this context, nanocomposites are attracting a great deal of attention as advanced nanocarriers for highly efficient delivery of drugs to treat cancer. Probably, due to their unique properties including retention effect, decreased toxicity, precise targeting and enhanced permeability[2].

Then, the aim was to synthesize functionalized carbon nanotubes (CNTf) associated with cobalt hexacyanoferrate (CoHCF) and folic acid (FA) and test their toxicity effects on breast cancer cells, here used MDA-MB 231 cell line. The synthesis of CoHCF/FA/CNTf was based on a precipitation method. The first step was the preparation of solutions A and B; solution A was a mixture of cobalt nitrate, sodium citrate, FA and CNTf, while solution B was potassium ferricyanide (III). Then, solutions were mixed by stirring for 1 hour and the mixture was aged at room temperature for 18 h[3]. Finally, the final nanocomposite was obtained after centrifugation with water and ethanol. In the Raman spectra, the presence of the carbon materials was confirmed by the characteristic bands: D (1345 cm^{-1}), G (1587 cm^{-1}) and 2D (2699 cm^{-1}). As for the spectrum of CoHCF, there are a vibrational band at 2112 – 2181 cm^{-1} and peaks around 510 cm^{-1}. The UV – Vis and photoluminescence spectra of the aqueous dispersions showed significant peaks at 400 – 600 nm.

Cell viability assay was performed at 5 concentrations (0.1, 0.2, 0.5, 0.8, and 1.0 mg/mL) of nanocomposites. At 0.2 mg/mL, higher cytotoxicity of CoHCF/FA/CNTf (68,96%) was observed compared to CoHCF/CNTf (44,44%) and CoHCF (37,88%) suggesting that nanocomposite is more toxic than controls. At concentrations ≥ 0.5 mg/mL, there are no significant difference of cytotocixity between CoHCF/FA/CNTf and CoHCF/CNTf. Both exhibited similarly percentage of cell death.

Characterizations proved the synthesis's success. The UV-Vis spectra exhibited strong absorption in the visible region and preliminar cell viability assays suggested a great potential of CoHCF/FA/CNTf against breast cancer treatment.

[1] SUNG, Hyuna et al. Global cancer statistics 2020: GLOBOCAN estimates of incidence and mortality worldwide for 36 cancers in 185 countries. **CA: a cancer journal for clinicians**, v. 71, n. 3, p. 209-249, 2021.

[2] LI, Jianmin et al. Recent advances in targeted drug delivery strategy for enhancing oncotherapy. **Pharmaceutics**, v. 15, n. 9, p. 2233, 2023.

[3] HAO, Yuting et al. Multifunctional Biodegradable Prussian Blue Analogue for Synergetic Photothermal/Photodynamic/Chemodynamic Therapy and Intrinsic Tumor Metastasis Inhibition. **ACS Applied Bio Materials**, v. 4, n. 9, p. 7081-7093, 2021.

Acknowledgments

CAPES, CNPq, FAPEMIG, INCT Nanocarbono, Instituto de Química – UFU, Universidade Federal de Uberlândia, INCT TeraNano.

Área: MAT

Synthesis and characterization of fluorescent mesoporous silica nanorods (MCM-41) labelled with fluorescein isothiocyanate (FITC)

Daniel P. Levita (IC),[1] Wilson S. do Nascimento (PQ)[1], Nathalia M. da Costa (PQ)[2], Aline F. M. da Silva (PQ)[1] and Célia M. Ronconi (PQ)[1*].

danielpl@id.uff.br; cmronconi@id.uff.br

[1]Departamento de Química Inorgânica, Universidade Federal Fluminense (UFF), 24020-141, Niterói, RJ, Brasil; [2]Programa de Carcinogênese Molecular, Instituto Nacional de Câncer (INCA), 20231-050, Rio de Janeiro, RJ, Brasil.

Keywords: *Silica nanoparticles, MCM-41, Nanorods, Fluorescein Isothiocyanate (FITC), Fluorescence, Drug delivery.*

Highlights

MCM-41 nanorods obtained by conjugating the fluorescein isothiocyanate (FITC) fluorophore display high fluorescence and superficial area. A drug delivery platform will be constructed based on the obtained nanoparticles.

Abstract

Mesoporous silica nanoparticles (MSNs) exhibit interesting properties for the development of drug delivery systems, such as a high surface-to-volume ratio and good biocompatibility, which makes it suitable for application in devices such as nanovalves. It also features a versatile chemistry through its terminal silanol (Si-OH) groups, and modulable morphology, as we explored and demonstrated that a drug delivery system based on rod-shaped MCM-41 can better internalize MCF-7 cancer cells.[1,2] Due to its chemistry, new molecules can bind to or adsorb in silica's surface, such as fluorophores, giving rise to new properties in the material. Herein, we describe an effective sol-gel based approach for the preparation of FITC conjugated MCM-41 nanorods. To our knowledge, FITC was conjugated only to spherical MCM-41 nanoparticles so far. The commercially available green, fluorescent dye FITC was embedded covalently into the silica matrix through coupling with 3-aminopropyltrimethoxysilane (APTMS). The material was characterized by powder X-ray diffraction (PXRD), scanning electron microscopy (SEM) and confocal microscopy (CM) (Figure 1a-c). The X-ray diffractogram (1a) reveals a major ((100) at 2,1º) and two minors ((110) at 3,7º; (200) at 4,3º) diffraction planes, confirming the hexagonal symmetry and structure of the MCM-41 rods, with a length of about 200 nm, as seen by SEM (1b). Intense molecular emission from FITC was observed by CM (1c), associated with an expected absorption centered at 485 nm. A specific area of 1040 m^2/g (BET method), adequate to transport drugs, and a BJH pore volume of 0,90 cm^3/g (1d), were obtained for the material. Our perspectives are to develop a new nanovalve based on these nanoparticles and proceed with biological tests.

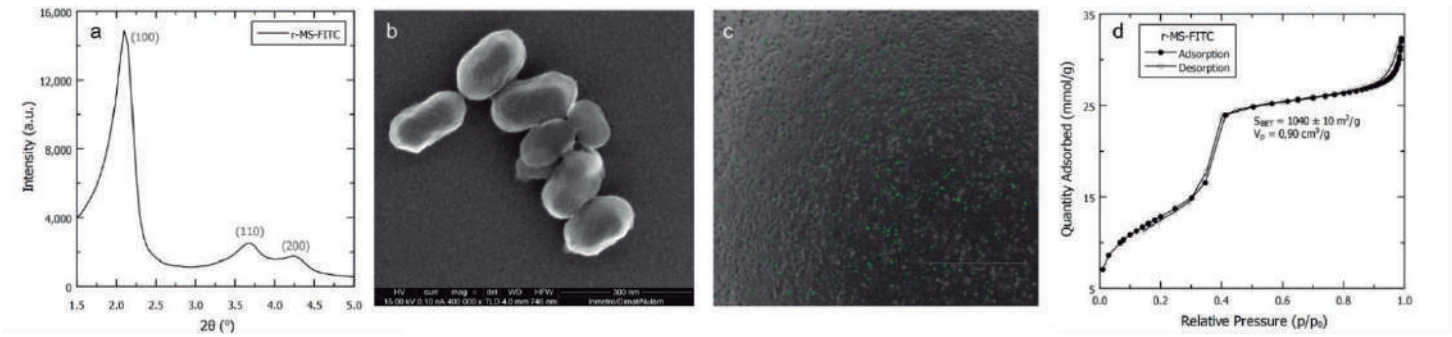


Figure 1. PXRD (a), SEM image (b), CM image (c) and N_2 Isotherms (d) of the FITC labelled MSNs.

[1] Noureddine, A. et al. *ACS nano*. **2023**, 17(17), 16308.
[2] Silva, A. F. M. Da et al. *ACS Applied Nano Materials*. **2022**, 13805.

Acknowledgments

CAPES, CNPq, FAPERJ (Programa Redes de Pesquisa em Nanotecnologia no Estado do RJ grant number E-26/010.000981/2019), PPGQ-UFF, LAME-UFF, LAMATE-UFF, LAMATE-UFRJ.

Área: MAT

Synthesis and characterization of high aspect Copper Nanowires

Barbara Perez G. Silva (PQ),[1*] Crystian W. C. da Silva,[1] Stefany R. Saraiva,[1] Larissa Otubo (PQ)[1]

barbara.silva@ipen.br

[1]*Centro de Ciência e Tecnologia de Materiais do Instituto de Pesquisas Energéticas e Nucleares (IPEN)*

Keywords: *Copper Nanowires, Polyol method*

Highlights

High aspect Copper Nanowires synthesis by polyol method; potential material to be applied in transparent conductive films.

Resumo/Abstract

Copper nanowires (CuNWs) are one-dimensional materials with excellent optical, electrical and mechanical properties. For this reason, they have gained attention to scientific community due to their applications possibilities, as optoelectronic devices.[1] In particular, copper is a very good candidate for commercial applications because of their high abundance and low cost, compared to silver, for example, that is the most used and studied metal for this kind of application. CuNWs can be obtained by different methods from the metallic precursor reduction, followed by the nucleation and growth. In this process, a surfactant is used as a capping agent to stabilize the nanostructures and a reducing agent to reduce the copper ions. Here, we present the synthesis of CuNWs using ethylene glycol (EG) as reducing agent, oleylamine and NaBr as capping agents, that adsorbs preferentially on {100} plane of copper, favoring the growth in [110] of nanowires,[2] as could be checked by XRD data and the peaks at 43°, 50° and 74° that correspond to the (111), (200) and (220) planes of Cu-fcc. The CuNWs were also observed by high resolution transmission electron microscopy (HRTEM) and it was possible to see the wires crystallinity and the amorphous region surrounding the structures. Uv-vis absorption spectra show a characteristic peak in 385 nm that can be attributed to the plasma resonance of CuNWs. Otherwise, there was identified the presence of copper oxide (Cu_2O) by XRD, suggesting that the reduction was not complete. The morphology was analyzed by scanning electron microscopy (SEM) and atomic force microscopy (AFM) where very long and thin structures could be observed. The CuNWs synthesized by salt-assisted polyol method are a very good candidate to be applied in transparent conductive films.

References

1. Huang, S.; Liu, Y.; Yang, F.; Wang, Y.; Yu, T.; Ma, D.; *Environ Chem Lett* **2022**, *20*, 3005. [https://doi.org/10.1007/s10311-022-01471-4]

2. Choi, Y.-H.; Chae, Y.-S.; Lee, J.-H.; Kwon, Y.; Kim, Y.-S.; *Electronic Materials Letters* **2015**, *11*, 735. [https://doi.org/10.1007/s13391-015-4502-6]

Agradecimentos/Acknowledgments

The authors thank IPEN/CNEN and CNPq for financial support and the support given by the Center for Lasers and Applications' Multiuser Facility and Laboratório de Microscopia e Microanálise at IPEN-CNEN/SP.

Área: MAT

Synthesis and Characterization of peanut shell biochar composite with Co(II) and Zn(II) double hydroxysalt for application in the degradation of Congo Red dye

Ralf R.R. Junior (PG),[1]* Fábio S. Lisboa,[1] Adhimar F. Oliveira. [1]

ralf.junior@unifei.edu.br; fabiolisboa@unifei.edu.br; adhimarflavio@unifei.edu.br

[1]*Instituto de Física e Química, UNIFEI.*

Palavras Chave: *Biochar; double hydroxy salts; composite; Congo Red dye removal;*

Highlights

The composite synthesized exhibited 98% removal of Congo Red dye within a span of 120 minutes.

Resumo/Abstract

Water, essential for life, is limited in its consumable form, and this fraction is susceptible to contamination by organic pollutants such as pharmaceuticals, dyes, hormones, and pesticides. The environmental challenges carries the risk of adverse effects on living organisms. In response to this concern, there is a rising interest in the development of methodologies, specifically directed towards ensuring the safety of water for human consumption. [1] The application of biochar composites in organic contaminants removal is a trend in environmental sciences, once biochar has the potential of its adsorption and the metallic particles can act in catalytic processes, providing its mineralization. [2]

In this study peanut shell biochar with Co(II) and Zn(II) double hydroxy salt composite was synthesized, such as the Zn-Co double hydroxy salt. The double hydroxy salt was synthesized by introducing a solution containing Zn^{2+} and Co^{2+} ions at pH 8. Similarly, the composite was prepared by incorporating both metallic ions into biochar suspended in water, with the pH regulated to 8. The materials were characterized and applied in Congo Red dye photocatalytic removal experiments. X-ray diffractograms in Figure 1 confirm the formation of distinct crystalline patterns, specifically zinc-cobalt hydroxysalts. The optical characterization indicates that the materials exhibit semiconductor behavior under visible light. In photocatalytic removal experiments with visible light, a substantial 98.06% reduction in dye concentration was achieved after 120 minutes, as shown in Figure 2.

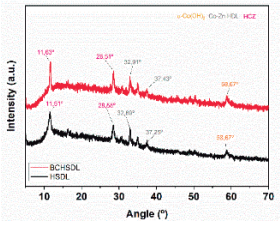


Figure 1 - XRD spectra of Co (II) and Zn(II) hydroxysalt and composite.

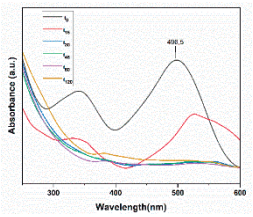


Figure 2 - *UV-Vis spectra of removal experiment.*

References

[1] Saidulu, D.; *et al.* **Journal of environmental Chemical Engineering**. 9, p. 105828, 2021.

[2] Lyu, H.; Zhang, Q.; Shen, B. **Chemosphere**, v. 240, p. 124842, 2020.

Acknowledgments

CAPES

PROGRAMA DE PÓS-GRADUAÇÃO MULTICÊNTRICO EM QUÍMICA DE MINAS GERAIS

LaCSin Laboratório Curie de Síntese

GCLAM Grupo de Compostos Lamelares

Área: MAT

SYNTHESIS AND CHARACTERIZATION OF POLYPHOSPHATE COACERVATES CONTAINING ELETRONIC RESIDUES

Aline Martins Feltran[1] (IC), Fabio José Caixeta[1] (PQ), Elias Paiva Ferreira Neto[2] (PQ), Sidney Jose Lima Ribeiro[1] (PQ), Douglas Faza Franco[1] (PQ).

aline.feltran@unesp.br

[1]*Instituto de Química, UNESP Araraquara;* [2]*Departamento de Química, UFSC*

Keywords: *Polyphosphates coacervates, electronic waste, Recycling, Rare Earth (RE).*

Highlights

The formation of a colloidal system from the chemical interaction between the polyphosphate solution with waste from the recycling of fluorescent lamps via coacervate route at room temperature.

Abstract

The polyphosphate coacervates (PCs) are colloidal systems obtained through the coacervation process at room temperature [1]. The coacervation process occurs through the liquid-liquid separation by the interaction between a concentrated solution of sodium polyphosphate with different metallic ions, such as Ca^{2+}, Mn^{2+}, Ni^{2+} among others [1]. In this work, we synthesized PC by adding electronic waste from the recycling of fluorescent lamps via a simple coacervation route at room temperature, using sodium polyphosphate $(NaPO_3)_n$ as a complexing agent. The polyphosphate coacervates were synthesized by two routes: **Route 1:** involved the direct addition of 0.01 and 0.025 mg of solid residue (waste) to 15 mL of $(NaPO_3)_n$ solution (4 M). The mixture was stirred slowly for 3 hours at room temperature, leading to a phase separation. The supernatant was then discarded, and the phase rich in colloids were dried in a desiccator for 10 days. **Route 2:** Initially, 250 mL of residue solution (1 mg m L^{-1}) was prepared using HCl (1 M). Subsequently, 15, 20, 25 and 30 mL of this solution were added to 15 mL of $(NaPO_3)_n$ (4 M), with the addition 5 mL of ethanol to induce the coacervation process. In this case, phase separation occurred, and the PCs were properly dried in a desiccator. The PCs were characterized through XRD analysis, Infrared and Photoluminescence spectroscopies. Visually, polyphosphate coacervates are opaque and hygroscopic. The preliminary results obtained from the XRD analysis indicated the presence of pyrophosphate and orthophosphate crystalline phases. The Infrared absorption spectra of the PCs from the two synthetic routes showed a shift in the two main vibrational modes of polyphosphate at 680 and 1080 cm^{-1}, assigned to the symmetric (P-O-P) and (P-O^-) stretches, respectively. In other words, this shift suggests the coordination of metal ions such as Ca^{2+}, Eu^{3+} and/or Tb^{3+} to the polyphosphate chains. The emission spectra of the PCs obtained from the route 1 exhibit electronic transitions at $^5D_0 \rightarrow {}^7F_2$ (614 nm) and $^5D_4 \rightarrow {}^7F_5$ (544 nm), indicating the presence of Eu^{3+} and Tb^{3+} ions, respectively. In contrast, the emission spectra of the PCs from route 2 show electronic transition at $^5D_0 \rightarrow {}^7F_2$ (614 nm) assigned to Eu^{3+} ions, indicating the coordination of the Eu^{3+} instead of Tb^{3+} to the polyphosphate in this synthetic route. In conclusion, the preliminary results indicate the feasibility of synthesizing polyphosphate coacervates (PCs) from fluorescent lamp residues. This method proves to be a simple, low-cost route that is highly effective in the separation of metal ions, such as Eu^{3+} and Tb^{3+}, facilitated by the use of $(NaPO_3)_n$ as a complexing agent.

References

[1] Franco, D. F. et al., J Sol-Gel Sci. Technol. 94, 531–543 (2020).

Acknowledgments

I would like to express my deep gratitude to CNPq (process number 407747/2022-2), to IQ-UNESP and to Photonics group, especially to my advisors Prof. Dr. Douglas F. Franco and Dr. Fábio J. Caixeta for all the assistance granted.

Área: MAT

Synthesis of a New Glycerol-Derived Eco-friendly Polymer by Photoinduced Thiol-Ene Reaction

Gabriel I. dos Santos (IC),[1*] Caroline Gaglieri (PD),[1] Fernanda B. Dos Santos (IC),[1] Gilbert Bannach (PQ),[1]

gabriel.i.santos@unesp.br

[1]*São Paulo State University (Unesp), School of Sciences, Chemistry Department, Bauru.*

Key words: *Photopolymerization, Renewable Resources, Thiol-ene, Glycerol, Maleic Anhydride.*

Highlights

A sustainable monomer was synthetized from Glycerol (a byproduct from biodiesel production) and maleic anhydride without solvents by a one-step reaction; The photopolymerization was used to reach a new renewable polymer by the thiol-ene reaction.

Abstract

Nowadays, with the increase in the consumption of polymeric materials from non-renewable sources, there is a strong demand for new eco-friendly/renewable raw materials and products in order to decrease the dependency on these non-renewable sources. In this context, it becomes necessary that new models of green synthesis and sustainable products be developed and seek to contemplate the principles of Green Chemistry [1]. As most polymeric materials come from finite sources such as petroleum and natural gas, glycerol (a byproduct from biodiesel production) and maleic anhydride emerge as proponents of green inputs for the production of renewable materials. In this case, the present work performed a one-step reaction between glycerol and maleic anhydride in order to obtain a monomer with available double bonds. The reaction was optimized by using sulfuric acid as an acid catalyst and its influence in the final product was investigated. The monomer produced was characterized by Proton Nuclear Magnetic Resonance (^{1}H-NMR), Mid-infrared spectroscopy analysis (MIR), and thermogravimetry–differential thermal analysis (TG–DTA) indicating that the reaction occurred successfully. A monomeric system was produced by mixing the renewable monomer obtained and the polythiol pentaerythritol tetrakis(3-mercaptopropionate), and then was photopolymerized under UV light irradiation (365 nm) in the presence of the photoinitiator 2,2-Dimethoxy-2-phenylacetophenone (DMPA) reaching a high value of conversion which was determined by MIR analysis observing the decrease in the double bonds band as expected in thiol-ene reactions [2]. The renewable polymer obtained (Figure 1) was characterized by TG-DTA and SEM analyses indicating that this new material has a thermal stability up to 61.0 ºC and a non-rough surface.

Figure 1 – Renewable polymer obtained after photopolymerization under UV light (365 nm).

References:

1. ANASTAS, P.; EGHBALI, N. Green chemistry: principles and practice. Chemical Society Reviews, v. 39, n. 1, p. 301-312, 2010.
2. MACHADO, T. O.; SAYER, C.; ARAUJO, P. HH. Thiol-ene polymerization: a promising technique to obtain novel biomaterials. European Polymer Journal, v. 86, p. 200-215, 2017

Acknowledgments

São Paulo Research Foundation (FAPESP, grants: 2021/02152-9, and 2022/03489-0), and CNPq (grants 303247/2021-5 and 150233/2022-1).

Área: MAT
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Synthesis of composites based on cerium hexacyanoferrate and carbon materials using the co-precipitation method.

João Leal da Silva (IC),[1] Diego Alves Peixoto (PQ),[1] Edson Nossol (PQ).[1]

jlealsilva@ufu.br

[1]*Instituto de Química, UFU*

Keywords: *Cerium Hexacyanoferrate, Graphene Oxide, Carbon Nanotubes, Energy Storage Devices.*

Highlights

In the present work, a novel composite of cerium hexacyanoferrate and carbon materials was obtained. The best control of particle size was obtained when the synthesis time was 3 hours.

Resumo/Abstract

Due to world increase in energy consumption, it is necessary to develop new forms of energy storage that offer an efficient alternative to current lithium-ion batteries. Prussian blue analogue based materials are starting to turn attention because of their properties and their ability to store alkaline/alkaline earth ions in their structure.[1] The present work aimed to synthesize cerium hexacyanoferrate (CeHCF) and its nanocomposites formed with graphene oxide (CeHCFGO) and carbon nanotubes (CeHCFCNTs). In addition, the electrochemical properties of the synthesized materials were evaluated for possible application in energy storage devices. Pure CeHCF and its composites with carbon materials were synthesized by co-precipitation method. To find the best conditions for obtaining the materials, synthesis parameters such as stirring time and concentration of reagents were studied. Furthermore, the addition of organic solvents to the reaction medium to control the morphology and size of CeHCF particles was also studied.

The results of infrared spectroscopy (FTIR) of the synthesized materials showed the typical C≡N bond around 2050 cm^{-1} present in the CeHCF structure. The bands located about 450 and 600 cm^{-1} are attributed to the Fe–C and Fe–C≡N bonds, respectively.[3] The Raman spectra of the synthesized materials showed vibrational modes located between 2050-2100 cm^{-1}, attributed to the interaction of the C≡N bonds with the Fe sites in different oxidation states. For composites, the presence of the D and G bands characteristic of carbon materials were observed, located at 1340 and 1580 cm^{-1}, respectively. Through the ratio between the intensities of the D and G bands, it was observed that CeHCF particles caused changes in the number of structural defects in carbon materials. Also was performed the Cyclic Voltammetry of CeHCF and its carbon composites, the observed voltametric profile presented the oxidation and reduction peaks referent to the Fe^{2+}/Fe^{3+} present in the structure of the compounds. The images taken by SEM showed that the different synthesis parameters were able to impact the formation of the material, in which the shortest magnetic stirring synthesis demonstrated particles of smaller and regular sizes.

Through the characterization of the material, it is possible to state that the synthesis was successfully, and future steps can apply it in energy storage devices.

Agradecimentos/Acknowledgments

UFU, FAPEMIG, CAPES, CNPq, INCT Nanocarbono and GMIT.

---

[1]Peng, J.; Li, C.; Yin, J.; Wang, J.; Yu, Y.; Shen, Y.; Fang, J.; Chen, A.; Xu, Y.; Rehman, R.; Fang, C.; Miao, L.; Jiang, R.; Li, Q.; Han, J.; Huang, Y. ACS Appl. Energy Mater. **2018**, *2*, 187-191.

[2]Oliveira, D.R.; Fernandes, D.S.; Carmo, D.R. Electroanalysis. **2020**, 32, 1524-1532.

[3]Peixoto, D.A.; Silva, S.C.; Borges, P.H.S.; Lima, R.C; Nossol, E. *J Mater Sci.* **2023**, *58*, 2993–3024.

Synthesis of FeHCF/Nb_2O_5 based filaments for the production of electrodes via 3D printing for the development of energy storage devices

Michele Verena C. O. da Silva (PG),[1*] Jéssica S. Stefano (PQ), Eduardo M. Richter (PQ), Rodrigo A. A. Munoz (PQ), Edson Nossol (PQ)*

*micheleverena066@gmail.com; enossol@ufu.br.

[1]*Chemistty Institute, Federal University of Uberlândia, Uberlândia, MG, Brazil*

keywords: *FeHCF, Nb Oxide, 3D-printed electrodes, Conductive filaments.*

Highlights

This work shows the electrochemical synthesis of filaments based on niobium oxide (Nb_2O_5), iron hexacyanoferrate (FeHCF) associated with carbon materials such as reduced graphene oxide (rGO), carbon black (CB) and the polymer polylactic acid (PLA) for the production of ready-to-use electrodes, which are additively manufactured (3D printed), without the need for additional treatments in order to overcome the limitations of commercial filaments already described in the literature, seeking to boost efficient and accessible electrochemical technologies, promoting the development of conductive filaments for the purpose of energy storage devices.

Abstract

3D printing technology has been widely explored in the field of chemistry, with applications in materials science, electrochemistry and analytical chemistry. Among the different 3D printing techniques available, fused deposition modeling (FDM) can be highlighted, due to its accessibility, and specially for the possibility of developing new printing materials (filaments) which can be produced in laboratory with the most varied compositions, allowing the production of filaments containing distinctive materials, ideal for the construction of electrochemical devices such as battery cathodes. However, the production of conductive filaments can be a challenge, since the addition of conductive fillers can make difficult the obtention of the electrode. In addition, the use of 3D-printed electrodes frequently requires pre-treatment or activation steps previous to their use to improve their conductivity. The present work presents the development and characterization of a compound, combining Nb_2O_5, FeHCF, rGO, CB, and the PLA polymer, for the production of conductive filaments with applications in energy storage devices. In this context, taking advantage of the properties of carbon materials, including excellent conductivity and high electrochemical stability, we propose the synthesis of FeHCF combined with Nb_2O_5 by coprecipitation. This material was then added to a reflux system, in conjunction with CB, rGO, PLA, and a mixture of solvents, and left under stirring and controlled temperature for 3 h. After recrystallization of PLA with ethanol, the composite material was obtained, and posteriorly the filament after an extrusion process. The Raman spectra of the 3D printed electrode revealed the presence of defects, sp^3 hybridization, vacancies, edges, and heteroatoms associated with the vibrational values D (1356 cm^{-1}) and G (1585 cm^{-1}). Furthermore, the presence of sp^2 carbon is attributed to the G band, and the two-dimensional signal is related to the two-dimensional order in the rGO plane. The characteristic band at (2150 cm^{-1}) of FeHCF was observed and attributed to the stretching vibration ν(CN), while the band (238 cm^{-1}), (695 cm^{-1}) is conditioned to NbO vibrations. To demonstrate the potential application, electrochemical measurements were carried out by cyclic voltammetry without any treatment steps. The voltammograms recorded at the FeHCF- Nb_2O_5/CB/rGO/PLA electrode exhibited two pairs of well-defined redox peaks (I and IV +0,2V), and (II and III +0,9V), that showed an increased response (55,1-times higher) in the presence of Nb_2O_5. Different works have discussed the composition, structure, and redox peaks of FeHCF-CB/rGO, and little is discussed about the presence of Nb_2O_5. The well-known insertion/disinsertion of cations in the FeHCF structure allowed the use of this material in a charge/discharge test, to posteriorly apply this material as battery cathode. Thus, a new and improved filament was successfully developed, with great potential to be applied as battery cathode with no further pre-treatment steps, driving to significant advances in the development of more efficient and affordable devices for practical application in energy storage devices.

Acknowledgments

We acknowledge to FAPEMIG, CAPES, CNPQ, INCT Nanocarbon for the financial support, and to NUPE and IQ-UFU groups.

1 Nossol, E; Zarbin, A. J. G. Electrochromic properties of carbon nanotubes/Prussian blue nanocomposite films. Sol. Energy Mater Sol. Cells, v. 109, p. 40–46, 2013a.
2 Cardoso, R. M, Rocha, D. P, Rocha, R.G. et al. 3D-printing pen versus desktop 3D-printers: Fabrication of carbon black/polylactic acid electrodes for single-drop detection of 2,4,6-trinitrotoluene. Anal Chim Acta. 2020;1132:10–9.
3 Richter, E. M. et al. Complete Additively Manufactured (3D-Printed) Electrochemical Sensing Platform. AnalChem. 2019;91(20):12844–51.
4 Silva, S. C; Nossol, E; Cardoso, R. M; et al. Reduced graphene oxide/multi-walled carbon nanotubes/prussian blue nanocomposites for amperometric detection of strong oxidants. Mat. Chem. Phys. 2020; 123011.

Área: MAT

Synthesis of $LiNbO_3$ using modified Pechini method: Rietveld refinement and photoluminescent properties

Wanison A. G. Pessoa Júnior (TM),[1*] Ingrity S. C. Sá (PQ),[2] Francisco X. Nobre (PQ),[3] Paulo R. C. Couceiro (PQ),[4] .

wanison.junior@ifam.edu.br

[1]Polo de Inovação - Inova, IFAM; [2]Instituto de Saúde e Biotecnologia Coari, UFAM; [3]Departamento de Química, Ambiente e Alimentos – CMC, IFAM; [4]Departamento de Química, UFAM.

Keywords: Lithium niobate, Pechini method, Rietveld refinement, Photoluminescence

Highlights

- The $LiNbO_3$ was obtained by a modified Pechini method.
- The desired material was successfully obtained by a low-cost and easy-to-execute method;
- $LiNbO_3$ showed 43.21% PL emission in the green region.

Abstract

Lithium Niobate, $LiNbO_3$ (LN) is one of the most interesting members of the niobate family because of its exceptional ferroelectricity, high Curie temperatures, photorefractive and photovoltaic behavior. This set of properties gives it a broad range of applications in actuators, waveguides, holographic memory devices and more recently Li-ion batteries. However, all these properties are strongly correlated to stoichiometry. A wide range of synthesis routes have been developed aiming to make the process easier, less expensive, and capable of maintaining the correct Li/Nb ratio to achieve the desired property. High temperatures and sensitive reagents problems can be sorted out by using the Pechini method (PM). The PM is a wet chemical method that uses an α-carboxylic acid (i.e. citric acid) as a chelating agent in the presence of ethylene glycol, thus ensuring homogeneity at the molecular level producing high-quality powders. In the present work, a modified PM was used to synthesize LN powders using ammonium niobium oxalate, lithium carbonate (Li_2CO_3), citric acid and ethylene glycol. The LN precursor was prepared by adding Li_2CO_3 to the niobium precursor solution in the molar ratio 1:1 (Li:Nb). This solution was then heated at 80 ºC to form a polyester, which was preliminarily calcined at 400 ºC for 2 hours to obtain a black powder, named puff. Finally, the NL was prepared by calcining the puff at 500 ºC. The X-ray diffraction (XRD) and Rietveld refinement (Figure 1a) revealed the formation of the pure phase of $LiNbO_3$, with a high degree of crystallinity, and trigonal structure phase of the space group *R-3c*. All indexed crystallographic planes were in agreement with the ICSD card n° 61118. The Rietveld refinement showed an excellent agreement between experimental and theoretical data, resulting in the quality parameters: R_{exp} = 10.09, R_p = 9.13, R_{wp} = 12.1 e χ^2 = 1.44, and network parameters: a=b= 5.1487 Å, c = 13.8521 Å, α=β= 90° and γ= 120°. The Photoluminescent spectrum (PL) of LN and its deconvolution (Figure 1b) showed a photoluminescent contribution in the green region of the electromagnetic spectrum, with maximum absorption at 527 nm and 43.21% PL emission, which implies the presence of intrinsic defects. These results indicated that LN was successfully obtained using the PM, which has the advantages of controlling size, morphology and stoichiometry, in addition to being an easy-to-execute, low-cost and mild-temperature route.

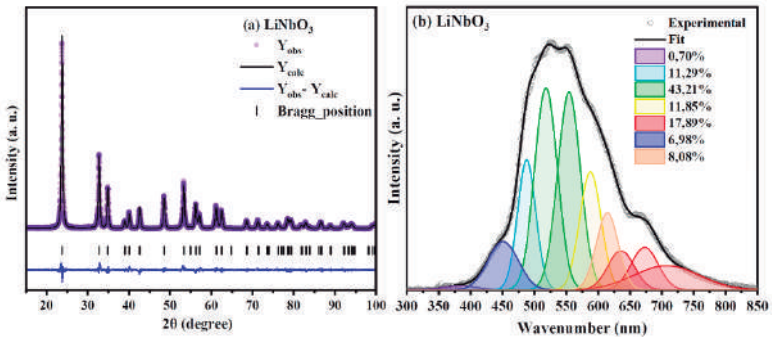


Figure 1. a) XRD and Rietveld refinement results and **b)** PL spectrum and its deconvolution of $LiNbO_3$.

Acknowledgments

The authors are grateful to IFAM, Central Analítica (IFAM CMC), and UFAM for analysis, as well as FAPEAM, CAPES (Finance Code 001), and CNPq for financial support.

Área: MAT

Synthesis of Pd Nanoparticle Supported on Aluminum Oxide by Mechanochemical Route and its application in Suzuki-Miyaura Reaction

Mattheus H. M. Mendes (PG), [1*] **Paulo F. M. de Oliveira (PQ).** [1]

mattheus.mendes@usp.br;

[1]*Instituto de Química, USP*

Palavras Chave: *Synthesis, Mechanochemistry, nanoparticle, Catalysis and Suzuki-Miyaura.*

Highlights

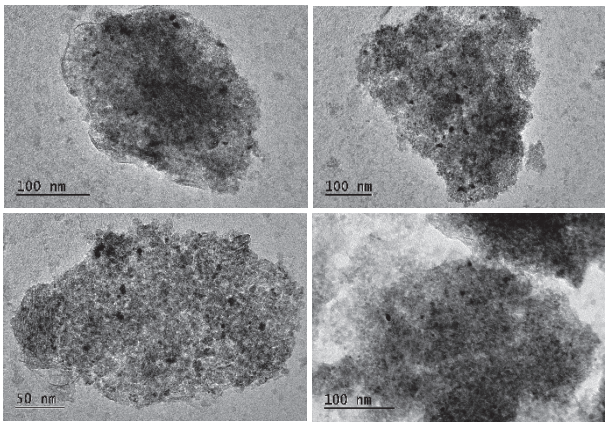
The Palladium nanoparticle supported on aluminum oxide synthetized by planetary milling was characterized by several techniques and was empolyed in organic solid-state Suzuki-Miyaura Reaction as a catalyst.

Resumo/Abstract

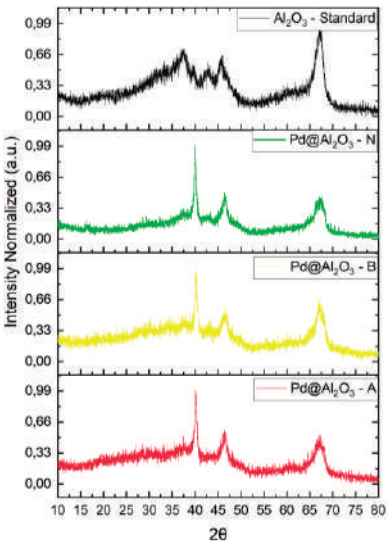
Mechanochemistry uses mechanical energy to promote chemical reactions in the solid state, dismissing, in the most of reactions, heating up and the use of toxic environmental solvents, being a potential green approach, alternative to conventional methods of synthesis.[1] Because of its advantages, different scientific areas have been using mechanochemistry to obtain a increase number of chemicals and materials,[2] including noble metallic nanoparticles.[3] In the synthesis of nanoparticles specifically, mechanochemistry can be used in two methods named as bottom-up or top down.[3] Metallic nanoparticles synthetized in the process can be used for many applications, for example catalysis, biosensing, imaging and energy.[4]

The bottom-up mechanochemical synthesis of noble metal nanoparticles are performed by planetary milling the metal precursor salt with the supporting oxide in the presence of a reducting agent. Specifically in this work, Pd^{2+} was reduced by $NaBH_4$ in the presence of Al_2O_3 as solid support. The nature of Al_2O_3 was also investigated, i.e. whether it is a neutral (N), basic (B) or acid (A) oxide. These materials were characterized by differents techniques as **(a)** Transmission Electron Microscopy (TEM), **(b)** Powder X Ray Diffraction (PXRD), X Ray Photoelectron Spectroscopy (XPS) etc, to confirm the presence of Palladium nanoparticles on the oxide sufarce.

a.



b.



The Palladium Supported synthetized was used as catalyst in Suzuki-Miyaura cross-coupling reactions, where all the reagents are in solid state.[5] The first catalysis was performed using the vibratory milling to obtain 4-biphenylcarboxaldehyde from biphenylboronic acid and 4-bromobenzaldehyde in basic environment. This product will be characterized and quantified by Gas Chromatography with Flame Ionization Detector acoupled (GC-FID), Nuclear Magnetic Resonance etc.

[1] A. A. L. Michalchuk, E. v. Boldyreva, A. M. Belenguer, F. Emmerling and V. v. Boldyrev, Front Chem, 2021, 9, 1–29. **[2]** W. Jones and M. D. Eddleston, Faraday Discuss., 2014, 170, 9–34. **[3]** P. F. M. de Oliveira, R. M. Torresi, F. Emmerling and P. H. C. Camargo, J Mater Chem A Mater, 2020, 8, 16114–16141. **[4]** C. Xu, S. De, A. M. Balu, M. Ojeda and R. Luque, Chemical Communications, 2015, 51, 6698–6713. **[5]** Klingensmith, L. M., Leadbeater, N. E. Ligand-free palladium catalysis of aryl coupling reactions facilitated by grinding. Tetrahedron Lett. 2003, 44, 765–768.

Agradecimentos/Acknowledgments

This work was financially supported by The São Paulo Research Foundation - FAPESP (FAPESP 2022/07640-4 and 2020/14955-6)

Área: MAT

Synthesis of sodium trititanate nanotubes by the hydrothermal method

Assis de O. Alves* (IC)[1]; Flávio M. Vichi (PQ)[1]

fmvichi@iq.usp.br; assis.alves@usp.br;

[1]*Department of Fundamental Chemistry, Institute of Chemistry, University of Sao Paulo (USP), São Paulo–SP, Brazil;*

Keywords:(sodium trititanate, nanotubes, hydrothermal method)

Highlights

We report the synthesis of $Na_2Ti_3O_7$ using the hydrothermal method, varying temperature, time and autoclave filling. Evaluate the nanostructures formed in post-thermal treatment. Characterization of the structure by XRD and the surface area and porosity by the BET isotherm.

Resumo/Abstract

Nanostructured titanates (TNS), obtained by alkaline hydrothermal treatment of TiO_2, are semiconductors widely studied for their properties such as surface area, porosity and ion exchange capacity. However, their morphology is heavily influenced by synthetic and post-reaction treatment conditions. In this study, synthesis parameters were varied in order to determine the morphology of the nanostructures. The materials were characterized by X-ray diffractometry (XRD), thermal analysis (TG, DTG and DSC), surface area analysis using the BET method by N_2 adsorption at 77 K, and transmission electron microscopy (TEM).

The nanotubes (Fig 1A) were obtained at 140ºC/ 24 h presented the diffraction pattern shown in Fig. 1B, and a surface area of 23 m^2g^{-1}. This value decreases as the calcination temperature increases, indicating an increase in crystallinity.

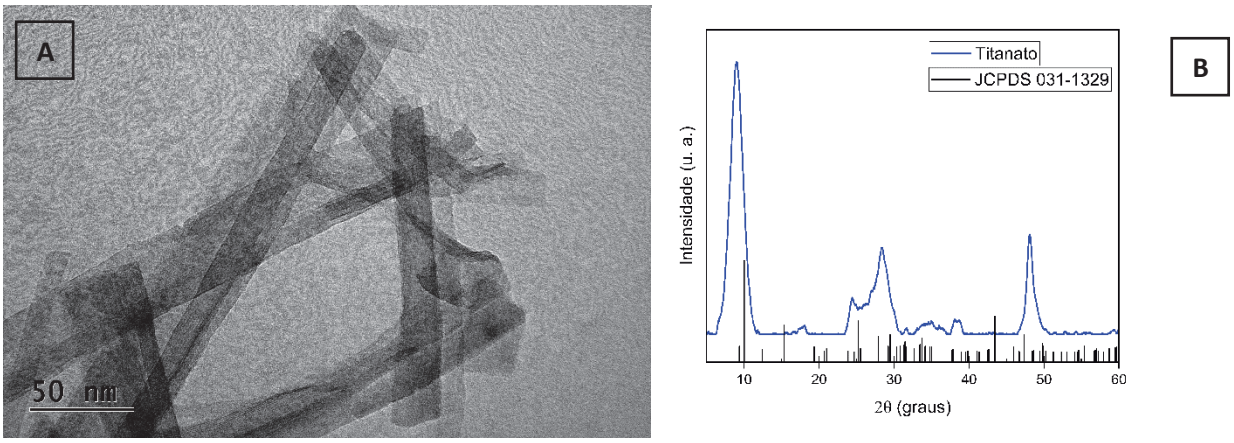


Figure 1: (A) TEM of nanotubes showing an average diameter of 7nm (B) XRD pattern of the particles showing a trititanate, $Na_aTi_3O_7$, crystal structure.

References

[1] Kasuga, T., Hiramatsu, M., Hoson, A., Sekino, T. and Niihara, K. (1999), Titania Nanotubes Prepared by Chemical Processing. Adv. Mater., 11: 1307-1311.

[2] Marina M. Leite, Vitor L. Martins, Flavio M. Vichi, Roberto M. Torresi; Electrochemistry of sodium titanate nanotubes as a negative electrode for sodium-ion batteries; Electrochimica Acta, Volume 331, 2020.

Agradecimentos/Acknowledgments

PROGRAMA UNIFICADO DE BOLSAS DE ESTUDO (PUB-USP), FAPESP, CNPq

Área: MAT

Synthesis of submicron inorganic particles based on lanthanides ions for random laser applications

Roberta S. Pugina (PQ),[1] Eloísa G. Hilário (PQ),[1] Tatiana Habib (PQ),[1] Manoel L. da Silva-Neto (PQ),[2] Lauro J.Q. Maia (PQ),[3] André L. Moura (PQ),[4] Anderson S.L. Gomes (PQ),[2] José Maurício Almeida Caiut (PQ).[1]*

caiut@ffclrp.usp.br

[1]Departamento de Química, FFCLRP; [2]Departamento de Física, UFPE; [3]Instituto de Física, UFG; [4]Instituto de Física, UFAL

Palavras Chave: *Spray pyrolysis, Rare earth materials, Stimulated emission, photonics.*

Highlights

Nd^{3+}: Inorganic particles without spurious phases have been prepared by spray pyrolysis.

The particles act as gain and scatter medium, leading to multidirectional laser emission

Resumo/Abstract

Optical materials for photonics and optoelectronics applications have been under demand for several decades, mainly due to the advantages of exploiting all-optical systems for a myriad of applications. On the other hand, the society has witnessed the development of nanoscience and nanotechnology, and once again when acting together, nanophotonic materials have found its own way into basic and applied science and technology. Among the diversity of nanomaterials exploited, rare earth-based materials in different formats, from bulk to powders and nanopowders have been in the forefront of many spectacular developments, leading to applications in biomedicine, environmental and optical communication systems. The NanoLum group at FFCLRP-USP report on the synthesis, characterization and application in random laser of Nd:YAG ($Y_3Al_5O_{12}$) and Nd:YAB (Nd:$Y_{1+x}Nd_xAl_3(BO_3)_4$), in the last samples, these particles were also decorated with nanometer diameter metallic (gold and silver) nanoparticles. Rare earth-based powder employed here was synthesized by the Spray Pyrolysis (SP) or Pechini method, leading to the preparation of $Nd3^+$ ions incorporated into YAG or YAB host, respectively, with submicron (600 nm average diameter), with ions concentration from 1 to 80%. Specifically on SP, this synthesis could produce particles in a few minutes, whereas the droplets stay in the pyrolysis zone for only 3–4 s, which prevent lanthanide clusters from arising and yield luminescent, spherical, highly doped Nd^{3+}:YAG particles without coalescence. The Nd:YAB submicron powder was independently decorated with gold and silver nanoparticles, using the atmospheric pressure plasma jet method. Powder X-Ray Diffraction (XRD), High-Resolution Transmission Electron Microscopy (HRTEM), and Selected Area Electron Diffraction (SAED) showed that the particles are well crystallized. Photoluminescence studies revealed the expected Nd^{3+} spectroscopic profile, and the narrow emission bands corroborate the assumption that the lanthanide ions replace Y^{3+} ions at the host. As a photonic application, the intense emission at 1064 nm, concerning the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition, was studied on random Laser emission as a result of different Nd^{3+} contents, and as the concentration of Nd^{3+} ion increases, the threshold energy decreases, e.g., the YAG doped with 5.0% of neodymium, the threshold was 0.2 mJ, almost five times lower than for the 2.5% concentration sample. Finally, a plasmonic enhancement on the RL threshold at different excitation wavelengths was carried out, exploiting the quantum effect. In conclusion, a Nd^{3+}:YAG or YAB micropowder Random Laser was demonstrated as a proof of concept for a future application, with characteristics similar to other Nd^{3+} based RL reported in the literature.

Agradecimentos/Acknowledgments

The authors acknowledge the Brazilian funding agencies FAPESP (Proc. Proc. 2019/18828-1 and 2021/08111-2) and Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) – Finance Code 001, as well as the University of São Paulo and The National Institute of Photonics – INFO (INCTs program) for financial support. CNPq is acknowledged for the grants received by José Maurício A. Caiut (303580/2021-6)

Área: MAT **N° de Inscrição: 138**

Synthesis of titanium- or silicon-doped calcium phosphate

Lauany M. Pontes [1]* (PG), João Vitor G. de Faria [1](PG), Lucas A. Rocha[1] (PQ), Eduardo J. Nassar [1] (PQ).

lauanymazzon@gmail.com; eduardo.nassar@unifran.edu.br

[1] Departamento de Química, UNIFRAN

Keywords: Biomateriais, Calcium phosphate, Bioactive Biomateriais, Biocompatibility.

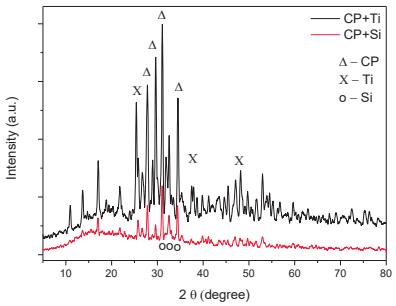
Highlights

Calcium phosphate (CP) occurs in the bone inorganic matrix. CP doping with titanium and silicon gives a biomaterial with improved mechanical and biological properties.

Abstract

The development of advanced materials aims to obtain new functionalities or to improve the existing ones. Biomaterials, which are under constant evolution, are examples of advanced materials. Human bone, based on calcium phosphate (CP), can be reproduced in the laboratory and can be tailored to add mechanical and biological properties. CP presents excellent biocompatibility and osteoconduction as well as bioactive properties; however, it has low resistance. To overcome this issue and to broaden its applications, this study focuses on adding chemical elements to the CP structure, to improve its properties. For this purpose, titanium (Ti) can be employed—Ti is non-cytotoxic, biocompatible, and resistant to corrosion, strain, and fracture, and it has excellent mechanical performance and low density. In turn, silicon (Si) is an oligoelement that occurs in the human body and which is important for bone mineralization and formation. Si addition to CP can provide enhanced bioactivity, allowing better tissue regeneration. Combining CP with Ti or Si may improve the biomaterial properties. We obtained CP by the precipitation method, from calcium nitrate and phophoric acid, as precursors. For the Ti-doped CP, titanium isopropoxide was used as precursor. As for the Si-doped CP, tetraethylsilicate was employed as precursor. Infrared spectroscopy analyses of the samples revealed bands at 1054 cm^{-1}, attributed to phosphate groups (P-O).

Figure 1: X-ray diffraction of the Ti- or Si-doped samples. The Δ, X, and O notations indicate the peaks due to CP, Ti anatase phase, and calcium silicate phase.



The X-ray diffractograms of the samples displayed peaks typical of calcium phoshate standard card n. 011-0177. After Si was added, peaks due to calcium silicate, standard card n. 01-1024, emerged. The Ti-doped samples displayed peaks due to the TiO_2 anatase phase, card n. 001-0562. Figire 1 shows the X-ray diffractograms of Ti-doped CP and Si-doped CP.

Acknowledgments

CAPES, CNPq, and FAPESP

Área: MAT

The impact of pKa on surface ligand composition via ligand exchange reaction in zirconia nanocrystals

Walter Sperandio Sampaio[1] (PG), Cleocir José Dalmaschio (PQ).

Cleocir.dalmaschio@ufes.br

[1]*Departamento de Química, Universidade Federal do Espírito Santo – Vitória/ES*

Surface Ligands, Ligand Exchange, Zirconia Nanocrystals, Colloidal Stability.

Highlights

Surface ligands present a crucial role in controlling nanocrystal growth and colloidal stability.
Ligand exchange, a key strategy, modifies nanomaterial surfaces without altering their characteristics.
Ligands exchange is more effective with lower pKa ligands, impacting surface composition.

Resumo/Abstract

Surface ligands are responsible for controlling growth and stabilizing the surface during production via chemical synthesis routes. Controlling the size, shape, and crystalline phase that the NCs exhibit yields different physicochemical effects; however, surface ligands can also affect NC behavior, either by surface passivation altering the bandgap in semiconductors or by enabling colloidal stability in different solvents [1]. Exchanging surface ligands in a second synthesis step has been a strategy employed to modify surface properties in nanomaterials and achieve desired behaviors without altering the characteristics of the produced nanocrystals [2].

A relationship exists between the amount of native surface ligands and the pKa value of solvents used in zirconia NC synthesis, where in oleic acid, the ligand quantity was higher than in benzyl alcohol and octyl alcohol [3]. This study investigated ligand preferences through a second synthesis step using the immersion method of NCs in solvent. Ligand exchange was performed using precursor solvents butyl alcohol and benzyl alcohol, which have similar pKa values, and oleic acid with the lowest pKa value.

Using the non-hydrolytic sol-gel chemical route with benzyl alcohol as the oxygen donor and zirconium butoxide as the precursor in butanol, ZrO2 NCs were synthesized with an approximate size of 5 nm, narrow size distribution, cubic crystalline phase, and isotropic morphology. Derived from synthesis reagents, butanoate and benzoate ligands cover the NC surface, forming a layer of native synthesis ligands [3].

FTIR analyses indicated that exchanging native ligands with excess precursor solvents does not entirely remove native ligands but significantly increases their quantity. Oleic acid was able to almost completely remove native ligands. Thermogravimetric analyses were used to quantify ligand from synthesis and presented after ligand exchange procedure. Results indicated a higher quantity of oleic acid covering the surface compared to native ligands, suggesting a preference for ligands with lower pKa values towards ZrO2 NC surfaces.

We conclude that ligand exchange occurs more with ligands having lower pKa values, and in solvents with similar pKa values ligands exchange does not occur. This work advances control over ligand layer composition through ligand exchange methods and the study of ligand interaction with zirconia nanocrystal surfaces.

References:

[1] M. A. Boles, D. Ling, T. Hyeon, and D. V. Talapin, Nat. Mater., vol. 15, no. 3, p. 364, 2016, doi: 10.1038/nmat4578.
[2] R. Deshmukh and M. Niederberger, Chem. - A Eur. J., vol. 23, no. 36, pp. 8542–8570, 2017, doi: 10.1002/chem.201605957.
[3] M. S. Santos, J. C. C. Freitas and C. J. Dalmaschio, CrystEngComm, vol. 22, no. 10, pp. 1802–1811, 2020, doi: 10.1039/c9ce01992h.

Agradecimentos/Acknowledgments

UFES, NCQP-UFES, LMC/LPT-UFES, CNPq, CAPES, FAPES.

Área: MAT

Thin and transparent films of PEDOT/gold nanoparticles: preparation and characterization

Eduarda Rubin (IC)[1], Carla Requena Klimpovuz (PG)[1] and Aldo José Gorgatti Zarbin (PQ)[1]*

eduarda.rubin@ufpr.br; carlaklimpovuz@ufpr.br; aldozarbin@ufpr.br

[1]Department of Chemistry, UFPR;

Key Words: Conductive Polymer, Nanoparticles, Thin Film, Nanocomposites

Highlights

Preparation of nanocomposites between PEDOT and gold nanoparticles (AuNPs) through spontaneous reaction, in the absence of polystyrene sulfonate (PSS). Thin films obtained with different proportions and reaction times, in a single step.

Abstract

Conductive polymers have unique electronic and optical properties. Among these polymers, (3,4-ethylenedioxythiophene) also known as PEDOT, presents high conductivity and good charge mobility due to non-covalent interactions between PEDOT chains.[1] Such polymer can be combined with gols nanoparticles (AuNPs), which present optical properties modulated according to their sizes and shapes. By varying reaction parameters, it is possible to obtain nanocomposites between PEDOT and AuNPs with synergistic properties. The aim of this work was to obtain nanocomposite thin films between PEDOT and AuNPs through a spontaneous reaction between the monomer EDOT and tetrachloroauricacid($HAuCl_4$), in the absence of PSS and in a single step. The nanocomposites were prepared through the liquid-liquid interfacial route, which consists of obtaining nanocomposite thin films at the interface between two immiscible solvents.[2] The two-phase systems studied were composed of an aqueous phase and an organic phase, containing EDOT and $HAuCl_4$, respectively. Six samples were obtained with different reaction times and different proportions between precursors. All the samples were obtained varying the ratio between the precurosos, and characterized by UV-Vis and Raman spectroscopy, XRD, and SEM-EDS. The characterizations show the spontaneous polymerization of EDOT concomitant to AuNPs formation. By varying the molar ratio of EDOT/$AuCl_4^-$, it was possible to obtain AuNPs of different sizes and nanocomposites with different electronic properties. Additional characterization techniques are being conducted to propose the mechanism of formation of these nanocomposites, as well as the type of interaction between AuNPs and PEDOT.

[1] YUK, H; Nature Comm, v. 11, 2020, p. 1604.

[2] Zarbin, A. J. G. Mater. Horiz. 2021, v. 8, p. 1409.

Acknowledgments

CNPq, CAPES, INCT NanoVida, INCT Nanocarbono and UFPR Scientific and Technological Initiation Coordination, GQM-UFPR

Área: MAT
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Towards Efficient Luminescent Materials: Triazine-Based TADF Emitters.

Hugo Gallardo (PQ),[1] Hugo Marchi Luciano (PQ),[2*] Marília Gabriela B. Cabral (PQ)[3], Fabrícia N. Silva (PQ)[4], Giliandro Farias (PQ)[1], Ivan H. Bechtold (PQ)[1], André A. Vieira (PQ)[4], Fabien Durola (PQ)[5], Harald Bock (PQ)[5].

hugo.gallardo@ufsc.br; hugo.marchi@udg.edu

[1]Departamento de Química, UFSC; [2]Institut de Química Computacional i Catàlisi, Universitat de Girona; [3]Centre for Organic and Nanohybrid Eletronics, Silesian University of Technology; [4]Departamento de Química, UFBA; [5]Centre de Recherche Paul Pascal, CNRS/Université de Bordeaux.

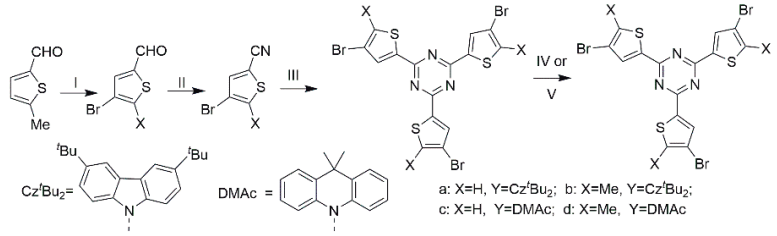
Key-words: *Donor-acceptor scaffolds, Electroluminescent dyes, Delayed fluorescence (DF).*

Highlights

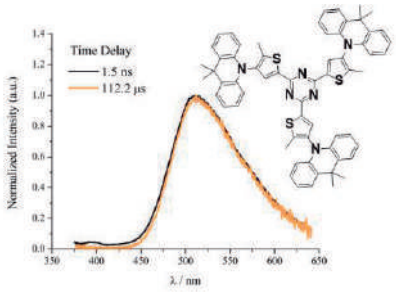
Recent advancements in Thermally Activated Delayed Fluorescence (TADF) materials exploit efficient singlet-triplet exciton transitions. Enhanced by sulfur-containing thiophene bridges, these materials exhibit both phosphorescence and TADF emission, promising for efficient electroluminescent dyes.

Resumo/Abstract

In recent years, significant advancements have been made in the development of Thermally Activated Delayed Fluorescence (TADF) materials. These materials possess a remarkable ability to efficiently utilize both singlet and triplet excitons for radiative transition, achieving high efficiency comparable to phosphorescent emitters while maintaining the stability of organic emitters. [1] Donor-acceptor scaffolds with an inner electron-accepting aromatic unit and three twisted outer electron-donating units exhibit enhanced oscillator strength compared to simple donor-acceptor systems. They are efficient electroluminescent dyes, as strong spin-orbit coupling (SOC) allows for fast singlet-triplet intersystem crossing leading to emission from both singlet and triplet states.[2] Significant progress has been made in the design of new TADF materials; however, a comprehensive understanding of the bridging connection between the Donor and Acceptor units remains largely unexplored. Therefore, a valuable strategy for obtaining new TADF materials is to explore various combinations of donor and acceptor components through the utilization of sulfur-containing thiophene rings. In a recent study conducted by our research group, we demonstrated that the incorporation of sulfur-containing thiophene bridges into D3A-type TTTs enabled the emission of RTP in solution.[3] However, the high value of ΔEST found in these materials made it impossible to obtain TADF. In light of this, we have now introduced sulfur-containing thiophene bridges between the donor and acceptor moieties in D3A-type triazines. The carbazole moiety in the triazine-thiophene structure allows for phosphorescence emission, while acridine derivatives exhibit TADF emission besides the phosphorescence in the solid state at low temperatures.



Scheme 1. I) Br2, AcOH, 3b: 60%; II) NH4OH(aq), I2, THF, 4a: 82%, 4b: 72%; III) CF3SO3H, 5a: 67%, 5b: 55%; IV) 3,6-di-tert-butyl-9H-carbazole, K2CO3, CuSO4.5H2O, 1-methylnaphthalene, 1a: 52%, 1b: 39%; V) 9,9-dimethyl-9,10-dihydroacridine, [Pd(OAc)2], Xphos, NaOt-Bu, toluene, 1c: 57%, 1d: 52%.



Agradecimentos/Acknowledgments

This work was funded by Capes-Cofecub, programme Eiffel, INCTcatálise/FAPESC/CNPq

References

[1] Shi, Y-Z. et al, *Chem. Sci.* 13, (2022), 3625-3651.
[2] Xie, F. M. et al, J. Mater. Chem. C. 8, (2020), 9476-9494.
[3] Luciano, H. M. et al, Chem. Eur. J. 29, (2023).

Área: MAT

Transparent glass composites with persistent luminescence: synthesis via viscous flow sintering and Synchrotron investigations

Roger G. Fernandes (PQ),[1-3] Elaine A. de Mattos (PG),[1] Victor M. P. da Silva (PG),[2] Danilo Manzani (PQ),[2] Veronica C. Teixeira (PQ),[3] Lucas C. V. Rodrigues (PQ).[1]*

lucascvr@iq.usp.br

[1]Department of Fundamental Chemistry, Institute of Chemistry, University of São Paulo IQ-USP; [2]Department of Analytical and Inorganic Chemistry, São Carlos Institute of Chemistry, University of São Paulo IQSC-USP; [3]Brazilian Synchrotron Light Laboratory (LNLS), Brazilian Center for Research in Energy and Materials (CNPEM)

Keywords: *Persistent luminescence, Glass Composite, Viscous Sintering, XRF nanomapping, XEOL*

Highlights

Transparent glass-ceramics with persistent luminescence were obtained via viscous sintering technique. Coherent X-ray synchrotron nanomapping was used to characterize the glasses microstructure.

Resumo/Abstract

In light of the rapid technological advancement, there is a growing interest in basic and applied research in physics, chemistry, and materials engineering focused on studying new multifunctional materials and techniques for modern applications. Here, we explored the incorporation of persistent luminescence particles (PeL) in glass through a process known as viscous flow sintering to obtain a transparent glass matrix composite material. Additionally, we investigated the potential dissolution of PeL within the glass matrix, potentially influencing glass crystallization and altering the material's physical and chemical characteristics. For this study, $SrAl_2O_4:Eu^{2+},Dy^{3+}$ (SAOED) synthesized via microwave-assisted solid-state reaction[1] was incorporated in soda-lime silicate glasses at temperatures ranging from 750-850 °C with or without low-pressure. In particular, we characterized the PeL before and after its incorporation in the glasses to compare the form parameters (size and shape), their distribution, and the optical properties. Finally, studies at CARNAUBA, the nanofocused coherent X-ray beamline of the Brazilian Synchrotron Light Laboratory (Sirius) indicated that X-ray Stimulated Optical Luminescence (XEOL) nanomapping (Fig 1d) is a more powerful tool than X-ray Fluorescence nanomapping (Fig. 1c) due to the X-ray attenuation from Silicon in the glass, blocking the emitted X-rays from particles deep inside the glass while their luminescence is not absorbed due to glass transparency (Fig. 1a).

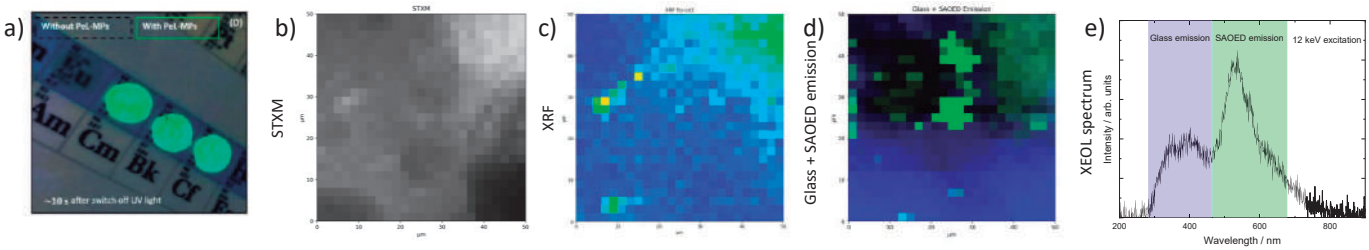


Figure 1. a) Photography of the PeL glasses after UV irradiation, b-d) Nanomapping at Carnauba using X-ray Transmission (b), X-ray Fluorescence (c) and XEOL (d). e) mean XEOL spectrum of the mapped region.

Reference:

1. Carvalho, J.M., Pedroso, C.C.S., Saula, M.S.N., Felinto, M.C.F.C., Brito, H.F. Molecules, 26 (2021) 2882.

Agradecimentos/Acknowledgments

FAPESP, CNPq, CAPES and LNLS-CNPEM

Área: MAT
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Unsaturation pattern modulates the activity of antiprotozoal acetogenins with microbial cell membrane models by Langmuir films

Matheus E. Rosa* **(PG),[1] Ivanildo A. Brito (PG),[2] João H. G. Lago (PQ),[2] Luciano Caseli (PQ),[1]**

matheus.elias@unifesp.br

[1]*Departamento de Química, UNIFESP;* [2]*Centro de Ciências Naturais e Humanas, UFABC*

Palavras Chave: *Langmuir, Acetogeninas, Modelo de membrana, Filmes, Produtos naturais, Nanomateriais.*

Highlights

The effects of three structurally similar acetylenic acetogenins on microbial cell membrane models by DPPE Langmuir films were evaluated, one being active against some protozoa cells. The unsaturated and bioactive one presents expulsion from the membrane at high surface pressures and destabilizes it. The results suggest that the unsaturation pattern of the alkylic chain affects the mechanism of action of these drugs in membranes.

Resumo/Abstract

Acetogenins are a natural product class showing bioactivity against microbial and tumor cells. Three acetylenic acetogenins from Porcelia macrocarpa have been isolated, presenting activity against Trypanosoma cruzi and Leishmania infantum protozoa. It was noted that the unsaturation pattern of the alkylic chains of these compounds determined their cytotoxicity since the more unsaturated one was active, while the others, more saturated, were inactive. This work studies the surface activity of those three acetogenins with cell membrane models of protozoa using DPPE Langmuir films. The results indicate that the unsaturated drugs tend to destabilize the film differently from the fully saturated ones. Also, the unsaturated compounds form filamentous aggregates on pressures up to 25 mN/m, inducing molecular rearrangements in the mixed films. These data might help understand the mechanism of action of these drugs in cell membranes.

Agradecimentos/Acknowledgments

CAPES, FAPESP, CNPq, UNIFESP, UFABC, SBQ

Recomendamos fortemente o uso da língua inglesa nos resumos, uma etapa importante na internacionalização do evento.

Área: MAT

Vanadium hexacyanoferrate cathodes for Zn-ion aqueous batteries using water-in-salt electrolyte in the presence of chlorine species

Samuel C. Silva (PG),[1]* David Hoang (PG),[2] Min Soo Jung (PQ),[2] Xiulei Ji (PQ),[2] Edson Nossol (PQ).[1]

samuelsilva73@gmail.com

[1]*Instituto de Química, Universidade Federal de Uberlândia;* [2]*Chemistry Department, Oregon State University*

Keywords: h*exacyanoferrates, aqueous batteries, zinc, chlorine*

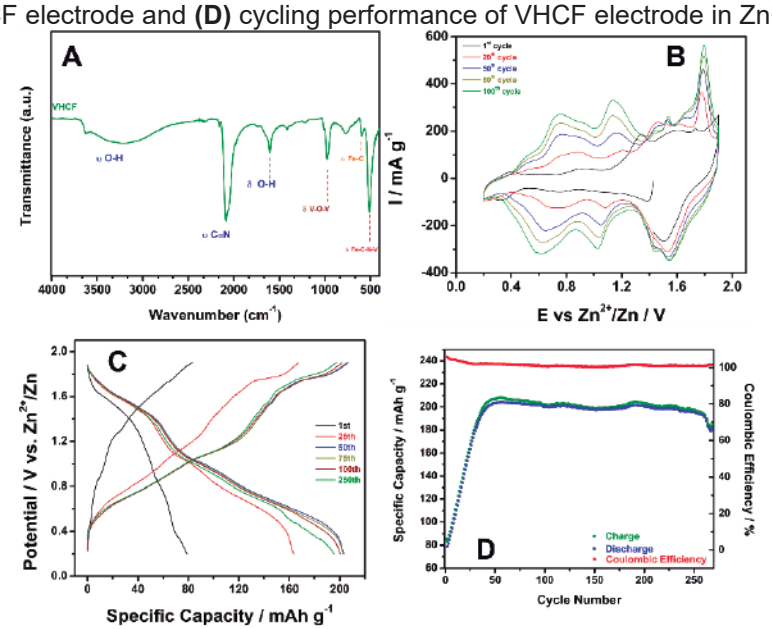
Highlights

Vanadium hexacyanoferrate is applied as a cathode in an aqueous Zn battery, with higher specific capacity and retention. The system is attractive due to chlorine chemistry and cost effectiveness.

Abstract

In the search for lowering energy costs and increasing sustainability, energy storage devices must embrace abundant materials. Ideally, showing high energy density and long-life cycles, like the promising aqueous zinc metal battery.[1] Vanadium hexacyanoferrate (VHCF) is of particular interest among cathodes materials because the associated reaction is facilitated by multi-electron transfer with V and Fe redox centers, capable of providing a higher specific capacity than other materials.[2] This work presents a synthesized VHCF through chemical coprecipitation and applied in a water-in-salt $ZnCl_2$ electrolyte Zn metal battery. Figure 1-A shows the infrared spectrum of the VHCF sample, exhibiting the characteristic vibrational modes of vC≡N, vFe–C and δFe–C≡N–V around 2086, 596 and 513 cm^{-1}, respectively. Figure 1-B presents the cyclic voltammetry of the prepared electrode, with the three redox pairs of the VHCF, attesting the effective synthesis of the material. Figure 1-C shows the galvanostatic charge and discharge experiment, with multiple electron processes and an activation process of the electrode over cycling, result in agreement with the profile observed on the cyclic voltammetry. Figure 1-D shows excellent capacity retention over 250 cycles at 100 mA g^{-1} current density, an excellent result for this material in the area. The specific capacity around 200 mAh g^{-1} with a coulombic efficiency around 99.9% is very promising. Studies are being conducted over the role of chlorine species on the specific capacity value and charge profiles observed.

Figure 1. (A) IR spectrum of VHCF sample, **(B)** Cyclic voltammetry of the VHCF electrode, **(C)** Galvanostatic charge and discharge of the VHCF electrode and **(D)** cycling performance of VHCF electrode in Zn^{2+} electrolyte.



[1] JI, X.; NAZAR, L. F. **Nature Sustainability**, 2024.
[2] KOKITS, O. *et al*. **Energy Storage Materials**, v. 63, 2023.

Acknowledgments

UFU, OSU, CAPES, FAPEMIG.

Área: QM

Variation in the amounts of dithiocarbimate anion present in layered compounds synthesized by different routes

[1]Eline Barbosa Ferreira* (PG), [1]Eder do Couto Tavares (PQ), [1]Fábio da Silva Lisboa (PQ)

*d2023103782@unifei.edu.br

[1]Institute of Physics and Chemistry, UNIFEI

Keywords: Dithiocarbimate, Layered Compounds, Thermogravimetric Analysis.

Highlights

The XRD results indicated the formation of functionalized and intercalated compounds; TGA suggests that the amount of DCBI in the ZHA-fDCBI and ZHA-iDCBI samples are, respectively, 20.44 and 32.28%.

Abstract

In this work, two new compounds formed by the potassium N-(4-methylphenylsulfonyl)dithiocarbimate dihydrate (DCBI) and zinc hydroxyacetate (ZHA) were synthesized by coprecipitation method. The only difference between the routes was the reagents' order of addition, which resulted in different solids.

For the compound ZHA, basal order peaks (001), (002), and (003) were observed [1]. The calculated value of the basal spacing was 13.60 Å. Comparing the ZHA and ZHA-iDCBI solids it is possible to notice a shift of the basal order peaks from 13.60 to 19.29 Å, which indicates the intercalation. On the other hand, the solid ZHA-fDCBI did not present a shift of basal order peaks; the calculated value of the basal spacing was 13.44 Å, which indicates a functionalization, as shown in Figure 1.

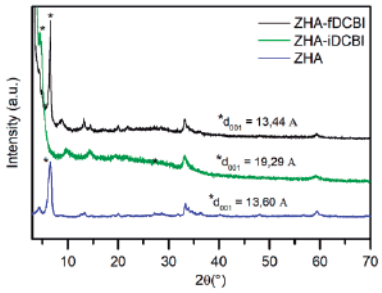


Figure 1 - DIffractograms of the solids ZHA, ZHA-fDCBI and ZHA-iDCBI.

The TGA-DTG measurement of ZHA-fDCBI, shown in Figure 2(a), revealed four mass loss events between 119 and 310 °C. The total mass loss corresponds to 23.13% [1]. The estimated amount of dithiocarbimate in the structure was 20.44%. Meanwhile, the thermal behavior of the ZHA-iDCBI solid can be observed in Figure 2(b). The total mass loss occurred in five events between 178 and 785 °C and totalized 46.57% [1]. The estimated amount of dithiocarbimate in the structure was 32.28%.

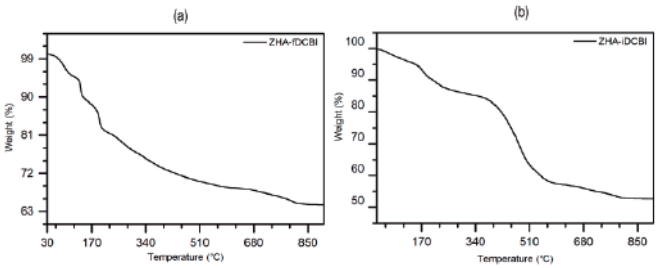


Figure 2 - Thermogravimetric Analysis of the solids ZHA-fDCBI (a) and ZHA-iDCBI (b).

It can be concluded that the route of synthesis influences the amount of DCBI in the solids ZHA-fDCBI and ZHA-iDCBI.

Acknowledgments

LaCSin PPGMQ-MG GCLAM Grupo de Compostos Lamelares

Reference

[1] Moezzi A, et al. Inorg. Chem. 52:95−102. 2013.

Área: MAT

Water Reactivity in Electrified Interfaces and the Simultaneous Production of Electricity and Green Hydrogen

Leandra P. Santos (PQ)[1], Diana Lermen (PG)[2], Rafael Galiza Yoshimura (PG)[2], Bruno Leuzinger da Silva (PG)[2], André Galembeck (PQ)[3], Thiago A. L. Burgo (PQ)[4], Fernando Galembeck (PQ)[1,2].

andre.galembeck@ufpe.br

[1]Galembetech Consultores Associados Ltda; [2]Instituto de Química, UNICAMP; [3]Departamento de Química Fundamental, UFPE; [4]Departamento de Química e Ciências Ambientais, UNESP

Palavras Chave: *hidrogênio verde, hidrovoltaicos, eletrização, interfaces.*

Highlights

This work describes the simultaneous generation of electric energy, green hydrogen and, hydrogen peroxide at room temperature, from water adsorbed in Al and nanographite electrodes. It results from the electrification of the surfaces made of aluminum and exfoliated and reassembled graphite.

Resumo/Abstract

The spontaneous electrification of surfaces and interfaces is a widespread but not often recognized phenomenon that is now finding applications in energy harvesting, sensing systems, and sustainable chemical synthesis. It arises from electron, ion, and material transfer, but achieving controlled charging states is still challenging. Recent discoveries show that charged water microdroplets and other water (liquid or vapor)/solid interfaces display hydrovoltaic effects, delivering power. Here, we demonstrate the simultaneous production of (green) hydrogen and electricity at room temperature and pressure from liquid water or vapor, delivering hydrogen peroxide as well. Different cell arrangements were assembled combining electrodes with acidic and alkaline surfaces where water molecules dissociate and adsorb, producing an electric potential difference. The electrodes are made of aluminum foil and exfoliated and reassembled graphite (ERG), which is formed by graphite nanoplates. W. Pauli said, "God made solids, but surfaces were the work of the devil." Interfacial electrification has been known for more than 2600 years, even before the devil was invented, but it has been poorly understood. Now, acknowledging water ionization on interfaces is providing a full toolbox for creating sustainable technologies.

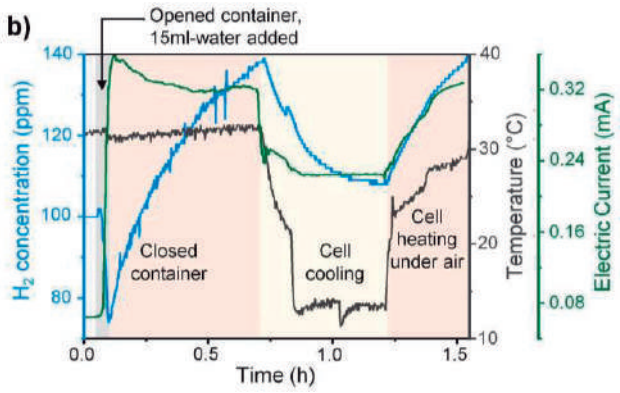


Figure. Hydrogen concentration (blue) and electric current (green) are delivered by the cell as a function of time. The cell is initially dry; as water is inserted in the cell, both electric current and hydrogen gas are produced.

Agradecimentos/Acknowledgments

INCT INOMAT (CNPq), INCT NanoVida (CNPq), CAPES, FAPESP.

MED

Química Medicinal

Sociedade Brasileira de Química

Área: MED
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

AI-Powered Drug Discovery: Unveiling 3CLpro Inhibitors via Structure- and Ligand-based virtual screening

Sabrina Silva-Mendonça (PG)[1,2], Christopher D. Jurisch (PG)[3], Donald Seanego (PQ)[3], Flavia S. N. Motta (PQ)[4], Beatriz S. A. Rodriguez[4], Gilberto S. M. Junior[4], Jeanette Liao[5], Sunniva Sigurdardóttir (PG)[5], Mariana Ortiz[6], Igor H. Sanches (PG)[1,2], Fabio M. de Oliveira (PQ)[1], Melina Mottin (PQ)[1,2], Rafael Guido[6], Glaucius Oliva[6], Izabela D. M. Charneau (PQ)[4], Per Sunnerhagen (PQ)[5], Kelly Chibale (PQ)[3], Richard Gessner (PQ)[3], Carolina Horta Andrade (PQ)[1,2*]

[1]Laboratory of Molecular Modeling and Drug Design (LabMol), Faculty of Pharmacy, Universidade Federal de Goiás, Goiânia, GO, Brazil; [2]Center for the Research and Advancement of Fragments and Molecular Targets (CRAFT), Faculdade de Ciências Farmacêuticas de Ribeirão Preto, USP, Ribeirão Preto, Brazil; [3]Holistic Drug Discovery and Development Center (H3D), University of Cape Town (UCT), Cape Town, South Africa; [4]Pathogen-Host Interface Laboratory, Department of Cell Biology, University of Brasília, Brasília, DF, Brazil; [5]Department of Chemistry and Molecular Biology, University of Gothenburg, Göteborg, Sweden; [6]Laboratory of Structural Biology and Pharmaceuticals (LaBEFar), Instituto de Física de São Carlos, Universidade de São Paulo, Brazil.

sabrinamendonca@discente.ufg.br; carolina@ufg.br

Keywords: *SARS-CoV-2, Virtual screening, protease, machine learning, docking.*

Highlights

Promising candidates specifically designed to inhibit SARS-CoV-2's 3CLpro enzyme, a critical target in combatting COVID-19. Developed predictive models for screening compounds, leading to LabMol-454 with IC_{50} of 27 μM, offering the potential for hit-to-lead optimization in the search for effective COVID-19 therapeutics.

Resumo/Abstract

The 3-Chymotrypsin-Like Protease (3CLpro) is crucial in replicating the SARS-CoV-2 virus, making it a significant target for COVID-19 drug development. Two drugs, ensitrelvir and nirmatrelvir, have been developed as inhibitors of 3CLpro and are recommended by the WHO and Japanese Government for treating non-severe COVID-19 and post-exposure prophylaxis. However, there is still a need for drugs for severe and critical cases, highlighting the need for further research. This study aimed to identify potential candidates by combining structure- and ligand-based computational approaches to screen available compounds. We developed predictive shape-based models, ensemble docking, and machine learning (ML) for 3CLpro using experimental data from the ChEMBL database, COVID Moonshot[3], and scientific literature. The best shape-based and ensemble docking models presented good validation results (AUC = 87%, EF = 7 and BEDROC = 60% and AUC = 87%, EF = 7.03 and BEDROC = 62%, respectively) for the top 10% of the ordered list. Moreover, the ML model combined ECFP4 fingerprints and Random Forest demonstrated good external classification power (ACC = 81%; MCC = 62%). Then, we used the best-validated models as filters for the virtual screening of the H3D and ChemBridge libraries. The compounds were then selected and prioritized for evaluation in yeast genetic trap assays and enzymatic (FRET) assays for 3CLpro. LabMol-454 emerged as the best compound from the virtual screening, with an IC_{50} of 27 μM. We also identified six other compounds with the highest potency of 80 μM, making them good starting points for hit-to-lead optimization.

Agradecimentos/Acknowledgments

The authors are grateful to the Brazilian funding agencies CNPq BRICS STI COVID-19 (#441038/2020-4), FAPEG (#202010267000272), and CAPES (financial code 001). We are grateful to ChemAxon (https://www.chemaxon.com/), Schröndiger (http://www.schrondiger.com/), and OpenEye Scientific Software Inc. (https://www.eyesopen.com/).

Referencias/References

[1]Jonathan Daniel Ip et al. eBioMedicine. 2023;91: 104559. https://doi.org/10.1016/j.ebiom.2023.104559; [2]Therapeutics and COVID-19: living guideline, 16 September 2022. Geneva: World Health Organization; 2022 (WHO/2019-nCoV/therapeutics/2022.5). License: CC BY-NC-SA 3.0 IGO; [3]Consortium TCM, Chodera J, Lee A, London N, Delft F von. ChemRxiv. 2020; doi:10.26434/chemrxiv.13158218.v1

Área:_MED_____

Anti-Trypanosomatidae profile of benzimidazole *N*-acylhydrazone

Laís G. Ramos (PG),[1,2*] Pedro M. C. Maynart (IC),[1,3] Juliana M. C. Barbosa (PG),[4] Kelly Salomão (PQ),[4] Policarpo A. Sales Junior (PQ),[5] Silvane M. F. Murta (PQ),[5] Valéria R. A. Pereira (PQ),[5] Rafaela S. Ferreira (PQ),[6] Talita C. D. Bernardes (IC),[6] Kátia R. de Souza (PQ),[2] Samir A. Carvalho (PQ)[1]

laisgomesramos@hotmail.com

[1]Instituto de Tecnologia em Fármacos - Farmanguinhos, Fundação Oswaldo Cruz, 21041-250, Rio de Janeiro, RJ, Brazil; [2]Laboratório de Físico-Química de Materiais, Seção de Engenharia Química, Instituto Militar de Engenharia, Praça General Tibúrcio 80, 22290-270 Rio de Janeiro, Brazil; [3]Instituto de Química, Universidade Federal do Rio de Janeiro; [4]Laboratório de Biologia Celular, Instituto Oswaldo Cruz, Fundação Oswaldo Cruz, 21040-900, Rio de Janeiro, RJ, Brazil; [5]Laboratório de Imunopatologia e Biologia Molecular, Departamento de Imunologia, Instituto Aggeu Magalhaes, Fundação Oswaldo Cruz, 50670-420, Recife, PE, Brazil; [6]Laboratório de modelagem molecular e planejamento de fármacos, Departamento de Bioquímica e Imunologia, Universidade Federal de Minas Gerais, Avenida Antônio Carlos, 6627, Belo Horizonte, MG, 31270-901, Brazil.

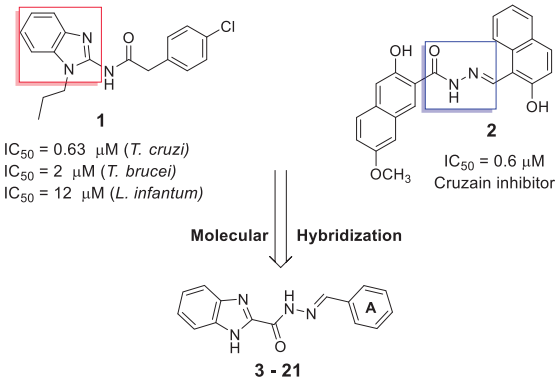
Keywords: *Antitrypanosomal, Benzimidazole, N-Acylhydrazone, Trypanosoma cruzi.*

Highlights

Novel benzimidazole *N*-acylhydrazones synthesized, exhibiting potent *anti*-Trypanosomatidae activity. One compound surpasses benznidazole, showing 46-fold stronger efficacy against *T. cruzi* amastigotes.

Resumo/Abstract

The privileged position of the *N*-acylhydrazone (NAH) structure[1] has been extensively exploited in the design of new bioactive compounds with diverse pharmacological profiles[2]. The pharmacophoric characteristics of this group have been identified during the process of developing cysteinyl protease inhibitors[3]. The present work outlines the synthesis of a novel group of benzimidazole derivatives with the objective of creating innovative prototypes for anti-Trypanosomatidae agents. The synthetic methodology practiced was reproducible, with global yields ranging from 33% to 57%. These new benzimidazoles derivatives (3 - 21) were structurally designed, exploring the molecular hybridization. In *T. cruzi in vitro* tests, we examine both circulating trypomastigote and intracellular amastigotes forms and of two different strains (Y and Tulahuen), which are crucial in drug development assays due to their presence in the vertebrate host during both the acute and chronic phases of Chagas' disease. The assessment against trypomastigotes and amastigotes forms of the Tulahuen strain of *T. cruzi* revealed compounds with greater active and selective compared to benznidazole.



1. C.D. Duarte, E.J. Barreiro, C.A.M. Fraga, Privileged structures: a useful concept for the rational design of new lead drug candidates, Mini Rev. Med. Chem. 7 (2007) 1108e1119.
2. C.A.M. Fraga, E.J. Barreiro, Medicinal chemistry of N-acylhydrazones: new lead-compounds of analgesic, antiinflammatory and antithrombotic drugs, Curr. Med. Chem. 13 (2006) 167e198.
3. R. Li, X. Chen, B. Gong, P.M. Selzer, Z. Li, E. Davidson, G. Kurzban, R.E. Miller, E.O. Nuzum, J.H. McKerrow, R.J. Fletterick, S.A. Gillmor, C.S. Craik, I.D. Kuntz, F.E. Cohen, G.L. Kenyon, Structure-based design of parasitic protease inhibitors, Bioorg. Med. Chem. 4 (1996) 1421e1427.

Agradecimentos/Acknowledgments

This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) – Finance Code 001 and the Carlos Chagas Filho Foundation for Research Support in the State of Rio de Janeiro (FAPERJ nos. 05/2020 and 29/2021). The authors also thank the Fundação de Amparo à Pesquisa do Estado de Minas Gerais (FAPEMIG – APQ 02816-21). PASJ is a research fellow of the Fundação de Amparo à Ciência e Tecnologia do Estado de Pernambuco (FACEPE).

Área: MED

Assessment of 1,2,3-Triazole-Selenide Hybrids as Potential Trypanothione Reductase Inhibitors: Implications for Trypanocidal Activity

João Victor Silva-Silva (PQ),[1*] Eliza Lima dos Santos (IC),[2] Leonardo L. G. Ferreira (PQ),[1] Aldo S. de Oliveira[3], Vanessa Nascimento[4], Adriano D. Andricopulo (PQ)[1]

jvictor.ssilva@ifsc.usp.br

[1]Laboratory of Medicinal and Computational Chemistry (LQMC), Center for Research and Innovation in Biodiversity and Drug Discovery (CIBFar), Institute of Physics of São Carlos, University of São Paulo (USP); [2] Laboratory of Antibody Engineering (LEA), Foundation Oswaldo Cruz Rondônia (Fiocruz); [3]Department of Exact Sciences & Education, Federal University of Santa Catarina, Campus of Blumenau; [4]SupraSelen Laboratory, Department of Chemistry, Federal University Fluminense, Institute of Chemistry.

Keywords: *Chalcogen, triazole, Trypanosoma cruzi, Molecular docking.*

Highlights

The synthetic 1,2,3-triazole-selenide hybrid, 4M-PT, previously evaluated, exhibits promising trypanocidal activity, possibly through modulation of trypanothione reductase, suggesting a potential mechanism of action against *Trypanosoma cruzi*.

Abstract

Chagas disease, caused by *T. cruzi*, is a significant public health concern affecting millions globally, particularly in Latin America. Current therapies face limitations, necessitating the development of new, safer, and more effective treatments. This study investigates the anti-*T. cruzi* activity of a novel 1,2,3-triazole-selenide compound (4M-PT**,** Fig. 1) and its interaction with the trypanothione reductase (TryR) enzyme, a potential target for drug development. The cytotoxicity (CC_{50}) of 4M-PT in HFF-1 fibroblasts and its effectiveness against intracellular amastigote forms were evaluated[1]. Molecular modeling studies explored the interactions between 4M-PT and the TryR enzyme (PDB ID 1BZL, 2.40 Å). Additionally, *in silico* prediction studies (pkCSM and SwissADME) on physicochemical and pharmacokinetic properties were conducted. Results indicate that 4M-PT exhibits comparable activity to benznidazole against *T. cruzi*, with IC_{50} values of 3.1 µM and 2.1 µM, respectively, while demonstrating low cytotoxicity (CC_{50} > 64 µM) and selectivity for the parasite (IS > 20.6). Analysis of the LUMO orbital (Fig. 1) highlights a specific aromatic segment, suggesting a potential mechanism for generating reactive oxygen species (ROS). Molecular modeling revealed relevant interactions with key residues of TryR (Cys53 and His461, Fig. 1). *In silico* evaluations, in line with Lipinski, Ghose, Veber, Egan, and Muegge criteria, underscore the potential of 4M-PT as a lead compound for developing new anti-parasitic agents for Chagas disease therapy. This comprehensive investigation provides valuable insights into the medicinal chemistry of trypanocidal agents and the potential role of trypanothione reductase as a therapeutic target.

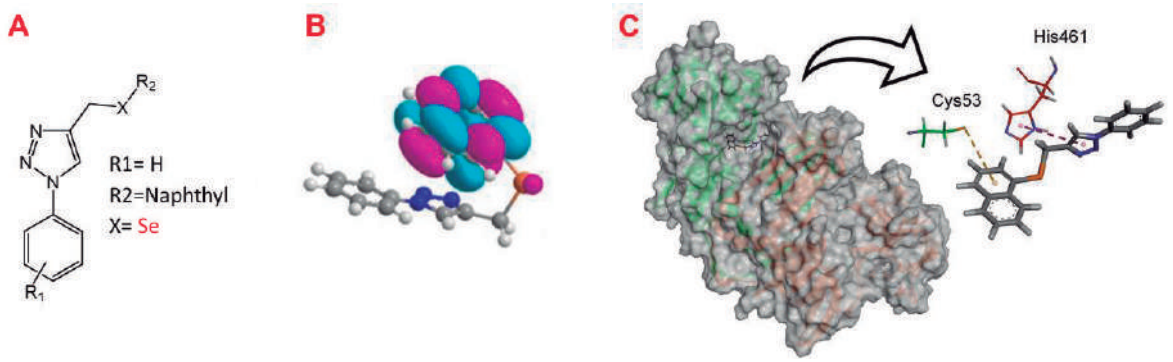


Figure 1. (a) Chemical structure of 4M-PT (b) LUMO surfaces for 4M-PT and (c) key interactions in the top docking pose of 4M-PT within the active site of 1BZL.

Acknowledgments

CIBFar-CEPID FAPESP #2013/07600-3, INCT BioNat FAPESP/ CNPq #2014/50926-0, FAPESP/DFG #2020/11967-3, FAPESP/DAAD PROPASP #2022/08333-8, Scholarship FAPESP # 2023/00242-6, and FAPESP #2023/14195-0.

[1] Chipoline et. al. European Journal of Medicinal Chemistry, Volume 243, 2022, 114687, ISSN 0223-5234, https://doi.org/10.1016/j.ejmech.2022.114687.

Area: MED

Calcogenonaphthoquinones-1,2,3- triazoles: synthesis and biological evaluation of promising structures against tuberculosis

Nathália L. B. Santos (PG),[1] Luana S. Gomes (PG),[1] Ruan C. B. Ribeiro (PG),[2] Alcione S. de Carvalho (PQ),[2] Maria Cristina S. Lourenço (PQ),[3] Vitor F. Ferreira (PQ),[2] Fernando C. da Silva (PQ),[2] Vanessa Nascimento (PQ).[1*]

nl_botelho@id.uff.br; nascimentovanessa@id.uff.br

[1]SupraSelen Laboratory – Department of Organic Chemistry – UFF; [2]LabSOA Laboratory – Department of Organic Chemistry – UFF; [3]Laboratory of Bacteriology and Bioassays – Campus Manguinhos – FIOCRUZ

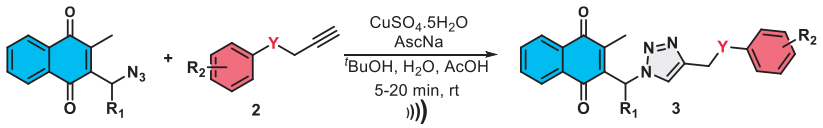
Keywords: *selenium; naphtoquinones; organochalcogens.*

Highlights

Synthesis and biological evaluation of promising structures against tuberculosis, considering the biological relevance of chalcogen groups, 1,4-naphthoquinone and the triazole nucleus.

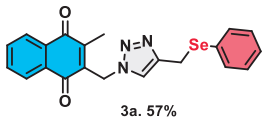
Abstract

The global public health challenge of combating tuberculosis persists. According to the World Health Organization (WHO), around 7.5 million people were diagnosed with tuberculosis (TB) worldwide in 2022. This is the highest number recorded since the WHO began global monitoring.[1] Furthermore, the growing prevalence of multidrug-resistant (MDR-TB) and extensively drug-resistant (XDR-TB) *Mycobacterium tuberculosis* (*Mtb*) strains underscores the urgency of the search for new, more effective therapeutic agents.[2] In this context, the combination of organochalcogens with naphthoquinones in the fight against TB has been shown to be promising.[3] Therefore, the aim of this work was to obtain new 1,2,3-triazole chalcogenonaphthoquinones and their application against TB. Thus, the target compounds were obtained through a "*click chemistry*" reaction between azide **1** derived from menadione and alkyne **2** containing chalcogen atoms (Se and S) catalyzed by Cu(I). From this methodology, it was possible to obtain 16 new molecules with good to excellent yields (Scheme 1). The synthesized compounds were evaluated against *Mtb* H37Rv ATCC 27294 and the most promising results were presented for the highlighted compounds. In addition, a complementary microbiological test was carried out to detect resistance against the *Mtb* T113 strain (resistant to rifampicin and isoniazid). Optimal results were achieved, with MIC values ≤ 3.12 µg/ml for the compounds, in relation to the standard (1.0 µg/ml). Additionally, a cytotoxicity test was carried out for the compounds in focus, according to scheme 1. In conclusion, a total of 16 new hybrid chalcogenonaphthoquinones were synthesized, with promising results against *M. tuberculosis.* The objective is to pursue further biological investigations on the cytotoxicity of the synthesized compounds to achieve reliable and conclusive outcomes.



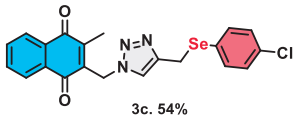
R_1 = aryl and alkyl; R_2 = H, 3-CF_3, 4-Cl, 2,4,6-CH_3, 4-CH_3, 2-CH_3, CH_2-furan, naphthyl
Y = Se e S

Target compounds with better biological results



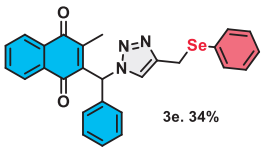
3a. 57%

Mtb H37Rv: MIC ≤ 6,25 µg/ml
Mtb T113: MIC ≤ 3,12 µg/ml
CC50 = não se aplica



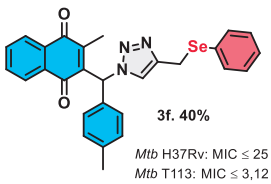
3c. 54%

Mtb H37Rv: MIC ≤ 3,2 µg/ml
Mtb T113: MIC ≤ 3,12 µg/ml
CC50 = não se aplica



3e. 34%

Mtb H37Rv: MIC ≤ 12,5 µg/ml
Mtb T113: MIC ≤ 3,12 µg/ml
CC50 > 100 µg/ml



3f. 40%

Mtb H37Rv: MIC ≤ 25 µg/ml
Mtb T113: MIC ≤ 3,12 µg/ml
CC50 > 67,54 µg/ml

Reaction scope

Compounds	R^1	R^2	E	Yield (%)
3a	H	Ph	Se	57%
3b	H	3-CF_3Ph	Se	93%
3c	H	2,4,6-CH_3Ph	Se	83%
3d	H	4-ClPh	Se	54%
3e	H	Naphthyl	Se	57%
3f	CH_3	Ph	Se	57%
3g	Ph	Ph	Se	34%
3h	4-CH_3Ph	Ph	Se	40%
3i	H	Ph	S	64%
3j	H	4-ClPh	S	85%
3k	H	4-CH_3Ph	S	79%
3l	H	2-CH_3Ph	S	48%
3m	H	CH_2-Furan	S	57%
3n	CH_3	Ph	S	48%
3o	Ph	Ph	S	65%
3p	4-CH_3Ph	Ph	S	59%

Scheme 1. Synthesis and biological evaluation of target compounds.

Acknowledgments

UFF, CAPES, FAPERJ, CNPq, PPGQ-UFF, SBQ-RJ

[1]WHO. *Global tuberculosis report* **2023**. [2]Falzon, F. *et al.*, *Eur. Respir. J.* **2015**, 45, 150–160. [3]Nascimento, V. *et al. Eur. J. Med. Chem.* **2021**, 209, 112859. [4]Nascimento, V. *et al. Eur. J. Med. Chem.* **2022**, 243, 114687.

Área: MED

Computational modeling of Angiotensin Converting Enzyme I inhibition by Ts3 and Ts10 toxins, present in the venom of the scorpion T*ityus serrulatus.*

Ana P. Contelli (IC),[1]* Gustavo C. Ferraz (IC),[1] Wítor R. Ferraz (PG),[2] André B. Penteado (PG),[2] Gustavo H.G Trossini (PQ),[2] Eliane C. Pedrozo (PQ).[1]

contelli@usp.br

[1]*Department of Chemical Engineering, Lorena School of Engineering – EEL/USP;*
[2]*Faculty of Pharmaceutical Sciences, University of São Paulo (FCF-USP).*

Keywords: *Neglected Diseases, Scorpion Poisoning, Tityus serrulatus, Angiotensin Converting Enzyme (ACE 1), Ts3, Ts10.*

Highlights

This study explores an alternative treatment for *Tityus serrulatus* poisoning, using molecular modeling to understand the inhibition of ACE 1 by the Ts3 and Ts10 toxins, present in the scorpion's venom.

Abstract

Accidents involving venomous animals are on WHO official list of neglected tropical diseases, wich persist in poor and marginalized areas, affecting more than a sixth of the world's population. In Brazil, the scorpion *Tityus serrulatus* accounts for the majority of these accidents. Although most cases receive treatment within three hours, a significant percentage (around 10%) of cases are delayed, which can result in complications such as acute pulmonary edema, the leading cause of death after *Tityus serrulatus* poisoning. Conventional anti-scorpion serum is produced from the plasma of horses hyperimmunized with *Tityus serrulatus* venom, but it requires specific storage and transport conditions, which makes it expensive, leading to uneven distribution of the drug and limiting access for small and riverside communities.Thus, there is a pressing need for alternative treatments to conventional antiscorpion serum, which can reduce production and distribution costs, expanding access to treatment. The angiotensin-converting enzyme (ACE 1) is associated with clinical manifestations of arrhythmia, respiratory and cardiac failure, shock and hypertension caused by *Tityus serrulatus* venom. Targeting this enzyme requires studying inhibitors to interrupt its effects. Understanding inhibitors of this enzyme can, of course, also be applied to combating hypertension. The well-known drug "Captopril" comes from the venom of the *Bothrops Jararaca* snake. There are also components in *Tityus Serrulatus* venom that may have antihypertensive properties. While there are conflicting findings from other researchers regarding the function of the Ts3 and Ts10 toxins from scorpion venom, this study aimed to clarify how these toxins interact with ACE 1 at a molecular level, in case it occurs. Ts10, a peptide consisting of 13 amino acids, with 12 being repeats, was compared to the first 13 amino acids of the N-terminal portion of Ts3, which comprises 64 amino acids. Initially, Ts3 was modeled using Alphafold, followed by protein-peptide docking using Hpepdock. Since there's no crystal structure of the Ts3 and Ts10 complex with ACE 1, a control complex between ACE 1 and a natural peptide inhibitor from the venom of the snake *Gloydius blomhoffii* (PDB code: 4APJ) was chosen. The method was validated through crossdocking (RMSD: 0.414, energy score: -109.772) and redocking (RMSD: 0.434, energy score: -117.036). It involved 35 runs with a limited number of amino acids known to be crucial for ACE inhibition, thereby restricting the size of the interaction box. Subsequently, docking between ACE 1 and the first four amino acids of the toxins' N-terminal portion resulted in an energy score of -112.077. As future steps, molecular dynamics will be employed to incorporate the remaining amino acids into the toxins and assess the stability of the complex.

Acknowledgments

UNIVERSIDADE DE SÃO PAULO
FACULDADE DE CIÊNCIAS FARMACÊUTICAS

Escola de Engenharia de Lorena
Universidade de São Paulo

PROGRAMA UNIFICADO DE BOLSAS DE ESTUDO PARA ESTUDANTES DE GRADUAÇÃO

Área: MED

Computational modeling of bradykinin (BK) potentiation by the Ts14 toxin, present in the venom of the scorpion *Tityus serrulatus.*

Gustavo C. Ferraz (IC),[1]* Ana P. Contelli (IC),[1] Wítor R. Ferraz (PG),[2] André B. Penteado (PG),[2] Eliane C. Pedrozo (PQ),[1] Gustavo H. G. Trossini (PQ).[2]

gugascabral@usp.br

[1]*Department of Chemical Engineering, Lorena School of Engineering – EEL/USP;*
[2]*Faculty of Pharmaceutical Sciences, University of São Paulo (FCF-USP).*

Keywords: *Tityus serrulatus, Neglected Tropical Diseases, Bradykinin, Hipotensive Toxin.*

Highlights

This research aims to study and develop the modeling interaction between Ts14 toxin and bradykinin B2 receptor, intending to explore an alternative treatment for some effects of *Tityus serrulatus* venom.

Abstract

Neglected tropical diseases (NTDs), according to the WHO (World Health Organization) classification, are endemic illnesses that persist in the most economically disadvantaged and marginalized populations in tropical countries. In this context, accidents caused by venomous animals and, in particular, scorpions, with their venoms made up of complex biochemical mixtures, are included. In Brazil, *Tityus serrulatus*, known as the yellow scorpion, is responsible for the majority of accidents, the most serious of which can cause pulmonary edema or cardiogenic shock. The prophylaxis used in these cases is the use of anti-scorpion serum (ASS), which, however, is a drug that is difficult to manufacture and maintain, with very specific temperature conditions. Thus, the possibility of evaluating new drugs that can precede the serum, inhibiting one or more effects of the scorpion accident, is of great pharmacological interest. Protein-protein interactions (PPIs) basically control all intra- and extra-cellular processes in living beings. In the case of scorpions, the focus is on ligand-receptor interactions. Considering the problem of hypertension as an effect of the animal's venom, the existence of a protein with a hypotensive function could have a prophylactic effect on the patient. In this sense, this work studies the Ts14 toxin (also known as TsHpt-I), a hypotensin present in the venom of *Tityus serrulatus*, with the aim of modeling the mechanism of action of bradykinin potentiation and evaluating the possibility of making it a prophylactic drug. Firstly, as there were no crystallized structures of the toxin, using AlphaFold 2.0, a model was developed and, understanding its agonist mechanism, the biochemical target was then aimed at. Using the crystal of the BK complex with the B2 (or B2R) receptor (PDB code: 7F6H), the interactions were demarcated for the validation phase of the docking methodology and platform. On the HPEPDock server, using a hybrid approach combining rigid and flexible coupling methods to predict interactions between proteins and peptide ligands, redocking was used, based on the energy minimization of the BK obtained from the mentioned crystal (RMSD: 0.695A and an energy score: -206.305) and a crossdocking with another crystal from the BK-B2R complex (PDB code: 7F2O) (RMSD: 0.503 and energy score: -361.74), varying the number of runs and the number of amino acids known as responsible for receptor activity. Then, docking was carried out between Ts14 and B2R, focusing on the C-terminal portion, which contains the proline doublet (main similarity with BK), finding poses correlated with the action of the agonist (energy scores around -143.843). For the next steps, molecular dynamics of the complex and the membrane receptor will be carried out, to evaluate the stability of this conformation.

Acknowledgments

UNIVERSIDADE DE SÃO PAULO
FACULDADE DE CIÊNCIAS FARMACÊUTICAS

Escola de Engenharia de Lorena
Universidade de São Paulo

CNPq

Área: MED

Coumarin-benzothiazole hybrids as dual inhibitors of acetylcholinesterase and butyrylcholinesterase for the treatment of Alzheimer's Disease

Raíssa G. Gouvêa (IC),[1] Mayra S. Coutinho (PG),[1] Fernanda P. Pauli (PQ),[1] Marcela C. de Moraes (PQ),[1] Luana da S. M. Forezi (PQ)[1]

raissagouvea@id.uff.br

[1] *Instituto de Química, Departamento de Química Orgânica, UFF.*

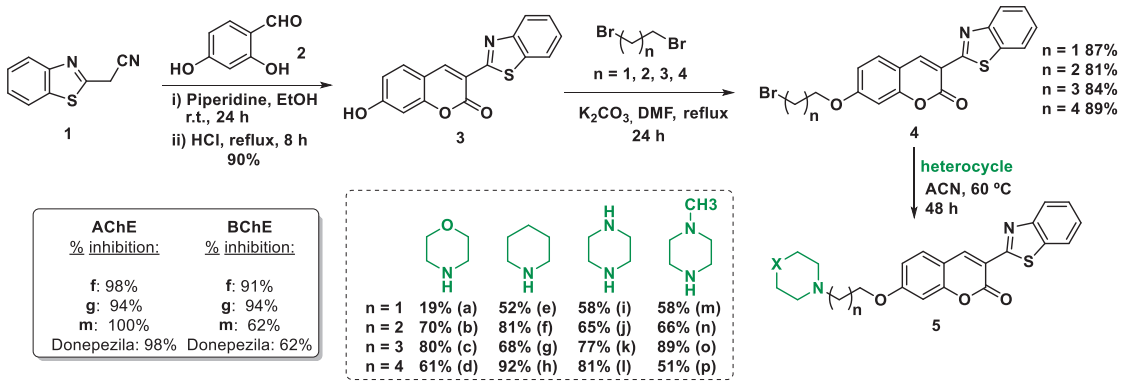
Keywords: *Coumarin, Benzothiazole, Alzheimer`s Disease, Cholinesterases.*

Highlights

Coumarin-Benzothiazole hybrids were synthesized with various nitrogen heterocycles to investigate their biological activity against Alzheimer's disease.

Abstract

In recent years, significant efforts have been directed toward the search for new molecules capable of acting in the treatment of Alzheimer's Disease (AD), which is one of the most serious public health problems worldwide.[1] The cholinergic hypothesis is the most extensively researched hypothesis for the cause of AD, which increasing cholinergic levels by inhibiting acetylcholinesterase (AChE) and butyrylcholinesterase (BuChE) is considered one of the promising therapeutic strategies that increase cognitive and neural cell function.[2] In this context, one important class of heterocycle compounds that were reported as cholinesterase inhibitors is coumarin, which is a building block for the preparation of molecular hybrids that can be used in multi-target strategies.[3] In this work, the desired hybrids **5** were synthesized via a Knoevenagel condensation reaction of benzothiazole **1** with 2,4-hydroxybenzaldehyde (**2**). Subsequently, the key intermediate **3** was *O*-alkylated with dibromoalkanes and next submitted to an S_N2 reaction using different nitrogen nucleophiles (Scheme 1). The hybrids underwent testing for inhibitory activity against AChE and BuChE and the results indicated that the **5m** exhibited superior inhibitory activity (100% inhibition, AChE) compared to the control (donepezila, 98%). Additionally, it showed inhibitory activity of 62% against BuChE (donepezil, 62%). Finally, **5f** and **5g** demonstrated inhibitory activity against both enzymes, exceeding 91% inhibition.



Scheme 1. Synthesis of coumarin-benzothiazole hybrids.

Acknowledgments

CAPES, FAPERJ and CNPq

[1] a) Sangi, D. P. *Química Nova* **2016**, *39*, 995-1006; b) Dementia – WHO (**2023**). Available in: < https://www.who.int/news-room/fact-sheets/detail/dementia>.
[2] Tripathi, A.; Choubey, P. K.; Sharma, P.; Seth, A.; Saraf, P.; Shrivastava S. K. *Bioorganic Chemistry* **2020**, *95*, 103506.
[3] a) Stefanachi, A.; Leonetti, F.; Pisani, L.; Catto, M.; Carotti, A. *Molecules* **2018**, *23*, 250; b) Ekström, F.; Gottinger, A.; Forsgren, N.; Catto, M.; Iacovino, L. G.; Pisani L.; Binda, C. *ACS Medicinal Chemistry Letters* **2022** *13*(3), 499-506.

Área: MED

Design, synthesis and anti-*Trypanosoma cruzi* evaluation of naphthoimidazole-nitroimidazole hybrids, derived from β-lapachone.

Thiago de Souza Dias Silva (FM)[1,2*], Afonso Santine M. M. Velez (PG)[2], Gabriel Amaral da Rocha Silva (IC)[2], Debora Decoté-Ricardo (PQ)[3], Marco Edilson F. de Lima (PQ)[2].

thiago-souzadias@hotmail.com; marcoedilson@gmail.com

[1]Colégio Estadual Dom Pedro II; [2]Instituto de Química; [3]Instituto de Veterinária, Universidade Federal Rural do Rio de Janeiro, Seropédica, RJ.

Key words: *Chagas disease, β-lapachone, Molecular hybridization, CuAAC reaction, Naphthoimidazoles, Nitroimidazoles.*

Highlights

We report herein the design and synthesis of new naphthoimidazole hybrids derived from β-lapachone and nitroimidazole cores present in known antiparasitic drugs. The novel hybrids obtained showed promising antiparasitic activities with good selectivity index.

Abstract

American trypanosomiasis, also known as Chagas disease (CD), is a parasitic disease caused by the hemoflagellate protozoan *T. cruzi* having some hematophagous triatomine insects as vectors. CD, in addition to being a social and public health problem, is classified by the World Health Organization (WHO) as one of the most neglected tropical diseases in the world. Currently, there are no effective therapeutic agents available to fight CD. The etiological treatment is carried out through the use of two old nitroheterocyclic drugs, benznidazole and nifurtimox. Both drugs do not show significant activity in the chronic phase of CD, requiring both a long treatment period and having severe adverse effects, which sometimes make treatment unfeasible[1]. Obtaining compounds derived from β-lapachone has been explored for the synthesis of new compounds with trypanocidal activity, with naphthoimidazole derivatives being the most promising. 6,6-dimethyl-2-(*p*-toluyl)-3,4,5,6 tetrahydrobenzo[7,8]chromeno[5,6-d]imidazole (N3), obtained by the condensation reaction between β- lapachone, ammonia and 4-methylbenzaldehyde, is a naphthoimidazole, derived from β-lapachone, which has activity against *T. cruzi* [2] and was chosen to undergo hybridization with pharmacophoric groups of commercial drugs with known antiparasitic activity, such as benznidazole and metronidazole, through the alkyne-azide cycloaddition reaction, catalyzed by copper (I) (CuAAC). In the molecular design of the novel derivatives prepared in this work (Figure 1), the position of the nitro group present in the imidazole centers has varied, with the aim of investigating the relationship between the different reduction potentials of each 2-, 4-, and 5-nitroimidazole species, relating the reduction potentials to the biological activities observed in the parasite cells[3]. Mixtures of regioisomer hybrids [(1) and (2); (3) and (4); (5) and (6)] were evaluated for the cytotoxicity profile against LLC-MK2 cells and for antiparasitic activity against *T. cruzi* (Tulahuen C2C4 LacZ strain).

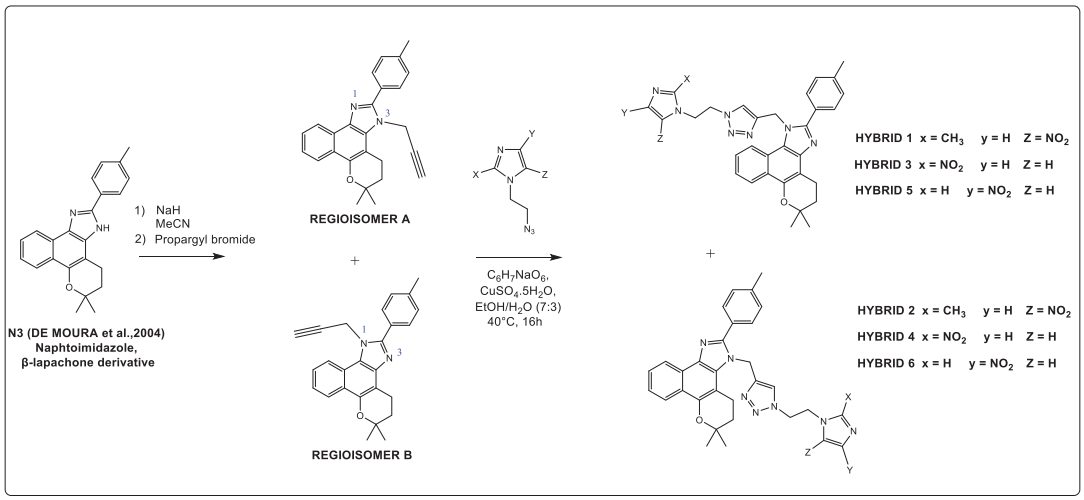


Figure 1. Synthetic route for the preparation of the new hybrids.

The preliminary results of IC_{50}/120h amastigotes and IC_{50}/120h LLC-MK2 were, respectively: mixture (1) and (2), 8.20 μM and 202.90 μM; mixture (3) and (4), 7.71 μM and 119.99 μM and, mixture (5) and (6), 8.02 μM; 98.68 μM. These results validated the molecular design used, generating optimized hybrid molecules, active against *T. cruzi* and with low toxicity towards host cells.

[1] WHO. Chagas disease (also known as American trypanosomiasis), 2024; [2] DE MOURA, K. C. G. et al. Studies on the trypanocidal activity of semi-synthetic pyran[b-4,3] naphtho[1,2-d]imidazoles from β-lapachone. European Journal of Medicinal Chemistry, 2004; [3] MORETH, M. et al. Nitroimidazoles - a promising class of compounds for the treatment of Tuberculosis. Revista Virtual de Química, 2010.

Acknowledgments

UFRRJ, CNPq, CAPES, FAPERJ.

Área: MED

Development and characterization of Nanostructured Lipid Carriers of 1,2,3-triazole trypanocide

Rafael P.R.F. Oliveira (PG)[1], Julia C.A. Souza (IC)[1], Daniel T.G. Gonzaga (PG)[2], Fernando de C. da Silva (PG)[3], Vitor F. Ferreira (PG)[1], Debora O. Futuro (PG)[1]

rrizzo@id.uff.br; cristina_julia@id.uff.br; danieltadeugonzaga@yahoo.com.br; fcsilva@id.uff.br; vitorferreira@id.uff.br; dfuturo@id.uff.br

[1]Departamento de Tecnologia Farmacêutica, Faculdade de Farmácia, UFF; [2]DEPFARM-FCBS, Campus Zona Oeste, UERJ. [3]Departamento de Química Orgânica, Instituto de Química, UFF

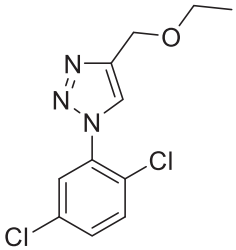
Palavras Chave: Triazole, *Nanostructured Lipid Carrier, Trypanocidal.*

Highlights

This work aims to develop nanostructured lipid carriers containing the triazole compound *Dan 65* which has discribed trypanocidal activity aiming to improve its solubility in water and its activity.

Resumo/Abstract

Five-member heterocyclic compounds containing nitrogen (azoles) are widely disseminated in nature and has several biological activities already described in the literature. The research group coordinated by Dr. Vitor Francisco Ferreira has dedicated efforts to the study of new derivatives of 1,2,3-triazoles and evaluate their biological activities such as the activity of the triazole derivative 1-(2,5-dichlorophenyl)-4-(ethoxymethyl)-1H-1,2,3-triazole or Dan 65 (**Figure 1**) against two strains of *Trypanosoma cruzi* (Y and Dm28-C) (GONZAGA *et al*, 2014; FARIA *et al.*, 2018).



(**DAN 65**)

Figure 1 1-(2,5-diclorofenil)-4-(etoximetil)-1H-1,2,3-triazol

A limitation found for the advancement in studies of the biological activity of the Dan 65 compound was its low solubility in aqueous solutions. Low aqueous solubility is a limit to the use of drug-candidate organic compounds in pharmaceutical preparations, especially those intended for oral administration, in this context, nanotechnology presents itself as an attractive approach to increase the solubility and stability of hydrophobic molecules (SCHITTNY *et al*, 2020).

This present work has the objective to development a nanostructured lipid carrier (NLC) containing a solid and a liquid lipid (Glyceryl Tristearate and Oleic Acid, respectively), Kolliphor® HS 15 as a surfactant and the active Dan 65 in its formulation with the aim of improving the aqueous solubility of this compound and seeking to improve its biological activity. The method employed for the development of NLC was an innovative one-pot microwave reactor-assisted technique. The particle size analysis of the proposed NLC was performed by dynamic scattering of light (DLS) and it presented particle size at the nanomeric scale (197nm) with a polydispersion index (PDI) of 18%. The encapsulation efficiency (EE) was done in an ultraviolet spectrophotometer with the aid of a calibration curve and showed 96% EE. This formulation will be submitted for activity studies against strains of Trypanosoma cruzi (Y and Dm28-C).

In conclusion, it was observed that it was possible to obtain an NLC containing nonpolar triazoles efficiently to improve the bioavailability of the compound.

GONZAGA, D.T.G. et all. 1-Phenyl- 1H- and 2-phenyl-2H-1,2,3-triazol derivatives: design, synthesis, and inhibitory effect on alpha-glycosidases. European Journal of Medicinal Chemistry, v. 74, p. 461-476, 2014.

FARIA, RX; GONZAGA, DTG; PACHECO, PAF; SOUZA, ALA; FERREIRA, VF; DA SILVA, FC. Searching for new drugs for Chagas diseases: triazole analogs display high in vitro activity against *Trypanosoma cruzi* and low toxicity toward mammalian cells. Journal of Bioenergetics and Biomembranes, v. 50, p. 81-91, 2018.

SCHITTNY, A.; HUWYLER, J.; PUCHKOV, M. Mechanisms of increased bioavailability through amorphous solid dispersions: a review. Drug Delivery, v. 27, n. 1, p. 110-127, 2020.

Agradecimentos/Acknowledgments

FAPERJ, CAPES, FIOCRUZ and CNPq

Área: MED

Discovery of Candidate Allosteric Inhibitors for the Dengue Virus NS5 RNA-dependent RNA polymerase: Exploring the Virtual Screening Strategy

Ana Carolina J. Oliveira* **(IC), Sarah H. Louzada (PG), Carlos Mauricio R. Sant'Anna (PQ)[1].**

anacarol04contato@gmail.com

[1]*Departamento de Química Fundamental, UFRRJ.*

Keywords: Dengue, NS5, Virtual screening, Molecular docking

Highlights

NS5 is involved in dengue virus genome replication. Candidate ligands for an NS5 allosteric site (N pocket) were found by a SBVS procedure with compounds from UFRRJ Chemistry Graduate Program theses.

Abstract

The first month of 2024 recorded a spike in dengue cases in Brazil. Effective drugs are necessary, since, to date, there is no specific treatment for the disease. The NS5 enzyme in involved in genome replication of the 4 main dengue serotypes (DENV-1, DENV-2, DENV-3 and DENV-4). Potent allosteric DENV-3 NS5 polymerase inhibitors were found to interact with an allosteric site called N pocket. Inhibitors that interact with the N pocket prevent conformational changes in the catalytic RNA-dependent RNA polymerase (RdRp) domain of NS5, necessary for its activity.[1] The Structure-Based Virtual Screening (SBVS) technique has been explored to search virtual chemical libraries for compounds with probable affinity for a target enzyme. The objective of this work is to use SBVS to find new candidate allosteric inhibitors of DENV NS5.

The protein targets were crystallographic structures of NS5 of DENV-3 containing allosteric inhibitors extracted from the Protein Data Bank. A set of 238 structures, containing synthetic compounds and natural products, was selected from the QV-PPGQ-UFRRJ database to be used in the SBVS study. QV-PPGQ-UFRRJ contains compounds from PhD and MSc theses from the Chemistry Graduate Program of UFRRJ; the structures were energy-minimized with the PM6 method available in Spartan'20 (Wavefunction). The docking was made with GOLD2023.2.0 (CCDC). The effect of NS5 conformational flexibility was partially included by docking all compounds into the allosteric site of three crystallographic structures that were cocrystallized with different inhibitors (PDB codes 5JJS, 5JJR and 53IQ)

In a previous redocking step with 5 different NS5 cocrystals, the GoldScore function presented the best performance for predicting the geometry of ligands at the N pocket, presenting the lowest average RMSD value (1.38 Å) of all scoring functions provided by GOLD2023.2.0 (CCDC).

Docking of the 238 compounds from QV-PPGQ-UFRRJ provided several good solutions. As a reference, an inhibitor with IC_{50} of 0.46 μM for NS5 RdRp[1] presented a score of 74.7, so we decide to discard solutions with scores lower than 70.0. For the remaining 14 molecules, the solution with the highest score among the 3 enzymes was selected, in which 5JJR better accommodates most compounds.

Table 1: compounds selected during docking and their highest scores (GoldScore) with NS5 structures

Compound code in QV-PPGQ-UFRRJ	5JJS	5JJR	5I3Q
PPGQ20070108	64.93	**70.32**	60.65
PPGQ20070121	**70.46**	64.97	66.64
MPPGQ1975C0119	60.28	**70.83**	58.87
PPGQ20070122	62.71	66.98	**72.15**
PPGQ201430118	65.27	**73.04**	68.88
PPGQ201430114	71.02	**74.92**	67.65
PPGQ20070111	**75.10**	69.47	60.95
PPGQ20070112	67.26	**76.17**	62.57
PPGQ20070102	66.11	**76.99**	66.23
PPGQ201430115	73.15	**77.32**	68.74
PPGQ20070113	76.70	**77.80**	67.85
PPGQ20070110	72.14	**81.41**	73.10
PPGQ201430113	74.59	**81.89**	76.70
MPPGQ2004A0128	**85.55**	69.15	57.70

The hydrophobic interactions and hydrogen bonds of the 14 best complexes were mapped with the PLIP web tool[2] to compare them with the original interactions recorded for cocrystallized ligands and the presence of interactions with residues essential for inhibition, such as Ser710, Arg729 and Arg737, which make up the binding site entrance of the RNA tunnel. As an example, MPPGQ2004A0128, in addition to being the best scored (85.55), interacts with Arg 737, Arg729, and other residues that promote better interaction with the site.

SBVS with molecular docking showed promising results for the search for allosteric inhibitors of DENV NS5 RdRp in the QV-PPGQ-UFRRJ database. The strategy made it possible to identify 14 candidate ligands for NS5 allosteric site, which could be explored in the future in inhibition studies of this enzyme.

[1] LIM, S. P. et al. *Plos Pathogens* **2016**, 12, e1005737..
[2] ADASME, M. F. et al. *Nucleic Acids Res.* **2021**, 49(W1), W530-W534.

Acknowledgments

Faperj, CNPq and CAPES.

Área: MED

Experimental and Computational Investigations on a Series of Drug Candidates for Chagas Disease

Gustavo A. V. Macêdo (IC),[1]* Leonardo L. G. Ferreira (PQ),[1] Thaynan A. B. Chagas (PG),[2] Fernando Coelho (PQ),[2] Adriano D. Andricopulo (PQ)[1]

gustavovieiraptc@gmail.com

[1]Laboratory of Medicinal and Computational Chemistry (LQMC), Center for Research and Innovation in Biodiversity and Drug Discovery (CIBFar), Institute of Physics of São Carlos, University of São Paulo (USP); [2]Laboratory of Synthesis of Natural Products and Drugs, Institute of Chemistry, University of Campinas, PO Box 6154, 13083-970, Campinas, SP, Brazil.

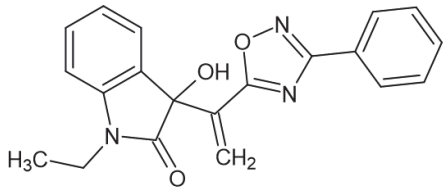
Palavras Chave:*(Chagas Disease, Leishmaniasis, Cell Assay, Cytotoxicity).*

Highlights

Chagas disease, caused by the parasite *Trypanosoma cruzi*, is endemic in 21 Latin American countries. There are 6–7 million people infected worldwide, with another 75 million at risk of contamination. Only two old nitro-heterocyclic drugs – benznidazole and nifurtimox – are available, and both have a number of limitations. In particular, we concentrate our efforts in the search of New Chemical Entities (NCEs) candidates for Chagas disease, which are urgently needed to enable new generations of therapies to save millions of lives.

Resumo/Abstract

According to the World Health Organization (WHO), Chagas disease is considered one of the most important Neglected Tropical Diseases (NTDs) in Latin American, due to their high incidence and substantial global impact on Disability-adjusted life years (DALYs). Although it is an urgent public health problem, therapeutic approaches still remain limited, with obsolete treatments of low efficacy and high toxicity. In this study, we describe the *in vitro* evaluation of the antiparasitic activities of several synthetic compounds aimed at identifying new small molecules having a combination of three important properties: (i) substantial antichagasic effects, evaluated against the intracellular amastigote forms of *Trypanosoma cruzi*; (ii) low cytotoxicity, assessed using HFF-1 fibroblasts and HepG2 hepatocytes; and, (iii) privileged drug-like characteristics. In this context, several oxadiazole derivatives showed potent *in vitro* activity against *T. cruzi*, with IC_{50} values varying from 2.30 μM to 25 μM. Benznidazole was used as the reference drug in all parasitic assays. The cytotoxicity was assessed through CC_{50} (HFF-1 and HepG2) values for the most promising compounds. The quantitative investigation of the drug-likeness of the most promising compounds was estimated with the StarDrop and Swiss ADME multi-parameter interfaces. The physicochemical properties and ADME parameters (molecular weight, clogP, solubility, rotatable bonds, flexibility, hydrogen bond donors, hydrogen bond acceptors, topological polar surface area, P450 metabolism, among others) indicate favorable pharmacokinetics and metabolism for drug discovery purposes. A representative compound of this series (**1**) is shown in Figure 1. This candidate possesses high potency ($IC_{50}^{T.cruzi}$ of 2.30 ± 0.21 μM) against the intracellular amastigote forms of *T. cruzi*, which is comparable or slightly superior to that of the standard drug benznidazole (IC_{50} of 5.60 ± 0.43 μM). In addition, it is highly selective ($CC50^{HFF-1}$ > 100 μM), indicating a safety window between the effective concentration against the parasite and the toxic concentration to the human cells. These easy-to-synthesize molecules represent novel chemotypes for the design of potent and selective lead compounds for Chagas disease drug discovery.



(**1**)

Agradecimentos/Acknowledgments

The authors acknowledge the financial support of FAPESP (#2022/16698-6 and #2013/07600-3) and CNPq.

Área: MED
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Identification of natural product molecules with key characteristics to act on some SARS-CoV-2 MPro variants

Simone Queiroz Pantaleão* **(PQ),[1] Patricia Gasparini* (PG),[1] Eric Allison Philot (PQ),[1] Yolanda Maria Barros Marcello (PG),[1] Rafael Plana Simões (PQ),[2] Angelo José Magro (PQ),[2] Ana Ligia Scott (PQ).[1]**

simone.queiroz@ufabc.edu.br; patricia.gasparini@ufabc.edu.br

[1]Computational Biology and Biophysics Laboratory, Universidade Federal do ABC (UFABC), Santo André, São Paulo, Brazil; [2]Department of Bioprocesses and Biotechnology, School of Agriculture (FCA), Universidade Estadual Paulista "Júlio de Mesquita Filho", (Unesp), Botucatu, São Paulo, Brazil;

Key words: SARS-CoV-2; *Mpro; Mutations; Natural products;*

Highlights

Continuing the previous study[1], we searched for natural product molecules capable of inhibiting Mpro containing the mutations: K90R, P99L, P108S and N151D.

Resumo/Abstract

In this stage of the research, we used Mpro structures with and without structural mutations to search for natural products with interesting physicochemical profiles for acting on variants of this protein. Firstly, we looked at Mpro's natural substrate (peptide (AVKLQNNE)) in terms of: (i) molecular lipophilicity potential (MLP) and polar surface area (PSA) using the Molinspiration tool; (ii) Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) using the WebMO tool. For the virtual screening, we used the NuBBE natural products database and the AutoDockVina program with flexibility for: HIS41, MET49, CYS145, HIS164, GLU166, LEU167, ASP187, GLN189. We applied the following filters: binding energy; calculation of ligand efficiency; combination of 03 or more types of molecular interactions detected by the BINANA algorithm; For the simulation of ADME-Tox properties (absorption, distribution, metabolism, excretion and toxicity), regarding the items: absorption (water solubility, Caco-2 permeability, human intestinal absorption, skin permeability, P-glycoprotein 12 substrate, P-glycoprotein inhibitor and glycoprotein II inhibitor); distribution (human steady-state volume of distribution - VDss, unbound fraction (human), blood-brain barrier permeability and central nervous system (CNS) permeability; metabolism - by substrate (CYP2D6 / CYP3A4) and inhibition (CYP1A2 / CYP2C19 / CYP2C9 / CYP2D6 / CYP3A4)); excretion (total and by the renal substrate OCT2); toxicity (AMES toxicity, hepatotoxicity, cardiotoxicity, mutagenicity genotoxicity, carcinogenicity, cytotoxicity, mitochondrial toxicity, nephrotoxicity, central nervous system toxicity, respiratory toxicity, skin sensitisation, acute oral toxicity and environmental toxicity for the species Tetrahymena pyriformis and Pimephales promelas); the SwissADME; pkCSM; ADMETLab; EmolTox and PHARMIT tools were used, and the 04 finalist molecules that met all the required parameters were: Ligand_120; Ligand_567; Ligand_1067 and Ligand_1770. The complexes formed will now be evaluated for their stability using molecular dynamics.

[1]Gasparini, P.; Philot, E. A.; Pantaleão, S. Q.; Torres-Bonfim, N. E. S. M.; Kliousoff, A.; Quiroz, R. C. N.; Perahia, D.; Simões, R. P.; Magro, A. J.; Scott, A. L. Unveiling mutation effects on the structural dynamics of the main protease from SARS-CoV-2 with hybrid simulation methods. Journal of Molecular Graphics & Modelling, v. 121, p. 108443-14, 2023.

Agradecimentos/Acknowledgments

CNPq (Grant number: 423717/2021-9), Fapesp (Grant Number: 2023/01920-8).

Área: MED

In silico studies of biflavonoids and triperpenes from the *Schinus terebinthiofolius* Raddi fruit and their action on human acetylcholinestarase

Jonhy Herbert (PG),[1] Késsia Souza Santos (PG),[1] Calila Teixeira Santos (PQ),[2] Manoelito C. dos Santos Junior (PQ),[1] Alexsandro Branco (PQ).[1,*]

jonhyherbert@gmail.com; branco@uefs.br

[1] *Departamento de Saúde, UEFS*; [2] *Instituto Federal de Ciências, IFBA*

Keywords: *Schinus terebinthifolius* Raddi, Acetylcholinesterase; Molecular docking, triterpene, biflavonoid

Highlights

The interactions of biflavonoids and triterpenes, characterized in the active extract of *Schinus terebinthifolius* raddi fruit on the active site of acetylcholinesterase using docking, were investigated.

Resumo/Abstract

Previous studies in our laboratory showed that the hydroalcoholic extract of *Schinus terebinthifolius* Raddi fruit, collected in the semiarid region of Brazil, inhibited the *in vitro* acetylcholinesterase in 59.6%. Molecular docking between biflavonoid and triterpenoid compounds, characterized in the above active extract by HPLC-MS and acetylchosterase, was performed in the FRED program to evaluate molecular affinity and intermolecular interactions. Molecular docking results show that the best biflavonoids were I6,II8-biapigenine (-5.97kcal/mol) and naringeninyl-apigenine (-5.69kcal/mol), while the 3,21-dihydroxy-tirucalla-24Z-en-27-oic acid (-7.80kcal/mol), 3β-hydroxy-tirucalla-7,24Z-dien-27-oic acid (Z-schinol) (-7.75kcal/mol) and 3,7-dioxo-tirucalla-8,24Z-dien-27-oic acid (-7.01kcal/mol) were the best triterpenoid compounds[1,2]. The intermolecular interactions with the triterpene Z-schinol with AChE show a hydrogen bond with His287 and hydrophobic interaction with Tyr72,Tyr341,Tyr124, Phe338, Phe297 and Trp286 (Figure 1). The results indicate that triterpenoid compounds have better affinity for the enzyme and the types of intermolecular interactions are in accordance with what has already been described in the literature[4].

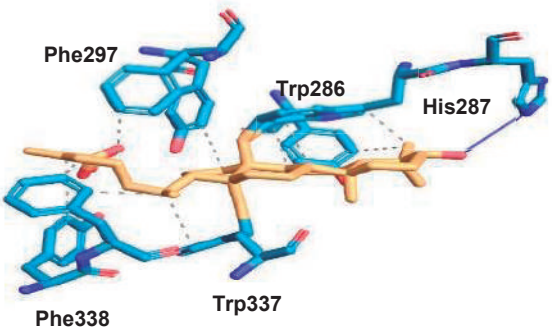


Figure 1. Intermolecular interaction map of Triterpenoid with orthostheric site of the AChE. Blue solid line: hydrogen bonds; Green dashed line; Gray dashed line: hydrophobic interaction

1. **J. Biomol.Struct. 2023, 1–15 2. Phytochemistry. 2022, 113182 3. Molecules. 2020, 25, 3353 4. JCIS Open 2023 12, 2, 100096.**

Agradecimentos/Acknowledgment

CNPq OpenEye fapesb CAPES

Área: MED

Investigation of the cytotoxicity of novel ruthenium(II)-diphosphine complexes as potential therapeutic agents against Chagas disease and visceral leishmaniasis

Analu Rocha Costa (PQ)[1], Felipe C. Demidoff (PQ)[2], Chaquip D. Netto (PQ)[3], Alzir Azevedo Batista (PQ)[2], Adriano D. Andricopulo (PQ)[1]

anallucosta@gmail.com

[1]*Laboratory of Medicinal and Computational Chemistry (LQMC), Center for Research and Innovation in Biodiversity and Drug Discovery (CIBFar), Institute of Physics of São Carlos, University of São Paulo (USP).*
[2]*Multidisciplinary Institute of Chemistry, Federal University of Rio de Janeiro, Macaé 35400-000, RJ, Brazil*
[3]*Department of Chemistry, Federal University of São Carlos, São Carlos 13565-905, São Paulo*

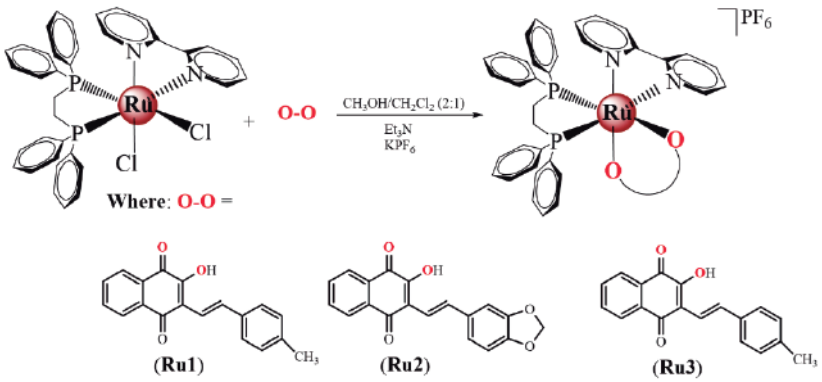
Keywords: ruthenium complexes, drug design, antileishmanial activity, Chagas diseases, Trypanosoma cruzi.

Highlights

Investigation of the biological activity of compounds against the intracellular amastigote forms of *Leishmania infantum* and *Trypanosoma cruzi*, which are the most relevant forms of the parasites for drug discovery assays.

Abstract

Chagas disease and leishmaniasis are considered by the World Health Organization (WHO) as two of the most important Neglected Tropical Diseases (NTDs). These infectious diseases affect millions of people and stand out mainly for their high incidence of disability and mortality. Currently, the therapeutic options available are limited and characterized by low efficacy and safety problems. The development of effective and safe therapeutic agents is an urgent medical need, especially in the most affected and vulnerable tropical and subtropical regions. In the present work, we aimed to synthesize, characterize, and evaluate the biological activity of three complexes with the general formula [Ru(NQ1)(dppe)(bpy)]PF_6 **(Ru1)**, [Ru(NQ2)(dppe)(bpy)]PF_6 **(Ru2)** and [Ru(NQ3)(dppe)(bpy)]PF_6 **(Ru3)** (Scheme 1). All complexes were characterized by molar conductivity, absorption spectroscopy in the infrared and UV-visible regions, nuclear magnetic resonance of $^{31}P\{^1H\}$, ^1H and $^{13}C\{_1H\}$, cyclic and differential pulse voltammetry and monocrystal X-ray diffraction. The voltammograms of the complexes, obtained in dichloromethane (1 mmol of PTBA), showed the oxidation potentials of Ru^{II}/Ru^{III}, presenting quasi-reversible processes. To this end, the antiparasitic potential of the new class of compound was determined using cisplatin, miltefosine and benznidazole as standard reference drugs. The results of the evaluation of the antiparasitic activities against the amastigote forms of *L. infantum* and *T. cruzi* showed that the ruthenium complexes are more potent than the corresponding free ligands. These findings are promising, indicating their potential for the design of new antiparasitic candidate drugs.



Scheme 1. Synthetic route of the ruthenium(II) complexes.

Acknowledgments

CNPq (project n. 152531/2022-0), CIBFar-CEPID FAPESP #2013/07600-3.

Área: MED

In vitro and in vivo evaluation of the [^{18}F]FAl-NOTA-PEG4-Rb9 peptide in a melanoma cancer model

Fabio L. N. Marques (PQ),[1*] Daniele de P. Faria (PQ),[1] Caroline C. Real (PQ),[1] Mara de S. Junqueira (PQ),[2] Fabricio C. Machado (PQ),[3] Alice S. Morais (PQ),[3] Carlos A. Buchpiguel (PQ),[1] Jose F. Perez (PQ).[3]

fabio.marques@fm.usp.br

[1]Departamento de Radiologia e Oncologia (LIM 43), Faculdade de Medicina, USP; [2]Centro de Investigação Translacional em Oncologia (LIM 24), ICESP-HC-FMUSP; [3]Recepta Biopharma SA.

Keywords: *Radioisotope, Fluorine-18, Radiolabeled peptide, Preclinical imaging, Melanoma.*

Highlights

This work describes the radiolabeling of the NOTA-PEG4-Rb9 peptide using [^{18}F]FAl^{2+}, the *in vitro* cell uptake, and *in vivo* and *ex vivo* biodistribution studies, in the murine melanoma B16F10-nex2 model.

Abstract

Introduction: Peptides are promising biomolecules for disease treatment. However, they can become a diagnostic agent or increase therapeutic potential when modified by introducing radioisotopes. [^{18}F]FAl-NOTA-PEG4-Rb9 is a cyclic amino acid sequence that potentially binds tumor or immunological cells. The biological behavior of the radiopeptide was evaluated *in vitro* by B16F10-nex2 melanoma tumor cell uptake, *in vivo* by dynamic positron emission tomography (PET) image, and *ex vivo* by radioactivity measurement in the organs. **Material and methods:** [^{18}F]F$^-$ was produced in a cyclotron by nuclear reaction ^{18}O(p,n)^{18}F, concentrated in the QMA cartridge, and eluted with NaAcO 0.2 M pH 4.1. Five µL of $AlCl_3$ 2 mM solution was added to 100 µL of [^{18}F]F$^-$ solution and incubated for 15 min at 21-23 °C. A different amount of NOTA-PEG4-Rb9 (1.5x10^{-8} to 6 x10^{-8} mol) was added to the [^{18}F]FAl^{2+} solution and heated for 15 min at 100 °C. Radiochemical yield (RCY) and in vitro stability were evaluated by HPLC. Samples with more than 95 % of RCY were incubated in B16F10-nex2 melanoma cells (1x 0^5 to 1x10^6) culture at 15/60/120 minutes (n=3). Uptake in dendritic and macrophage cells (5x10^5 to 1x10^6) was evaluated at 120 minutes. *In vivo,* PET imaging (n=3) was performed on a preclinical PET system in a dynamic sequence for 60 min on B16F10-nex-2 tumor-bearing C57Bl/6 mice (Figure 1). *Ex vivo* biodistribution was done by euthanizing the animal at the end of the imaging process; the organs were harvested and weighed; their radioactivity was measured in a gamma counter. Radioactivity in urine content (n=2) was analyzed by HPLC. **Results:** [^{18}F]FAl-NOTA-PEG4-Rb9 was prepared with RCY>95%, using a peptide mass of 150 µg (6 x10^{-8} mol), and it was stable in the labeling solution for 6 h. Uptake in B16F10-nex-2 was proportional to cell population reaching a maximum value of 0.9 % at 1x10^6 cells/120 min. The macrophage uptake was statistically significant compared to the dendritic cell at 5x105 concentrations. *In vivo,* biodistribution showed slow kidney elimination and high bone cumulation determined by ROI kinetic curves. *Ex vivo* uptake, at 120 min, were: kidney = 16.13 ± 5.61%, bone = 28.45 ± 14.02%, blood = 1.29 ± 0.05%, tumor = 1.03 ± 0.48%. Degradation products were found in urine, with a retention time (rt) of 2.7 min, in similar time associated with [^{18}F]FAl^{2+}, another in 10.6 and 11.1 min, with the complete disappearance of the product signal (rt =15.2 min). **Conclusion:** The [^{18}F]FAl-NOTA-PEG4-Rb9 was efficiently prepared, and the B16F10-nex-2 tumor cell uptake was appropriate and higher than that of dendritic and macrophage cells. The preliminary *in vivo* and *ex vivo* evaluation shows a high kidney elimination and bone uptake, which can be associated with peptide degradation products observed in urine content. Additional investigations must be performed to determine the peptide degradation profile.

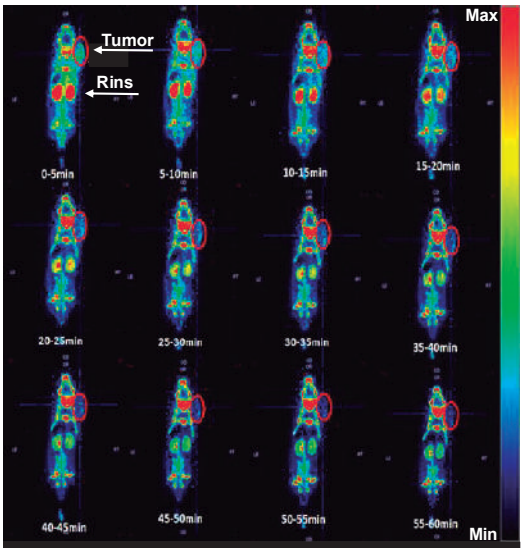


Figure 1. Dinamic image of the ([^{18}F)FAl-NOTA-PEG4-Rb9

Acknowledgments

To FINEP/Brazil Grant 03.14.0198.00

Área: MED

Modelagem molecular de triazóis como reativadores da acetilcolinesterase humana inibida pelos agentes neurotóxicos VX e Novichok A-242

Fernanda F. P. F. Pires (PG)[1], Samir F. de A. Cavalcante (PG)[2], Joyce S. F. Diz (PG) [1]*.

fernanda.pires@ime.eb.br; samirfac@gmail.com, joycediz@ime.eb.br

[1]Instituto Militar de Engenharia, IME; [2]Instituto de Defesa Química, Biológica, Radiológica e Nuclear, IDQBRN.

Palavras Chave: *Molecular Modeling, Neurotoxic Agents, Reactivation of acetylcholinesterase.*

Highlights

Triazoles as potential reactivators of human acetylcholinesterase inhibited by nerve agents VX and Novichok A-242.

Virtual Screening, Molecular Docking and Molecular Dynamics studies. “Near Attack Conformation (NAC)” as evaluation criteria to point the best reactivators.

Resumo/Abstract

Os agentes neurotóxicos são compostos organofosforados considerados inibidores irreversíveis da enzima acetilcolinesterase (AChE), e podem provocar a síndrome colinérgica, por impedirem a hidrólise do neurotransmissor acetilcolina nas sinapses[1]. Como forma tradicional de tratamento, utilizam-se como antídotos os compostos quaternários de oximas piridínicas, tais como a pralidoxima (2-PAM), a obidoxima e a oxima HI-6. Estes reativadores não são universais, de forma que podem não ser tão eficientes contra todos os tipos de neurotóxicos[2]. Além disso, eles apresentam limitada permeabilidade no sistema nervoso central devido à hidrofilicidade das moléculas. Estudos mostraram que modificações estruturais envolvendo o aumento da lipofilicidade podem proporcionar melhor permeação pela barreira hematoencefálica (BHE)[3], e consequentemente melhor eficiência das substâncias como reativadoras da enzima inibida. Neste contexto, 24 (vinte e quatro) compostos triazólicos que diferem entre si pela lipofilicidade foram avaliados por estudos de *docking* molecular na enzima inibida por VX e pelo agente *Novichok* A-242, utilizando-se o programa *Molegro Virtual Docker*[4], e os resultados foram avaliados pela abordagem “*Near-Attack Conformation* (NAC)”, que considera a distância entre os átomos envolvidos na reação de inibição, e ainda o ângulo de ataque do composto triazólico ao organofosforado. Os resultados obtidos sugerem que os compostos avaliados possuem potencial reativador da enzima inibida. Os melhores resultados serão submetidos a estudos de dinâmica molecular e de cálculo de energia livre, com o objetivo de corroborar os resultados de *docking*, e de obter-se valores de energia livre de interação com métodos mais robustos de cálculo.

1. PETRONILHO, E. C; FIGUEROA-VILLAR, J. D. Agents for Defense Against Chemical Warfare: Reactivators of the Inhibited Acetylcholinesterase with Organophosphorus Neurotoxic Compounds. **Revista Virtual de Química,** v. 6, n. 3, p. 671-686, 2014. DOI: 10.5935/1984-6835.20140042

2. JOKANOVIĆ M.; STOJILJKOVIĆ M. P. Current understanding of the application of pyridinium oximes as cholinesterase reactivators in treatment of organophosphate poisoning. **European Journal of Pharmacology**, v. 553, n. 1-3, p. 10-17, 2006. DOI: 10.1016/j.ejphar.2006.09.054

3. FAIZ, M. N. *et al.* Recent developments on oximes to improve the blood brain barrier penetration for the treatment of organophosphorus poisoning: a review. **RSC Advances**, 2020. DOI: 10.1039/c9ra08599h

4. THOMSEN, R.; CHRISTENSEN, M. H. MolDock: a new technique for high-accuracy molecular docking. **Journal of Medicinal Chemistry**, v. 49, n. 11, p. 3315-3321, 2006. DOI: 10.1021/jm051197e

Agradecimentos/Acknowledgments

O presente trabalho está sendo realizado com o apoio da Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – Brasil (CAPES).

Área: MED

Molecular docking analysis of benzoxaboroles as candidate inhibitors of *Leishmania braziliensis* Endonuclease CPSF3

Layla D. de Araújo (IC), Carlos Mauricio R. Sant'Anna (PQ)

layladorbacao@gmail.com; santanna@ufrrj.br

Departamento de Química Fundamental, UFRRJ

Keywords: *Leishmania brazilienzis*, CPSF3, Homology modeling, Benzoxaboroles , Molecular docking.

Highlights

L. infantum CPSF3 endonuclease inhibitors were evaluated by molecular docking as ligands of *L. infantum* and *L. braziliensis* enzymes. The compounds presented very similar interactions with both enzymes.

Abstract

Leishmaniasis is a neglected tropical disease caused by protozoa of the genus *Leishmania*, whose clinical manifestations differ according to the species of *Leishmania* involved. Existing drugs for treating the disease have high toxicity, making it necessary to search for new ones. In a recent study, benzoxaboroles with excellent activity against *L. donovani* and *L. infantum*, parasites that cause visceral leishmaniasis (VL), were identified[1]. Detailed mode of action studies confirmed the active compounds act as inhibitors of the parasites' cleavage and polyadenylation specificity factor (CPSF3), a zinc-containing endonuclease.

Due to the encouraging results presented by benzoxaboroles against *L. infantum*, the objective of this work was to analyze by theoretical methods the potential of the same compounds as candidate CPSF3 inhibitors of *L. braziliensis*, comparing the interactions of the compounds with the enzymes of both species. *L. braziliensis* is one of the species responsible for mucocutaneous leishmaniasis, which causes ulcers on the skin and mucous membranes. It is the most important *Leishmania* species, not only in Brazil, where around 21,000 cases are recorded each year on average, but throughout Latin America, with a wide distribution, from Central America to northern Argentina.

Since there are no crystallographic structures available for *L. braziliensis* and *L. infantum* CPSF3, 3D models were constructed from the enzymes' sequences extracted from UniProtKB/Swiss-Prot database. Models were prepared by homology modeling with the Swiss-Model online server (https://swissmodel.expasy.org/) using templates with 46% and 53% sequence identity with targets, respectively. The structures of the 10 most active compounds (values of intramacrophage *L. infantum* EC_{50} between 0.5 and 1.6 μM) extracted from ref. 1 were constructed and optimized with the semi-empirical method PM6, available in Spartan'20 (Wavefunction, Inc). The compounds were constructed with a boronate group, since CPSF3 contains a zinc-activated water that is expected to react with the oxaboroles leading to the formation of a negatively charged boronate species that coordinates the active site zinc ions, mimicking the substrate RNA phosphate.[1] To study interactions with the CPSF3 models of each protozoan species, molecular docking runs were made with the GoldScore scoring function of GOLD 2022.3.0 (CCDC) in duplicate. The following table presents the highest score value for each compound extracted from the duplicate docking runs. All compounds docked very well in both enzymes an there is a high correlation between scores obtained with both species (R = 0.86), indicating a strong similarity in the interaction patterns.

	Fitness score (GoldScore) in CPSF3	
Compound[1]	*L infantum*	*L. braziliensis*
5	64.64	63.89
6	65.42	67.38
9	69.27	68.34
12	69.56	70.29
13	69.72	67.76
17	68.49	68.93
19	69.07	69.53
25	66.34	63.93
28	64.45	64.04
30	70.45	72.54

The results presented here are indicative that the compounds identified by Mowbray and colleagues as active against *L. infantum* also have potential activity against *L. braziliensis*, based on a very similar interaction profile with the enzyme related to the benzoxaboroles activity, CPSF3, from both parasite species.

[1] MOWBRAY, C. E. *et al. J. Med. Chem.* **2021**, 64,16519-16176.

Acknowledgments

CNPq, FAPERJ

ÁREA: MED

Molecular hybridization: a useful tool in the design of novel curcumin-nitroimidazole derivatives potentially active against *Trypanosoma cruzi*.

Jayane Clys C. dos Santos (IC),[1] Jorge Lucas F. Lacerda (PG),[1] Afonso Santine M. M. Velez (PG),[1] Debora Decoté-Ricardo (PQ),[2] Marco Edilson F. de Lima (PQ).[1]* jayclys@ufrrj.br; marcoedilson@gmail.com*

[1]Instituto de Química - Universidade Federal Rural do Rio de Janeiro, Seropédica, RJ; [2]Instituto de Veterinária - Universidade Federal Rural do Rio de Janeiro, Seropédica, RJ.

Keywords: *Chagas disease, Diarylheptanoides, Nitroreductases, Cytotoxicity, Medicinal chemistry of natural products.*

Highlights

This work shows the synthesis planning of curcumin *O*-alkylated with nitroimidazoles-like molecular hybrids aiming to potentialize the biological profile of the natural diarylheptanoid against *T. cruzi* amastigotes.

Abstract

The Chagas disease (CD) is a parasitic illness caused by hemoflagellate parasite *T. cruzi*. CD affects around 8 million people worldwide, being concentrated in peripheral and rural areas in Latin America. Due to the lack of access by the population to diagnostic methods, and adequate treatments, is registered that around 30,000 new cases and 10 thousand people die per year by CD consequence, which makes around 75 million people vulnerable to parasitic infection.[1] Furthermore, the drugs known and currently used to treat CD, are benznidazole (**4**) and nifurtimox (the second been banned in Brazil, due to their genotoxicity), which aren't effective and are toxic to the patients, due to the capacity to release reactive oxygen and nitrogen species (ROS and RNS) at the organism, causing oxidative stress at spidering cells.[2]

In the search for novel alternatives to CD treatment our group (LaQuiMed-UFRRJ), in previous works, realized a series of studies in the trypanocidal activity of main natural products (diarylheptanoids) from *Curcuma longa* dry rhizomes, that consists of majority in curcumin (**1**, CUR), desmethoxycurcumin (**2**, DMC) and bisdesmethoxycurcumin (**3**, BDMC, **Figure 1**).

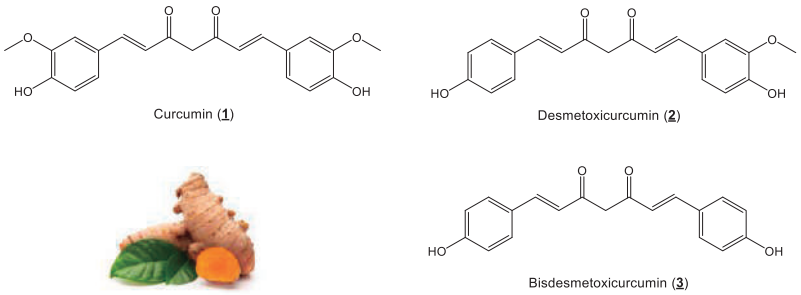


Figure 1 – Majority natural curcuminoids isolated from *C. longa* rhizomes.

These natural curcuminoids showed an important antiparasitic activity against amastigotes forms of *T. cruzi* (Tulahuen C2C4 LacZ strains), with adequate cytotoxicity profile against LLC-MK2 cells, that presents IC_{50} values 17,75 ± 6,88 μM to CUR, 31,31 ± 0,77 μM to DMC and 17,61 ± 0,26 μM to BDMC.[3,4] This set of results may be attributed to the antimitotic feature of curcuminoids, due its capacity to interacts with tubulin (essential protein to the parasite's proliferation), since it acts directly on the *T. cruzi* cell cycle, making its a possible molecular target to CD chemotherapy.[3]

Aiming to potentialize the anti-*T. cruzi* activity of curcumin (**1**), a series of curcumin-nitroimidazole hybrids (**5 – 7**, ***Figure 2***) were designed and synthesized with the goal of to affect the *T. cruzi* cells in two different ways, since the nitroimidazole can interact with the trypanothione reductase, generating toxic intermediates to the parasite because this enzyme is responsible to avoid oxidative stress, ensuring it viability. The evaluation of the new hybrids is underway.

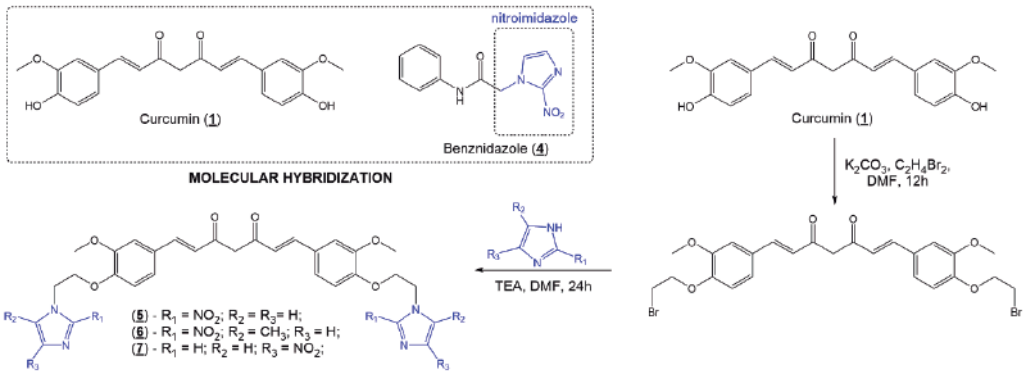


Figure 2 – Curcumin-nitroimidazoles hybrids molecular planning and the synthetic scheme.

[1] **PAN-AMERICAN HEALTH ORGANIZATION/ WORLD HEALTH ORGANIZATION** - https://www.paho.org/pt/brasil; [2] KANESHIMA, E. N. et alActa Scientiarum. Health Science, v. 34, n. 0, 19 dez. 2012. [3] SUETH-SANTIAGO, V. *et al.* **PLoS ONE** 11(9): e0162926; [4] BARREIRO, E. J.; FRAGA, C. A. M. Química Medicinal: As Bases Moleculares da Ação dos Fármacos. [s.l: s.n.].

Acknowledgments

CNPq, CAPES, FAPERJ

Área: MED

Molecular Modeling and Structural Comparison of *Leishmania* Sirtuin 2 Enzymes, an Epigenetic Target in Drug Discovery

Andre Berndt Penteado (PG),[1*] Gustavo H.G Trossini (PQ).[1]

andre.berndt.penteado@usp.br; trossini@usp.br

[1]*Department of Pharmacy, School of Pharmaceutical Sciences, University of São Paulo, SP, Brazil.*

Palavras Chave: *Comparative Modeling, Molecular Dynamics, Sirtuin 2-related protein 1, Leishmania, MM/PBSA, Structure-Based Drug Design.*

Highlights

Sirtuin 2 models from species of *Leishmania* and the human homolog were built by Comparative Modeling. Molecular Dynamics were employed to evaluate the residues involved in their substrates' binding.

Resumo/Abstract

Leishmaniasis are neglected diseases that affect a large part of the world's population, mainly in developing countries, causing major socioeconomic impacts. The medications available to treat these diseases are ineffective and have serious adverse effects. The process of researching new drugs involves, among other things, a selection of biochemical targets essential for the survival and development of the causative agent. In this sense, Sirtuin 2, an epigenetic enzyme with hydrolase activity essential for the survival of parasites of the genus *Leishmania*, presents itself as an interesting target in the search for new drugs against these parasites. Structure-Based Drug Design requires knowledge of the three-dimensional structure of the target protein. Therefore, the structural elucidation and a detailed study of Sirtuins from various species of the genus *Leishmania* presents itself as an important approach in the application of this strategy in the search for chemotherapeutic agents. To date, in the *Trypanosomatidae* family, the only experimentally resolved three-dimensional structure of a Sirtuin 2 enzyme is that of the *Leishmania infantum* species Sirtuin 2-related protein 1 (Protein Data Bank accession code 5OL0). Thus, this work applied the Comparative Modeling approach using the software Modeller in the construction of Sirtuin 2-related protein 1 (Sir2rp1) models of the species *L. infantum*, *L. major*, and *L. braziliensis*, whose amino acid sequences were retrieved from the UNIProt database. The constructed models were validated by means of the Modeller's DOPE score function and the servers PROCHECK, MolProbity and QMEAN, evaluating their stereochemical quality and their folding. The Sirtuin 2 natural ligands were superimposed in the built models using the PyMol software and the validated complexes were submitted to Molecular Dynamics simulations through the GROMACS package. The refined complexes were then analyzed by means of the softwares PyMol and LigPlotPlus and the packages GROMACS and gmx_MMPBSA, and the substrates' binding sites and the relevant amino acid residues involved in their binding and recognition were studied. The application of Molecular Modeling is an alternative for the structural study of homologous enzymes, making it possible to elucidate the points of interaction and the selectivity for substrates and modulators of these parasitic hydrolases. A comparative study between these enzymes expressed by different parasitic species provided us with an understanding of structural differences between them and in relation to the human homologous protein. The Comparative Modeling of the human Sirtuin 2 and its homologues from the species *L. infantum*, *L. major*, and *L. braziliensis*, the Molecular Dynamics simulations conducted with the constructed and validated enzymatic models complexed with their natural ligands, the calculations of the energy of interaction between the models and their substrates and the comparative structural study carried out between them provides us with a theoretical basis for the search for novel Sirtuin 2 inhibitors that are more selective and potent against the parasitic enzymes, paving the way for the development of safer and more effective leishmanicidal drug candidates.

Agradecimentos/Acknowledgments

CAPES, CNPq, FAPESP and FUSP

Área: ORG

Molecular modeling studies of arginase inhibitors from *Leishmania (L.) amazonensis*

Camilo H. S. Lima (PQ),[1] Priscila G. Camargo (PQ),[2] Magaly G. Albuquerque (PQ),[1] Carlos R. Rodrigues (PQ),[2]

camilolima@iq.ufrj.br; priscilagcmg@gmail.com

[1]Laboratório de Modelagem Molecular (LabMMol), Instituto de Química, Universidade Federal do Rio de Janeiro; [2]Faculdade de Farmácia, Departamento de Fármacos e Medicamentos, Universidade Federal do Rio de Janeiro

Palavras-Chave: *CoMFA, Molecular Docking, Molecular Dynamics, Antileishmanial, Neglected Diseases.*

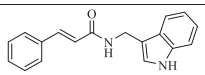
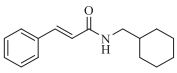
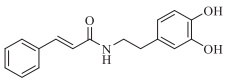
Highlights

3D-QSAR models constructed to identify arginase inhibitors.
Two compounds were selected by molecular docking study with protein sites.
Molecular dynamics demonstrated the potential binding interaction.

Abstract

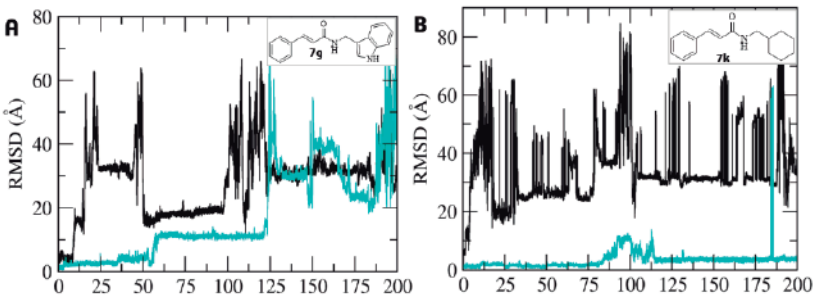
Leishmaniasis is a disease caused by protozoa of the genus *Leishmania*, mainly in tropical countries. It affects millions due to poor social conditions and economic development[1]. The primary treatment involves pentavalent antimonial drugs, which are highly toxic and resistant[2]. Arginase is vital in pathogenicity and contributes to a higher infection rate[3]. This study helps design arginase inhibitors for leishmaniasis treatment. CoMFA 3D-QSAR[4] models were constructed using 34 inhibitors from different chemical classes against arginase from *L. amazonensis*. The QSAR predictions showed an excellent correlation between experimental and calculated pIC_{50} values (Table 1). Two cinnamide compounds, **7g** and **7k**, with similar structures to the reference inhibitor, were identified. The molecular docking study identified the favorable hydrophobicity contribution of phenyl and cyclohexyl groups as substituents in the protein site. The results of molecular dynamics studies (Figure 1) indicate that the molecule **7g** has a stronger binding affinity (ΔG= -86.2±8.84 kJ/mol) to the active site than to the allosteric site (ΔG= -56.2±8.15 kJ/mol). Conversely, the molecule **7k** shows a more favorable binding to the allosteric site (ΔG= -69.3±7.37 kJ/mol) compared to the active site (ΔG= -31.3±9.26 kJ/mol). These findings suggest that the two molecules may have different mechanisms of action and could potentially guide the development of more effective arginase inhibitors for treating Leishmaniasis.

Table 1. Predicted pIC_{50} values for **7g** and **7k**, and reference compound from CoMFA model C*sp3*.

Compounds	Structures	pIC_{50Pred}
7g		5.169
7k		5.151
Reference		5.811

pIC_{50Exp} of reference compound = 5.886 μM

Figure 1. RMSD analysis of **7g** (**A**) and **7k** (**B**) in the active (black) and allosteric (cyan) sites.



Acknowledgments

The authors wish to thank FAPERJ (E-26/205.966/2022, E- 26/205.967/2022, SEI-260003/019723/2022) and CENAPAD - SP.

References

[1]World Health Organization (WHO). Leishmaniasis. https://www.who.int/health-topics/leishmaniasis (2024). [2]Pradhan, S., Schwartz, R. A., Patil, A., Grabbe, S. & Goldust, M. Treatment options for leishmaniasis. *Clin. Exp. Dermatol*. 47, 516–521 (2022). [3]Pessenda, G. & da Silva, J. S. Arginase, and its mechanisms in Leishmania persistence. *Parasite Immunol.* 42, (2020). [4]Ragno, R. www.3d-qsar.com: a web portal that brings 3-D QSAR to all electronic devices—the Py-CoMFA web application as a tool to build models from pre-aligned datasets. *J. Comput. Aided. Mol*. Des. 33, 855–864 (2019).

Área: MED
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Naphthoquinone-1*H*-1,2,3-triazole Hybrids: Design, Synthesis and Evaluation as Inductors of ROS-Mediated Apoptosis in the MCF-7 Cells

Acácio S. de Souza (PQ),[1*] Deborah S. Dias (PG),[2] Ruan C. B. Ribeiro (PQ),[3] Dora C. S. Costa (PQ),[3] Laís M. Marins (IC),[3] Matheus G. de Moraes (PG),[3] Sandy P. Valle (IC),[3] Claudio J. C. de Carvalho (PG),[3] Gustavo S. G. de Carvalho (PG),[3] Angélica L. N. Mello (PQ),[2] Mauro Sola-Penna (PQ),[4] Luana da S. M. Forezi (PQ),[3] Vitor F. Ferreira (PQ),[1] Patrícia Zancan (PQ),[2] Fernando de C. da Silva (PQ).[3]

acacio.farma@gmail.com

[1]Departamento de Tecnologia Farmacêutica, Faculdade de Farmácia, UFF; [2]Departamento de Biotecnologia Farmacêutica, Faculdade de Farmácia, UFRJ; [3]Departamento de Química Orgânica, Instituto de Química, UFF; [4]Departamento de Biotecnologia Farmacêutica, Faculdade de Farmácia, UFRJ.

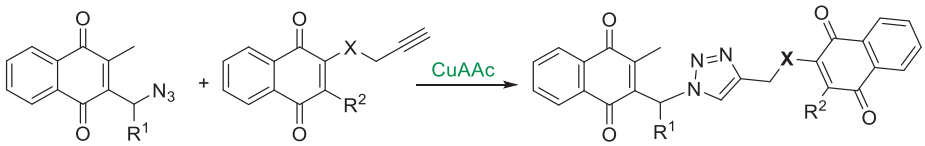
Keywords: *Anticancer, Mannich bases, Molecular Hybrids.*

Highlights

Rational design, synthesis and antitumor activity of new potential selective drugs against breast cancer.

Abstract

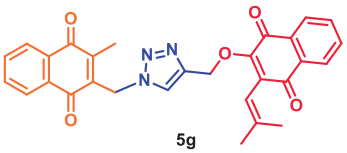
The search for novel anticancer drugs is essential to expand treatment options, overcome drug resistance, reduce toxicity, and promote innovation.[1] The importance of these studies lies in their contribution to advancing cancer research and enhancing patient outcomes in the battle against cancer. Here, we developed new asymmetric hybrids containing two different naphthoquinones linked by a 1,2,3-1*H*-triazole nucleus (**5**), which are potential new drugs for cancer treatment. For the synthesis of the news naphthoquinone hybrids **5**, the azido-menadiones **1** were reacted with propargylated naphthoquinones **2-4** through a CuAAC reaction[2] to furnish **5a-q** (52-63%).



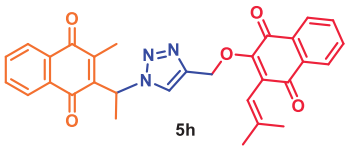
Scheme 1. Synthesis of naphthoquinone-1*H*-1,2,3-triazole hybrids**.**

The antitumor activity of the novel compounds was tested using the breast cancer cell lines MCF-7 and MDA-MB-231, using the non-cancer cell line MCF10A as control. Our results showed that two substances tested (**5g** and **5h**) presented potential antitumor activity against the breast cancer cell lines. These potential drugs were effective in reducing cell viability and promoting cell death of the tumor cell lines, exhibiting minimal effects on the control cell line (Table 1). The mechanism of action of the novel drugs was assessed revealing that both drugs increased reactive oxygen species production with consequent activation of the AMPK pathway.

Table 1. IC_{50} values of compounds **5g** and **5h.**



Cell line[a]	IC_{50} 5g (μM)	IC_{50} 5h (μM)	Doxorubicin (μM)
MCF10A	n.d.	n.d.	n.d.
MCF-7	4.4 ± 0.9	4.3 ± 1.1	1.1 ± 0.3
MDA-MB-231	11.1 ± 2.3	9.2 ± 2.1	n.d.



[1] Lopes, G. *JAMA Oncol.* **2023**, *9*(4), 461-462.
[2] Silva, B. N. M.; Pinto, A. C.; Silva, F. C.; Ferreira, V. F.; Silva, B. V. *J. Braz. Chem. Soc.* **2016**, *27*, 2378-2382.

Acknowledgments

FAPERJ, CAPES, FIOCRUZ and CNPq.

Área: MED

New chalcogen-functionalized naphthoquinones: design, synthesis, and cytotoxic activity against Oral Squamous Cell Carcinoma (OSSC)

Luana S. Gomes (PG),[1*] Érica O. Costa (IC),[1] Thuany G. Duarte (IC),[1] Thiago S. Charret (PG),[4] Raquel C. Castiglione (PQ),[5] Rafael Loureiro Simões (PQ),[6] Vinicius D. B. Pascoal (PQ),[4] Thiago H. Döring (TC),[7] Fernando C. da Silva (PQ),[2] Vitor F. Ferreira (PQ),[3] Aldo S. de Oliveira (PQ),[7] Aislan C. R. F. Pascoal (PQ),[4] André L. de S. Cruz (PG)[8] and Vanessa Nascimento (PQ).[1]

luanagomes@id.uff.br; luanagomes@id.uff.br

[1]SupraSelen Laboratory, Department of Organic Chemistry, Federal University Fluminense, Institute of Chemistry, Niterói-RJ; [2]Applied Organic Synthesis Laboratory (LabSOA), Institute of Chemistry, Universidade Federal Fluminense, Niterói-RJ; [3]Faculty of Pharmacy, Research and Development Laboratory in Pharmaceutical Technology, Niterói-RJ; [4]Research Laboratory of Natural Products and Bioactive Molecules, Fluminense Federal University (ISNF-UFF), Nova Friburgo-RJ; [5]Clinical and Experimental Research Laboratory in Vascular Biology (BioVasc), Rio de Janeiro-RJ; [6]Cellular and Molecular Pharmacology Laboratory, Biomedical Center, Rio de Janeiro-RJ; [7]Department of Exact Sciences and Education, Federal University of Santa Catarina, Blumenau-SC; [8]Physiopathology Laboratory, Institute of Medical Sciences, Macaé-RJ.

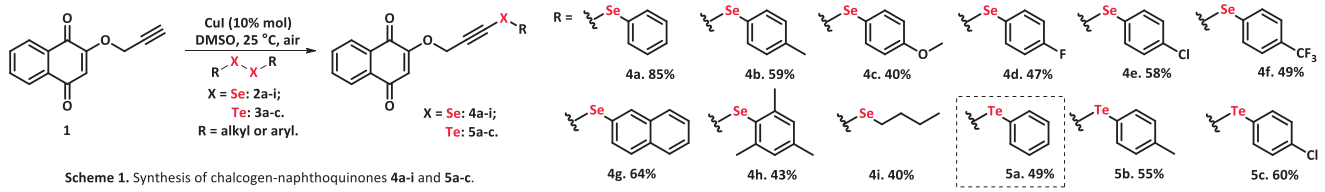
Palavras Chave: *Drug development, Anticancer activity, Organochalcogen compounds, Targeted synthesis*.

Highlights

Organochalcogen compounds were synthesized, showed strong anticancer effects against SCC-9 cells, especially (**5a**). The experiments performed included cytotoxicity, selectivity, and in silico studies.

Resumo/Abstract

Oral squamous cell carcinoma (OSCC) is the sixth most common malignant tumor in humans, accounts for about 2% of all cancer cases and approximately 350,000 new cases are diagnosed globally each year, resulting in up to 170,000 annual mortalities. Chemotherapy is an important part of OSCC treatment and is frequently used in conjunction with radiotherapy and surgery. Unfortunately, the establishment of multi-drug resistance mechanisms in specific cell types has been frighteningly rapid, resulting in treatment failures.[1] In light of this difficulty, the development of new treatment options using more effective medications is becoming increasingly necessary. In this context, chalcogens-containing compounds and naphthoquinones can be a good alternative to new medicines due to their potential therapeutic efficacy and unique modes of action.[2,3] Therefore, in this work, twelve new compounds were synthesized (**4a-i** and **5a-c**) using a CuI-catalyzed Csp-chalcogen bond formation method. The methodology produced outstanding results, with yields ranging from 30 to 85% (**Scheme 1**).



Scheme 1. Synthesis of chalcogen-naphthoquinones **4a-i** and **5a-c**.

To assess the compounds' potential antineoplastic capabilities, an MTT cell viability experiment was first performed on the twelve samples, which demonstrated dose-dependent cytotoxicity in SCC-9 cells, outperforming carboplatin. In particular, the tellurium-containing compound (**5a**) an IC_{50} = 1.648 µM, demonstrated high selectivity for these cells with a S.I. = 3.53. In silico studies also revealed that compound (**5a**) inhibits tubulin polymerization, interfering with microtubule production and mitotic spindle function (**Figure 1**). This prevents cell division and induces apoptosis. Furthermore, compound (**5a**) avoids P-glycoprotein, crucial for overcoming multidrug-resistant tumor mechanisms, making it a promising candidate for targeted cancer treatment while sparing normal cells.

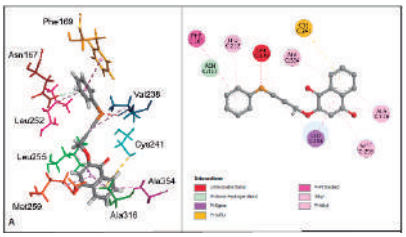


Figure 1. 3D view and 2D diagram of ligand-receptor interactions between Tubulin protein and **5a**.

Agradecimentos/Acknowledgments

UFF, CAPES, FAPERJ and CNPq.

[1] (a) Yang, Z. *et al. Oncoimmunology,* **2021**, 10, e1938890; (b) Wang, Z. *et al. BMC Cancer*, **2023**, 23, 2.
[2] (a) Pereyra, C. E. *et al. Cancer Cell Int.,* **2019**, 19, 1-20; (b) Hu, J. *et al. Molecules,* **2023**, 28, 1304.

ÁREA: MED

Novel curcuminoids with anti-*Trypanosoma cruzi* activity against amastigotes forms, a structural design study

Jorge Lucas F. Lacerda (PG),[1] Jayane Clys C. dos Santos (IC),[1] Afonso Santine M. M. Velez (PG),[1] Debora Decoté-Ricardo (PQ),[2] Carlos Maurício R. Sant'Anna (PQ),[1] Marco Edilson F. de Lima (PQ).[1]* jorge.llacerda@ufrrj.br; marcoedilson@gmail.com*

[1]Instituto de Química - Universidade Federal Rural do Rio de Janeiro, Seropédica, RJ; [2]Instituto de Veterinária - Universidade Federal Rural do Rio de Janeiro, Seropédica, RJ.

Keywords: *Chagas disease, Bioisosterism, Curcumin, (Bis)styryl-pyrimidines, Docking, Cytotoxicity.*

Highlights

This work shows the design and synthesis of novel curcuminoids planning from non-classic bioisosterism strategy aiming to potentialize the biological profile and stability of the natural diarylheptanoids against *T. cruzi* amastigotes.

Abstract

Chagas disease (CD) is caused by the hemoflagellated parasite *Trypanosoma cruzi,* affecting 8 million people worldwide and causing 30,000 infections and 10,000 deaths per year. This parasitic disease is endemic in Latin America, both in rural and peripheral areas, being classified by WHO as a neglected tropical disease, principly due to the difficult access of infected patients to both effective treatments and diagnostics. This epidemiological scenario makes around 75 million people vulnerable to this parasitic infection.[1]

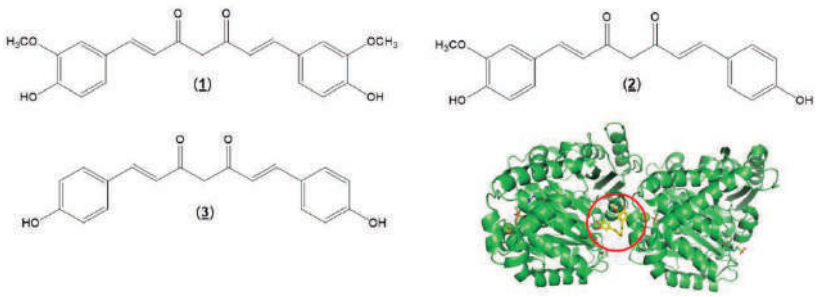


Figure 1 – Natural curcuminoids and their bind pocket at *T. cruzi*'s tubulin.

The only two drugs are now available to the CD treatment, benznidazole and nifurtimox (wish was prohibited in Brazil due to its genotoxicity), aren't effective due their low efficacy in the chronic phase of inffection, and both drugs are toxic, because they can cause oxidative stress to the host's organism due to its ability of release reactive oxygen and nitrogen species (ROS and RNS) related to these drugs.[2]

Our research group (LaQuiMed – UFRRJ) investigated the anti-*T. cruzi* activities of curcumin (**1**, CUR), desmethoxycurcumin (**2**, DMC) and bisdesmethoxycurcumin (**3**, BDMC, **Figure 1),** the major's constituents by the dry rhizomes of the medicinal plant, *Curcuma longa*. They were evaluated by molecular docking in *T. cruzi* tubulin as their molecular target, since they can cause mitotic catastrophe, and affect the parasite like the antimitotic drugs do.[3]

in this work, the curcuminoids CUR, DMC and BDMC were tested against amastigotes *T. cruzi* forms (LLC-MK2 infected by Tulahuen strains) and presented the IC_{50} values of 17.75 ± 6.88 μM, 31.31 ± 0.77 μM, and 17.61 ± 0.26 μM respectively. These results were compared with *in silico* results obtained by molecular docking of a new tubulin homology model.

Despite presents promising results against the parasite, the curcuminoids significantly present cytotoxicity to the host cells. To enhance the anti-*T. cruzi* activity and the selectivity of these substances, novel *bis*-styrylpirimidines analogues (**4** – **5**, **Figure 2**) were elaborate with non-classic bioisosterism, *in silico and in vitro* studies as medicinal chemistry tools aiming to reach a better biological profile for the new series planned.[3, 4]

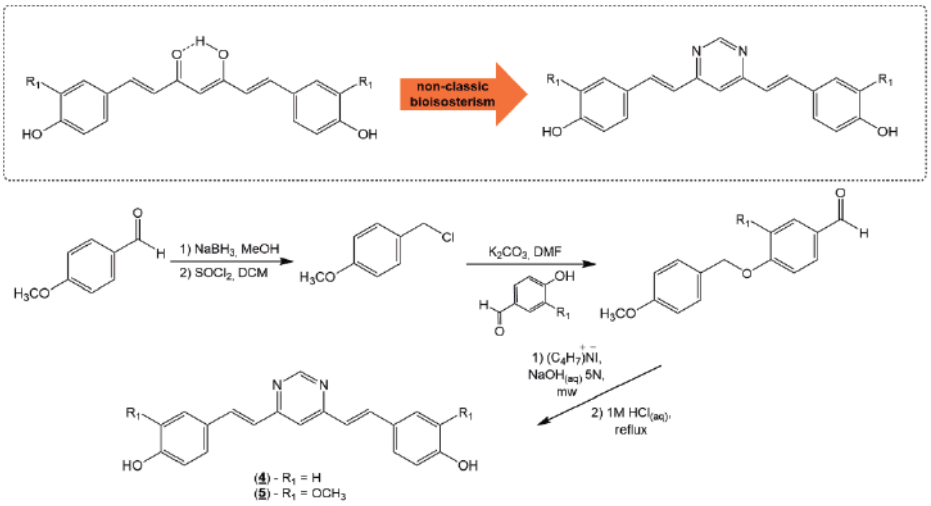


Figure 2 – *bis*-styrylpyrimidines molecular analogues planning; and the synthetic route develloped.

[1] **PAN-AMERICAN HEALTH ORGANIZATION/ WORLD HEALTH ORGANIZATION** - https://www.paho.org/pt/brasil; [2] KANESHIMA, E. N. et al. Acta Scientiarum. Health Science, v. 34, n. 0, 19 dez. 2012. [3] SUETH-SANTIAGO, V. *et al.* **PLoS ONE** 11(9): e0162926; [4] BARREIRO, E. J.; FRAGA, C. A. M. Química Medicinal: As Bases Moleculares da Ação dos Fármacos. [s.l: s.n.].

Acknowledgments

CNPq, CAPES, FAPERJ

Área: MED
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Novel Naphthoquinone Derivatives with anti-*Mycobacterium tuberculosis* Activity

Alcione Silva de Carvalho (PC),[1] Beatriz Cunha Tolla de Oliveira (IC),[1] Dandara de Paula Candido (PG),[2] Carlos Mauricio R. Sant'Anna (PQ),[2] Fernando de Carvalho da Silva (PQ),[3] Maria Cristina da Silva Lourenço,[4] Vitor Francisco Ferreira (PQ).[1]

alcionecarvalho1570@gmail.com.; vitorferreira@id.uff.br

[1]Laboratório de Inovação em Química e Tecnologia Farmacêutica LabIQTF, FF-UFF; [2]Departamento de Química Fundamental, IQ-UFRRJ; [3] Laboratório de Síntese Orgânica Aplicada LabSOA,. IQ-UFF, [4] Plataforma de Bioensaios de Tuberculose-FIOCRUZ
Keywords: *Tuberculosis, Molecular Hybridization, Quinones, Medicinal Chemistry*

Highlights

Napthoquinone hybrids have been synthesized through a well-established synthetic methodology. The preliminary results showed good activity against *Mycobacterium tuberculosis*.

Abstract

Tuberculosis (TB) is an infectious, transmissible disease and despite being preventable and curable disease, 1.6 million people die from tuberculosis each year, making it the leading cause of infectious death worldwide. A major issue is the increase in cases of multidrug-resistant and extensively resistant strains of *M. tuberculosis*. Naphthoquinones are one of the classes that has been highlighted in terms of anti-TB activity with various therapeutic targets against *M. tuberculosis*. Continuing our contributions to the fight against tuberculosis, in this work we present the design, synthesis and biological evaluation of 11 naphthoquinone derivatives (**5-15**), as anti-*M. tuberculosis* agents, possible inhibitors of the enzyme shikimate kinase (Mtb-SK), enzyme present only in *M. tuberculosis*, essential for the synthesis of aromatic amino acids essential for Mycobacteria. The medicinal chemistry strategy was molecular hybridization (**Fig. 1**).

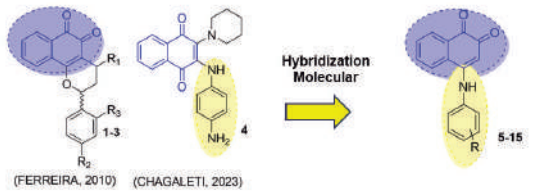
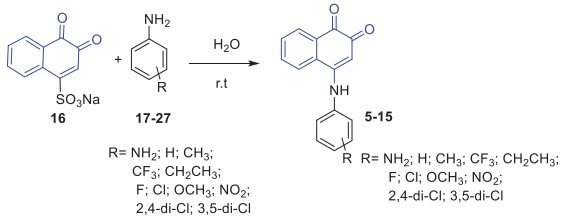


Figure 1: Design of naphthoquinone derivatives as possible anti-TB agents.

The synthesis is described in the **Scheme 1**. Five derivatives showed good activity against *M. tuberculosis*. The most active was the 4-((4-methoxyphenyl) amino) naphthalene-1,2-dione (**12**) derivative with an MIC of 21.33 µM, equipotent to the ethambutol and 36 times more potent than pyrazinamide, drugs used in tuberculosis chemotherapy.



Scheme 1. Synthetic route of new derivatives **(5-15).**

Cytotoxicity testing on HepG2 cells of the active substances is currently being carried out. A molecular docking study with GOLD2023.2.0 (CCDC) was done to evaluate the interaction profile of **5-15** with Mtb-SK. The Mtb-SK 3D structure was obtained in the Protein Data Bank (code 1WE2) and the GoldScore fitness function was used in the docking procedure. The structure contains as ligands Mg^{2+}, ADP and shikimate. The compounds were prepared and energy minimized with the PM6 method in Spartan'20 (Wavefunction) and then docked at the shikimate binding site, after removal of the ligand and water molecules. Compound **4** was used as a reference, since it was previously shown to be an Mtb-SK inhibitor (CHAGALETI, 2023). Docking studies were also implemented after replacement of ADP by a modelled ATP molecule, since it is one of the substrates of Mtb-SK. With both the ADP- and the ATP-containing Mtb-SK structures, all naphthoquinones presented favourable interactions in the shikimate binding site.
A novel series of naphthoquinones were obtained in excellent yield. Preliminary anti-TB activity of these compounds showed good activity. This study can aid in the design of new hit compounds.

FERREIRA, S.B. *et al* 2010 *Arch. Pharm.*, *343*, 81-90; CHAGALETI, B.K. *et al* 2023 *J. Biomol. Struct. Dyn.*, *28*, 1-17

Acknowledgements

PIBIC-CNPq; CAPES; FAPE

Área: *MED*

Planejamento, Síntese e Caracterização de uma nova bis-benzamidina com potencial atividade antileishmania

Jonas T. Xavier (IC)[1], Aurea Echevarria(PQ) [2], Cláudio Eduardo Rodrigues-Santos (PQ) [1,2]

jonastxavier@gmail.com; claudioers@ufrrj.br

[1]*Departamnteo de Química Orgânica, Instituto de Química - Universidade Federal Rural do Rio de Janeiro (UFRRJ), Seropédica, RJ,* [2]*Programa de Pós-graduação em Química Orgânica-UFRRJ.*

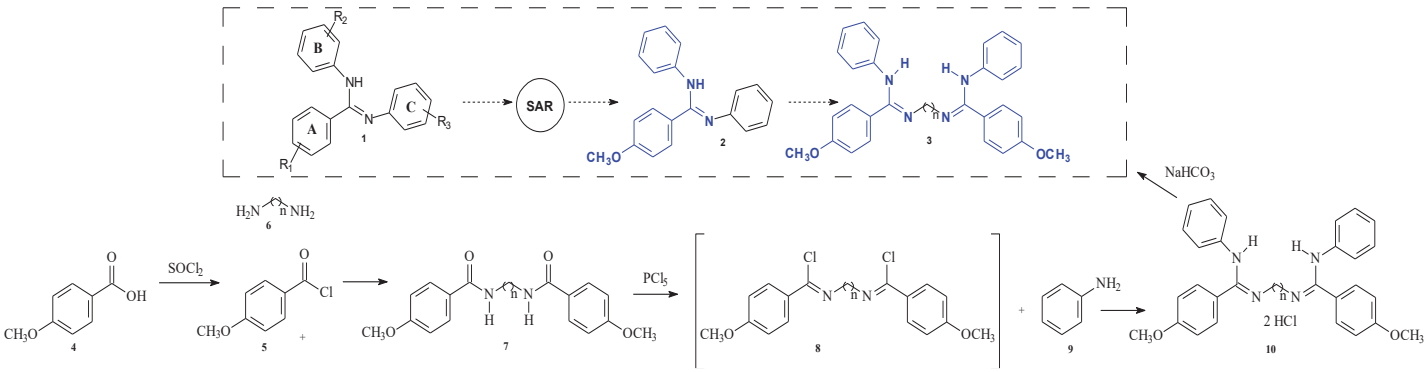
Palavras Chave: *Bis-benzamidinas, SAR, Atividade antileishmania,*

Highlights

Planning, Synthesis, and Characterization of a New Bis-benzamidine with Potential Anti-leishmanial Activity.
In this study, a new derivative of the bisamidine class with potential anti-leishmania activity was planned, synthesized, and characterized.

Resumo/Abstract

A leishmaniose é uma parasitose que promove manifestação cutânea, mucosa, mucocutânea e visceral. Nesse contexto, a organização Mundial da Saúde emitiu uma resolução que determina a leishmaniose como uma das doenças tropicais mais negligenciadas no mundo. A única forma de tratamento para tal doença é a quimioterapia, os fármacos de primeira escolha quanto os de segunda escolha precisam ser administrados em uma unidade de saúde, sua administração é via venosa, com exceção da milftefosina. Entretanto, todos os fármacos possuem efeitos colaterais acentuados. O grupo de pesquisa NUSQMED (Núcleo de síntese e Química Medicinal) tem evidenciado que os compostos da série *N*-R_2, *N'*-R_3-diaril-R_1-benzamidínicos (**1**) exibem uma atividade anti-leishmania promissora. Vários substituintes em diferentes posições foram inseridos nos anéis aromáticos (A, B, C), e por meio da análise da relação entre a estrutura e a atividade biológica (SAR), identificou-se o composto N,N'-diaril-4-metoxi-benzamidina (**2**) como particularmente interessante. Este composto demonstrou uma elevada atividade leishmanicida frente a *L. amozenensis* (14 µM), associada a uma baixa citotoxicidade para o hospedeiro. Estudos indicaram que o possível mecanismo de ação envolve a inibição das enzimas óxido nítrico sintases do parasita. Com base neste protótipo e considerando os resultados promissores dos derivados bis-amidínicos na literatura, foi planejado a nova bis-amidina **3**, **(Esquema 1)** com diferentes espaçadores (n).



Esquema 1. Rota sintética e planejamento dos derivados Bis-amidínicos

Neste trabalho sintetizou o composto **3** (n=2). A partir do ácido benzóico (**4**), obtivemos o cloreto de acila (**5**), que foi adicionado a uma solução de 10% NaOH com etilenodiamina (**6**, n=2) para formar a amida **7** (n=2), obtendo o rendimento de 29 %. A amida **7** (n=2) foi submetida a refluxo em tolueno e PCl_5 por 18h, originando o cloreto de imidoíla (**8**). Em seguida, *in situ*, adicionou-se anilina (**9**) à solução, resultando no produto **10** (n=2), diprotonado, com rendimento de 29 %. Posteriormente, este foi submetido a desprotonação por 26 h numa solução de bicarbonato de sódio a 10% m/v, seguido da extração do produto **3** (n=2) com clorofórmio. Tanto a amida (**7**) quanto a bis-benzamidina (**3**, n=2) foram analisadas por meio de espectros de RMN de ^1H e ^{13}C. Os compostos **10** (n=2) e **3** (n=2) serão enviados para avaliação da atividade anti-leishmania.

Agradecimentos/Acknowledgments

Os autores agradecem a CAPES, CNPq, e a FAPERJ

Área: MED

Quinazoline-Chalcone Hybrids as Tubulin Colchicine-Binding Site Inhibitors for Antimetastatic Cancer Drug Discovery

Maynara Afonso(IC)*,[1] Matheus da Silva Souza (PG),[1] Eduardo Mass (PQ),[2] Dennis Russowsky (PQ),[2] Adriano Defini Andricopulo (PQ).[1]

maynara.afonso@usp.br

[1]Laboratory of Medicinal and Computational Chemistry (LQMC), Center for Innovation in Biodiversity and Drug Discovery (CIBFar), Institute of Physics of Sao Carlos, University of Sao Paulo - USP; [2]Department of Organic Chemistry, Institute of Chemistry, Federal University of Rio Grande - UFRGS.

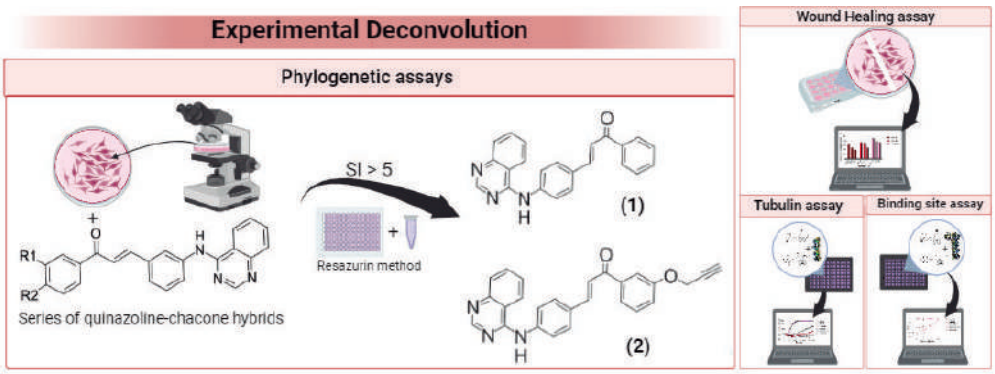
Palavras Chave: *Breast cancer, Medicinal chemistry, Tubulin, Quinazoline-chalcones, Metastasis.*

Highlights

The investigation of cytotoxic target tubulin in metastatic breast cancer, from phylogenetic assays to the identification of the binding site on the target protein.

Resumo/Abstract

Breast cancer can be characterized by abnormal and rapid proliferation of mammary tissue cells in a disordered manner. Among the different types and subtypes of breast cancer is triple-negative breast cancer (TNBC), which accounts for about 10 to 15% of all breast cancer cases. Cytotoxic therapy usually targets both healthy and tumor cells, and, then, selective drugs are a promising medical approach. In this context, the present study aimed to evaluate through biological assays a series of compounds using tubulin, a validated molecular target. The protein tubulin affects the polymerization capacity of microtubules and selectively impairs the proliferation of TNBC cells of the MDA-MB-231 cancer cell lineage. For this purpose, a series of ten synthetic hybrid compounds of quinazoline-chalcones, previously having in vitro activity for MDA-MB-231 cells, with a selectivity index (SI) greater than 5 (in comparison to healthy human fibroblasts HFF-1) were selected. The two most promising compounds (**1** e **2**) were characterized in migration assays, and for the ability to modulate tubulin polymerization. In addition, competitive binding site assays were conducted to determine the binding site of these compounds. The results of tubulin polymerization assays demonstrated that compounds **1** and **2** exhibit inhibitory activity, with IC_{50} values of 5.71 µM and 3.17 µM, respectively. These findings suggest their potential to interfere with the formation and stabilization of microtubules, which are essential structures for various cellular functions, including cell division. The results of the binding site competition assays indicated that the inhibition is due to the binding of **1** and **2** to the colchicine binding site. These compounds have shown promising characteristics for future medicinal chemistry efforts towards the development of new drug candidates for TNBC therapy.



Acknowledgments

The authors are grateful to CNPq – Brazil (project nº 138066/2022-1), FAPESP – Brazil (project nº 2018/25289-7) and CIBFar for all the support.

Rho-associated protein kinase (ROCK) chemical space analysis for design and synthesis of new inhibitors

Lucas S. Franco (PD),[1,2,3] Pedro S. M. Pinheiro (PQ),[2,3] Gabrielli A. I. Martins (IC),[2] Nicole S. Lemos (IC),[2] Eliezer J. Barreiro (PQ),[1,2,3] Carlos A. M. Fraga (PQ)[1,2,3]

silvafrancolucas@gmail.com; cmfraga@ccsdecania.ufrj.br

[1] *Programa de Pós-Graduação em Farmacologia e Química Medicinal, Instituto de Ciências Biomédicas, Universidade Federal do Rio de Janeiro, Avenida Carlos Chagas Filho, 373, Ilha do Fundão, Rio de Janeiro, RJ, Brasil;*
[2] *Laboratório de Avaliação e Síntese de Substâncias Bioativas (LASSBio, http://www.lassbio.icb.ufrj.br), Instituto de Ciências Biomédicas, CCS, Universidade Federal do Rio de Janeiro, Cidade Universitária, Rio de Janeiro, RJ, Brasil;*
[3] *Instituto Nacional de Ciência e Tecnologia de Fármacos e Medicamentos (INCT-INOFAR; http://www.inctinofar.ccs.ufrj.br/), CCS, Universidade Federal do Rio de Janeiro, Cidade Universitária, Rio de Janeiro, RJ, Brasil.*

Keywords: ROCK, Kinase, Inhibitors, Chemical Space

Highlights

Chemical space analysis of Rho-associated protein kinase (ROCK) led to the identification of key structural patterns associated with its inhibitors and the design of new ROCK inhibitor candidates.

Abstract

Rho-associated protein kinases (ROCKs) are serine/threonine kinases. To date, there are four approved ROCK inhibitors (ROCKi) for the treatment of glaucoma and ocular hypertension, cerebral vasospasm, and graft-versus-host disease. However, it has been suggested that ROCKi may be useful for the treatment of additional pathologies, such as neurodegenerative diseases, making the development of new ROCKi interesting.[1] Chemical space analysis provides a means of understanding the chemical basis for the design of new inhibitors.[2] In this work, ROCK inhibitors were extracted from ChEMBL database. A total of 166 ROCK1 inhibitors and 218 ROCK2 inhibitors ($pIC_{50} \geq 7$) were subjected to clustering analysis. Chemical space analysis of ROCKi was generated in the KNIME platform. PCA-based silhouette scores indicated that hierarchical clustering had better performance for both ROCK1 (0.91, k = 3) and ROCK2 (0.92, k = 3) datasets. For both datasets, the presence of densely populated clusters of molecules was observed for ROCK1 (159 molecules), and for ROCK2 (199 molecules). Sparse data points represented peptides and staurosporine derivatives. The most populated clusters of each dataset were further analyzed using MDS for dimensionality reduction. In this step, silhouette scores indicated that k-means had better performance for both ROCK1 (0.44, k = 4) and ROCK2 (0.47, k = 6) datasets. The K-medoids algorithm was employed to assign the main representative chemotypes of each cluster. For ROCK1, 7-azaindole, pyridine and indazole derivatives were detected. For ROCK2, 7-azaindole, 4-phenylpyridine, indazole, 4-amino-thieno[3,2-*c*]pyridine, indole, and phthalazinone derivatives were detected (Figure 1). Based on chemical space information, docking was performed using CCDC GOLD 2023.3.1 for 7-azaindole or pyridine ring containing compounds from the LASSBio Chemical Library.[3] This led leading to the design of new derivatives (Figure 1), which were synthesized in two steps from commercial 7-azaindole-3-carboxaldehyde and 4-pyridinyl-carboxaldehyde. NMR spectra were obtained using a Varian 400-MR and HPLC analysis was performed to determine relative purity of the compounds (>95%, 254 nm).

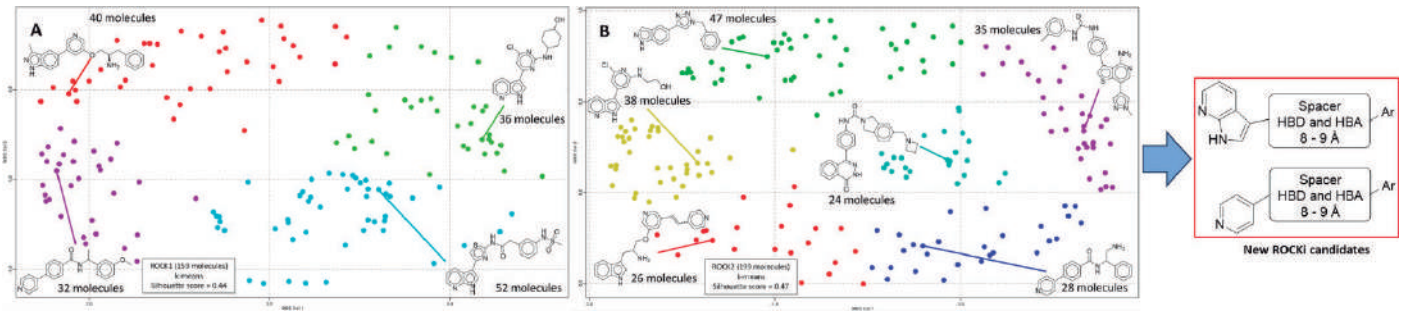


Figure 1: Chemical space of ROCK inhibitors for the design of new ROCKi candidates

References: 1. Hensel, N., Rademacher, S., Claus, P. *Frontiers in Neuroscience*, 2015, 9, 198.
2. Beroza, P. et al. *Nature Communications*, 2022, 13, 6447.
3. Franco, L. S., Maia, R. C., Barreiro, E. J. *RSC Medicinal Chemistry*, 2021, 12, 110.

Acknowledgments

INCT-INOFAR (CNPq Nº 465.249/2014-0), FAPERJ and CNPq.

Área: MED

Síntese de bavachalcona (BVC) e sua atividade antiviral contra o vírus Mayaro (MAYV)

Otávio H.L. Soares (PG),[1*] Maria B.S. Costa (PG),[1] Nancy Juaréz (PG),[2] Ana C.G. Jardim (PQ),[2] Luis O. Regasini (PQ).[1*]

otavio.henrique@unesp.br; luis.regasini@unesp.br

[1]Instituto de Biociências, Letras e Ciências Exatas, Unesp São José do Rio Preto; [2]Instituto de Ciências Biomédicas, UFU.

Palavras Chave: *síntese, chalcona, antiviral, bavachalcona, Mayaro, arbovírus.*

Highlights

Bavachalcona (**BVC**) foi sintetizada em cinco etapas, com rendimento global de 7%, sendo capaz de inibir a replicação do vírus Mayaro (EC_{50} = 14,4 μM).

Resumo

O vírus Mayaro (MAYV) foi isolado em 1954 em Trinidad e Tobago, sendo o agente etiológico da febre Mayaro, que apresenta sintomatologia similar a outras arboviroses, incluindo dengue, zika e chikungunya. Tendo em vista, a ausência de fármacos antivirais e vacina contra essa doença, a qual exibe caráter altamente negligenciado, o presente estudo visou investigar a bavachalcona (**BVC**) como potencial agente anti-MAYV. **BVC** foi sintetizada em 5 etapas, empregando reação de *O*-prenilação e rearranjo sigmatrópico, que permitiram a *C*-prenilação na posição 5' (anel A). Outras etapas incluíram o uso do grupo protetor metoximetila e condensação de Claisen-Schmidt. Os ensaios biológicos indicaram valores de EC_{50} = 14,4 μM (inibição da replicação viral), CC_{50} = 38,5 μM (toxicidade contra células de rins de macaco) e IS = 2,7 (índice de seletividade). Esses dados sugerem um ponto de partida para a descoberta de agentes anti-MAYV, uma vez que há poucas substâncias com essa bioatividade descritas na literatura.

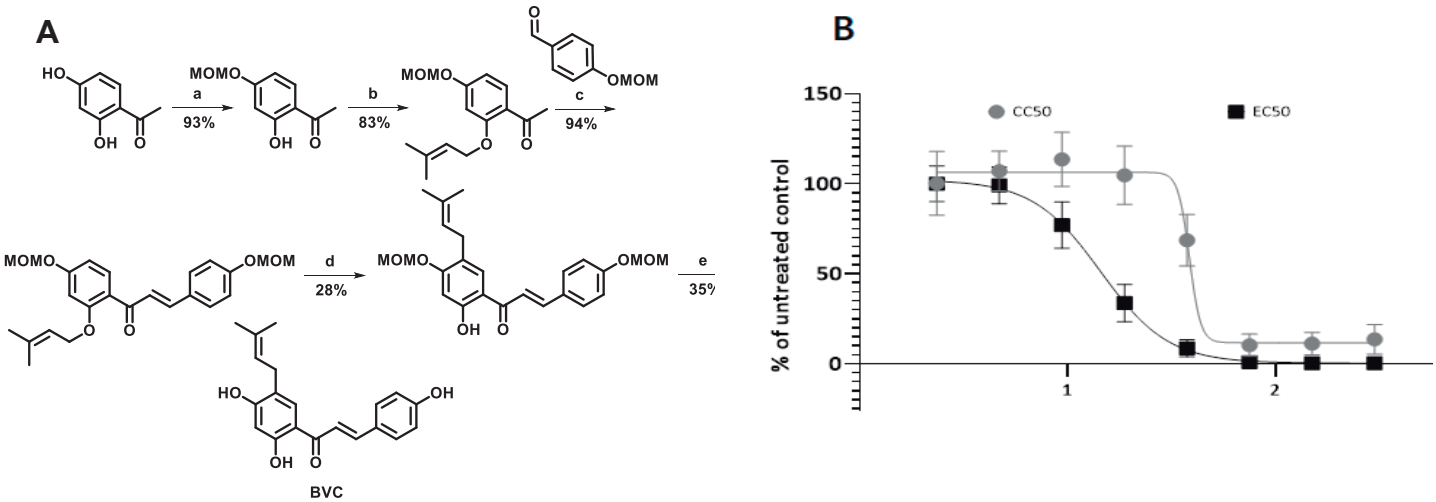


Figura A Síntese de BVC. a) MOMCl, K_2CO_3, acetona, 0 ºC → ta, 3 h; b) brometo de isoprenila, K_2CO_3, acetona, 0 ºC → ta, 24 h; c) 3,0 M NaOH, EtOH, rt, 8 h, d) Montmorilonita K10, DCM, 0 ºC → ta, 30 min; e) HCl 1 mol L^{-1}, MeOH:THF (1:1), 55 ºC, 6 h. MOM = metoximetila. **Figura B. Atividade Anti-MAYV de BVC.** CC_{50} = concentração tóxica contra 50% de células VeroE6 e EC_{50} = concentração capaz de inibir em 50% a replicação de MAYV.

Agradecimentos

Fapesp, CNPq, CAPES e PPG Química IBILCE.

Área: MED

Screening for inhibitors of methylthioadenosine phosphorylase from *Schistosoma mansoni* in *Hymenaea stigonocarpa*

Lucas G. do Amaral (IC),[1] Miguel F. S. de Abreu (IC),[1] Renato C. S. Lessa (PG),[1] Pamella C. O. de Oliveira (PG),[1] Martin Albino (PQ),[2] Claudio Sangregorio (PQ),[2] Vanessa G. P. Severino (PQ),[3] Marcela C. de Moraes (PQ).[1]*

amaral_lucas@id.uff.br; mcmoraes@id.uff.br

[1]Departamento de Química Orgânica, UFF; [2]Università degli Studi di Firenze, Itália; [3]Instituto de Química, UFG

Palavras Chave: *Schistosomiasis, Enzymes, Screening assays, Inhibitory potential.*

Highlights

*Sm*MTAP enzyme was immobilized onto magnetic cobalt ferrite nanoparticles, and its activity was monitored by HPLC-DAD. The novel activity assay was employed in screening of inhibitors in natural products. The extract from the stem of *H. stigonocarpa* was identified as a promising source of *Sm*MTAP inhibitors.

Resumo/Abstract

Enzyme immobilization on magnetic particles is an effective approach to enhance enzyme stability, facilitate easy recovery and reuse, and reduce costs[1]. This approach can be successfully applied in the development of new screening assays in the realm of the drug discovery and development process. Enzyme inhibitors are a class of drugs used to treat several diseases. In infectious diseases, enzyme inhibitors can target enzymes crucial to the parasite's survival. One such disease is schistosomiasis, caused by the *Schistosoma mansoni* parasite, which affects populations in 78 countries worldwide. *S. mansoni* relies solely on the salvage pathway for its purine supply. The enzyme 5'-deoxy-5'-methylthioadenosine phosphorylase (MTAP) plays a critical role in this biochemical pathway and represents an attractive target for the development of novel drugs against schistosomiasis[2]. Thus, in this study, the *Sm*MTAP enzyme was covalently immobilized on cobalt ferrite magnetic nanoparticles and its activity was monitored through the direct quantification of the adenine formed from the adenosine phosphorolysis by HPLC-DAD. Chromatographic separation of adenosine and adenine was conducted in an octadecyl column (150 × 4.6 mm i.d., 3 µm, Sigma Aldrich), using a solution of NH_4OAc (20 mmol.L^{-1}, pH 6.0)/ACN (95:5) as mobile phase, at a flow rate of 0.8 mL.min^{-1}. Catalytic reaction was performed at 21°C under constant agitation, using 5 µg of *Sm*MTAP-coated magnetic nanoparticles (MNPs) and 40 µmol.L^{-1} of the substrate adenosine in a 100 mmol.L^{-1} phosphate buffer at pH 7.4. After characterizing the immobilized *Sm*MTAP through kinetic and stability assays, the function-based assay was employed in inhibitor screening using natural product extracts at 200 µg.mL^{-1} as a library[3]. The extracts of the bark, stem, and roots of *H. stigonocarpa* exhibited the highest inhibition level in the initial screening assays, and their IC_{50} values ranged from 8 to 62 µg.mL^{-1}. The *H. stigonocarpa* stem extract, which furnished the lowest IC_{50}, was selected to establish the inhibition profile by HPLC and microfractionation. First, the fingerprint chromatogram of the selected extract was assessed by HPLC analysis using H_2O and ACN, both acidified with 0.1% formic acid, as mobile phase and employing a gradient elution (from 85:15 to 4:96, v/v), at 0.8 mL.min^{-1}, in a total run time of 70 min. The analytical column used was an octadecyl column (250 × 4.6 mm i.d., 5 µm, Supelco Ascentis). An analytical-scale microfractionation of the selected extract enables assessing the inhibitory activity of each 12s microfraction, yielding a biochromatogram that evidenced the inhibition percentage as a function of the microfraction retention time. The *Sm*MTAP inhibition profile indicates the elution of inhibitors at 31.5 min retention time. Then, affinity selection-mass spectrometry assays (AS-MS) were performed with the active and inactive *Sm*MTAP to assess the affinity ratio for all the ligands present in the selected extract. By analyzing the fished-out ligands in a UPLC-HRMS system, the features will be annotated and evaluated individually. So, this work describes the development of a new screening assay for the identification of *Sm*MTAP inhibitors and the study of *H. stigonocarpa* stem extract as a source of bioactive compounds using inhibition profiling and AS-MS approaches.

References: 1) De Moraes, M.C; *et al Anal Bioanal Chem., 405*, 4871–4878, **2013**. 2) Gryssels, B.; *et al The Lancet*, *368* (9541), 1106–1118, **2006**. 3) Trindade Ximenes, I. A.; *et al*. *J Pharm. and Biomed Anal.*, *204*, 114-286, **2021**.

Agradecimentos/Acknowledgments

FAPERJ, CAPES and CNPq

Área: MED

Synthesis and biological evaluation of purine-benzohydroxamates as potential inhibitors of PI3K and HDAC6 for the treatment of hematologic malignancies

João P.F. Verotti (IC)[1], Karoline B. Waitman (PG)[1], Jorge A.E.G. Carlos (PG)[1], Mônica F.Z.J. Toledo (TC)[1], Letícia V. Costa-Lotufo (PQ)[1], João A. Machado-Neto (PQ)[1], Maurício T. Tavares (PQ)[2], Roberto Parise-Filho (PQ)[1]

jpverotti@gmail.com; roberto.parise@usp.br

[1]*Laboratory of Design and Synthesis of Bioactive Substances (LAPESSB), Department of Pharmacy, Faculty of Pharmaceutical Sciences, University of São Paulo (USP)*

[2]*Department of Cancer Biology, Dana-Farber Cancer Institute, Boston, MA, 02115, United States*

Palavras Chave: *HDAC6, PI3K, hybridization, multi-target approach, dual inhibitors, hybrids, hematological cancer.*

Highlights

Hybrid PI3K/HDAC6 inhibitors has been designed for treating hematologic cancer; Three hybrids were obtained in 3-steps synthetic route. Future biological evaluation will assess its cytotoxicity potential.

Resumo/Abstract

Cancer is a pathology characterized by the disorderly and accelerated proliferation of abnormal and undifferentiated cells, wherein a significant number of genes undergo mutations. Crucial pathways, such as PI3K (phosphoinositide 3-kinase) and HDAC6 (histone deacetylase 6), are frequently altered in leukemia tumor cell lineages. In this context, Hybrid Inhibitors have shown remarkable potential in combating cancer development by simultaneously blocking multiple signaling pathways. This study aims to synthesize PI3K/HDAC6 hybrid molecules, based on the pharmacophores of selective inhibitors for each chosen target: idelalisib and nexturastat A, as illustrated in **figure 1**.

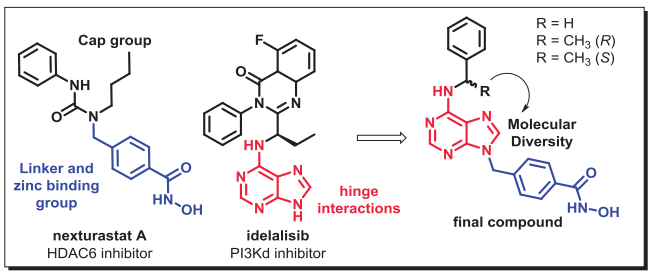
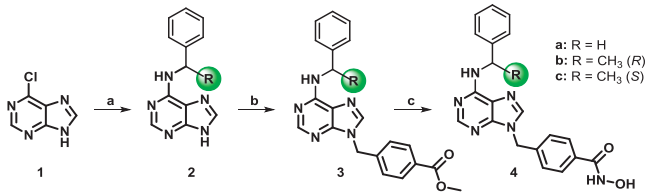


Figure 1: Design of the hybrid inhibitor.

As depicted in **Scheme 1**, hybrid compounds were synthesized by reacting 6-chloropurine **(1)** with substituted benzylamines. This step primarily involved an aromatic nucleophilic substitution (SNAr), leading to the formation benzylamine-purine intermediates **(2)**. These intermediates were then subject to the reaction with methyl 4-(bromomethyl)benzoate through bimolecular nucleophilic substitution (SN2), yielding methyl ester benzoate intermediates **(3)**. Following this, intermediates **(3)** will undergo a reaction with hydroxylamine (NH_2OH) to produce corresponding hydroxamates **(4)**.



Reagents and conditions: a) 7-substituted-benzylamines (1 eq.), Triethylamine (1,66 eq.), n-butanol, reflux, 18 h; b) Methyl-4-(bromomethyl)benzoate (1 eq.), K_2CO_3 (3 eq.), acetone, reflux, 18 h; c) NH_2OH (50 eq.), NaOH (8 eq.), THF-MeOH-Dioxane (1:1:1), 0 °C - r.t., 2 h.

Scheme 1. Synthetic route for hybrid compounds.

At the current stage, intermediates **2a-c** and **3a-c** have been synthesized, with yields of 55% and 81%, respectively. These results highlight a promising and feasible synthetic pathway for the final compounds. Characterization of these compounds was comprehensively conducted using ^1H and ^{13}C Nuclear Magnetic Resonance (NMR). The purity of the compounds was determined to be high (>95%). Following this, the compounds will undergo biological activity evaluation through cytotoxicity and mechanistic assays in various cancer cell lines, including Jurkat (T-cell acute lymphoblastic leukemia), Namalwa (B-cell acute lymphoblastic leukemia), MCF-7 (breast cancer), and HCT 116 (colon cancer).

Agradecimentos/Acknowledgments

The authors are grateful to the Faculty of Pharmaceutical Sciences of University of São Paulo, which allowed the development of this work, and fellowship #2023/13499-5, grant #2021/08260-8, from São Paulo Research Foundation (FAPESP).

Área: MED

SYNTHESIS AND *IN SILICO* AND *IN VITRO* STUDIES OF NEW HETEROCYCLES ANALOGOUS TO CHALCONES

Tamires da Silva Alves (PG)*[1,3], Amanda Perim Teixeira (IC)[2], Leandro Louback da Silva (PQ)[2], Adriana de Oliveira Gomes (PQ)[3], Nelilma Correia Romeiro (PQ)[1]

nelilmaromeiro@gmail.com; salves.tamires@gmail.com

[1]*Laboratório Integrado de Computação Científica-LICC- IMQ CM/UFRJ*

[2]*Laboratório Integrado de Pesquisa -LIP - ICF CM/UFRJ*

[3]*Laboratório Integrado de Pesquisa Computacional -LIPCOM - ICF CM/UFRJ*

Keywords: *Chalcones, Organic synthesis, Anticholinesterase activity, Molecular docking*

Highlights

Synthesis of seven new heterocyclic chalcone derivatives. *In vitro* analysis of anticholinesterase activity. *In silico* studies using molecular *docking*, theoretical prediction of ADMET parameters.

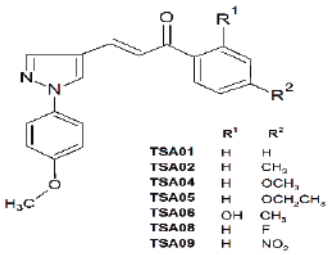
Abstract

Chalcones are alpha-beta unsaturated ketones that link two aromatic rings. Studies confirm that chalcones possess various biological activities, such as anti-inflammatory, antiparasitic, antiviral, and antitumoral properties. Their synthesis occurs through the condensation between an aldehyde group and an aromatic ketone, employing methodologies like the Claisen-Schmidt reaction. Therefore, chalcones and their derivatives are considered promising candidates in the search for new substances with biological activity. In this work, new heterocyclic derivatives were synthesized, and *in vitro* analysis of their activity against acetylcholinesterase and butyrylcholinesterase was conducted. Additionally, *in silico* studies were performed using molecular *docking*, along with the theoretical prediction of the physicochemical and toxicological profiles of these analogs. The synthetic methodology involved an adapted method of condensation between substituted aromatic arylhydrazines and 1,3-dicarbonyl reagents to facilitate cyclizations, leading to pyrazole-type ring formations. The substituted pyrazolic aldehyde was obtained through the Duff reaction. Subsequently, the obtained pyrazolic aldehyde reacted with substituted aromatic ketones in a basic environment using the Claisen-Schmidt reaction, resulting in the formation of seven 1-(4-methoxyphenyl)-1*H*-pyrazol-4-yl]-1-phenylprop-2-en-1-one derivatives. *In vitro* analysis of human acetylcholinesterase (hAChE) and butyrylcholinesterase (hBuChE) inhibition was assessed using the Ellman method. *Docking* analysis was conducted using GOLD, where the 3D structures of the target proteins were obtained from the Protein Data Bank. Ligands underwent optimization through PM7 and DFT levels. Predictions of ADMET parameters were performed using the admetSAR 2.0 server, SwissADME, Pred-hERG, and Molinspiration. The seven compounds were synthesized using the proposed methodology with yields above 50%, and their structures were elucidated through NMR. Regarding the inhibitory activity of AChE, compounds TSA01, TSA04, TSA06, and TSA08 exhibited the best enzymatic inhibition profile, exceeding 60%. However, none of the compounds showed significant pharmacological activity against BuChE.

Figure 1: Effect on the activity of human acetylcholinesterase (hAChE) and butyrylcholinesterase (hBuChE).

Enzyme Inhibition - % of Control		
	mean ± mean deviation	
	AChE	BuChE
Blank (no enzyme)	0 ± 1.9	0 ± 1.6
CONTROL	100 ± 2.2	-0.1 ± 0.6
DMSO (0,15%)	98.1 ± 3.7	-3.8 ± 2.3
RIVASTIGMINE (50 µM)	97.8 ± 1.1	98.9 ± 1.7
TSA01 (150 µM)	67.3 ± 3.1	11.5 ± 1.7
TSA02 (150 µM)	57.3 ± 2.8	-3.7 ± 2.6
TSA04 (150 µM)	65.7 ± 2.3	-2 ± 2.1
TSA05 (150 µM)	48.1 ± 3.3	-2.8 ± 1.2
TSA06 (150 µM)	63.7 ± 2.7	2.3 ± 2.3
TSA08 (150 µM)	63.6 ± 4.7	3.6 ± 3.7
TSA09 (150 µM)	50.5 ± 4.6	-0.2 ± 4.9

Figure 2: General structure of synthetic derivatives.



Acknowledgements

FAPERJ/CNPq/CM UFRJ Macaé

Área: MED

Synthesis, characterization, and β-lactamases inhibition activity of a novel zinc(II) complex with probenecid

Wilton R. Lustri (PQ)[1*], Silmara C. Lazarini (PQ)[1], Flávia A. Resende (PQ)[1], Bruna Cardinali Lustri (PQ)[2], Cristiano Gallina Moreira (PQ)[2], Douglas H. Nakahata (PQ)[5], Adriano M. Gonçalves (PQ)[1,6,7], Nailton M. Nascimento-Júnior (PQ)[4], Pedro P. Corbi (PQ)[2]

wrlustri@uniara.edu.br

[1] Department of Biological and Health Sciences - University of Araraquara - UNIARA, Laboratory of Bacterial Cellulose and Medicinal Chemistry (CBQUIM), 14801-320 Araraquara, São Paulo, Brazil
[2] Institute of Chemistry, University of Campinas – UNICAMP, 13083-970 Campinas, São Paulo, Brazil
[3] São Paulo State University – UNESP, School of Pharmaceutical Sciences, 14801-903 Araraquara, Brazil.
[4] São Paulo State University (Unesp), Institute of Chemistry, Department of Biochemistry and Organic Chemistry, Laboratory of Medicinal Chemistry, Organic Synthesis and Molecular Modeling (LaQMedSOMM), 14800-060, Araraquara, São Paulo, Brazil.
[5] Donostia International Physics Center, Paseo Manuel de Lardizabal 4, Donostia, Spain.
[6]College of Veterinary Medicine and Animal Science, University of São Paulo (USP) - São Paulo, Av. Prof. Dr. Orlando Marques de Paiva, 87, São Paulo 13690-970, Brazil
[7]School of Education, University of São Paulo (USP) - São Paulo, Av. da Universidade, 220, São Paulo 05508-040, Brazil

Key words: *Probenecid, β-lactamases, ESBL inhibition, CTX-M15, TEM-1B*

Highlights

Extend-spectrum β-lactamase inhibition CTX-M15, TEM-1B by Zn-PROB complex.
Absence of mutagenic activity by Ames test.
Absence of cytotoxicity in J774 cell line model.

Abstract

β-Lactamases, enzymes that hydrolyze and inactivate β-lactam antibiotics such as penicillin, cephalosporins and carbapenems, are considered the main determinants of the increasing prevalence of multidrug-resistant (MDR) Gram-negative pathogens, constituting a significant global concern, especially in relation to strains producing Extended-Spectrum β-Lactamase (ESBL), such as clinical isolates *Escherichia coli* EC958 (CTX-M15)[1,2] and *E. coli* BR43 (TEM-1B) [1,3]. Here, we describe the synthesis, characterization, and inhibitory activity of ESBL, produced by *E. coli* EC958 (CTX-M15) and *E. coli* BR43 (TEM-1B) activity of a zinc(II) complex with probenecid (Zn-PROB). The complex was prepared by the reaction of an alkaline methanolic solution containing 1.0 mmol of probenecide with 1.0 mmol of $ZnSO_4$. The synthesis was carried out under constant stirring and at room temperature for 2 hours. The white solid obtained was collected by filtration, washed with cold water and dried in a desiccator for 2 hours. The complex is soluble in DMSO. Infrared (IR) spectroscopic analyses suggest that ligand coordination of PROB to Zn(II) occurs by the oxygen atoms the COO^- group present in its structure. The molecular docking predicted interactions between Zn-PROB and key amino acid residues of both CTX-M-15 and TEM-1B ESBL. The in vitro diffusion assay demonstrated that Zn-PROB complex was capable of inhibiting CTX-M-15 and TEM-1B ESBL produced by E. coli EC958 and E. coli BR43 seeded on Luria Bertani agar containing 100 $\mu g \cdot mL^{-1}$ of ampicillin (AMP) by the formation of an inhibition zone around the well containing 1.0 mg $\cdot mL^{-1}$ of Zn-PROB, using wells with only the PROB ligand as controls. The minimum inhibitory concentration of the β-lactamases TEM-1B and CTX-M-15 (MICβ) was evaluated, and the results demonstrated that the inhibitory concentration was $19.7 mmol \cdot L^{-1}/269 mmol \cdot L^{-1}$ (Zn-PROB /AMP) while the bacterial strains were resistant to higher concentrations of PROB/AMP ($175 mmol \cdot mL^{-1}/269 mmol \cdot mL^{-1}$). The Ames test indicated the absence of mutagenic activity, and *in vitro* cell viability analysis, using UVEC and HaCat normal cell lines, demonstrated absence of cytotoxicity. Such results open a perspective for *in vivo* tests to evaluate the potential use in the treatment of infections caused by ESBL-producing bacteria.

1. W.R. Lustri, et al. J. Inorg. Biochem (2023).
2. B.M. Forde, et al. PLOS ONE (2014).
3. P. da Silva et al., Braz. J. Microbiol. (2021)

Acknowledgments

The authors would like to thank to CAPES, FAEPEX, FAPESP (grant # 2021/07458-9, 2021/08717-8, 2018/12590-0), FUNADESP and CNPq (Brazilian agencies).

Área: MED

Synthesis of dihidroquinolinone derivatives and evaluation of their potential against *T. Cruzi* intracellular amastigotes *in vitro* and *in silico*

William C. L. Silva (PG),[1*] **Lucas F. Moreira (PG)[1], Mirian Claudia S. Pereira (PQ)[2], Warley S. Borges (PQ),[1]**

William_lima.xp@outlook.com; Warley.borges@ufes.br

[1]*Chemistry Departament, Federal University the Espírito Santo – UFES,* [2]*Fundação Oswaldo Cruz.*

Key words: *Dihidroquinolinone derivatives, T.Cruzi, Intracellular amastigotes, Chagas disease, Docking molecular.*

Highlights

Synthesis of benzylated ethers and 1,2,3-triazoles derived from 7-hydroxy-3,4-dihydroquinolin-2(1H)-one; *In vitro* evaluation against intracelular amastigotes; *In silico* evaluation against the cruzin protease (3KKU).

Abstract

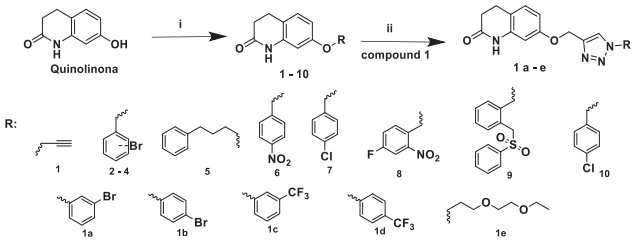
Introduction

Even at this moment, Chagas disease is a public health problem that mainly affects populations in conditions of social vulnerability.[1] Although several proteases related to the development of the parasite have been discovered, the scarcity and inefficiency of treatments are still recurrent.[2] In this context, the synthesis of new chemical entities becomes eminent and quinolinones, due to their broad spectrum of action in different available drugs, stand out as potential building blocks for possible new bioactive compounds.[3-7]

Results and Discussion

In this work, the synthesis of a series of compounds derived from 7-hydroxy-3,4-dihydroquinolin-2(1H)-one (quinolinone) (**scheme 01**), was carried out through nucleophilic substitution reactions (**step i**) and 1,3 dipolar cycloaddition (**step ii**) with good to moderate yields.

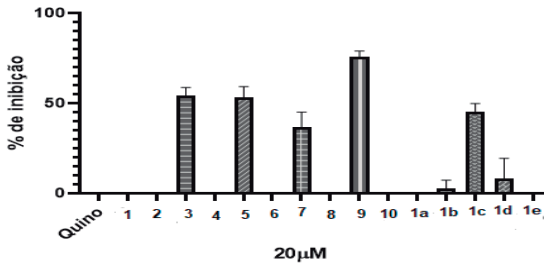
Scheme 01: Synthesis of 7-hydroxy-3,4-dihydroquinolin-2(1H)-one derivatives.



Reactions condictions: Quinolinone (0,308 mmol),K_2CO_3 (0,770mmol), halides (0,46 mmol), DMF,(i); Ascorbato de sódio, DMF, CuSO4 0,1M, MW, 150W, 80ºC, 10'(ii).

All compounds obtained were evaluated against intracellular amastigotes at 20µmol. Among the compounds tested, only five demonstrated an inhibitory potential greater than 40%.

Figure 01: Graph of the inhibitory percentage of compounds synthesized against *T. Cruzi in vitro*.



In order to corroborate the experimental data and understanding possible interactions, molecular docking was carried out against the 3KKU protease (Cruzaine) and will be rationalized by comparison with experimental data observed *in vitro*.

Conclusion

It can be inferred that 2-quinolinone derivatives showed improved activity against intracellular amastigotes compared to the original substrate. It was observed that the presence of bulkier and electronegative atoms in the "ortho" and "para" positions of the aromatic ring contributed significantly to the activity. It was also observed that the extension of the chain by an alkyl moiety as in **5** showed an improvement in inhibition compared to the extension by a more rigid, aromatic chain, as in the triazole ring in **1c**, possibly favoring varied states of conformation of the molecule and interactions hydrophobic.

References:

Acknowledgments

Área: MED

Synthesis of pyrrolidine derivatives, targeting the α7 and α4β2 nicotinic acetylcholine receptors.

Bruna C. L. Domingues (PG),[1]*, Gustavo C. Monteiro (PQ),[1] Nailton M. Nascimento-Júnior (PQ).[1]

bruna.lopes@unesp.br

[1]*Laboratory of Medicinal Chemistry, Organic Synthesis and Molecular Modeling (LaQMedSOMM), Department of Biochemistry and Organic Chemistry, Institute of Chemistry, São Paulo State University (Unesp)*

Keywords: *α7* nAChRs, *α4β2 nAChRs*, Alzheimer's disease, Nicotine dependence, Synthesis of pyrrolidine derivatives.

Highlights

The project aims to synthesize fragments with potential activity against α7 and α4β2 nAChRs, which are related to Alzheimer's disease (AD) and dependence caused by psychoactive substances.

Abstract

Among the nAChRs present in the central nervous system, the α7 and α4β2 subtypes are more abundant than the others, and ligands for these receptors have great potential as therapeutic agents. For example, they could be useful in discovering new therapies for the treatment of Alzheimer's disease and nicotine addiction.[1] In this context, based on previous work carried out in our research group, involving the structural design and in silico screening of compounds for the α7 and α4β2 nAChRs, eight derivatives containing a pyrrolidine moiety were selected for the synthesis stage, shown in **Figure 1**.[2] The first step consists of the occurrence of protection between Boc-L-proline and the corresponding anilines. To date, compounds **19b**, **19c**, **19q** and **19r** were obtained, showing yields of 23%, 75%, 94% and 20%, respectively. Subsequently, two steps will be carried out, one to remove the Boc protective group, followed by a reduction of the carbonyl to deliver product **10**.

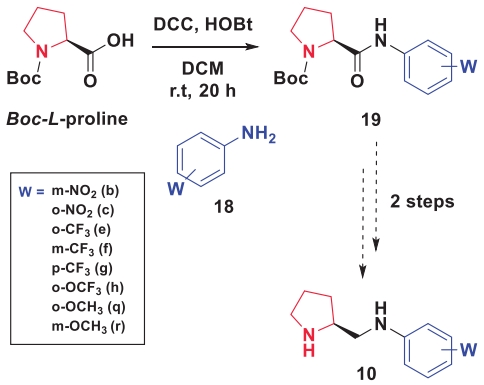


Figure 1: Synthetic route to obtaining pyrrolidine derivatives.

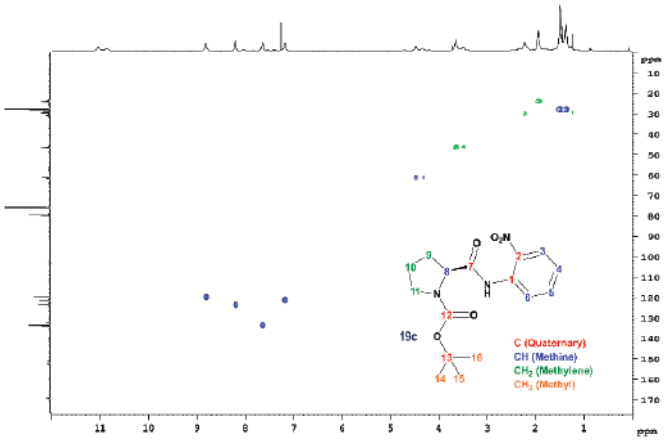


Figure 2: HSQC (600 MHz) **19c**.

To characterize the compounds, nuclear magnetic resonance (1H, 13C, HSQC and TOCSY) and infrared analyzes were carried out. **Figure 2** shows the HSQC spectrum of the **19c** molecule, which, together with the other resonance experiments mentioned above, allowed us to exclude signals from its carbon atoms and confirm that the desired molecule was obtained.

From the data obtained, it is interesting to observe that, regardless of the activating ($-OCH_3$) or deactivating ($-NO_2$) nature of the ring substitute, when they are ortho-substituted in relation to the amino group of aniline, the yields are Os greater benefits when compared to those equal in meta position to the amino group. This fact makes us realize that the position is more relevant than the electronic nature of the groups in terms of performance.

[1] SURESH, A.; HUNG, A. Molecular simulation study of the unbinding of α-conotoxin [Y4E]GID at the α7 and α4β2 neuronal nicotinic acetylcholine receptors. **J. Mol. Graph. Model.**, v. 70, p. 109-121, Sep. 2016.

[2] DASH, J. *et al*. "On water'' Promoted Ullmann-type C−N Bond-forming Reactions: Application to Carbazole Alkaloids by Selective N-Arylation of Aminophenols. **J. Org. Chem.**, v. 83, n. 14, p. 7347–7359, Feb. 2018.

Acknowledgments

CNPq (scholarschip). FAPESP (2018/0087-7). IQ – UNESP (equipments used for characterization).

Área: MED

SYNTHESIS OF UNNATURAL AMINO ACIDS AS KEY FRAGMENTS FOR SARS-CoV-2 3CL M^{pro} MAIN PROTEASE INHIBITORS

Vinícius G. Roqueto (IC), Wellington F. de Souza (PG), Carlos A. Montanari (PQ).

vini.g_roqueto@usp.br; Carlos.Montanari@usp.br

Medicinal and Biological Chemistry Group, IQSC-USP. - Av. Trabalhador Sanarlense, 400 – 13566-590 – São Carlos, Brasil.

Cysteine protease inhibitors, SARS-CoV-2 3CL M^{pro}, Building blocks, Unnatural amino acids, Negishi coupling.

Highlights

Synthesis and characterization of building blocks of SARS CoV-2 3 CL M^{pro} inhibitors.
Synthesis of unnatural amino acids.
Negishi coupling in protected serine.
Strategies to increase compound yield.

Abstract

Despite the success in the application of the vaccines against the new coronavirus and the announcement by the World Health Organization of the end of the pandemic state of emergency, studies related to SARS-CoV-2, including the development of drugs to treat COVID-19, continue to be extremely relevant for medicinal chemistry and public health given the potential economic and social threats, especially, considering that the Omicron variant has demonstrated resistance to Nirmatrelvir, a drug approved for the treatment of the disease. Consequently, this work focuses on designing inhibitors for the main protease of SARS-CoV-2 (3CL Mpro) and strives to synthesize, purify, characterize and scale up the fundamental building blocks for innovative inhibitors. Herein, the fragments consist of unnatural amino acids synthesized from methyl (2S)-2-{[(tert-butoxy) carbonyl]amino}-3-hydroxypropanoate, which is, essentially, serine with the carboxyl and amine functional groups protected as ester and carbamate, respectively. This compound is converted through a nucleophilic substitution reaction into methyl (2R)-2-{[(tert-butoxy)carbonyl]amino}-3-iodopropanoate, an alkyl iodide. Subsequently, it undergoes a Negishi cross-coupling reaction involving organozinc and palladium catalysts such as Pd(amphos)Cl2 and Pd2(dba)3, along with brominated heteroaryls moieties, to form a carbon-carbon bond amidst different aromatic heterocycles and the side chain of the protected unnatural amino acid as exemplified in Figure 1 (a). In this perspective, some brominated heteroaryls were used as 2-bromopyrazine, 3-Bromo-7-azaindole, 4-Bromo-7-azaindole, 5-Bromo-7H-pyrrolo [2,3-d]pyrimidine, 3-Bromopyridazine, 5-Bromopyrimidine, 6-Bromo-7H-purine, 6-Bromoquinoxaline, 2-Bromoquinoxaline, 3-Bromo-1H-pyrrolo[2,3-c]pyridine, 3-Bromobenzo[b]thiophene, 5-Bromobenzothiophene. The strategy of employing unnatural amino acid fragments represents modernity in medicinal chemistry, as they have been utilized to increase the diversity and coverage of compounds by combining them in different positions, as depicted in Figure 1 (b). Additionally, this strategy seeks to enhance the protease affinity for the inhibitors and modulate their solubility, ensuring they continue soluble in water while remaining permeable to the cell membrane. In the characterization of these compounds, it was observed that the synthesis methodology proved suitable for yielding the final products, accompanied by a significant increase in the solubility of the end compounds.

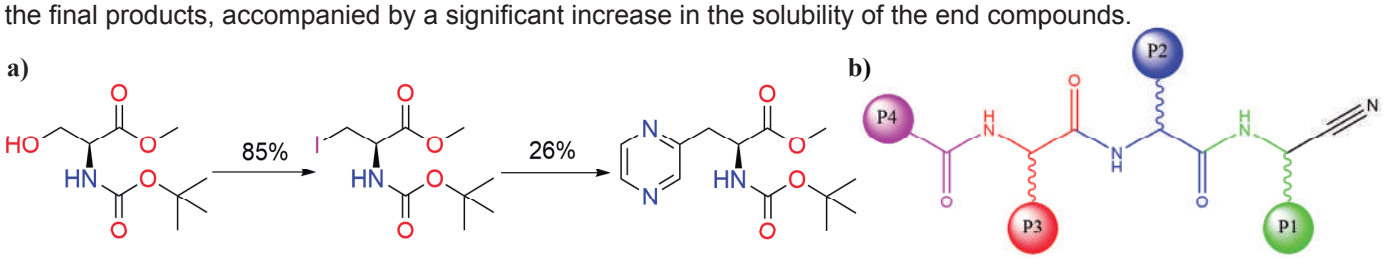


Figure 1. a) Example of synthetic route of fragments used in different positions of the inhibitors scaffold. **b)** 2D scaffold representation of tripeptidyl nitrile inhibitors: P1, P2, P3 and P4 are modified to optimize the interaction with the S1, S2, S3, and S4 subsites of the protease.
Source: Own preparation.

Acknowledgments

Instituto de Química de São Carlos (IQSC-USP); FAPESP (2022/01393-5, 2023/13679-3).

Área: _____MED_____

The Unified Latin American Natural Product Database: LANaPDB

Marilia Valli (PQ),[1] Alejandro Gómez-García (PG),[2] Vanderlan da Silva Bolzani (PQ),[3] José L. Medina-Franco (PQ),[2] Adriano D. Andricopulo (PQ),[1]

marilia.valli@ifsc.com.br

[1]*Laboratory of Medicinal and Computational Chemistry (LQMC), Center for Research and Innovation in Biodiversity and Drug Discovery (CIBFar), Institute of Physics of São Carlos, University of São Paulo (USP), Av. João Dagnone, n° 1100, São Carlos, SP, Brazil*

[2]*DIFACQUIM Research Group, Department of Pharmacy, School of Chemistry, Universidad Nacional Autónoma de México Avenida Universidad 3000, Mexico City 04510, Mexico*

[3]*Nucleus of Bioassays, Biosynthesis and Ecophysiology of Natural Products (NuBBE), Department of Organic Chemistry, Institute of Chemistry, Universidade Estadual Paulista Júlio de Mesquita Filho (UNESP), 14800-900 Araraquara-SP, Brazil*

Keywords: *chemical space; chemoinformatics; databases; Latin America; natural products.*

Highlights

The first version of LANaPDB was developed as an effort to unify natural products databases from six countries. Chemical properties of pharmaceutical interest of the compounds were analyzed.

Abstract

Latin America is extraordinarily rich in biodiversity, with many countries classified as megadiverse. This region represents a remarkable source of bioactive molecules and potential drug candidates. This has encouraged the development of databases and the implementation of those that are under development. Databases containing natural products from Latin American countries, such as NaturAr (Argentina), $NuBBE_{DB}$ (Brazil), UNIIQUIM and BIOFACQUIM (Mexico), CIFPMA (Panama), NAPRORE-CR (Costa Rica), LAIPNUDELSAV (El Salvador), and PeruNPD (Peru) represent the state of the art in developing Latin American natural products databases. The current version of LANaPDB unifies the information from six countries and contains 12,959 chemical structures. The database is freely available at https://github.com/alexgoga21/LaNaPDB. The long-term goal of the project is to collect, unify and standardize the Latin American NP collections available in the public domain into one public database. As part of this study, we analyzed the structural content and determined some physicochemical properties of pharmaceutical interest of the compounds in LANaPDB. We also represent coverage in the chemical space of compounds in LANaPDB using the concept of a chemical multiverse.

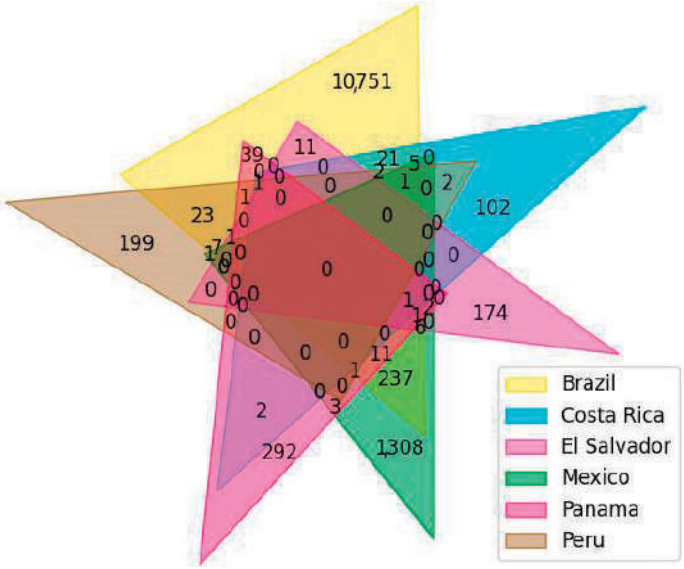


Figure 1. Venn diagram showing the number of unique compounds per country in the analyzed databases.

Acknowledgments

CIBFar-CEPID FAPESP #2013/07600-3, INCT BioNat FAPESP/ CNPq #2014/50926-0, FAPESP/DFG #2020/11967-3, FAPESP/DAAD PROPASP #2022/08333-8, and Scholarship CNPq #382044/2013-1.

ORG

Química Orgânica

Sociedade Brasileira de Química

Área: ORG
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

A green approach for the synthesis of Isocoumarin derivatives using Trichloroisocyanuric Acid (TCCA)

Luiz Eduardo Welter (PG),[1*] Antonio Luiz Braga (PQ),[1].

luiz.welter@posgrad.ufsc.br

[1]*Departamento de Química, UFSC, 88040-970, Florianópolis, Brazil.*

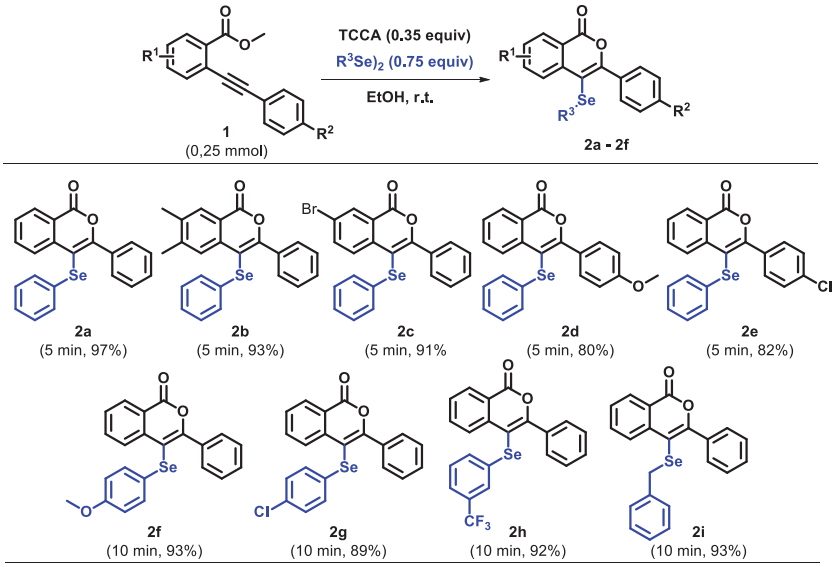
Palavras Chave: *Trichloroisocyanuric Acid, Isocoumarins, Electrophilic Cyclization, Green Approach.*

Highlights

Synthesis of 4-(arylselanyl)-1H-isochromen-1-ones by trichloroisocyanuric acid (TCCA) with diorganoyl diselenide. Electrophilic cyclization of 2-(alkynyl)esters. Satisfactory yields (up to 97%) and good tolerance to substituent groups.

Resumo/Abstract

Heterocycle compounds derived from coumarins and isocoumarins have been explored for many years due to their different properties, such as their antitumor[1], anti-inflammatory[2] and antimicrobial[3] biological activities. In organic synthesis, different methodologies have been developed to obtain these compounds, but the search for green approach still remains a challenge[4-6]. In this way, TCCA becomes an alternative to the use of other oxidizing reagents, as it has high solubility, low toxicity and a good cost-effectiveness ratio[7,8]. We have therefore developed a new protocol for the synthesis of 4-(arylselanyl)-1H-isochromen-1-ones **2** promoted by the electrophilic selenium species formed *in situ* by the reaction between TCCA and the respective diorganoyl diselenide. The protocol involves 0.35 equivalents of TCCA and 0.75 equivalents of diorganoyl diselenide in ethanol (3 mL) for the cyclization reaction of *o*-(alkynyl)-esters **1**. The reaction, conducted at room temperature for 5 to 10 minutes, produced the desired products **2a-2i** in yields of up to 97% (Scheme 1).



Sheme 1: Reaction conditions for the synthesis of 4-(arylselanyl)- 1H-isochromen-1-ones **2** from *o*-(alkynyl)-esters **1** and products obtained.

References: [1]Das, V. *et al. Naunyn. Schmiedebergs. Arch. Pharmacol.* **394**, 1437–1449 (2021). [2]Ramanan, M. *et al. Eur. J. Med. Chem.* **124**, 428–434 (2016). [3]Ferrazzoli Devienne, K. *et al. Phytomedicine* **12**, 378–381 (2005). [4]Yao, T. & Larock, R. C. *J. Org. Chem.* **68**, 5936–5942 (2003). [5]Sperança, A. *et al. J. Org. Chem.* **76**, 6789–6797 (2011). [6]Goulart, H. A. *et al. J. Org. Chem.* **86**, 14016–14027 (2021). [7]Mendonça, G. F. & Mattos, M. C. S. *Curr. Org. Synth.* **10**, 820–836 (2014). [8]Doerner, C. V. *et al. New J. Chem.* **47**, 5598–5602 (2023).

Agradecimentos/Acknowledgments

LabSelen
CNPq Conselho Nacional de Desenvolvimento Científico e Tecnológico
INCT catálise
CAPES

Área: ORG

α-Xyloidone as a synthetic platform: an approach for direct synthesis of new dithioethers with activity against oral squamous cell carcinoma

Helena G. Fernandes (IC)[1], Thaís B. Santos (PG)[1], Sara T. B. Leal (IC)[1], Rafaella M. de A. C. Ribeiro (IC)[1], Alex de S. C. L. Canuto (PG)[2], Bruno K. Robbs (PQ)[2], Vitor F. Ferreira (PQ)[3], David R. da Rocha* (PQ)[1]

hgfernandes2003@gmail.com; davidrocha@id.uff.br

[1]Universidade Federal Fluminense, Departamento de Química Orgânica, Niterói, RJ; [2]Universidade Federal Fluminense, Instituto de Saúde de Nova Friburgo, Nova Friburgo, RJ ; [3]Universidade Federal Fluminense, Faculdade de Farmácia, Niterói, RJ

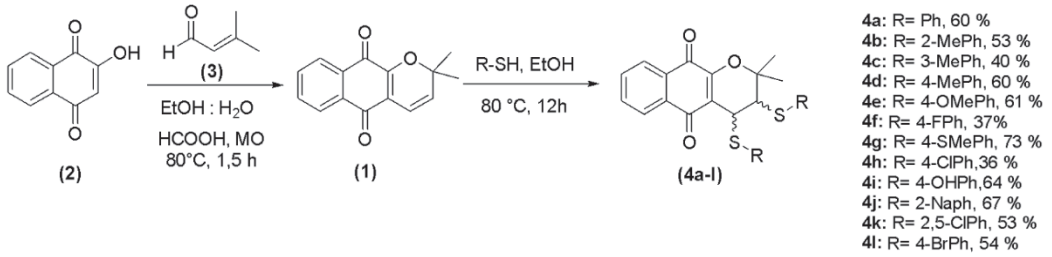
Palavras Chave: *Piranonaftoquinonas, Adição direta, Tiolapachonas, Câncer*

Highlights

First report of dithiolapachones through direct functionalization of α-xyloidone with activity against squamous cell carcinoma of the human tongue

Resumo/Abstract

As piranonaftoquinonas são uma classe de substâncias abundantes na natureza e devido ao seu perfil biológico são amplamente exploradas na literatura, destacando-se as xiloidonas e lapachonas [1].Embora a funcionalização desses compostos seja principalmente baseada em modificações utilizando as lapachonas como precursores, as xiloidonas também podem ser usadas como plataformas sintéticas. Essa abordagem ainda é restrita a reações que levam inicialmente à formação de lapachonas mais simples [2], sendo necessário reações subsequentes para a obtenção de seus derivados mais complexos estruturalmente. Sendo assim, o objetivo deste trabalho consiste na síntese de novos tioéteres, a partir da funcionalização direta da α–xiloidona (**1**) e posterior avaliação da atividade antitumoral em linhagens de carcinoma espinocelular oral. A estratégia sintética (**Esquema 1**) se inicia pela obtenção da α–xiloidona (**1**) através da condensação de Knoevenagel seguida de ciclização intramolecular entre lausona (**2**) e o aldeído α,β-insaturado (**3**) [3]. Os tioéteres (**4a-l**) são obtidos através da adição direta de diferentes tióis comerciais, resultando em doze tiolapachonas inéditas com rendimentos variando de 36 a 73%. Dez tioéteres foram avaliados frente a linhagem de carcinoma espinocelular de língua humana (SCC-9), dentre os quais oito apresentaram atividade, com IC_{50} variando de 15,27 a 46,50 μM, sendo mais ativas que a carboplatina (IC_{50} carboplatina= 49,77 μM).



	4a	4b	4c	4d	4e	4f	4g	4h	4i	4j
SCC-9 IC_{50} em μM	26,26	34,77	15,27	30,85	46,50	35,25	ND	33,28	17,24	ND

Esquema 1. Obtenção dos tioéteres (**4a-l**) e IC_{50} para linhagem SCC-9; IC_{50} Carboplatina= 49,77 μM

[1] Ferreira, S. *et al*. *Rev. Virtual Quim*. **2010**, *2*, 140-160.
[2] Lee, Y. *et al*. *Synthesis* **2005**, 3026-3034.
[3] Rocha, D. *et al*. *Tetrahedron*, **2014**, *70*, 3266-3270.

Agradecimentos/Acknowledgments

PPGQ-UFF, CNPq, CAPES e FAPERJ

Área: ORG

An Alternative Synthesis of Dobutamine Using Continuous Flow and Electrosynthesis

Pedro P. de Castro (PQ),[1] Pedro M. Santucci (PG),[1] Timothy J. Brocksom (PQ),[1] Kleber T. de Oliveira (PQ)[1*]

pedro.possa@ufscar.br; kleber.oliveira@ufscar.br

[1]*Departamento de Química, UFSCar*

Palavras Chave: API, continuous flow, electrosynthesis.

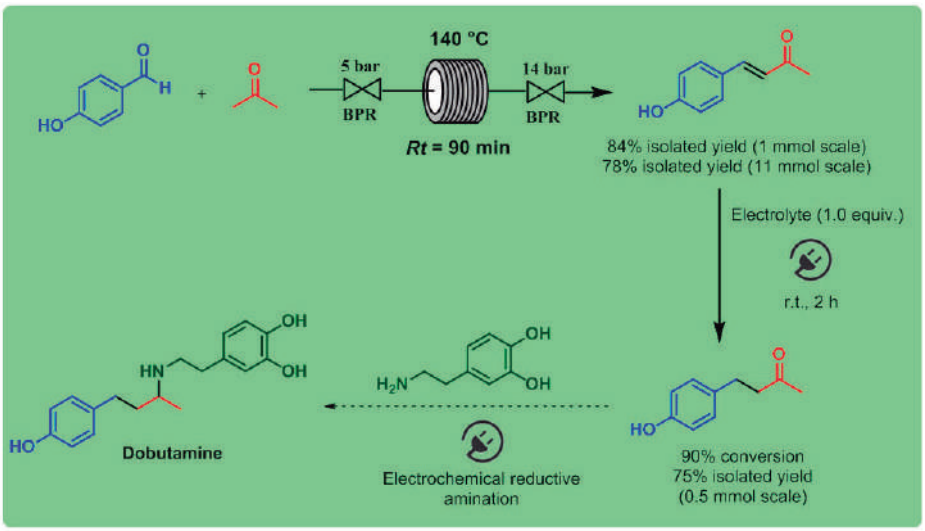
Highlights

A new three-step route for the preparation of the API dobutamine is presented using alternative technological tools, such as continuous flow and organic electrosynthesis.

Abstract

The use of alternative technological tools (e.g., continuous flow, photocatalysis and electrosynthesis) for the preparation of active pharmaceutical ingredients (APIs) and fine chemicals has the potential to solve long-standing problems associated with traditional chemical synthesis, especially those related to the use of hazardous reagents.[1] The traditional synthesis of the API dobutamine, a β_1-agonist widely used in the treatment of cardiogenic shock and heart failure,[2] involves the use of hydrides or hydrogen gas associated with transition metals, and generally includes the use of protecting groups. In this context, an alternative synthetic strategy for the preparation of this API is presented (Scheme 1). The methodology initiates through the continuous flow aldol condensation between acetone and 4-hydroxybenzaldeyde. After an extensive optimization, TFA plus morpholine were chosen as the best catalysts, affording the desired enone in up to 84% isolated yield, with a productivity of up to 2.18 g day^{-1} and a residence time of only 90 minutes (against 24 hours in batch). The electrochemical reduction of the enone was carefully evaluated, including the optimization of electrodes, electrolyte, reaction time and the use of additives, affording the product in up to 75% yield. The last step (electrochemical reductive amination) is under development and will be reported in due time.

Scheme 1. Synthetic approach to dobutamine.



References: [1] *Chem. Rev.* **2016**, 116, 10276–10341; [2] *Crit. Care Explor.* **2023**, 28, e0962.

Agradecimentos/Acknowledgments

FAPESP (grants 2021/13924-2 (P.P.C.), 2023/04020-8 (K.T.O)), CAPES, and CNPq.

Área: ORG

A Palladium-photocatalyzed Heck reaction for the synthesis of C3-alkylated coumarins.

Camila Pelizzer de Oliveira (IC),[1] Clarice Alves Dale Caiuby (PQ),[1] Marco Antonio Barbosa Ferreira (PQ),[1]*

camilapelizzer@estudante.ufscar.br; clarice@ufscar.br; marco.ferreira@ufscar.br*

[1]*Departamento de Química, UFSCar*

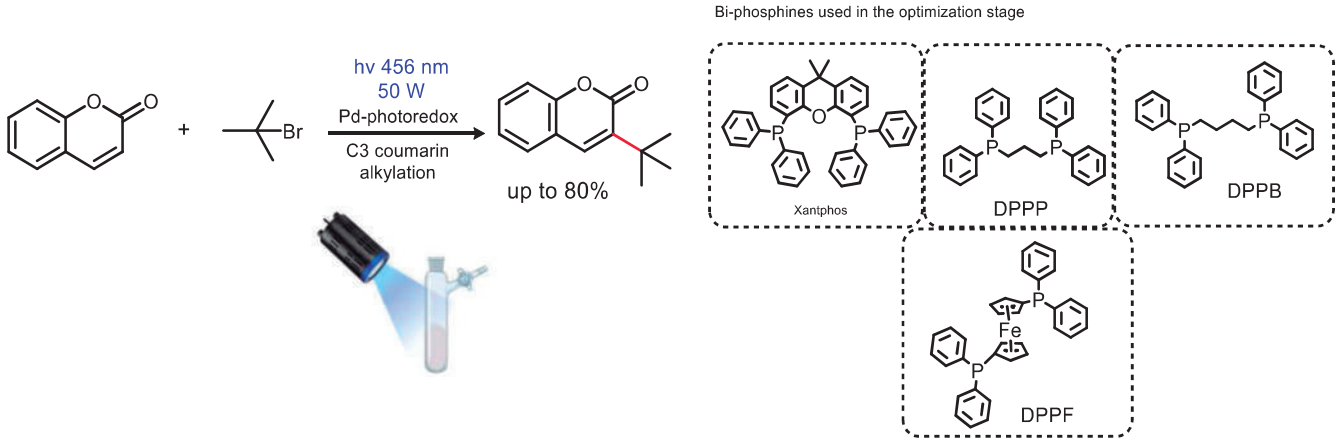
Palavras Chave: *Transition Metal Catalysis, Photochemistry, Coumarin, Organic Synthesis*

Highlights

Palladium photoredox strategy to explore C3-alkylation of coumarins using alkyl halides. The combination of a palladium source, phosphine ligands and visible light provides the desired product in high yield and regioselectivity via Heck reaction.

Resumo/Abstract

The pursuit of enhanced efficiency in chemical processes has remained a longstanding priority[1]. In this regard, the significance of employing palladium as a catalyst is noteworthy, given its crucial role in enabling the functionalization of a variety of substrates[2]. The photocatalyzed Heck reaction is a powerful strategy for C–C bond formation under mild conditions, using visible light as an energy source[3]. Coumarin-based compounds exhibit important pharmacological activities and are frequently used in medicinal chemistry[4]. The C3-functionalization of coumarins represents a valuable synthetic strategy to modulate their biological properties. In this work, we obtained C3-alkylated coumarins by palladium-photoredox Heck reaction using alkyl halides as radical precursors. This transformation is catalyzed by a visible light-photoactive complex formed from a palladium source and the combination of mono- and biphosphines, providing the desired product in good yields (up to 80% yield) as a single regioisomer.



References: [1] P. Marion, B. Bernela, A. Piccirilli, B. Estrine, N. Patouillard, J. Guilbot, F. Jérôme, Green. Chem. 2017, 19, 4973–4989. [2] (a) He, J.; Wasa, M.; Chan, K. S. L.; Shao, Q.; Yu, J. Q. Chem. Rev. 2017, 117 (13), 8754–8786. (b) Biffis, A.; Centomo, P.; del Zotto, A.; Zecca, M. Chem. Rev. 2018, 118 (4), 2249–2295. [3] G. A. M. Jardim, J. A. Dantas, A. A. Barboza, M. W. Paixão, M. A. B. Ferreira, Synthesis 2022, 54, 4629–4645. [4] (a) Matos, M. J.; Vazquez-Rodriguez, S.; Santana, L.; Uriarte, E.; Fuentes-Edfuf, C.; Santos, Y.; Muñoz-Crego, A. *Med. Chem.* **2012**, *8*, 1140. (b) Matos, M. J.; Vazquez-Rodriguez, S.; Santana, L.; Uriarte, E.; Fuentes-Edfuf, C.; Santos, Y.; Muñoz-Crego, A. *Molecules* **2013**, *18*, 1394. (c) Gualandi, A.; Rodeghiero, G.; Della Rocca, E.; Bertoni, F.; Marchini, M.; Perciaccante, R.; Jansen, T. P.; Ceroni, P.; Cozzi, P. G. Chem. Commun. 2018, 54, 10044. (d) Abdallah, M.; Hijazi, A.; Graff, B.; Fouassier, J. P.; Rodeghiero, G.; Gualandi, A.; Dumur, F.; Cozzi, P. G.; Lalevée, J. Polym. Chem. 2019, 10, 872.

Agradecimentos/Acknowledgments

(2023/05757-4); (2020/10246-0); (2022/11314-5); (2021/12394-0); (2022/14197-0).

Área: ORG

Application of electrossynthesized copper (I) acetylide as catalyst in solvent-free propargylamine and triazole synthesis

Chrystian de Oliveira Bellin* **(PG),[1] Mauro Chierici Lopes (PQ),[1] Giancarlo Di Vaccari Botteselle (PQ).[1]**

chrystianbellin@gmail.com

[1]*Departamento de Química, UNICENTRO*

Palavras Chave: *Organic Synthesis, solvent-free, catalysis, propargylamines, triazoles.*

Highlights

Cheap and easily obtainable catalyst;

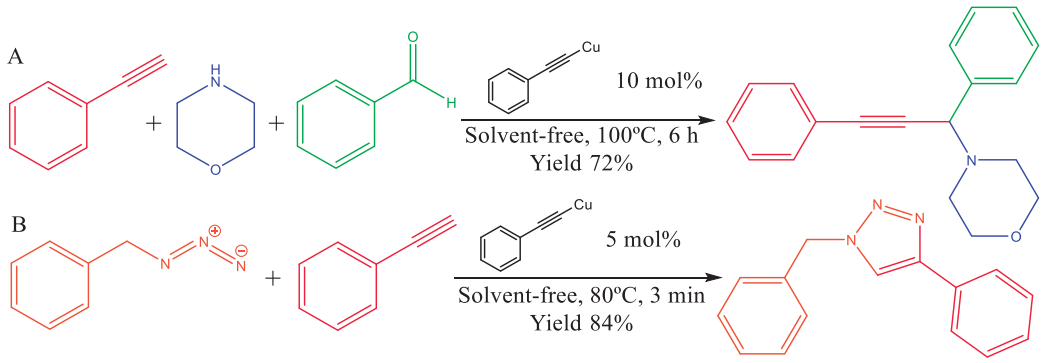
Novel application of copper (I) acetylides in eco-friendly synthesis;

Good to great yields;

Resumo/Abstract

Propargylamines and triazoles are intermediates for the synthesis of many heterocyclic compounds. Also, its derivatives have biological activity and are suitable for pharmacological use[1,2]. For the synthesis of both propargylamine and triazole, transition metals' nanoparticles, in special copper, are usually employed as catalysts to produce acetylides, intermediates in the reaction mechanism. However, the synthesis of these nanoparticles is usually complex and slow, its use is limited due to its tendency to oxidation in atmospheric conditions and the catalysts can be only used for few reactional cycles before losing catalytic activity[3]. It is known that it is possible to electrossynthesize copper (I) acetylides through the electrodissolution of metalic copper[4]. In this work, an electrossynthesized copper (I) acetylide was applied as catalyst in solvent-free propargylamine and 1,2,3-triazole synthesis as shown in figure 1. The yields were good but reaction conditions are yet to be optimized. Our next goals are to evaluate the possibility of recovery of the catalyst and to develop a method to make electrossynthesis of propargylamines.

Figure 1 – A) Reactional scheme for propargylamine synthesis. B) Reactional scheme for 1,2,3-triazole synthesis.



1 - LAUDER, K. et al. Synthesis and Reactivity of Propargylamines in Organic Chemistry. **Chemical Reviews**, American Chemical Society, 27 dez. 2017.

2 - CHAUDHARY, P. M. et al. Exploration of click reaction for the synthesis of modified nucleosides as chitin synthase inhibitors. **Bioorganic and Medicinal Chemistry**, v. 17, n. 6, p. 2433–2440, 2009.

3 - SAHA, T. K.; DAS, R. Progress in synthesis of propargylamine and its derivatives by nanoparticle catalysis via A3 coupling: A decade update. **ChemistrySelect**, v. 3, n. 1, p. 147–169, 10 jan. 2018.

4 - SEAVILL, P. W.; HOLT, K. B.; WILDEN, J. D. Electrochemical synthesis of copper(i) acetylides: Via simultaneous copper ion and catalytic base electrogeneration for use in click chemistry. **RSC Advances**, v. 9, n. 50, p. 29300–29304, 2019.

Agradecimentos/Acknowledgments

Área: ORG

A Regioselective and Solvent-free Synthesis of 4-cyano-1,5-diaryl-1*H*-1,2,3-Triazoles *via* Mechanochemistry

Edson de O. Lima Filho (PQ),[1] Fernando de C. da Silva (PQ).[1]*

Edson_olf@id.uff.br; fcsilva@id.uff.br

[1]*Laboratório de Síntese Orgânica Aplicada, Universidade Federal Fluminense.*

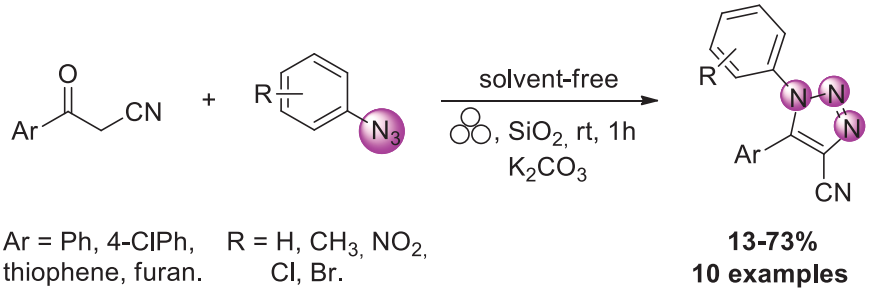
Keywords: Cycloaddition, heterocycles, ecofriendly, green synthesis.

Highlights

- Efficient Broad-Scope Synthesis of 4-cyano-1,5-diaryl-1*H*-1,2,3-triazoles.
- Scaffolds significance in medicinal chemistry.
- Solvent-free condition.

Resumo/Abstract

Due to their vast applications, a wide variety of methods are described for the preparation of 1,2,3-triazoles. The development of efficient and straightforward methods for the synthesis of 1,2,3-triazoles have led to an exponential growth of this field in the last decades, with several compounds containing these scaffolds having displayed a wide range of biological activities.[1] Herein we described an innovative method to afford 4-cyano-1,5-diaryl-1*H*-1,2,3-triazoles formation. It was obtained 10 examples after applying a broad-spectrum of azides and commercially available α-keto nitriles under mild and solvent-free conditions via mechanochemistry in short reaction time (**Scheme 1**). Highlighting, thiophene and furan derivatives are unpublished. The reduced reaction time, when compared to the traditional method, and the simple isolation of the product (filtration) make this methodology very attractive for the synthesis of derivatives with potential biological activity.[2,3]



Scheme 1. Mechanochemical method developed to obtain 4-cyano-1,2,3-triazoles.

References

1. Forezi, L. S. M.; Lima, C. G. S.; Amaral, A. A. P.; Ferreira, P. G.; de Souza, M. C. B. V.; Cunha, A. C.; da Silva, F. C.; Ferreira, V. F. *Chem. Rec.* **2021**, *21*, 2782– 2807.

2. Liu, P.; Clark, R. J.; Zhu, L. *J. Org. Chem.* **2018**, *83*, 5092-5103.

3. Wang, L.; Peng, S.; Danence, L. J. T.; Gao, Y.; Wang, J. *Chem. Eur. J.* **2012**, *18*, 6088-6093.

Agradecimentos/Acknowledgments

CAPES, CNPq, FAPERJ and FIOCRUZ.

Área: ___ORG_____
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Arylamino-naphthoquinones as new synthetic platforms to produce anticancer drugs

Acácio S. de Souza (PQ),[1] Gabriel N. da Silva (IC),[1] Luana da S. M. Forezi (PQ),[2] Fernando de C. da Silva (PQ),[2] Vitor F. Ferreira (PQ)[1]

gabrielns@id.uff.br; acacio.farma@gmail.com

[1] *Faculdade de Farmácia, Departamento de Tecnologia Farmacêutica, Universidade Federal Fluminense, UFF.*
[2] *Laboratório de Síntese Orgânica Aplicada, Universidade Federal Fluminense, Instituto de Química, Niterói-RJ, Brazil.*

Keywords: *Coupling reaction, Triazole, Molecular Hybridization, Heterocycles.*

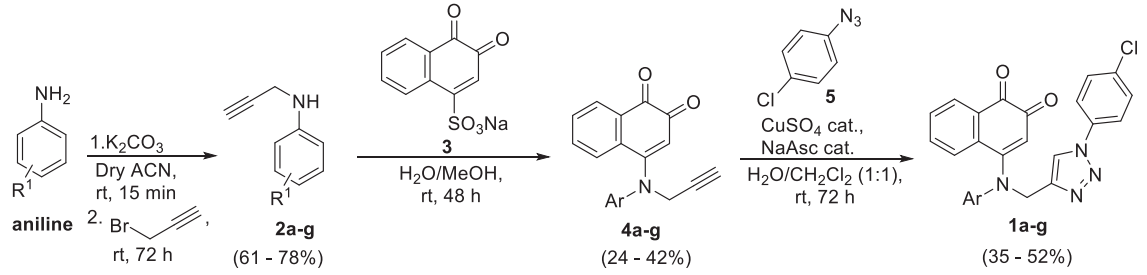
Highlights

Cancer is one of the world's most important diseases, causing millions of deaths every year. Synthesis of new naphthoquinone-triazole hybrids as prototypes of anticancer drugs, exploring the coupling reaction.

Abstract

Cancer is one of the world's most important diseases, causing millions of deaths every year.[1] In addition to the health and socio-economic impacts, the low selectivity against healthy cells, side effects, and resistance developed by tumors make it increasingly necessary to research and develop of new drugs that provide more effective treatments.[2] In this scenario, 1,2-naphthoquinones and 1,2,3-triazoles have been attracting attention for their anticancer properties, either individually or in the form of hybrid substances.[3] The limitations of producing 4-arylamino-1,2-naphthoquinone-triazole hybrids via alkylation with propargyl bromide or direct insertion of triazole rings are a challenge. The alkylation of the oxygen atom in position C-2 of the naphthoquinone ring with propargyl bromide, for example, is frequently reported, forming 4-arylimino derivatives as the main products.[4] This work aims to develop the synthesis of 4-arylamino-1,2-naphthoquinone-triazole hybrids (**1**) by exploiting the reaction between arylamines **2** and the naphthoquinone derivative **3**, to develop prototype candidates for new drugs against cancer.

The synthetic methodology chosen for the synthesis of type **1** hybrids is a three-step synthesis (Scheme 1). The first stage consisted of the alkylation of commercial anilines with propargyl bromide to provide the type **2** derivatives.[5] To carry out the second stage, different methods were studied to promote the nucleophilic substitution reaction most efficiently between the secondary anilines **2** and the 1,2-naphthoquinone salt derivative **3**, the critical step. After finding the best condition, the products of type **4** were obtained in yields of between 24-42%. Finally, a copper (I)-catalyzed 1,3-dipolar cyclization reaction was carried out between the derivatives **4** and the 4-Cl-phenyl azide (**5**), previously synthesized from commercial anilines, to provide the hybrids **1** in 35-52% yields.



a: R= H; **b:** R= 4-CH_3; **c:** R= 4-OCH_3; **d:** R= 4-Cl; **e:** R= 3,4-OCH_3; **f:** R= 3,5-OCH_3; **g:** R= 3,4,5-OCH_3

Scheme 1. Synthesis of 4-arylamino-1,2-naphthoquinone-triazole hybrids.

[1] World Health Organization. Cancer. In: https://www.who.int/news-room/fact-sheets/detail/cancer. Accessed 28/01/2024.
[2] Lopes, G. *JAMA Oncol.*, **2023**, *9*(4), 461-462.
[3] Xu, Z.; Zhao, S. J.; Liu, Y. *Eur. J. Med. Chem.* **2019**, *183*, 111700.
[4] Ribeiro, R. C. B.; Ferreira, P. G.; Borges, A. A., *et al. Beilstein, J. Org. Chem.*, **2022**, *5*(18), 53-69.
[5] Sakai, N.; Hori, H.; Ogiwara, Y. *Eur. J. Org. Chem.*, **2015**, 1905–1909.

Agradecimentos/Acknowledgments

FAPERJ, CAPES, FIOCRUZ and CNPq.

Área:_____ORG_____

A Shorter, Faster and Better Yielding Multistep Synthesis of Benzocaine: An Update Undergraduate Experiment for Teaching Telescopic Synthesis

Leonardo Antonelli (PG),[1] Talita Nascimento (PG),[1] Viviane Costa de Souza (PG),[1] Mauricio M. Victor (PQ),[1] Silvio Cunha (PQ),[1,2*]

antonellileonardo@hotmail.com; *silviodc@ufba.br

[1]Instituto de Química, Universidade Federal da Bahia - UFBA, Brazil; [2]Instituto Nacional de Ciência e Tecnologia em Energia e Ambiente - INCT, Brazil.

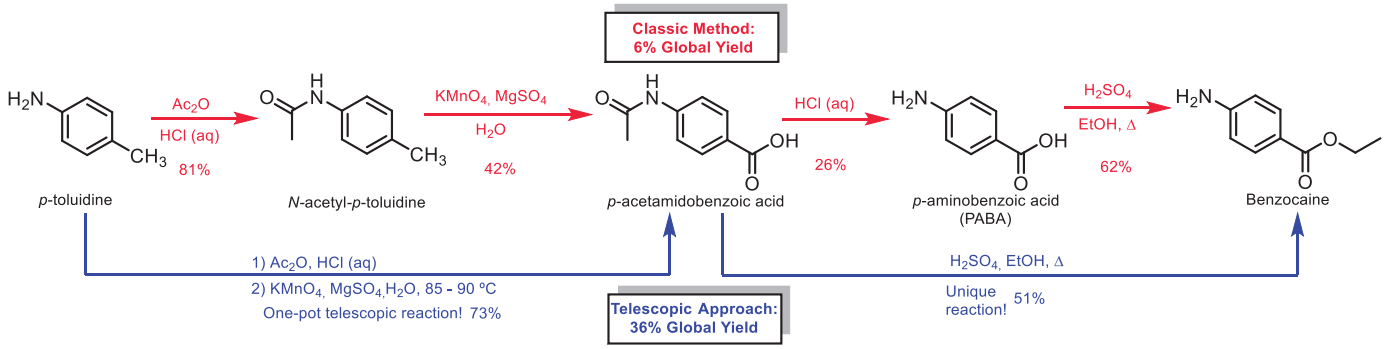
Palavras Chave: *Benzocaine; Multistep Synthesis; Hands-on Chemistry; Laboratory Experiment.*

Highlights

- The traditional four-step synthesis of benzocaine by undergraduate students was optimized by replacing the first two steps to a telescopic approach and by removing the third and unnecessary step, the total amount of needed experimental classes for the synthesis was reduced from four to only two. The average global yield of the students in the synthesis was increased from 6% to 36%.

Resumo/Abstract

Benzocaine is a well-known local anesthetic due to its high efficiency, low cost and rapid absorption through skin and mucous.[1] This compound has been used as a motivational synthetic target in experimental organic chemistry classes that aim to teach undergraduate students about planning and conducting multistep syntheses.[2] In this work, the traditional synthetic procedure applied in the experimental classes was optimized achieving a reduction in one day on the three original needed experimental classes by incorporating a one-pot telescopic step and bypassing one unnecessary step. In addition, the paper chromatography technique was introduced in the slow oxidation step of the synthesis, allowing the students to monitor the completion of the reaction during the entire process, leading to a time reducing up to 80% in this step. These modifications were carefully evaluated and also were tested by chemistry undergraduate students, to evaluate the suitability of the modified experiment. Besides the reduction of the total amount of needed experimental classes to reach the target molecule, the final results of the students have shown an improvement in global yield from (5.7 ± 3.7) % to (35.7 ± 5.8) %.



1. Khair-Ul-Bariyah, S.; Arshad, M.; Ali, M.; Din, M. I.; Sharif, A.; Ahmed, E. Benzocaine: Review on a Drug with Unfold Potential. *Mini-Reviews in Medicinal Chemistry*, **2020**, *20* (1), 3.
2. Kremer, C. B. The Laboratory Preparation of a Simple Vitamin: p-aminobenzoic acid. *J. Chem. Educ.* **1956**, *33* (2), 71.

Agradecimentos/Acknowledgments

We would like to thank the students who performed the original and the optimization experimental procedures. This work was financed by the Brazilian agencies CAPES, CNPq and FAPESB.

Área: ORG

A theoretical view on the stereochemistry of 1,3-benzoxazol-2-(3*H*)-ylidenes obtained from double vinylic substitution

Ana Julia F. Souza (IC),[1] Matheus P. Freitas (PQ),[2] Julliane Yoneda (PQ),[1] Diego P. Sangi (PQ) [1]*

dpsangi@id.uff.br *

[1] *Departamento de Química, Universidade Federal Fluminense;* [2] *Departamento de Química, Universidade Federal de Lavras,*

Keywords: Stereochemistry; 1,3-benzoxazol-2-(3H)-ylidenes; Ketenedithiacetals; Vinylic substitution.

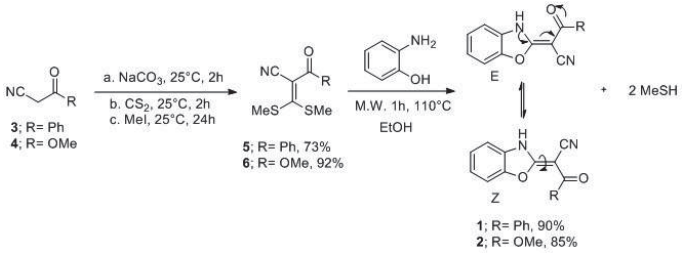
Highlights

A theoretical view on the stereochemistry of 1,3-benzoxazol-2-(3H)-ylidenes.
Synthesis of benzoxazoles derivatives with biological activity.
Relative stability of diastereoisomers.

Resumo/Abstract

Ketenedithioacetals have widespread use in organic chemistry, being important building blocks to obtain heterocyclic scaffolds using many different methods.[1] Polarized ketenedithioacetals are substrates to vinylic substitutions using 2-aminophenols as nucleophiles to produce benzoxazoles.[2] Benzoxazoles play an important role in discovering novel agrochemicals of different classes, especially herbicides, and are known for their large spectrum of pharmacological properties, that are highly dependent on the stereochemistry for an optimal enzyme induced-fit.

In our search for novel biologically active benzoxazoles, 1,3-benzoxazol-2(3*H*)-ylidene-3-oxo-3-phenylpropanenitrile (**1**) and methyl-1,3-benzoxazol-2(3*H*)-ylidene(cyano)acetate (**2**) have been prepared through double vinylic substitution of a ketenedithioacetal, as shown in Scheme 1. However, it is unclear whether the *E* stereoisomer is the single product in solution due to the establishment of an NH···O=C intramolecular hydrogen bond giving rise to a thermodynamic product or if the ene moiety undergoes free rotation due to a resonance structure that allows for conformational isomerization (and an average conformation would then be observed).[2]



Scheme 1. Synthetic route to obtain **1** (R = Ph) and **2** (R = OMe), which resonates allowing for conformational isomerization.

According to the DFT calculations, the rotational barriers of both **1** and **2** were computed as high as 20 (Z → E) to 35 (E → Z) kcal mol^{-1}, which prevents fast, free rotation at room temperature (Figure 1). For instance, the rotation time constants for ethane and butane are about 12 ps and 40 ps, respectively.[3] The C=C rotation barrier of typical alkenes is about 60 kcal mol^{-1}, while the corresponding value for the N-C(=O) bond of amides is 21 kcal mol^{-1}.[3] A barrier of 20 kcal mol^{-1} corresponds to an interconversion rate of 1.3 × 10^{-2} s^{-1} at 25° C, that is, a half-life ($t_{1/2}$) of about 1 minute; $t_{1/2}$ for a barrier of 25 kcal mol^{-1} at 25° C is 66 hours.[4] Therefore, as the isomers of **1** and **2** could be separated at room temperature and analytically distinguished by NMR spectroscopy, only one form is produced, which is the thermodynamically most stable isomer *E*.

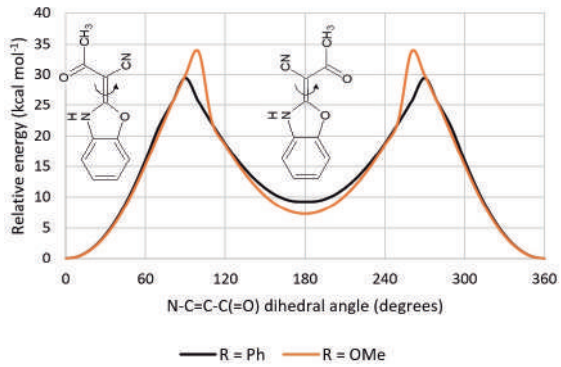


Figure 1. Relative energy of isomers.

The *E* isomer is the single form observed experimentally because it is 8.1 and 6.2 kcal mol^{-1} more stable than the *Z* isomer (for **1** and **2**, respectively), according to B3LYP-GD3(BJ)/DGTZVP calculations, because interaction corresponding to a C=O···H−N intramolecular hydrogen bonding.

1. Huang et al. *Tetrahedron Lett.* **2020**, *61*, 151363. 2. Sangi et al. *Pest Manag. Sci.* **2019**, *75*, 262-269. 3. Zheng et al.*Science*. **2006**, *313*, 1951-1955. 4. Eliel E. L.; Wilen, S. H., John Wiley & Sons: Hoboken, **1994**.

Agradecimentos/Acknowledgments

FAPERJ

Área: ORG
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Beyond Medicine: Paracetamol as Reagent in the Multicomponent Synthesis of 1,3-Benzoxazine

Leonardo Antonelli (PG),[1] Rosiene Reis Mattos (PQ),[2] Mauricio M. Victor (PQ),[2] Silvio Cunha (PQ),[1*]

antonellileonardo@hotmail.com; *silviodc@ufba.br

[1]Instituto de Química, Universidade Federal da Bahia - UFBA, Brazil; [2]Instituto Nacional de Ciência e Tecnologia em Energia e Ambiente - INCT, Brazil.

Palavras Chave: *Undergraduate Experiment; Active Pharmaceutical Ingredient; Multicomponent Reactions; Hands-on Chemistry.*

Highlights

An undergraduate experiment involving solid-liquid extraction, spectroscopic characterization and the multistep synthesis of a 1,3-benzoxazine derived from paracetamol extracted from Tylenol® tablets was developed.

Resumo/Abstract

This work developed a simple practical class involving the extraction and application of paracetamol from Tylenol® tablets (Figure 1) in the multicomponent synthesis of a 1,3-benzoxazine (Figure 2) as an effective strategy for teaching the features of multicomponent reactions, a topic not prevalently discussed in the undergraduate environment. The extractionprocedures were tested with students and proved to be reproducible, recovering the paracetamol with an average 83%. The synthetic procedures are simple and requires no catalysts, additives, heating or even stirring, and the 1,3-benzoxazine was obtained in an average 28% yield. This practical class was efficient to teach and discuss the multicomponent reactions features besides solid-liquid extraction, spectroscopic characterization and multi-step mechanism discussion, also encouraging the students to realize that everyday materials can be used as chemical reagents. Students' motivation in all experimental stages indicated that this strategy combined enjoyment and pedagogical interest.

Figure 1. Sequential steps for the extraction of paracetamol by solid-liquid extraction with boiling ethyl acetate.

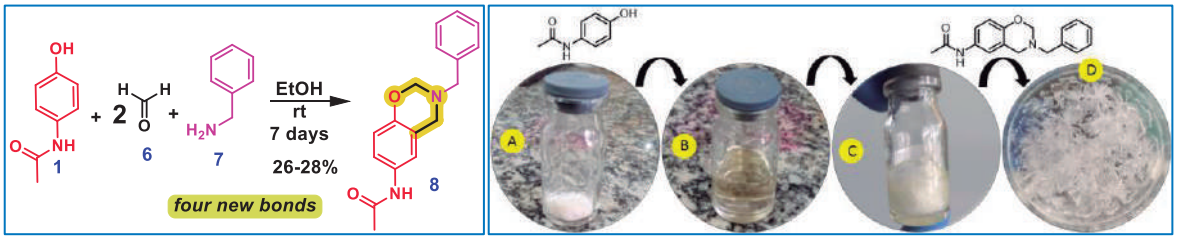


Figure 2. Reaction scheme of the multicomponent synthesis of the 1,3-benzoxazine from the extracted paracetamol (left). Sequential steps of the reaction, involving the addition of the reagents at room temperature and only needing to leave the crystals of the product to form out of the solution from the starting class until the following week.

Agradecimentos/Acknowledgments

We would like to thank the students from the three semesters who performed the experiments using the optimized procedures. This work was financed by the Brazilian agencies CAPES, CNPq, and FAPESB.

Área: ORG

Bifunctional nucleophile bearing imidazole and hydroxamic acid for catalytic dephosphorylation reactions

Gabriella A. Borim (IC),[1] Patrícia M. Soares (PG),[1] Valmir B. Silva (PQ),[2] Julien Legros (PQ),[2] Elisa S. Orth (PQ).[1]

gabriella.borim@ufpr.br

[1]Departamento de Química, UFPR; [2]Laboratoire COBRA UMR CNRS 6014, Universitè de Rouen Normandie.

Palavras Chave: Agrochemical, *Detoxification, Neutralization, Kinetics.*

Highlights

- Targeting a faster neutralization of organophosphates with a bifunctional nucleophile.
- The hydroxamate site acts as a nucleophile, while the imidazole as general base catalyst.

Resumo/Abstract

Organophosphates are an environmental concern due to their use in agrochemicals and chemical weapons, with threatening public health issues. This class of compounds is known by its toxicity and high stability, making it important design molecules able to promote their dephosphorylation, thus neutralize and lead to less toxic products. The present study focuses in proposing a novel bifunctional nucleophile containing an imidazole and hydroxamic acid moieties (IMZ-HA) with the aim of achieving a synergistic neutralization effect against diethyl-2,4-dinitrophenylphosphate (DEDNPP - Figure 1). The reactions were monitored by the absorption in the UV-Vis region (Figure 2) and the pH rate profile (Figure 3) shows a pronounced behavior: extremely higher than the spontaneous reaction and also higher than the bare nucleophiles (imidazole and benzohydroxamic acid). This evidences a cooperativity among the groups and a bifunctional catalysis is proposed: hydroxamate attacks the phosphorus and the nucleophile is regenerated through a general base catalysis by the imidazole group. Therefore, the classical suicidal nucleophilic attack by hydroxamic groups is avoided and the nucleophile is recovered: is catalytic. Thus, the bifunctional nucleophile proposed has the potential to act as molecular catalyst, accelerating reactions that would otherwise take a long time to complete: millions of years in such a couple of minutes.

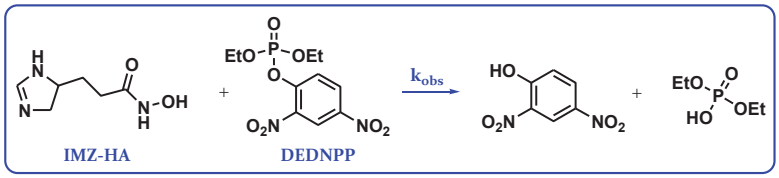


Figure 1. Representation of reaction between IMZ-HA and DEDNPP.

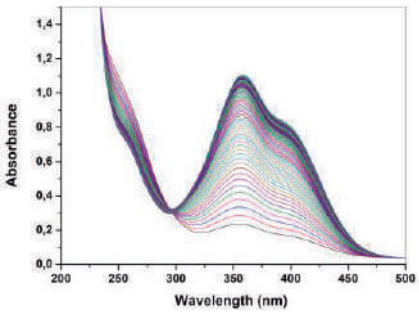


Figure 2. UV-Vis spectra for reaction of IMZ-HA with DEDNPP.

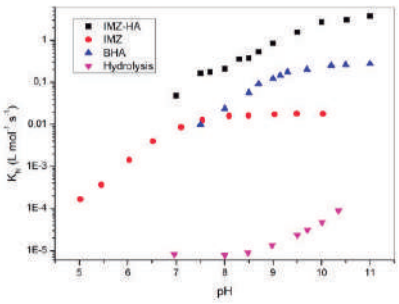


Figure 3 Kinetic pH rate profile for the reaction of DEDNPP with IMZ-HA, imidazole (IMZ), benzohydroxamic acid (BHA) and its spontaneous hydrolysis at 25ºC.

Agradecimentos/Acknowledgments

UFPR, CAPES, CNPq, L'Oréal UNESCO-ABC, PhosAgro/UNESCO/IUPAC, INCT NanoVida, INCT Nanocarbono.

Área: ORG

Controlling the synthesis of tetralactam macrocycle-based [2]- and [3]-rotaxanes by the stopper choice

Tainára Orlando (PQ),[1]* Gustavo H. Weimer (PG),[2] Paulo R. S. Salbego (PQ),[2] Marcos A. P. Martins (PQ).[2]

tainaraorland@gmail.com

[1]LAITEC, Academic Department of Chemistry, Federal Technological University of Paraná (UTFPR), Medianeira Campus, PR, Brazil; [2]NUQUIMHE, Department of Chemistry, Federal University of Santa Maria (UFSM), Santa Maria, RS, Brazil.

keywords: Rotaxane, Mechanically interlocked molecule, Intercomponent interactions, Synthesis.

Highlights

The synthesis of [2]- and [3]rotaxanes was assessed using a asymmetric two-station thread. When a secondary amide is used as stopper in the second portion of the thread the [3]rotaxane is obtained.

Abstract

Supramolecular chemistry has many fronts of study.[1] One of the most recent focus is the development of molecules designed to, at a molecular level, have programmable properties.[2] Rotaxanes are candidates for this use and can be considered as molecular machines when they perform movements controlled by external stimuli.[3] In this context, the synthesis of new rotaxanes is important for the development of the area. More specifically, when it comes to rotaxanes, the two-component compounds are the great majority found. The controlled synthesis of rotaxanes with more than two components is still a field to be explored, especially amide-benzylic rotaxanes. In most cases, [3]rotaxanes are obtained from threads containing two symmetric stations,[4,5] or as an undesired product of [2]rotaxane synthesis. Based on this, in the present work we seek to understand the formation of amide-benzylic [3]rotaxanes using a thread containing a common station (succinamide) and an unusual station (triazole-carbonyl). The succinamide station is already known to be a good station for the synthesis of rotaxanes,[6] and at the second station, triazole is a good substitute for the amide group, as it mimics its electronic properties, having the hydrogen bond acceptor behavior. Additionally, these stations are very close together in the thread, as far as we know, being unusual for this type of rotaxane. Thread modifications were carried out to prove the ideal conditions for [3]rotaxane formation. Five new threads were synthesized and used in the rotaxane synthesis (Figure 1).

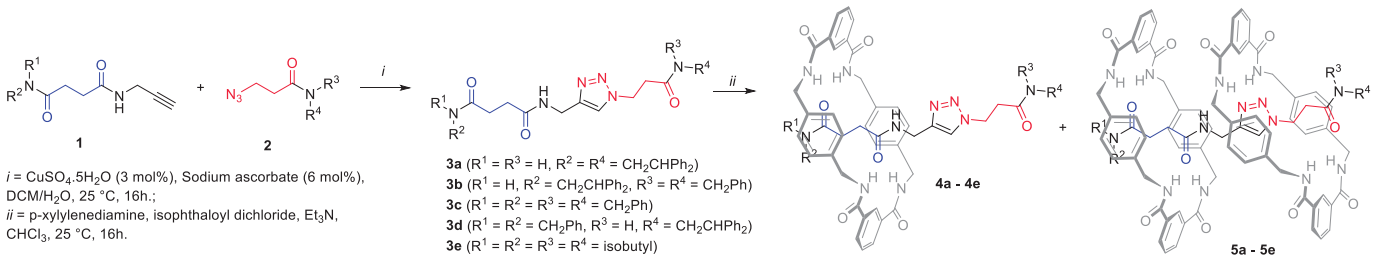


Figure 1. Synthesis of threads **3** and rotaxanes **4** and **5**.

The threads synthesis was carried out through a click reaction with the union of two fragments, forming the asymmetrical two station-thread providing yields between 46 and 75%. The synthesis of rotaxanes was carried out through the clipping reaction where the macrocycle is formed around the thread, generating the rotaxane molecule.[7] The **3b-e** generate [2]rotaxane molecules (yield of 3.7 – 33.1%) and only the **3d** generated the [3]rotaxane molecule (yield of 5.5%). The [3]rotaxane formation is due to the presence of a stopper containing a secondary amide that allowed the formation of an additional macrocycle at the triazole-carbonyl station, which could be due to less steric hindrance or the presence of new intercomponent interactions. Additionally, the macrocycle preference for the succinic station was confirmed by both solution and solid-state experiments.

1. *Chem. Soc. Rev.*, 2009, **38**, 1802. 2. *Chem. Rev.*, 2015, **115**, 10081–10206. 3. *Chem. Soc. Rev.*, 2017, **46**, 2592–2621. 4. *ChemPhysChem*, 2016, **17**, 1902–1912. 5. *Org. Chem. Front.*, 2021, **8**, 4202–4210. 6. *European J. Org. Chem.*, 2018, **2018**, 4978–4990. 7. *Angew. Chemie Int. Ed. English*, 1997, **36**, 728–732.

Acknowledgments

The authors acknowledge the UTFPR, UFSM, CAPES, CNPq, and FAPERGS.

Área: ORG

Copper-Mediated C—H Bond Oxidation in Synthetic Studies of Complex Diterpenes

Lucas D.P. Gonçalves (PG),[1*] Julian C.S. Pavan (PG),[2] Vladimir C.G. Heleno (PQ),[2] Emilio C. de Lucca Jr. (PQ).[1]

l239920@dac.unicamp.br

[1] *Instituto de Química, Universidade Estadual de Campinas;* [2] *Núcleo de Pesquisa em Ciências Exatas e Tecnológicas, Universidade de Franca.*

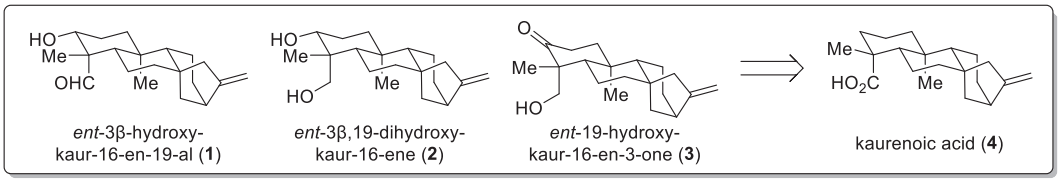
Keywords: *C—H oxidation, Catalysis, Natural products, Diterpenes*

Highlights

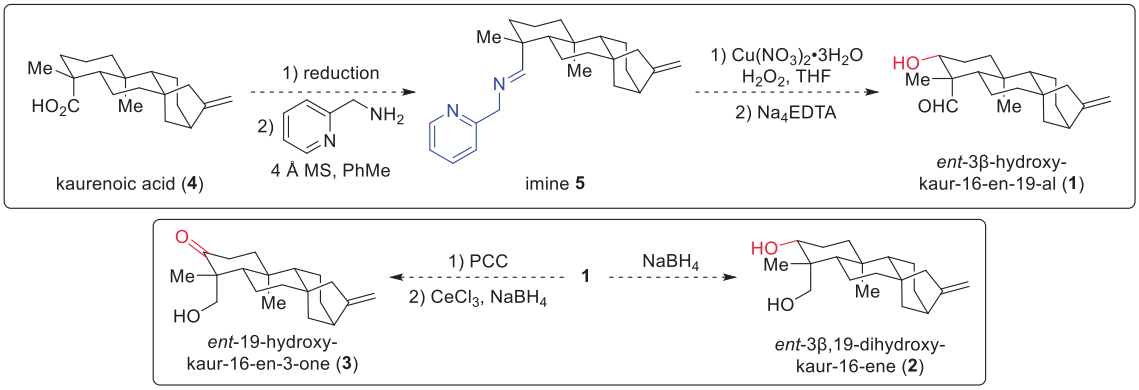
Studies toward the synthesis of complex natural *ent*-kaurene diterpenoids. Our approach is based on the directed selective copper-mediated C—H bond oxidation of derivatives of kaurenoic acid.

Abstract

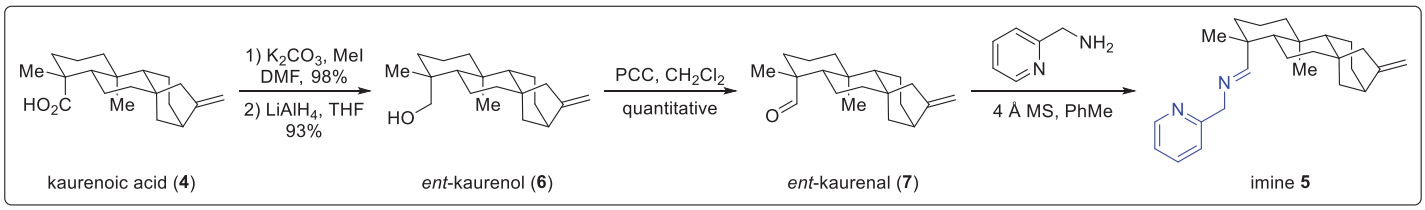
This study aims to investigate a synthetic route to obtain the natural products **1**–**3**,[1] through oxidation of C—H bonds as the key step. Since these natural products have an *ent*-kaurene carbon skeleton, we propose synthesizing them from kaurenoic acid (**4**).



In view of recently reported synthesis of *ent*-trachylobanes through a copper-mediated oxidation of a C—H bond,[2] we propose to use this strategy in the synthesis of natural products **1**–**3**.



By employing these reactions, we have progressed in our efforts to synthesize the natural product **1**. The next steps involve the oxidation of a C—H bond to achieve the product **1** and the correction of oxidation states to obtain the products **2** and **3**.



References:

(1) a) Dutra, L. M.; Bomfim, L. M.; Rocha, S. L. A.; Nepel, A.; Soares, M. B. P.; Barison, A.; Costa, E. V.; Bezerra, D. P. *Bioorganic Med. Chem. Lett.* **2014**, *24*, 3315. b) Yin, Z.-Y.; Dai, Y.; Hua, P.; Sun, Z.-J.; Cheng, Y.-F.; Yuan, S.-H.; Chen, Z.-Y.; Gu, Q. *Bioorg. Chem.* **2019**, *92*, 103292.

2) Wein, L. A.; Wurst, K.; Magauer, T. *Angew. Chem. Int. Ed.* **2022**, *61*, e202113829.

Acknowledgments

The authors thanks IQ/UNICAMP, UNIFRAN, FAPESP, FAEPEX, CNPq, and CAPES.

Área: ORG

Development of Coumarin-Selenotriazole Hybrids via Sequential Functionalization of 4-Hydroxycoumarin.

Cristal V.T. Martins (PG),[1] Analice G.R. da Cruz (IC),[2] Acácio S. de Souza (PQ),[1] Pâmela S. Cordeiro (PG),[2] Vanessa Nascimento (PQ),[2] Fernando de C. da Silva (PQ),[2] Luana da S.M. Forezi (PQ)[2,*]

cristalvirginia@id.uff.br; luanaforezi@id.uff.br

[1]Faculdade de Farmácia, Departamento de Tecnologia Farmacêutica, Universidade Federal Fluminense; [2]Instituto de Química, Departamento de Química Orgânica, Universidade Federal Fluminense.

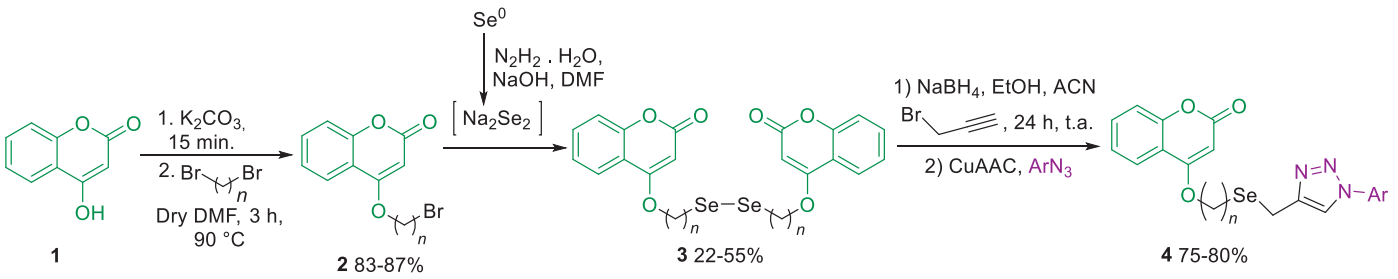
Keywords: 4-Hydroxycoumarin, organoselenium, chalcogen, heterocycles, bioactivity.

Highlights

Coumarins, organoselenium compounds, and triazoles individually exhibit numerous biological properties.
Development of coumarin-selenotriazole hybrids via sequential functionalization of 4-hydroxycoumarin.

Abstract

The exploration of novel bioactive molecules begins with their relevance in the literature, such as 4-hydroxycoumarins (**1**), triazoles, and organoselenium compounds. These entities have been the subject of pharmacological studies, revealing diverse biological properties when evaluated individually. Thus, the objective of this work is the development of new coumarin-triazole hybrids Se-linked, obtained via sequential functionalization of 4-hydroxycoumarin (**1**, Scheme 1). The synthetic pathway initiates with the alkylation reaction of **1** with the corresponding dibromoalkanes (83-87%), followed by the reaction of these alkylated intermediates with sodium diselenide, generated *in situ*, forming the diselenides **3** in moderate yields (22-55%). A methodological investigation was carried out to ascertain the optimal reaction conditions to be followed. All diselenides were acquired as yellow solids, and with the alkyl chain increase, the diselenide exhibited a more pronounced yellow hue. Finally, an alkylation reaction of **3** with propargyl bromide was performed, followed by a CuAAC reaction between the formed propargylated monoselenide and the desired azide. The targeted hybrids **4** (75-80%) will have their biological properties evaluated in subsequent studies.



Scheme 1. Synthesis of coumarin-selenotriazole hybrids.

1. Krief A.; Derock M. *Synlett* **2005**, *6*, 1012–1014.
2. Forezi, L. S. M.; Froes, T. Q.; Cardoso, M. F. C.; Maciel, C. A. O.; Nicastro, G. G.; Baldini, R. L.; Costa, D. C. S.; Ferreira, V. F.; Castilho, M. S.; Silva, F. C. *Current Topics in Medicinal Chemistry* **2018**, *18*, 149-156.

Acknowledgments

FAPERJ, CAPES and CNPq.

Área: ORG

Development of Novel Triazoles Derived from 4-Hydroxy-3-Aryl-Coumarins: Exploring Potentially Bioactive Substances

Analice G.R. da Cruz (IC),[1] Cristal V.T. Martins (PG),[2] Yuri P.V. Carvalho (IC),[1] Edson Evangelista (PQ),[1] Luana da S.M. Forezi (PQ)[1,*]

analiceg@id.uff.br; luanaforezi@id.uff.br

[1]Departamento de Química Orgânica, Instituto de Química, UFF; [2]Departamento de Tecnologia Farmacêutica, Faculdade de Farmácia, UFF.

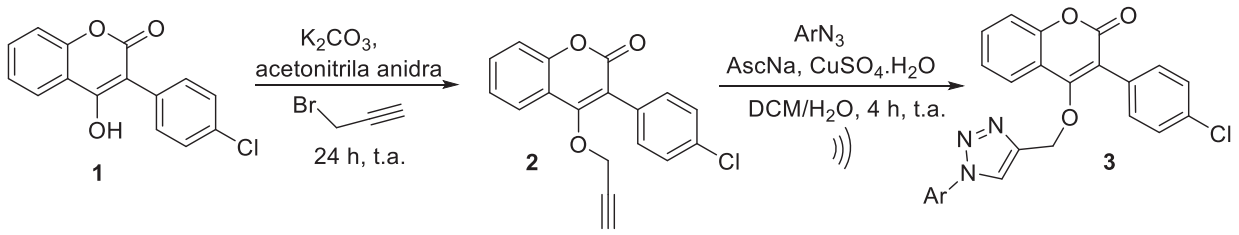
Keywords: Coumarins, 1,2,3-Triazoles, Bioactivity.

Highlights

Coumarins and triazoles exhibit numerous individual biological properties. Development of novel triazoles derived from 4-hydroxy-3-aryl-coumarins.

Abstract

4-Hydroxy-coumarins constitute an important class of bioactive coumarin derivatives. Many of them display biological activities such as anticoagulant, antibacterial, and anti-inflammatory properties. It has been shown that 4-hydroxy-coumarins bearing an aryl group in the 3-position, inhibit cell proliferation.[1] Thus, the objective of this work is the development of new potentially bioactive triazoles derived from 4-hydroxy-3-aryl-coumarins (Scheme 1). For the preparation of the target compounds **3**, the 4-hydroxy-3-aryl-coumarin **1**, previously obtained in our research group from the reaction of 4-hydroxycoumarin with the desired diazonium salt, was reacted with propargyl bromide in the presence of potassium carbonate in anhydrous acetonitrile for 24 hours at room temperature. Subsequently, intermediate **2** underwent a 1,3-dipolar cycloaddition reaction to form the hybrids **3** in good yields. After obtaining all the desired hybrids **3**, they will undergo biological evaluation.



Scheme 1. Synthesis of coumarin-triazole Hybrids.

1. Serra, S. et al. *Bioorganic & Medicinal Chemistry Letters* **2012**, *22*, 5791–5794.
2. ABO-SALEM, H. M. et al. New sulfonamide-tethered coumarin derivatives as potential DNA gyrase inhibitors: Design, synthesis, antimicrobial evaluation, and in silico study. Journal of Molecular Structure **2024**, v. 1296, p. 136860–136860.
3. Franco, D. et al. *A importância das cumarinas para química medicinal e o desenvolvimento de compostos bioativos nos últimos anos* **2020**. Química Nova,

Acknowledgments

FAPERJ, CAPES and CNPq.

Área: ORG
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Develop Scale up of Triazole-quinoline Intermediates in Project of Potent Anti-SARSCoV-2 and Anti-*Plasmodium* activity.

Victória Toledo Diniz Camargo (IC),[1,2] Alcione Silva de Carvalho (PC),[1,2] Fernando de Carvalho da Silva (PQ),[2] Vitor Francisco Ferreira (PQ).[1]

victoriacamargo@id.uff.br; vitorferreira@id.uff.br

[1]Laboratório de Inovação em Química e Tecnologia Farmacêutica Lab IQTF, Departamento de Tecnologia Farmacêutica, FF-UFF; [2]Laboratório de Síntese Orgânica Aplicada LabSOA, IQ-UFF

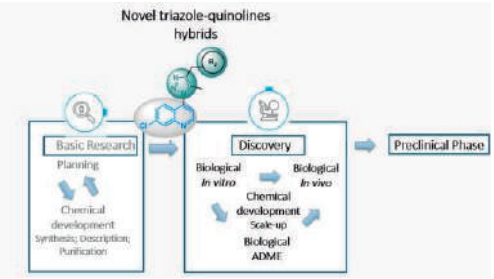
Keywords: *scale up, heterocycles, anti-SARSCoV-2, anti-Plasmodium*

Highlights

Initial findings indicated significant activity against SARSCoV-2 and *P. falciparum* by a novel group of triazolo-quinolines. The objective of this project is scale-up of these compounds.

Introduction

Although malaria is a preventable and curable disease, research and development (R&D) of alternative substances to treat the different types of *Plasmodium* that exist are still necessary. Over the past decade, resistance to antimalarial drugs has increased, posing a threat to global malaria control efforts. In the same vein, COVID-19 requires R&D efforts to contain the spread of a new strain of coronavirus. In line with this mission, our research group has planned, synthesized, and evaluated a new family of triazolo-quinolines. Some of these substances have shown high activity against SARSCoV-2 and *P. falciparum in vitro* with low cytotoxicity. Moving forward, the next phase, *in vivo* testing and pharmacokinetic assays, necessitates the scale-up of these substances (Scheme 1). Therefore, this work aims at the scale-up of these compounds. In this study, we assess the technical feasibility by examining different parameters such as reagent stoichiometry, reaction time, temperature, and the use of ultrasound for the synthesis of key intermediates.

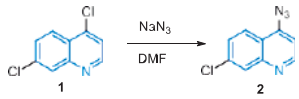


Scheme 1. Stage of the R&D process.

Results and Discussion

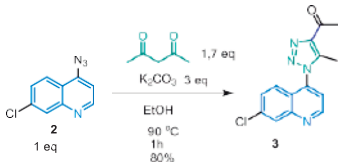
The studied parameters for the synthesis of the first key intermediate are illustrated in Table 1.

Table 1. Results of parameter studies for scaling up the key intermediate **2**.



	Temp. (0ºC)	Time (h)	Equiv.	Ultrasonic bath	Results
1	65	24	1:2	No	1+2
2	80	24	1:2	No	1+2
3	110	24	1:2	No	1+2+subproduct
4	65	24	1:2	Yes	1+2
5	65	24	1:3	Yes	1+2
6	65	24	1:5	Yes	1+2
7	80	7	1:3	No	2

With a 4-fold increase for the synthesis of key intermediate **2**, it was seen that only entry 7 was ideal for obtaining the product. A difference in isolation was also noted. Following filtration with ice water, the intermediate was obtained with a 88% yield. For the scale-up of the synthesis of intermediate **3**, no difference was observed in producing it (Scheme 2).



Scheme 2. Scale-up of intermediate triazole-quinoline (**3**).

Conclusions

Scale-up of key intermediates were successfully obtained.

CNPQ; CAPES; FAPERJ

Área: ORG

Electrochemical investigation of quinones substituted by selenium and cyanide

Danielly S. C. Silva (PG),[1] Allan dos S. Lessa (IC),[1] Marília O. F. Goulart (PQ),[2] Thaíssa L. Silva (PQ),[1] Vinicius Del Colle (PQ)[1,3]*.

danielly.silva@arapiraca.ufal.br; delcolle@arapiraca.ufal.br

[1]*Universidade Federal de Alagoas – Campus de Arapiraca – Núcleo de Ciências Exatas (NCEx), Arapiraca-AL.*
[2]*Universidade Federal de Alagoas, Instituto de Química e Biotecnologia (IQB), Maceió-AL.*
[3]*Instituto Tecnológico de Aeronáutica, Departamento de Química, São José dos Campos-SP.*

Palavras Chave: *Eletroquímica, Quinonas, Voltametria Cíclica.*

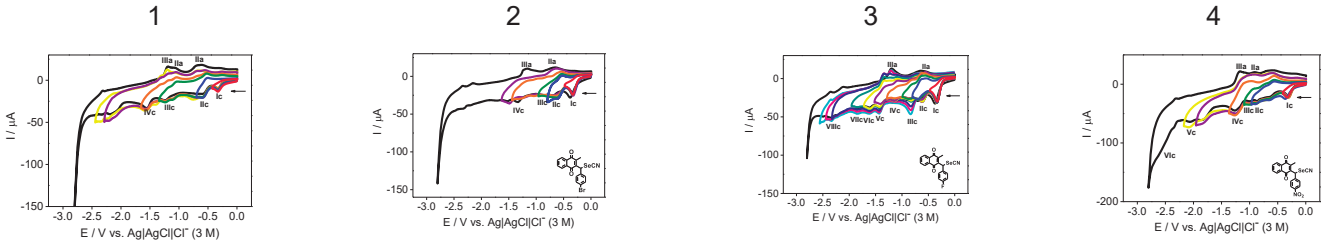
Highlights

This work investigates the electrochemical behavior of a series of compounds substituted with selenium and cyanide, in order to understand the redox action of these compounds.

Resumo/Abstract

As quinonas são um grupo de moléculas que possuem atividade dual (antioxidante e pró-oxidante)[1,2] e potencial redox influenciado pelos substituintes.[1,2] Desta forma é possível eletroquimicamente obter informações relevantes para uma possível elucidação dos mecanismos de ação de compostos de interesse biológico e, assim, investigar as propriedades redox destes compostos. Os estudos eletroquímicos foram realizados numa célula convencional de três eletrodos: carbono vítreo (trabalho), platina (contra-eletrodo) e Ag/AgCl (referência). Os voltamogramas cíclicos (VCs) de quatro quinonas hidridizadas com selênio e cianeto, e substituídas com átomos eletroretiradores (Figura 1) foram registrados em meio aprótico (ACN + $TBAPF_6$) para assemelhar-se ao ambiente lipofílico, típico de membranas celulares. As análises foram realizadas entre 0 – -2,7 V e, para todos os compostos, obteve-se um perfil complexo com quatro picos catódicos, diferente do comportamento habitual das quinonas. O primeiro processo, Ic, é de natureza irreversível e aparece em potenciais próximos a -0.35 V. IIc aparece em seguida, em potenciais mais negativos e com natureza quase-reversível em todas as amostras. As demais ondas podem estar relacionadas à formação de quinonametídeos via eliminação redutiva.[3] É possível notar que, como esperado, à medida que se aumentou a capacidade eletroretiradora dos átomos substituintes, o deslocamento no potencial do pico apresentou valores mais positivos, visto que substituintes eletroretiradores diminuem a energia do LUMO e o processo de redução é facilitado.[4] Esse estudo traçou o perfil eletroquímico de uma série de quinonas substituídas com selênio e cianeto que mostraram atividade eletroquímica complexa na durante a varredura catódica dos voltamogramas. Portanto, compreender a bioativação redox é fundamental nos estudos do desenvolvimento de novos compostos candidatos a protótipos de fármacos.

Figura 1. VCs das quinonas (1 mmol L^{-1}) estudadas em ACN + $TBAPF_6$ (0,1 mol L^{-1}). Eletrodo de carbono vítreo, v = 100 mV s^{-1}.



Referências

[1] EL-NAJJAR, N. et al. The chemical and biological activities of quinones: overview and implications in analytical detection. **Phytochemistry Research**, v. 10, 353-370, 2011.

[2] XAVIER, André Felippe de Almeida et al. Análise eletroquímica de quinonas bioativas: o caso das selenoquinonas. 2021.

[3] ABREU, F. C. et. al. Nitrooxyquinones: synthesis, X-ray diffraction and electrochemical studies. **Tetrahedron Letters**, v. 43, 8153–8157, 2002.

[4] SILVA, Thaissa Lúcio et al. Avaliação de substâncias de interesse biológico com propriedades anti e pró-oxidantes. 2014.

Agradecimentos/Acknowledgments

FAPEAL, CNPq, CAPES e INCT-Bioanalítica.

Área: ORG

Epoxide opening catalyzed by Europium Fumarate via mechanochemistry.

José Robson da Silva Filho (PQ)[1], Cristiane Kelly de Oliveira (FM)[2], Ivani Malvestiti (PQ)[1].

Joserobson.silvafilho@ufpe.br

[1]*Departamento de Química Fundamental, UFPE;* [2]*Escola de Referência em Ensino Médio Professor Ernesto Silva.*

Palavras Chave: *Mechanochemistry, catalysis, europium, epoxides.*

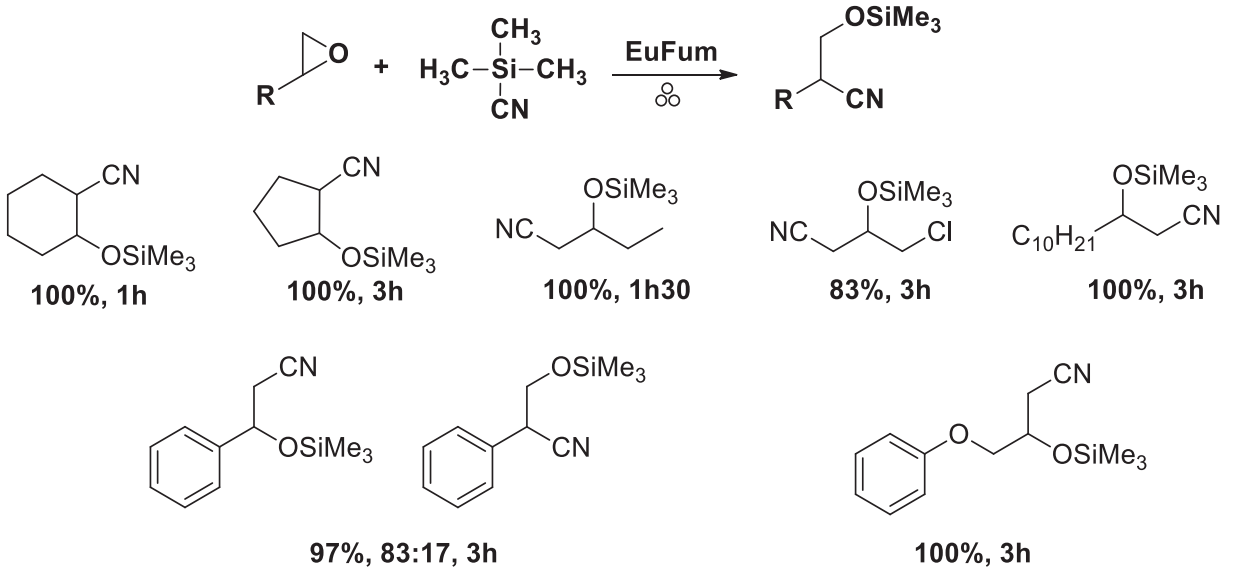
Highlights

This study demonstrates the opening of epoxides via mechanochemistry with TMSCN catalyzed by europium. Showing selectivity for the C-C bond formation, regioselectivity, short reaction times, and conversions above 80%, these data indicate potential for further investigations under more green conditions.

Resumo/Abstract

Mechanochemistry, a green technique, has been widely spread in organic chemistry, allowing solvent-free reactions, reducing waste and energy consumption. This study presents the opening of epoxides via mechanochemistry, catalyzed by Eu(III), with TMSCN as nucleophile. Seven epoxides of various sizes, both symmetric and asymmetric, were employed, and the formation of both regioisomers was observed only with styrene oxide. Furthermore, the formation of only the nitrile was confirmed through infrared measurements and gas chromatography (GC). The results indicate that nucleophilic attack occurred at the less substituted carbon of the epoxide, consistent with the literature on lanthanide-catalyzed epoxide opening. The method presents energy efficiency, short reaction times, and the possibility of avoiding the isolation step by column chromatography, as the samples were simply dried and analyzed without the need for additional purification. Except for the reaction with 2-(chloromethyl)-oxirane which showed the product in 83% along with starting material, further optimization was still required. Conversions were determined by gas chromatography and gas chromatography-mass spectrometry, while product characterization was performed by ^{1}H and ^{13}C NMR and compared with the literature. With excellent conversions (>80%) and reaction times of up to 3 hours, this study indicates new possibilities for using mechanochemistry on epoxide opening under greener conditions. Tests were also initiated with $TMSN_3$ as nucleophile in the opening of cyclohexene oxide, which already shows 80% conversion. The results obtained so far demonstrate the potential for expanding the scope of reaction and preparing organic compounds quickly and more environmentally friendly.

Scheme 1: Scope of epoxide opening with TMSCN catalyzed by Europium fumarate, via mechanochemistry.



Agradecimentos/Acknowledgments

UFPE, Capes, CNPq, FACEPE e Secretaria de Educação e Esportes de Pernambuco (SEE).

Área: ORG

Estudo de metabolômica por RMN de ^{1}H do óleo essencial extraído de resíduos de bergamota Freemont para aplicações em Biotecnologia.

Yasmim A. Sousa (IC),[1*] Aniele B. Dias (M),[2], Paula S. Penteado (D)[3], Patrícia M. da Conceição (PQ)[4], Fernando A. de Azevedo (PQ)[5], Tatiana S. Ribeiro (PQ).[6]

yasmim2k11@gmail.com

[1]UFSCar-campus Araras, Curso de Bacharelado em Biotecnologia; [2]UFSCar-campus Sorocaba/Mestrado em Ciência dos Materiais; [3]UFSCar-campus São Carlos/Doutorado em Química; [4]UFSCar-campus Araras DDR-CCA; [5]Centro de Citricultura Sylvio Moreira-IAC Cordeirópolis; [7]UFSCar-campus Araras/DCNME-CCA.

Palavras Chave: *Cultivares de citros, Freemont bergamota, RMN, óleo essencial, metabolômica, resíduos.*

Highlights

^{1}H NMR Metabolomic study of essential oil extracted from Freemont bergamot residues for biotechnology applications.

Extraction of essential oils from Freemont bergamot residues; Metabolomic study by ^{1}H NMR.

Resumo

Os óleos essenciais majoritariamente são compostos formados por terpenos, chegando a uma fração de 85% a 99%[1], e podem ser definidos como uma combinação de compostos voláteis, de baixo peso molecular e de caráter hidrofóbico[2], onde se destaca os efeitos antioxidante e antimicrobiano. Sabe-se que as atividades biológicas atribuídas aos óleos essenciais dependem de um conjunto de compostos específicos, e pode estar associado a fatores, como localização geográfica da plantação, época de colheita, clima, tipo de espécie e técnicas de extração[2]. O Brasil se destaca por ser o maior produtor mundial de laranja e de suco de laranja, e o segundo maior produtor de citros[3], produzindo quantidade significativa de resíduos. A espectroscopia de RMN de ^{1}H merece destaque para avaliar o perfil de metabolômica de plantas, visto que são análises de compostos orgânicos que possuem alto teor de hidrogênio, um núcleo com $I \neq 0$, 99,98% de abundância natural e, portanto, alta sensibilidade, permitindo o mapeamento dos metabólitos secundários presentes. Portanto, este trabalho visou extrair óleo essencial de resíduos de casca da cultivar bergamota freemont (coleção do IAC-Cordeirópolise), pelo método de hidrodestilação, e investigar por RMN de ^{1}H os principais metabólitos presentes (Figura 1) e de acordo com a literatura[4], com perspectiva de encapsulamento e avaliação de atividade biológica. Estudos estão em andamento, com outras técnicas de RMN associadas, e óleos de cultivares inéditas estão sendo extraídos.

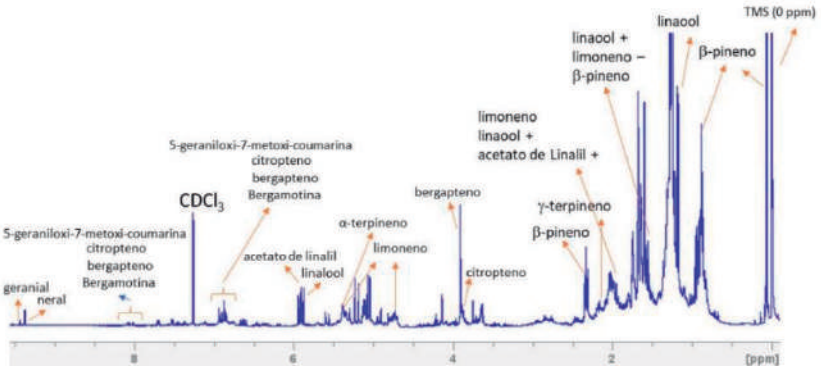


Figura 1. RMN de ^{1}H do óleo essencial de resíduos da bergamota Freemont (em $CDCl_3$, ref. TMS, δ/ppm).

Referências: [1] MEHL, F.; MARTI, G.; BOCCARD, J.; DEBRUS, B.; MERLE, P.; DELORT, E.; BAROUX, L.; RAYMO, V.; VELAZCO, M. I.; SOMMER, H.; WOLFENDER, J.; RUDAZ, S. Differentiation of lemon essential oil based on volatile and nonvolatile fractions with various analytical techniques: a metabolomic approach. **Food Chemistry**, v. 143, p. 325-335, 2014. [2] DIMA, C.; DIMA, S.. Essential oils in foods: extraction, stabilization, and toxicity. **Current Opinion in Food Science**, v. 5, p. 29-35, 2015. [3] FRIZZO, C. D.; LORENZO, D.; DELLACASSA, E. Composition and Seasonal Variation of the Essential Oils from Two Mandarin Cultivars 441 of Southern Brazil. **Journal of Agricultural and Food Chemistry**, v. 52, n. 10, p. 3036-3041, 2004. [4] SALVINO, R. A.; AROULANDA, C.; DE FILPO, G.; CELEBRE, G.; DE LUCA, G. Metabolic composition and authenticity evaluation of bergamot essential oil assessed by nuclear magnetic resonance. Analytical and Bioanalytical Chemistry, v. 414, p. 2297-2313, 2022.

Agradecimentos

Ao CNPq pela bolsa PIBIC concedida, CAPES, FAPESP,

Área: ORG

Estudo Metodológico para a Obtenção de Sulfetos Simétricos e Dissimétricos a partir de Sais De Bunte

Vitor Emanuel Simette Zerger (PG),[1*] Rogério Aparecido Gariani (PQ),[1]

vitor.esz@edu.udesc.br;

[1]*Departamento de Química, Universidade do Estado de Santa Catarina, SC, Joinville, CEP 89219-710, Brazil; do Estado de Santa Catarina*

Palavras Chave: Sais de Bunte, Organocalcogênio, Dihidropirimidinona, Química verde.

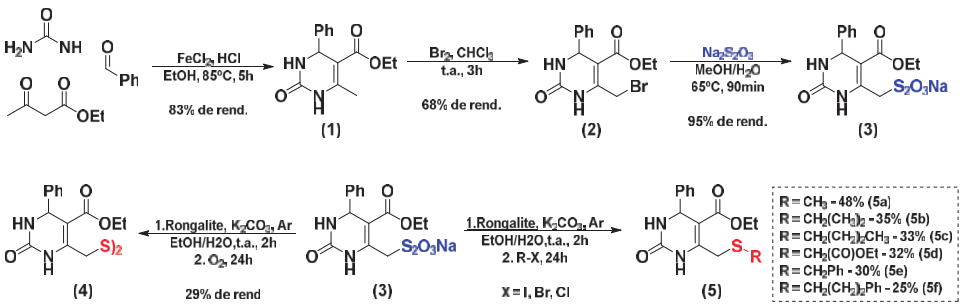
Highlights

The pursuit of sustainable methodologies for synthesizing sulfur-containing organic compounds is increasingly vital in the chemical industry. A promising approach involves utilizing Bunte salts as precursors for sulfides and selenides, providing a practical alternative to conventional organometallic methods. Reducing these salts, coupled with investigating gentle agents like rongalite, sodium borohydride, and sodium dithionite, holds significant promise for crafting bioactive compounds. Moreover, combining dihydropyrimidinones with Bunte salts offers fresh routes for discovering pharmacologically relevant compounds due to the therapeutic significance of their starting materials.

Resumo/Abstract

A busca por metodologias sustentáveis na síntese de compostos orgânicos contendo enxofre está ganhando destaque na indústria química. Uma abordagem promissora é a utilização de sais de Bunte como precursores na obtenção de sulfetos, oferecendo uma alternativa viável aos métodos tradicionais que envolvem organometálicos. O estudo metodológico concentra-se na síntese de sais de Bunte, que são materiais de fácil manipulação devido à sua. O objetivo do trabalho é a síntese de sulfetos híbridos a dihipirimidinona, dada as características biológicas das dihidropirimidinonas podem apresentar melhorias em outras áreas terapêuticas.

Figura 1 – Síntese geral de sulfetos e dissulfetos a partir do sal de Bunte



Fonte: elaborado pelo autor

Durante a otimização das variáveis, incluindo o redutor, estequiometria, temperatura, solvente e método de extração, foram avaliadas. Todos os compostos foram caracterizados por RMN e EMAR. O estudo da obtenção de sulfetos por meio de sais de Bunte é uma alternativa promissora, eliminando o uso de compostos organometálicos. Como próximos passos, iremos explorar haletos de alquila e outros eletrófilos, tais como, aceptores de Michael, epóxidos, cloretos de acila e anidridos, para ampliar a gama de compostos e permitir avaliações biológicas mais abrangentes.

Agradecimentos/Acknowledgments

Aos órgãos de fomento CAPES, CNPq e FAPESC, pelo apoio financeiro durante o trabalho.

Área: ORG

Evaluation of skin-health effects of polysaccharides from wild "jelly mushrooms"

Mateus A. V. Oliveira (PG) [1]*, Dirce Leimi Komura (PQ)[1], Elaine R. Carbonero (PQ)[1]

***augustomateus734@gmail.com; elaine_carbonero@ufcat.edu.br**

[1] Instituto de Química, UFCAT; [2] Instituto Federal de Educação, Ciência e Tecnologia do Maranhão (IFMA), Campus São João dos Patos.

Palavras Chave: *Jelly mushroom*, *Auriculariaceae, Polysaccharides, Antioxidant activity*, Cerrado biome

Highlights

This study to investigate the skin-health potential of the polysaccharide-rich extracts from a wild *Auricularia sp.* mushroom collected in Cerrado biome.

Resumo/Abstract

The increased demand for skin-friendly products has stimulated the development of natural ingredient-based cosmeceutical preparations. In this context, fungal polysaccharides have received special attention due to their promising potent efficacy in wound healing, moisturizing, antiaging, and whitening. Among the numerous macrofungi, *Auricularia* spp. stands out due to the unusual structures and physiological activity of their polysaccharides[1]. Due to numerous wild species of Auricularia and the scarce studies related to their carbohydrates, the present research aims to evaluate the potential of native macrofungi as a source of bioactive polysaccharides for cosmeceutical formulations. For this, the polysaccharides of the basidioms of *Auricularia* sp. (62 g), collected in the cerrado region in Catalão-GO, were obtained by successive aqueous extraction (10 ºC and 96 ºC). Each extract was filtered, and the combined aq. extracts were evaporated to a small volume. Afterward, the polysaccharides were recovered by ethanolic precipitation, followed by centrifugation at 5000 rpm at 20 ºC for 10 min. The resulting polysaccharide precipitates were dissolved in H_2O, dialyzed (10-12 kDa membranes) against distilled water for ~20 h to remove low-molecular-weight carbohydrates, and freeze-dried, resulting in the main fractions named A-EAF, A-EPAQ, and A-EAQ. Three-dimensional structures of A-EPAQ, and A-EAQ-S-I fractions were evaluated by Congo Red assay [2]. For both fractions, a behavior similar to that of carrageenans was observed, where the λ_{max} of the complex first increases and gradually stabilizes as the alkaline concentration increases (0.1 to 0.5 M), suggesting unusual multiple helix structures. Antioxidant activity was carried out with A-EPAQ and A-EAQ-S-I fractions, using the ability of polysaccharides to scavenge DPPH (1,1-Diphenyl-2-picryl-hydrazyl) radical [3]. Briefly, 1 ml sample solution at various concentrations (1 mg/ml to 2 mg/ml) was mixed with DPPH solution to 100 uM final concentration. The mixture was placed in the dark for 30 min, and the absorbance at 517 nm was immediately measured using a UV/Vis spectrophotometer (Kasvi). Ascorbic acid was used as a positive control, and distilled water was used as a negative control. According to preliminary data, the polysaccharide fractions obtained by hot aqueous extraction (A-EPAQ and A-EAQ-S-I fractions) decreased the DPPH radical, suggesting that it has antioxidant activity. In order to correlate the results obtained with the chemical structure of these polymers, analyses to verify the monosaccharide composition, type of glycosidic bond, homogeneity, degree of branching, and presence of acetyl groups are being performed.

References:

[1] Mapoung S, et al. Skin wound-healing potential of polysaccharides from medicinal mushroom *Auricularia auricula-judae* (Bull.). *J Fungi (Basel)*, 7(4), 247, 2021. doi: 10.3390/jof7040247

[2] Guo X, et al. Triple-helix polysaccharides: formation mechanisms and analytical methods. *Carbohydr. Polym.,* 262, 117962, 2021. https://doi.org/10.1016/j.carbpol.2021.117962

[3] Sharma O P, and Bhat T K. DPPH antioxidant assay revisited. *Food Chemistry*, 113(4), 1202-1205, 2009. https://doi.org/10.1016/j.foodchem.2008.08.008

Agradecimentos/Acknowledgments

This study was supported by the Federal University of Catalão (UFCAT) and financed in part by the Fundação de Amparo à Pesquisa do Estado de Goiás (FAPEG).

Área: ORG

Exploring the formation of new C-C bonds through the reaction of sulfur ylides with epoxides.

Aislan L. da Silva (IC)*, **Viktor S. Câmara (PQ), Antonio C. B. Burtoloso (PQ).**

aislanlemesilva@usp.br; antonio@iqsc.usp.br

[1]*São Carlos Institute of Chemistry, IQSC - USP.*

Keywords: *Ylides, epoxides, oxetanes.*

Highlights

The present work proposes the synthesis of a library of epoxides with different reactivity patterns, as well as the study of their behavior in the reactions with α-carbonyl sulfoxonium ylides.

Resumo/Abstract

Sulfur ylides constitute a chemical class that is currently establishing itself as versatile substrates in organic synthesis. Their structural characteristics confer them an ambiphilic nature, allowing sulfur ylides to participate in reactions with various electrophiles and nucleophiles. Despite α-carbonyl sulfoxonium ylides having a wide range of synthetic applications, one of the less explored applications is their use as nucleophiles in epoxide ring-opening reactions, with such reaction being only explored with the highly reactive dimethylsulfoxonium methylide. Recently, we performed the synthesis of 14 examples of 2-hydroxyindolin-3-ylidene from the reaction of the epoxide indole with α-carbonyl sulfoxonium ylides (Figure 1)

Based on this observation, we decided to explore the reaction of sulfoxonium ylides with classic epoxides, aiming for the formation of functionalized oxetanes (Figure 2). We started evaluating parameters such as different catalysts, solvents, temperature, and reaction time. However, none of the conditions tested furnished the desired product. Finally, considering the lack of success during the tests, efforts were made to synthesize more reactive epoxides. We applied methods already described, such as the Corey and Chaykovsky epoxidation, and obtained four epoxides in good yields (Figure 3). The reaction of these epoxide with sulfoxonium ylides will be explored.

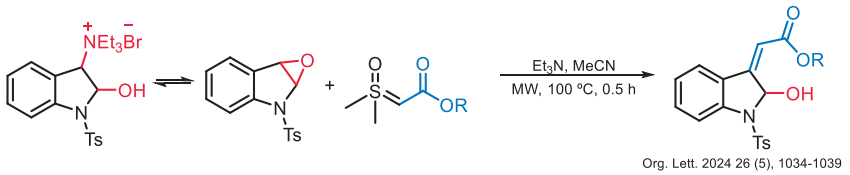


Figure 1: Epoxide ring opening of indole epoxide by α-carbonyl sulfoxonium ylide

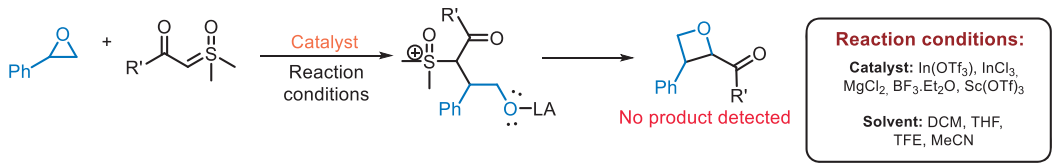


Figure 2: Test conducted for epoxide ring-opening aiming at the formation of oxetanes.

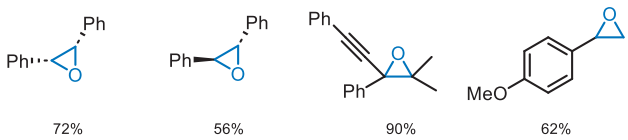


Figure 3: Synthesized epoxides.

References: Camara *et.al. 2024 Org. Lett 26 (5), 1034-1039*; Okuma *et. al.* 1983 J. Org. Chem. 48, 25, 5133–5134

Agradecimentos/Acknowledgments

FAPESP

Área: ORG

Exploring the Origins of the Supramolecular Similarity in Organic Crystal Structures: A Fresh Perspective based on a Multi-Parameter Approach

Paulo R. S. Salbego (PQ)[1*], Tainára Orlando (PQ)[2], Bryan B. Menezes (PQ)[1], Leandro C. Lopes (PG)[3], Darlon A. M. Neumann (IC)[3], Valquiria P. Andrade (PQ)[3], Mateus Mittersteiner (PG)[3], Marcos A. P. Martins (PQ).[3]

paulosalbego@gmail.com

[1]NUQUIMHE, Department of Engineering and Environmental Technology (DETA), Federal University of Santa Maria (UFSM), Frederico Westphalen Campus, RS, Brazil; [2] Academic Department of Chemistry, Federal Technological University of Paraná (UTFPR), Medianeira Campus, PR, Brazil; [3]NUQUIMHE, Department of Chemistry, Federal University of Santa Maria (UFSM), Santa Maria, RS, Brazil.

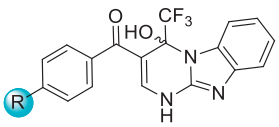
keywords: Supramolecular Chemistry; Supramolecular Similarity; Crystalline Structure; Crystal Engineering.

Highlights

It was possible to uncover the origins of the supramolecular similarity between a series of five organic structures using the similarity indices I^X and crystallization mechanism proposals.

Abstract

Research on supramolecular similarity in crystalline structures is of the utmost importance to the pharmaceutical industry and the development of new materials, since crystal structures with supramolecular similarity may have similar properties.[1] Hence, searching for tools that can help shed more light on the isostructurality in crystals and how to modulate structures to obtain the desired properties is pivotal. In this sense, this study pursued to propose the origins of the supramolecular similarity between a series of five benzimidazole derivatives structures (**Figure 1**).[2] The benzimidazole scaffold was chosen as it is present in molecules of major interest due to its wide range of biological/pharmacological activities. Our findings indicated that the similarity occurs due to the approximation of the initially formed one-dimensional nuclei during crystallization. To achieve these insights, supramolecular comparisons were carried out by calculating the quantitative similarity indices I^X (X = D, C, or G) based on geometric (I^D), contact area (I^C), and stabilization energy (I^G) parameters.[3] The multiparameter index I^{DCG} demonstrated distinct similarity regions in the supramolecular comparisons. All structures with substituents (**2**–**5**) presented a high similarity when compared amongst each other; the unsubstituted compound **1** was the only one with a low similarity after being compared to the rest of the series. To understand how supramolecular similarity arises and how the crystals were formed in this series of compounds, crystallization mechanisms were proposed using a retrocrystallization process.[4] The crystallization mechanisms proposed for all structures presented two main stages. In the first stage, one-dimensional nuclei formation occurs, which is assisted by hydrogen bond interactions combined with π···π interactions, showing the dominance stabilization energy parameter. After the first stage, the one-dimensional nuclei present a pattern of approximation (interaction) similar to compounds **2**–**5**; this led to crystal lattices with high supramolecular similarity. Nevertheless, given the absence of a substituent, compound **1** favored a distinct complementarity between the one-dimensional nuclei, giving rise to a crystal lattice distinct from compounds **2**–**5**. It was possible to uncover the origins of the supramolecular similarity between **2**–**5** (and the dissimilarity with compound **1**) using the similarity indices I^X and crystallization mechanism proposals. From this, we reinforce that isostructurality must be seen as a broad concept and consider a supramolecular perspective using quantitative and comparable parameters to classify regions of similarity. In the way we see it, we need to discuss more *Supramolecular Similarity* instead of only *Isostructurality* because the supramolecular environment is pivotal in understanding this phenomenon.



Compound	R
1	H
2	Me
3	OMe
4	Cl
5	Br

Figure 1. The crystalline structures used in this study.

References: 1. *CrystEngComm* **2020**, 22, 7193–7203. 2. *EurJOC* **2020**, 2020, 6478–6484. 3. *ACS Omega*, **2019**, 4, 9697–9709. 4. *Cryst. Growth Des*. **2023**, 23, 8, 5548–5563.

Acknowledgments

The authors acknowledge the UFSM, CAPES, CNPq, and FAPERGS.

Área: ORG

Guardians of Authenticity: Unveiling Counterfeit Spirits through Bottle Cap Analysis using Time-Domain Nuclear Magnetic Resonance

Jéssica T. Lima (PG eTM),[1]* Sônia F. Zawadzki (PQ),[1] Frederico L.F. Soares (PQ),[1] Kahlil S. Salome (PQ),[1] Andersson Barison (PQ),[1] Tiago B. Moraes (PQ),[2] Caroline R.M. D'Oca (PQ).[1]

jess.delima@ufpr.br

[1]Department of Chemistry, UFPR; [2]Department of Biosystems Engineering, USP.

Keywords: *Distilled Spirits, Counterfeit Spirits, TD-NMR, FT-IR, Forensic Chemistry.*

Highlights

A novel method to identify counterfeit spirits. FT-IR and TD-NMR reveal molecular dynamics changes. TD-NMR is a powerful tool for detecting counterfeit spirits through bottle caps.

Resumo/Abstract

The illegal alcoholic beverage market constitutes 25% of global trade[1], posing health risks and tax-related issues. A prevalent practice involves reusing original bottles to maintain genuine packaging. This includes reusing seals and caps and using materials to imitate authenticity. Originals often undergo heating during refilling, simulating sealing. Despite similarities, production in packaging industries differs in color, thickness, and hardness. This creates opportunities for fraud, prompting the need for a methodology to investigate alterations in plastic caps and seals, aiming to identify adulteration or counterfeiting in alcoholic beverages. This study employs a robust methodology, analyzing original, suspicious, or commercially acquired samples through FT-IR and TD-NMR. Chemometric techniques, including PLS-DA, and DD-SIMCA, reveal exceptional separation among sample groups, as depicted in Figure 1. The comprehensive approach aims to identify and understand the alteration of plastic caps and seals, contributing to the detection of adulteration or counterfeiting in alcoholic beverages.

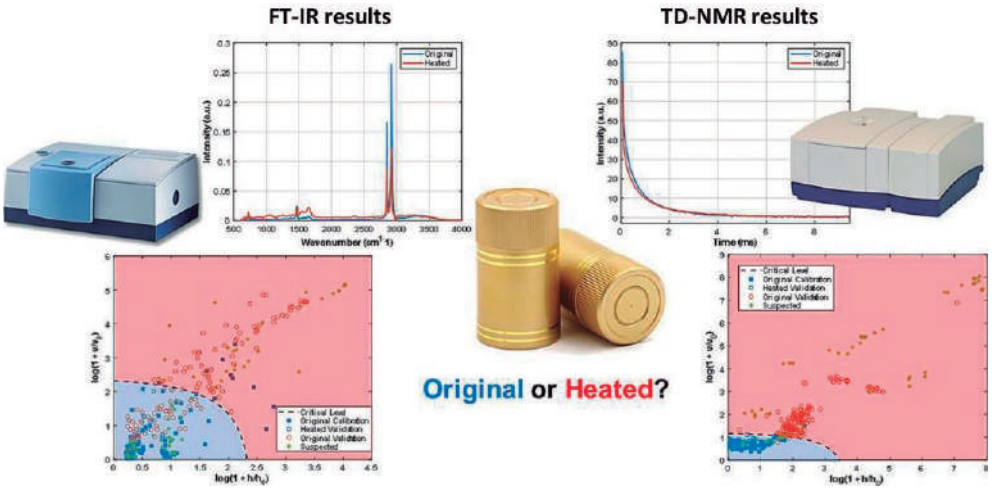


Figure 1. DD-SIMCA prediction models based on vibrational and relaxation data.

The chemometric analysis, particularly utilizing TD-NMR data, exhibited an exceptional capability to recognize heated bottle caps—a telltale sign often linked to the illicit practice of refilling brand spirits with inferior substitutes or counterfeit liquors. With an impressive accuracy rate of 98%, this approach allows for the rapid and straightforward identification of heated bottle cap samples by acquiring T_2 relaxation curves through the CPMG pulse sequence, directly from the sample, without any pre-treatment. The benchtop TD-NMR system emerges as a versatile and reliable instrument in the battle against counterfeiting, offering the advantages of being cost-effective and robust. This innovative methodology marks a significant contribution to forensic practices, enhancing our ability to combat fraudulent activities in the spirits industry.

[1]WHO - World Health Organization. Global Status Report on Alcohol and Health 2018. (2018). Geneva.

Agradecimentos/Acknowledgments

To the Brand Protection Group (BPG) and to the Brazilian Federal Police that kindly provided the bottle caps samples. To the funding agencies for providing the spaces and equipment used.

Área: CAT

Immobilization of $[Ru(bpy)_2Cl_2].2H_2O$ in Covalent Organic Frameworks as a New Strategy for the Development of Heterogeneous Photocatalysts

Gabriel Almeida Mendonça da Silva [1](IC), Marcos A. S. Francisco [1](PG), Leandro S. de Abreu [1](PQ), Pierre M. Esteves [1]*(PQ), Raoni Schroeder B. Gonçalves [1]*(PQ)

1: Instituto de Química – Universidade Federal do Rio de Janeiro (IQ-UFRJ)
** raoni.schroeder@iq.ufrj.br, pesteves@iq.ufrj.br*

Keywords: COFs, Ruthenium, Photocatalysis.

Highlights

A new heterogeneous photocatalyst is prepared through the anchoring of $[Ru(bpy)_2Cl_2].2H_2O$ onto a Covalent Organic Framework (COF) named RIO-55. The composite displayed promising results for the photosensitized generation of singlet oxygen.

Resumo/Abstract

In recent years, photocatalytic reactions have gained increasing attention within the scientific community. Key photocatalysts include inorganic complexes and organic dyes, usually employed in the homogeneous phase, which presents challenges for their recovery.[1] In this context, the heterogenization of these catalysts enables us to capitalize on both aspects – the high catalytic efficiency of these species and the benefits of heterogeneous catalysis, such as the easy recovery of the photocatalyst, and minimal product contamination. However, the success of this approach relies predominantly on the use of supports compatible with the catalytic process and the implementation of efficient immobilization strategies.

Aiming to develop a Ru based heterogeneous photocatalyst, we proposed the anchoring of $[Ru(bpy)_2Cl_2].2H_2O$ complex in a Covalent Organic Framework (COF) named RIO-55. This COF features aza-imine groups in its structure, which can serve as a potent π acceptor. Recent studies have demonstrated that the complexation of Ru with ligands of this type can result in a bathochromic shift in the transition bands related to metal-ligand charge transfer, compared to pyridinic ligands. Additionally, higher oxidation potentials have been observed for these complexes.[2] Therefore, in addition to serving as a support, it is proposed that the COF will act as an active component of the catalyst, modulating the properties of the metal center.

The synthesis of COF RIO-55 was carried out using the solvothermal method, through the reaction between bismarck Brown (Y) and triformylphloroglucinol.[3] Characterization was performed through infrared spectroscopy (IR), N_2 adsorption and desorption isotherms, with the surface area determined by the BET method. The synthesis of *cis*-$Ru(bpy)_2Cl_2.2H_2O$ was carried out through the reaction between hydrated ruthenium(III) chloride, 2,2'-bipyridine, and lithium chloride in N,N-Dimethylformamide at room temperature for 8 hours.

The anchoring of the ruthenium complex was achieved by reacting the $[Ru(bpy)_2Cl_2].2H_2O$ complex with RIO-55, using ethanol as a solvent, under reflux for 72 hours. The resulting material underwent repeated washings with ethanol using a Soxhlet extractor. Subsequently, the composite was characterized through X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy-dispersive spectroscopy (EDS). Analyses were conducted on RIO-55 before and after the incorporation of the ruthenium complex. XRD revealed a decrease in crystallinity after ruthenium anchoring, while SEM-EDS confirmed the retained morphology, with 1.9% of Ru relative to the material's mass being dispersed on the surface. The use of the catalyst as a photosensitizer for singlet oxygen generation is being investigated in our laboratory.

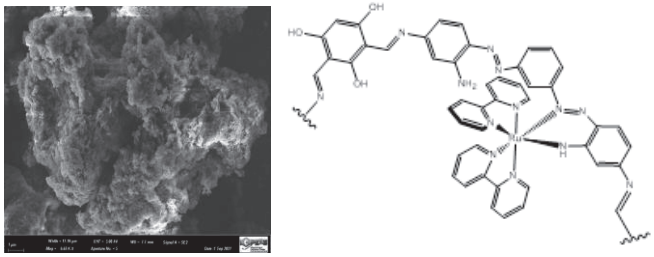


Figure1: Scanning electron microscopy (SEM) of $Ru(bpy)_2$@RIO-55.

Agradecimentos/Acknowledgments

To CNPq, FAPERJ, CAPES for their financial support.

[1]**KÖNIG**, B. *European J. Org. Chem.*, 2017, 1979.
[2]**MONDAI**, B. *Dalton Trans.*, 2000, 4209.
[3]**MAIA**, R. et al. *Crystal Growth and Design*, 2018, 5682.

Área: ORG

Investigating the mechanism for the synthesis of mesotrione herbicide analogues by means of DFT

Roberto M. de Oliveira (IC)*, Carolina G. de S. Lima (PQ), Rodolfo G. Fiorot. (PQ).

robertomello@id.uff.br

[1]*Departamento de Química Orgânica, UFF.*

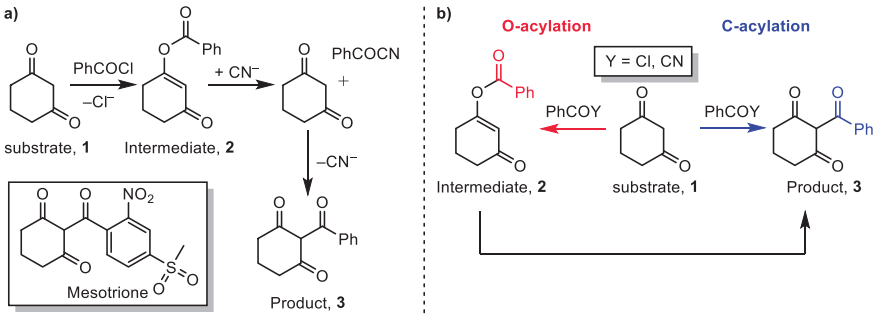
Keywords: computational chemistry, green chemistry, molecular modeling, reaction mechanism.

Highlights

Exploration of the energy profile of the mechanism for the synthesis of mesotrione analogues, via DFT methods, to understand the role of the cyanide in the reaction, aiming to propose a sustainable alternative pathway.

Resumo/Abstract

Mesotrione (scheme 1a) is a selective herbicide that works via inhibition of the enzyme 4-hydroxyphenylpyruvate dioxygenase (HPPD)[1]. Due to its high selectivity, low environmental impact and low toxicity, this herbicide is widely used, especially in corn fields. However, its main synthetic route employs the hazardous cyanide anion, formed *in situ*. The present work aims to comprehend the role of the cyanide in the reaction mechanism to propose a more environmentally friendly synthetic route. To this end, computational simulation was carried out using the DFT approach, with the DFT method ωB97X-D/def2-TZVPP and implicit solvation with the model IEFPCM, using water as solvent. According to literature[2], when the substrate **1** reacts with benzoyl chloride (PhCOCl), the intermediate **2** is formed. This, in the presence of cyanide ions, regenerate substrate **1** and releases benzoyl cyanide (PhCOCN) in the reaction medium. When **1** reacts with PhCOCN, product **3** is formed, with a structure analogous to mesotrione (scheme 1a). To understand this chemoselectivity, the energy variation in the formation reaction of O-acylation and C-acylation was compared for both acylating agents and their respective reaction barriers (scheme 1b).



Scheme 1. A) Sequence of reaction steps to form the product **3**; b) O-acylation and C-acylation reactions from the substrate **1**.

The calculations showed that the energy change (ΔE), in kcal mol^{-1}, for the reactions with PhCOCl for O-acylation and C-acylation were respectively –19.1 and –24.6 and for the reactions with PhCOCN obtained 5.6 and 0.4. Furthermore, the C-acylation product was more stable by 3.0 kcal mol^{-1}. The calculated energy barriers for the O-acylation and C-acylation using PhCOCl were 7.3 and 12.0 in kcal mol^{-1}, respectively, indicating a kinetic preference towards formation of the intermediate **2**. On the other hand, the reactions with PhCOCN resulted in barriers of 20.2 and 10.8 kcal mol^{-1} for the O-acylation and C-acylation, respectively, indicating a kinetic preference for the formation of the product **3**. While C-acylation with PhCOCl is thermodynamically more favorable, the preference for the O-acylation probably occurs due to the low barrier compared to C-acylation. In addition to the O-acylation reaction with PhCOCN being less thermodynamically favorable in relation to C-acylation, the difference between the two barriers is considerable, which would drive the formation to the desired product, in accordance with the literature[2]. Therefore, the preference for the reaction path is kinetic for the reaction with PhCOCl, and not only kinetic but also with a thermodynamic influence for PhCOCN. We will then investigate the factors controlling chemoselectivity to propose a sustainable synthetic route.

References: [1] Mitchell, G.; Bartlett, D.W.; Fraser, T.E.M. et al. *Pest Manag Sci*, *57*, p. 120, **2001**; [2] Yu, M.; Fan, H.; Cao, C. et al. *J Flow Chem*, *12*, p. 197, **2022**.

Agradecimentos/Acknowledgments

Acknowledgments: FAPERJ, CNPq e CAPES.

Área: ORG

Iron- and manganese-catalyzed oxidation of aromatic sulfides

Anna Beatriz Facundo E Silva (IC),[1] Milena Cristina Vieira Fernandes (PG),[2] Emilio Carlos de Lucca Júnior (PQ).[1] *

eluccajr@unicamp.br; m222555@dac.unicmap.br

[1]*Instituto de Química, Universidade de Campinas, CEP. 13083-970, Campinas, São Paulo, Brasil.*

Palavras Chave: Oxidation, Sulfides, PDP system, Funcionalization.

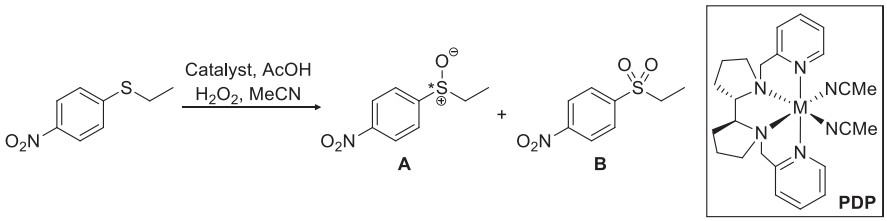
Highlights

Sulfoxides are interest for pharmaceutical area and organic synthesis. Therefore, we used FePDP and MnPDP catalysts to oxidize sulfides in order to obtain sulfoxides and avoid overoxidation.

Resumo/Abstract

Given the interest of our research group in using active species of iron-oxo and manganese-oxo for oxidations such as hydroxylations, epoxidations, and lactonizations, we asked ourselves if FePDP and MnPDP could promote the oxidation of sulfides to sulfoxides in high yields and avoid overoxidation to sulfones. Various reaction conditions were investigated and, depending on temperature, oxidant equivalents, and catalyst, different products were obtained (Table 1). In the Table 1 we observe that by changing the catalyst and the reaction temperature it was possible to obtain only the sulfoxide.

Table 1. Optimization of reaction conditions.



Catalyst	H_2O_2 (equiv.)	Addiction method	Temperature (°C)	Yield B (%)	Yield A (%)
Fe-PDP	3.6	Iterative	rt	98	0
Without	3.6	Iterative	rt	0	28
Fe-PDP	1.2	Iterative	rt	51	41
Fe-PDP	4.5	Slow	rt	67	0
Mn-PDP	4.5	Slow	0	0	23

References: [1] *Chem Commun* **2009**, 6129-6144; *Chem Rev* **2007**, 107, 5133-5209. [2] *JACS* **2003**, 125, 6610-6611.

Agradecimentos/Acknowledgments

FAPESP (Grants 2021/07167-4 and 2018/04837-6), CNPq, and Capes for financial support.

Area: ORG

Mechanochemical valorisation of the bio-based nitrogenated furan 3A5F

Bruna Butke de Souza (PG),[1] Renan Rodini Mattioli (PG),[1] Camila Souza Santos (PQ),[1] Pedro Dominguez Branco (PG),[1] Julio Cezar Pastre (PQ).[1]*

b261083@dac.unicamp.br; jpastre@unicamp.br

[1]Institute of Chemistry, University of Campinas (UNICAMP), 13083-970, Campinas, SP, Brazil;

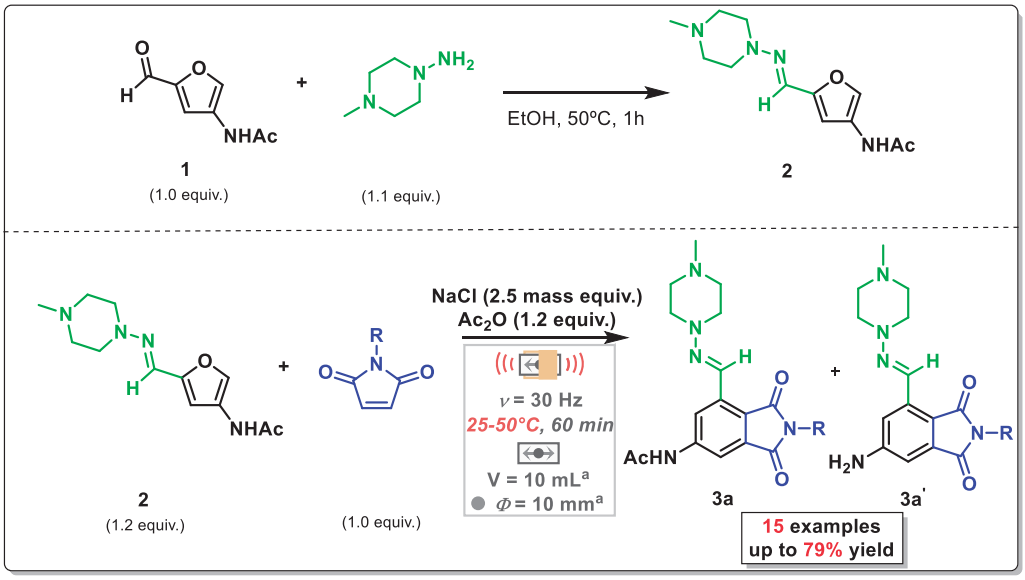
Key words: *Biomass Valorisation, Chitin Biomass, Mechanochemistry, Green Chemistry.*

Highlights

Synthesis of new aromatic derived from renewable resources. Valorisation of chitin biomass by Mechanochemistry. Use of a commercially available hydrazine to promote aromatisation.

Resumo/Abstract

Since the beginning of the chemical industry, aromatic compounds have played a crucial role in the production of high added-value chemicals. Currently, fossil carbon sources are still the predominant starting materials for the synthesis of aromatic. To minimize the carbon footprint of nitrogen containing chemicals, the use of furans derived from chitin has become an affordable and promising source for nitrogen fixation in compounds with high added-value. In this sense, our goal is to promote the preparation of aromatic compounds from renewable sources using enabling technologies. In this work, we address the challenge of using the chitin-derived furan 3-acetamido-5-furfural aldehyde (**3A5F**), to favour the formation of 4-acetylaminophthalimides using Mechanochemistry, as a more sustainable and cleaner synthesis compared to the classical methods in solution-phase. We also investigated the use of a less toxic and commercially available hydrazine in order to promote the synthesis of 4-acetylaminophthalimides from **3A5F** in yields ranging from 20–79% (**Scheme 1**).



Scheme 1. Synthetic route for the production of nitrogenated aromatic compounds from the chitin-derived furan **3A5F**.

Agradecimentos/Acknowledgments

The authors gratefully acknowledge financial support from the São Paulo Research Foundation – FAPESP (BBS, 2023/01238-2; RRM, 2019/26450- 9 and 2022/03872-8; CSS, 2022/00774-5; PDB, 2023/01232-4; JCP, 2021/06661-5), the Brazilian National Council for Scientific and Technological Development – CNPq (JCP, 308540/2021-2), and the Coordination for the Improvement of Higher Education Personnel – CAPES (RRM, Finance Code 001).

Área: ORG

Menadione as Synthetic Plataform for 1,2,3-Triazoles Hybrids in The Search for New Drug Prototypes

Gustavo Senra G. De Carvalho (PQ),[1] Raquel N. Simões (IC),[1] Mariana O. L. Desmarais (IC),[1] Daniel T. G. Gonzaga (PQ),[2] Fernando de Carvalho (PQ),[1]

senradcarvalho@gmail.com

[1] *Universidade Federal Fluminense, Instituto de Química, Laboratório de Síntese Orgânica Aplicada, Niterói-RJ, 24210-141, Brazil.*
[2]*Universidade do Estado do Rio de Janeiro, Campus Zona Oeste, Campo Grande-RJ, 20950-000, Brazil.*

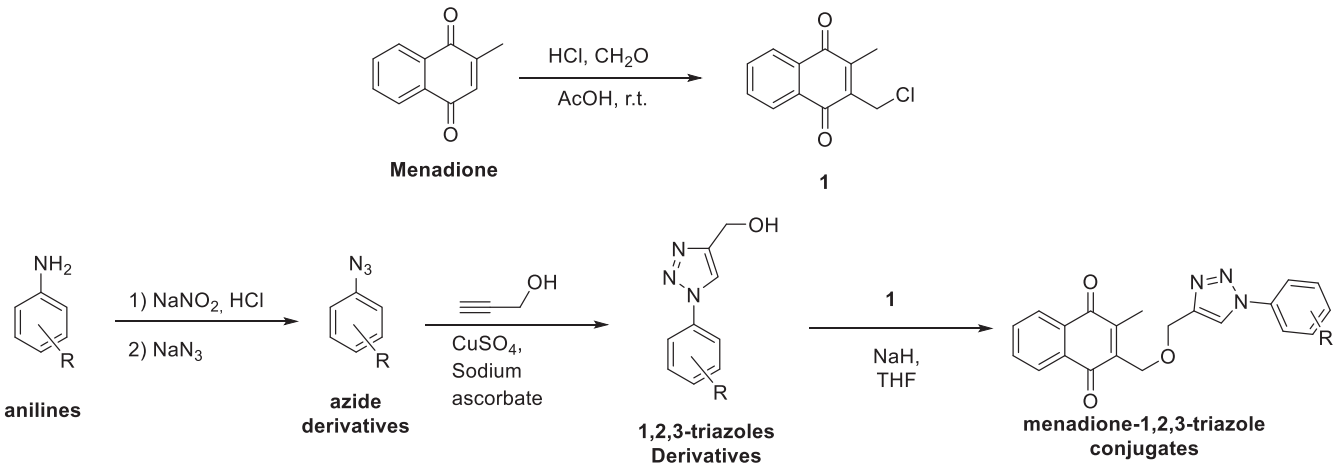
Palavras-Chave: *Vitamin K3, Heterocycles, Click Chemistry*.

Highlights

This work now proposed will address various aspects of the chemical conjugation of menadione nuclei (vitamin K3) to 1,2,3-triazole nuclei with a view to obtaining new bioactive substances against various diseases.

Resumo/Abstract

Menadione is a naphthoquinone and has attracted much attention due to its wide range of biological activities, such as: anticancer, antibacterial, antifungal, antimalarial, antichagasic and anthelmintic.[1] The presence of an α,β-unsaturated diketone in the quinone structures allows them to receive electrons through reduction processes, followed by oxidation, establishing a redox cycle.[2] In these cases, the redox cycle of menadione, followed by the generation of reactive oxygen species (ROS), resulted from interactions between nucleophilic biomolecules and the 1,4-naphthoquinone nucleus of menadione and its derivatives.[3] On the other hand, heterocyclic rings with nitrogen atoms are the most commonly used molecular fragments in drug design using the tools of medicinal chemistry. 1,2,4-triazole rings are part of an extensive family of medications that are in use on the pharmaceutical market.[4] In this sense, in this work we aimed to synthesize novel derivatives of menadione-1,2,3-triazole conjugates. The synthetic methodologies to obtain the proposed conjugated compounds originate from the methylenechlorinated intermediate of menadione **1** (97% yield). This compound opens possibilities for coupling to nucleophilic synthons of interest such as azides (up to 95% yield) and 1,2,3-triazole derivatives (up to 90% yield) as shown in Scheme 1. After the complete synthesis and characterization of all conjugated compounds, they will be sent for evaluation of their biological activities.



Scheme 1. Synthetic route toward menadione-1,2,3-triazole conjugates.

Agradecimentos/Acknowledgments

LabSOA FAPERJ CNPq CAPES

References

[1] *Nature Communications* **2016**, *7*, 13401.
[2] *PLoS One* **2015**, *10*, e0144033.
[3] *RSC Advances* **2018**, *5*, 67909-67943.
[4] *Journal of Medicinal Chemistry* **2014**, *57*, 5845.

Área: ORG

Microfluidic synthesis of artificial intelligence-generated compounds potentially bioactive against COVID-19

João Victor X. da Silva[1,2] (IC), Ingrid C. Chipoline[1,2] (PQ), Marcos V. da Silva Santana[2] (PQ), Natalia L. V. Ranke[2] (PQ), Rafael F. Dantas[2] (PQ), Luciano P. Gomes[2] (PQ), Sabrina B. Ferreira[1] (PQ), Floriano P. S. Júnior[2]* (PQ).

ximenes@gradu.iq.ufrj.br; floriano@ioc.fiocruz.br

[1]Laboratório de Bioquímica Experimental e Computacional de Fármacos, Instituto Oswaldo Cruz, Fiocruz, RJ, Brasil; [2] Laboratório de Síntese Orgânica e Prospecção Biológica, Departamento de Química Orgânica, Universidade Federal do Rio de Janeiro, RJ, Brasil.

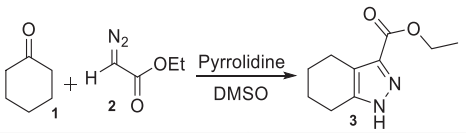
Keywords: *Continuos flow, generative model, microchip, Mpro, SARS-CoV-2.*

Highlights

Accelerating the pre-clinical drug discovery process. Combination of predictive and synthetic technology. Prediction of potentially bioactive drugs using AI. Microfluidic synthesis as a more efficient alternative.

Resumo/Abstract

Artificial Intelligence (AI) is a technology that is increasingly gaining prominence in various areas of human life. In the natural and biological sciences, for instance, it has emerged as a tool to accelerate the design phase in the cycle of discovering new drugs. One application of AI in drug discovery is generative computational models, which can design new molecules with potential biological activity[1]. Flow synthesis is another technology that has been explored to optimize the process of obtaining new drugs. Specifically, one cutting-edge technology is on-chip synthesis, which utilizes microfluidics to improve yields, reduce reaction time, and contribute to green chemistry[2]. Therefore, the aim of this study was to combine AI and on-chip synthesis to obtain new drug candidates more quickly and efficiently. Initially, COVID-19 was our primary focus, by employing a generative model[3] to create a library of over 10,000 new molecules based on known inhibitors of the Mpro of SARS-CoV-1 and 2 viruses. Using this library, a cascade of filters was applied, including the novelty of the compound, types of reactions involved in its synthesis, classification of potential inhibitors using molecular docking, among other filters, resulting in the selection of 4 molecules for synthesis with a high degree of novelty. In parallel with these theoretical studies, methodological tests were conducted for the implementation of the flow system, comparing it with a reaction already established in the research group[3]. In this methodology, by utilizing the flow system, it was possible to reduce the reaction time from 24 hours to 5 minutes, along with an increase in the reaction yield, as seen in **Table 1**. This confirmed the efficiency of the assembled system, ready to be used for producing the molecules planned by AI. Consequently, the reagents have already been obtained, and, as customary in this area of organic synthesis, the batch reaction has been performed for substance 6 (**Table 1**). The product was obtained with a 10% yield and confirmed through ^{1}HNMR analysis. An improvement is expected when transferring the reaction to the chip system. Furthermore, the other substances are in the process of synthesis, and all will be evaluated as inhibitors of the Mpro of SARS-CoV-2.



Batch reaction	Chip reaction
24 hours	**5 minutes** (residence time)
Room temparature	Room temperature
Magnetic stirring	83,4 $\mu.s^{-1}$ (flow rate)
60% yields	95% yields
< 99% convertion	> 99% convertion

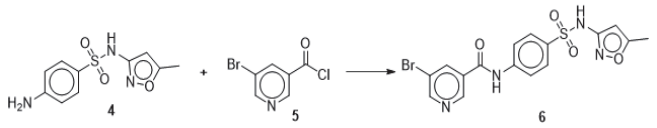


Table 1: On the left, a comparison of reactions in a batch and in flow. On the right, a reaction where it was possible to obtain the product predicted by AI.

Agradecimentos/Acknowledgments

The authors would like to thank CAPES, FAPERJ, CNPq and INOVA-Fiocruz

[1] Wang, H; et al. *Nature*, 620, 7972, 47–60, **2023**.
[2] Liu, Y; Jiang, X. *Lab on a Chip*, 17, 23, 3960–3978, **2017**.
[3] Santana, M. V. S.; Silva-Jr, F. P. *BMC Chemistry*, 5, 8, **2021**.

Área: ORG

Molecular Design Based on Artificial Intelligence and Synthesis of new peptidomimetic inhibitors of the SARS-CoV- 2 Mpro enzyme

Ana Beatriz C. Gonçalves (IC),[1] Pedro H.O. Borges (PG),[1] Natalie F. Araujo (PG),[1] Floriano P. S. Junior (PQ),[2] Sabrina B. Ferreira (PQ).[1*]

anabe@ufrj.br; sabrinab@iq.ufrj.br

[1]Universidade Federal do Rio de Janeiro, Instituto de Química, Laboratório de Síntese Orgânica e Prospecção Biológica (LaSOPB), Rio de Janeiro, RJ, Brasil; [2]Fundação Oswaldo Cruz, Instituto Oswaldo Cruz, Laboratório de Bioquímica Experimental e Computacional de Fármacos (LaBCEFar), Rio de Janeiro, RJ, Brasil.

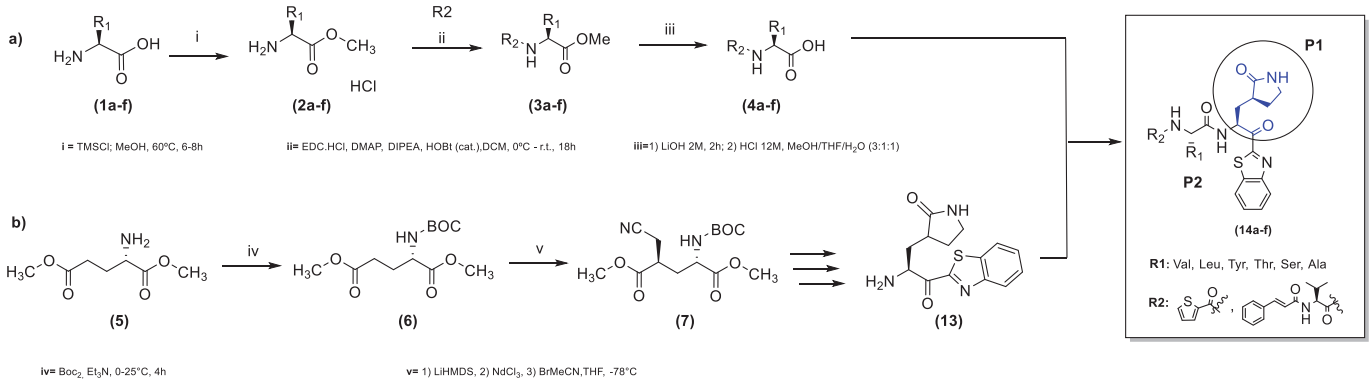
Palavras Chave: *SARS-CoV-2, artificial intelligence, Mpro inhibitors, peptidomimetic.*

Highlights

The A.I. model developed by our group suggested new peptidomimetic molecules against the SARS-CoV-2 Mpro, which are currently being studied by molecular docking and synthesized.

Resumo/Abstract

The SARS-CoV-2 coronavirus, responsible for the global pandemic of the COVID-19 disease, led to several negative impacts across the world.[1] Inhibitors of the viral main protease **(Mpro)**, responsible for the viral replication in cells, have become a key subject of research through computational approaches derived from artificial intelligence **(A.I.)** methods, which are an important tool to design and propose new potentially active molecules. Our aim is to synthesize, through peptide coupling methods, the compounds designed by our group's A.I. model, which is based on known SARS-CoV inhibitors.[2] To obtain the glutamine analog at position P1 **(in blue)**, compound **6** was obtained in **route b**, starting from the protection of the diester **(5)** with Boc_2O, achieving a yield of 45%. Subsequently, an α-cyanomethylation reaction of compound **6** was attempted; however, no product formation occurred. It was observed that the inclusion of Lewis acids, such as NdCl3, favored this reaction, resulting in a yield of 28%.[3] This step, derived from a convergent route, will be coupled with compounds **4a-f (route a)** to obtain the final molecule **14a-f**. The synthesized molecules will be characterized by NMR and infrared spectroscopy. Thus, our objective is to synthesize new peptidomimetic inhibitors developed by AI, optimizing reactions for better yields, and evaluating their interactions with Mpro through molecular docking **(Scheme 1).**



Scheme 1: (a) Peptide-coupling step. (b) α-cyanomethylation reaction of glutamic acid methyl diester.

1.Dai, W. et al. Design, Synthesis, and Biological Evaluation of Peptidomimetic Aldehydes as Broad-Spectrum Inhibitors against Enterovirus and SARS-CoV-2. *Journal of Medicinal Chemistry*, v. 65, n. 4, p. 2794–2808, **2022**.

2.Santana, M. V. S.; Silva-Jr, F. P. De novo design and bioactivity prediction of SARS-CoV-2 main protease inhibitors using recurrent neural network-based transfer learning. *BMC Chemistry*, v. 15, n. 1, p. 1–20, **2021**.

3. QIN, H. et al. Optimized Synthesis of a Key Intermediate of Nirmatrelvir. *Organic Process Research and Development*, v. 27, n. 1, p. 78–83, **2023**.

Agradecimentos/Acknowledgments

The authors acknowledge and thank PIBIC, CNPq, CAPES, Fiocruz and UFRJ for the financial and structure support.

Área: ORG

Molecular docking to predict the interaction of piperine with the enzyme acetylcholinesterase for Alzheimer's disease treatment.

Gabriela Z. Beretta (IC),[1*] Ian R. G. Godoi (M),[2] Aniele B. Dias (M),[2] Thiago H. Doring (D),[3] Adriano D. Andricopulo (PQ),[3] Leonardo L. G. Ferreiro (PQ),[3] Tatiana S. Ribeiro (PQ).[4]

gabriela.beretta@estudante.ufscar.br

[1]UFSCar-campus Araras, DCNME-CCA/Curso de Licenciatura em Química; [2]UFSCar-campus Sorocaba/Mestrado em Ciência dos Materiais ;[3]USP-campus São Carlos/Instituto de Física de São Carlos; [4]UFSCar-campus Araras DCNME-CCA.

Keywords: *Black Pepper, Piperina, Alzheimer's disease, Molecular Docking, Acetylcholinesterase.*

Highlights

Use of piperine to control Alzheimer's Disease (AD - neurodegenerative disease) through Molecular Docking that verifies interaction with the enzyme acetylcholinesterase (responsible for the advancement of AD).

Abstract

Alzheimer's disease (AD) is a neurodegenerative illness characterized by progressive loss of cognitive functions, it is the most common dementia nowadays, causing degeneration and death of brain cells. There is no treatment or medication capable of reversing, only pharmacological strategies that can inhibit its progression. Several studies have shown that piperine (alkaloid extracted from black pepper) has anti-inflammatory and antioxidant potential, those being essential mechanisms to control AD[1]. Therefore, this work study the interaction between piperine and acetylcholinesterase.

Piperine has the possibility of binding to the enzyme acetylcholinesterase, suggesting an inhibitory action that may act to slow down the progression of AD. For this to occur, the ligand must be coupled to the active site of the enzyme and inhibit it. This process happens via several intermolecular interactions. Acetylcholinesterase has the role of hydrolyzing acetylcholine (neutotransmitter present in the synaptic clefts). Thus, the lower the levels of acetylcholinesterase in the body, the slower the progression of AD. Molecular coupling studies were conducted with diferente scoring funtions, using as a reference the ligand cocrystallized with acetylcholinesterase (PDB 4M0E), with Root Mean Square Deviation (RMSD) less than 1 Å for all scoring functions. The RMSD is a measure of the average distance between atoms of overlapping structures, which was calculated between the resulting ligand and receptor positions. The scoring functions GoldScore, ChemScore, Astex Statistical Potential (ASP) and ChemPLP were used, providing a quantitative parameter regarding the ligand-receptor interaction[2]. Molecular coupling data are presented in Table 1 and Figure 1.

Table 1. Position, score and RMSD functions for docking into the acetylcholinesterase (PDB 4M0E) structure.

Functions	Position	Score	RMSD
GoldScore	4	58,197	0,365
ChemScore	1	38,483	0,218
ASP	4	51,963	0,242
ChemPLP	10	78,047	0,170

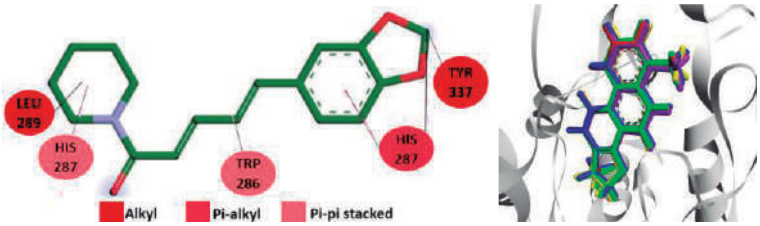


Figure 1. Coupling of piperine with the acetylcholinesterase and the connections responsable for the interaction.

The maximum value of the ChemPLP scoring function for piperine was 75.19 (position 1), procimal to the cocrystallized ligand (maximum values), which suggests the potential of piperine to interact with the enzyme and inhibit its activity, indicating its usefulness in further studies for AD therapy (piperic acid and aminoguanidine derivative)[2].

References: [1] MAHDY, K.; SHAKER, O.; WAFAY, H.; NASSAR, Y.; HASSAN, H.; HUSSEIN, A. Effect of some medicinal plant extracts on the oxidative stress status in Alzheimer's disease induced in rats. **European Review for Medical and Pharmacological Sciences**, v. 16, n. 3, p. 31-42, 2012.

[2] GUEDES, I. A.; de MAGALHÃES, C. S.; DARDENNE, L. E. Receptor–ligand molecular docking. **Biophysical Reviews and Letters**, v. 6, p. 75-87, 2014.

Acknowledgments

CCA LAB.COMAM FAPESP CNPq CAPES

Scholarship 14950-0

Área: ORG

Novel Mannich bases from enaminonaphthoquinones and preformed eletrophiles

Vinícius S. Cunha (PG)[1]*, Artur M. S. Silva (PQ)[2], Sandro J. Greco (PQ)[1].

cunha.vini@hotmail.com

[1]Departamento de Química, Universidade Federal do Espírito Santo (UFES), Vitória, Espírito Santo, CEP.: 29075-910; [2] REQUIMTE & Department of Chemistry, Universidade de Aveiro (UA), Aveiro, 3810-193, Portugal.

Keywords: *2-amine-1,4-naphthoquinone, Mannich's bases, Eschenmoser's salt, pyrrolidinemethyleneammonium chloride.*

Highlights

In this study, seven novel Mannich bases were developed using enaminonaphthoquinones and pre-formed electrophiles. The compounds exhibit inhibitory capacity against cancer cell lines.

Resumo/Abstract

The Mannich reaction is an amino alkylation that consists of the condensation of a substrate containing at least one active hydrogen, a non-enolizable carbonyl compound, and a primary, secondary, or ammonia in hydrochloride form. (BLICKE,1942) Modern versions use pre-formed electrophilic reagents to replace the amines and the carbonyl compound, ensuring a higher concentration of iminium ion in the reaction medium and minimizing reactional disadvantages. (AREND, WESTERMAN and RISCH, 1998) While various substrates with active hydrogen have been used in Mannich reactions (ROMAN, 2015), the application of enaminonaphthoquinones for this purpose is practically unexplored. This work aims to prepare novel Mannich bases **2-8** (Fig. 1) with antitumor activity (Table 1) by aminomethylation of enaminonaphthoquinones **1a-d** with pre-formed electrophiles, such as Eschenmoser salt **9** and pyrrolidinemethyleneammonium chloride **10**.

Figure 1. Preparation of Mannich's bases **2-8.**

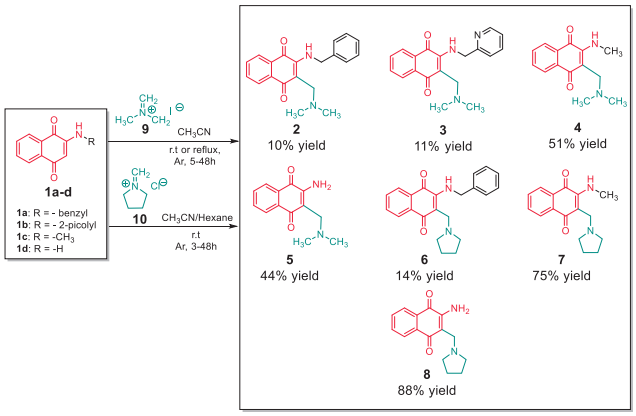


Table 1. Percentage of growth inhibition (IC%) of the compounds against tumor cell lines at single

Cell Lines Samples	PC-3		SNB-19		HCT-116	
	% Inhibition	Standard Deviation	% Inhibition	Standard Deviation	% Inhibition	Standard Deviation
2	72,999	2,457	**80,820**	1,809	**87,914**	2,269
3	**94,172**	0,518	**91,222**	0,303	**93,498**	0,087
4	**83,440**	1,441	**88,734**	0,058	**92,448**	0,115
5	**84,790**	1,088	**87,254**	0,324	**93,498**	0,087
6	**86,860**	0,780	**84,078**	0,735	**88,322**	0,457
7	76,844	0,634	64,121	0,793	6,144	3,455
8	**91,631**	0,324	31,12	0,101	**94,299**	0,075

Legend: Highlight in bold for inhibition values above 75%.

All Mannich bases exhibited cytotoxicity against cancer cell lines (SNB-19 = human glioblastoma, HCT-116 = human colon carcinoma, PC-3 = human prostate carcinoma, HL-60 = human leukemia). They were more cytotoxic than the enaminonaphthoquinones used as starting materials. (LEMOS, *et al.*, 2021)

Agradecimentos/Acknowledgments

CNPq CAPES FAPES LabPetro UFES

Área: ORG

Novos Aciclonucleosídeos Quinolonocarboxamídicos como Potenciais Agentes Anti-SARS-CoV-2

Rodrigo L. M. Gomes (PG)[1], Ana B. C. Araújo (IC)*[1], Maria C. B. V. de Souza (PQ)[1],Fernanda da C. S. Boechat (PQ)[1]

[1]*Universidade Federal Fluminense, Instituto de Química, Departamento de Química Orgânica – Outeiro de São João Batista s/nº, Niterói / RJ, 24020-141 *e-mail: calana@id.uff.br, fernandacostasantos@id.uff.br*

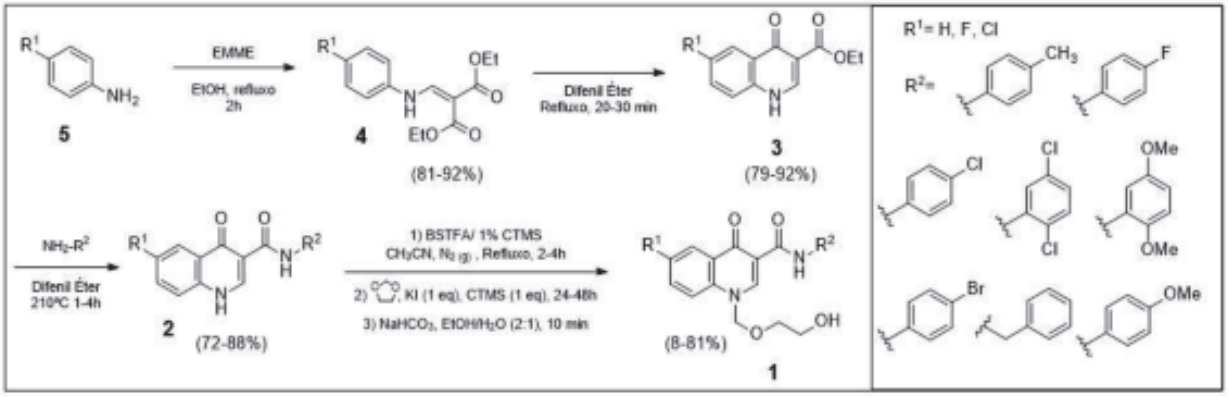
Palavras Chave: *COVID-19, Antiviral, 4-Quinolona, Carboxamida, Aciclonucleosídeos*

Highlights

Synthesis of new Acyclic 4-quinolone-3-carboxamide derivatives with potential anti-SARS-CoV-2 activity. Synthesis of acyclonucleosides derived from 4-quinolone-3-carboxamide precursors by Vorbruggen methodology.

Resumo/Abstract

A COVID-19, doença proveniente da infecção pelo vírus SARS-CoV-2, foi uma dasmais preocupantes pandemias (2020-2023), com atualmente 760 milhões de casos confirmados, dos quais 6,9 milhões culminaram em óbito. O vírus é altamente transmissível e mesmo que já existam antivirais aprovados para uso emergencial em pacientes internados, as medidas profiláticas como o distanciamento social, medidas de higienização e a vacinação em massa continuam sendo as principais formas de combate à doença. Mesmo assim, face à mutabilidade desse tipo viral, é imprescindível que se continuem as pesquisas na busca de novos agentes anti-SARS-CoV-2. Neste contexto, substâncias derivadas de nucleosídeos mostram-se interessantes candidatos, pela possível inibição de enzimas envolvidas em diferentes etapas do processo de replicação viral, o que inclui os fármacos Remdesivir e Molnupiravir, atualmente empregados no tratamento de casos mais graves da doença. Aciclonucleosídeos como o Aciclovir atuam de forma similar aos derivados de nucleosídeos no organismo. Neste contexto, este trabalho tem como objetivo realizar a síntese e avaliação biológica de derivados aciclonucleosídeos contendo o núcleo quinolonocarboxamídico em sua estrutura. Os aciclonucleosídeos (1) foram obtidos a partir de suas respectivas 4-quinolono-3-carboxamidas (2), através da metodologia de Vorbruggen adapatada, conforme descrito no Esquema 1. Até o momento, os derivados foram obtidos com rendimentos que variaram entre 8 a 81%. Uma vez obtidos e devidamente caracterizados, estas substâncias serão encaminhadas para avaliação de atividade antiviral frente o vírus SARS-CoV-2.



Esquema 1: Síntese dos aciclonucleosídeos propostos..

Agradecimentos/Acknowledgments

CNPq, FAPERJ, CAPES (Finance Code 0001)

[1] Organização Mundial da Saúde . Disponível em <https://covid19.who.int/>. Acesso em 13/09/2023.
[2] Brandariz-Nuñez, D.; Correas-Sanahuja, M.; Maya-Gallegos, S.; Herranz, I. M. Journal of Clinical Pharmacy and Therapeutics, 2021, 46, 918.

Área: _ ORG____

One-Pot Synthesis of Novel Isatin-Thiazole Hybrids with Potential Anti-inflammatory Profile

Isadora Maria Gouveia Andrade (PG),* Mariana de Oliveira Leal Desmarais (IC), Mayane Barbosa dos Santos (PG), Carolina Guimarães de Souza Lima (PQ), Luana da Silva Magalhães Forezi (PQ), Fernando de Carvalho da Silva (PQ).

imgandrade@id.uff.br;

Laboratório de Síntese Orgânica Aplicada, Universidade Federal Fluminense, Instituto de Química Niterói-RJ, 24210-141, Brazil.

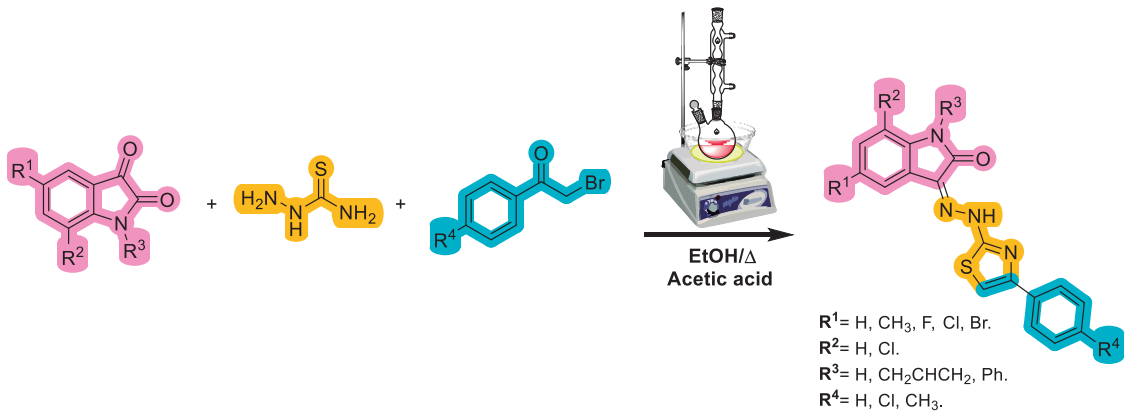
Keywords: *Heterocycle, Inflammation, Drug Development.*

Highlights

Molecular hybridization is a modern strategy for safer and more effective drugs. Isatin and thiazole as versatile building blocks for the next generation of drugs with anti-inflammatory profiles.

Resumo/Abstract

The manipulation of specific aspects in the molecular structure of chemical compounds has been a subject of research in the field of medicinal chemistry, resulting in a significant number of studies.[1] Molecular hybridization is a modern design approach based on the recognition and combination of pharmacological subunits from two or more bioactive derivatives, aiming to promote a more selective, resilient, less toxic, and devoid of undesired side effects activity profile.[1,2] In this context, isatin and its derivatives interact with benzodiazepine receptors such as the ligand-gated ion channel monoamine oxidase B (MAO-B) in the brain and reduce the formation of cyclic guanosine receptor γ-aminobutyric acid (GABA), which can mediate sedative, hypnotic, analgesic, and other important effects on the central nervous system (CNS).[3] Thus, this study focuses on the synthesis of new isatin-thiazole hybrids through a one-pot reaction, aiming to explore their potential as promising bioactive compounds. The synthesis methodology was based on the work of Veeranna et al.[3], involving the mixing of isatin and its derivatives in a 1:1 ratio with thiosemicarbazide, derivatives of 2-bromoacetophenone, and acetic acid (2/3 drops) in ethanol under reflux for 3-6 hours, yielding 46 to 90% (Scheme 1). The product was isolated and recrystallized in ethanol. The isatin-thiazole conjugates showed good yields in relatively short reaction times, consolidating as an effective methodological approach. Currently, the anti-inflammatory profile is still being investigated.



Scheme 1. Schematic route for the synthesis of novel isatin-thiazole hybrids.

Agradecimentos/Acknowledgments

CAPES, CNPq and FAPERJ.

[1] Marchesi, E.; Perrone, D.; Navacchia, M. L. *Pharmaceutics. Multidisciplinary Digital Publishing Institute*, **2023,** 15, 2185.
[2] Viegas-Junior, C.; Barreiro, E.; Fraga, C. *Bentham Science*, **2020**, 18, 348-407.
[3] Montes, G.C.; da Silva, B. N. M.; Rezende, B.; Sudo, R. T.; Ferreira, V. F.; da Silva, F. C.; Pinto, A. C.; da Silva, B. V.; Zapata-Sudo, G. *Molecules*, **2017**, 22, 800.

Área: ORG

Parametrization of phosphine ligands in Palladium photocatalyzed Heck reaction.

Mateus Oliveira Costa (PG),[1] Davi Madureira de Medeiros (IC),[2] Marco Antonio Barbosa Ferreira (PQ).[1*]

Mateuscosta0595@gmail.com; marco.ferreira@ufscar.br*

[1]*Departamento de Química, UFSCar;*

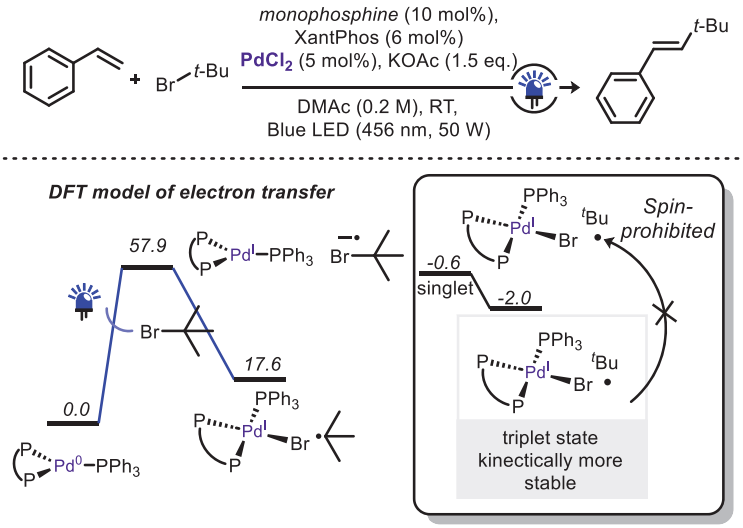
Palavras Chave: *Palladium, Phosphine, Photocatalysis, Heck.*

Highlights

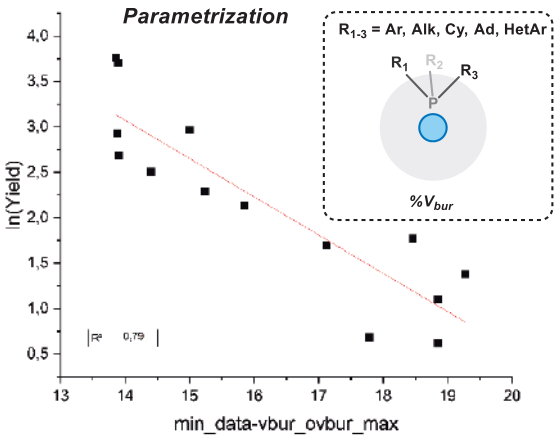
Pd-photoredox coupling reaction. Relationship between the structure of the complex's ligands and the system's reactivity. Correlation between phosphorous steric environment and yield.

Resumo/Abstract

Photochemical reactions involving palladium are in the initial stage of development its synthetic potential has been progressively explored in the face of new chemical transformations, such as coupling reactions the focus of this work. Although some theoretical and experimental studies have been reported about the mechanism of these transformations, there are, to date, no studies about the relationship between the structure of the complex's ligands and the system's reactivity in organic transformations. In particular, the way in which the dual ligand system acts, using mono- and bidentate phosphines[1]. In this work we are studying the relationship between the ligand structure and chemical reactivity in Pd-photoredox reactions with the aim of identifying essential structural characteristics that describe the catalytic activity of these systems in the face of chemical transformations. To this end, we evaluated structurally diverse photo-responsive ligands to visible light based on phosphines described in the literature[2].



The correlation experimental data obtained in our laboratory show little relevance of electronic factors in obtaining the product, the importance of a sterically unhindered environment in the monophosphine ligand seems to play a big role in the reaction yield, which could be associated with the stabilization of hybrid alkyl Pd^{I}-radical triplet state. DFT calculations are under investigation to confirm the key step indicated by parametrization results.



References: [1]Wang, G.-Z. Shang, R. Cheng, W.-M. Fu, Y. *J. Am. Chem. Soc.* **2017**, *139*, 18307. [2]Gensch, T. *et. al. ACS Catalysis*. **2022**, *12*, 7773.

Agradecimentos/Acknowledgments

(2022/11314-5) (140710/2022-1)

Área: ORG

Phenolic compounds profiled in *Eugenia arenosa and Eugenia anomala* hydroethanolic leaf extracts.

Catarina dos Santos (PQ),[1*] Thalison Amorim de Souza (PQ)[2] catarina.santos@unesp.br;

[1]Department of Biological Sciences, Faculty of Sciences and Letters, University of São Paulo State (UNESP), [2]Multi-user characterization and analysis Laboratory - Federal University of Paraiba

Keywords: Myrtaceae, phenolic compounds

Highlights

Eugenia arenosa and *Eugenia anomala* hydroethanolic were profiled by high-resolution HPLC-ESI-MS and HPLC-DAD-ESI-Ion-Trap(-). This analysis showed both extracts are rich in phenolic acids, catechins, flavonoids, and flavonols, which could be potentially useful in our research group's future biological studies.

Abstract

The Myrtaceae are used in folk medicine for diabetes, hypertension, and ulcers. These activities are frequently attributed to their phenolics[1]. Therefore, these bioactive molecules must be identified in crude extracts before isolation to rationalize which procedure could be applied to these substances. Continuing studies of Myrtaceae conducted by our research group, we aimed to profile the phenolics in extracts using mass spectrometry data from the *Eugenia arenosa* (HEar) and *Eugenia anomala* (HEan) hydroethanolic leaves extracts**.** Extracts were provided from the dried leaves collection at Estação Ecológica de Santa Bárbara (Águas de Santa Bárbara, SP) after maceration (1:10 plant/solvent ratio, 3x2h, r.t), filtration, and evaporation in rotaevaporator[1]. An HPLC Shimadzu (Kyoto, Japan) coupled with a MicroTOF II (Bruker Daltonics, Billerica, MA, USA) with an electrospray ion (ESI) source was used to acquire high-resolution mass spectra in negative mode. The used parameters were previously reported[2,3]. The MS/MS spectra extracts were analyzed by liquid chromatography coupled to a mass spectrometer HPLC-DAD-ESI-Ion-Trap(-) (Figure 1-2).

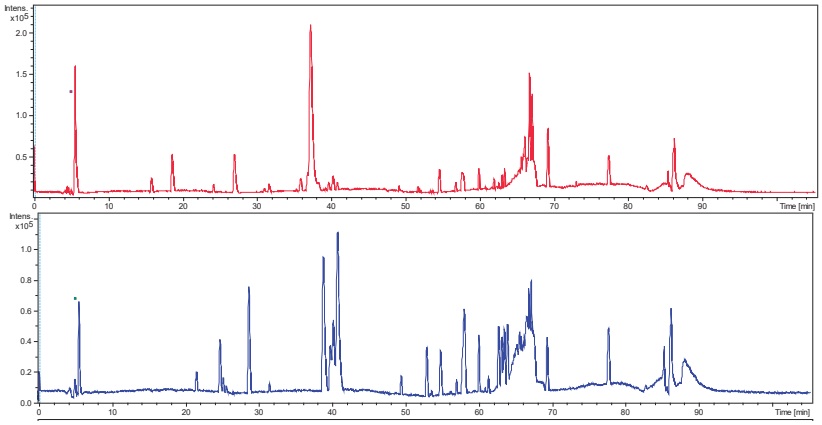


Figure 1- *Eugenia anomala* and *Eugenia arenosa* chromatogram.

HEan and HEar presented a similar profile compared to other Myrtaceae already described by our group[1]. They are also rich in phenolic acids, catechins, flavonoids and flavonols. However, HEan and HEar differences in chemical profile could be originate some new and/or improved biological activities. For this reason, more studies are underway in our lab.

Formula $[M-H]^-$	Theoretical mass $[M-H]$ *m/z*	Experimental mass $[M-H]^-$ *m/z*	Δm (ppm)	MS/MS fragments *m/z*	Compound identification	Extracts
$C_7H_5O_5$	169.0137	169.0136	-0.58		Gallic acid	HEan
$C_7H_{11}O_6$	191.0561	191.0559	1.3	127, 163	Quinic acid	HEan, HEar
$C_9H_9O_5$	197.0455	197.0454	1.9		Syringic acid	HEan
$C_{15}H_{13}O_6$	289.0715	289.0710	1.0		Catechin	HEan, HEar
$C_{15}H_{13}O_7$	305.0661	305.0655	-2.1		Epigallocatechin	HEan
$C_{20}H_{17}O_{11}$	433.0776	433.0774	0.50	300, 271, 151,	Quercetin–3-O-β–D-pentoside	HEan, HEar
$C_{21}H_{19}O_{11}$	447.0933	447.0940	-2.50		Quercetin-3-O-β–rhamnoside	HEan
$C_{22}H_{17}O_{11}$	449.0725	449.0713	2.8		Myricetin-3-arabinofuranoside	HEan
$C_{18}H_{23}O_{14}$	463.0891	463.0882	-1.92	316	myricitrin	HEan, HEar
$C_{42}H_{39}O_{24}$	927.1837	927.1821	1.7	463 316	Myricitrin dimer	HEan, HEar

Figure 2- Main phenolics profiled from *Eugenia arenosa* and *Eugenia anomala*

[1] Santos et al. *Molecules* **2018**, *23*, 986; [2] Dantas, CAG, et al. *Phytochemical Analysis*. 2021; 32(6): 1011– 1026. Silva, J. P., et al. (2022). Journal of Natural Products, 85(9), 2184-219

Acknowledgments

47ª Reunião Anual da Sociedade Brasileira de Química: *"A centralidade da Química na educação do cidadão e na inovação científica e tecnológica"*

Sociedade Brasileira de Química (SBQ)

Profa. Rosana Marta Kolb for plant collection.

Área: ORG

Preparation of isatin, indirubin and tryptanthrin hydrazones, oximes and functionalization with carbohydrate

Ana Flávia dos Santos Fuzaro* **(PG),[1] Danilo de Souza Costa (PG),[1] Mauro Vieira de Almeida (PQ)[1] and Richard Michael Grazul (PQ)[1]**

ana.fuzaro@estudante.ufjf.br; ana.fuzaro@estudante.ufjf.br

[1] *Departamento de Química, Instituto de Ciências Exatas, Universidade Federal de Juiz de Fora, 36036-900, Juiz de Fora – MG, Brasil.*

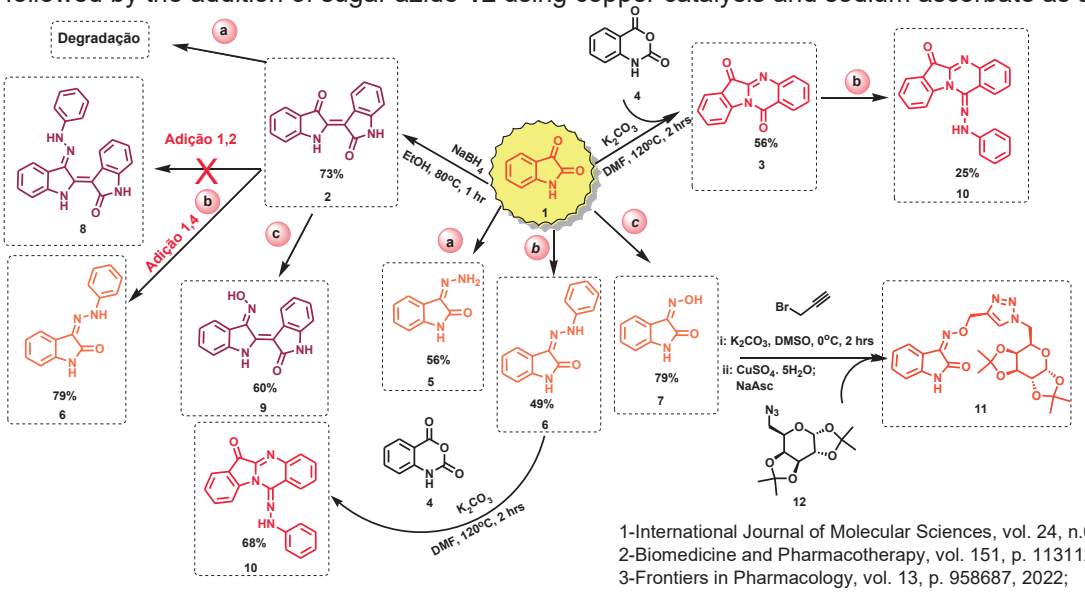
Palavras Chave: *Isatin; Indirubin; Tryptanthrin; hydrazones; oximes; sugar.*

Highlights

Isatin, indirubin and tryptanthrin show anticancer activity *in vitro* and *in vivo*. Functionalization with oximes and carbohydrates may improve activity and pharmacological parameters.[1,2]

Abstract

The natural compounds indirubin **2** and tryptanthrin **3** can be synthesized from isatin **1**. Indirubin **2** (73% yield) is produced through a reductive coupling reaction with $NaBH_4$, while tryptanthrin **3** (57% yield) is synthesized via condensation in a basic medium with isatoic anhydride **4**.[1,2] Functionalizing these indole alkaloids may yield potential pharmaceutical prototypes, and chemical modifications could enhance both physical and chemical properties. Attempts to functionalize these alkaloids with hydrazine hydrate **(Scheme 1a)**, phenyl hydrazine **(Scheme 1b)**, and hydroxylamine hydrochloride **(Scheme 1c)** were successful, resulting in isatin hydrazone **5** (56% yield), isatin phenyl hydrazone **6** (49% yield), and isatin oxime **7** (79% yield). However, subjecting indirubin **1** to the same conditions **(a** and **b)** did not yield the desired products. The reaction with hydrazine hydrate produced decomposition products, and the reaction with phenyl hydrazine led to the formation of isatin phenyl hydrazone **6**.
The indirubin oxime **9**, and tryptanthrin phenyl hydrazone **10** have been previously reported.[1,3] However, the yield of **10** increased to 68% in the condensation between phenyl hydrazone isatin **6** and isatoic anhydride **4.** One application of the synthesized compound **7** is in the *click* reaction, where hydrophilic substrates such as carbohydrate moiety can be employed. Specifically, isatin oxime **7** reacted with propargyl bromide at 0 °C, in basic medium, followed by the addition of sugar azide **12** using copper catalysis and sodium ascorbate as a reducing agent.



1-International Journal of Molecular Sciences, vol. 24, n.02, p. 1450, 2023;
2-Biomedicine and Pharmacotherapy, vol. 151, p. 113112, 2022;
3-Frontiers in Pharmacology, vol. 13, p. 958687, 2022;

Scheme 1: Functionalization of isatin, indirubin and tryptanthrin: a) H_2NNH_2 H_2O, EtOH, 80°C, 24hrs; b) $PhNHNH_2$, EtOH, 80°C; c) $HONH_2.HCl$, pyridine, 60°C, 2hrs.

Acknowledgments

FAPEMIG, CAPES and CNPq for financial support.

Área: ORG

Preparation of triarylimidazoles using niobium catalysts

Ana Carolina de O. Pereira (IC),[1] Pamella Monte (IC),[1] José C. Barros (PQ),[1*] Tiago Lima Silva (PQ)[2]

ana.oliveira@gradu.iq.ufrj.br; jbarros@iq.ufrj.br

Instituto de Química – Universidade Federal do Rio de Janeiro (IQ-UFRJ); Universidade Federal do Rio de Janeiro, Campus Macaé.
Keywords: *Niobium, Catalysis, Triarylimidazoles.*

Highlights

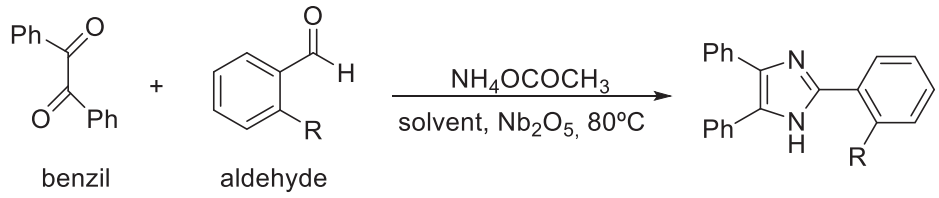
In this projetc, the synthesis of triarylimidazoles, like lophine, is presented utilizing niobium catalysts on diferents solvents such as dioxane, propylene glycol and solvent free conditions. The reactions were conducted with both benzaldehyde and salicylaldehyde.The catalyst proved to be effective for synthesis.

Resumo/Abstract

Niobium (Nb) is an element with atomic number 41, belonging to the class of transition metals in group 5 of the periodic table. It is usually employed in the technology field and used in car batteries. In Organic Chemistry it is used as catalysts – like niobium oxide (Nb_2O_5) among others - in the formation of heterocycles such as imidazoles. These structures show diverse pharmacological activities, for example anti-inflammatory[1,2].

This work aims to evaluate the use of niobium oxide as a catalyst for the synthesis of triarylimidazoles, such as lophine (2,4,5-triphenylimidazole), by the reaction between aldehydes (salicylaldehyde or benzaldehyde) and benzil in presence of ammonium acetate as ammonia source. The reactions were carried out in the presence of different solvents, like dioxane, propylene glycol or under solvent-free conditions. The products were characterized by gas chromatography coupled to mass spectrometry (GC/MS), by Nuclear Magnetic Resonance (NMR) and Infrared (IR) spectroscopy.

After optimisation of the reaction conditions (*e.g.* solvent, amount of catalyst) and followed by purification by column chromatography lophine was obtained with an yield of 36%, while others heterocycles are still under investigation.



R = H, OH.
Solvent = Dioxane or Propylene glycol.

Figure 1: General scheme of synthesis of triarylimidazoles.

Agradecimentos/Acknowledgments

To CNPq, FAPERJ, CAPES for their financial support.

1: ALMEIDA, G. C *et al*. Nióbio: salvação ou promessa brasileira do século 21. **Ciência Hoje**, 2019. V. 356.
2: BRUZIQUESI, Carlos GO *et al*. Nióbio: um elemento químico estratégico para o Brasil. **Química nova**, v. 42, p. 1184-1188, 2020.

Área: QPN

Prospecção Fitoquímica e Atividade Biológica da Espécie Pleroma hirsutissimum: Uma Contribuição à Flora Endêmica da Região dos Lagos- RJ

Yasmim Souza de Oliveira (IC)[1], Ray de Siqueira Pereira (IC)[1], Renan Rangel Moraes (PQ)[2], Vinicius Fernandes Moreira (PQ)[1*]. yasmim.souza@gsuite.iff.edu.br; vinicius.moreira@iff.edu.br.

[1] Instituto Federal Fluminense campus Cabo Frio; [2] Universidade do Estado do Rio de Janeiro.

Palavras Chave:*Atividade biológica, Flavonoides, Fitoquímica, Pleroma.*

Highlights

Phytochemical Screening and Biological Activity of the Pleroma hirsutissimum Species: A Contribution to the Endemic Flora of the Lakes Region - RJ

Exploring the endangered Pleroma hirsutissimum in Rio's restingas to save its unique biochemistry and ecology;P. hirsutissimum: A critical study on its survival amid Rio's real estate boom.

Resumo/Abstract

As Restingas Fluminenses, especialmente próximas a Cabo Frio, destacam-se pela sua riqueza taxonômica de vegetais superiores, sendo considerada um dos principais Centros de Diversidade Vegetal do Brasil. Contudo, vem enfrentando ameaças devido à urbanização e especulação imobiliária, o que impacta negativamente sua biodiversidade. Diante disso, ressalta-se a importância de estudos para a conservação de espécies ameaçadas, como a *Pleroma hirsutissimum*, endêmica dessa região e classificada como Criticamente em Perigo. Este trabalho propõe-se a primeira prospecção fitoquímica de extratos das folhas dessa planta, visando ampliar o conhecimento sobre a espécie e contribuir para sua conservação, que não era coletada por pesquisadores há quase 40 anos. Após identificação da espécie com a colaboração do JBRJ, os extratos brutos obtidos por percolação de solventes de diferentes polaridades, concentrados com evaporador rotativo e submetidos a teste de reações características esperadas para identificação dos principais metabólitos secundários. Os testes foram realizados nos laboratórios do IFF Cabo Frio, e a prospecção fitoquímica com extrato metanólico, apresentaram resultados positivos para Saponinas, Taninos, Cumarinas, Flavonóides e Fitoesteróis. Na realização de uma análise em Cromatografia Líquida de Alta Eficiência acoplado à espectrometria de massas (CLAE-MS) com a colaboração da UERJ, foram obtido cerca de 80 sinais de compostos orgânicos, que através de comparação com dados da literatura e biblioteca do software, foi possível identificar a presença de diversos sinais correspondentes a Flavonoides. Sabe-se que os flavonóides possuem propriedades anti-inflamatórias e antioxidantes, e os resultados obtidos até o momento mostraram-se promissores quanto a continuação da pesquisa, com a realização de novas análises cromatográficas e mais testes, como testes histoquímicos, isolamento e identificação desses flavonoides, avaliação de toxicidade frente *Artemia salina*, testes antioxidante e outros testes de atividades biológicas, para maiores informações a respeito dos constituintes químicos da *P. hirsutissimum.*

Agradecimentos/Acknowledgments

Agradecemos ao Conselho Nacional de Desenvolvimento Científico - CNPQ, Instituto Federal de Educação, Ciência e Tecnologia Fluminense - IFF *Campus* Cabo Frio,Universidade do Estado do Rio de Janeiro - UERJ, e Instituto de Pesquisa Jardim Botânico do Rio de Janeiro - JBRJ.

Área: ORG

PZQ resistance studies using efflux pumps: synthesis of new probe molecules

Camilla Thomaz da Silva Oliveira* **(PG)[1,2], Floriano P. S. Junior (PQ),[2] Sabrina B. Ferreira (PQ).[1]***

camillathomaz@iq.ufrj.br; sabrinab@iq.ufrj.br

[1]Universidade Federal do Rio de Janeiro, Instituto de Química, Laboratório de Síntese Orgânica e Prospecção Biológica. Rio de Janeiro, Brasil; [2] Instituto Oswaldo Cruz, Laboratório de Bioquímica Experimental e Computacional de Fármacos, FIOCRUZ, Rio de Janeiro, Brasil.

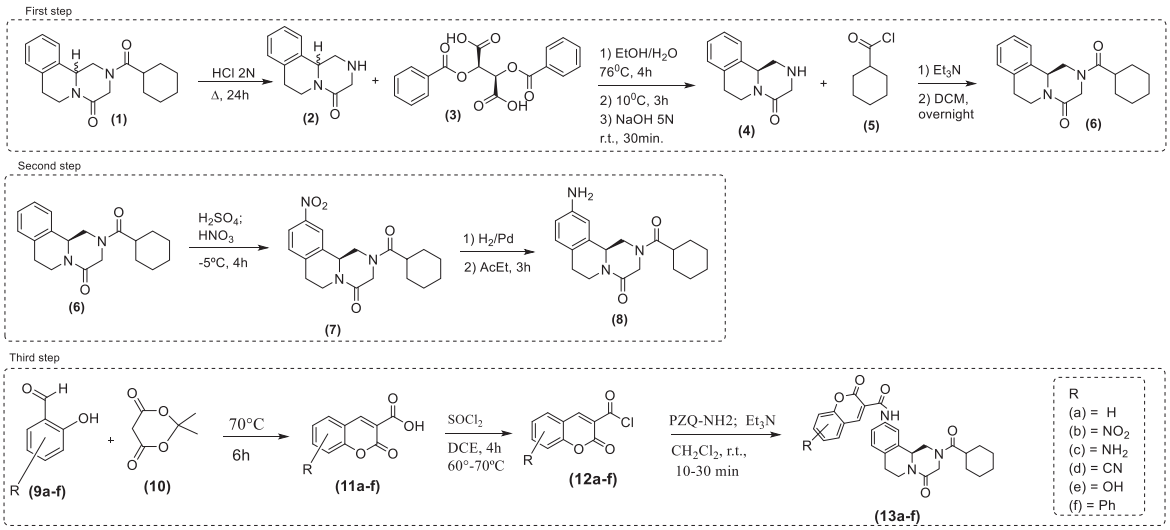
Keywords: synthesis, probe molecules, praziquantel, fluorescent

Highlights

Praziquantel fluorescent derivatives. Synthesis of probe molecules. Derivatives of coumarin. Efflux pumps as a resistance system.

Abstract

Schistosomiasis is one of the most important neglected tropical diseases. Nowadays praziquantel is the major drug used for treatment against all forms of schistosomiasis. To better understand the mechanism of action of praziquantel, some fluorescent derivatives have been synthesized and used as probes to understand the mode of interaction of the drug with the Schistosoma[1] and to determine the molecular target of this drug[2]. Currently, there are reports in the literature relating the appearance of resistance to treatment of schistosomiasis due to PZQ acting as a efflux substrate to Pgp-like or MRPs. Coumarins can be used to achieve the desired goal, as they have excellent fluorescent properties.[3] The objective of this work is to synthesize new molecules derived from (R)-praziquantel with substituted coumarins by varying the R groups of coumarin to increase the fluorescence of the synthesized compound. The first step begins with the hydrolysis of the praziquantel **(1)** racemic mixture followed by the use of the configuration driver (-)dibenzoyl-L-tartaric acid **(3)** to finally restore the structure of praziquantel in the configuration (R) **(6)**. The second step begins with the nitration of the compound **(6)**, followed by the reduction of the nitro group **(7)** to form (R)-PZQ-NH_2 **(8)**. The third stage begins with the synthesis of coumarin-3-carboxylic acid **(11a-f)** with the use of Meldrun acid and substituted salicylaldehydes **(9a-f)**, then acid chloride **(12a-f)** is formed with the use of thionyl chloride ($SOCl_2$) and finally the synthesis of fluorescent derivatives **(13a-f)** with coupling of (R)-PZQ-NH_2 **(8)** with coumarins **(12a-f)**.



1 - Y. Xie, Y. Li, Y. Wu, C. Liu, X. Li, X. Fan. Synthesis of fluorescent derivatives of praziquantel: cell-imaging and interaction with Schistosoma japonicum cercariae. Org. Biomol. Chem., **2013**, 11, 5989–5993.

2 –D. J. Sprague, M. Kaethner, S. Kyu, C. M. Rhor, J. L. Harris, D. Maillard, T. Spangenberg, B. Lundstrom-Stadelmann, J. S. Marchant. The Anthelmintic Activity of Praziquantel Analogs Correlates with Structure-Activity Relationship at $TRPM_{PZQ}$ Orthologs. ACS Medicinal Chemistry Letters, **2023**, 14, 1537-1543.

3 - X. Fu, X. Wang, J. Chen, D. Wu, T. Li, X. Can, J. Qin. Synthesis, fluorescence properties, and antiproliferative potencial of several 3-oxo-3H-benzo[f]chromene-2-carboxylic acid derivates. Molecules, **2015**, 20, 18565-18584.

Acknowledgments

The authors would like to thank CAPES, CNPq, LaBRMN and FIOCRUZ.

Área: ORG

Recent advances in the synthesis and functionalization of 4-aminopyrrolo[2,1-f][1,2,4]triazine

Geovana Fontes Vargas (IC),[1] Vinícius Rodrigues Durães Pereira (PG),[1] Giuliano Cesar Clososki (PQ),[2] Giovanni Wilson Amarante (PQ).[1]*

geovanavargas47@gmail.com; giovanni.amarante@ufjf.br

[1]Departamento de Química, UFJF, [2]FCFRP, USP-SC

Keywords: *Remdesivir, Pyrrolotriazine, Functionalization, C-glycosylation.*

Highlights

An alternative route for the synthesis of 4-aminopyrrolo[2,1-f][1,2,4]triazine was proposed, in addition to two new functionalization methodologies not yet described in the literature.

Resumo/Abstract

In 2019, the pandemic of the respiratory syndrome known as COVID 19 emerged, causing several losses in the global socioeconomic sphere.[1] Remdesivir was the first drug approved in Brazil to contain it. Due to its structural complexity and currently synthesis routes, high production costs are associated, making imperative the search for faster and more economical methodologies.[2] One of its most relevant fragments is the *N*-heterocycle 4-aminopyrrolo[2,1-f][1,2,4]triazine, which couples to ribose through *C*-glycosylation. The functionalization of pyrrolotriazine represents a crucial step for the success of this reaction.[3] Therefore, in the present work, the synthetic route of pyrrolotriazine was initially optimized, obtaining a final yield of 71% after 3 steps (Figure 1), since the highest yield reported in the literature was 59% in a 2-step route.[4] For the functionalization of this material, iodination methodologies using *N*-iodosuccinimide are described in the literature. However, in 2022, List and co-workers reported the existence of an intrinsic nucleophilicity of pyrrolotriazine.[5] In order to verify this statement, direct functionalization of pyrrolotriazine was carried out using only molecular iodine and DMF, obtaining an isolated yield of 71 % (Figure 2a). Furthermore, when protecting the amino group with BOC, an isolated yield greater than 99% was obtained (Figure 2b). Thus, not only was the direct reactivity of pyrrolotriazine proven against a strong electrophile, such as iodine, but a new methodology was also developed for its direct functionalization, something new in the literature.

Figure 1: Pyrrolotriazine synthesis route

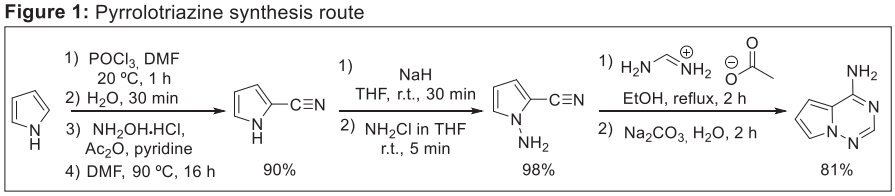
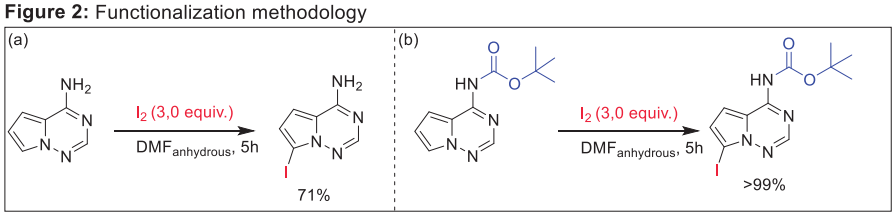


Figure 2: Functionalization methodology



(1) OPAS. Histórico da pandemia de COVID-19. Organização Pan-Americana da Saúde. Disponível em: <https://www.paho.org/pt/covid19/historico-da-pandemia-covid-19>. Access in 25 de janeiro de **2023**.
(2) DOS SANTOS, J. A. et al. Klein's Remdesivir-nucleobase synthesis revisited: Chemoselective cyanation of pyrrol-2-carboxaldehyde. *J. Braz. Chem. Soc.* **2021**, 32 (7), 1391-1395.
(3) BRAGA, T. et al. Avanços recentes na síntese do remdesivir, molnupiravir (EIDD-2801) e tenofovir: moléculas promissoras no tratamento da COVID19. *Quím. Nova.* **2022**, 45 (1), 53-73.
(4) PAYMODE, D. J. Expanding Access to Remdesivir via an Improved Pyrrolotriazine Synthesis: Supply Centered Synthesis. *Org. Lett.* **2020**, 22 (19), 7656–7661.
(5) OBRADORS, C. et al. Direct and Catalytic *C*-Glycosylation of Arenes: Expeditious Synthesis of the Remdesivir Nucleoside. *Angew. Chem. Int. Ed.* **2022**, 61 (11), e202114619.

Agradecimentos/Acknowledgments

The authors are grateful for the generous financial support from CAPES (Finance Code 001), CNPq, UFJF, FAPEMIG, and Rede Mineira de Química.

Área: ORG

Regiodivergent Addition of Anilines and Phenolates to *p*-Benzoquinones Ring

Maria Tereza M. Martins (PG)[1], Talita O. C. Leite, Searitha C. Rodrigues (PG) [1], Beatriz L. C. de Carvalho, Raphael S. M. de Moraes (PG) [1], Gabriel T. de A. Pinto (PG) [1], Ana Beatriz M. Botelho (IC) [1], Camille C. Cruz (IC)[1], Anna Claudia Cunha (PQ) [1]*

mariaterezamartins@id.uff.br; annacunha@id.uff.br

[1]Universidade Federal Fluminense, Instituto de Química, Departamento de Química Orgânica, Programa de Pós-Graduação em Química, 24020-141, Niterói, Rio de Janeiro, Brazil

Keywords: Benzoquinone, regiodivergent addition, anilines, phenoxides.

Highlights

The regiodivergent addition of anilines and phenolates to *p*-benzoquinones can lead to different products depending on the reaction conditions and the substituents on the reactants.

Abstract

Quinone compounds are widely found in various families of plants, fungi, and certain animals. Numerous of them play crucial roles in many biochemical processes. For example, coenzyme Q10, also known as ubiquinone, is an essential component in cellular respiration and ATP production in many organisms, including humans[1]. Moreover, quinone ring constitutes a common structural unit not only in well-known antitumoral drugs[2] but also in compounds with diverse pharmacological activities, including antimicrobial, antiparasitic, and fungicidal properties[3,4]. Quinones can exert their therapeutic effect by acting as prooxidants, reducing oxygen to reactive oxygen species (ROS) and as electrophiles, forming covalent bonds with tissue nucleophiles[5]. Due to versatile biological activity and chemical reactivity of quinones, our research group has explored different methodologies that lead to the development of synthetically modified compounds[5]. Within this context, we report the synthesis of aminobenzoquinones **4** and aryloxy-benzoquinone derivatives **5** via regio-divergent conjugate nucleophilic addition of amines **2** and phenoxides **3** to the 2-bromo-1,4-benzoquinone ring of compound **1**,[6] which is a potential synthetic building block in the design of biological molecules.

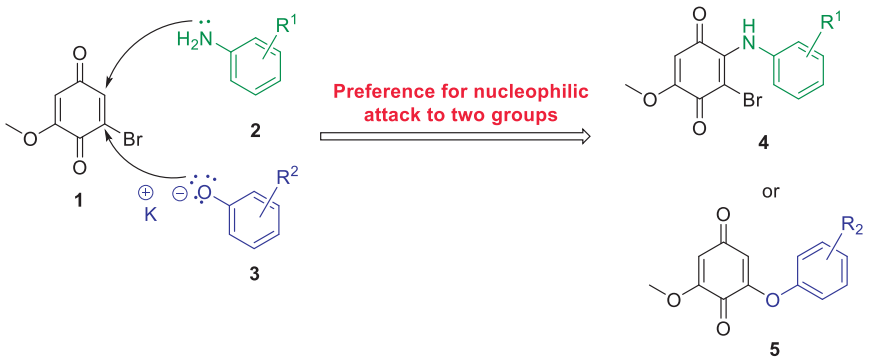


Figure: Regiodivergence of the nucleophilic attack.

Acknowledgments

CAPES, UFF, PPGQ-UFF, FAPERJ, PIBITI/CNPq.

References:

(**1**) Zhang, Y.; Liu, J.; Chen, X.; Chen, C.-Y. O. *Food Funct.*, **2018**, 9 (11), 5653–5659.
(**2**) Ferreira, V. F.; de Carvalho, A. S.; Ferreira, P. G.; Lima, C. G. S.; de C. da Silva, F. *Med Chem.*, **2021**, 17 (10), 1073–1085.
(**3**) da Silva, R. E.; de Oliveira Silva Ribeiro, F.; de Carvalho, A. M. A.; Daboit, T. C.; Marinho-Filho, J. D. B.; Matos, T. S.; Pessoa, O. D. L.; de Souza de Almeida Leite, J. R.; de Araújo, A. R.; dos Santos Soares, M. J. *Microb Pathog.*, **2020**, 149, 104513.
(**4**) Abraham, I.; Joshi, R.; Pardasani, P.; Pardasani, R. T. J. Braz. *Chem. Soc.*, **2011**, 22 (3), 385–421.
(**5**) Dias, F.; Guerra, F.; Lima, F.; de Castro, Y.; Ferreira, V.; Campos, V.; Fernandes, P.; Cunha, A. J. Braz. *Chem. Soc.,* **2021**,32 (3) 476-489.
(**6**) Da Silva, H. C.; Leite, T. O. C.; Rodrigues, S. C.; De Carvalho, B. L. C.; Martins, M. T.; Fiorot, R. G.; Dias, F. R. F.; Campos, V. R.; Ferreira, V. F.; Cunha, A.C.; De Almeida, W. B. ACS *Omega.*, **2022**, 7, 44, 40241–40256.

Area: ORG

Rotaxanes containing macrocycle derived from crown ether: study of intercomponent interactions

Paloma Neves de Oliveira (PG),[1] Gustavo Weimer (PG),[2] Marcos A. P. Martins (PQ),[2] Tainára Orlando (PQ).[1]*

palomatga2@gmail.com; tainaraorland@gmail.com

[1]Academic Department of Chemistry, Federal Technological University of Paraná (UTFPR), Medianeira Campus, PR, Brazil; [2]NUQUIMHE, Department of Chemistry, Federal University of Santa Maria (UFSM), Santa Maria, RS, Brazil.

Keywords: Rotaxanes, crown ether, intercomponent interactions, contact area, stabilization energy.

Highlights

Rotaxanes with a macrocycle derived from crown ether present more energetic intercomponent interactions when the thread has an associated charge compared to a neutral thread.

Abstract

Rotaxanes are molecules formed by a linear molecule with stopper groups at the ends, called thread, and by a macrocyclic molecule that is incorporated in the center of the thread.[1] These components are connected by a mechanical bond and the main movements they carry out are rotation and translation.[1] Compounds of this type can be categorized as molecular machines when, under external stimulus, it is possible to manage the movements of molecular components.[2] Intercomponent interactions between the constituent parts, such as the thread and the macrocycle, play a crucial role in these movements, influencing their nature and execution.[3] Therefore, understanding these interactions is fundamental for the design of new rotaxanes, whether to facilitate their synthesis or to control and predict their movements, aiming for their use as molecular machines.[3] Rotaxanes are based in different macrocycles, among them are: metal-ligand based macrocycle, amide based macrocycle, $CBPQT^{4+}$, pillar[5]arene, calix[6]arene, cucurbit[6]uril, α- cyclodextrin and crown ethers.[4] This work concentrated into rotaxanes with crown ether-derived macrocycles, which have the potential to be employed in the development of mechanical nanodevices,[5] including exploration to create a multi-state molecular abacus,[5] as well as advanced methods of controlled drug delivery.[6] Based on this, this work focuses on the study of intercomponent interactions of rotaxanes containing macrocycle derived from crown ether. To this, a search was carried out in the Cambridge Structural Database (CSD), in the ConQuest search interface using the term 'rotaxan', selecting single-crystalline and non-disordered structures, and only organic molecules. Resulting in a set of 299 structures, of which 12 structures containing the macrocycle derived from the crown ether were manually selected. To evaluate intercomponent interactions, contact area and intercomponent stabilization energies data were collected. The contact area was determined from the Voronoi-Dirichlet Polyhedron using the ToposPro program, and the stabilization energies of the molecules were calculated using data obtained from the MOPAC software (PM6-D3H4 method). With these data, it was possible to verify that the contact area remains constant even with the variation in intercomponent energy of the molecule. It can be seen that rotaxanes containing charged threads have a greater intercomponent stabilization energy (about -86 kcal mol^{-1}) compared to rotaxanes containing neutral thread (about -31 kcal mol^{-1}), having a difference of -55 kcal mol^{-1} which results in 180% stabilization energy gained. Furthermore, it was also possible to notice that when there is a charge greater than 1, it becomes even more energetic, but does not reach the value of twice. It is crucial to investigate intercomponent stabilization energy when analyzing rotaxane molecules. In this way, the present study contributes significantly to the understanding of intercomponent interactions in rotaxane models that incorporate a crown ether-derived macrocycle. The results indicated notable differences in stabilization energies between rotaxanes containing charged and neutral threads. Therefore, understanding these interactions is crucial for the synthetic development of new rotaxane models.

1 *J Mol Liq*, 2023, **385**, 122291. 2 *Chem Soc Rev*, 2017, 46, 2592–2621. 3 *Quim Nova*, 2021, **44**, 76–85. 4 *Chem Rev*, 2015, 115, 7398–7501. 5 *J Am Chem Soc*, 2021, **143**, 8046–8055. 6 *Supramol Chem*, 2019, 31, 221–238.

Acknowledgments

The author acknowledges CNPq, CAPES, and UTFPR.

Área: ORG

Síntese de 4-aminometileno-7-metoxicumarinas e investigação do potencial antioxidante

Leonardo de Oliveira Aguiar (PQ)[1], João Felipe Silva Oliveira (IC)[1], Oscar Caetano Silva Neto (PQ)[2], Silvio Cunha (PQ)[3], Jorge Mauricio David (PQ)[2]

leonardo.aguiar@uesb.edu.br; jmdavid@ufba.br

[1]AGUIARLAB, Departamento de Ciência e Tecnologia, UESB, Jequié – BA; [2]GPPN, Departamento de Química Orgânica, Instituto de Química da UFBA, Salvador – BA. [3]GPSQ, Departamento de Química Orgânica, Instituto de Química da UFBA, Salvador – BA.

Palavras-Chave: *cumarina, N-alquilação, antioxidante, síntese orgânica.*

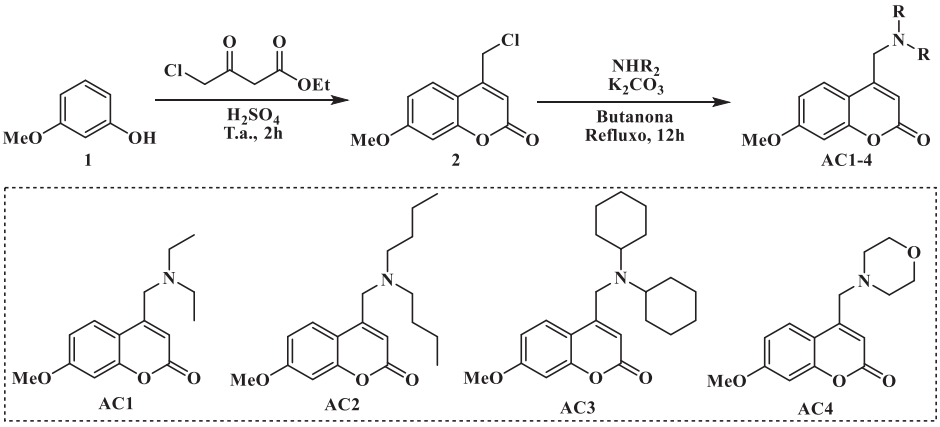
Highlights

Synthesis of four new 4-aminomethyl-7-methoxycoumarins and evaluation of their antioxidant potential. This work describes the synthesis of new *N*-coumarin derivatives through *N*-alkylation reaction and shows the results of antioxidant activities based on assay employing DPPH.

Resumo

Derivados cumarínicos são amplamente utilizados como preparações farmacológicas devido à sua diversidade de aplicações. Obter cumarinas por síntese orgânica segue sendo uma estratégia eficiente devido à rapidez e eficiência dos métodos sintéticos. O núcleo cumarínico é também passível de modificação estrutural via diferentes metodologias de reação, permitindo o acesso a novos compostos derivados.

Neste trabalho, 3-metoxifenol (**1**) foi o substrato para obtenção da 4-clorometileno-7-metoxicumarina (**2,** 82%), por meio de ciclização de Pechmann catalisada por ácido sulfúrico. Em seguida, quatro aminas secundárias foram utilizadas como reagentes nucleofílicos, para promover *N*-alquilação no carbono halogenado da cumarina, empregando-se butanona como solvente de reação. Os produtos, 4-aminometileno-7-metoxicumarinas (**AC1-4**), foram obtidos com rendimentos que variaram entre 55 e 83%. Após caracterização por técnicas espectrométricas, os produtos-alvo foram submetidos ao ensaio de avaliação do potencial antioxidante, frente ao radical DPPH, de modo que, em comparação com o padrão ácido gálico, o composto AC1 apresentou uma ligeira atividade, todavia não excedeu os 25% em concentração 250 $\mu g.mL^{-1}$.



Agradecimentos/Acknowledgments

UESB, UFBA, CNPq

Área: ORG

Síntese de derivados 6-azido-4-quinolono-3-carboxamídicos com potencial atividade antitumoral

Jordana de Paula Alves (IC),[1*] Letícia M. dos Santos (IC),[1*] Thiago M. Do Vale (PG),[1] Rodrigo L. M. Gomes,[1] Aislan Cristina Rheder Fagundes Pascoal (PQ),[2] Vinícius Dávila Bitencourt Pascoal (PQ),[2] Pedro Netto Batalha (PQ), [1] Maria Cecília B. V. de Souza (PQ),[1] Fernanda S. Boechat (PQ).[1]

gomesrodrigo@id.uff.br; fernandacostasantos@id.uff.br;

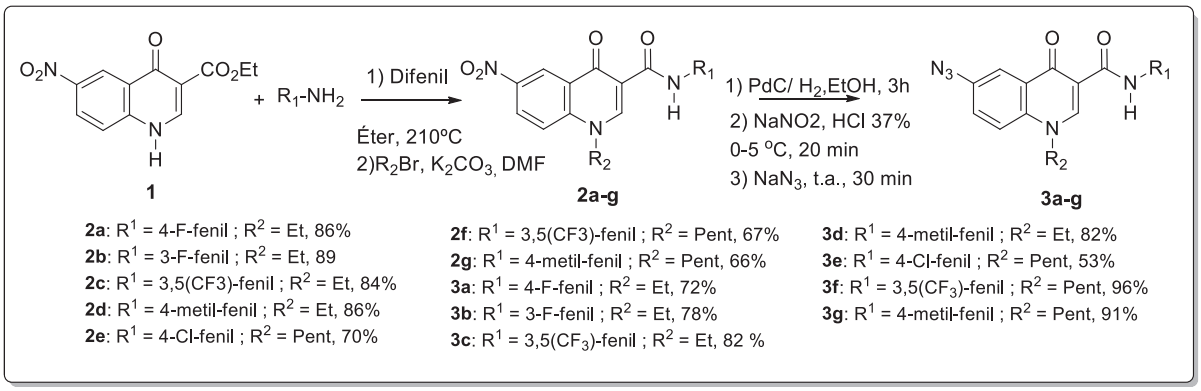
[1]*Laboratório de Nucleosídeos, Heterociclos e Carboidratos, Departamento de Química Orgânica, UFF;*
[2]*Grupo de Pesquisa de produtos naturais e moléculas bioativas- Laboratório Multiusuário de Pesquisa Biomédica- ISNF-UFF*
Palavras Chave: *quinolonas. 4-oxoquinolinas, atividade antitumoral*

Highlights

Design, synthesis and antitumoral evaluation of 4-quinolone derivatives in the search of new anticancer agents. Synthetic methodology validation for obtaining 6-azido-4-quinolone derivatives using diazotization reaction.

Resumo/Abstract

O câncer é o principal problema de saúde pública no mundo, se incluindo entre as quatro principais causas de morte na maioria dos países. O tratamento eficaz do câncer, com menores efeitos colaterais e melhora da qualidade de vida do paciente oncológico ainda é um grande desafio e a busca de agentes antitumorais com melhor potência terapêutica e menores efeitos colaterais motiva pesquisas no mundo inteiro. Quinolonas se constituem em uma classe de agentes quimioterápicos com grande biodinamicidade. Essas substâncias são capazes de inibir a Topoisomerase do tipo IV, enzima alvo do mecanismo de ação antibacteriana. De forma análoga, 4-quinolonas também podem inibir o crescimento das células cancerígenas via inibição da Topoisomerase II humana. Neste contexto, o presente trabalho tem como objetivo obter uma série de compostos 6-azido-4-quinolo-3-carboxamídicos **3a-i** (Esquema 1), bem como avaliar a sua atividade antiproliferativa na busca de novos agentes antitumorais



A 6-nitro-4-oxoquinolina **1**, sintetizada previamente a partir da metodologia clássica de Gould Jacobs, foi submetida a uma reação de substituição nucleofílica à carbonila, utilizando-se diferentes anilinas como nucleófilos. Esta reação foi seguida de uma reação de *N*-alquilação a partir de brometo de etila ou de pentila como agentes alquilantes. Esta medodologia possibilitou a obtenção dos derivados **2a-e**, que foram submetidos à reação de hidrogenação catalisada por paládio, seguido de uma diazotação e posterior reação com azida de sódio, obtendo-se os derivados **3a-g**, com rendimentos que variaram entre 53 e 96%. Estes compostos sintéticos foram devidamente caracterizados e encaminhados para avaliação de sua atividade antitumoral, onde ensaios preliminares indicam que a substância **3d** foi capaz de inibir células tumorais cervicais em concentrações menores que 10 μM.

Agradecimentos/Acknowledgments

O presente trabalho foi realizado com apoio da Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) - Código de Financiamento 001; CNPq; FAPERJ; PPGQ-UFF; PROAP-UFF.

Área: ORG

Síntese de intermediários sintéticos para obtenção de derivados diamínicos de 6-(triazolil)-4-quinolonas com perfil anti-*Leishmania*

Felipe G. Z. Segura (IC),[1] Amanda R. P. Costa (PG),[1] Fernanda da C. S. Boechat (PQ),[1] Maria Cecília B. V. de Souza (PQ),[1] Pedro N. Batalha (PQ).[1]

felipezapata@id.uff.br;

[1]*Departamento de Química Orgânica, Universidade Federal Fluminense*

Palavras-Chave: *Quinolona, Triazol, Leishmania, Heterociclos.*

Highlights

Synthesis of 6-(triazolyl)quinolone diaminic derivatives with anti-*Leishmania* profile. Synthesis and evaluation of 6-(triazolyl)quinolone diaminic derivatives as new potential agents with anti-*Leishmania* profile.

Resumo/Abstract

As leishmanioses são um conjunto de doenças causadas por protozoários do gênero *Leishmania* e da família Trypanosomatidae. Clinicamente a doença pode ser expressa de três formas: leishmaniose visceral, cutânea e mucocutânea. Essa doença afeta principalmente países em desenvolvimento, que não são alvos de interesses econômicos das grandes indústrias farmacêuticas. Os tratamentos existentes para tais doenças são associados à problemas como alto custo, alta toxicidade, baixa biodisponibilidade oral e resistência medicamentosa. Levando isso em conta, justifica-se o interesse no desenvolvimento de novas substâncias bioativas eficazes, seguras e seletivas. Neste projeto foi planejada a síntese dos derivados diamínicos de 6-(triazolil)quinolonas, tendo em vista que os núcleos triazólicos[1] e diamínicos[2] têm potencial anti-*Leishmania* previamente descritos. Já o núcleo 4-quinolônico é de interesse do nosso grupo de pesquisa e está presente em substâncias com reportada atividade anti-*Leishmania.*

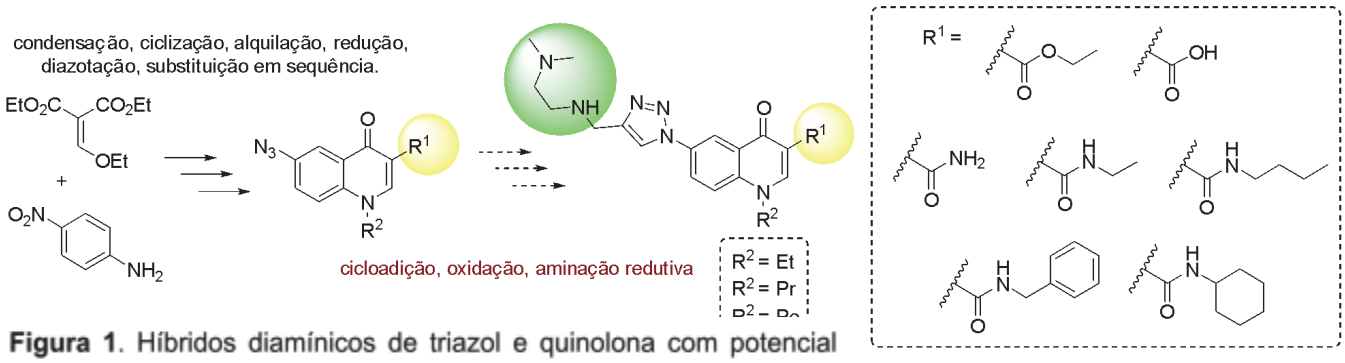


Figura 1. Híbridos diamínicos de triazol e quinolona com potencial anti-*Leishmania*.

A rota sintética planejada para síntese destas substâncias, envolve nove etapas, de forma linear. Até o momento 11 intermediários sintéticos, dos quais seis são inéditos, foram obtidos e devidamente caracterizados via métodos espectroscópicos de análises. Como perspectiva, as substâncias planejadas poderão ser sintetizadas após mais três etapas reacionais. Uma vez obtidos, estes também terão suas estruturas elucidadas via métodos espectroscópicos de análises e, posteriormente, serão submetidos à ensaios de atividade biológica anti-*Leishmania*, em colaboração com os grupos de pesquisa das Profas. Drª. Marcela Cristina de Moraes (GQO-UFF) e Drª. Luzineide Wanderley Tinoco (IPPN-UFRJ).

Agradecimentos/Acknowledgments

CNPq, FAPERJ, PPGQ-UFF, PROAP-UFF, CNPq-PIBIC, CAPES (Finance Code 001).

[1] Bonandi, E. et al. *Drug Discovery Today*, **2017**, 22, 10, 1572-1581.
[2] Martín-Montes, Á. et al. *ACS Infectious Diseases*, **2021**, 7(12), 3168–3181.

Área: ORG

Síntese de novas tionaftoquinonas contendo o núcleo 1*H*-1,2,3-triazol com potencial atividade tripanocida

Thaís B. Santos (PG),[1] Diana P. de Abreu (IC),[1] Vítor F. Ferreira (PQ),[2] David R. da Rocha (PQ),[1]

thaisbarreto@id.uff.br

[1]Departamento de Química, Universidade Federal Fluminense; [2]Faculdade de Farmácia, Universidade Federal Fluminense

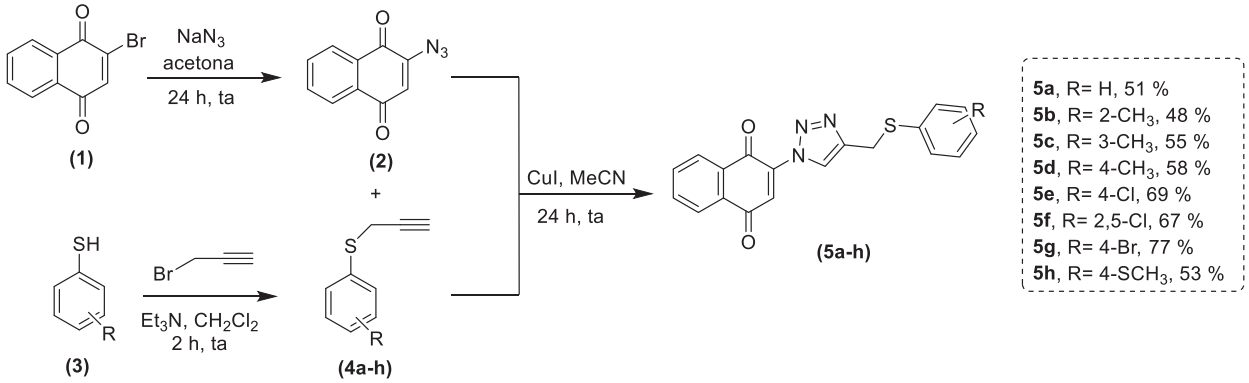
Palavras Chave: *Doença de Chagas, naftoquinonas, tioéteres, núcleo triazólico, cicloadição 1,3-dipolar*

Highlights

Synthesis of new thionaphthoquinones-linked 1*H*-1,2,3-triazoles with potential tripanocidal activity.

Resumo/Abstract

As naftoquinonas são uma classe de substâncias encontradas na natureza e amplamente relatadas na literatura, principalmente por causa de seus perfis biológicos variados.[1] Do ponto de vista sintético, estas ganham destaque pelo uso como plataforma sintética, uma vez que podem sofrer modificações em seu arranjo e assim, levar a formação de novos derivados com potencial atividade biológica. Nesse cenário, pode-se ressaltar a associação entre o núcleo naftoquinônico e 1,2,3-triazólico como estratégia para obtenção de novas substâncias que demonstraram atividade tripanocida.[2] Em relação a Doença de Chagas, há uma lacuna no que tange o tratamento desta que é a principal doença tropical negligenciada, especialmente pela falta de medicamentos eficazes, sendo necessário novos estudos nessa área.[3] Assim, o objetivo deste trabalho é a síntese de tionaftoquinonas triazólicas inéditas, com posterior avaliação da atividade tripanocida. Para isso, a metodologia empregada envolve a síntese convergente apresentada no Esquema 1. Inicialmente a 2-azidonaftoquinona **(2)** é obtida a partir do tratamento da 2-bromonaftoquinona **(1)** com azida de sódio.[4] Simultaneamente, os tioéteres **(4)** são preparados através de uma reação de substituição dos tiofenolatos pelo brometo de propargila.[5] Por fim, uma reação de cicloadição 1,3-dipolar catalisada por cobre entre a 2-azidonaftoquinona **(2)** e os respectivos tioéteres **(4)** permitiu a síntese das tionaftoquinonas contendo o núcleo triazólico **(5a-h)** com rendimentos variando de 48% a 77%.[6] Assim, neste trabalho foram sintetizadas dezessete moléculas, das quais oito são as tionaftoquinonas triazólicas inéditas que serão enviadas posteriormente para avaliação da atividade tripanocida.



Esquema 1. Síntese das tionaftoquinonas triazólicas **(5a-h)**

[1]Santos, T. B. *et al*. *Pharmaceuticals* **2023**, *16*, 1577.
[2]da Silva Júnior, E. N. *et al. Eur. J. Org. Chem.* **2012**, *52*, 304-312.
[3]De-Fuentes-Vicente, J. A. *et al*. *Trop. Med. Infect. Dis.* **2023**, *8*, 360.
[4]Sarkar, S. K. *et al*. *J. Am. Chem. Soc.* **2015**, *137*, 4207-4214.
[5]Martzel, T. *et al*. *Eur. J. Org. Chem.* **2018**, *36*, 5069-5073.
[6]Cardoso, M. F. C. et al. *Eur. J. Med. Chem.* **2014**, *84*, 708.

Agradecimentos/Acknowledgments

PPGQ-UFF, CAPES, CNPq e FAPERJ

Área: ORG

Síntese de novos análogos de aciclonucleosídeos fosfonatos (ANPs) derivados de ácidos 4-quinolono-3-carboxílicos 7-substituídos como potenciais antivirais.

Luiza Cardoso de Castro Carrilho Soares (IC),[1] Guilherme C. Valles (IC),[1] Alan G. de Souza (PG),[1]* Letícia V. Faro (PQ),[1] Fernanda C. S. Boechat (PQ),[1] Maria Cecília B. V. de Souza (PQ).[1]

castroluiza@id.uff.br; mceciliabvs@gmail.com

[1]*Instituto de Química, Departamento de Química Orgânica, UFF.*

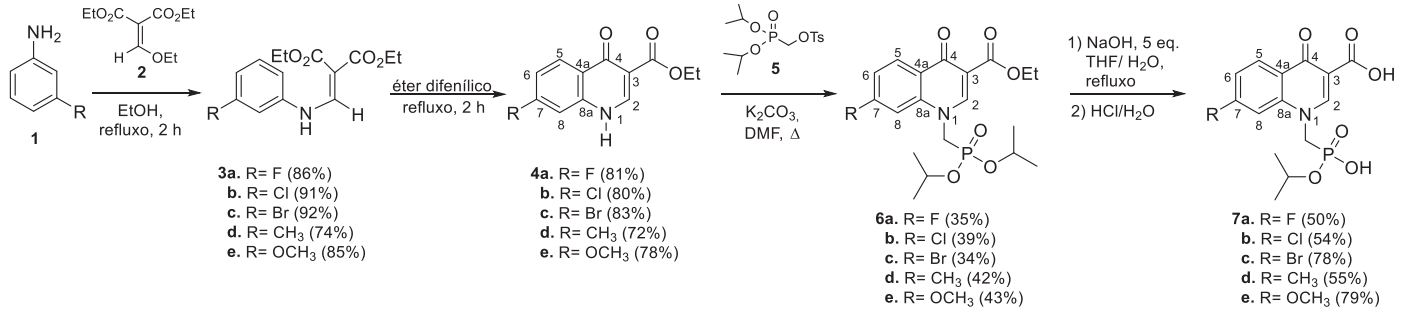
Palavras-Chave: *Aciclonucleosídeo, Quinolona, Fosfonato, Antiviral.*

Highlights

Synthesis of novel acyclonucleoside phosphonates (ANPs) analogues derived from 7-substituted 4-quinolone-3-carboxylic acids as potential antivirals.
Viral infections represent a major public health challenge, necessitating the continuous development of new antivirals to address drug resistance and adapt to constantly evolving viruses.

Resumo/Abstract

As infecções virais são um dos principais desafios de saúde pública, sendo necessário o contínuo desenvolvimento de novos antivirais para seu enfrentamento, para o combate à resistência a medicamentos e para adaptação a vírus em constante evolução. Os aciclonucleosídeos fosfonatos (ANPs) constituem uma classe de fármacos que se tornaram essenciais no tratamento de infecções virais. A primeira geração de fármacos ANPs, como tenofovir (TFV), adefovir (HPMPA) e cidofovir (HPMPC), mostrou ser altamente eficaz e assim a síntese de novos fosfonatos antivirais tem sido uma estratégia amplamente adotada, e a proteção do grupo fosfonato faz com que os derivados se constituam em pró-drogas. O sucesso alcançado com compostos como o fumarato de tenofovir disoproxil (TDF), o tenofovir alafenamida (TAF) e o adefovir dipivoxil (ADV), disponíveis comercialmente para o tratamento da AIDS e da hepatite B, destaca a eficácia dessa abordagem. Nesse sentido, foi sintetizada uma série de novos análogos de aciclonucleosídeos fosfonatos derivados de ácidos 4-quinolono-3-carboxílicos 7-substituídos **7**, através da sequência reacional que envolveu a reação entre as anilinas **1** e o etoximetilenomalonato de dietila (**2**), gerando os anilinoacrilatos de etila **3**, que por ciclização térmica produziram as 4-quinolonas **4**. Estas, submetidas à reação de *N*-alquilação com diisopropil-*p*-toluenosulfoniloximetanofosfonato (**5**), previamente sintetizado, levaram aos intermediários ANPs 4-quinolonônicos **6**, que foram convertidos aos ANPs **7** por hidrólise básica, seguida de neutralização do meio reacional. Os novos derivados sintetizados e descritos neste trabalho tiveram suas estruturas caracterizadas por análise espectral na região do infravermelho e por de RMN de ^{1}H, de ^{13}C-APT e de ^{31}P, e serão submetidos a avaliação de sua atividade antiviral frente aos vírus SARS-CoV-2, HIV-1 e arbovírus, sendo os estudos realizados por grupos de pesquisas da UFF e da FIOCRUZ-RJ.



Esquema 1. Esquema reacional para obtenção dos análogos de ANPs derivados de ácidos 4-quinolono-3-carboxílicos 7-substituídos.

Agradecimentos/Acknowledgments

O presente trabalho foi realizado com apoio da Fundação de Amparo à Pesquisa do Estado do Rio de Janeiro (FAPERJ), do Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) e da Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) - Código de Financiamento 001.

Área: ORG

Síntese e caracterização de ligantes orgânicos para obtenção de complexos metálicos com propriedades magnéticas

Alan G. de Souza (TC),[1] Thomaz de A. Costa (PG),[1] Maria das Graças F. Vaz (PQ),[1] Pedro N. Batalha (PQ).[1]*

alangoncalves@id.uff.br; pedrobatalha@id.uff.br

[1]*Instituto de Química, Universidade Federal Fluminense (UFF), Niterói, RJ, Brasil.*

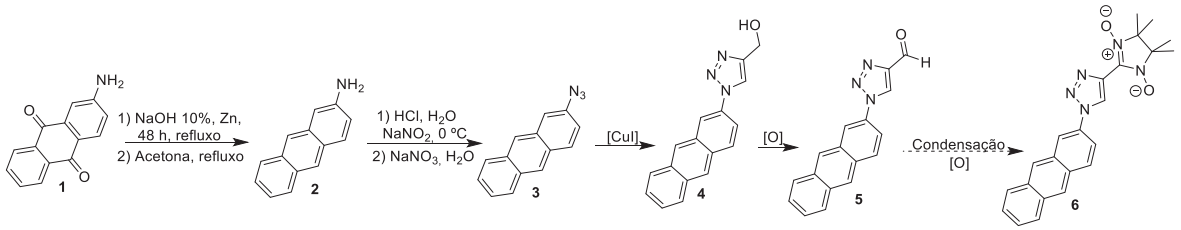
Palavras-Chave: Ligantes Orgânicos, Complexos Metálicos, Radicais, Sistemas Magnéticos.

Highlights

Technical support for the synthesis and application of organic ligands and their metal complexes. The synthesis of structurally designed ligands for the construction of technological metallic complexes and in the application in the Inorganic Synthesis of magnetic molecular systems, will be discussed.

Resumo/Abstract

Os radicais nitronil nitróxido (NN) são importantes blocos construtores para a obtenção de sistemas magnéticos moleculares de interesse, tais como sistemas heterometálicos do tipo 2p-3d-4f,[1] e de cadeias magnéticas unidimensionais[2]. Os radicais NN são estáveis devido à deslocalização eletrônica entre os átomos de O-N-C-N-O permitindo sua manipulação em temperatura ambiente e conferindo dois sítios de coordenação equivalentes nos átomos de oxigênio. Esse tipo de composto possui uma versatilidade atribuída por conta da facilidade da obtenção de radicais NN com substituintes diversificados[3] a partir de um aldeído segundo o método de Ullman.[4] Isso confere aos radicais NN a possibilidade de possuir múltiplos sítios de coordenação e possuir ligantes volumosos, por exemplo. A proposta de um novo aldeído precursor contendo os grupamentos triazol e antraceno para obtenção de um radical NN inédito será apresentada nesse trabalho. Desta forma, foram exploradas diferentes metodologias sintéticas, como a Reação de Diazotação[5,6] para a obtenção desse aldeído. A sequência sintética se iniciou com a hidrólise da 2-aminoantraquinona **1** para obtenção do 2-aminoantraceno **2** que foi submetido a reação de diazotação para gerar o respectivo 2-azidoantraceno **3**. Este, foi submetido a reação de cicloadição 1,3-dipolar catalisada por cobre para levar ao intermediário **4**, que através de oxidação branda gerou o aldeído **5** que será utilizado para obtenção do radical nitronil nitróxido **6**. O precursor **5** foi obtido, bem como os seus respectivos intermediários, e está em fase de caracterização estrutural por meio de análises de espectrofotometria de Infravermelho, Ressonância Magnética Nuclear de ^{1}H e massas de alta resolução. A síntese do radical **6** será realizada e este será utilizado como ligante para a obtenção de sistemas magnéticos moleculares.[7]



Esquema 1. Esquema reacional para obtenção do ligante Nitrosil.

Referências:

1. Vaz, M. G. F. & Andruh, M. *Coordination Chemistry Reviews*, 2021, 427, 213611.
2. Meng, X.X., Shi, W. and Cheng, P. *Coordination Chemistry Reviews*. 2019, 378, 134-150.
3. Luneau, D. European Journal of Inorganic Chemistry. 2020, 597–604.
4. Ullman, E.F., Call, L. and Osiecki, J.H. *The Journal of Organic Chemistry*. 1970, 35, 3623-3631.
5. Hajipour, A.R. and Abrishami, F. *Journal of Applied Polymer Scienc.* 2012, 124, 1757-1763.
6. Jaafar, Z.; Chniti, S.; Sassi, A.B. *et al*. *Journal of Molecular Structure*. 2019, 1195, 689-701.
7. Batalha, P. N.; Mocanu, T.; Calancea, S; Vaz, M. G. F. & Andruh, M. Journal of Molecular Structure, 2022, 1259, 132703.

Agradecimentos/Acknowledgments

O presente trabalho foi realizado com apoio da Fundação de Amparo à Pesquisa do Estado do Rio de Janeiro (FAPERJ), do Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) e da Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) - Código de Financiamento 001.

Área: ORG

Síntese e caracterização de Zn-MOFs com ligante quinolínico

Vinicius H. de Carvalho (IC),[1]* **Lais Cristina Augusto (PG)**[1] **and Luiz C. da Silva-Filho (PQ).**[1]

vinicius.hesiquel@unesp.br

[1]*Departamento de Química, Faculdade de Ciências, UNESP campus Bauru.*

Palavras Chave: *Metal-Organic Frameworks, Quinoline, Synthesis.*

Highlights

Synthesis and characterization of Zn-MOFs with quinolinic ligand. A one-pot reaction to obtain a quinoline derivative. New crystalline structure synthesis.

Resumo/Abstract

Metal-Organic Frameworks (MOFs) are porous molecules formed from the interaction of metal ions and organic ligands, constituting a coordination compound.[1] Among their characteristics, high crystallinity, porosity, a large surface area, and a wide range of applications[2] are highlighted. They can be utilized for storage,[3] catalysis,[4] gas adsorption,[5] among other purposes. This project aims to synthesize and characterize a new zinc-based metal-organic framework with a quinoline derivative as the ligand.

To obtain Zn-MOF, two reaction steps are necessary. The first step is a multicomponent reaction (MCR) using 4-carboxybenzaldehyde (**1**) and 4-carboxyaniline (**2**) and phenylacetylene (**3**) catalyzed by $NbCl_5$.[6] The second step involves the reaction of the quinoline derivative (**4**) with the chosen metal salt, in this case $Zn(NO_2)_3$, and methanoic acid as a modulator. (Scheme 01)

The structure of quinoline 4 was confirmed by NMR and the synthesized Zn-MOF has a crystalline structure, confirmed by the PXRD (Figure 01). The PXRD pattern obtained from the Zn-MOF differs from the zinc nitrate PXRD, consulted on the crystalline structure basis, CRYSTMET, proving that a new crystalline network was formed during the synthesis. New characterizations are underway to prove the structure.

Scheme 01. Synthesis of Zn-MOFs (**5**).

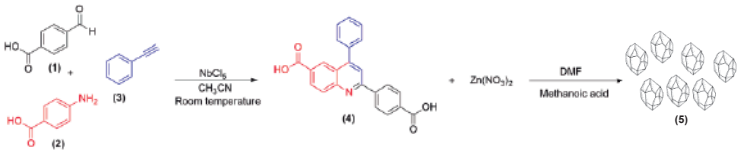
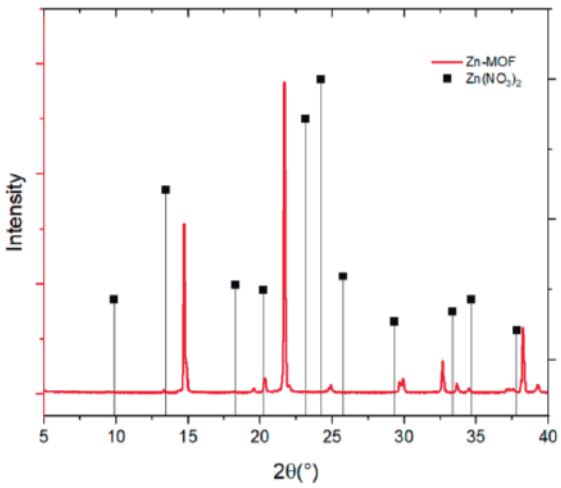


Figure 01. PXRD pattern for the synthetized MOF and zinc nitrate peaks.



[1]Batten, S. R.; *et al. CrystEngComm* **2012**, *14*, 3001.; [2]Frem, R. C. G.; *et al. Quim. Nova* **2018**, *41*, 1178; [3]Song, Z.; *et al. Nano Lett.* **2016**, *16*, 3309; [4]Llabrés i Xamena, F. X.; *et al.* RSC Publ.: London, **2013**; [5]Férey, G.; Serre, C.; *Chem. Soc. Rev*. **2009**, *38*, 1380; [6]Andrade, A.; *et al. J. Heterocyclic Chem.* **2015**, *52*, 273.

Agradecimentos/Acknowledgments

FAPESP
unesp UNIVERSIDADE ESTADUAL PAULISTA "JÚLIO DE MESQUITA FILHO"
Faculdade de Ciências
LSOP Laboratório de síntese orgânica e processos

Área: ORG

Síntese e prospecção biológica de derivados 4-quinolono-3-acilhidrazonas como potenciais candidatos anti-HIV-1

Yuri I. M. Silva (FM)[1], Paulo R. S. Stephens (PQ)[2], Vitor W. Rabelo (PQ)[2], Izabel C. P. Paixão (PQ)[2] Maria C. B. V. de Souza (PQ), [1] Fernanda da C. S. Boechat (PQ) [1]

inacioyuri@id.uff.br;

[1]Laboratório de Nucleosídeos, Heterociclos e Carboidratos (LNHC), Departamento de Química Orgânica, Universidade Federal Fluminense, Niterói; [2]Instituto de Biologia, Universidade Federal Fluminense, Niterói.

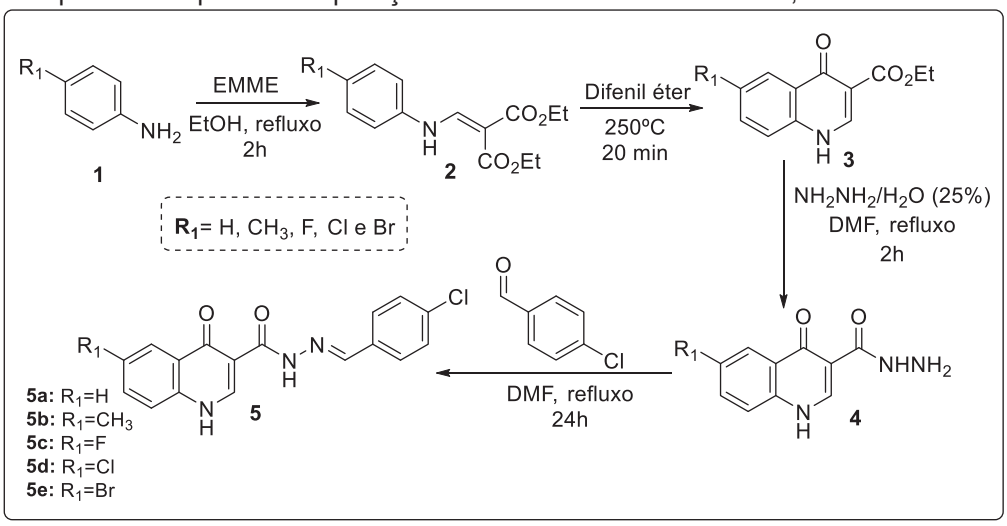
Palavras-Chave: *4-quinolone; acylhydrazone; HIV-1; Antiviral.*

Highlights

Synthesis of 4-quinolone-3-acylhydrazone derivatives as potential anti-HIV-1 substances. A large number of 4-quinolone derivatives are heterocyclic compounds with biological activity widely described in the literature. In this work, the proposed compounds were synthesized and their anti-HIV activity is being evaluated.

Resumo/Abstract

O Vírus da Imunodeficiência Humana (HIV) foi descrito em 1983 como agente causador da Síndrome da Imunodeficiência Adquirida (AIDS) e continua sendo uma questão mundial de assistência à saúde.[1] A Transcriptase Reversa (RT) do HIV-1 é o principal alvo dos medicamentos antirretrovirais disponíveis na clínica, por ser uma enzima multifuncional no ciclo de vida do vírus. Entretanto, a alta taxa de mutação da RT confere resistência contra os inibidores desta enzima e este fator se mostra uma grande barreira na luta contra a infecção pelo vírus HIV.[2] Muitas substâncias contendo o núcleo 4-quinolônico possuem aplicação clínica como antibacterianos, além de outras atividades ditas não clássicas, como por exemplo a antiviral, sendo o Elvitegravir, um exemplo disto.[3] Neste trabalho, derivados do tipo 4-quinolono-3-acilhidrazonas foram sintetizados e estão sendo avaliados frente ao HIV-1. Inicialmente, anilinas devidamente substituidas **(1a-e)** foram submetidas a uma reação de condensação com etoximetilenomalonato de dietila (EMME), seguida de ciclização térmica, para formação das 4-quinolonas **(3a-e)**. Posteriormente estas substâncias reagiram com monoidrato de hidrazina, para a obtenção das hidrazidas **4a-e**. Estes derivados, por sua vez, foram reagidos com *p*-clorobenzaldeído sob catálise ácida obtendo-se os produtos **5a-e** (Esquema 1) com rendimentos que variaram entre 35 e 45%. As substâncias foram caracterizadas por métodos físicos de análise. Ensaios preliminares indicam que o derivado **5a** foi capaz de inibir a transcriptase reversa (Tabela 1) do vírus, e se mostrou menos citotóxico que o fármaco de referência (AZT). As demais substâncias seguem em avaliação biológica.



Esquema 1: Rota sintética para obtenção dos compostos **5a-e.**

Tabela 1: Composto **5a** em comparação com o primeiro fármaco aprovado no tratamento da AIDS (**AZT**).

Composto	CC_{50}(μM)	EC_{50}(μM)	SI
5a	719,07±382,94	3,37±1,22	213,4
AZT	128±2,8	0,16±0,01	800

Agradecimentos/Acknowledgments

CNPq, PPGQ-UFF, PROAP-UFF, CAPES, FAPERJ

SANTOS, L. H.; et al., **Memórias Instituto Oswaldo Cruz**, 2015, 110 (7), 847-864.
FERREIRA, R. C. S.; et al., **Química Nova**, 2010, 33 (8), 1743- 1755.
AHMED, A.; DANESHTALAB, M., **Journal of Pharmacy and Pharmaceutical Sciences**, 2012, 15 (1), 52-72.

Área: ORG

Síntese Regiosseletiva de Anidrido Hetero-Aromático *Via* Rearranjo de Curtius Empregando Sonoquímica

Patrick P. Pimentel (PG)[1,2] Juliana A. Francisco (IC),[1] Erica N. D. Figueiredo (IC),[1] Pedro A. R. Lessa (IC),[1] Evanoel Crizanto de Lima (PQ)[1*]

pppatrickpedro@gmail.com; evanoel.crizanto@gmail.com

[1]Laboratório de Catálise e Síntese de Substâncias Bioativas, Centro Multidisciplinar UFRJ-Macaé, Pólo Ajuda, Macaé-RJ; [2]Laboratório de Catálise e Síntese (CSILab), sala 413, Instituto de Química, Campus do Valonguinho, Universidade Federal Fluminense, Centro, Niterói-RJ.

Palavras Chave: *Química verde, Ultrassom, Rearranjo de Curtius, Anidrido Quinolínico.*

Highlights

Regioselective Synthesis of Hetero-Aromatic Anhydride via Curtius Rearrangement Using Sonochemistry.

Resumo/Abstract

A promoção de reações químicas pelo ultrassom é um fenômeno físico baseado no processo de criar, aumentar e implodir microbolhas de vapor e gases em um líquido, denominado cavitação, promovendo efeitos de ativação em reações químicas.[1] No ciclo de compressão seguinte, essas cavidades colapsam quase instantaneamente com a liberação de grandes quantidades de energia nas imediações das microbolhas. Estima-se que as temperaturas atinjam até vários milhares de Kelvin e pressões de várias centenas de atmosferas sejam produzidas.[1,2] Em 2014, Sarmiento-Sánchez e colaboradores publicaram um trabalho para síntese de diversos anidridos *via* rearranjo de Curtius[3], dentre os quais pode-se destacar o anidrido azaisatoico, intermediário-chave de interesse em nosso grupo de pesquisa. Para sua obtenção, o anidrido quinolínico foi empregado como material de partida e foi utilizado um longo tempo reacional de 17h, a uma temperatura específica de 53 °C, e mais 2h de refluxo. A temperatura exata de 53 °C dificulta a reprodutibilidade do aquecimento em placas convencionais de laboratório, que não possuem precisão no controle e aumento da temperatura. Ademais, como o anidrido quinolínico não possui simetria molecular, há possibilidade da formação de dois isômeros, os quais foram obtidos sem regiosseletividade no trabalho de Sánchez, em uma proporção de 56:44 (regioisômeros 8-azaisatoico e 5-azaisatoico, respectivamente). O objetivo deste trabalho é a síntese do anidrido 8-azaisatoico a partir do anidrido quinolínico, utilizando ultrassom como uma abordagem alternativa e reprodutível, e investigar sua influência sobre a obtenção do produto através do rearranjo de Curtius e sobre a regiosseletividade da reação. Primeiramente, investigou-se a mesma condição reacional descrita no artigo (anidrido quinolínico em THF, 1 mM, e trimetilsililazida, 1,05 equiv.) com intuito de se comparar o resultado, somente alterando a temperatura da reação, desta vez à temperatura ambiente, empregando-se sonoquímica. A reação terminou em apenas três horas, tendo sido acompanhada por CCF a cada 30 minutos. O produto foi filtrado e enviado para a análise de Cromatografia Gasosa acoplada à Espectrometria de Massas, utilizando metanol como solvente. A metodologia desenvolvida se mostrou efetiva para a obtenção do produto alvo, com rendimentos de até 90% e regiosseletividade de 10:1, que pôde ser observada através da análise de RMN de ^{1}H. Esta abordagem apresentou experimental significativamente mais simples do que o descrito na literatura, tempo reacional mais curto e ainda dispensa a necessidade de lavagem do produto obtido, simplificando não só a síntese como também o isolamento do produto final e minimizando o uso de solvente. Todas essas melhorias representam um grande ganho no aspecto verde do procedimento, tornando-o mais econômico e ambientalmente amigável.

Referências:

[1] Einhorn, C. *et. al. Synthesis* **1989**, 787; [2] Lenardão, E. J. *et. al. Quim. Nova* **2003**, *26,* 123**;** [3] Sarmiento-Sánchez, J. I. *et. al. Quim. Nova* **2014**, *37,* 1297.

Agradecimentos/Acknowledgments

Authors thank Faperj and CNPq for financial support and Farmanguinhos for analytical data.

Área: ORG

Selective *O*-alkylation of Lawsone Using Sulfonic Acid-functionalized Chitosan as a Biodegradable Heterogeneous Organocatalyst

Iva S. de Jesus (PQ),[1,*] Juliana B. de Pontes (IC),[1] Fernando de C. da Silva (PQ),[2] Vitor F. Ferreira (PQ).[1]

ivasouza.quimica@gmail.com

[1]*Faculdade de Farmácia, Departamento de Tecnologia Farmacêutica, Universidade Federal Fluminense, UFF.*
[2]*Laboratório de Síntese Orgânica Aplicada, Universidade Federal Fluminense, Instituto de Química, Niterói-RJ, 24210-141, Brazil.*

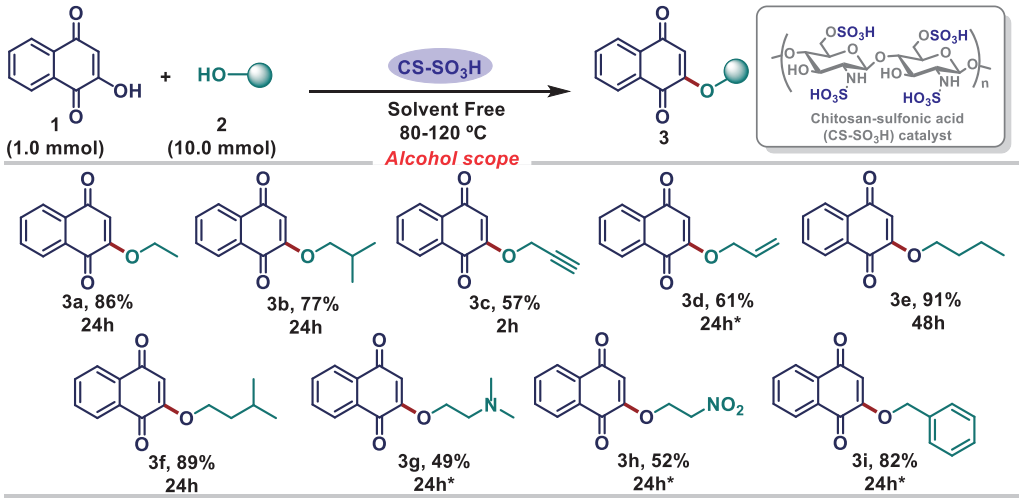
keywords: *Lawsone, Acidic Chitosan, Alkylation Heterogenous Organocatalyst.*

Highlights

Herein, we described for the first time, a rapid and scalable direct *O*-alkylation of lawsone with different alcohols using acid chitosan (CS-SO_3H) as a heterogeneous organocatalyst. Products are obtained with good yields, solvent-free, and short reaction times. Recycling of the catalyst and regioselectivity of the method were evaluated.

Abstract

Naphthoquinone is a privileged structural motif frequently found in biologically relevant compounds.[1] Furthermore, their electrophilic and nucleophilic properties make them valuable building blocks for the synthesis of chemical architectures containing this core.[2,3] Thus, this work reports a rapid, and scalable direct *O*-alkylation of lawsone using acid chitosan (CS-SO_3H) as a biodegradable, easily accessible, and recyclable heterogeneous organocatalyst. The synthesis of the 2-alkyloxy-1,4-naphthoquinones (**3**) was performed by reacting lawsone (**1**) with different alcohols (**2**) in the presence of CS-SO_3H as a heterogeneous organocatalyst, solvent-free in heating. The scope of this transformation exhibits high compatibility with several alcohols without the need for conversion into its respective bromide, as reported in previous works, and the corresponding products were isolated in good yields. Importantly, this reaction is facilitated by the activation of the carbonyl group of lawsone **1** due to its protonation by the acidic catalyst CS- SO_3H. This facilitates the nucleophilic attack from alcohol **2** to form the tetrahedral intermediate which, after eliminating water, provides the respective alkylated product.



*Reactions were performed using acetonitrile as a solvent (5.0 M).

Scheme 1. Synthesis of 2-alkyloxy-1,4-naphthoquinoes promoted by CS-SO_3H.

1. Beerhues, L.; Liu, B. Biosynthesis of biphenyls and benzophenones – evolution of benzoic acid-specific type III polyketide synthases in plants. *Phytochemistry* **2009**, *70*, 1719–1727;
2. Liu, B.; Raeth, T. A novel 4-hydroxycoumarin biosynthetic pathway. *Plant Mol. Biol.* **2010**, *72*, 17–25;
3. Xu, B.; Gao, Y.; Han, J.; Xing, Z.; Zhao, S.; Zhang, Z.; Ren, R.; Wang, L. Hypervalent Iodine(III)-Mediated Tosyloxylation of 4-Hydroxycoumarins. *J. Org. Chem.* **2019**, 84, 10136–10144.

Acknowledgments

CAPES, CNPq, FAPERJ.

Área: ORG

Solvent Effect in the Groebke-Blackburn-Bienaymé Reaction: A Theoretical and Experimental Investigation

Marcelo H.R. Carvalho (PG),[1] Pedro P. de Castro (PQ),[2] Pedro de S. Beck (PG),[3] Hélio F. dos Santos (PQ),[1] Brenno A.D. Neto (PQ),[3] Giovanni W. Amarante (PQ).[1*]

carvalho.mhr@gmail.com; giovanni.amarante@ufjf.br

[1]*Departamento de Química, UFJF;* [2]*Departamento de Química, UFSCar;* [3]*Instituto de Química, UnB*

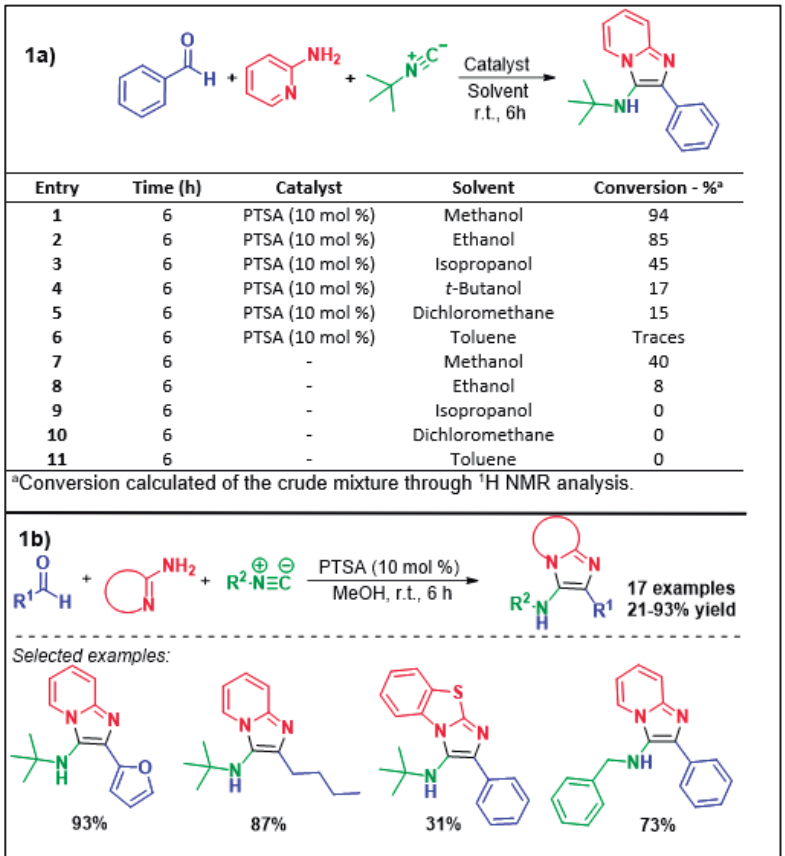
Keywords: *Multicomponent Reaction, Solvent Effect, GBB, Heterocycles.*

Highlights

Experimental and theoretical investigations of the Groebke-Blackburn-Bienaymé reaction were carried out, evidencing the solvent effect for this transformation.

Resumo/Abstract

Multicomponent reactions are important transformations in organic synthesis, allowing access to compounds with high molecular complexity from simple substrates. A notable characteristic of this class of reactions is the involvement of three or more reactants in a one-pot system, affording the products with high atomic economy.[1] For example, the Groebke-Blackburn-Bienaymé (GBB) reaction involves an aldehyde, an isocyanide, and a cyclic amidine as starting materials, providing derivatives of imidazo[1,2-*a*]heterocycles as products. Based on our results obtained for the Ugi multicomponent reaction, in which we found that methanol can play an important role in the mechanism,[2] our initial hypothesis is that something similar could occur with the GBB reaction. A careful analysis of different solvents with varying dielectric constants showed that protic polar organic solvents were more effective, with the best yield obtained when methanol (and other alcohols) were used (Figure 1a). After reaction optimization, we prepared a diverse scope of 17 examples, varying each of the three components, obtaining isolated yields between 21% and 93% (Figure 1b). Control experiments using growing loadings of methanol as an additive instead of a solvent for the reaction, promoted an increase in terms of yields. Mechanistic investigation using density functional theory (DFT) calculations were carried out, and a plausible alternative mechanism was evaluated. It was revealed that methanol (or other alcohols) may participate through an alternative reaction pathway, which differ from the classic mechanism (without alcohol participation), explaining the experimental results.



Entry	Time (h)	Catalyst	Solvent	Conversion - %[a]
1	6	PTSA (10 mol %)	Methanol	94
2	6	PTSA (10 mol %)	Ethanol	85
3	6	PTSA (10 mol %)	Isopropanol	45
4	6	PTSA (10 mol %)	*t*-Butanol	17
5	6	PTSA (10 mol %)	Dichloromethane	15
6	6	PTSA (10 mol %)	Toluene	Traces
7	6	-	Methanol	40
8	6	-	Ethanol	8
9	6	-	Isopropanol	0
10	6	-	Dichloromethane	0
11	6	-	Toluene	0

[a]Conversion calculated of the crude mixture through ^{1}H NMR analysis.

Figure 1. a) Optimization of reactional conditions. b) Substrate scope of GBB adducts.

(1) Carvalho, M. H. R.; Castro, P. P.; Amarante, G. W. Recent Synthetic Developments of Asymmetric Multicomponent Transformations: Strecker, Mannich, Passerini and Ugi Reactions. *J. Braz. Chem. Soc.* **2023**, *34* (8), 1041-1070.

(2) Carvalho, M. H. R.; Ribeiro, J. P. R. S.; De Castro, P. P.; Passos, S. T. A.; Neto, B. A. D.; Dos Santos, H. F.; Amarante, G. W. Solvent Dependent Competitive Mechanisms for the Ugi Multicomponent Reaction: A Joint Theoretical and Experimental Study in the α-Acyl Aminocarboxamides vs α-Amino Amidines Formation. *J. Org. Chem.* **2022**, *87* (16), 11007-11020.

Agradecimentos/Acknowledgments

The authors are grateful for the generous financial support from CAPES (Finance Code 001), UFJF, FAPEMIG, FAPESP, FAPDF and Rede Mineira de Química.

Área: ORG

SOLVENT-FREE SUSTAINABLE SYNTHESIS OF L-PIROGLUTAMIC ACID

Fernando Barretto (PG)[1,2*] and Silvio Cunha (PQ)[1,2]

1) Instituto de Química, Universidade Federal da Bahia, UFBA, 40170-115

2) INCT-Instituto Nacional de Ciência e Tecnologia em Energia e Ambiente, Universidade Federal da Bahia, UFBA, 40170-230

****e-mail:** fernando.barrettto@hotmail.com*

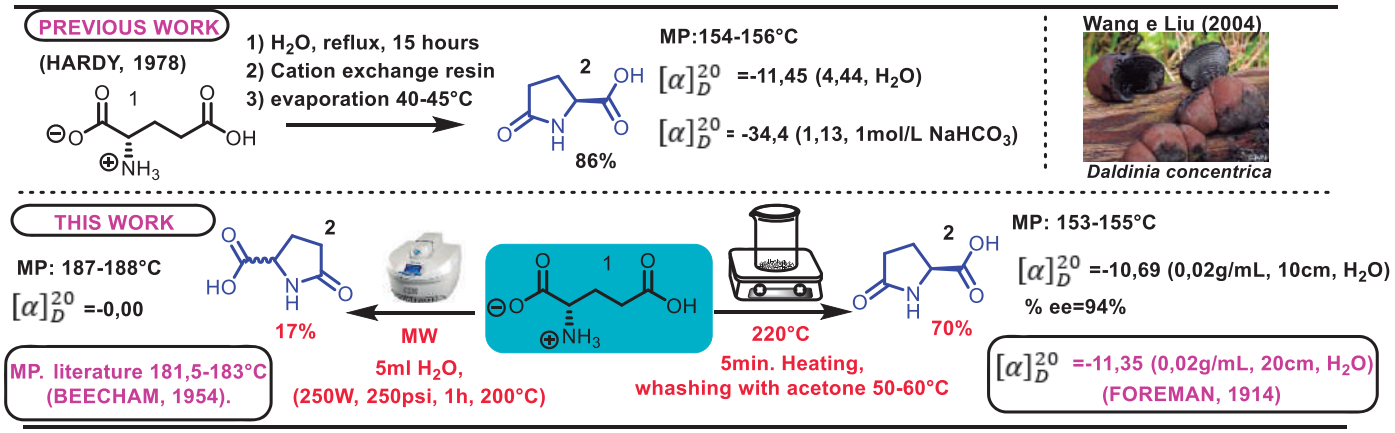
Palavras Chave:*(glutamic acid, pyroglutamic acid).*

Highlights

We developed a fast and practical synthesis of L-pyroglutamic acid starting from L-glutamic acid.

Resumo/Abstract

L-glutamic acid is one of the 22 amino acids found and holds biological importance as it serves as one of the main excitatory neurotransmitters in the human brain and is also used in the food industry.[1] L-pyroglutamic acid **(2)** is a natural product found in the fungus *Daldinia Concentrica* and has been used as a target molecule in the synthesis of DKPs alkaloids.[2] Its synthesis was first developed from L-glutamic acid **(1)**.[3] The synthesis reported by Hardy (1978) is the most practical. Divergences were observed regarding its synthesis, specific rotation reading and spectroscopic data. In this work, we developed a fast preparation using L-glutamic acid **(1)** as an accessible starting material, in the synthesis of pyroglutamic acid **(2)**. Firstly, the synthesis was tested using microwave condition, however, the product **(2)** was obtained with low yield and in racemic form. Other reactions were tested, such as reflux with water and mechanochemical condition, but reagent was recovered. Then, the solid-state reaction was investigated and **1** left in a hotplate (220°C) until complete fusion within 5 minutes. Then, the reaction was cooled to room temperature and allowed to crystallize at room temperature, solid formed was washed with hot acetone, and the product was obtained by simple vacuum filtration. The product **(2)** was obtained with 70% yield in chiral form, $[\alpha]_D^{20}$= -10.69, and an %ee of 94%. Therefore, L-pyroglutamic acid was formed in an unprecedented and sustainable wayfrom L-glutamic acid **(1)**.



*1 a) ANDERSEN, Jens V. et al. Neuropharmacology, 196, 108719, **2021**. b) RIBEIRO J., V., D.Sc., Suplementação de ácido glutâmico e de glutamina em dietas para frangos de corte. Tese de doutorado, Universidade Federal de Viçosa, **2015**. c) ALVES, S. S. M.Sc. Adição de glutamina mais ácido glutâmico em dietas para porcas lactantes e ou leitões na creche. Dissertação mestrado, Universidade Federal de Viçosa, **2013**. d) DO NASCIMENTO T. L. P. et al. Journal of Health Sciences, 14, **2012**. e) SHIH, I.-L.; VAN, Y.-T.; SHEN, M.-H. Mini reviews in medicinal chemistry, 4, 179-188, **2004**. f) SOUZA, J. G. DE L. DE. Produção de ácido L-glutâmico por bactéria de ácido lático. Tese de doutorado, Universidade de Lavras-MG, **2022**.*

*2 a) WANG, Fei; LIU, Ji-Kai. Helvetica Chimica Acta, 87, 2131-2134, **2004**. b) PARRISH, D. A.; MATHIAS, L. J. The Journal of Organic Chemistry, 67, 1820-1826, **2002**.*

*3 a) ARNOW, L. E.; OPSAHL, J. C. Journal of Biological Chemistry, 134, 649-651, **1940**. b) FOREMAN, F. W. Biochemical Journal, 8, 481, **1914**. c) HARDY, P. M. Synthesis, 1978, 290-291, **1978**.*

Agradecimentos/Acknowledgments

CAPES, FAPESB, INCT, CNPq, and DQ-UFSCAR

Área: ORG_____
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Studies on C1'-Quaternized *C*-Nucleosides: Novel Isoxazolyl Nucleoside Synthesis and Perspectives

Sarah M. R. do Nascimento (PG),[a] Julia de Paula Santos (IC), [a] Leandro Soter de Mariz e Miranda (PQ)*[a]

sarahrodrigues17.ufrj@gmail.com; julia.psantos1864@gmail.com; leandrosoter@iq.ufrj.br

[a] *Biocatalysis and Organic Synthesis Group, IQ-UFRJ Universidade Federal do Rio de Janeiro, Av Athos da Silveira Ramos 149, Centro de Tecnologia, Bl A, 21941909 Ilha do Fundão, Rio de Janeiro, Brazil.*

Palavras Chave: *nucleosides, 1,3-dipolar cycloaddition, quaternization*

Highlight

Studies on C1'-Quaternized *C*-Nucleosides: novel Isoxazolyl Nucleoside Synthesis and Perspectives

- Quaternized *C*-alkynyl-Ribosides of the type **2** are versatile intermediate on the synthesis of different nucleosides obtained in 55% global yield in three steps.
- The reaction of riboside **2** with nitrile oxides furnishes quaternized isoxazolyl-nucleosides.

Abstract

5'-Phosphorylated nucleosides, termed nucleotides, are a class of molecules present in all living organisms and viruses. These molecules and their polymers are responsible for many vital processes such as storing, transcription, and translation of genetic information. Over the last century, these vital roles have fueled the interest of researchers to develop structural analogues that could interfere with these processes. Special attention was given to analogues that could interfere with the transcription and translation of genetic information and disrupt the cell division process.

As part of our efforts in the study of C1'-quaternized *C*-ribonucleosides, we decided to continue to explore the versatility of the ribosylpropiolate **2** in the reaction with nitrile oxides for the synthesis of C1'-quarternized C-isoxazolyl-ribonucleosides.

For such, the alkynylation of the ribonolactone **1** with the lithium propiolate followed by the quenching of the intermediate hemiketal with acetic anhydride furnished the crude ribosyl-propiolate, which was carried out to cyanation obtaining the pure **2β** anormer as the major anomer in 55% global yield after chromatographic purification. The reaction of **2β** with different nitrile oxides derived from the oxidation of the respective oxime yielded the isoxazoles of type **4** regioselectively**.** These quaternized nucleosides can be further used as substrates for spirocyclic nucleoside synthesis as depicted in Scheme 1.

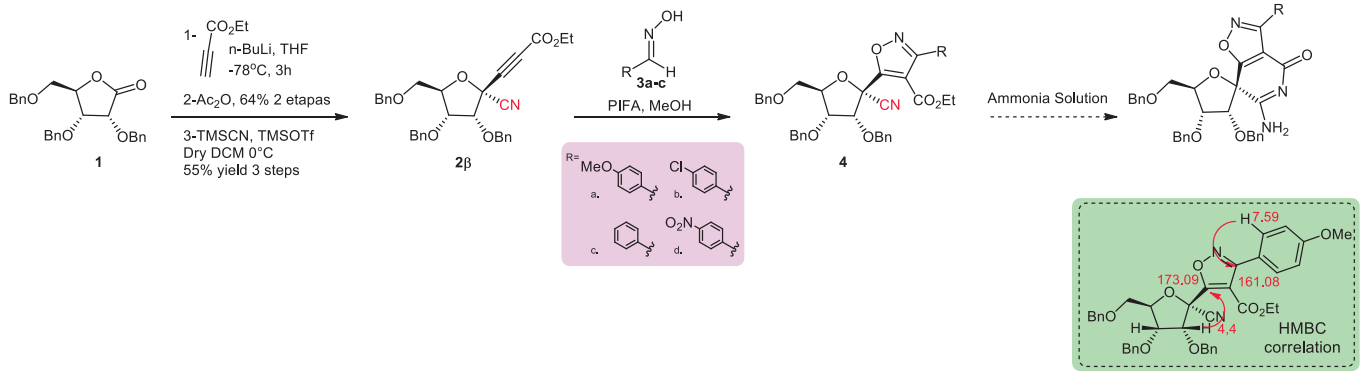


Figure 1. The synthesis of quarternized nucleosides **4**

Acknowledgments

FAPERJ CNPq CAPES

Área: ORG

Superior stability of benzoyl-selenoesters over acetyl-selenoesters on lipase-catalyzed reactions

Ana Letícia W. da Silva (IC),[1] Willian Patrick Oliveira da Silveira (IC),[1] Leandro Piovan (PQ).[1]*

ana.waszak@ufpr.br; lpiovan@ufpr.br

[1]*Departamento de Química - Laboratório de Síntese Química e Enzimática (LaSQuE), Universidade Federal do Paraná - UFPR*

Palavras Chave: *Selenoesters, Lipases, Nucleophiles, Benzoyl donor*

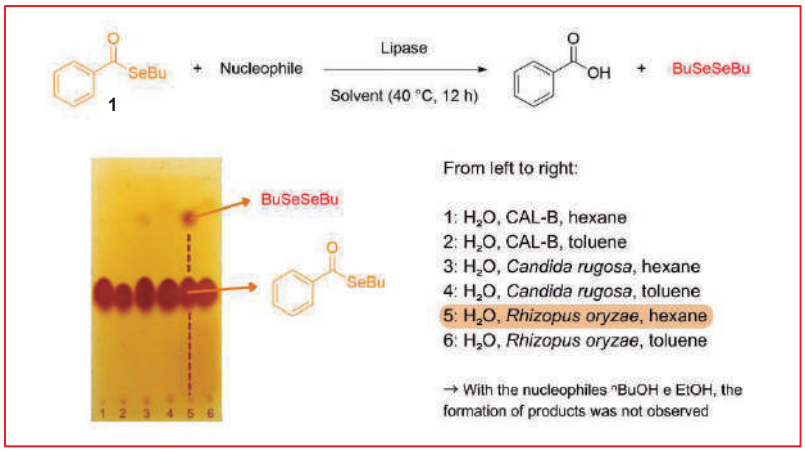
Highlights

Selenoesters as benzoyl donors. Lipase-catalyzed reactions. Different stabilities of acetyl versus benzoyl-selenoesters.

Resumo/Abstract

Organoselenium compounds have been described in the literature for their most diverse potentials, including antiviral and antimicrobial activity, and as key intermediates in organic and inorganic synthesis[1-3]. Initially considered possibly toxic and difficult to handle, in-depth studies indicate the biological and chemical potential of molecules containing the chalcogen Selenium[1] since the last century. The selenoesters, a subclass of organoselenium compounds, are examples of broadly applied Se-containing compounds mainly used as acyl donors in organic synthesis[3].

Recently, selenoesters were applied as acyl donors in lipase-catalyzed reactions with promising results[3]. Hence, we decided to evaluate the selenoesters' potential as benzoyl donors in this work. Therefore, Se-butyl benzoate (**1**) was used as substrate in the EKR reaction under different conditions: the assays were carried out using the lipases CAL-B, *Candida rugosa,* and *Rhizopus oryzae*; *n*-butanol, ethanol, and water as nucleophiles in hexane and toluene as solvents under 40 °C in batch mode.



Scheme 1. Enzymatic kinetic resolution of compound **1**.

After 12 h, was observed the occurrence of reaction in only two of the conditions (*Candida rugosa*, H_2O, hexane e *Rhizopus oryzae*, H_2O, hexane), where the second one demonstrated the higher formation of the co-product BuSeSeBu, even though the starter reagent was not wholly consumed (Scheme 1). It is concluded that the benzoyl group donation reaction from selenoesters is slower than the acyl group donation reaction described previously[3]; therefore, the benzoyl-selenoesters are more stable than the acyl ones.

[1]Back, Thomas G., ed. *Organoselenium chemistry: a practical approach*. OUP, **1999**.
[2]L. L. Baldassari, D. S. Lüdtke, *Chem. Eur. J.* **2021**, 27, 8656
[3]Zugman, T.; da Silva Durigon, M. C.; Campos, S. K.; da Silva, R. R.; da Silva, T. S.; de Oliveira, A. R. M.; Piovan, L. *ChemistrySelect* **2022**, 7 (48).

Agradecimentos/Acknowledgments

UFPR UNIVERSIDADE FEDERAL DO PARANÁ · PPGQ-UFPR · LaSQuE Laboratório de Síntese Química e Enzimática · CAPES · CNPq

Área: ORG

Symmetrical benzalazines with enhanced emission in acidic medium as potential sensing materials for the detection of strong acids

Bruno G. Lopes (PG),[1] Lidiane G. de Araujo (PG),[1] Rafael G. Soares (IC),[1] Claudio G. Lima Junior (PQ),[1] Rodrigo Cristiano (PQ),[1] Boniek G. Vaz (PQ),[2] Gabriel F. dos Santos (PQ).[2]

bruno.galdino.lopes@academico.ufpb.br;

[1]Departamento de Química, UFPB; [2]Instituto de Química, UFG.

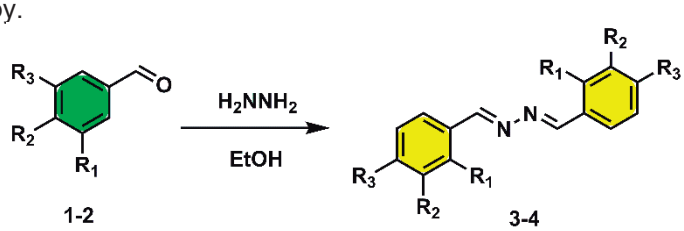
Keywords: *Aggregation-induced emission, Azines, Acid sensor, Chromophores, ESIPT, AIE.*

Highlights

Benzalazines in this work are obtained by easy synthesis from aldehydes and hydrazines in good yields. Films of the materials are luminescent chromophores when exposed to concentrated HCl vapors and the process is thermally reversible.

Abstract

Fluorophore molecules with Aggregation Induced Emission (AIE) have attracted the attention of many researchers due to their unique properties and applications in various technological fields.[1] Among several classes of small molecules, azines have been shown advantages, such as simplicity, low-cost obtation, and high sensitivity of real-time detection in vitro and in vivo settings.[2] Furthermore, these materials have been widely used as fluorescent molecular sensors for various analytes, OLED devices, and liquid crystal displays (LCD).[3] Some of these AIEgens are responsive to external stimuli such as pH variation, temperature change, mechanical stress, photonic irradiation, etc. In this context, we show the synthesis and characterization of two azine molecules (**3** and **4**). These compounds are non-luminescent either in solution or solid phase but became very strong emitters after protonation in acidic solutions and in thin films exposed to concentrated HCl vapor. Synthesis was carried out according to **Scheme 1**. The structures of the products were determined by IR, ^{1}H, and ^{13}C NMR and HRMS. The optical properties were studied by UV-vis and Fluorescence spectroscopy.



Comp.	R_1	R_2	R_3
3	H	$OC_{10}H_{21}$	OCH_3
4	$OC_{10}H_{21}$	H	$OC_{10}H_{21}$

Scheme 1: Synthesis of studied benzalazines

Both compounds exhibited a strong absorption band around 350 nm and a very weak emission ranging from 420 to 500 nm (ϕ ~ 0.001). In a 10% HCl solution, they became yellow chromophores (λmax.abs. ~ 410 nm), and their emission increased 60 to 90 times (ϕ = 0.09 for 3, ϕ = 0.06 for 4) with increased Stokes shifts (λmax.em. ~ 520 nm). Similar patterns were also observed for their solid films when exposed to HClconc. vapors. We also found that the optical changes are reversible upon heating. Analyzes carried out using IR and NMR indicate that such compounds undergo protonation in the azine nitrogen, which corroborates the large Stoke shifts, with a possible excited state intramolecular proton transfer (ESIPT) mechanism.

Acknowledgments

Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Instituto Nacional de Ciência e Tecnologia em Ciências Moleculares (INCT-Cimol).

Reference

1. Adamczyk, J. A. *et al.* Photophysical properties of novel fluorescent thin solid layers based on the Aggregation Induced Emission of alkoxy-substituted salicylaldehyde azines. *J. Lumin.* **229**, 117668 (2021).
2. Zhang, Y., Wang, C. X. & Huang, S. W. Aggregation-induced emission (AIE) polymeric micelles for imaging-guided photodynamic cancer therapy. *Nanomaterials* **8**, (2018).
3. Kagatikar, S. & Sunil, D. Aggregation-induced emission of azines: An up-to-date review. *J. Mol. Liq.* **292**, 111371 (2019).

Área: ORG

Synthesis and antitumoral activity of Selenium-containing α-hydroxy esters

Maria Clara da Silva Durigon (PG),[1] Andressa Dalolio Valente (PG),[2] Rian Richard Santos de Farias (PG),[2] Francielle Pelegrin Garcia (PQ),[2] Celso Vataru Nakamura (PQ),[2] Leandro Piovan (PQ).[1]*
durigon.mariaclara@gmail.com; lpiovan@quimica.ufpr.br
[1]Departamento de Química, UFPR; [2]Centro de Ciências da Saúde, UEM

Palavras Chave:*(Selenium compounds, α-hydroxy esters, Antitumoral, HeLa, Cervical carcinoma).*

Highlights

Novel selenium-containing α-hydroxy esters were synthesized and evaluated using HeLa cervical carcinoma cells, showing promising results.

Resumo/Abstract

The biological application of selenium-containing molecules as an antitumoral agent is a growing field in medicinal chemistry.[1,2] Even so, using these compounds as antitumoral agents for human cervical carcinoma HeLa is still poorly explored.[3] In this work, the syntheses of selenocompounds **MC08-14** were achieved using a classic transesterification methodology, with isolated yields ranging from 37 to 54% (Figure 1).

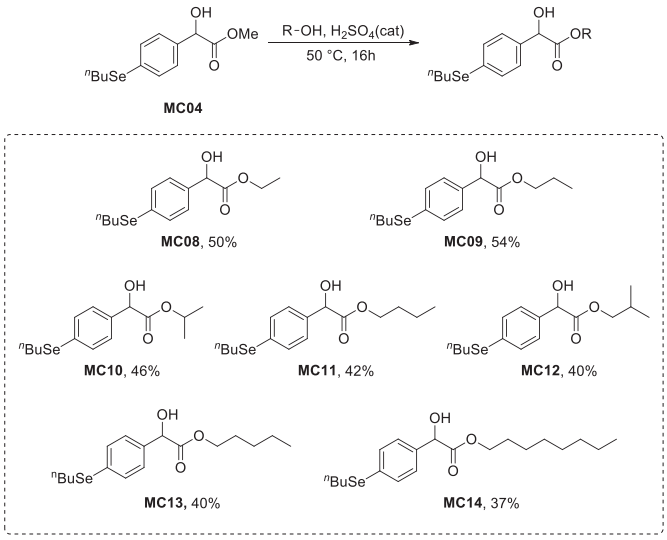


Figure 1 – Synthetic route for α-hydroxy esters **MC08-14**.

MC04 and **MC08-14** were tested as antitumoral agents using the HeLa cell line. The results demonstrated that compounds **MC09-12** were active against HeLa cells, with IC_{50} ranging from 27.0 ± 3.0 and 42.6 ± 8.6 μM.

Table 1 – IC_{50} of tested compounds against HeLa cell line.

Compound	IC_{50} HeLa (μM)
MC04	95.0 ± 3.4
MC08	58.6 ± 0.3
MC09	42.6 ± 8.6
MC10	39.4 ± 4.9
MC11	27.0 ± 3.0
MC12	33.4 ± 9.0
MC13	53.1 ± 7.6
MC14	62.5 ± 13.8
Doxorrubicine	8.2 ± 4.9

In summary, **MC09-12** showed promising antitumoral activity in the cervical cancer cell line and can be considered leads for new Se-containing compounds.

1. Debnath, S.; Agarwal, A.; Kumar, N. R.; Bedi, A. *Futur. Pharmacol.* **2022**, *2*, 595–607.
2. Garbo, S.; Di Giacomo, S.; Łażewska, D.; Honkisz-Orzechowska, E.; Di Sotto, A.; Fioravanti, R.; Zwergel, C.; Battistelli, C. *Pharmaceutics* **2023**, *15*, 1–32.
3. Chuai, H.; Zhang, S. Q.; Bai, H.; Li, J.; Wang, Y.; Sun, J.; Wen, E.; Zhang, J.; Xin, M. *Eur. J. Med. Chem.* **2021**, *223*, 113621.

Agradecimentos/Acknowledgments

The authors thank CAPES and CNPq for their financial support and also UFPR for the support in the development of this work.

Área: MAT

Synthesis and application of quinoline derivatives as photoiniciators in photopolymerization reactions

Emily Bassani de Barros* **(IC),[1] Ilana Sganzerla Rosário (PG),[1] Vitor Fernandes Moreno (PG),[1] Luiz Carlos Da Silva Filho (PQ)[1]**
*e-mail: **emily.bassani@unesp.br**

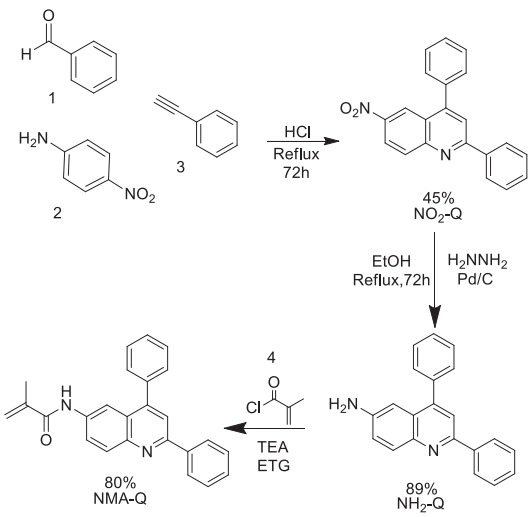
[1]Department of Chemistry, São Paulo State University (UNESP), School of Sciences, 17033-360, Bauru, São Paulo, Brazil
Keywords: quinoline derivatives, photopolymerization, photoinitiator, luminescent polymers, multicomponent reactions

Highlights

Fast and efficient photopolymerizations. Production of fluorescent polymers. Photopolymerization carried out under blue and UV light irradiation.

Abstract

In this study, we present our findings regarding the synthesis, characterization, and application of a new quinoline derivative (Scheme 1) designed to serve as a Type II photoinitiator in the photopolymerization reaction of the monomer urethane dimethacrylate (UDMA), which is commonly employed in resin formulations for dental restoration. Methacrylated aminoquinoline (NMA-Q) was obtained in three steps with good yield, commencing with a Multicomponent reaction followed by the reduction of the nitro group and the methacrylation of the amino group. Photolysis analyses of this derivative (NMA-Q) and it's synthetic intermediates (NO2-Q and NH2-Q) (Figure 1) demonstrate that the formation of reactive species occurs within the first second of light exposure, providing clear evidence of the photosensitivity of these molecules. All the synthesized quinoline derivatives were tested as photoinitiators in the UDMA photopolymerization reaction using a Kessyl lamp under 370 nm irradiation, resulting in polymers with a conversion rate of up to 40% in approximately 60 seconds. These results closely resemble those achieved with camphorquinone, a commercial photoinitiator. Importantly, the polymers obtained exhibit fluorescent characteristics (Figure 2), which could be particularly relevant for applications in fields such as dentistry.



Scheme 1. Synthesis of quinoline derivatives

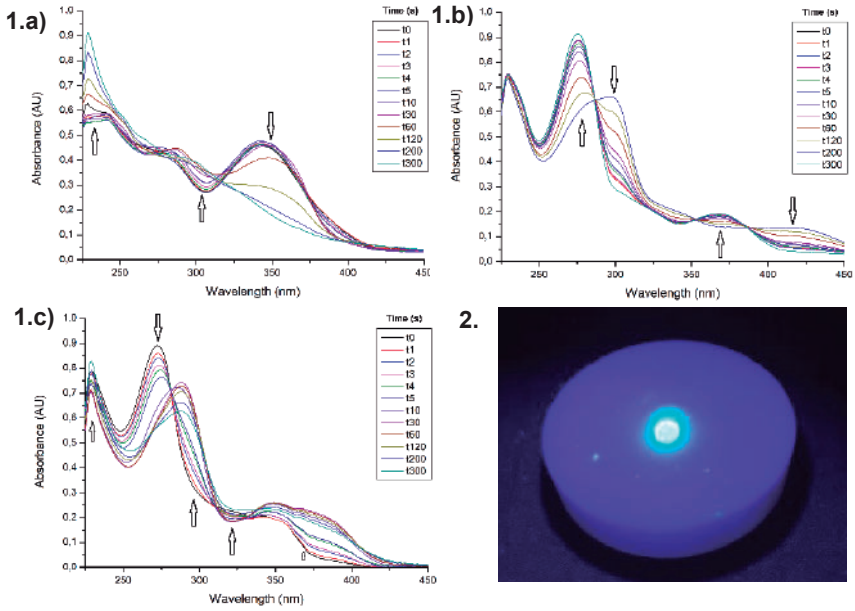


Figure 1. Photolysis behavior of a) NO_2-Q, b) NH_2-Q and c) NMA-Q.
Figure 2. Luminescent polymer of UDMA using quinolinic PI's

[1]. Moszner, N.; Völkel, T.; Fischer, U. K.; Klester, A.; Rheinberger, V., Angew. Makromol. Chem. 1999, 265 (1), 31–35.
[2]. Alarcon, R. T.; dos Santos, G. C.; de Oliveira, A. R.; da Silva-Filho, L. C.; Bannach, G., J. Appl. Polym. Sci. 2019, 136 (19), 47461.
[3]. Fouassier, J. P.; Lalevée, J. Photoinitiators for Polymer Synthesis; John Wiley & Sons, 2013

Acknowledgments

The authors would like to thank FAPESP (2018/09235-4 and 2018/14506-7), CAPES (88882.330148/2019- 01 e 88887.827622/2023-00), CNPq (10594) and Pró-Reitoria de Pesquisa da UNESP (PROPe-UNESP) for their financial support.

Área: ORG

Synthesis and Biological Activity of Bis-acylhydrazones

Claudio L. Donnici (PQ),[1] Hélcio C. Marcondes (PG),[1] Jacqueline A. Takahashi,[1,2] Marina A. Costa (PQ)[1,3]

cdonnici@terra.com.br; helciomarcondes@gmail.com; marina.avilacosta@hotmail.com

[1]*LASELORG-QUIM,* [2]*Laboratório de Biotecnologia e Bioensaios/Depto. de Química, UFMG;* [3]*Faculdade de Tecnologia, UNB*

Palavras Chave: *bis-acil-hidrazonas, síntese, micro-ondas, ultrassom, atividades biológicas.*

Highlights

Twenty bis-acylhydrazones were synthesized and their antibacterial, anticancer, anticonvulsant, antifungal and antitrypanosomal activities were evaluated.

Resumo/Abstract

N-acylhydrazones (NAHs) have been one of the most promising, useful and versatile functional groups in medicinal chemistry to generate a huge number of hit and lead compounds that act on various types of molecular targets. The great interest on these compounds is even more remarkable due to the easeness of synthesis, since they are usually prepared by a condensation reaction between aldehydes or ketones with hydrazides. The present work reports the synthesis of twenty bis-N-acylhydrazones and their preliminary biological investigation as antibacterial, anticancer, anticonvulsant, antifungal and antitrypanosomal agents. The twenty bis-NAHs were obtained, in good yelds (70-86%), from the condensation reaction of 2,2′-thiobis acetic- (**1b**), 2,2′-sulfinylbisacetic- (**2b**), 2,2′-sulfonyl bisacetic- (**3b**), 3,3'-thiobis propionic- (**4b**), and 2,2'-oxy bisacetic- (**5b**) N,N'-bishidrazides with the following heteroaromatic aldehydes: furfural (**i**), 5-nitro-furfural (**ii**) 2-thiophenecarboxaldehyde (**iii**) and 2-pyridine carbaldehyde (**iv**) (**Figure 1**). The N,N'-bis hidrazides(**1b-5b**) were prepared (70-88%) by the reaction of the corresponding diethyl esters (**1a-5a**) with hydrazine hydrate using ultrasound irradiation and these esters were obtained by optimized Fischer esterification reaction (75-90%), under microwave irradiation, from the analogous carboxylic acids (**1-5**) as starting materials. All precursors, intermediates and final products were fully characterized and their molecular structures were confirmed using spectroscopic analysis. The bis-acylhydrazones were submitted to several biological activity investigations, such as: antibacterial (*Bacillus cereus*, *Citrobacter freundii, Listeria monocytogenes* and *Pseudomonas aeruginosa*), anticancer (colon (HCT116), leukemia (HL60), prostate (PC3), glioblastoma (SF-295) and breast (MX1)), antifungal (*Aspergillus fumigatus, Candida* (*C. albicans*, *C. famata*, *C. glabrata, C. krusei, C. parapsolisis* and *C. tropicalis*), *Cryptococcus neoformans*, *C. gatti*, *Paraccocidioides brasiliensis* and *Sporotrix schenkii*), anticonvulsant and antitrypanosomal. It is remarkable that some of these bis-NAHs showed promising pharmacological results and, in addition, low cellular toxicity was observed in *in vitro* tests indicating a highly favorable safety profile, essential for future medical applications.

n = 1, **X** = S, **Het** = Fur (**I.i**); **n** = 1, **X** = SO, **Het** = Fur (**II.i**);
n = 1, **X** = SO_2, **Het** = Fur (**III.i**); **n** = 2, **X** = S, **Het** = Fur (**IV.i**); **n** = 1, **X** = O, **Het** = Fur (**V.i**)
n = 1, **X** = S, **Het** = 5-NO_2Fur (**I.ii**); **n** = 1, **X** = SO, **Het** = 5-NO_2Fur (**II.ii**);
n = 1, **X**= SO_2; **Het** = 5-NO_2Fur (**III.ii**); **n** = 2, **X** = S, **Het** = 5-NO_2Fur (**IV.ii**); **n** = 1, **X** = O, **Het** = 5-NO_2Fur (**V.ii**)
n = 1, **X** = S, **Het** = Th (**I.iii**); **n** = 1, **X** = SO, **Het** = Th (**II.iii**);
n = 1, **X** = SO_2, **Het** = Th (**III.iii**); **n**=2, **X** = S, **Het** = Th (**IV.iii**); **n** = 1, **X** = O, **Het** = Th (**V.iii**)
n = 1, **X** = S,**Het** = Py (**I.iv**); **n** = 1, **X** = SO, **Het** = Py (**II.iv**);
n = 1, **X** = SO_2; **Het** = Py (**III.iv**); **n** = 2, **X** = S, **Het** = Py (**IV.iv**); **n** = 1, **X** = O, **Het** = Py (**V.iv**)

n = 1, **X** = S (**1b**); **n** = 1, **X** = SO (**2b**);
n = 1, **X** = SO_2 (**3b**); **n** = 2, **X** = S (**4b**);
n = 1, **X** = O (**5b**)

Figure 1. Retrosynthetic analysis for bis-acylhydrazones (**1b-5b**) from bis-hydrazides and heteroaromatic aldehydes (**Het**)

Agradecimentos/Acknowledgments

CNPq, FAPEMIG (CEX PPM 00281-17), CAPES (Finance Code 001, INCT-MIDAS)

Área: ORG

Synthesis and phytotoxicity of amides derived from carvacrol

Patrícia F. Pinheiro (PQ)*,[1] Alícia C. T. da Silva (IC),[1] Ulisses A. Pereira (PQ),[2] Bruna V. Paes (PG),[3] Bernardo L. Rodrigues (PQ),[3] Milene M. Praça-Fontes (PQ)[4], Angel A. R. Despaigne (PQ)[1].

areciod@ufv.br; patricia.pinheiro@ufv.br

[1]Departament of Chemistry, UFV; [2]Institute of Agricultural Sciences, UFMG; [3]Departament of Chemistry, UFMG; [4]Department of Biology, UFES

Keywords : *Herbicides, Semi-synthetic, Natural Phenol, N-Phenyl-2-phenoxyacetamides.*

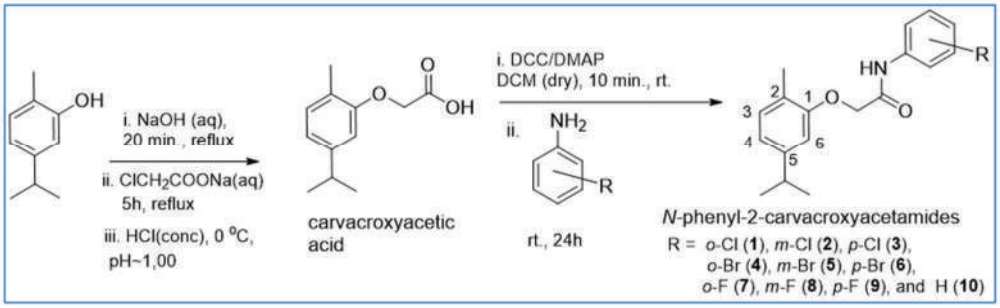
Highlights

New *N*-phenyl-2-carvacroxyacetamides with potential herbicidal activity. Molecules containing chlorine (*ortho*) and bromine (*para)* in the *N*-phenyl group showed significant phytotoxicity in lettuce.

Resumo/Abstract

Herbicides play a crucial role in controlling weeds in crops, ensuring greater quality and productivity. However, their frequent use has caused environmental contamination and health problems in humans[1]. With increasing weed resistance to commercial herbicides, there is a growing need for new herbicides that are less toxic and more selective. One approach is to use natural products or their derivatives, such as semi-synthetic compounds[2].

Phenols, including carvacrol found in essential oils such as oregano and rosemary, are notable for their phytotoxic activity. Therefore, this work aimed to synthesize and evaluate the phytotoxic activity of new amides derived from carvacrol. Initially, carvacroxyacetic acid was synthesized with a structure similar to the commercial herbicide, 2,4-dichlorophenoxyacetic acid (2,4-D), with a yield of 68%[3]. This acid was used in Steglich amidation reactions to produce ten new *N*-phenyl-2-carvacroxyacetamides, with yields ranging from 11% to 60% (Scheme 1). The synthesized compounds were characterized by mass spectrometry, ^{1}H and ^{13}C NMR. Crystals suitable for X-ray diffraction were obtained for the compound containing fluorine (**9**) in the *para* position of the *N*-phenyl group from a chloroform solution (Figure 1).



Scheme 1. Synthetic Route to obtain *N*-phenyl-2-carvacroxyacetamides.

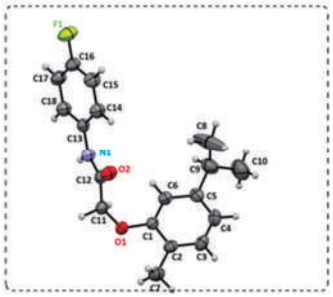


Figure 1. Ortep representation of **9** ($C_{18}H_{20}FNO_2$).

These compounds were then tested *in vitro* against the germination and root growth of *Lactuca sativa* and *Sorghum bicolor* at a concentration of 3 mmol L^{-1} in suspensions containing 1% Tween 80 (w/v). Compounds containing chlorine in the *ortho* position and bromine in the *para* position of the *N*-phenyl group significantly inhibited germination and root growth only of *L. sativa*. Therefore, substituted *N*-phenyl-2-carvacroxyacetamides, considered semi-synthetic compounds because they are derived from natural phenol, can serve as inspiration for new molecules with selective herbicide potential.

References

[1]Kubiak, A.; Wolna-Maruwka, A. et al. *Agronomy*, **12**, 1808 (2022).
[2]Berestetskiy, A. *Plants* **12** (2), 234 (2023).
[3]Alves, T. A.; Pinheiro, P. F. et al. *Ind. Crops Prod.*, **114**, 59 (2018).

Agradecimentos/Acknowledgments

CNPq, FAPEMIG, CAPES, UFV

Área: ORG

Synthesis and structure-activity relationships of novel biphenyl containing tetronamides with cyanobactericidal activity

Júnio Gonçalves Silva (PQ),[1] Amanda Silva de Miranda (PQ),[1] Daiane Szczerbowski (PQ),[1] André M. Oliveira (PQ),[2] Giuseppe Forlani (PQ),[3] Luiz Claudio Almeida Barbosa (PQ)[1]

lcab@outlook.com

[1]Departamento de Química, Instituto de Ciências Exatas, UFMG; [2]Departamento de Controle Ambiental e Química, CEFET-MG (Campus Contagem); [3] Department of Life Science and Biotechnology, University of Ferrara, Ferrara (Italy).

Keywords: *Algaecidal activity, Tetronamides, Hill's reaction, QSAR.*

Highlights

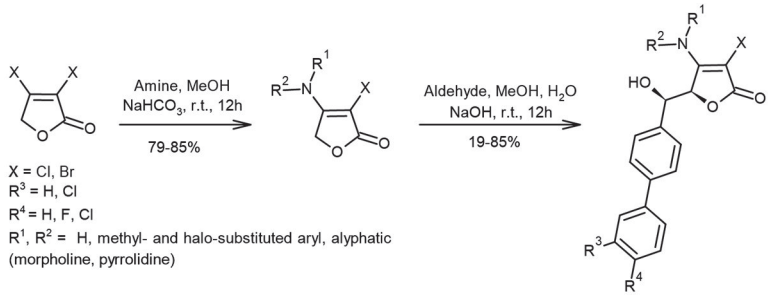
New cyanobactericidal tetronamides were synthesized

Six tetronamides inhibited *S. elongatus* growth with IC_{50} of 2 μM

QSAR studies highlight the relevance of biphenyl and *N*-aryl groups for activity

Abstract

Cyanobacterial blooms have detrimental effects on aquatic ecosystems and water quality. Their control has become more challenging due to climate changes and the discovery of effective and environmentally safe agents to control cyanobacterial bloom is greatly desirable. We report the synthesis of 20 novel tetronamides (Scheme 1), designed from cyanobactericidal biphenyl tetronamides previously identified by our group,[1] and the evaluation of their effect on the growth of cyanobacterium *Synechococcus elongatus*. Six compounds presented excellent cyanobactericidal activity, with an IC_{50} of 2 μM (Figure 1) and showed no significant inhibition of photosynthesis or impact on the growth of plant *Raphanus sativus* at 10 μM. QSAR and PCA studies (Figure 2) suggested the biphenyl, *N*-aryl and NH moieties to be crucial for activity. In summary, our findings expanded the knowledge on the SAR of cyanobactericidal tetronamides and led to the discovery of promising leads for the development of new algaecides.



Scheme 1. Synthesis of tetronamides

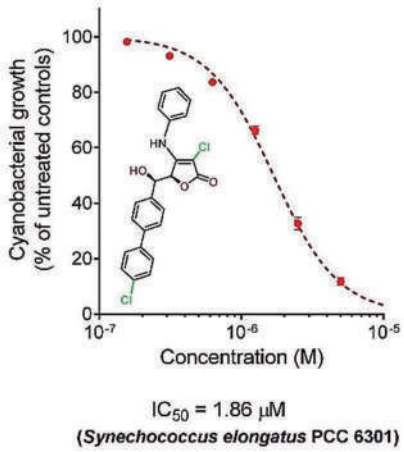


Figure 1. Cyanobactericidal activity of the most active tetronamide

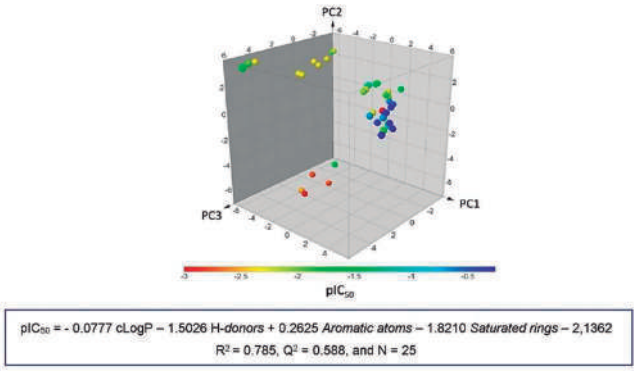


Figure 2. PCA plots and QSAR model

[1] Acosta, J. A.; Karak, M.; Barbosa, L. C.; Boukouvalas, J.; Straforini, A.; Forlani G. Pest Manag Sci. 2020, 76, 379–788

Acknowledgments

CEFET-MG, UFMG, FAPEMIG, CNPq, CAPES, University of Ferrara

Área: ORG

Synthesis of 1,3-diazepine derived of ketenedithioacetals

Ana Júlia F. Souza (IC),[1] Samanta Freitas (IC),[1] Maxwel E. Bille (IC),[1] Diego P. Sangi (PQ) [1]*

anajfs@id.uff.br ; dpsangi@id.uff.br *

[1] *Instituto de Ciências Exatas, Departamento de Química, Universidade Federal Fluminense, Volta Redonda - RJ*

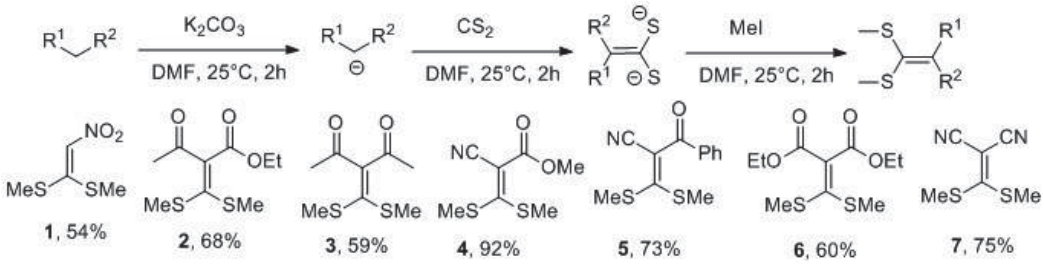
Keywords: 1,3-diazepine derivatives; Ketenedithioacetals; Synthesis.

Highlights

Ketenedithioacetals are interesting building blocks to produce heterocyclic compounds.
Synthesis of 1,3-diazepine derivatives with potencial biological activity by double vinylic substitution of dithioacetals.

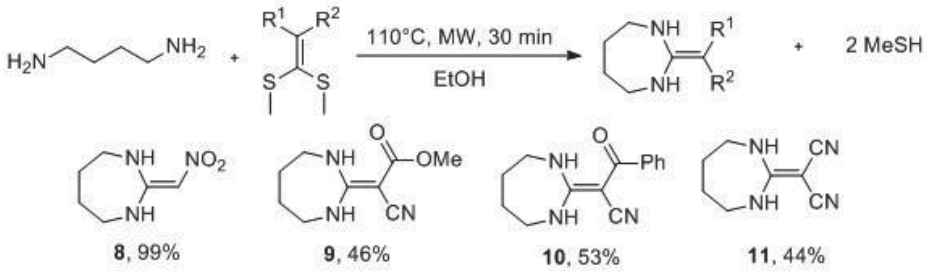
Resumo/Abstract

Diazepines is a privileged class of structure, because they are capable of providing compounds with a lot of biological activities, as antibiotics, anti carcinogenic, antivirals, including activity in cardiovascular disorders.[1] Due to the diazepines importance and potential biological activity, there is great interest in the development of new efficient and cost-effective methods for synthesis of new diazepine compounds.
Ketenedithioacetals have been recognized as useful building blocks in many chemical transformations, including double vinylic substitution of methylsulfanyl groups, in order to produce heterocyclic compounds in a unique step.[2] So, in this work, we decided to investigate their application on the synthesis of 1,3-diazepine derivatives.
Using a three steps one-pot reaction, constituted by i) deprotonation of hydrogen active compounds; ii) addition on carbon disulfide; iii) dimethylation of sulfides, we synthesize seven ketenedithioacetals as indicated in Scheme 1.



Scheme 1. Synthesis of ketenedithioacetals.

The presence of electronegative groups in the compounds **1-7** is an important factor to promote a nucleophilic substitution of methylsulfanyl groups through an elimination-addition mechanism.[2] Using microwave irradiation assisted synthesis, we promote the reaction between ketenedithioacetals and 1,4-diaminebuthane to obtain diazepine compounds by vinylic substituition (Scheme 2).



Scheme 2. Synthesis of diazepine compounds.

Only the reactions using compounds **1**, **4**, **5** e **7** were successful and produced the diazepine derivatives **8-11** that were identified by ^{1}H and ^{13}C NMR. These compounds will be submitted to biological evaluation to elucidate their potential.

1. Maleki A. Tetrahedron Letters. 54, 2055-2059, 2013.
2. Sangi, D. P et al. Brazilian Chemical Society. 25, 887-889, 2014.

Agradecimentos/Acknowledgments

FAPERJ

Área: ORG

Synthesis of 3-alkylseleno-alanine from diselenide and ß-chloro-alanine, evaluation in drug delivery systems and photodynamic therapy

Matheus Rick Gomes (PG),[1] Adriana Passarella Gerola (PQ),[1] Camila F. F. Marin (PQ).[1]

matheus.r.gomes@posgrad.ufsc.br

[1]Departamento de Química, UFSC.

Palavras Chave: Selenium, Amino acid, Surfactant, Photodynamic therapy, Nanoparticle, Drug delivery.

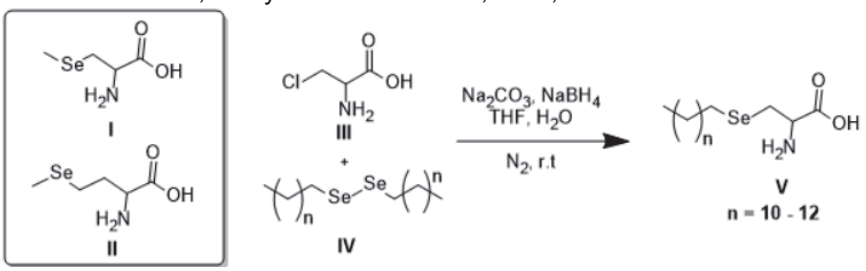
Highlights

Synthesis of 3-alkylseleno-alanine from diselenide and ß-chloro-alanine, evaluation in drug delivery systems and photodynamic therapy This study aims to synthesize a novel surfactant containing selenium within an amino acid segment. The synthesized material will be employed in the development of delivery systems for photodynamic therapy.

Resumo/Abstract

Selenium is an essential metalloid for the human body, present in enzymes in the form of its two amino acids, selenocysteine and selenomethionine (**I** and **II** in Scheme 1). Selenium serves both catalytic and structural functions in enzymes, attracting researchers who have observed increased catalytic power over selenium-containing amino acids in enzyme structures.[1] Furthermore, studies have demonstrated that selenium, whether in organic, inorganic, or selenoprotein forms, exhibits anticarcinogenic or antimutagenic properties, making it a promising candidate for anticancer therapies.[2] When applied in release systems, it is reported that selenium-containing nanoparticles can make treatment more selective for cancer cells and protect drugs against side reactions in the physiological environment. Selenium-containing surfactants are responsive to oxidizing environments due to their hypervalence and reactivity to radicals.[3] This has led us to consider how surfactants with selenium in their structure would act in PDT. We aim to assess whether the presence of selenium in 3-alkylseleno-alanine leads to increased effectiveness of the treatment.

In this scenario, aiming to study a surfactant containing selenium and amino acid in its structure, the synthesis of novel 3-alkylseleno-alanine (**V**) is proposed by cleavage of diselenide (**IV n=10**) to generate nucleophilic species and substitute ß-chloro-alanine (**III**). The molecule was characterized by mass spectrometry and nuclear magnetic resonance spectroscopy, and in the future, analyzes such as DRX, TGA, FTIR and DSC should be carried out.



Scheme 1. Structures of selenocysteine (**I**), selenomethionine (**II**) and synthesis of 3-alkylseleno-alanine (**V**)

[1]Roy, G., Sarma, B.K., Phadnis, P.P. et al. Selenium-containing enzymes in mammals: Chemical perspectives. J Chem Sci 117, 287–303 (2005) [2] Brigelius-Flohé, R. (2008), Selenium Compounds and Selenoproteins in Cancer. Chemistry & Biodiversity, 5: 389-395. [3]Fan Y, Cai S, Xu D, Sun Q, Liu X, Zhang Y, Fang Y. Reversible-Tuning Krafft Temperature of Selenium-Containing Ionic Surfactants by Redox Chemistry. Langmuir. 2020 Apr 7;36(13):3514-3521.

Agradecimentos/Acknowledgments

UNIVERSIDADE FEDERAL DE SANTA CATARINA · CNPq · fapesc · INCT catálise · CAPES

Área: ORG

Synthesis of aromatic imidazole derivatives

Daniel Florêncio Filho (PG), Valéria Belli Riatto (PQ), Mauricio Moraes Victor (PQ)

vriatto@ufba.br; danffilho@live.com

Instituto de Química, Departamento de Química Orgânica, UFBA;

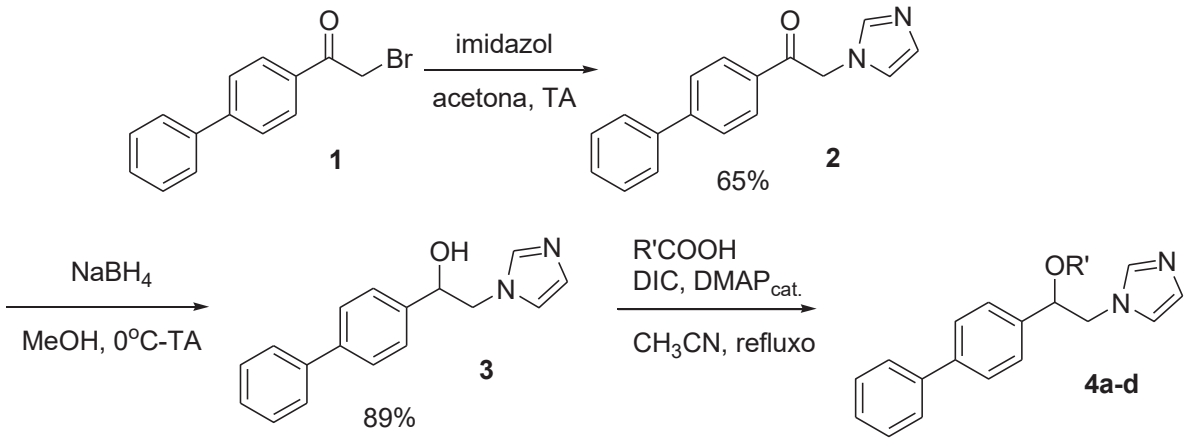
Palavras Chave: *derivados imidazólicos, ésteres polifuncionalizados, bisfenil acetofenona*

Highlights

Synthesis of esters derived from imidazoles, antifungal activity

Resumo/Abstract

A síntese de novos compostos é um processo dinâmico, especialmente quando se trata da funcionalidade complexa dos grupos presentes nas moléculas. Esta dinâmica enriquece os compostos em termos de estabilidade, reatividade e potencial atividade biológica e medicinal, entre outras características importantes.[1] Em particular, os grupos azóis têm se destacado por sua associação com atividades biológicas relevantes, como atividade antibiótica, antifúngica e antiparasitária.[2] Neste trabalho foram preparados ésteres poli funcionalizados, derivados de compostos imidazo-cetônicos (Esquema 1). Estes derivados vêm apresentando promissoras atividades biológicas e estão sendo encaminhados para investigação de suas atividades antifúngicas. Partindo-se da 4'-fenil-bromoacetofenona **1**, foi possível obter o derivado ceto-imidazólico **2**, pela reação com imidazol em acetona, em 65% de rendimento. A cetona **2** foi reduzida na presença de $NaBH_4$, em 89% de rendimento, e o álcool **3** foi submetido à esterificação de Steglich, variando-se a natureza do ácido carboxílico, gerando os ésteres **4a-d**, como apresentado na Tabela 1.



Esquema 1. Síntese dos ésteres **4a-d**

Éster	R´	Rendimento (%)
4a	4-cloro-benzoato	42
4b	oleato	95
4c	valeroato	83
4d	crotonato	33

Tabela 1. Síntese dos ésteres **4a-d**

[1]CHINCHILLA, R. *Molecules* 2022, 27, 825. [2]DOGAN, I.S. et al., *European Journal of Medicinal Chemistry* 2017, 130, 124-138.

Agradecimentos/Acknowledgments

UFBA, CNPq, Cienam, INCT Energia e Ambiente

Área: ORG

Synthesis of benzimidazoles and benzoxazoles derived of ketenedithiacetals

Maxwel E. Bille (IC),[1] Gabriel R. Antunes (IC),[1] Giovanni Y. Silva,[1] Diego P. Sangi (PQ) [1]*

maxwelbille@id.uff.br ; dpsangi@id.uff.br *

[1] *Departamento de Química, Universidade Federal Fluminense*

Keywords: Synthesis; Benzimidazoles; Benzoxazoles; Ketenedithiacetals; Vinylic substitution.

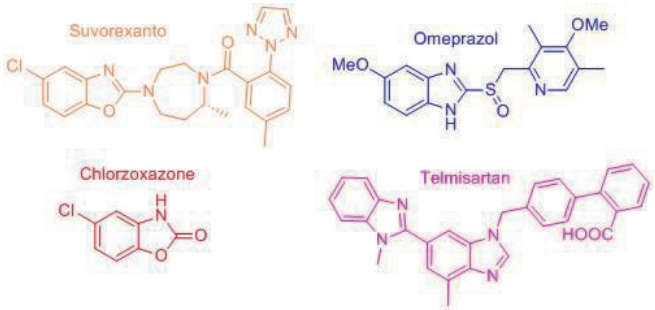
Highlights

Preparation of ketenedithioacetals
Ketenedithioacetals as substrates to double vinylic substitution.
Synthesis of benzoxazoles and benzimidazoles with potential biological activity.

Resumo/Abstract

Benzimidazoles and benzoxazoles are among the oldests N-heterocyclic compounds, consisting of a bicyclic structure formed by the union of a benzene and an imidazole or oxazolidine, respectively.[1,2]
Benzoxazoles and benzimidazoles have many documented biological activity, including drugs such as insomnia modulators (Suvorexant), muscle relaxant (Chlorzoxazone), gastric juice secretion inhibitors (Omeprazole) and antihypertensives (Telmisartan).[1,3]

Figure 1. Benzoxazole and benzimidazoles drugs.



The main method used in the synthesis of benzoxazoles and benzimidazoles is the condensation of o-aminophenols or o-phenylenediamines with carbonyl compounds, however there are limitations in the structures that can be produced. In this work, we investigated the use of kethenedithioacetals as substrates for the synthesis of benzoxazoles and benzimidazole derivatives with potential biological activity.
In the first part of this work we synthesized a series of polarized kethenedithioacetals (**1-8**), for this we used a three-step one-pot reaction: i. Deprotonation of compounds containing active hydrogens; ii. Addition to carbon disulfide; iii. Methylation of sulfides.[4]
The presence of electron-withdrawing groups makes methylsulfanyl groups susceptible to nucleophilic substitution by an addition-elimination mechanism. Therefore, we employed 2-aminophenols and o-phenylenediamine in an attempt to produce benzoxazoles and benzimidazoles derivatives by double vinylic substitution. To our surprise only ketenedithiacetals **1**, **5**, **6** and **8** were able to produce benzimidazoles. and **1**, **5** and **6** benzoxazoles.

Figure 2. Synthesis of kethenedithioacetals.

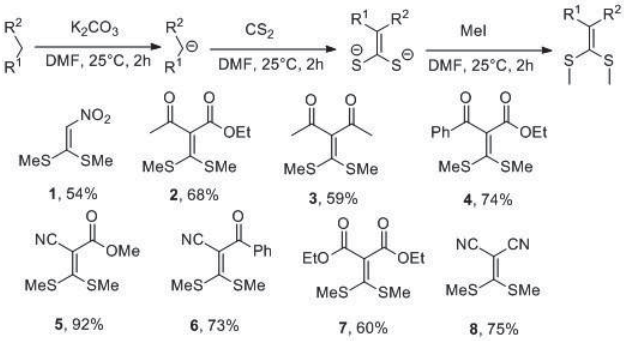
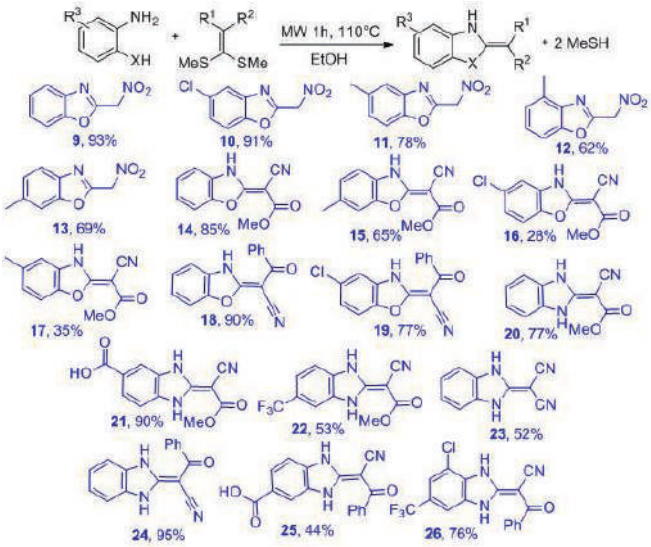


Figure 3. Synthesis of benzoxazoles and benzimidazoles.



Using this method we obtain 11 benzoxazoles and 7 benzimidazoles with moderate to good yields. At this moment, we are studying their potential biological activity.

1. Ebenezes et al. Results in Chemistry, 5, 100925, **2023**. 2. Sangi et al. *Pest Manag. Sci.* **2019**, *75*, 262-269. 3. Wong X. K.; Yeong, K. Y. Chem. Eur. **2021**, *16*, 3237-3262. 4. Thomae et al. Tetrahedron, 65, 2009,10453-10458, **2009**.

Agradecimentos/Acknowledgments

FAPERJ

Área: ORG

Synthesis of bis-amides by Ugi 4-Component Reaction for herbicidal application

Giuliana Pavaneli (PG)[1*], Eron R. Bueno (IC)[1], Emerson A. Abreu (IC)[1], Caroline D. R. M. D'Oca (PQ)[1]

pavaneli@ufpr.br; carolinedoca@ufpr.br

[1]*Grupo de Síntese Orgânica Medicinal e Agroquímica (SOMA), Departamento de Química, UFPR, 19032, Curitiba-PR, 81531-990, Brasil;*

Palavras Chave: *Ugi reaction, amide, multicomponent reaction, synthesis, agrochemistry*

Highlights

Ugi 4-Component Reaction was applied to synthesize bis-amides using the commercial herbicide 2,4-D as the carboxylic acid, diversifying the chain mostly by different isocyanides.

Abstract

Research in new agrochemical alternatives from renewable resources, considering environmental impact minimization, can contribute towards sustainable development, given Brazil's status as one of the largest herbicide consumers, along with China and the United States. The Ugi four-component reaction (U-4CR) stands as a prominent multicomponent reaction (MCR) widely utilized for generating peptide-like α-acyloxycarboxamides[1]. This versatile reaction employs carboxylic acids, amines, aldehydes, and isocyanides, offering a platform for constructing molecular libraries with remarkable flexibility across various reactants. The resultant structurally diverse products hold potential for further modification, yielding complex molecules with diverse biological activities, including pharmaceuticals, agrochemicals, and natural products[2,3]. Notably, this approach facilitates the creation of tunable-properties molecules endowed with enhanced lipophilic characteristics, rendering them pertinent for numerous biological applications[4,5]. Recent investigations within our research group have unveiled the feasibility of enhancing the effectiveness and degradability of commercial herbicide molecules through strategic modifications, such as incorporating fatty chains[6]. Building upon this finding, we have successfully synthesized 12 new bis-amides via U-4CR, utilizing the widely available herbicide 2,4-D (2,4-Dichlorophenoxyacetic acid) as the carboxylic acid. With yields ranging from 41% to 85%, these bis-amides were generated using five different isocyanides, four of which feature fatty chains while one is aromatic. Presently, our primary focus centers on evaluating the herbicidal potential of these compounds against various invasive species that pose significant threats to agriculture in Paraná state.

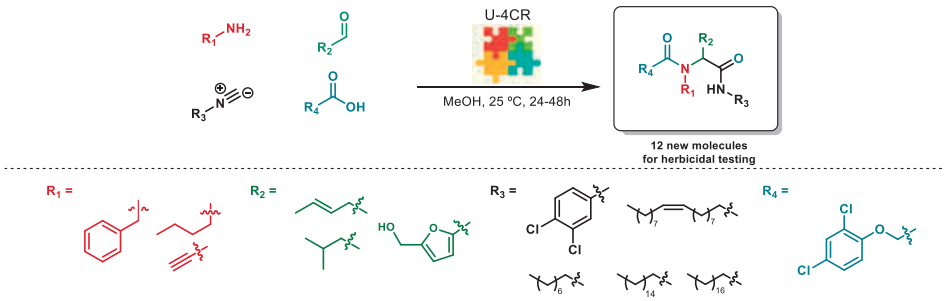


Figure 1. Scheme of the U-4CR synthesis of new bis-amides for herbicidal testing

[1] Wiemann J.; Heller, L.; Csuk, R. Eur. J. Med. Chem., v. 150, p. 176–194, 2018.
[2] A. Váradi; T. C. Palmer; R. Notis Dardashti; S. Majumdar; Molecules, 21, p. 1–22, 2016.
[3] Lamberth, C. Bioorg. Med. Chem., p. 115471, 2020.
[4] D'Oca, C. D. R. M.; Mass, E. B.; Ongaratto, R. F.; et al. New J. Chem., v. 44, n. 31, p. 13230–13239, 2020.
[5] Treptow, T. G. M.; Figueiró, F.; Jandrey, E. H. F.; et al. Eur. J. Med. Chem., v. 95, p. 552–562, 2015.
[6] Porciuncula, L. M.; Teixeira, A. R.; Santos, M. F. C.; D'Oca; et al. Chem. Phys. Lip., 231, 104947, 2020.

Acknowledgments

The authors would like to acknowledge Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES).

Área: ORG

Synthesis of C(2)-arylindole derivatives as potential antileishmanial agents

Daniel G. Rocha (IC),[1] Bruno M. S. Santos (PG),[1] Thais G. Silva (PG),[1] Fernanda G. Finelli (PQ).[1]*

daniel.rguarda@gmail.com; finelli@ippn.ufrj.br

[1]*Instituto de Pesquisas de Produtos Naturais, UFRJ*

Keywords: *photocatalysis, indole, arylation, diazo compounds, antileishmanial activity.*

Highlights

Protozoan diseases pose global health threats, necessitating innovative treatments. Indole nucleus is promising for drug development. This study synthesizes a range of C(2)-arylindoles using photoredox arylation, aiming to evaluate their leishmanicidal activity.

Abstract

Protozoan diseases represent a significant global health threat, particularly impacting vulnerable populations due to inadequate investment in drug discovery, resulting in limited therapeutic options often plagued by low efficacy and toxicity. The emergence of drug-resistant strains further emphasizes the urgent need for innovative treatments. In this context, the indole nucleus has emerged as a promising molecular scaffold for developing novel drug candidates.[1] Recently, thiazolidine-based compounds were tested against of *Leishmania major* promastigotes using *in vitro* primary screen and dose-response assays. Among the most active compounds, the C(2)-arylindole hybrids exhibited the clearest structure-activity relationships, while also displaying low toxicity to human fibroblasts. These compounds were prepared by a classical Fischer synthesis from *N*-arylhydrazines and ketones, limited to four arylindole analogues containing phenyl or phenyls substituted with *p*-Cl, *p*-Br and *p*-NO_2 groups.[2] In this work we present the synthesis of a comprehensive series of C(2)-arylindoles employing a straightforward methodology for the photoredox arylation of indoles, developed by our group, aiming to evaluate their leishmanicidal activity and study possible mechanisms of action involved.

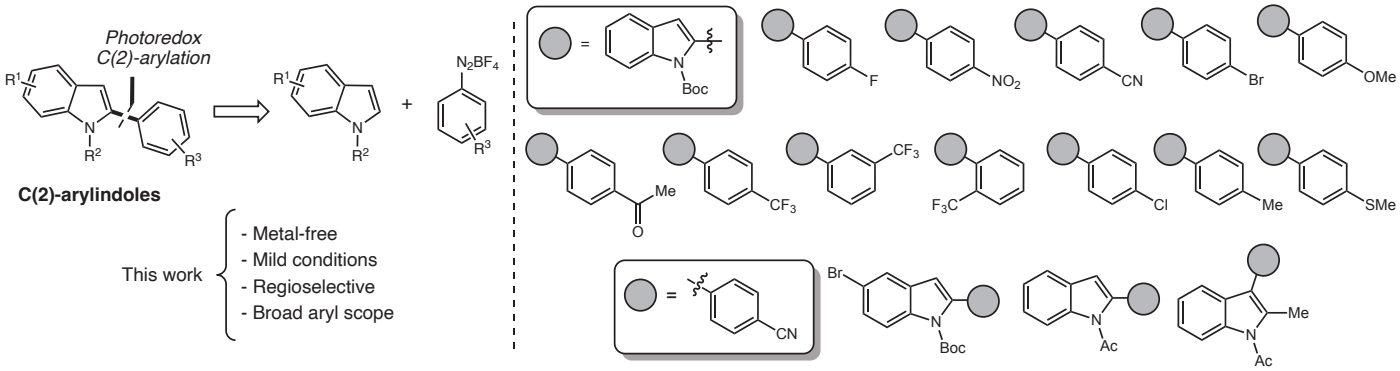


Figure 1. C(2)-arylindoles synthetized in this work.

The intermediates compounds were synthesized from *N*-Boc-indole and the corresponding aryl diazonium salts in DMSO and KH_2PO_4 after 3 hours exposed to a 10 W blue LED at room temperature in 25-89% yields. After some failed attempts, the remotion of Boc group is being carried out through an overnight reaction with $NaBH_4$ in DMSO at 110 ºC. As a perspective, these compounds will be evaluated for their leishmanicidal potential and as inhibitors of Ornithine Decarboxylase, an enzyme which plays an important role in the growth and proliferation of the parasite.

Acknowledgments

CNPq CAPES FAPERJ

[1] Pacheco, P. A. F.; Santos, M. M. M. *Molecules* **2022**, *27*, 319. [2] Schadich et al. *Bioorg. Med. Chem. Lett.* **2020**, *30*, 127616.

Área: ORG

Synthesis of (+)-cannabidiol and evaluation of its anxiolytic-like effect

Kawana Rosa (PG), Marcos Accioly Jr. (PG), Andressa G. Gabriella (PQ), Suzete M. Cerutti (PQ), and Cristiano Raminelli (PQ)*

kawana.rosa@unifesp.br; *raminelli@unifesp.br

Instituto de Ciências Ambientais, Químicas e Farmacêuticas, Universidade Federal de São Paulo, Diadema, SP, Brazil

Keywords: *Cannabinoids; Asymmetric synthesis; ent-CBD; Anxiolytic activity*

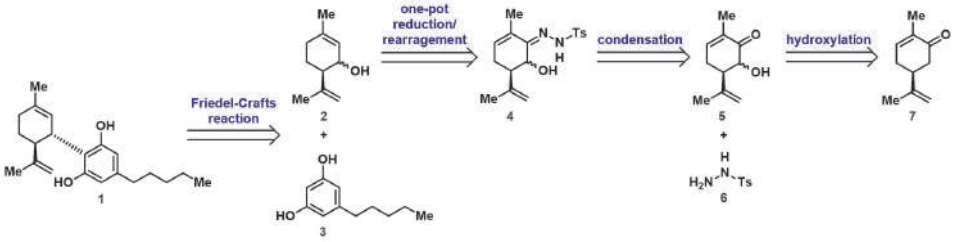
Highlights

ent-CBD was synthesized in 6 steps with an overall yield of 3.2%. A highly diastereoselective Friedel-Crafts reaction was employed. Data suggest an anxiolytic-like effect of *ent*-CBD in mice.

Resumo/Abstract

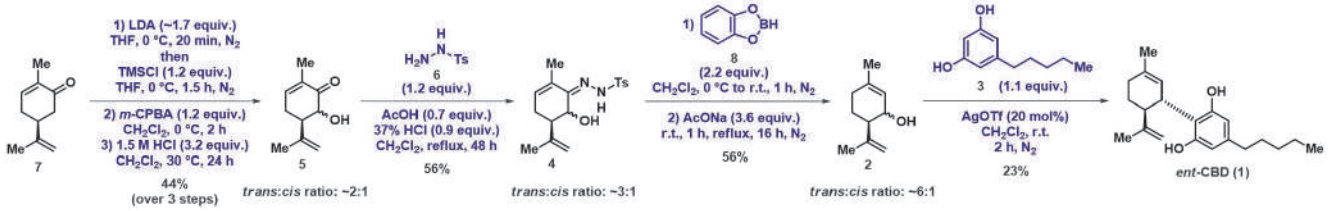
(-)-Cannabidiol (CBD) is a terpenophenolic phytocannabinoid, which was recently approved for the treatment of epileptic seizures associated with the Lennox-Gastaut and Dravet syndromes.[1] In this work, we accomplished the synthesis of (+)-cannabidiol (*ent*-CBD, **1**), the non-natural enantiomer of CBD, which has been involved in a limited number of pharmacological studies, using (*S*)-(+)-carvone (**7**) as starting material,[2] through a highly diastereoselective Friedel-Crafts reaction,[3] according to the retrosynthetic analysis outlined in **Scheme 1**.

Scheme 1. Retrosynthetic analysis for (+)-cannabidiol (**1**).



ent-CBD (**1**) was synthetized by converting (*S*)-(+)-carvone (**7**) into the diastereoisomeric mixture **5**, which was subjected to a condensation with *p*-tosyl hydrazide (**6**), allowing the formation of **4**. One-pot reduction/rearrangement of **4** was promoted using catecholborane (**8**) to give the diastereoisomeric mixture **2**,[2] which was allowed to react with olivetol (**3**) using 20 mol% of AgOTf,[3] affording (+)-cannabidiol (**1**) (**Scheme 2**).

Scheme 2. Synthesis of (+)-cannabidiol (**1**).



ent-CBD (**1**) was synthesized in 6 steps with an overall yield of 3.2%, employing in the key step a AgOTf-catalyzed Friedel-Crafts reaction.

Pharmacological studies using the plus maze discriminative avoidance task (PM-DAT) as a model to evaluate both anxiolytic-like and memory effects were carried out with young adult and aged male mice.[4] Our data suggest that *ent*-CBD (**1**) presents an anxiolytic-like effect in male mice at a dose of 20 mg/kg (**Figure 1**).

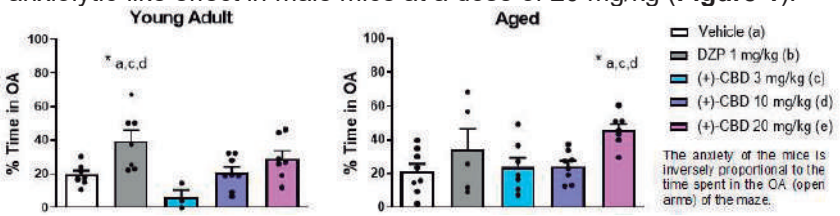


Figure 1. Anxiolytic-like effect of (+)-cannabidiol (**1**) in male mice.

[1] Morales, P.; Reggio, P. H.; Jagerovic, N. *Front. Pharmacol.* **2017**, *8*, 422.
[2] Golliher, A. E.; Tenori, A. J.; Dimauro, N. O.; Mairata, N. R.; Holguin, F. O.; Maio, W. *Tetrahedron Lett.* **2021**, *67*, 152891.
[3] Accioly Jr., M. Dissertation (Master of Science), PPGQ-CTS (UNIFESP), **2023**.
[4] Solani, A., Kubota, S. M., Corrêa, M. F., Cerutti, S. M., Fernandes, J. P. F. *Behav. Brain Res.* **2020**, *377*, 112230.

Acknowledgments

We are grateful to FAPESP and CNPq for the financial support. K.R. thanks CAPES for the scholarship.

Área: ORG

Synthesis of corrosion inhibitors heterocycles

Giovanni Y. Silva (IC),[1] Gabriel R. Antunes (IC),[1] Ana J. F. Souza (IC),[1] Elivelton A. Ferreira (PQ),[1] Diego P. Sangi (PQ)[1]*

giovanniyuri@id.uff.br ; dpsangi@id.uff.br *

[1] *Departamento de Química, Universidade Federal Fluminense*

Keywords: Synthesis; Heterocycles; Corrosion inhibitors.

Highlights

Preparation of 1,1-bis(methylsulfanyl)-2-nitroethylene.
1,1-bis(methylsulfanyl)-2-nitroethylene as substrates to vinylic substitution.
Synthesis of heterocycles water soluble corrosion inhibitors.

Resumo/Abstract

Corrosion is a natural phenomenon that has economic consequences. Steel structures can suffer from severe damage, due to electrochemical reactions caused by the environment.[1,2]

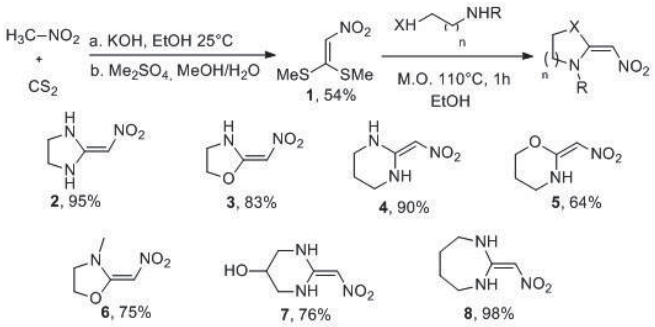
Most of commercially available inhibitors are toxic compounds, therefore, it's necessary to replace them with more environmentally friendly inhibitors.[1,2]

In many industries, hydrochloric or sulfuric acids are used at concentrations up to 20% in pickling processes to remove scale with organic inhibitors being used to prevent corrosion of steel.[1]

Most efficient inhibitors are heterocyclic organic compounds containing nitrogen, oxygen, or sulfur atoms, with conjugate p double or triple bonds that increase the electron density on the molecule and can donate electron pairs to facilitate adsorption on the metal surface.

Ketenedithioacetals have widespread use in organic chemistry, being important building blocks to obtain heterocyclic scaffolds.[3] In this work, we prepare 1,1-bis-methylsulfanyl-2-nitroethylene and used it as substrates to double vinylic substitution, in order to produce some water solubles heterocycles and test them as corrosion inhibitors.

Figure 1. Synthesis of heterocycles by double vinylic substitution.



Dithioacetal **1** was prepared deprotoneting nitromethane using potassium hydroxide, to produce a carbanion that is able to attack carbon disulfide producing a salt that was isolated by filtration. In a second step we alkylated the salt using dimethyl sulfate, resulting in 1,1-bis-methylsulfanyl-2-nitroethylene with 54% of yields.[4]

The compound **1** was employed as substrate to double vinylic substitution using ethylenediamine, 2-aminoethanol, 1,3-aminopropane, 3-aminopropanol and 1,4-diaminobutane as nucleophiles, in order to produce respectively 2-nitromethylene imidazolidine, oxazolidine, hexahydropyrimidine, oxazinane and diazepine with moderate to good yields.[4]

All the compounds **2-8** showed good water solubility, facilitating corrosion tests. For the corrosion analyses, The working electrode was a piece of SAE 1020 steel with dimensions of 2.5 2.5 0.13 cm. The surfaces of the SAE 1008 and SAE 1020 carbon steels were polished with different grade emery papers (200, 400, 600, 800, and 1200), followed by rinsing with deionized (Milli-Q) water. For each steel sample, a geometrical area of 1 cm2, delimited by an O-ring, was exposed to the electrolytes.

The steels were exposed to the electrolytes (aqueous solutions containing 5.4 and 2.7 mol L-1 of the acids HCl and H_2SO_4, respectively) and different inhibitors (compounds **2-8**). All the synthesized heterocyclic compounds showed corrosiion inhibitory activity proved by weight loss of the steel and electrochemical measurements (Non published data and published in references 1 and 2).

In conclusion, using the double vinylic substitution on 1,1-bis-methylsulfanyl-2-nitroethylene, we synthesize seven heterocycles of the five to seven members that are water soluble and have the ability to inhibit corrosion of the steel.

1. Silvério et al. Materials Research. 2024, 27:e20230197.
2. Silva et al. Chem. Eng. Commun, 2021, 1940154.
3. Huang et al. *Tetrahedron Lett*. 2020, *61*, 151363.
4. Sangi et al. J. Braz. Chem. Soc., 2014, 25(5), 887-889.

Agradecimentos/Acknowledgments

FAPERJ

Área: ORG

Synthesis of Coumarin-Naphthoquinones Hybrids Triazole Linker-based with Potential Pharmacological Action in the Treatment of Neglected Diseases

Robson C. da Silva (PG),[1] Douglas C. A. Pinto (PQ),[1] Gustavo S. G. de Carvalho (PQ),[1] Vítor F. Ferreira (PQ),[2] Luana da S. M. Forezi (PQ),[1] Fernando de C. da Silva (PQ)[1]

robsoncs@id.uff.br

[1] Laboratório de Síntese Orgânica Aplicada, Universidade Federal Fluminense, Instituto de Química, Niterói-RJ, 24210-141, Brazil.
[2] Faculdade de Farmácia, Universidade Federal Fluminense, Niterói-RJ, 24241-000, Brazil.

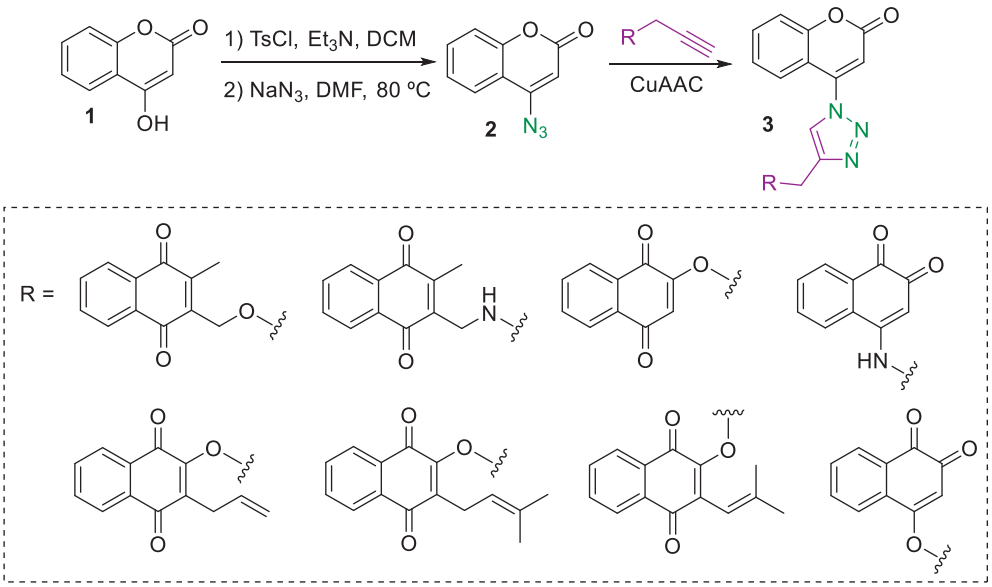
Keywords: *Coumarins, Naphthoquinone, Click Chemistry, Heterocycle*.

Highlights

Coumarins are a privileged building block for obtaining new drug candidates. Synthesis of coumarin-naphthoquinone hybrids and evaluation against neglected diseases such as Leishmaniasis, Chagas Disease, Yellow Fever, Dengue, and Tuberculosis.

Abstract

Coumarins have a remarkable ability to exert non-covalent interactions in protein structures, enzymes, and receptors of living organisms, providing them with a broad spectrum of biological activities.[1] Naphthoquinones exhibit high pharmacophoric potential for use in the treatment of various diseases.[2] The ability of 1,2,3-triazole rings to engage in hydrogen bonding and dipole interactions enhances solubility and binding to biomolecular targets.[3] Thus, this work involves the synthesis of coumarin-naphthoquinones hybrids triazole Linker-based **3** through CuAAC between azide **2** and different alkynes (Scheme 1). After the complete characterization of all hybrids, they will undergo evaluation to assess their biological activities.



Scheme **1.** Synthesis of coumarin-naphthoquinone hybrids triazole linker-based.

[1] *Chemical Biology & Drug Design* **2018**, *92*, 1888-1898; [2] *Current Organic Synthesis* **2016**, *13*, 334-371; [3] *Topics in Heterocyclic Chemistry* **2014**, 40, 117-165.

Acknowledgments

CAPES, CNPq and FAPERJ

Área: ORG

Synthesis of Dialkynyl-*N*-(het)arylpyrroles with promising photophysical properties

João Pedro S. S. C. Thomaz (IC),[1] Thiago J. Peglow (PQ),[1] Patrick C. Nobre (PQ),[1] Vanessa Nascimento (PQ)[1*]

jsenna@id.uff.br; nascimentovanessa@id.uff.br.

[1]*Laboratório SupraSelen, Departamento de Química Orgânica, Universidade Federal Fluminense - UFF.*

Keywords: *Cross-coupling reactions, chromophores, photophysics, heterocyclic compounds.*

Highlights

In this study we developed the synthesis of new (alkynyl)arylpyrrole-based fluorophores bearing different combinations of donor-acceptor moieties.

Abstract

Push-pull chromophores are known as substances formed by a conjugated π-system, which are able to absorb wide bands in a spectrum attributed to intramolecular charge transfer between electrons.[1] Since photophysical properties are linked to these conjugated system, some applications are achievable in organic photovoltaic (OPV) cells.[1] Plus, the presence of heteroaromatic rings frequently brings interesting properties to the overall system, including elevated polarizability, intense charge transfer upon electronic excitation, chemical inertness, and thermal stability.These rings also serve as donor or acceptor moieties due to the presence of one or more heteroatoms.[2] The synthesis of dialkynyl-*N*-(het)arylpyrroles, proposed in this work, occurs through a three-step process.[3] In step 1, a bromination reaction was promoted via electrophilic aromatic substitution (S_EAr) using amino(het)aryl derivatives **1a-c**, *N*-bromosuccinimide (NBS) and acetonitrile as solvent. In step 2, derivatives **2a-c** were subjected to a Clauson-Kaas reaction using 2,5-dimethoxytetrahydrofuran, under reflux temperature (118 °C) in acetic acid. Finally, in step 3, derivates **3a-c** will undergo a Sonogashira-type cross-coupling reaction Thus, the reaction was conducted in the presence of the corresponding (het)arylpyrrolyl bromides **3** (2.0 mmol) and alkynes **4a-c**, $PdCl_2(PPh_3)_2$ and CuI with triphenylphosphine as a catalytic system, into a mixture of diethylamine and dimethylformamide as solvent. The reaction was performed under microwave irradiation at 120 °C for 30 minutes giving yields of 53-77% (Table 1).

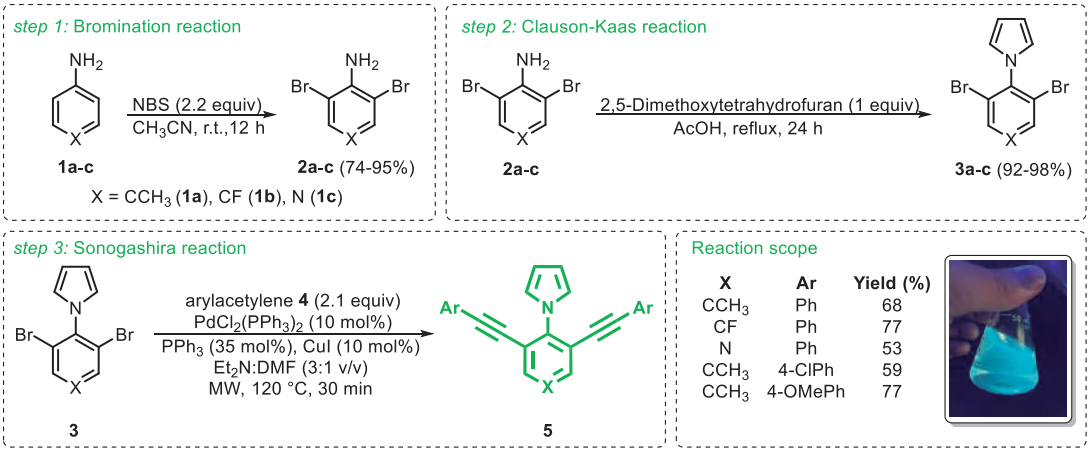


Table 1. Steps for the synthesis of key compounds **5**.

In conclusion, we carried out the synthesis of dialkynyl-*N*-(het)arylpyrroles, through three easy-to-execute reaction steps with good yields. Using the method described, we synthesized five derivatives of interest, including these two that are unpublished in the literature. The compounds were sent for photophysical evaluation with partner groups and the results are promising. Furthermore, new synthetic applications for these intermediates are being developed in the laboratory.

Acknowledgments

UFF, CNPq, CAPES, FAPERJ.

[1] (a) P. Pierrat, et al. *Eur. J. Org. Chem.* **2019**, 4341-4348; (b) K. Do, et al. *Sol. Energy Mater. Sol. Cells* **2013**, *115*, 52-57; (c) K. Do, et al. *Dyes Pigm.* **2015**, *120*, 126-135; (d) Y. Lin, et al. *Chem. Soc. Rev.* **2012**, *41*, 4245-4272.

[2] T.-D. Kim, K.-S. Lee, *Macromol. Rapid Commun.* **2015**, *36*, 943-958.

[3] P. Pierrat, S. Hesse, C. Cebrián, P. C. Gros, *Org. Biomol. Chem.* **2017**, *15*, 8568-8575.

Área: ORG

Synthesis of fluorophores BODIPY for DSSC application

Nicole A. Camargo (IC),[1] Richard S. Araujo (IC),[1] Bruna H. Cortes (IC),[1] Samara R. Amorim (IC),[1] Geovanna D. O. Rafael (IC),[1] Lorena B. Braz (IC),[1] Paula Romanhi (PG),[2] Luana A. Machado (PQ),[3] Leandro F. Pedrosa (PQ).[1,2*]

nicoleandrade@id.uff.br; leandropedrosa@id.uff.br

[1] Instituto de Ciências Exatas, Departamento de Química, UFF; [2] Programa de Pós-Graduação em Química, Instituto de Química, UFF; [3] Instituto de Ciências Exatas, Departamento de Química, UFMG.

Palavras Chave: *BODIPY, Boron-dipyrromethene, DSSC, Fluorophores.*

Highlights

Synthesis of metal-free organic photosensitizer, with a BODIPY moiety and a malononitrile acting as an anchoring group for application in solar cells.

Resumo/Abstract

Dye-sensitized solar cells (DSSCs) offer a compelling alternative to traditional semiconductor-based solar cells due to limitations in widely used constructs. With the aim of replacing metal-complex dyes like ruthenium dye, various chromophores, including boron-dipyrromethene (BODIPY) derivatives, stand out as promising photosensitizers in DSSCs.[1] Research indicates their efficacy as light absorbers for converting solar energy into electricity. In recent years, our research group has concentrated on developing fluorophores based on BODIPY, a versatile compound widely utilized in diverse research areas such as chemosensors, photosensitizers and OLEDs.[2] In this study, we employed straightforward synthetic methods to acquire formylated BODIPY dyes, by selective oxidation with PCC of α-methyl,[3] serving as intermediates for the introduction of malononitrile, as an anchor group, through Knoevenagel condensation reaction [4] (*Figure 1*). The photophysical, electrochemical and photovoltaic properties, as well as electrochemical impedance are being systematically investigated.

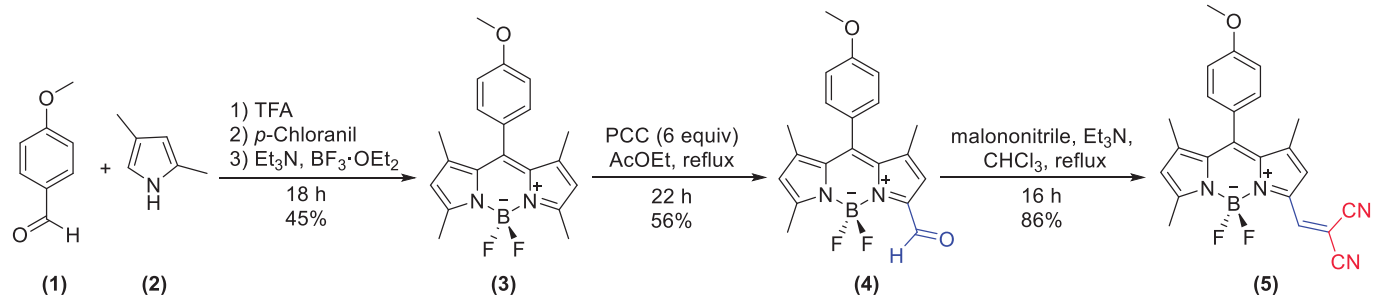


Figure 1. Synthetic route to the BODIPY dyes.

Agradecimentos/Acknowledgments

CAPES, CNPq, FAPERJ, UFF.

[1] Rahman, S.; et al. *RSC Adv.*, **2023**, *13*, 19508.
[2] Machado, L. A.; et al. *J. Fluor. Chem.* **2019**, *220*, 9.
[3] Ramos-Torres, Á.; et al. *Org. Lett.* **2019**, *21*, 4563.
[4] Sritharan, S. R.; et al. *RSC Adv.*, **2017**, *7*, 8922.

Área: ORG

Synthesis of Ibuprofen Using Enabling Technologies: Electrosynthesis and Photocatalysis under Continuous Flow Conditions

Maria F. A. Magalhães (PG),[1] Guilherme M. Martins (PQ),[1] Timothy J. Brocksom (PQ),[1] Kleber T. de Oliveira (PQ).[1*]

mmagalhaes@estudante.ufscar.br; kleber.oliveira@ufscar.br

[1]*Departament of Chemistry, Federal University of Sao Carlos (UFSCar);*

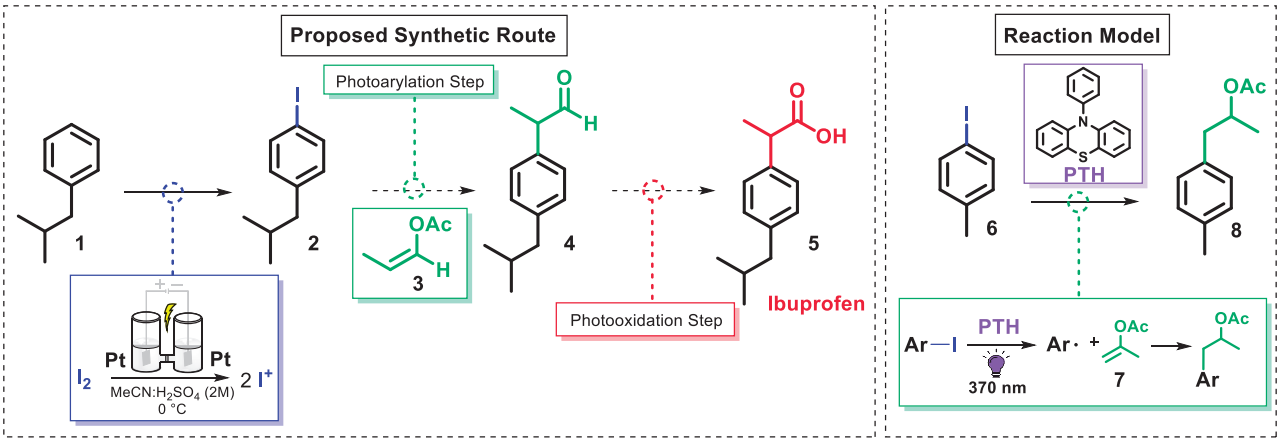
Keywords: Ibuprofen, Electrosynthesis, Photoarylation, Photooxidation, Flow Chemistry.

Highlights

A new synthetic route to obtain Ibuprofen has been developed using advanced technologies such as electrosynthesis and continuous flow chemistry. The process involves a highly regioselective iodination step utilizing I^+ ions generated at the anode of a divided cell,[1] followed by photoarylation[2,3] and photooxidation.[4]

Resumo/Abstract

Previsously, *p*-iodoisobutylbenzene (**2**) was obtained through the iodination of isobutylbenzene (**1**) by the electrophile I^+ generated at the anode of a divided cell (first step, scheme 1). This batch reaction yielded compound **2** in a 90% yield with a 7:1:92 *o:m:p* ratio. The reaction was also explored under continuous flow conditions, resulting in a 74% yield of product **2** and an 8:5:87 *o:m:p* ratio.



Scheme 1: Synthesis of Ibuprofen using enabling technologies.

Herein, in the photoarylation step, the conditions were first evaluated using a reaction model and commercially available reagents, iodotoluene (**6**) and isopropenyl acetate (**7**). 10-phenylfenotiazine (PTH) was used as photocatalyst for generating the aryl radical that can add to the enol acetate **7,** thus yielding the product **8** in 49-54% yield. The synthesis of enol acetate **3** has been successfully performed and will be applied under optimized conditions for aldehyde **4** in both batch and flow conditions. Subsequently, the final reaction step (photooxidation) will be performed to produce Ibuprofen (**5**).

Agradecimentos/Acknowledgments

The authors would like to thank the São Paulo Research Foundation FAPESP (grant numbers: 2023/04020-8 (K.T.O.), 2022/00074-3 (G.M.M.) and 2022/10687-2 (M.F.A.M.)) as well as the Conselho Nacional de Pesquisa - CNPq (K.T.O. research fellowship 303890/2019-3) and CAPES - Financial Code 001.

1 K. Kataoka, Y. Hagiwara, K. Midorikawa, S. Suga and J. Yoshida, *Org. Process Res. Dev.*, 2008, **12**, 1130–1136.

2 A. A. N. de Souza, N. S. Silva, A. V. Müller, A. S. Polo, T. J. Brocksom and K. T. de Oliveira, *J. Org. Chem.*, 2018, **83**, 15077–15086.

3 A. J. Boyington, C. P. Seath, A. M. Zearfoss, Z. Xu and N. T. Jui, *J. Am. Chem. Soc.*, 2019, **141**, 4147–4153.

4 K. T. de Oliveira, L. Z. Miller and D. T. McQuade, *RSC Adv.*, 2016, **6**, 12717–12725.

Área: ORG

Synthesis of *N*-phenyl-2-phenoxyacetamides from Eugenol with Anti-inflammatory Potential

Vitor Emanuel M. de A. Giostri (IC),[1] Patricia Fontes Pinheiro (PQ).[1]*

uranium@duck.com; patricia.pinheiro@ufv.br

[1]*Department of Chemistry, UFV.*

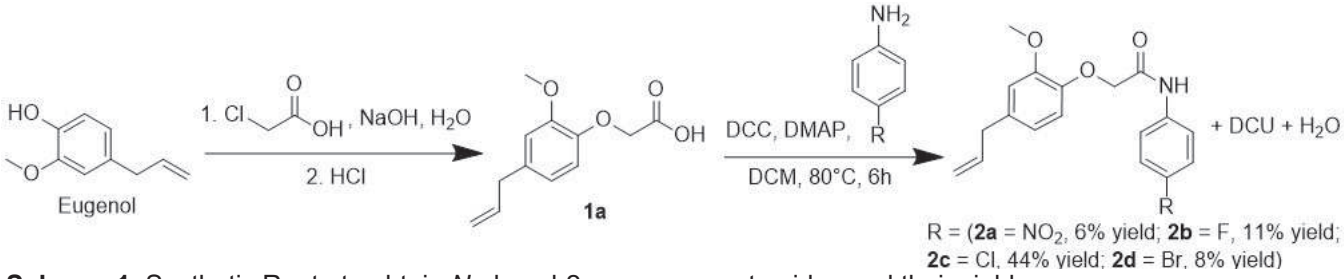
Keywords: Eugenol, Anti-inflammatory, PPARγ Agonist, Synthesis, Steglich Amidation.

Highlights

►*N*-Phenyl-2-eugenoxyacetamides synthesized by Steglich amidation. ►Steglich amidation at a higher temperature and shorter time than usual. ►Three new compounds may have anti-inflammatory activity.

Resumo/Abstract

Eugenol, the main component of Clove essential oil, is a natural phenol with a plethora of biological properties[1]. This compound has been studied for its anti-inflammatory activities[2]. Literature reports indicate that *N*-phenyl-2-phenoxyacetamides derived from eugenol possess the innate structure of PPARγ agonists, with PPARγ being a nuclear hormone receptor shown to be crucial for inflammation control[3]. Therefore, these substances are deemed relevant for developing novel anti-inflammatory agents. As such, this study is aimed on synthesizing *N*-phenyl-2-phenoxyacetamides for evaluation of anti-inflammatory activity in subsequent research stages. The synthesis of *N*-phenyl-2-phenoxyacetamides was conducted in two steps (Scheme 1). Initially, compound **1a** was synthesized via Williamson ether synthesis. The reaction was refluxed for 24h under alkaline conditions. Then, it was acidified until compound **1a** precipitated. The solid was subsequently purified using chemically active liquid-liquid extraction, with a yield of 36%. For the amidation step, various synthetic routes were explored, but the final products were only detected through Steglich amidation. Initially, the Steglich reaction was conducted at room temperature, however compound **2a** was not detected after 24h. To increase the reaction rate, a higher temperature test was performed. Compounds **2a-2d** were then synthesized at 80°C and 6h in a sealed tube using the DCC (*N*,*N'*-dicyclohexylcarbodiimide)/ DMAP (4-dimethylaminopyridine) method (Scheme 1). The DCU (*N*,*N'*-dicyclohexylurea) byproduct was separated by filtration, and the excess aniline was protonated using PTSA (*p*-toluenesulfonic acid) to facilitate purification. Products **2a-2d** were purified via column chromatography utilizing silica gel stationary phase and hexane:ethyl acetate mixture (1:1, v/v) mobile phase. All synthesized compounds were characterized by mass spectrometry, ^{1}H and ^{13}C NMR, COSY, and HSQC. The progress of the reactions was monitored by gas chromatography coupled with mass spectrometry (GC-MS) and the synthesis's second step is being optimized.



Scheme 1: Synthetic Route to obtain *N*-phenyl-2-eugenoxyacetamides and their yields.

Compounds **2b**, **2c**, and **2d** are novel. While the synthesis of compound **2a,** which has exhibited anti-inflammatory activity[3], has been previously reported using a different route and reagents with more toxicity. The new molecules were synthesized in a two-step process and hold promise for developing novel anti-inflammatory agents.

References: [1]Ulanowska, M.; Olas, B. *Int. J. Mol. Sci.* **2021**, 22, 3671. [2]Sushma, D.; Chauhan, S. *et al. Inflammopharmacol* **2023**. [3]Anjum, N. F.; Shanmugarajan, D. *et al. Molecules* **2023**, 28, 3899.

Agradecimentos/Acknowledgments

FAPEMIG, CNPq / PIBIC, CAPES, UFV/DEQ.

Área: ORG

Synthesis of monoketone curcuminoids for biological evaluation

Gabriela Fernanda Nascimento da Silva (IC)[1*], Mirela Inês de Sairre (PQ)[1]

nascimento.gabriela@aluno.ufabc.edu.br; mirela.sairre@ufabc.edu.br

[1]Center for Natural and Human Sciences, Universidade Federal do ABC, Avenida dos Estados, 5001, 09210-170 Santo André, SP, Brazil.

Keywords: Condensation, Curcumin, Niobium.

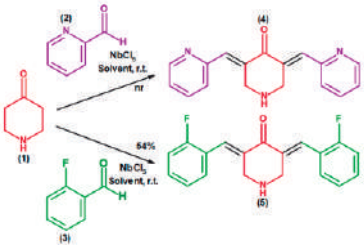
Highlights

Niobium pentachloride ($NbCl_5$) was used as a heterogeneous catalyst for the synthesis of monoketone curcuminoids from Claisen-Schmidt condensation in an acid medium.

Abstract

Curcumin is the most abundant and biologically active compound present in the rhizomes of *Curcuma longa L*. However, it is poorly bioavailable and has low chemical stability under physiological conditions, in addition to being a photosensitive compound. Monoketone curcuminoids can exhibit biological activities while maintaining structural characteristics essential for activities with simpler and more stable structures.[1] According to schemes 1 and 2, monoketone curcuminoids **4**, **5**, **9** and **10** were prepared by Claisen-Schmidt condensation under acidic conditions. The use of a niobium acid compound (niobium pentachloride - $NbCl_5$) as a reaction promoter has proven effective in the reaction tests carried out so far. $NbCl_5$ spontaneously releases hydrochloric acid into the reaction medium and favors the reaction by increasing the reactivity of the aldehyde due to its action as a Lewis acid.

Scheme 1 - Synthesis of curcuminoids 4 and 5.



Scheme 2 - Synthesis of curcuminoids 9 and 10.

The synthetic methodology using $NbCl_5$ in acetic acid at room temperature (r.t.) has presented difficulties in the isolation step of the pure product. The product **5** (EF24) was obtained in the form of acetic acid salt. Treatment of the precipitate formed in the reaction with a solution of potassium carbonate and acetone allowed the formation of the free base as a product, which was obtained in 54% yield. EF24 showed potent schistosomicidal activity *in vitro* that varies according to parasite isolate.[3] Table 1 shows some reaction tests for the synthesis of compound **9**. After the reaction time, the product isolation procedure was varied, resulting in a 66% yield in entry 3. Compound **10** was obtained in 64% yield by applying the same procedure studied for the synthesis of compound **9**. The development of synthetic methodology has shown promise for the preparation of new monoketone curcuminoids.

Table 1 - Reaction tests for the synthesis of compound 9.

Entry	Solvent	Reaction condition	Procedure	Yield*
1	Acetic Acid	1.5 eq. Aldehyde, 6 h	Crude product was vacuum filtered and washed with cold ethanol; the removal of the niobium compound was carried out by silica gel filtration using ethyl acetate as eluent.	43%
2	Acetic Acid	1.5 eq. Aldehyde, 6 h.	The solvent was removed in a rotary evaporator; the removal of the niobium compound was carried out by silica gel filtration using ethyl acetate as eluent; the solid product was recrystallized using ethanol and water (98:2 ratio).	37%
3	Acetic Acid	1.5 eq. Aldehyde, 6 h.	Crude product was filtered using a sintered plate funnel system, infusoria mixture and filter paper; the removal of the niobium compound was carried out by silica gel filtration using ethyl acetate as eluent.	66%

* isolated product

[1] Vieira, T.M. et al. *Future Pharmacol.* **2024**, *4*, 54-76; [2] Arpini, B. H. et al. *Curr.Org. Synthesis*, **2015**, 12, 570-583; [3] Magalhães, L. G.; Sairre, M. I. et al. *Chemico-Biological Interactions* **2022**, *368*, 110191.

Acknowledgments

FAPESP, CNPq, CAPES, CEM-UFABC, CBMM.

Área: ORG

Synthesis of new 1,2,3-triazoles glycoconjugates via enaminones

Eduardo N. C. Junior (PG),[1] Camilla D. Buarque (PQ),[2] Sabrina B. Ferreira (PQ).[1*]

eduardonunes@pos.iq.ufrj.br; camilla.buarque@puc-rio.br; sabrinab@iq.ufrj.br

[1]Universidade Federal do Rio de Janeiro, Instituto de Química, Laboratório de Síntese Orgânica e prospecção Biológica (LaSOPB), Rio de Janeiro, RJ, Brasil; [2]Pontifícia Universidade Católica do Rio de Janeiro, Departamento de Química Laboratório de Síntese Orgânica (LabSint), Rio de Janeiro, RJ, Brasil.

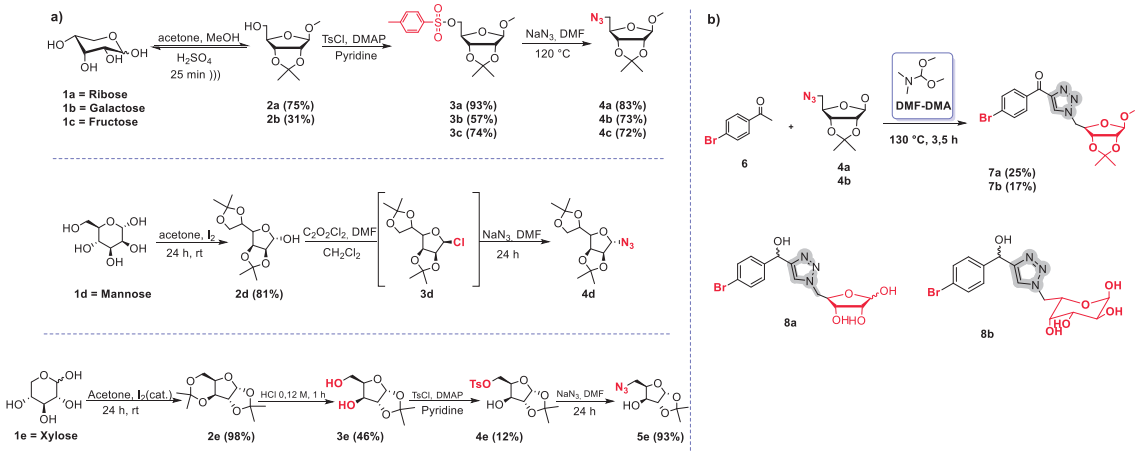
Palavras-Chave: *1,3-dipolar cycloaddition, 1,2,3-triazole, Carbohydrate, Glycoconjugate.*

Highlights

1,3-dipolar cycloaddition reaction between enaminones and azides derived from carbohydrates.

Abstract

1,2,3-triazoles are an important scaffold in medicinal chemistry with potential pharmacologic activities.1 Considering previous works at LaSOPB - UFRJ involving carbohydrates[2] and Labsint - PUC-Rio, focusing on 1,3-dipolar cycloaddition to synthesize bioactive triazoles, [3,4] our study starts by generating azides from carbohydrates **1a-e**. This involves a series of steps including hydroxyl group protection and conversion to improved leaving groups, resulting in impressive azide yields of 72% to 93%, as shown in Scheme 1a. Subsequently, employing a simplified methodology, we synthesized 1,2,3-triazoles **7a** and **7b** through a one-pot 1,3-dipolar cycloaddition reaction, yielding purified products in 17% and 25% yields, respectively, as depicted in Scheme 1b. This streamlined synthesis not only enhances triazole glycoconjugate production efficiency but also opens promising avenues for exploring their pharmacological properties and therapeutic potential.



Scheme 1: (a) Synthesis of azides derived from carbohydrates; **(b)** Synthesis of 1,2,3-triazole glycoconjugates **7a** and **7b** and final product **8a** and **8b**.

This work presents a simpler methodology that opens possibilities to obtain 1,2,3-triazoles. Ongoing efforts are focused on optimizing conditions to enhance results, with compounds **7c-e** currently undergoing purification. Future directions involve reducing compounds **7a-e** and conducting pharmacological evaluations to elucidate their potential therapeutic applications.

1. Bakulev, V. A., Beryozkina, T., Thomas, J., Dehaen, W. *European J. Org. Chem.* **2018**, 262.
2. Evangelista, T. C. S. et al. *Journal of Carbohydrate Chemistry*, **2021**, 40, 5, 243.
3. Almeida-Souza, F. *et al. J. Med. Chem.*, **2021**, 64, 12691.
4. Bacalhau, M. et al.. *European Journal of Pharmacology*. **2023,** 938, 175396.
5. Gaspar, F. V et al. *Tetrahedron*, **2022**, 120, 132856.

Acknowledgments

The authors would like to thank CAPES, FAPERJ, CNPq and UFRJ for their funding and structural support.

Área: ORG

Synthesis of new 4-quinolone-3-hydroxamic acids with potential anti-Alzheimer activity

Joice Cristina de O. Andrade (PG),[1] Mayra da S. Coutinho (PG),[1] Maria Cecília B. V. de Souza (PQ),[1] Marcela Cristina de Moraes (PQ),[1] Pedro N. Batalha (PQ),[1] Fernanda da C. S. Boechat (PQ)[1].

joicecristina@id.uff.br

[1]Universidade Federal Fluminense, Instituto de Química, Departamento de Química Orgânica – Outeiro de São João Batista s/nº, Niterói / RJ, 24020-141

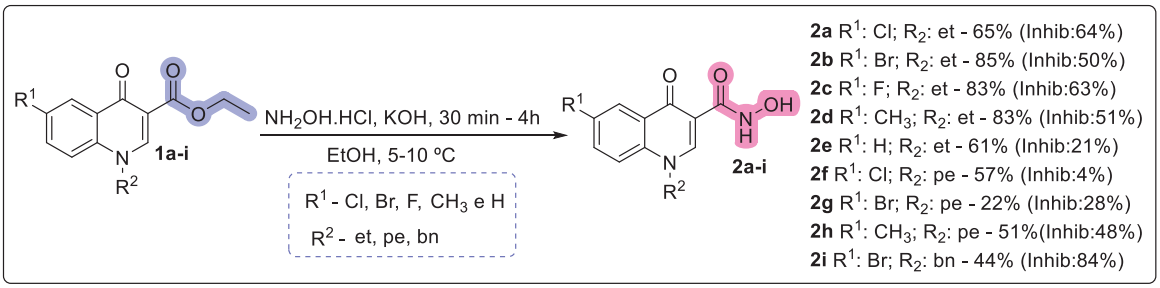
Palavras Chave: *Hydroxamic acids, 4-quinolone, Synthesis, Anti-Alzheimer activity*

Highlights

Synthesis of hydroxamic acids derived from 4-quinolone ester precursors and inhibitory study conducted by the Ellman colorimetric method of the obtained substances.

Resumo/Abstract

Alzheimer's disease (AD) is a chronic, progressive neurodegenerative pathology of probable multifactorial etiology. It presents cognitive impairment as a symptom and is linked to about 80% of dementia cases in individuals over 65 years old. Considering its high mortality rate and the projected increase in cases by 2050, the search for bioactive substances for AD treatment is an area of interest in Medicinal Chemistry[1]. Based on this fact, 4-quinolone derivatives and the the hydroxamic acid functional group (HA - C=ONHOH) are important structures associated with the development of anti-Alzheimer substances, due to data regarding their action against neurodegenerative diseases such as Parkinson's and Alzheimer's, the latter also being associated with the inhibition of the AChE enzyme[2]. Thus, the objective of this work is the structural modification of the 4-quinolone nucleus **1a-i** through the introduction of the HA group to obtain derivatives **2a-i**.



Scheme 1: Synthesis of 4-quinolone-3-hidroxamic acid derivatives **2a-i**.

The HA derivatives obtained were synthesized through a nucleophilic substitution reaction at the ester group **1a-i** using the hydroxylamine previously obtained by treating $NH_2OH.HCl$ with KOH in methanolic medium as the nucleophile **(Scheme 1)**. The synthesis resulted in nine substances with yields ranging from 22-85%, which were subsequently structurally characterized by physical analysis methods (m.p., IR, MS, ^1H and ^{13}C NMR). These substances were subjected to the Ellman method for the inhibitory study of the AChE enzyme using Donepezil as reference (98% inhibition). The inhibition observed for these HA exhibited values between 4 and 84%, with the highest inhibition associated with substance **2i**. Thus, the synthesis of HA and the inhibitory study towards AChE enzyme showed promising results given the inhibition above 60% for three of the obtained substances. Additionally, molecular docking studies and calculation of the IC_{50} of the synthesized substances will be further investigated.

1.Qiu, W. Q.e M. F. Folstein. **Neurobiology of Aging**, v. 27, n. 2, p. 190-198, 2006.
2.Aleksandrova, Y. et al. **International Journal of Molecular Sciences**, v.24, n. 11, 2023.

Agradecimentos/Acknowledgments

CNPq, FAPERJ, CAPES (Finance Code 0001)

Área: ORG

Synthesis of new 5-(1*H*-1,2,3-triazol-1-yl)-1,4-naphthoquinones With Trypanocidal Potential

Cássia C. de Oliveira (IC),[1] Leonardo G. C. de Moraes (PG),[1] Thaís B. Santos (PG),[1] Diana P. de Abreu (IC),[1] Vitor F. Ferreira (PQ)[2] e David R. da Rocha (PQ)[1,*]

cassia_oliveira@id.uff.br; davidrocha@id.uff.br

[1]*Instituto de Química, Departamento de Química, UFF, Niterói, RJ, Brasil;*
[2]*Departamento de Tecnologia Farmacêutica, Faculdade de Farmácia, UFF, Niterói, RJ, Brasil.*

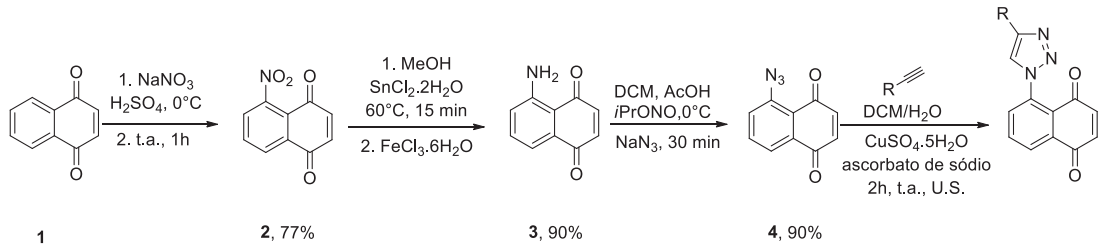
Palavras Chave: *Naftoquinonas, Heterociclos, Triazóis, Doenças Negligenciadas.*

Highlights

This project presentes an important innovation in the field of modifications in naphthoquinones, specifically by modifying naphthoquinones aromatic rings with a direct bond to triazole moiety.

Resumo/Abstract

As naftoquinonas compõem o maior grupo da classe das quinonas, sendo esses compostos naturais utilizados há séculos pela humanidade para a obtenção de compostos ativos frente diversas doenças, principalmente, pela capacidade de induzir a formação de espécies reativas de oxigênio (ERO).[1] Esse projeto tem como objetivo fazer a introdução do núcleo triazólico no anel aromático da 1,4-naftoquinona **(1)**, contendo diferentes substituintes, com foco na obtenção de compostos úteis para o tratamento da doença de Chagas e leishmaniose. A rota sintética empregada se iniciou com uma reação de nitração na 1,4-naftoquinona **(1)** originando, assim, a 5-nitro-1,4-naftoquinona **(2**, 77%**)**,[2] que por sua vez sofreu redução do grupo nitro, dando origem à 5-amino-1,4-naftoquinona **(3**, 90%**)**.[2] A seguir, foi realizada uma reação de diazotação no grupamento amino, resultando em um sal diazotado, que sofreu substituição nucleofílica aromática para fornecer o intermediário chave da série, a 5-azido-1,4-naftoquinona **(4**, 90%**)**.[2] Por fim, realizou-se a reação de **4**, tanto com alcinos comerciais quanto com tióis propargilados, por meio de uma cicloadição catalisada por Cu I, levando à formação de 14 derivados triazólicos inéditos do tipo **5**,[3] até o presente momento, destacando-se que alguns outros derivados ainda serão sintetizados por esta metodologia.



5a, R= CH_2S(4-Me-Ph), 24%
5b, R = CH_2SPh, 53%
5c, R = CH_2S(2,5-diCl-Ph),47%
5d, R = CH_2S(4-Br-Ph), 56%
5e, R = CH_2S(2-benzotiazol), 47%
5f, R = Ph, 51%
5g, R = But, 46%
5h, R = Pr, 36%
5i, R = 4-Pent-Ph,46%
5j, R = $CH(Me)(OH)_2ChM$, 39%
5k, R = CH_2S(3-Me-Ph), 21%
5l, R = CH_2S(2-Me-Ph), 27%
5m, R = CH_2S(4-NO_2-Ph), 58%

Esquema 1. Rota sintética para a síntese dos derivados triazólicos

Referências:
[1] Ferreira, V. F. et. al. Quím.Nova. 2003, 407-416.
[2] Shvsbergat, M. S. A. et. al. 1985, 2154.
[3] Pacheco, P.A. F. et. al. Bioorg. Med. Chem. 2019, 10, 2016.

Agradecimentos/Acknowledgments

CNPq, CAPES, FAPERJ.

Área: ORG

Synthesis of new biomass-derived diols for polymerization reactions

Jéssica Ribeiro da Silva (IC)*, Jorge Andrés Mora Vargas (PG), Antonio Carlos Bender Burtoloso (PQ).

Jessicaribeiro19@usp.br; antonio@iqsc.usp.br

São Carlos Institute of Chemistry IQSC-USP

Keywords: *Biomass-derived monomers, Aldehydes, Diols, Thiols, Sustainable Chemistry.*

Highlights

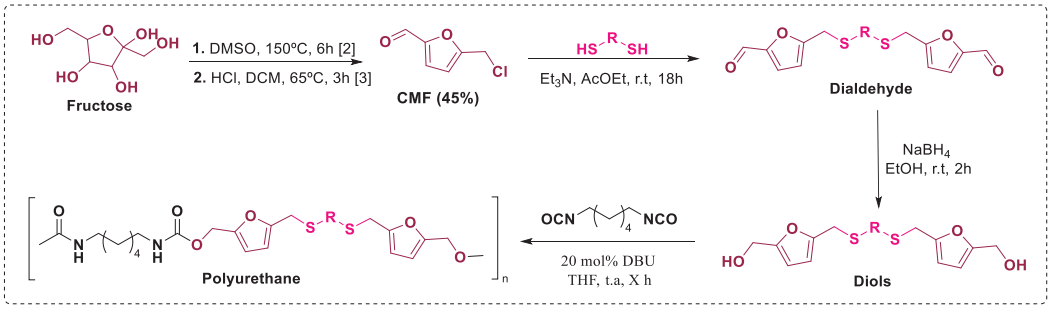
Synthesis of new added-valued compounds from 5-(chloromethyl)furfural

Synthesis of new diols and aldehydes in good yields

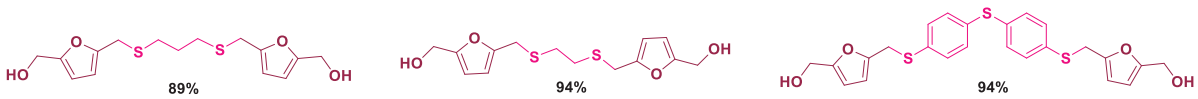
Resumo/Abstract

Polyurethanes (Pus) are polymeric materials that have a wide range of applications in various industrial fields. The main production of PUs occurs through the polyaddition reaction between diisocyanates and polyols, however, these starting materials are conventionally obtained from petroleum sources. In this work, we showcase the synthesis of new diols (to be used in polymerizations) from the nucleophilic substitution reaction between 5-(chloromethyl)furfural (CMF) and dithiols. CMF is a promising biomass molecular platform obtained by the treatment of raw biomass, cellulose, or sugars with commercial hydrochloric acid. Initially, we investigated the best reaction conditions using monothiols and CMF. Under our optimized reaction condition for the substitution reaction, the desired product could be obtained in excellent yields (up to 97%). After finding this best reaction condition, we next extend it to the synthesis of the desired diols. Several diols could be readily prepared in 89-94% yields, after a two-step sequence (coupling and reduction). It is worth noting that one of the prepared diols could already be applied in the synthesis of a new polyurethane. In summary, a novel way to prepare biomass-derived diols was disclosed, starting from fructose.

Figure 1. Synthesis of new added-valued compounds from CMF and thiols.



Diols prepared:



References

[1] GÓMEZ-JIMÉNEZ-ABERASTURI, O; OCHOA-GÓMEZ, J. R.. *Journal of Chemical Technology & Biotechnology*, v. 92, n. 4, p. 705-711, **2017**.
[2] AMARASEKARA, A. S.; WILLIAMS, L. D.; EBEDE, C. C. *Carbohydrate research*, v. 343, n. 18, p. 3021-3024, **2008**.
[3] MASCAL, M. *ChemSusChem*, v. 8, n. 20, p. 3391-3395, **2015**.

Agradecimentos/Acknowledgments

FAPESP CNPq CAPES IQSC MINISTÉRIO DA EDUCAÇÃO PÁTRIA AMADA BRASIL Research Centre for Greenhouse Gas Innovation

Área: ORG

Synthesis of new bis-1,2,3-triazole glycoconjugates with fungicidal potential

João Pedro de Paiva S. Duarte (IC), Ingrid C. Chipoline (PQ), Sabrina B. Ferreira* (PQ).

joaop.duarte@gradu.iq.ufrj.br; *sabrinab@iq.ufrj.br

Universidade Federal do Rio de Janeiro, Instituto de Química, Laboratório de Síntese e Prospecção Biológica, Rio de Janeiro, RJ, Brasil

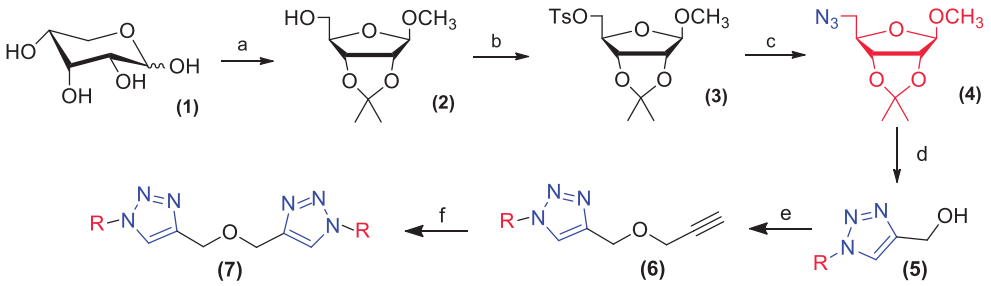
Keywords: Antifungal, Carbohydrate, Galactose, Heterocycles, Mannose, Ribose.

Highlights

The fusion of carbohydrates, facilitated by the triazole rings present in each one of them, originates molecules that can be of great importance in the fight against fungi.

Abstract

Triazole rings are aromatic heterocycles, of synthetic origin and their derivatives have proven biodynamicity, demonstrating activities such as antiviral, antibacterial, antitumor, and antifungal, the latter being the activity of interest for the work in question.[1] These molecules can be used as spacers in organic synthesis, commonly appearing linked to other classes. In this sense, carbohydrates represent another class of substances with reported antifungal potential, among other activities.[2] Thus, the objective of this work is to efficiently synthesize new glycoconjugated bis-1,2,3-triazoles, varying the carbohydrate portion, which are D-ribose (**1**), D-galactose, D-mannose, D-fructose and D-xylose. Using (**1**) as shown in the scheme, the synthesis began with the protection of the hydroxyls, followed by the addition of the tosyl group, obtaining compound (**3**). Later, the azido group was introduced through a nucleophilic substitution, allowing the formation of the first triazole ring (**5**) through a 1,3-dipolar cycloaddition reaction. To form bistriazole, the hydroxyl of (**5**) was propargylated, obtaining compund (**6**). Then, starting from the terminal alkyne (**6**) and the initial azido-carbohydrate (**4**), the second cycloaddition reaction was carried out, obtaining the final product (**7**).



a. Acetone, MeOH, H_2SO_4,))), 25 min, 71% yield; **b**. TsCl, Pyridine, DMAP, 20h, r.t., 79% yield; **c**. NaN_3, DMF, reflux, 20h, 120ºC, 53% yield. **d.** Propargyl alcohol, $CuSO_4 . 5H_2O$, Sodium ascorbate, H_2O, reflux, 16h, 50ºC, 69% yield. **e.** DMF, NaH, Propargyl bromide,))), 30 min, 79% yield. **f.** Azide (carbohydrate), $CuSO_4 . 5H_2O$, Sodium ascorbate, H_2O, $CHCl_3$,))), 3h, 2% yield. R=carbohydrate

It is worth noting that the 5 types of carbohydrates will be combined with each other, generating 15 new molecules that can be unprotected to have free hydroxyls, thus obtaining 15 other compounds. The first product, the combination of two portions of the carbohydrate D-ribose, has already been obtained and characterized by ^{1}H and ^{13}C NMR and infrared. All 30 will be tested for antifungal activity.

Acknowledgments

The authors gratefully acknowledge the financial support from FAPERJ, CNPq, Fiocruz and UFRJ.

[1]Shalini, K. *et al. Beilstein J. Org. Química* (**2011**), 7, 668-677. [2]Evangelista, T. C. S. *et al. Journal of Carbohydrate Chemistry* (**2021**), 40, 243-268.

Área: ORG

Synthesis of new Bisnaphthoquinone-1,2,3-triazole hybrids with potential pharmacological action

Douglas C. Alcântara Pinto (PQ),[1,*] Gustavo Senra G. De Carvalho (PQ),[1] Robson C. Da Silva (PG),[1] Mariana O. L. Desmarais (IC),[1] Vítor F. Ferreira (PQ),[2] Fernando de Carvalho da Silva (PQ)[1]

douglasdoti@hotmail.com

[1] *Laboratório de Síntese Orgânica Aplicada, Universidade Federal Fluminense, Instituto de Química, Niterói-RJ, 24210-141, Brazil.*
[2] *Faculdade de Farmácia, Universidade Federal Fluminense, Niterói-RJ, 24241-000, Brazil.*

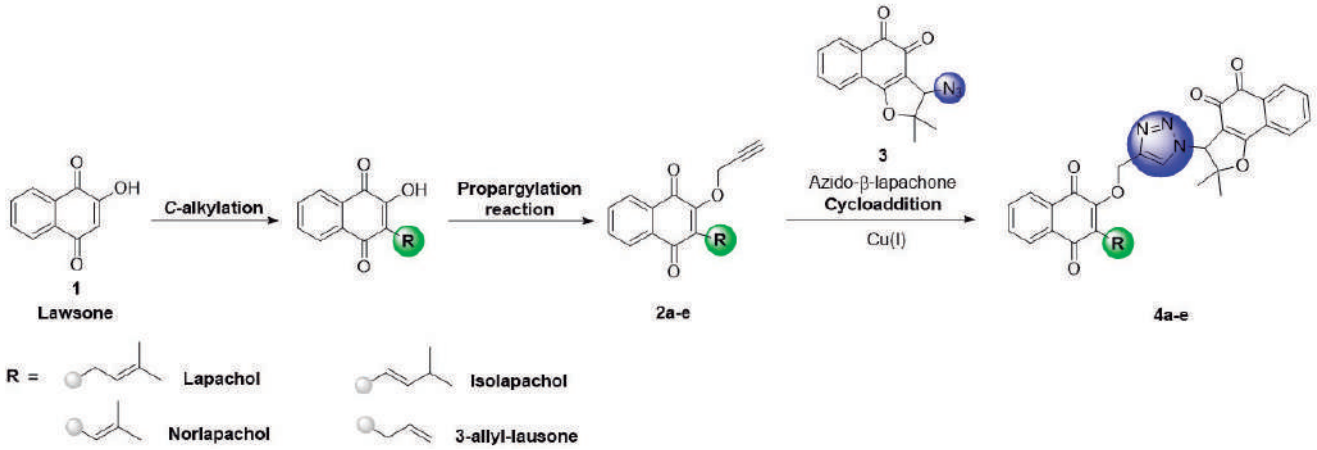
Keywords: *Naphthoquinone, 1,2,3-triazole, Click Chemistry, heterocycle*.

Highlights

The use of naphthoquinones and their derivatives obtained through modifications in their structures can provide molecules with potential therapeutic activity. Naphthoquinones can act on the redox cycle and promote an increase in the levels of reactive oxygen species and, thus, play an important role in the processes of apoptosis. Thus, in the present work, the synthesis of new, new bisquinone-1,2,3-triazole hybrids was carried out via click chemistry reaction.

Resumo/Abstract

Synthetic and natural naphthoquinones have a wide spectrum of applications in several areas, especially in medicinal chemistry. These naphthoquinones, which are significantly relevant, have high clinical potential in the treatment of various diseases.[1] There are reports that naphthoquinones containing the pyranic ring have bioactivity against several microorganisms and cancer cell lines due to their ability to accept one or two electrons in the cycle redox, generating reactive oxygen species (ROS).[2] In this way, quinones have cytotoxic action and lead cells to programmed cell death (apoptosis).[3] Especially, β-Lapachone, there is great interest due to its notable anticancer activity.[4] On the other hand, heterocyclic rings such as 1,2,3-triazoles are extremely important in bioactive compounds, being present in the structure of several drugs.[5] Taking into account all these factors, this work aimed to synthesize new bisquinone-triazole hybrids through Cu(I)-catalyzed Huisgen cycloaddition between *O*-propargylated 1,4-naphthoquinones **2a-e** and azido-lapachone **3**, as shown in Scheme 1. Compounds **2a-e** were synthesized, in good yield (40-84%). and characterized. Triazole derivatives **4a-e**, in yield (38-95%), were obtained and characterized. After complete characterization of all synthesized Bis-naphthoquinone-1,2,3-triazoles, their *in vitro* evaluation as pharmacological agents will be carried out.



Scheme 1. Synthetic route toward new bis-naphthoquinone-1,2,3-triazole hybrids.

References

[1] *Current Organic Synthesis* **2016**, *13*, 334-371; [2] *Journal of the American Chemical Society* **2011**, *133*, 11557-11571; [3] Current Pharmaceutical Design **2016**, 22, 5899-5914; [4] *Bioorganic & Medicinal Chemistry* **2008**, *16*, 5635-5643; [5] *Journal of Medicinal Chemistry* **2014**, *57*, 5845-5859.

Acknowledgments

LabSOA, FAPERJ, CNPq, CAPES

Área: ORG

Synthesis of New Hybrid 1,2,3-Triazoles and Imidazopyridine Derivatives with Potential Application as Inhibitors of RNA-Polymerase of SARS-CoV-2.

Rayanne L. N. Lima (IC),[1] Gabriel A. S. Aquino (PG),[1] Floriano P. S. Junior (PQ),[2] Sabrina B. Ferreira (PQ).[1]*

rayannelessa82@gmail.com; sabrinab@iq.ufrj.br

[1]Universidade Federal do Rio de Janeiro, Instituto de Química, Laboratório de Síntese Orgânica e Prospecção Biológica. Rio de Janeiro, Brasil; [2] Instituto Oswaldo Cruz, Laboratório de Bioquímica Experimental e Computacional de Fármacos, FIOCRUZ, Rio de Janeiro, Brasil.

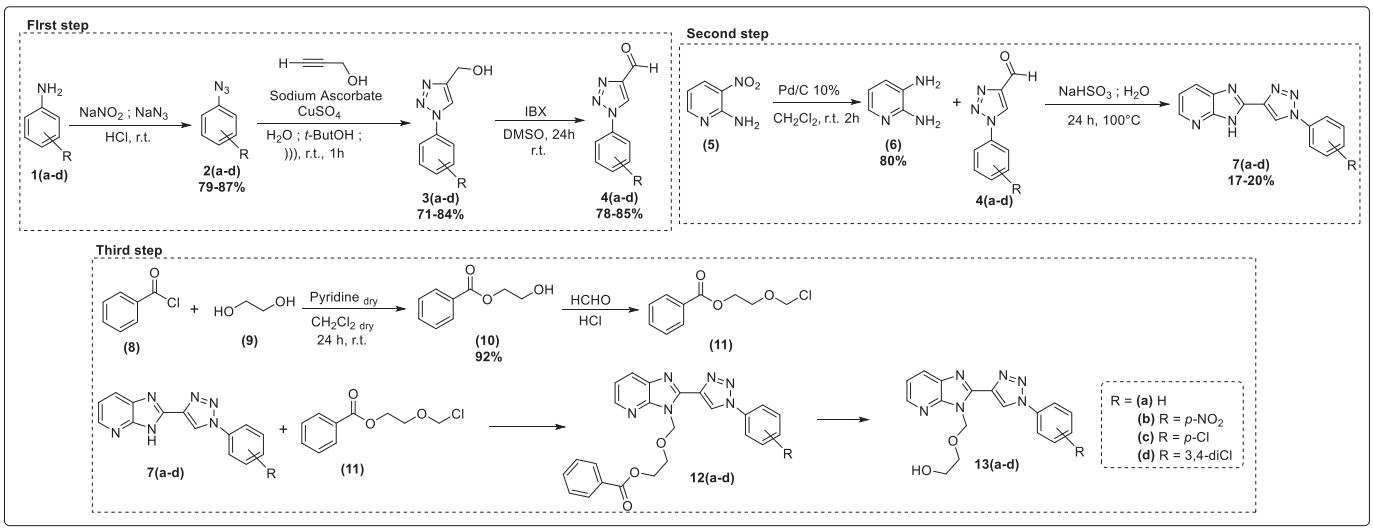
Keywords: *COVID-19, SARS-CoV-2, RNA-Polymerase, 1,2,3-Triazole, Imidazopyridine*

Highlights

Synthesis of new hybrid molecules containing nitrogenated heterocycles with possible applicability in the treatment of COVID-19 as inhibitors of RNA-polymerase.

Abstract

SARS-CoV-2 is a positive single-strand RNA virus responsible for the respiratory disease COVID-19, which gave rise to the pandemic in 2020 and caused the death of more than 6 million people worldwide.[1] The virus contains a heterotrimeric protein called RNA-dependent RNA polymerase, which acts in the replication and transcription of its genome.[2] Even with the new advancements regarding combating the disease through the development of vaccines and some drugs, there is a necessity for research on the development of new antivirus drugs since the virus may suffer mutations, possibly generating new strains. Few drugs are approved to treat COVID-19 due to low efficiency and side effects.[3] This work aims to synthesize new hybrid molecules containing imidazopyridine and 1,2,3-triazole rings with possible applicability in the treatment of COVID-19 through the inhibition of the enzyme RNA-polymerase. The first route started with the synthesis of aromatic azides **(2a-d)** from commercial anilines **(1a-d)**, followed by a Huisgen 1,3-dipolar cycloaddition to obtain alcohols containing 1,2,3-triazoles ring **(3a-d)**, which were oxidized using IBX to generate aldehydes **(4a-d)**. The second route started with the synthesis of the compound 2,3-diaminopyridine **(6)** from 2-amino-3-nitropyridine **(5)** through hydrogenation, which was reacted to the aldehydes to form the imidazopyridine ring. In the third part of the route, benzoyl chloride **(8)** was reacted with ethylene glycol **(9)** to generate 2-hydroxybenzoate **(10)**, which will be reacted to the imidazopyridine derivative, followed by the hydrolysis of the ester to obtain the final compounds **(13a-d)**.



[1] FERNANDES, Q. et al. Emerging COVID-19 variants and their impact on SARS-CoV-2 diagnosis, therapeutics, and vaccines. Annals of Medicine, v. 54, n. 1, p. 524–540, 31 dez. 2022.

[2] ZHOU, Z.; ZHU, Y.; CHU, M. Role of COVID-19 Vaccines in SARS-CoV-2 Variants. Frontiers in Immunology, v. 13, p. 898192, 20 maio 2022.

3 BRAY, M. Highly pathogenic RNA viral infections: Challenges for antiviral research. Antiviral Research, v. 78, n. 1, p. 1–8, abr. 2008.

Acknowledgments

The authors would like to thank CNPq, LABRMN, and FIOCRUZ.

Área: ORG

Synthesis of new nicotinic acetylcholine receptor ligands with therapeutic potential in CNS disorders

Rodrigo G. Agostinho (IC),[1] Daniel G. Rocha (IC),[1] Lívia C. R. M. da Frota (PQ)[1], Nailton M. do Nascimento Júnior (PQ),[2] Fernanda G. Finelli (PQ)*[1]

rodrigogarciaagostinho@gmail.com; finelli@ippn.ufrj.br

[1]Instituto de Pesquisa de Produtos Naturais, UFRJ; [2]LaQMedSOMM UNESP

Palavras Chave: *nicotinic derivatives, copper-catalyzed O-arylation, neurodegenerative diseases*

Highlights

Acetylcholine nicotinic receptors modulation. Copper-catalyzed *O*-arylation reaction. Therapeutic potential for Alzheimer's, neuroprotection, smoking cessation, schizophrenia, and anxiety disorders.

Abstract

Considerable evidence supports the therapeutic potential of selective neuronal nicotinic acetylcholine receptor (nAChR) ligands in various central nervous system (CNS) diseases. Studies using (-)-nicotine, a nonselective nicotinic agonist, indicate promising prospects. However, due to unfavorable pharmacokinetics, gastrointestinal and cardiovascular effects, sleep disturbances, and addiction risks associated with nicotine, it is unlikely to be the preferred therapeutic agent.[1] Nicotine analogs with extended side chains have shown high affinity for nAChR, but the synthesis of these compounds has been limited to nucleophilic substitution reactions, which have drawbacks such as the need for pre-activation of starting materials, low atom economy, and the formation of numerous by-products.[2] In this context, we present in this work an efficient synthesis of arylprolinols, nicotine analogs, using copper-catalyzed *O*-arylation as a key step, providing a cost-effective and versatile alternative.[3]

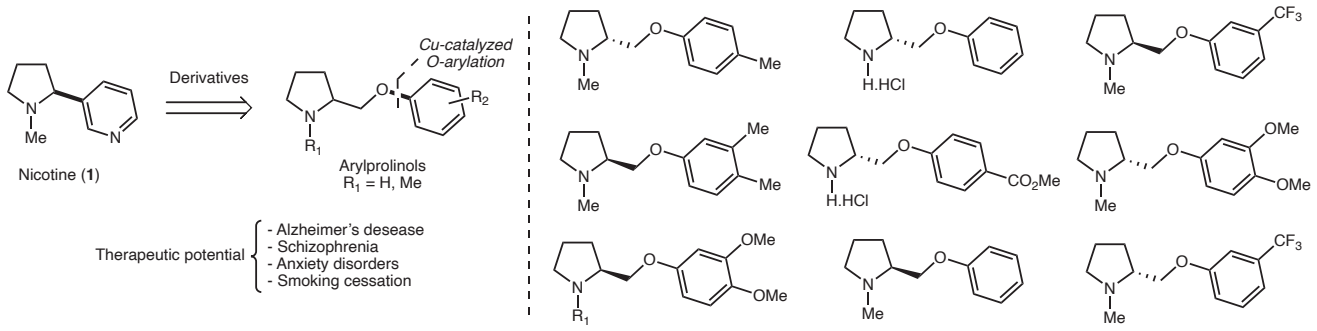


Figure 1. Nicotine derivatives synthetized in this work.

Ten synthetic targets were selected through virtual screening and synthesized in 3-4 steps. Initially, (*R*)- and (*S*)-*N*-Boc-prolinol, starting materials for the *O*-arylation step, were prepared from D- and L-proline in 58% yields after 2 steps. Copper-catalyzed *O*-arylation was carried out between prolinols and different boronic acids, obtaining yields of 12-88%. The respective hydrochlorides were prepared by deprotecting the nitrogen in acidic conditions in 64-94% yields. The methylated derivatives were obtained through *N*-methylation in 37-95% yields. The target compounds were submitted to *in vitro* cytotoxic activity test and were well tolerated. As a perspective, these nicotinic analogues will be evaluated for their potential of enhance cognitive function in neurodegenerative models.

Acknowledgments

To Prof. Diego Allonso (FF-UFRJ) for the preliminary biological assays.

[1] a) Jones, C. K., et al., Neuropsychopharma **2011**, 37, 16; (b) Radek, R. J., et al., Curr. Pharm. Design **2010**, 16 (3), 309-322; (c) Francotte, P., et al., Curr. Med. Chem. **2004**, 11 (13), 1757-1778; (d) Tonder, J. E.; Olesen, P. H., *Curr. Med. Chem.* **2001**, *8* (6), 651-674.
[2] Bolchi, C., et al., *J. Med. Chem.* **2015**, *58* (16), 6665-6677.
[3] Gandeepan, P.; Muller, T., et al., *Chem. Rev.* **2019**, *119* (4), 2192-2452.

Área: ORG

Synthesis of new quinoline-sulfonamide hybrids with potential activity against *P. falciparum*

Alexandra S. Santoro* **(PG)[1], Nubia Boechat (PQ)[2], Luiz C. S. Pinheiro (PQ)[3], Vinícius R. Campos (PQ)[1]**

***alexandrasantoro@id.uff.br**

[1]*Departamento de Química Orgânica, UFF;* [2]*Fundação Oswaldo Cruz, Farmanguinhos;* [3]*Departamento de Ciências, UERJ;*

Palavras Chave: *Quinolina, Sulfonamida, Malária, Plasmodium falciparum.*

Highlights

Optimization of prototype **I** to obtain new compounds with antimalarial activity.

Resumo

A malária, doença causada pelo protozoário do gênero *Plasmodium*, é considerada uma grave ameaça à saúde pública mundial. Segundo a OMS, foram estimadas mais de 619 mil mortes somente em 2021[1]. Os principais fármacos utilizados no tratamento da malária são os derivados quinolínicos, derivados da artemisinina e os antifolatos, onde se destacam a cloroquina e a sulfadoxina. No entanto, a diminuição da eficácia desses medicamentos clássicos pode ser atribuída às cepas resistentes[2]. A síntese e atividade de uma série de compostos híbridos planejados a partir da cloroquina e sulfadoxina foi publicada[3]. O composto mais potente da série apresentou atividade *in vitro* contra *P. falciparum* (IC_{50} de 0,09 μM) e nos testes *in vivo* contra *P. berghei* inibiu 49% da parasitemia com uma dose de 20 mg/kg, após o quinto dia de inoculação, contribuindo para a descoberta do composto protótipo **I** (Figura 1-A). Nesse trabalho propõe-se a otimização do protótipo **I** para obtenção de novos derivados com atividade antimalárica.

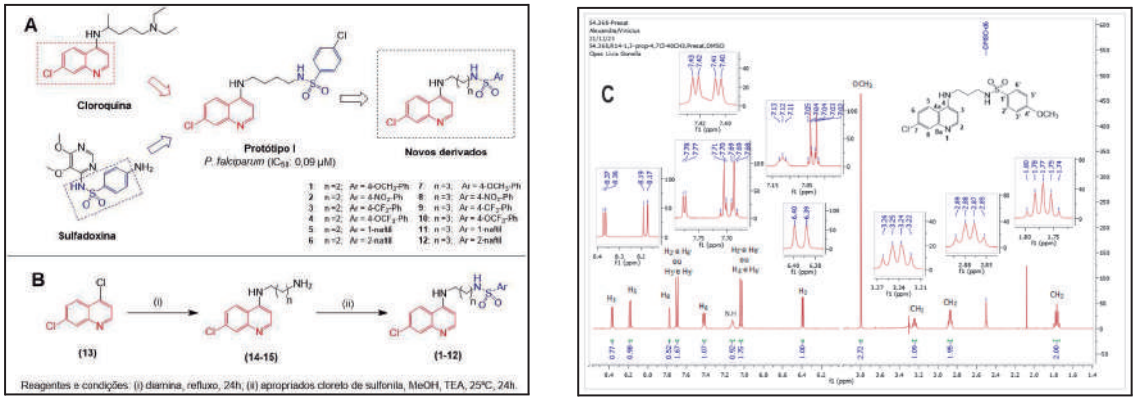


Figura 1. A: Planejamento dos novos derivados híbridos quinolina-sulfonamidas. B: Síntese dos novos derivados **(1-12)**. C: Espectro de RMN de ^{1}H do derivado **1** (500 MHz, solvente DMSO-d^6)

A reação de substituição nucleofílica entre a 4,7-dicloroquinolina **13** e as respectivas diaminas, fornecem os intermediários **14** (n = 2) e **15** (n = 3) que por sua vez vão reagir com os apropriados cloretos de sulfonila para a obtenção dos novos derivados **(1-12)**[3] (Figura 1-B). Como resultados preliminares tem-se a obtenção do derivado **1** com 70% de rendimento, cujo espectro de RMN ^{1}H é apresentado na Figura 1-C. Os compostos sintetizados terão suas estruturas elucidadas por IV, RMN de ^{1}H, ^{13}C e EM e serão enviados para a avaliação *in vitro* contra *P. falciparum*.

Referências: [1.] https://www.who.int/teams/global-malaria-programme/reports/world-malaria-report-2022. Acessada 12/01/2024.
[2.] Int. J. Parasitol. Drugs Drug Resist. 16 (2021) 102-118. DOI: 10.1016/j.ijpddr.2021.05.007.
[3.] Bioorg. Med. Chem. 23 (2015) 5979-5984. DOI: 10.1016/j.bmc.2015.06.056.

Agradecimentos

Os autores agradecem a LASINTHET, PPGQ-UFF, UERJ, FIOCRUZ, CNPq, CAPES, FAPERJ e a SBQ.

Area: ORG

Synthesis of new selenides derived from carvacrol with potential pharmacological activity

Millena da C. Silva (IC),[1] Thiago J. Peglow (PQ),[1] Luana da S. Gomes (PG),[1] Vanessa Nascimento (PQ)[1]

millenas@id.uff.br; nascimentovanessa@id.uff.br

[1]*Departamento de Química Orgânica, Instituto de Química, Universidade Federal Fluminense*.

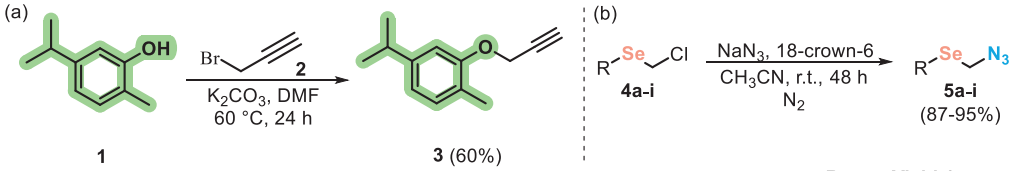
Keywords: Selenides, Carvacrol, Triazoles, Click chemistry.

Highlights

In this work, a series of new 1,2,3-triazole selenides derived from carvacrol with possible therapeutic properties were synthesized.

Abstract

The synthesis of new molecules is essential for the development of more effective, safe and specific drugs. In addition, exploring different chemical structures makes it possible to find compounds that can interact selectively with biological targets, resulting in more efficient treatments. In this sense, natural products have emerged as an excellent alternative for the synthesis of new molecules due to the possibility of guaranteeing fewer side effects. Carvacrol is a phenolic monoterpenoid that has several pharmacological properties, such as antimicrobial, anti-inflammatory, antimicrobial and neuroprotective activities.[1] In addition, organoselenium compounds are also an excellent alternative, as they have antioxidant and neuroprotective activities.[2] Therefore, this work aims to combine different groups of interest, such as the natural product carvacrol (2-methyl-5-isopropylphenol), a portion of organoselenium and the triazole, using the molecular hybridization strategy. Thus, propargyl carvacrol **3** was synthesized from commercial carvacrol **1** through an *O*-alkylation reaction using propargyl bromide **2** (Figure 1a).[3] On another route, the azides **5a-i** were synthesized in the presence of chlorides **4a-i**, sodium azide and 18-crown-6 in acetonitrile as solvent (Figure 1b).[3] Finally, through a copper-catalyzed azide-alkyne cycloaddition reaction (CuAAC) between propargylated carvacrol **3** and azide-containing selenides **5a-i**, triazole products **6a-i** were obtained after 24 h in moderate to good yields (44-63%) (Figure 1c).



R	Yield 6 (%)
H	63
4-OMe	60
4-Me	48
1,3,5-tri-Me	53
4-Cl	44
Naphthyl	45
Thiophenyl	49
Butyl	50
Benzyl	60

Figure 1. a) Lawsone propargylation reaction **3**; b) Reaction of formation of azides **5**; c) Synthetic route for obtained the products **6a-i**.

In conclusion, we have developed a simple method based on the click chemistry reaction for the synthesis of carvacrol derivatives. Furthermore, it should be noted that the synthesized compounds will be sent to collaborating groups so that their pharmacological properties can be evaluated.

Acknowledgments

UFF, CNPq, CAPES, FAPERJ.

---

[1] Javed, H. et al. *Curr. Neuropharmacol*. **2023**, *21*, 1421; [2] Belenichev, I. F. et al. *Res. Results Pharmacol*. **2021**, *7*, 29; [3] Gomes, L. S. et al. *RSC Av*. **2023**, *13*, 34852.

Área: ORG

Synthesis of Novel Iminocoumarin-Benzothiazole Hybrids for Application as Photosensitizers for Dye-Sensitized Solar Cell

Maria Vitória S. F. Gomes (IC),[1] Amanda de A. Borges (PG),[1] Edson Evangelista (PQ),[1] Luana da S. M. Forezi (PQ)[1,*]

mariavsfg@id.uff.br; luanaforezi@id.uff.br

[1]*Laboratório de Síntese Orgânica Aplicada, Instituto de Química, Departamento de Química Orgânica, UFF, Niterói-RJ, Brazil.*

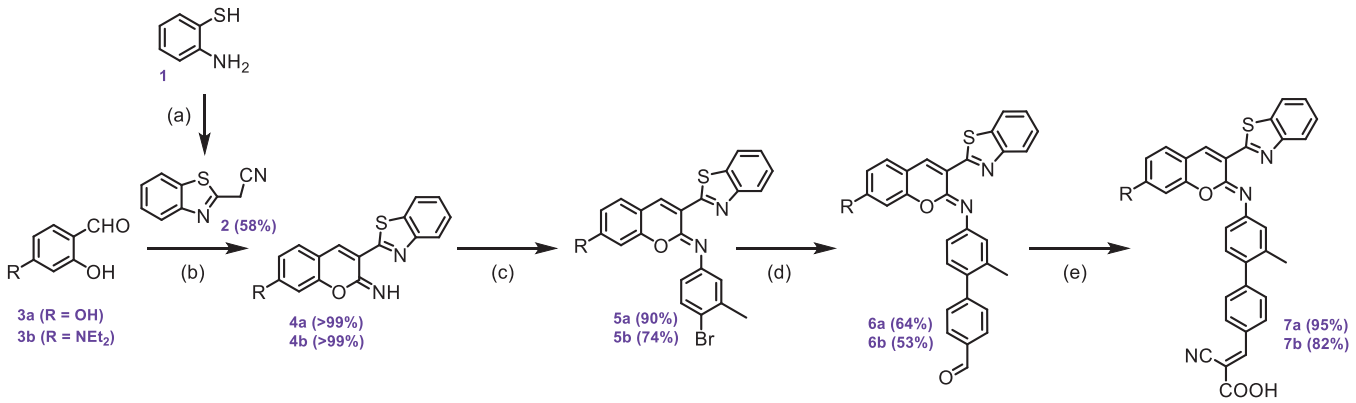
Keywords: *Coumarins, heterocycles, Photosensitizers, DSSCs.*

Highlights

Novel Iminocoumarin-Benzothiazole Hybrids for Application as Photosensitizers for Dye-Sensitized Solar Cell. Iminocoumarin-benzothiazole hybrids were obtained with satisfactory yields. Photophysical properties and their electrochemical behaviors were evaluated.

Abstract

In recent years, coumarin derivatives have generated significant interest in their applications in dye-sensitized solar cells (DSSCs) due to the ease of modifying their photophysical properties through the introduction of substituents/groups. Thus, the present work reports the synthesis of iminocoumarin-benzothiazole hybrids to investigate their potential applications as sensitizers in DSSCs (Scheme 1). Initially, 2-aminothiophenol (**1**) underwent a cyclization reaction with malonitrile in ethanol and acetic acid, yielding benzothiazole **2**. Subsequently, **2** underwent a Knoevenagel condensation reaction with 2-hydroxybenzaldehyde (**3**) in the presence of piperidine and ethanol, resulting in iminocoumarins **4**. The reaction of **4** with 4-bromo-3-methylaniline produced the desired intermediates, 2-phenyliminocoumarins **5**. These intermediates underwent a Suzuki coupling reaction with 4-formylphenylboronic acid to form **6**. Finally, the condensation reaction between **6** and cyanoacetic acid, led to photosensitizers **7** in good yields (82-95%).



Scheme 1. Synthesis of iminocoumarin-benzothiazole hybrids **7**. Reagents and solvents: a) malonitrile, EtOH, AcOH; b) EtOH, piperidine; c) 4-bromo-3-methylaniline, AcOH; d) 4-formylphenylboronic acid, $K_2CO_{3(aq)}$, THF, $Pd(PPh_3)_4$; e) $NCCH_2COOH$, piperidine, ACN.

1. Mandal, S.; Kandregula, G. R. *Journal of Photochemistry and Photobiology A: Chemistry* **2023**, *435*, 114300.
2. Endo, S.; Hu, D.; Suyama, M.; Matsunaga, T.; Sugimoto, K.; Matsuya, Y.; El-Kabbani, O.; Kuwata, K.; Hara, A.; Kitade, Y.; Toyooka, N. *Bioorganic & Medicinal Chemistry* **2013**, *21*, 6378–6384.
3. Huang, Z-S.; Cai, C.; Zang, X-F.; Iqbal, Z.; Zeng, H.; Kuang, D-B.; Wang, L.; Meier, H.; Cao, D. *Journal of Materials Chemistry A* **2015**, *3*, 1333–1344.
4. Martins, S.; Candeias, A.; Caldeira, A.T.; Pereira, A. *Dyes and Pigments* **2019**, *174*, 108026.

Acknowledgments

FAPERJ, CNPq and CAPES.

ÁREA: Química Orgânica

Synthesis of *O*-prenylated phenolics esters with potential activity against *Trypanosoma cruzi* amastigotes.

Fábio da Rocha Teixeira (IC),[1] Lucas de Oliveira Pires (PG),[1] Afonso Santine M. M. Velez (PG),[1] Marco Edilson F. de Lima (PQ),[1] Debora Decoté-Ricardo (PQ),[2] Rosane Nora Castro (PQ)[1]* fabiorteixeira@ufrrj.br; noraufrrj@gmail.com*

[1]Instituto de Química - Universidade Federal Rural do Rio de Janeiro, Seropédica, RJ; [2]Instituto de Veterinária - Universidade Federal Rural do Rio de Janeiro, Seropédica, RJ.

Keywords: *Chagas Disease, cinnamic acids, benzoic acids, cytotoxicity.*

Highlights

This work shows the synthesis of *O*-prenylated derivatives of different phenolic acids aiming to evaluate their biological activity against *Trypanosoma cruzi* amastigotes.

Abstract

Phenolic acids (PAs) are a widespread group of natural products found in different plant species as a product of their secondary metabolism; the most common PAs are hydroxybenzoic and hydroxycinnamic acids with promising biological properties, such as antioxidant, antimicrobial, and antiparasitic.[1] Chagas Disease (CD) is illness caused by *Trypanosoma cruzi* infection, affecting about 6 to 7 million people around the world. Since it was first described by Carlos Chagas (1909), the two drugs available for CD therapy (benznidazole and nifurtimox) are still in use despite the high toxicity in association with long-term treatments.[2] Naturally occurring PAs and their esters are described with anti-*T. cruzi* activity, and the coupling of an isoprenoid moiety to phenolic groups is often associated with and improvement of the biological properties.[3] The aim of this work was to investigate the toxicity of methyl esters prepared from cinnamic (**1** – **4**) and benzoic acids (**5**, **6**) against amastigote forms of *T. cruzi*, in comparison with their respective *O*-prenylated analogues (**7** – **12**). The PAs derivatives obtained in this work are described in **Figure 1**.

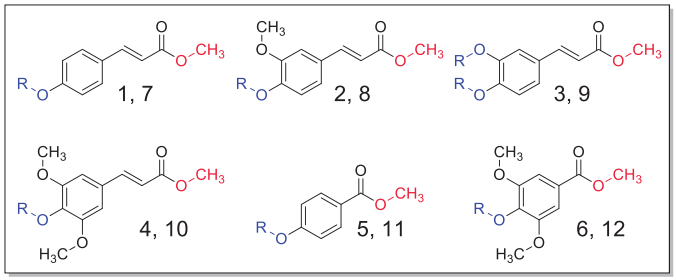


Figure 1 – Structure of the derivatives evaluated in this work: **1** – **6** phenolic esters (**R = H**) and **7** – **12** (**R = -$CH_2CHC(CH_3)_2$**).

PAs esters (**1** – **6**) were prepared using Fischer reaction under reflux using methyl alcohol and catalytic amounts of H_2SO_4, affording yields from 83 to 98%; respectively, their *O*-prenylated analogues were synthesized using K_2CO_3 (1,5 eq.) and prenyl bromide (1,5 eq.) in acetone at room temperature (overnight), and the yields ranged from 68 to 90%. All the compounds were characterized using ^1H and ^{13}C NMR spectroscopy, as well as LC-MS with 98% of purity. The compounds were evaluated for their toxicity against *T. cruzi* (Tulahuen C2C4 Lac-Z) and cytotoxicity (LLC-MK2). The toxicity assays against amastigotes and cytotoxicity were found to be dependent on both the hydroxyl groups available and type of carboxylic acids. Among the tested compounds, the *O*-prenylated derivative **10** was the most active (IC_{50} = 48.47 μM), while the respective non-prenylated ester showed no activity at the maximum concentration (IC_{50} > 100 μM). This result suggests that *O*-prenylation may be enhancing the activity; compounds **3** and **9** have also shown promising results against *T. cruzi* (IC_{50} 75,66 and 84,41 μM, respectively). In addition, the derivative **12** (benzoic analogue of **10**) showed no activity against amastigotes at the maximum tested concentration (100 μM), suggesting that both the *O*-prenylated side-chain and cinnamic ester moiety are preferable for *T. cruzi* activity (**Figure 2**).

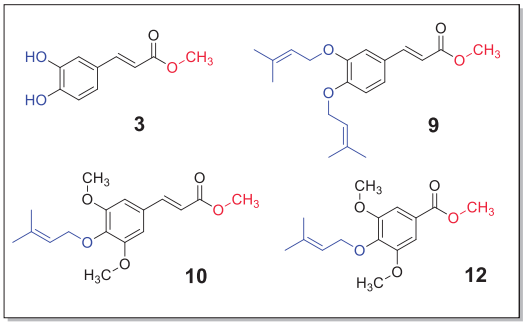


Figure 2 – Structure of the derivatives highlighted in this discussion.

. The compounds showed no relevant toxicity in the cytotoxic assays against LLC-MK2 cells. Furthermore, new PAs esters and derivatives will be prepared to provide more information about the structure-activity relationships for the series highlighted in this study, contributing to the discovery of new therapies against CD.

[1]MARCHIOSI, Rogério et al. **Phytochemistry Reviews**, v. 19, p. 865-906, 2020; [2]ABRAS, Alba et al. **Clinical Microbiology Reviews**, v. 35, n. 2, p. e00152-21, 2022; [3]SILVA, Matheus L. et al. **Química Nova**, v. 46, p. 39-42, 2023.

Acknowledgments

CAPES, FAPERJ, CNPq

Área: ORG

Synthesis of pyrazoles derivatives with potential biological activity.

Gabriel R. Antunes (IC),[1] Felipe P. Machado (PG)[2] Àurea Echevarria (PQ),[2] Diego P. Sangi (PQ).[1]*

gabrielrodriguesantunes@id.uff.br; dpsangi@id.uff.br*

[1]*Instituto de Ciências Exatas, Universidade Federal Fluminense, Volta Redonda- RJ;*
[2] *Instituto de Química, Universidade Federal Rural do Rio de Janeiro, Seropédica -RJ*

Palavras Chave: *Heterociclic synthesis, Pyrazoles, Kethenedithioacetals.*

Highlights

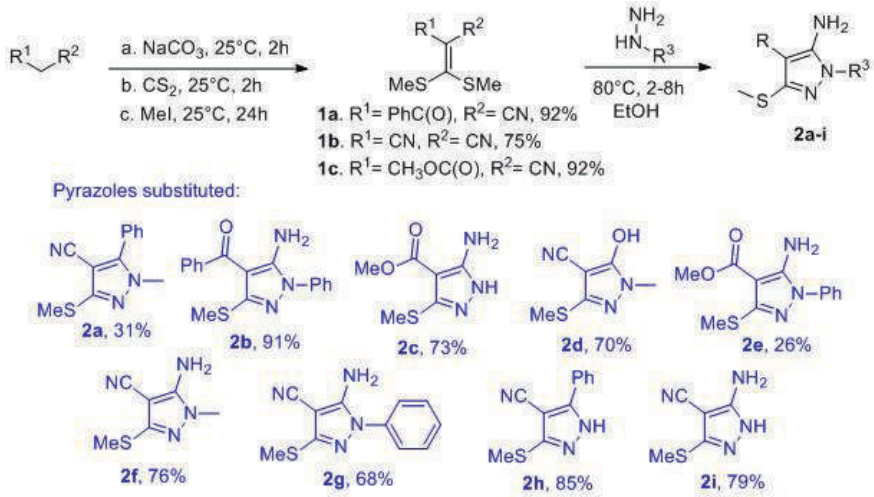
The pyrazole heterocycle is a privileged structure with many biological applications. We synthetized substituted pyrazoles using kethenedithioacetals as building blocks.

Abstract

Pyrazoles constitute an important class of heterocyclic compounds. This class has a great versatility of biological activities, including antifungical (Penthiopyrad), antiviral (Pyrazofurin), anagesical (Difenamizole) and anti-inflamatory (Celecoxibe). Due to these important applications, there are many methods to synthesize pyrazoles. In this work, we applied the vinylic substitution in ketenedithioacetals using hydrazines as nucleophiles, in order to prepare tri and tetra-substituted pyrazoles derivatives.[1]

In the first step, we prepared ketenedithiacetals with a three steps one-pot procedure constituted by, i) deprotonation of compounds containing active hydrogens; ii) addition of carbanion on the carbon disulfide; iii) methylation of sulfide groups using iodomethane (Scheme 1).[2]

In the second part, we submitted the kethenedithioacetals **1a-c** to reactions with three hydrazines**,** hydrazine hydrate, phenylhydrazine and methyl hydrazine. An equimolar solution of a kethenedithioacetal and a hydrazine in ethanol was refluxed in a round bottom flask**.** We observed a vinylic substitution and a cyclization producing pyrazoles derivatives **2a-i**, that were purified by recrystallization in boiling ethanol (chromatographic column was needed in some cases) (Scheme 1).[3]



Scheme 1. Synthesis of pyrazoles.

Using vinylic substitution followed by a cyclization, we prepare nine pyrazoles that will be submitted to evaluation, in selected biological targets.

1. Andrew W. Brown, in Advances in Heterocyclic Chemistry, 2018.
2.Thomae et al. Tetrahedron, 65, 2009,10453-10458, 2009.
3. Sangi et al. J. Braz. Chem. Soc., 2014, 25(5), 887-889.

Acknowledgments

FAPERJ

Área: ORG
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Synthesis of Selenylated Indolic Amide Alkaloids Using an I_2/DMSO Protocol as Promising Anti-Alzheimer's Agents: A Rational Design Approach

Angelica Justino (PG)[1]*, Aldo S. de Oliveira (PQ)[2], Antonio L. Braga (PQ)[1].

justino.a@posgrad.ufsc.br;

[1]*Department of Chemistry, UFSC, 88040-970, Florianópolis, Brazil.*
[2]*Department of Exact Sciences and Education, UFSC, 89036-004, Blumenau, Brazil.*

Keywords: *Iodine catalysis, Indole alkaloids selenilated, Indole synthesis, Indole amide, Alzheimer, Molecular docking.*

Highlights

New selenylated indolic amide alkaloids with exceptional blood-brain barrier permeability, were synthesized with high yields (54-99%) using an efficient I_2/DMSO method developed in our lab.
Compound **4a** demonstrates potential for Alzheimer's therapy by modulating acetylcholinesterase activity.

Resumo/Abstract

The study advances the field of medicinal chemistry by introducing an efficient approach to synthesize selenylated indole alkaloids derivatives, targeting anti-Alzheimer properties [a-e]. Utilizing the efficient I_2/DMSO system developed in our lab, this research achieves functionalization at the crucial 2-position of the indole ring [f], with an optimized reaction producing the desired products in up to 94% yield. Specifically, molecule **4a** emerges as a standout, demonstrating favorable interactions with acetylcholinesterase, a key enzyme in Alzheimer's pathogenesis. This methodical and rational design not only uncovers a new class of potential therapeutic agents but also highlights the significance of integrating selenium and indole structures in drug discovery for Alzheimer's disease, presenting promising preliminary outcomes.

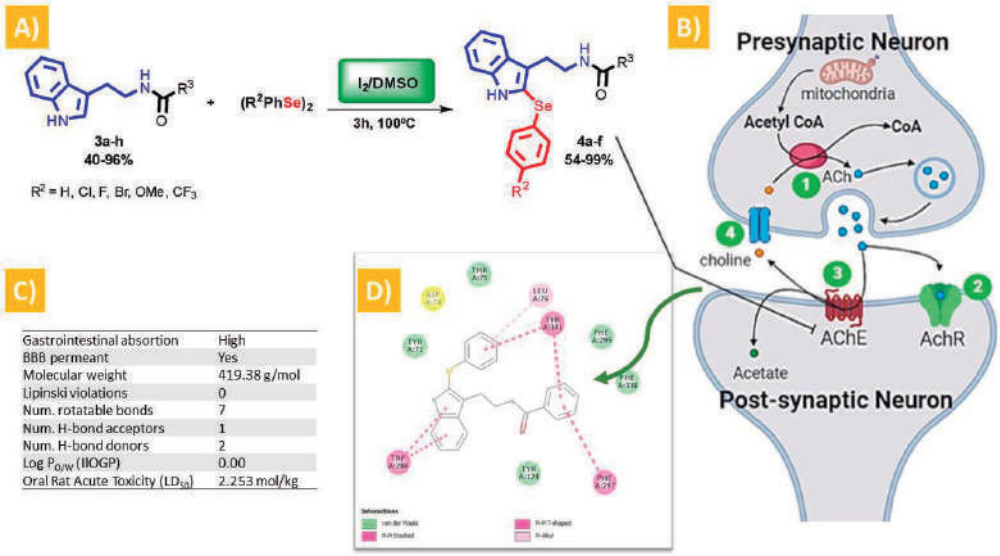


Figure 1. A) Synthesis conditions for selenylated indolic amide alkaloids. **B)** Cholinergic pathway scheme: 1) ACh synthesis, 2) Reuptake via AchR, 3) ACh degradation by AChE to choline and acetate. **C) 4a** characteristics and drug-likeness. Data from https://biosig.lab.uq.edu.au/ **D)** 2D diagrams of **4a** interactions at acetylcholinesterase catalytic site. Created with Biovia Discovery Studio Visualizer.

References: a) Sravanthi & Manju, Eur. J. Pharm. Sci. '16, 91, 1–10. **b)** Reich & Hondal, ACS Chem. Biol. '16, 11, 821–841. **c)** Barbosa et al., Curr. Med. Chem. '22. **d)** Scheide et al., Org. Biomol. Chem. '20, 18, 4916–4921. **e)** Chalupova et al., Eur. J. Med. Chem. '19, 168. **f)** Azeredo et al., J. Org. Chem. '14, 79, 4125–4130.

Agradecimentos/Acknowledgments

UNIVERSIDADE FEDERAL DE SANTA CATARINA
LabSelen
CNPq Conselho Nacional de Desenvolvimento Científico e Tecnológico
INCT catálise
CAPES

Synthesis of Substituted Phthalimides from 3A5F by the Hydrazone Formation Strategy.

Pedro Dominguez Branco (PG),[1] Camila Souza Santos (PQ),[1] Bruna Butke de Souza (PG),[1] Renan Rodini Mattioli (PG),[1] Julio Cezar Pastre (PQ).[1]*

p223264@dac.unicamp.br; jpastre@unicamp.br

[1]*Institute of Chemistry, State University of Campinas (UNICAMP).*

Keywords: *Nitrogenated aromatics, Diels–Alder, Chitin Biomass, Green chemistry.*

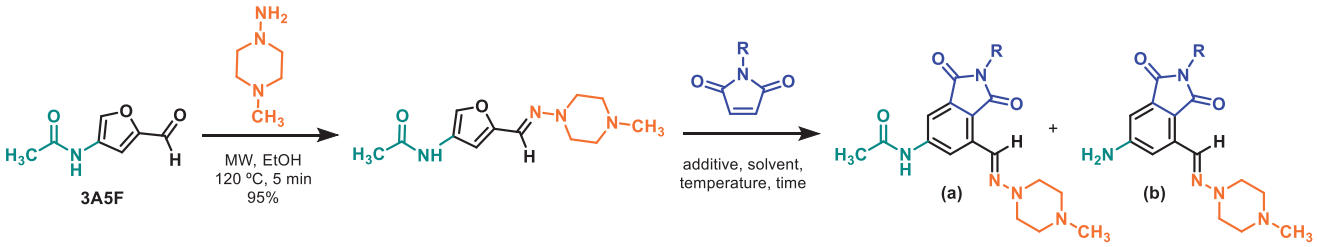
Highlights

3A5F is obtained from *N*-acetylglucosamine (NAG), a biobased compound of economic importance in shell biorefinery.

New nitrogenated aromatics were synthesized from renewable sources and fully characterized.

Resumo/Abstract

Aromatic compounds containing nitrogen atoms in their structure are still obtained from non-renewable sources with the incorporation of nitrogen from ammonia, which is industrially produced by the highly energy demanding Haber process. To minimize the carbon footprint of nitrogen containing chemicals and drive the production of nitrogenated aromatic compounds in a Haber-independent manner, the use of furans derived from *N*-acetylglucosamine (NAG), a chitin-based compound, has become an affordable and promising source for nitrogen fixation in high added-value compounds. Herein, we address the challenge of using a chitin-derived furan, 3-acetamido-5-furfural (**3A5F**), an electron poor furan, to favor the formation of Diels–Alder (DA) adducts and sequential aromatisation to form 4-acetylaminophthalimides. Thus, the hydrazone formation strategy afforded the synthesis of 4-acetylaminophthalimides from **3A5F** in one-pot sequential DA/aromatization reactions selectively yielding the desired aromatic in up to 60% yield. Microwave irradiation was also employed to shorten reaction time. The scope expansion to other dienophiles is in progress and it will lead to the synthesis of novel aromatics.



Entry	Solvent	Additive	Temperature (°C)	Time	Yield of a/b (%)
1	EtOH	-	50	15 h	46/10
2	MeCN	-	50	15 h	45/9
3	DMSO	-	50	15 h	48/7
4	EtOH	-	r.t.	15 h	45/8
5	EtOH	MsOH	50	3 h	48/9
6	EtOH	*N*-methylimidazole·HSO_4	50	3 h	47/8
7	EtOH	*N*-methylimidazole·HSO_4	r.t.	4 h	49/7
8	EtOH	*p*-TsOH	50	3 h	42/12
9	EtOH	TFA	50	3 h	51/6
10	THF	Ac_2O and H_2SO_4	50	1 h	40/0
11	EtOH	$MgSO_4$	50	15 h	45/10
12	MeCN	Ac_2O	50	2 h	60/0
13	MeCN	Ac_2O	120 (MW)	15 min	55/0

Agradecimentos/Acknowledgments

The authors gratefully acknowledge financial support from the São Paulo Research Foundation – FAPESP (RRM, 2019/26450-9 and 2022/03872-8; CSS, 2022/00774-5; BBS, 2023/01238-2; PDB, 2023/01232-4; JCP, 2021/06661-5), the Brazilian National Council for Scientific and Technological Development – CNPq (JCP, 308540/2021-2), and the Coordination for the Improvement of Higher Education Personnel – CAPES (RRM, Finance Code 001).

Área: ORG

Synthesis of water-soluble organophotocatalysts via benzyne chemistry

Bruno H. Rita (PG)[1] and Cristiano Raminelli (PQ).[1,*]

b.rita@unifesp.br; raminelli@unifesp.br

[1] *Instituto de Ciências Ambientais, Químicas e Farmacêuticas, Universidade Federal de São Paulo, Diadema, SP, Brasil*

Keywords: *Green chemistry; Benzyne chemistry; Organophotocatalysis; Water-soluble anthraquinone*

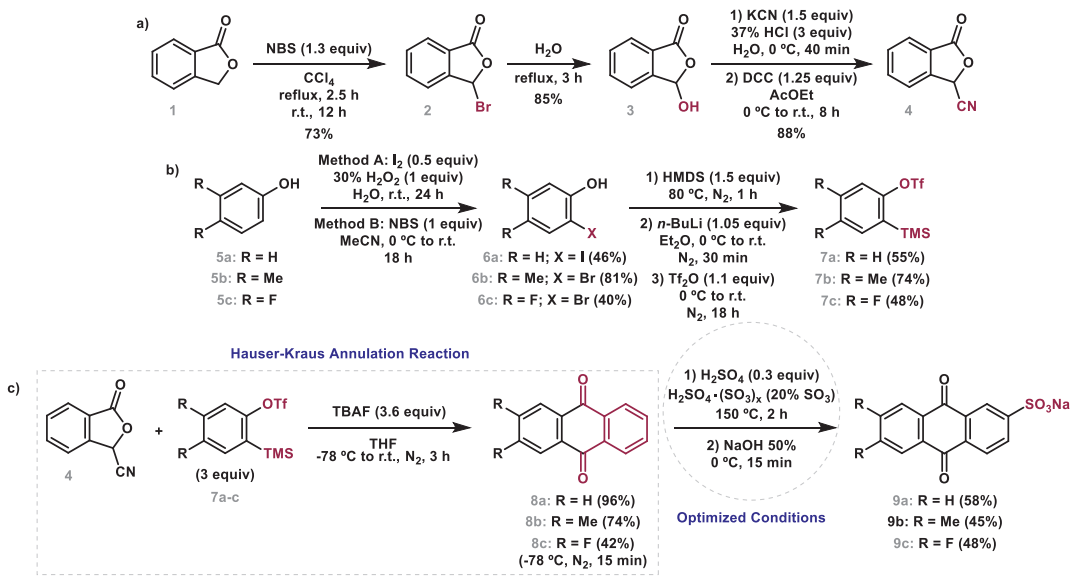
Highlights

Synthesis of water-soluble anthraquinones using benzyne chemistry under mild conditions. Water-soluble organophotocatalysts for hydrogen peroxide production. Reactions with hydrogen peroxide in water.

Resumo/Abstract

Benzyne and its derivatives have found application in total synthesis of natural products[1] and preparations of functional materials.[2] In this work, we are employing benzyne chemistry in the synthesis of water-soluble organophotocatalysts[3] via the Hauser-Kraus annulation reaction.[4] Initially, phthalide (**1**) was allowed to react with *N*-bromosuccinimide (NBS) in CCl_4 to give 3-bromophthalide (**2**). Then, compound **2** was treated with water under reflux, affording 3-hydroxyphthalide (**3**). Intermediate **3** was subjected to the reaction with KCN and HCl in distilled water, followed by treatment with *N*,*N'*-dicyclohexylcarbodiimide (DCC) in AcOEt, to provide 3-cyanophthalide (**4**)[4] (**Scheme 1a**). Phenols **5** were subjected to halogenation reactions using iodine (I_2) with 30% (w/v) hydrogen peroxide (H_2O_2) (Method A) and *N*-bromosuccinamide (NBS) in MeCN (Method B) to give 2-iodophenol (**6a**) and bromophenols **6b,c**, respectively. Then, compounds **6** were treated with 1,1,1,3,3,3-hexamethyldisilazane (HMDS), followed by reaction with *n*-butyllithium (*n*-BuLi), to result in the corresponding silylated lithium phenolates via retro-Brook-type rearrangement, which reacted with triflic anhydride (Tf_2O), affording 2-(trimethylsilyl)aryl triflates **7**[4] (**Scheme 1b**). Water-soluble anthraquinones **9** were synthesized through the route outlined in **Scheme 1c**. 3-Cyanophthalide (**4**) and 2-(trimethylsilyl)aryl triflates **7** were treated with TBAF in THF to provide anthraquinones **8**, which upon sulfonation and acid-base reactions (extensively optimized), furnished water-soluble anthraquinones **9**, that is, organophotocatalysts for the *in situ* generation of hydrogen peroxide, with application in organic transformations that use water as a solvent[3] (**Scheme 1c**).

Scheme 1. a) Synthesis of 3-cyanophtalide (**4**). **b)** Synthesis of aryne precursors **7a-c**. **c)** Synthesis of water-soluble anthraquinones **9**.



1. Krishna, R. B.; Moncy, S. H.; Mohan, C. *Org. Biomol. Chem.* **2023**, *21*, 479.
2. Pozo, I.; Guitián, E.; Pérez, D.; Peña, D. *Acc. Chem. Res.* **2019**, *52*, 2472.
3. (a) Yuan, B.; Mahor, D.; Fei, Q.; Wever, R.; Alcalde, M.; Zhang, W.; Hollmann, F. *ACS Catal.* **2020**, *10*, 8277. (b) Burek, B.O.; Bormann, S.; Hollmann, F.; Bloh, J. Z.; Holtmann, D. *Green Chem.* **2013**, 1. (c) Renirie, R.; Aubry, J. M.; Hartog, A. F.; Schoemaker, H. E.; Alsters, P.; Wever, R. *Adv. Synth. Catal.* **2003**, *345*, 849.
4. Perecim, G. "Estudos Visando Sínteses Totais de Substâncias Bioativas". Tese de Doutorado. Programa de Pós-Graduação em Biologia Química. Universidade Federal de São Paulo - Campus Diadema. 242, 2020.

Agradecimentos/Acknowledgments

We are grateful to FAPESP and CNPq for the financial support. B.H.R. thanks CAPES for the scholarship.

Área: ORG

The elusive synthesis of boroquinolines via A^3 coupling reaction

Richard S. Araújo (IC),[1] Nicole A. Camargo (IC),[1] Bruna H. Cortes (IC),[1] Samara R. Amorim (IC),[1] Paula Romanhi (PG),[2] Luana A. Machado (PQ),[3] Leandro F. Pedrosa (PQ).[1,2*]

richard_santos@id.uff.br; leandropedrosa@id.uff.br

[1] Instituto de Ciências Exatas, Departamento de Química, UFF; [2] Programa de Pós-Graduação em Química, Instituto de Química, UFF; [3] Instituto de Ciências Exatas, Departamento de Química, UFMG.

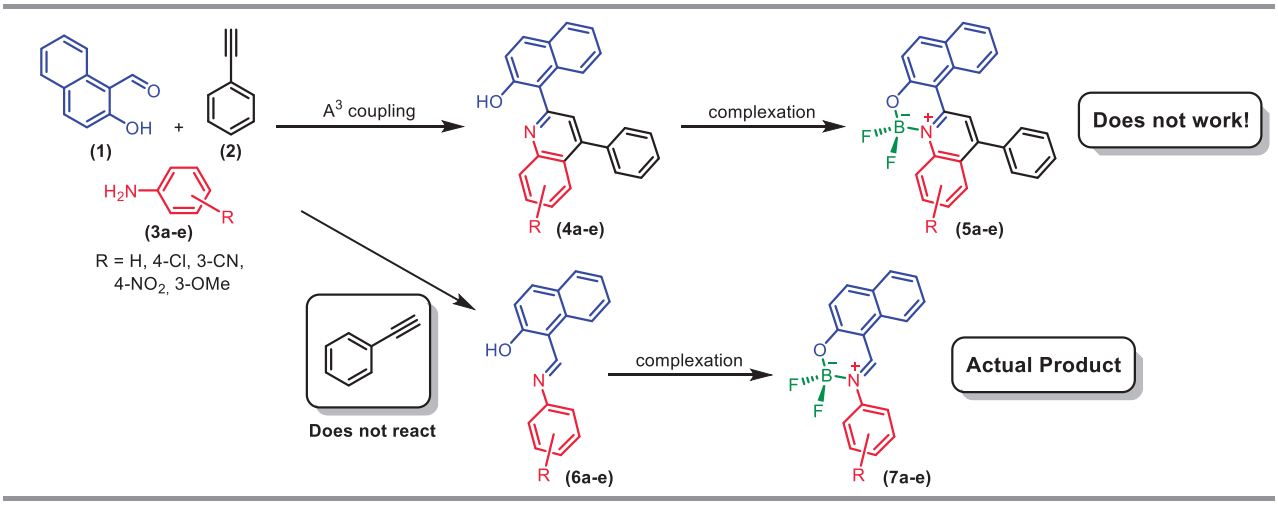
Palavras Chave: *A^3 Coupling, Boroquinolines, DSSC.*

Highlights

The attempts of synthesizing boroquinolines via A^3 Coupling in our lab led to no avail, resulting in an intermediate compound that our group already produce, leading us to investigate what went wrong.

Abstract

Quinoline derivatives have a wide variety of applications in many fields of research, such as pigments and pharmaceutical usages,[1] the same goes for BF_2 coordinated complexes such as BODIPYs that can be used as chemosensors, biochemical markers and photosensitizers.[2] In recent years, our research group have focused in combining those two classes of compounds to further study their interactions and applications as dyes in DSSCs.[2] The A^3 coupling reaction was our first attempt in producing those compounds (***Scheme 1***), for being rather straightforward and not requiring harsh reaction conditions.[3] Unfortunately, all attempts led us to a rather curious path. Although the physical characteristics and melting point of some of our compounds matched those of the articles we followed, our NMRs never matched with the proposed structure of our target compounds, revealing to us that we were actually synthesizing a class of compounds already known to our group. The BORANILs, compounds already synthesized by our group via other methods. Our work does not stop here as we keep developing new methods to reach our current goal.



Scheme 1. Route followed for the synthesis of boroquinolines and our actual product after analysis.

Acknowledgments

CAPES, CNPq, FAPERJ, UFF.

[1] Lewinska, G.; et al. *J Mater Sci: Mater Electron* **2021**, *32*, 18451.
[2] Bozzi, I. A. O.; et al. *Chem. Eur. J.* **2023**, e202303883.
[3] Yadav, C. S.; et al. *ChemistrySelect* **2018**, *3*, 12576.

Área: ORG

TiO_2-catalyzed C3-direct diazenylation of 4-hydroxycoumarin and lawsone with diazonium salts

Yuri P. V. Carvalho (IC),[1] Edson Evangelista (PQ),[1] Iva S. de Jesus (PQ),[2] Luana da S. M. Forezi (PQ)[1*]

yu_carvalho@id.uff.br; luanaforezi@id.uff.br

[1]*Instituto de Química, Departamento de Química Orgânica, UFF;* [2]*Faculdade de Farmácia, Departamento de Tecnologia Farmacêutica, UFF.*

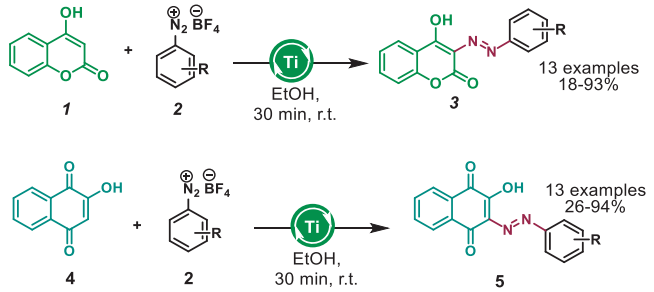
keywords: *Coumarin, Lawsone, Heterogeneous catalysis, Diazonium salts, Direct diazenylation.*

Highlights

A rapid and scalable direct diazenylation of 4-hydroxycoumarin and Lawsone, catalyzed by TiO_2, was described. The products were obtained with favorable yields, at room temperature and short reaction times. The recycling potential of the catalyst and the regioselectivity of the method were evaluated.

Abstract

Coumarins and naphthoquinones represent important classes of substances frequently found in biologically relevant compounds.[1,2] Moreover, their antioxidant properties and ability to participate in redox reactions make them relevant in pharmaceutical research, exploring their therapeutic potential. Their electrophilic and nucleophilic properties make them valuable building blocks for the synthesis of bioactive compounds.[3] Thus, it becomes necessary to study new synthetic methodologies for obtaining substances containing these cores. In this context, this work reports a rapid, and scalable direct diazenylation of 4-hydroxycoumarin employing an easily accessible and recyclable, heterogeneous catalyst (TiO_2). The synthesis of the 3-azo-4-hydroxycoumarins (**3**) and 3-azo-lawsones (**5**) was performed by reacting 4-hydroxycoumarins (**1**) or lawsone (**4**) with different diazonium salts (**2**) in the presence of TiO_2 and ethanol. The scope of this transformation exhibits high compatibility with electron-rich as well as electron-poor diazonium salts, and the corresponding products were isolated in good yields, at room temperature, and with short reaction times. Importantly, the hydroxy group at the C-4 position for 4-hydroxycoumarin was considered to be a directing group, and it was proposed that the formation of titanium enolate intermediate is a requirement for the advancement of the C3-diazenylation developed.



Scheme 1. Synthetic routes to obtain 3-azo-4-hydroxycoumarins **3a-m** and 3-azo-lawsones **5a-m.**

1. Hisham, S.; Salim, M. F. Z.; Chaibi, F. Z.; Sulaiman, L.; Bakar, A. A.; Tajuddin, H. A.; Sarih, N. M.; Abidin, Z. Z. Influence of PMVEMA-ES and 4-hydroxycoumarinhydrazone dyes on the physico-optical properties of PMMAcoating films. *Polymer Bulletin* **2022**, 79, 8669–8693;
2. Yuce-Dursun, B.; Danış, O.; Ozalp, L.; Sahin, E.; Demir, S.; Erdem, S. S.; Ogan, A. In vitro and in silico investigation of inhibitory activities of 3-arylcoumarins and 3-phenylazo-4-hydroxycoumarin on MAOisoenzymes. *Structural Chemistry* **2023**, 34, 1715–1729;
3. Abdou, M. M.; Gizawy, M. A.; Shamsel-Din, H. A. Green synthesis, radioiodination and in vivo biodistribution of5-(2-hydroxyphenyl)-2,4-dihydro-3H-pyrazol-3-one derivatives as potential candidates for lung imaging. *Applied Radiation and Isotopes* **2024**, 203, 111096.

Acknowledgments

CAPES, CNPq, FAPERJ.

Área: ORG

TiO_2-catalyzed direct diazenylation of cyclic dicarbonyls with diazonium salts

Maria Eduarda S. Rodrigues (IC),[1] Emelli P. Hayashi (TM),[1] Yuri P. V. Carvalho (IC),[1] Edson Evangelista (PQ),[1] Luana da S. M. Forezi (PQ)[1,*]

maria_esr@id.uff.br; luanaforezi@id.uff.br

[1]*Instituto de Química, Departamento de Química Orgânica, UFF.*

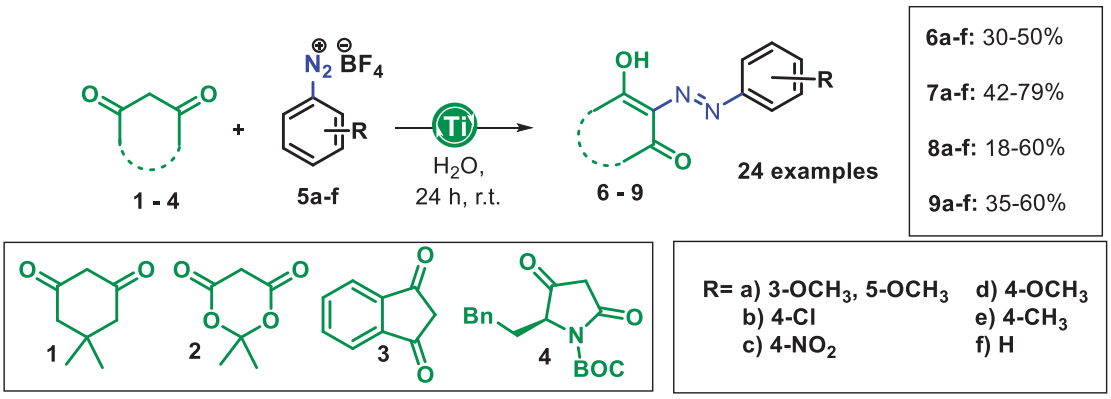
Keywords: *Heterogeneous catalysis, Diazonium salts, diazenylation, Cyclic dicarbonyls.*

Highlights

The present work presents a methodology for direct, simple, and scalable diazenylation of cyclic dicarbonyl compounds. The products were obtained in good yields at room temperature. Catalyst reuse was evaluated, and the reaction was optimized to its most efficient condition.

Abstract

Azo compounds are important structures in medicinal chemistry and have been widely applied as a building block for substances that have a range of biological activities.[1,2] The cyclic α-azo β-dicarbonyl compounds presented in this work were obtained through the reaction between different cyclic dicarbonyls against diazonium salts with different substituents **5a-f** in the presence of TiO_2, as catalyst, in water at room temperature (Scheme 1). The scope of this transformation displays the simplicity and efficiency of the methodology developed, where different compounds with electron-donating and electron-withdrawing groups were obtained, also highlighting the versatility of the methodology. It is important to highlight that the existence of the keto-enol tautomerism present in the initial carbolic is altered after the reaction, meaning that the products have a preference for adopting the enol tautomer after the addition of the azo group. All products were obtained in satisfactory yields.



Scheme 1: synthesis of cyclic α-aryl β-dicarbonyl compounds

1. Das, R.; Kundu, T.; Basumatary, J. Visible light mediated organocatalytic dehydrogenative aza-coupling of 1,3-diones using aryldiazonium salts. *RSC Adv*. **2023**, 13, 3147;
2. Zarei. A.; Khazdooz, L.; Soltani, S.; Chermahini, A. N.; Aghaei, H.; Abbaspourrad, A. Synthesis of arylhydrazone-based molecular switches using aryldiazoniumsilica sulfate nanocomposites and analysis of their isomerization. *Dyes and Pigments* **2021**, 194, 109544;
3. Abdulla, H. O.; Scaringi, S.; Amin, A. A.; Mella, M.; Protti, S.; Fagnoni, M. Aryldiazenyl Radicals from Arylazo Sulfones: Visible Light-Driven Diazenylation of Enol Silyl Ethers. *Adv. Synth. Catal*. **2020**, 362, 2150 – 2154;
4. Abbas, M. M.; Negi, G. Synthesis of Some Novel Heterocyclic Azo-Dye by Usingmeldrum's Acid. *Heterocycl. Lett.* **2021**, 11, 4, 555-558.

Acknowledgments

CAPES, CNPq, FAPERJ.

Área: ORG

Unraveling Reaction Mechanisms: Identifying Isomeric Intermediates with IRMPD Spectroscopy and IMS Techniques

Thiago Carita Correra (PQ)

tcorrera@iq.usp.br

Department of Fundamental Chemistry, Institute of Chemistry, University of São Paulo Av. Prof. Lineu Prestes, 748, Cidade Universitaria, São Paulo, São Paulo, 05508-000, Brazil.

Keywords:*(Mass Spectrometry, Reaction Mechanism, Ion Spectroscopy, Ion Mobility, Polymerization, Catalysis)*

Highlights

Isomeric reaction intermediates have different roles on the reaction mechanism/outcome.

Ion spectroscopy and ion mobility can be used for the identification of isomers without reference standards helping to characterize reaction intermediates and to differentiate reaction pathways.

Abstract

Understanding the intricate pathways of chemical reactions demands investigation of transient species, particularly isomeric intermediates, which often dictate the outcome of complex transformations. This abstract discusses the role of Ion Mobility Spectrometry (IMS) and Infrared Multiphoton Dissociation (IRMPD) spectroscopy in deciphering such intermediates.

IMS offers insights into the structural diversity of ions based on their interaction with a buffer gas, allowing the resolution of isomeric species. Coupled with IRMPD spectroscopy, which promotes the IR photofragmentation of ions to determine their infrared spectrum, it is possible to carry out the precise characterization of reactive intermediates without the need for reference standards. Notably, this synergy allows for the interrogation of species that evade conventional isolation methods or possess fleeting lifetimes that do not allow for reference standard preparation.

In this context, we will demonstrate how the use of IRMPD spectroscopy and IMS was instrumental for the evaluation of a series of reactions, including reactions catalyzed by metal and organometallic and polymerization reactions, exemplified in Figure 1.

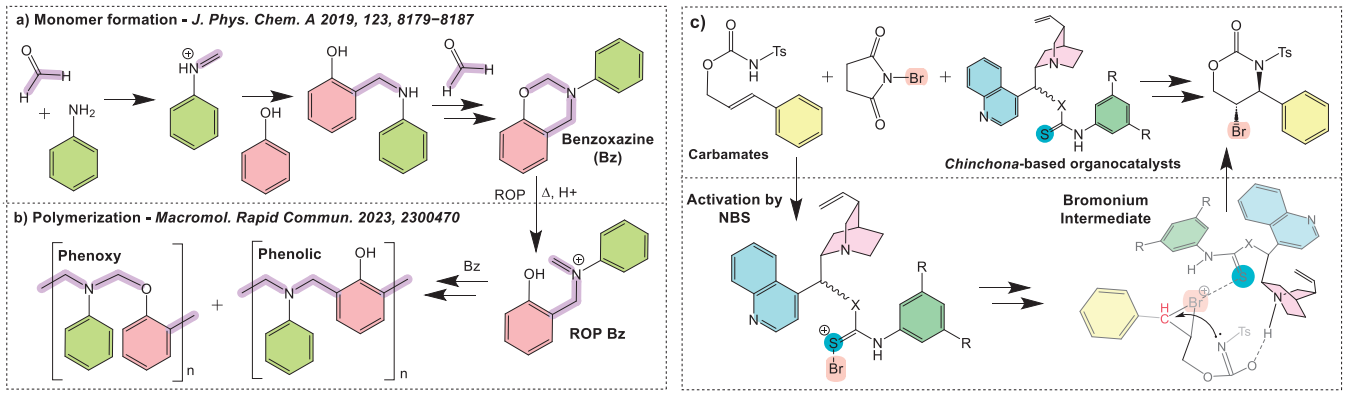


Figure 1. Some reaction mechanisms evaluated by IRMPD spectroscopy and IMS to be discussed.

By providing direct access to elusive intermediates, these advanced mass spectrometry techniques offer invaluable opportunities for elucidating many other reaction mechanisms with detail and accuracy.

Acknowledgments

FAPESP (grants 2014/15962-5, 2015/08539-1, 2019/25634-9, 2021/06726-0, 2022/00498-8), CAPES (grant 23038.006960/2014-65) and CNPq (305858/2020-3 and 306701/2023-5).

QPN

Produtos Naturais

Sociedade Brasileira de Química

Área: QPN
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Activity against bacterial spot of the passion fruit of xanthones isolated from the endophytic fungus *Guignardia manguiferae*

Andrey Moacir do R. Marinho (PQ),[1,2] Viviane Vasconcelos Gracia (PG),[2] Joselina A. Carvalho (PG),[1] Victoria Lopes Ribeiro (IC),[1] José Edson de S. Siqueira[1] (PG), Luana Cardoso de Oliveira[2] (PQ) e Patrícia Santana B. Marinho[1] (PQ).

andrey@ufpa.br

[1]PPGQ, Universidade Federal do Pará; [2]PPGQ, Universidade Federal do Sul e Sudeste do Pará

Key words: secondary metabolites, endophytic fungi, pesticide, passion fruit.

Highlights

Isolation of compounds from the fungus *Guignardia manguiferae*, search for bioactive compounds, new xanthone, passion fruit bacterial spot.

Abstract

Endophytic fungi, which are those that live in symbiosis in plant tissues, have been the subject of research in both chemistry and biotechnology, as they can provide secondary metabolites with various applications. The *Guignardia* genus includes approximately 330 identified species of fungi. A series of bioactive secondary metabolites have been isolated from *Guignardia* fungi, including tricycloalternarenes, vermistatin derivatives, sesquiterpenes, meroterpenoids, among others, many of which are metabolites with antimicrobial activities. The pathogenic bacterium *Xanthomonas axonopodis pv. passiflorae* causes bacterial spot, bacteriosis or oily spot, a disease frequently found on passion fruit. The disease attacks the aerial parts of the plant and can cause the leaves to dry out and fall off, affect the vessels of the thinner stems causing premature death of the plant and cause dark green to brown lesions on the fruit, as well as reducing yields. The aim of this study was to isolate compounds with antimicrobial activity from extracts of the endophytic fungus *G. manguiferae*. The fungus was cultivated in rice medium and after 21 days the ethyl acetate extract (AcOEt) was obtained by maceration. Column chromatography (CC) was used to fractionate the AcOEt extract and isolate the substances, using silica gel or sephadex as the stationary phase and pure solvents and a mixture of solvents in increasing polarity gradients as the mobile phase. The structural elucidation of the substances was carried out by 1H and 13C NMR and two-dimensional experiments (COSY, HSQC and HMBC) and mass spectrometry. Three xanthones known as Sydowinol, Sydowinin A, and a new Sydowin-type xanthone were isolated. The isolated substances were tested for their antimicrobial capacity and showed good results against four virulent strains of *X. axonopodis pv. passiflorae*. The results show that compounds obtained from endophytic fungi can be used as an alternative source to synthetic pesticides against passion fruit diseases.

Agradecimentos/Acknowledgments

The authors would like to thank CNPq (grant 310540/2022-4), FAPESPA and CAPES

Área: QPN

Alcaloides aza-antracênicos com ação citotóxica de *Porcelia ponderosa*

Carlos H. Totini dos Santos (PG)[1], Ranyelison S. Machado (PQ)[2], Emerson A. Oliveira (PQ)[2], Rodrigo E. Tamura (PQ)[2], João Henrique G. Lago (PQ)[1]*

carlos.totini@ufabc.edu.br

[1]Centro de Ciências Naturais e Humanas (CCNH), Universidade Federal do ABC, Santo André – SP; [2]Laboratório de Biologia Molecular do Câncer, Universidade Federal de São Paulo, São Paulo, SP, Brazil

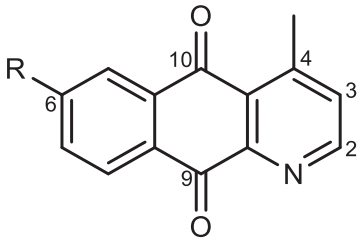
Palavras Chave: *Aza-antraquinonas; DU145;* Porcelia ponderosa

Highlights

Cytotoxic azaanthracene alkaloids from *Porcelia ponderosa*. Fractionation of CH_2Cl_2 extract from roots of *Porcelia ponderosa* afforded two chemically related azanthacene alkaloids - cleistopholine and 6-methoxy-cleistopholine - both actives against tumor prostate DU145.

Resumo

O presente trabalho descreve a investigação da ação antitumoral de alcaloides obtidos do extrato CH_2Cl_2 das raízes de *Porcelia ponderosa.* Para tanto, o material vegetal foi inicialmente extraído com hexano e posteriormente com CH_2Cl_2. O extrato em CH_2Cl_2 foi fracionado via técnicas cromatográficas clássicas resultando, até o momento, nos alcaloides **1** e **2**. Os espectros de RMN de ^{1}H para **1** e **2** revelaram sinais característicos para alcaloides do tipo aza-antracênicos, evidenciados pelos sinais de H-2 em δ 8,89/8,84 (d, *J* = 4,8 Hz), de H-3 em δ 7,48/7,46 (d, *J* = 4,8Hz) e do grupo metílico localizado em C-4 em δ 2,90/2,89 (s), confirmando o esqueleto aza-antraquinônico com a unidade 4-metil-piridina conservada. Diferentemente do espectro de RMN de ^{1}H de **1**, que mostrou sinais de hidrogênios de um sistema *orto*-substituído entre δ 7,20 - 7,80 (H-5 a H-8), para a substância **2** foram observados sinais em δ 7,74 (d, *J* = 2,7 Hz, H-5), 7,28 (dd, *J*= 8,7 e 2,7 Hz, H-7) e em 8,18 (d, *J*= 8,7 Hz, H-8), indicativos de um sistema aromático 1,2,4-trissubstituido. Esse perfil, associado a presença de um sinal adicional em δ 4,00 (s), referente a um grupo metoxílico, permite inferir o posicionamento desse grupo em C-6 no alcaloide **2** estando o mesmo ausente em **1**. Os espectros de RMN de ^{13}C para os alcaloides **1** e **2** revelaram, dentre outros, dois sinais referentes as carbonilas C-9 e C-10 em δ 184,9/182,1 e 183,9/182,2, respectivamente. O posicionamento do grupo metoxílico em C-6 foi confirmado pela proteção em C-9 para **2**, quando comparado com o derivado **1**, ocasionado pelo aumento da densidade eletrônica exercida pelo efeito de ressonância. Finalmente, as fórmulas moleculares dos alcaloides **1** e **2** foram confirmadas como $C_{14}H_{11}NO_2$ e $C_{15}H_{12}NO_3$, devido aos sinais em *m/z* 224,05 e 254,07, respectivamente. Assim, com base nos dados da literatura[1], os compostos foram identificados como cleistofolina (**1**) e 6-metóxi-cleistofolina (**2**), ambos isolados pela primeira vez em *P. ponderosa*. Apesar do primeiro relato na espécie, ambos alcaloides foram isolados anteriormente na espécie *P. macrocarpa*, destacando-se a ocorrência restrita desta classe de alcaloides nas famílias Annonaceae[1] e Papaveraceae[2].



1 R= H
2 R= OMe

Ambos os alcaloides foram testados, *in vitro*, frente a linhagem celular de câncer de próstata (DU145). Após incubação a 100 µM, foram observadas reduções de 90 e 50% de viabilidade celular para **1** e **2**, respectivamente. Por outro lado, quando testados a 50 µM, as taxas de redução na viabilidade celular foram determinadas como 75 e 10% para **1** e **2**, respectivamente. Desta forma, é possível inferir que o alcaloide **1** apresenta maior ação do que **2** frente a linhagem testada, possivelmente causada pela ausência do grupo metoxílico em C-6. Frente aos resultados obtidos, pode-se sugerir que a cleistofolina (**1**) pode ser considerada um protótipo interessante em futuros estudos para o desenvolvimento de fármacos para o tratamento do câncer de próstata.

Referências: [1]Chaves *et al., J. Nat. Prod.*, 64, 240-242, 2001; [2]Ma & Wei & Sang, *Chem. Nat. Comp.*, 56, 292-295, 2020.

Agradecimentos

UFABC, CAPES, CNPq e FAPESP.

Área: QPN

Annotation of azaphilones produced by Penicillium meliponae using LC-MS data and molecular networking.

Eldrinei G. Peres (PG),[1] Thiago F. Souza (PG),[2] Carlos V. A. da Silva (PG),[1] Felipe M. A. da Silva (PQ),[3] Emmanoel V. Costa (PQ),[1] Lívia S. de Medeiros (PQ),[4] Gilvan F. da Silva (PQ), [2] Hector H. F. Koolen (PQ).[5]*

eldrineibk96@gmail.com; hkoolen@uea.edu.br

[1]Departamento de Química, UFAM; [2]Embrapa Amazonia Ocidental; [3]Centro de Apoio Multidisciplinar, UFAM; [4]Instituto de Ciências Ambientais Químicas e Farmacêuticas, UNIFESP; [5]Grupo de Pesquisa em Metabolômica e Espectrometria de Massas, UEA.

Palavras Chave: *Metabolomic, OSMAC, Penicillium, Azaphilones, Molecular Networking.*

Highlights

Endophytic fungi are important sources of diverse molecules. Changes in constitution and cultivation conditions have shown metabolic variability. *P. meliponae* is an excellent producer of azaphilones.

Abstract

Species of fungi belonging to the genus *Penicillium* are among the main microorganisms known for their ability to produce bioactive molecules with various biotechnological applications. Despite the large number of studies involving the chemical characterization of species within this genus, new species are continually being discovered capable of producing a wide variety of molecules. This study aimed to utilize a metabolomics approach through mass spectrometry and molecular networking for a comprehensive characterization of the secondary metabolites of *Penicillium meliponae* (MMSRG-058), an endophytic fungus isolated from the stem of the Amazonian plant *Duguetia stelechantha* (Annonaceae). To obtain extracts of *P. meliponae*, fermentative cultures were performed using the OSMAC (One Strain Many Compounds) method, which comprised four different culture media, potato-dextrose-yeast (PDY), Czapek, International *Streptomyces* Project 2 (ISP2), and meat medium (ME), under two conditions, static and shaken. Both the liquid fraction and the mycelium were used, and two extracting solvents, ethyl acetate and methanol, were employed. The extracts were analyzed using HPLC-HRMS/MS and molecular networking. The analysis of both the networks and manual interpretation of MS/MS spectra allowed for the annotation of over 30 molecules, including polyketides belonging to the subclass of azaphilones. Among them, notable compounds include esclerotioramine, isochromophilone I, II, VI, and IX, esclerotiorin, and ocrephilone, widely described in the literature for their important bioactivities such as antimicrobial[1], anti-inflammatory[2], antioxidante[3], and cytotoxic properties[4]. Additionally, *P. meliponae* showed a great adaptive and biosynthetic capacity in different media and conditions, producing distinct molecules and, in some cases, specific molecules. Chemical characterization through the metabolomics approach proved to be of great importance for understanding the extensive metabolic capacity of the fungal species, particularly for the production of polyketides with bioactive properties.

[1] HEBRA, T. et al. Dereplication, annotation, and characterization of 74 potential antimicrobial metabolites from *Penicillium Sclerotiorum* using t-SNE Molecular Networks. **Metabolites**, v. 11, n. 7, p. 444, 2021.

[2] TANG, J. L. et al. Azaphilone alkaloids with anti-inflammatory activity from fungus *Penicillium sclerotiorum* cib-411. **Journal of agricultural and food chemistry**, v. 67, n. 8, p. 2175-2182, 2019.

[3] DOS SANTOS, P. O. et al. Antioxidant and antibacterial activities of the chlorine pigment sclerotiorin from *Penicillium mallochii* and its chemotaxonomic significance. **Biochemical Systematics and Ecology**, v. 86, p. 103915, 2019.

[4] SON, S. et al. Structures and biological activities of azaphilones produced by *Penicillium* sp. KCB11A109 from a ginseng field. **Phytochemistry**, v. 122, p. 154-164, 2016.

Acknowledgments

The authors would like to thakk the funding agences Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES-finance code 001), Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) and Fundação de Amparo à Pesquisa do Estado do Amazonas (FAPEAM).

Área: QPN

A novel dimeric sesquiterpene and other compounds of *Guatteria olivacea*

Emille Wannick Reinaldo da Silva (PG)[1*], Luiz Henrique de Amorim Pereira (PG)[1], Mariana Costa Aragão (PG)[1], Ana Rita Rodrigues de A. S. Brilhante (PQ)[1], Morgana de Souza Araújo (PG)[2], Antônio Carlos Webber (PQ)[3], Emmanoel Vilaça Costa (PQ)[2], Yuri Mangueira do Nascimento (PQ)[1], Marcelo Sobral da Silva (PQ)[1,4], Josean Fechine Tavares (PQ)[1,4]

emillewannick@ltf.ufpb.br; yurimangueira@ltf.ufpb.br

[1]Postgraduate Program in Natural and Synthetic Bioactive Products, UFPB; [2]Department of Chemistry, UFAM; [3]Department of Biology, UFAM; [4]Department of Pharmaceutical Sciences, UFPB

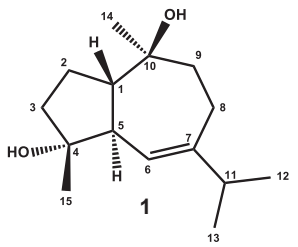
Annonaceae, Terpenes, Chromatography, Spectroscopy

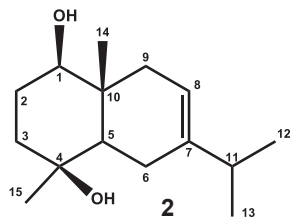
Highlights

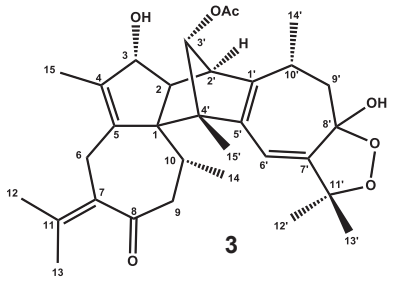
This study of the *Guatteria olivacea* (Annonaceae) resulted in the isolation of 2 sesquiterpenes, which were identified for the first time in this species, in addition to a novel dimeric sesquiterpene.

Abstract

The genus *Guatteria* comprises approximately 307 species widely distributed throughout Mesoamerica, the Caribbean, and South America, with significant diversity in the Amazon region. Chemically, its species consist of isoquinoline and aporphine alkaloids, sesquiterpene lactones with a guaianolide skeleton, as well as monoterpenes and sesquiterpenes that constitute their essential oils. From one of its species, *Guatteria olivacea*, primarily found in the Amazonas, Acre, and Pará regions, the presence of alkaloids and terpenoids with *in vitro* antitumoral activity has been reported. In this study, efforts were made to expand knowledge about this plant through a phytochemical investigation of its hexane extract. For this purpose, plant material was collected in Manaus, Amazonas, Brazil, and subjected to extraction with *n*-hexane. The obtained extract (EH) was fractionated by column chromatography, resulting in 31 fractions analyzed by thin-layer chromatography (TLC) and high-performance liquid chromatography on an analytical scale (HPLC). Among these fractions, fraction 25 (200 mg) was chosen for the isolation of its constituents using preparative-scale HPLC, leading to the isolation of three chemical compounds. These compounds were identified through nuclear magnetic resonance (1D and 2D NMR), comprising two sesquiterpenes (alismoxide - 1, oplodiol - 2), isolated for the first time in *G. olivacea*, and a novel dimeric sesquiterpene named guatteriolivol (3). The obtained results significantly contributed to the chemical knowledge of this species and the Annonaceae family.







References:

ARAÚJO, M. S. et al. Isoquinoline-derived alkaloids from the bark of *Guatteria olivacea* (Annonaceae). **Biochemical Systematics and Ecology**, v. 92, p. 104105, 2020.

COSTA, E. V. et al. A novel eudesmol derivative from the leaf essential oil of *Guatteria friesiana* (Annonaceae) and evaluation of the antinociceptive activity. **Zeitschrift für Naturforschung C**, v. 78, p. 169-177, 2022.

GALVÃO, A. F. et al. Antitumor Effect of *Guatteria olivacea* RE Fr. (Annonaceae) Leaf Essential Oil in Liver Cancer. Molecules, v. 27, n. 14, p. 4407, 2022.

MAAS, P. J. M. et al. Twelve new and exciting Annonaceae from the Neotropics. **PhytoKeys**, v. 126, p. 25, 2019.

Acknowledgments

CAPES · inct institutos nacionais de ciência e tecnologia · Finep INOVAÇÃO E PESQUISA · IPEFARM · LMCA Laboratório Multiusuário de Caracterização e Análises

Área: QPN

Antifungal activity of *Physalis angulata* against *Candida* species enhanced by the action of red LED light

Bianca B. de Alencar (IC)[1]*, Wanderson Z. Cosme (PG)[1], Matheus H. F. Dias (PG)[1], Maria L. F. R. de Melo (IC)[1], Camila C. B. Medeiros (PG)[2], Rosemeire C. L. R. Pietro (PQ)[2], Fabiano G. Silva (PQ)[3], Regina H. Pires (PQ)[1], Ana H. Januário (PQ)[1].

bibiancab901@gmail.com

[1]Universidade de Franca, UNIFRAN; [2]Universidade Estadual Paulista "Júlio de Mesquita Filho", Unesp-Araraquara; [3]Instituto Federal de Educação, Ciência e Tecnologia Goiano, IF-Goiano.

Keywords: *Light-emitting diode, Solanaceae, Phototherapy, Photodynamic inactivation.*

Highlights

This study reports the antifungal activity of the methanolic fraction of *Physalis angulata* against *Candida* strains, both with and without the association of red LED light.

Abstract

Physalis angulata L., commonly known as “camapú”, “balãozinho”, and other names, holds dual significance, both economically (in the synthesis of withanolides and physalins) and medicinally (exhibiting bioactivities against viruses, tumors, and microbes)[1]. This study primarily aimed to evaluate the antifungal properties of the methanolic fraction PA-2F against *Candida* species, both with and without irradiation using a Light Emitting Diode (LED) in the red spectrum. The chloroform extract from the leaves of *P. angulata* branches was fractionated in silica under vacuum, providing the PA-2F(MeOH) fraction. Subsequently, this fraction underwent further purification through exclusion chromatography and flash chromatography using the Büchi Pure 850® equipment, leading to the isolation of compound 1. The antifungal activity of the PA-2F fraction, ranging from 15.62 to 2.000 µg/mL, was tested against *Candida* species, including *C. albicans* ATCC 90028, *C. glabrata* ATCC 2001, and *C. parapsilosis* ATCC 90018. Biofilms were formed in 96-well microplates, exposed to PA-2F, and irradiated with red LED (590 nm, 3.000 mW-3.0 J/cm^2) continuously for 10 minutes[2]. The biofilm inhibitory concentration (CBIM) was determined using the total plate count method. The experiments were performed in triplicate. Results from compound 1's ^{1}H and ^{13}C NMR spectrum, along with a band at λ_{max}=230 nm, suggested a vitasteroid structure, the details of which are currently under investigation. The CBIM obtained for all *Candida* species exceeded 2.000 µg/mL. However, exposure of biofilms to 250 µg/mL of PA-2F followed by red LED irradiation caused a significant reduction of 4.88±0.12, 4.29±0.15, and 4.16±0.06 Log10 CFU/mL for *C. albicans*, *C. glabrata*, and *C. parapsilosis*, respectively, compared to unexposed and non-irradiated biofilms, demonstrating the fungicidal activity of the fraction. These results highlight the potential of combining phytochemistry with phototherapy for fungal control.

References

[1] Maciel, O. A, *et al*. Atena. 3, 175-187, 2021.

[2] Sanitá, P.V, *et al*. Lasers in Medical Science. 33, 709-717, 2018.

Acknowledgments

This research was supported by CAPES, CNPq and FAPESP.

Área: QPN

Antifungal metabolites produced by *Penicillium* sp. CMLD 17, a new species of fungus associated with the Atlantic Forest termite *Anoplotermes pacificus*

Giordanno Di Gioia (PG)[1] *, Jullio Kennedy C. Soares (PG)[1], Fabiana Elaine Casarin dos Santos (PQ)[2], Lívia Soman de Medeiros (PQ)[3].

gioia.silva@unifesp.br; livia.soman@unifesp.br

[1] Instituto de Ciências Ambientais Químicas e Farmacêuticas, UNIFESP; [2] Laboratório Termitologia, [3] Laboratório de Química Bio-Orgânica Otto Richard Gottlieb (LaBiORG)

Keywords: *Termites, Fungi, Chemical ecology, Antimicrobials, Symbiosis*

Highlights

Metabolic organic extracts produced by *Penicillium* sp. CMLD 17, a new fungal species isolated from the termite nests of *Anoplotermes pacificus*, showed antifungal activity against the entomopathogens *Beauveria bassiana, Metarhizium Anisopliae* and *Isaria javanica*.

Abstract

Termites (Blattodea: Isoptera), like other eusocial insects, have some characteristics that could make them more susceptible to being affected by entomopathogens. They store food in their nests and live in high population density, which enables microbial growth and spread in the colony. One of the strategies that evolved in this group of insects is the association with microorganisms that produce antimicrobial agents. Therefore, this study aims to identify molecules produced by the new fungus species *Penicillium* sp. CMLD 17, isolated from the termite *Anoplotermes pacificus* nests, and to verify their antimicrobial potential to assist in the understanding of the likely chemical and biological roles from the association between the fungus and the termite in nature. Preliminary data obtained by analysis of the extracts of the isolate *Penicillium* sp. CMLD 17 via UHPLC-DAD-QTOF-MS/MS, combined with chemical dereplication, led to the annotation of some polyketides that belong to the azaphilones subclass. Some of the annotated compounds have antifungal activity reported in the literature. An antifungal susceptibility assay (poison plate) was performed to evaluate the capability of the extracts to inhibit the growth of three entomopathogenic fungi (*Beauveria bassiana* IBCB 66, *Metarhizium anisopliae* IBCB 425 and *Isaria javanica* IBCB 638) at a concentration of 1 mg.mL^{-1}. All the extracts presented some inhibition in the entomopathogen's growth when compared to the negative control, ranging from 26% to 81%. The max inhibition belonged to the acetone-methanol extract from the mycelium growth in Potato dextrose broth, ranging from 74% to 81%. These results may be evidence that *Penicillium* sp. CMLD 17 and its compounds have ecological importance in the defense of *A. pacificus* from entomopathogens and the isolation and recognition of these molecules can contribute to a better understanding of its role.

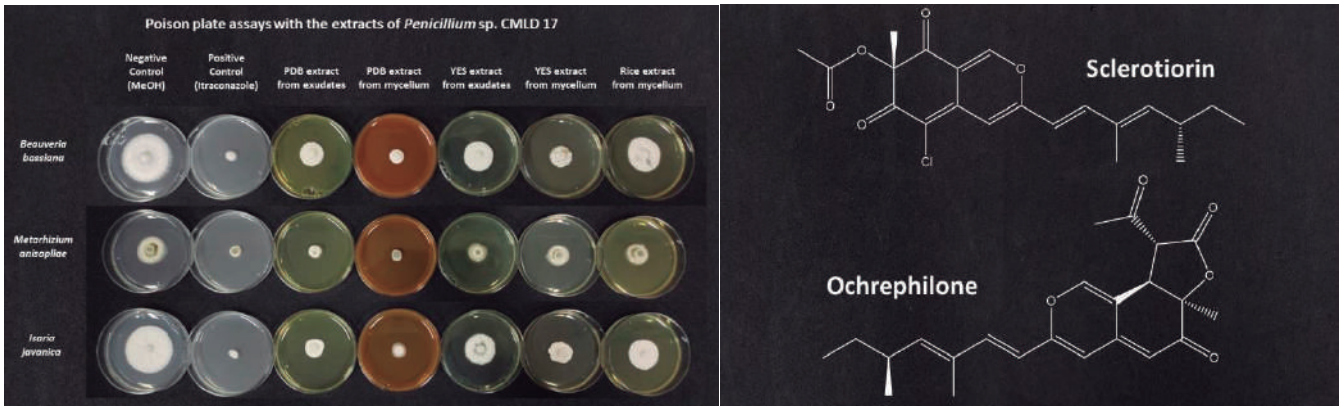


Figure 1. Poison plate assays of *Penicillium* sp. CMLD 17 against *B. bassiana*, *M. anisopliae* and *I. javanica* and two azaphilones (sclerotiorin and ochrephilone) annotated in the extracts of *Penicillium* sp. CMLD 17.

Agradecimentos/Acknowledgments

The authors thank the funding institutions CAPES (88887.840196/2023-00) and FAPESP (2020/08270-0) for financial support.

Área: QPN

Antimicrobial activity from extracts of endophytic fungi isolated from *Calea pinnatifida*

Bianca B. Fernandes (PG)[1*], Marcelo J. P. Ferreira (PQ)[2], Lhaís A. Caldas[3], Jackson Monteiro (PG)[1], Renata C. Pascon[1], Marcelo A. Vallim[1], Suzan P. Vasconcellos (PQ)[1], Patricia Sartorelli (PQ)[1].

bianca.barna@unifesp.br; psartorelli@unifesp.br

[1] Instituto de Ciências Ambientais, Química e Farmacêutica, UNIFESP; [2] Instituto de Biociências, USP, [3]Netherlands Institute of Ecology, NIOO-KNAW, Holanda.

Palavras Chave: *Calea pinnaifida, endophytic fungi, dereplication, antimicrobian activity, molecular network.*

Highlights

Six endophytic fungi were obtained from the leaves of Calea pinnatifida; were cultivated and their metabolic extracts analyzed by HPLC-MS/MS; compounds from different classes were annotated using the GNPS platform; promising biological activities against pathogenic strains; A wide variety of endophyte genera was observed in just one host.

Resumo/Abstract

Endophytic microorganisms, associated with medicinal plants or plants of some economic value, have stood out for producing a great diversity of classes and metabolites. *Calea pinnatifida* is a plant belonging to the Asteraceae family and is widely used in folk medicine to treat stomach aches, giardiasis and amoebiasis. However, this species has not been investigated in relation to its endophytic microbiota. In this work six endophytic fungi isolated from the leaves of the plant and identified, by sequencing DNA Internal Transcribed Spacer (ITS), as *Colletotrichum* sp. (CPFF12, CPFF14 and CPFF16), *Pestalotiopsis* sp. (CPFF42), *Nigrospora* sp. (CPFF52) and *Hypomontagnella* sp. (CPFF41). After cultivation in BD broth medium, extracts were obtained using ethyl acetate and analyzed by liquid chromatography coupled to mass spectrometer (UHPLC-HRMS/MS) in association with the Global Natural Product Social Molecular Networking (GNPS), in order to organize and dereplicate the extracts. Thus compounds, already described in the literature, such as the terpene fusaproliferin and the lignan niranthin, were annoted in the metabolome of the fungi of genera *Colletotrichum* and *Nigrospora*. Additionally, these extracts were submitted to evaluation of antimicrobial activity against pathogenic bacteria and yeast and all the extracts showed some kind of inhibition against the strains of *E. coli*, *S. aureus* and *C. albicans*, both for disk diffusion and minimum inhibitory concentration. In this way, it was possible to observe the variety of classes of compounds produced by different genera of microorganisms within a single host, highlighting the potential for biological application due to the significant activities against pathogens, making new studies an inexhaustible source of new discoveries and perspectives.

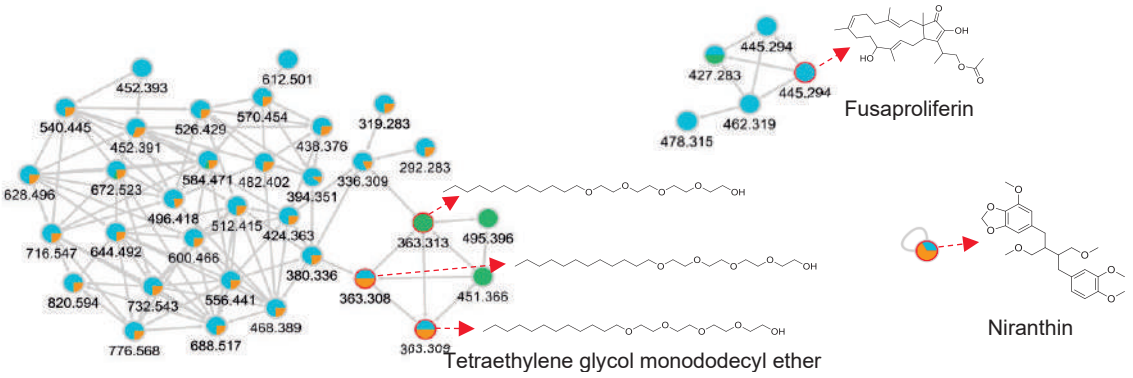


Figure: Molecular network created by GNPS. Colors of the nodes: Green: CPPF41|CPFF42; Blue: CPFF12|CPFF14|CPFF16; Orange: CPFF52. Red frames: molecules annotated by GNPS. Edge labels between nodes represent m/z differences.

Acknowledgments

To the collaborators and funding agencies: Capes, CNPq and FAPESP.

Área: QPN

Antioxidant activity test of “Maria Bonita Pepper” cultivar essential oil

Aniele Beatriz Dias (PG),[1*] Ian Raffaello Gallo Godoi (PG),[1] Gabriela Zutin Beretta (IC),[2] Virgínia Cláudia Paulino Silva (PQ),[3] Fernando César Sala (PQ),[3] Tatiana Santana Ribeiro (PQ)[2]

aniele@estudante.ufscar.br

[1]Programa de Pós-Graduação em Ciência dos Materiais - PPGCM, UFSCar; [2]Universidade Federal de São Carlos - UFSCar, [3]Departamento de Ciências da Natureza, Matemática e Educação - DCNME, UFSCar; [3]Departamento de Biotecnologia, Produção Vegetal e Animal, UFSCar.

Keywords: *DPPH, antioxidant test, essential oil, "Maria Bonita Pepper”, "Biquinho Pepper”.*

Highlights

“Maria Bonita Pepper” had superior antioxidant ability in comparison with “Biquinho Pepper” (42.5% DPPH inhibition). Results contribute to future applications in the food and pharmaceutical industries.

Abstract

The present work evaluated the antioxidant activity of “Maria Bonita Pepper” essential oil, obtained from “Biquinho Pepper” seed crosses from UFSCar - Araras germplasm bank[1]. Comparative analysis was conducted concerning the antioxidant activity documented in the literature for “Biquinho Pepper” essential oil[2]. The methodology relies on the DPPH (2,2-diphenyl-1-picrylhydrazyl) radical capture by antioxidant[3]. "Maria Bonita" cultivar essential oil was extracted through hydrodistillation using a Clevenger extractor. Resulting sample was combined with dichloromethane in a separation funnel to facilitate the target mixture removal. After dichloromethane evaporation, the oil obtained was transferred to an amber flask, resulting in a final yield of 4.8 mg.

In DPPH methodology, solutions were prepared using ethyl alcohol as the solvent, and the quantities were related to the mass obtained during the extraction. Quercetin was used as a comparative factor to evaluate the antioxidant action of “Maria Bonita" cultivar. Samples were prepared by weighing 4.8 mg for 50 mL of solvent, while the DPPH solution was prepared with 2.4 mg for 100 mL of alcohol. Absorbances were measured at a wavelength of 517 nm. Absorbance results were 0.200 for DPPH, 0.115 for the sample solution, and 0.009 for the quercetin solution. When calculating the percentage of reduced DPPH, the study revealed “Maria Bonita Pepper" exhibited a 42.5% inhibition rate of the radical. In comparison, “Biquinho Pepper” studies indicate 33.17% inhibition rate (standard deviation 0.08%)[2]. Thus, we can conclude that “Maria Bonita Pepper” demonstrated a significant ability to inhibit DPPH radical, surpassing the percentage observed in the “Biquinho Pepper”. These results highlight the antioxidant potential of the “Maria Bonita Pepper”, suggesting its interest as a natural source of bioactive compound. This study contributes to the comprehension of the beneficial potential of this cultivar, paving the way for future research and applications in the food and pharmaceutical industries. Metabolomic studies by NMR and GC-MS are underway to identify the metabolites of this cultivar, as well as nanoencapsulation methods to be tested as prototypes for bioinsecticides and fungicides.

References:

[1] Campo & Negócio, 2020. Maria bonita: A nova pimenta brasileira. Available in: https://revistacampoenegocios.com.br/maria-bonita-a-nova-pimenta-brasileira/#:~:text=A%20Maria%20Bonita%20(MB)%20foi,existe%20e%20a%20mais%20importante. Access in: 23 jan. 2024.

[2] Mariano, B. J. et al. Biquinho pepper (Capsium chinense): Bioactive compounds, in vivo and in vitro antioxidant capacities and anti-cholesterol oxidation kinetics in fish balls during frozen storage. Food Bioscience, 47, 101647, 2022.

[3] Brand-Williams, W., Cuvelier, M.E. and Berset, C. (1995) Use of a Free Radical Method to Evaluate Antioxidant Activity.

Acknowledgments

PPGCM CIÊNCIA DOS MATERIAIS · FAPESP · UFSCAR ARARAS LAB.COMAM · CNPq · CAPES

Área: QPN

Anti-Plasmodial Brominated Metabolites from the Marine Sponge *Aplysina alcicornis*

Cauê A. W. Zuccarino (IC),[1*] Andrés F. T. Peña (PG),[1*] Giovana R. Mendes (PG),[2] Antonio G. Ferreira (PQ),[3] Eduardo Hajdu (PQ),[4] Rafael V. C. Guido (PQ),[2] Roberto G. S. Berlinck (PQ)[1]

cauezuccarino@usp.br; andres.torres@usp.br; rgsberlinck1010@outlook.com

[1]Instituto de Química de São Carlos, USP-IQSC; [2]Instituto de Física de São Carlos, USP-IFSC; [3]Departamento de Química, UFSCAR; [4]Museu Nacional, UFRJ.

Keywords: *Screening, bromotyrosine, Antiplasmodial, Aplysina*

Highlights

Anti-Plasmodial Brominated Metabolites from the Marine Sponge *Aplysina alcicornis*

Sponges have diverse and bioactive secondary metabolites. A chemo-biological investigation of *A. alcicornis* led to the isolation of brominated compounds some of which active against *P. falciparum*.

Resumo/Abstract

Malaria is a potentially fatal disease caused by the parasite *Plasmodium falciparum*. In 2021, the World Health Organization (WHO) estimated 249 million cases and more than 608,000 deaths, mainly in tropical countries. This represents a 2.46% increase in new cases and a small decrease in the mortality rate compared to previous years [1]. Currently, artemisinin-based drugs are the gold standard treatment against malaria and have saved a millions of lives. However, the emergence of parasites resistant to standard antimalarials, including artemisinin and its derivatives, highlights the importance of discovering new bioactive compounds as lead candidates for malaria. In this sense, new bioactive compounds of natural product origin is an important approach to identify new antimalarial agents [2], [3].

In the present investigation we evaluated the biological and chemical profiles of aqueous and organic extracts obtained from the marine sponge *Aplysina alcicornis*. Purifications of these extracts by size-exclusion chromatography and solid-phase extraction (SPE-C18) provided enriched fractions, which were subjected to evaluation of their antiplasmodial activity against *P. falciparum* (3D7 strain, chloroquine-sensitive) and HPLC-UV-MS analyses. Twelve fractions obtained from the *A. alcicornis* extract were screened and evaluated, 7 of which displayed ≥ 90% *P. falciparum* inhibitory activity. Selected fractions were purified by HPLC-UV, resulting in the isolation of 10 compounds. The structures of the above compounds were identified by NMR and MS-based analyses. The anti-plasmodial activity of pure compounds indicated some potent activity, at low μM level.

[1] https://www.who.int/teams/global-malaria-programme/reports/world-malaria-report-2023.

[2] Penna-Coutinho, J. et al., *Int. Jour. Parasit.*, **2021,** *17*, 150–155. https://doi.org/10.1016/j.ijpddr.2021.09.003

[3] Kyei-Baffour, K. et al., *Bioorg. Med. Chem.*, **2020,** *28*, 115678. https://doi.org/10.1016/j.bmc.2020.115678

Agradecimentos/Acknowledgments

The authors thank FAPESP (2023/02821-3; 2019/17721-9; 2015/01017-0), CNPq and CAPES for the financial support and scholarships.

Área: QPN

Antischistosomal potential of dehydrodieugenol-loaded silver nanoparticles formed *in situ* by coupling oxidation of eugenol

Larissa V. F. Oliveira (PQ),[1*] Dalete Christine S. Souza* (PG),[1] Fernanda F. Camilo (PQ),[2] Marisi G. Soares (PQ),[3] Rayssa A. Cajas (PG),[4] Maria E. Cirino (PG),[4] Josué de Moraes (PQ),[4] João Henrique G. Lago (PQ)[1]

joao.lago@ufabc.edu.br; larissa.verena@ufabc.edu.br

[1]Center of Natural Sciences and Humanities, Federal University of ABC (UFABC); [2]Institute of Environmental, Chemical and Pharmaceutical Sciences, Federal University of São Paulo (UNIFESP); [3]Institute of Chemistry, Federal University of Alfenas (UNIFAL); [4]Research Center for Neglected Diseases, Guarulhos University (UNG)

Keywords: *Silver nanoparticles, green synthesis, dehydrodieugenol,* S. mansoni, C. elegans

Highlights

This work reports the *in situ* preparation of dehydrodieugenol-loaded silver nanoparticles by coupling oxidation of eugenol provided by clove oil and the evaluation of their antischistosomal activity.

Abstract

Schistosomiasis is a significant neglected disease that affects approximately 250 million people globally. Since praziquantel is the only available drug for treating schistosomiasis, there is a critical need to identify new anthelmintic compounds, especially from natural sources.[1] To enhance the activity of various natural products, one potential avenue involves combining them with silver nanoparticles (AgNP).[2] Based on this approach, this work aimed to prepare dehydrodieugenol-loaded silver nanoparticles, *in situ*, through an oxidation coupling reaction of eugenol provided by clove oil. The antischistosomal activity of the dehydrodieugenol conjugated with AgNP (NatProd-AgNP) was assessed against *S.mansoni* adult worms and the toxicity of the samples was evaluated using a mammalian cell line model and an in vivo model (C. elegans) (Figure 1). For comparison, isolated eugenol, dehydrodieugenol (DHDG), and AgNP dispersions prepared through a conventional chemical method were also evaluated.

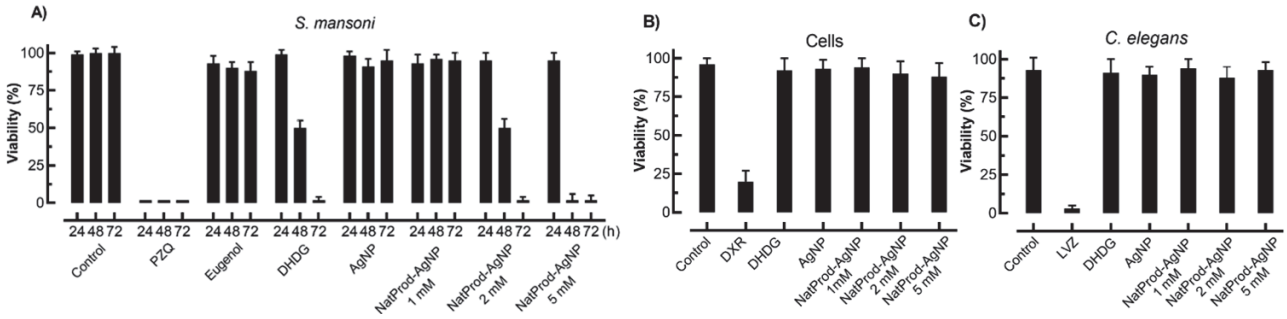


Figure 1. A) Anthelmintic assays on *S. mansoni* adult worms ex vivo after 24, 48, and 72 hours of incubation. B) Cytotoxicity assays on Vero cells. C) Toxicity assays on C. elegans. Praziquantel (PZQ), levamisole (LVZ), and doxorubicin (DXR) were used as positive controls against schistosomes, cells, and C. elegans, respectively.

In Figure 1A, it is noticeable that eugenol and silver nanoparticles prepared through a chemical method (AgNP) exhibited no activity against *S. mansoni*. In contrast, the prepared green silver nanoparticles (NatProd-AgNP) demonstrated significant activity, resulting in 100% worm mortality within 72h and 48h for samples at 2 and 5 mM concentrations, respectively. This efficacy is likely attributed to the combination of silver nanoparticles and DHDG since this is the product of the oxidative coupling of eugenol in the presence of Ag^+. Moreover, pure DHDG when tested independently, also exhibited activity, leading to 100% mortality of worms after 72 hours. Remarkably, the combined product exhibited a faster onset of activity compared to isolated DHDG. Importantly, the toxicity assays revealed that none of the tested samples exhibited toxicity towards both cells and the animal model. Therefore, this study not only enhances the understanding of the application of phytochemical-conjugated nanoparticles but also represents a significant step toward the development of novel anthelmintic agents.

References: [1]Azevedo C.M, et al. *Molecules,* **2023**, 28, 6807. [2]Joshi G, et al. *J Control Release*, **2021**, 339, 51.

Acknowledgments

FAPESP (Grants 2021/07971-8, 2021/07297-5 and 2021/02789-7).

Área: QPN

Aporphinoid alkaloids isolated from the bark of branches of *Annona amazonica* (Annonaceae)

Aldimara Faba Martins (PG),[1,*] Maria Lúcia Belém Pinheiro (PQ),[1] Waldireny Rocha Gomes (PQ),[2] Felipe Moura Araújo da Silva (PQ),[3] Hector Henrique Ferreira Koolen (PQ),[4] and Emmanoel Vilaça Costa (PQ).[1,*]

***** aldimaramartinsbioqui@gmail.com / evc@ufam.edu.br

[1]Departamento de Química, UFAM (DQ/UFAM), Manaus-AM; [2]Faculdade de Ciências Farmacêutica, UFAM (FCF/UFAM), Manaus-AM; [3]Central Analítica, UFAM (CA/UFAM), Manaus-AM; [4]Escola Superior de Ciências da Saúde, UEA, Manaus-AM.

Palavras Chave: *Annona amazonica, Annonaceae, Aporphinoid alkaloids, Dereplication; Chemical profile.*

Highlights

1. Six compounds were isolated from the bark of branches of *Annona amazonica*. **2.** The isolated compounds belong to the class of aporphinoid alkaloids and terpenoid. **3.** Among these, only three were identified as the alkaloids liriodenine, dicentrinone and nordicentrine, the others are under analysis. 4. Dicentrione and nordicentrine are described for the first in the *A. amazonica* as well as in the genus *Annona*.

Resumo/Abstract

Annona amazonica R.E. Fries is a tropical tree that grows up to 20-25 m tall popularly known as 'araticum árvore gigante', 'araticum', and 'ata', found from Panama to South America. In Brazil this species commonly occurs in the Amazon, mainly in the states of Amazonas and Pará. According to literature, there are three studies with *A. amazonica*.[1] One that describes the presence of cyanogenic constituents in the leaves, fruits and seeds,[2] other that describe the isolation and identification of aporphinoid alkaloids, terpenoids, and fatty acids from the heartwood,[1] and one that describes the studies of essential oils from the leaves and twigs,[3] data that has not been published. On the other hand, there are no reports for the study of the fixed constituents from the bark of the branches of *A. amazonica*, the object of study of our research group GEQBiom (*Grupo de Estudo de Química de Biomoléculas*). The hexane and methanolic extracts were obtained by maceration method at room temperature. After drying and calculating the yields, they were subjected to chemical profile analysis by mass spectrometry. Having observed the presence of nitrogenous constituents, the methanolic extract was subjected to acid-base treatment [4] in search of the alkaloid constituents present in the alkaloid fraction. The alkaloid fraction was also subjected to chemical profile analysis and dereplication. The analysis of the chemical profile (dereplication) in the *APCI+* positive mode highlighted several ions of even mass attributed to the presence of isoquinoline alkaloids in the methanolic extract and alkaloid fraction. The phytochemical study of the alkaloidal fraction resulted in the isolation of six compounds, five belonging to the class of alkaloids and one to sesquiterpene class (Figure 1). Classical chromatographic techniques (CC and TLC), and spectroscopic (^{1}H and ^{13}C 1D/2D NMR) and spectrometric (MS) analysis were used for the isolation and identification of the chemical compounds, respectively, leading to the present moment the identification of three known alkaloids, liriodenine (**1**), dicentrinone (**2**) and nordicentrine (**3**). Liriodenine has already been described in the species under study, while dicentrinone and nordicentrine are the first records in the species and in the genus itself. All identified alkaloids appear in the analysis of both the methanolic extract and the alkaloid fraction chemical profile. The dereplication study of these alkaloids confirms their presence in the methanolic extract and alkaloid fraction.

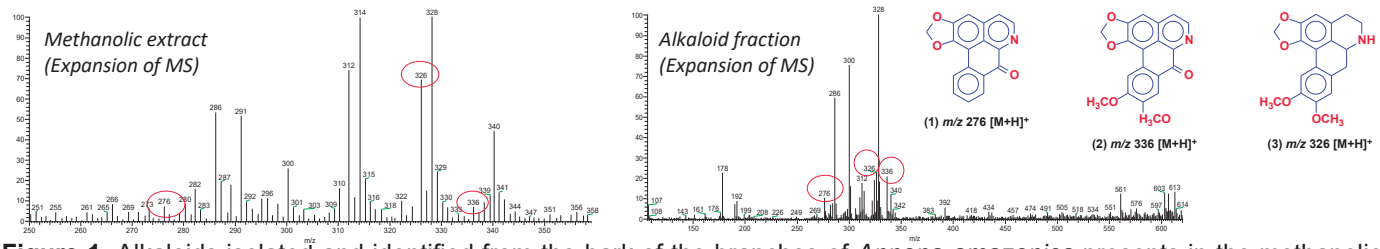


Figure 1. Alkaloids isolated and identified from the bark of the branches of *Annona amazonica* presents in the methanolic extract and alkaloid fraction.

References: [1] Pinheiro, M.L.B., *et al. J. Braz. Chem. Soc.*, 20 (6), 1095-1102, 2009; [2] Thomsen, K.; Brimer, L.; Bot. J. Linnaeus Soc. 1997, 124 (3), 273-294; [3] Alcântara, J.M., *et al. VII SBOE - Simpósio Brasileiro de óleos essenciais*, UFOPA, 2013; [4] Costa, E.V., *et al. J. Nat. Prod.*, 69, 292-296, 2006.

Agradecimentos/Acknowledgments

The authors are grateful to CAPES, CNPq, FAPEAM, Institutos Nacionais de Ciência e Tecnologia (INCT/CNPq Grant: 465357/2014-8), and UFAM for financial support, and CA/CAM/UFAM for NMR and MS analysis.

Área: _____QPN_____

Applicability of endophytic fungi as a source of active secondary metabolites, for biotransformation, agriculture, bio- and phytoremediation

Humberto E. Ortega (PQ),[1,2,3*] **Daniel Torres-Mendoza** (PQ),[1,4] **Luis Cubilla-Ríos** (PQ).[1,2,3]

humberto.ortegad@up.ac.pa

[1]*Departamento de Química Orgánica, Facultad de Ciencias Naturales, Exactas y Tecnología, Universidad de Panamá;* [2]*Sistema Nacional de Investigación (SNI);* [3]*Laboratorio de Bioorgánica Tropical, Universidad de Panamá;* [4]*Vicerrectoría de Investigación y Postgrado, Universidad de Panamá.*

Keywords: *Endophytic fungi, secondary metabolites, biotransformation, bioremediation, phytoremediation.*

Highlights

Endophytic fungi colonize the internal tissue of plants without causing harm or disease.
In the past decade, the number of patents has increased to apply endophytic fungi for agricultural, bio-, and phytoremediation purposes, and for the production of active natural products with biomedical applications.
They are an important source of active natural products with great chemical diversity which is largely untapped.
In some cases, they can produce the same secondary metabolites of their host plants that are medically important drugs.
The genus *Aspergillus* is the most dominant, representing a rich source of diversity of bioactive natural products.

Abstract

Plant endophytic fungi spend all or part of their lives inside host tissues without causing disease symptoms. They can colonize the plant to protect against predators, pathogens, and abiotic stresses generated by drought, salinity, high concentrations of heavy metals, UV radiation, and temperature fluctuations. They can also promote plant growth through the biosynthesis of phytohormones and nutrient acquisition, and they could be an alternative source of secondary metabolites for applications in medicine, pharmacy, and agriculture. In this work, we present the results obtained from three reviews: 1) patents related to endophytic fungi applicability for abiotic stress tolerance and growth promotion of plants, as agents for biocontrol of herbivores and plant pathogens and bio- and phytoremediation applications; 2) patents related to secondary metabolite production and biotransformation; 3) and endophytic fungi compounds published from January 2015 to December 2020 that were cataloged as unprecedented, rare, uncommon, or possessing novel structural skeletons. The two most patented genera of fungi for different applications and as a source of novel secondary metabolites were *Aspergillus* and *Penicillium*. Fungi that could increase the capacity of CO_2 absorption by plants, degradation, and biotransformation of waste, enhance food production without altering its quality or those that provided drought resistance/nutrient absorption capability to plant species related to human or animal feeding could be areas of significance to develop new applications and patents provide an outstanding field for further studies. About two decades ago, the study of endophytic fungi as producers of active molecules was emphasized due to obtaining compounds originally produced by plants or due to the production of novel secondary metabolites. Thus, fungi from the genera *Aspergillus*, *Fusarium*, *Penicillium,* and *Pestalotiopsis* have been recognized as producers of anticancer compounds and have pharmaceutical potential. It is estimated that only around 1% of the microorganisms have been cultivated, and within these groups, endophytic fungi correspond to the least studied.

References:

1. Ortega, H.E.; Torres-Mendoza, D.; Caballero E., Z.; Cubilla-Rios, L. *J. Fungi* **2021**, 7, 570.
2. Ortega, H.E.; Torres-Mendoza, D.; Cubilla-Rios, L. *Microorganisms* **2020**, 8, 1237.
3. Torres-Mendoza, D.; Ortega, H.E.; Cubilla-Rios, L. *J. Fungi* **2020**, *6*, 58.

Acknowledgments

This project was supported by the National Research System (SNI), and the National Secretariat for Science and Technology of Panama (SENACYT). The authors thank the University of São Paulo, Brazil, for granting access to Portal de Periodicos CAPES/MEC.

Área: *QPN*

A study on the influence of different particle sizes on the antioxidant activity of ethanolic extracts of rosemary (*Rosmarinus Officinalis L.*)

Rayane Cristina da Silva Santos (PG)[1*], Tayná de S. V. Moura (PG)[1], Felipe Silva Semaan (PQ)[2], Kátia Regina de Souza (PQ)[1].

rayanne.cristina@ime.eb.br

[1]*Seção de Ensino de Engenharia Química, Instituto Militar de Engenharia, 22290270 RJ, RJ, Brasil;*
[2] *Departamento de Química Analítica, Instituto de Química, Universidade Federal Fluminense, 24020007 Niterói, RJ, Brasil.*

Palavras Chave: *Rosemary, Granulometry, Antioxidant Activity, Total Phenolics, UV-vis, Biodiesel.*

Highlights

The research investigates how different particle sizes can influence the antioxidant activity of the ethanolic extract of rosemary, a plant recognized for its application in cooking and medicine.

Resumo/Abstract

O biodiesel, por ser higroscópico e possuir alta reatividade com o oxigênio, sofre oxidação, o que resulta em curto tempo de vida útil e consequentemente, prejuízos severos ao motor que o utiliza. Diante disso, é importante adotar medidas para melhorar a resistência desse biocombustível e, consequentemente, aumentar o tempo de vida útil dele, como a adição de antioxidantes sintéticos ou naturais.

O alecrim é uma erva com propriedades antioxidantes, amplamente disponível na natureza, tendo o seu extrato etanólico como fonte promissora de compostos fenólicos em altas concentrações, podendo assim, ser utilizado para melhorar a estabilidade oxidativa do biodiesel. Tendo em vista isso, o trabalho em questão foi baseado no estudo da influência de diferentes granulometrias na atividade antioxidante de extratos etanólicos de alecrim, uma abordagem não explorada na literatura.

Para isso, os extratos foram obtidos seguindo metodologia conhecida[1], mas com algumas adaptações. A determinação do teor de fenólicos totais para cada *mesh* foi realizada empregando o reagente Folin-Ciocalteau e espectrofotometria UV-Vis (ʎ= 760 nm), e a atividade antioxidante foi, pela mesma técnica (ʎ= 517 nm), determinada empregando o método de sequestro de radicais DPPH▪. Após a realização das análises, os resultados obtidos sobre a atividade antioxidante foram comparados com os de um dos antioxidantes sintéticos mais utilizados, BHT, conforme Quadro 1.

Quadro 1. Resultados da Análise da Atividade Antioxidante.

Amostras	N	Quantidade de leitura	Abs ± SD	AA(%) ± SD
Extato *Mesh* 20	9	3 x 9	0,021 ± 0,001	99,481 ± 0,035
Extrato *Mesh* 32	9	3 x 9	0,030 ± 0,002	99,261 ± 0,056
Extrato *Mesh* 80	9	3 x 9	0,021 ± 0,001	99,468 ± 0,028
Extrato *Mesh* 100	9	3 x 9	0,027 ± 0,001	99,321 ± 0,035
Extrato *Mesh* >100	9	3 x 9	0,036 ± 0,003	99,102 ± 0,086
BHT	1	3 x 1	0,162 ± 0,001	95,942 ± 0,014

Com base no Quadro 1, foi possível observar uma relação entre diferentes granulometrias e as atividades antioxidantes para respectivos extratos etanólicos de alecrim, não sendo, porém, possível, verificar um aumento gradual inversamente proporcional ao tamanho do grão, como esperado. Tal fato pode ser explicado pela compra de dois lotes diferentes do alecrim. Portanto, o trabalho permitiu observar a importância da padronização desde a compra, pois isso poderia ter minimizado as diferenças obtidas nos valores de absorbância e atividade antioxidante de cada *mesh*, e evidenciar o desenvolvimento de metodologias e pesquisas para o aumento da qualidade do combustível, a fim de reduzir a emissão de poluentes, podendo o extrato etanólico de alecrim substituir parcialmente ou integralmente o BHT, uma vez que todos os *meshes* apresentaram atividade antioxidante maior do que a dele conforme mostrado no Quadro 1.

Agradecimentos/Acknowledgments

Este estudo foi financiado em parte pela Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) - Código Financeiro 001, FAPERJ (Projetos n^{os}: E-26/210.022/2021 e E-26/211.062/2021), Universidade Federal Fluminense (UFF) e Instituto Militar de Engenharia (IME).

[1] MEDEIROS, M. L. Extrato de Alecrim (Rosmarinus officiallis L.): Um antioxidante eficiente para uso no biodiesel. 2013. 75 f. Tese (Doutorado em Química), Centro de Ciências Exatas e da Natureza, Universidade Federal da Paraíba, Paraíba.

Área: QPN

Atividade alelopática, estudo químico e rendimento do extrato bruto e do óleo essencial das folhas de *Peperomia pelúcida* (Itacoatiara-Amazonas).

Mateus Feitosa Santos (IC)[1], Sulcimilena Mady Flores (TC/PG)[1], Ília Gilmara Carvalho dos Santos (PQ)[1] Eldon Carlos dos Santos Colares (PQ)[2], Márcio Laranjeira Anselmo (PG)[1], Nívea Cristina G. Munin (PQ)[1].

[1]*Universidade Federal do Amazonas, Instituto de Ciências Exatas e Tecnologia- (ICET), Itacoatiara, Amazonas.*
[2]*@Pharbox, comércio varejista de produtos farmacêutico, Manaus, Amazonas.*

Palavras Chave: *Alelopatia, Peperomia pellucida, Herbicida natural, Óleo essencial.*

Highlights

Allelopathic activity, chemical study and yield of crude extract and essential oil of Peperomia pellucida leaves (Itacoatiara-AM). Through secondary metabolism, plants can produce substances such as essential oils, and we can extract extracts from them. Peperomia pellucida has been studied because its bioactive activities. The essential oil and the extract were studied for their allelopathic potential against gherkin and cherry tomato seeds, both the essential oil and the extract inhibited seed germination.

Resumo/Abstract

A família Piperaceae abriga filogeneticamente espécies produtoras de óleos essenciais e extratos que apresentam amplo espectro de atividades biológicas, dentre estes, há o efeito tóxico contra diversas pragas agrícolas e plantas daninhas. Dentre os gêneros botânicos desta família destaca-se o gênero Peperomia que abriga a espécie *Peperomia pellucida*, conhecida como erva de jabuti que possui diferentes atividades biológicas[1]. Todavia, não existem relatos do potencial alelopático do óleo e do extrato da folha da espécie, o que contribui para que pesquisas desta natureza despertem o interesse da comunidade científica. O objetivo deste trabalho foi avaliar o rendimento, o perfil químico e atividade alelopática do óleo essencial e extrato das folhas de *Peperomia pellucida*, coletadas em Itacoatiara-AM, sobre as sementes de maxixe (*Cucumis anguria* L.) e tomate-cereja (*Solanum lycopersicum* var. *cerasiforme*). As folhas de *Peperomia pellucida* foram coletadas verdes, parte foi separada para extração do óleo essencial a partir da técnica de hidrodestilação da biomassa fresca, em aparelho tipo Clevenger, por 4 horas. O rendimento do óleo foi calculado v/m. A análise da composição química do óleo essencial foi por cromatografia gasosa acoplada à espectrometria de massas (Shimadzu GCMS-QP2010) e a identificação dos constituintes foi baseada na interpretação de seus respectivos espectros de massa, cálculo do índice de retenção e comparados com dados da literatura. A outra parte das folhas coletadas foram secas em estufa e trituradas em moinho de facas. O extrato bruto foi caracterizado por ensaios cromáticos segundo Matos (2009)[2]. Os ensaios alelopáticos consistiram em avaliações diárias do desenvolvimento de sementes de maxixe e tomate-cereja submetidas às concentrações de 0,1 e 1 % do óleo essencial e do extrato. Os parâmetros: porcentagem de germinação, tempo médio de germinação, velocidade de germinação, vigor das sementes pelo índice de velocidade de sementes e o comprimento da raiz primária foram determinados e analisados estatisticamente (software SISVAR). O rendimento do extrato seco foi de 4,6 % e do óleo essencial 0,89 %. O óleo essencial apresentou como constituintes majoritários: α-pineno (9,08 %), β-pineno, (5,06 %), limoneno (4,27 %), β-elemeno (6,51 %), curzereno (11,03 %), germacreno B (12,3 %), óxido de cariofileno (6,29 %) e germacrona (18,6 %). O extrato apresentou: flavonas, flavanonas, flavonóis, terpenos, saponinas e taninos. O óleo e o extrato apresentaram atividade alelopática sobre as sementes testadas, assim como compostos de interesse farmacológico. Por meio de estudos que garantam a segurança de uso para humano e organismos não alvos, o óleo essencial e o extrato de *P. pellucida* podem ser importantes candidatos a herbicidas naturais, todavia, faz-se necessário realização testes complementares que possam elucidar os mecanismos que estes produtos naturais utilizam para impedir a germinação das sementes.

[1]De Souza, J. A., & Sousa, Z. L. (2018). Estudo da atividade biológica do extrato etanólico da Peperomia pellucida (L.) Kunth. REVISTA CEREUS, 10(4), 147-159;
[2]MATOS, F.J.A. Introdução à Fitoquímica Experimental. 3 ed. Fortaleza: Edições UFC,2009.

Agradecimentos/Acknowledgment

PROGESP e PROEG da UFAM pelas bolsas de IC e monitoria de M.F.S.; FAPEAM pela bolsa de mestrado de M.L.A..

Área: QPN

Avaliação da atividade anti-*Trypanosoma cruzi* do óleo essencial de *Vernonanthura polyanthes* e efeitos sinérgicos de sesquiterpenos majoritários

Felipe S. Sales (PG),[1*] Thais A. Costa-Silva[2], André G. Tempone[3], João Henrique G. Lago (PQ).[1]

felipe.sales@ufabc.edu.br

[1]Centro de Ciências Naturais e Humanas (CCNH) Universidade Federal do ABC, UFABC, SP; [2]Instituto de Inovação em Biotecnologia, SENAI, SP; [3]Laboratório de Fisiopatologia, Instituto Butantan, SP.

Palavras Chave: *óleo essencial; sesquiterpenos; efeito sinérgico;* Vernonanthura polyanthes; Trypanosoma cruzi.

Highlights

Evaluation of anti-*Trypanosoma cruzi* activity of essential oil from *Vernonanthura polyanthes* and synergistic effects of main sesquiterpenes. In the present work, four sesquiterpenes from the essential oil of *V. polyanthes* were tested individually and in binary combination (1:1) against trypomastigote forms of *T. cruzi*.

Resumo

A Doença de Chagas, causada pelo protozoário *Trypanosoma cruzi*, impacta milhões de pessoas globalmente, especialmente nas Américas[1]. As opções de quimioterapia são restritas ao benznidazol e ao nifurtimox, com diversos efeitos adversos[2]. Diante dessa problemática, a necessidade de buscar novos agentes antiparasitários torna-se evidente. A espécie *Vernonanthura polyanthes* ("assa-peixe") é conhecida pelo acúmulo de triterpenos e flavonoides bioativos, inclusive com ação anti-*T. cruzi*. Adicionalmente, estudos anteriores mostraram que o óleo essencial dessa espécie apresenta expressiva ação frente a *Leishmania infantum*[3]. No presente trabalho, o óleo essencial de *V. polyanthes* foi extraído por hidrodestilação e analisado por CG-EM. Quimicamente, esse se mostrou constituído majoritariamente por sesquiterpenos, em especial biciclogermacreno (9,8%), β-cariofileno (11,8%), α-humuleno (12,8%) e germacreno D (16,4%). Quando o óleo bruto foi testado frente as formas tripomastigotas de *T. cruzi*, foi observado um valor de CE_{50} de 11,5 µg/mL, similar ao padrão benznidazol (CE_{50} = 18,7 µg/mL), com reduzida toxicidade frente as células NCTC (CC_{50} > 200 µg/mL). Visando avaliar os efeitos individuais destes sesquiterpenos, foi observado que germacreno D e biciclogermacreno foram os compostos mais ativos, com CE_{50} de 17,8 e 16,3 µg/mL, respectivamente, enquanto que β-cariofileno e α-humuleno mostram menor potencial, cada um com CE_{50} de aproximadamente 27 µg/mL. Frente a esse resultado, foi investigado o efeito na atividade anti-*T. cruzi* de misturas binárias de cada um dos sesquiterpenos majoritários (proporção 1:1, m/m), como demostrado na Tabela 1.

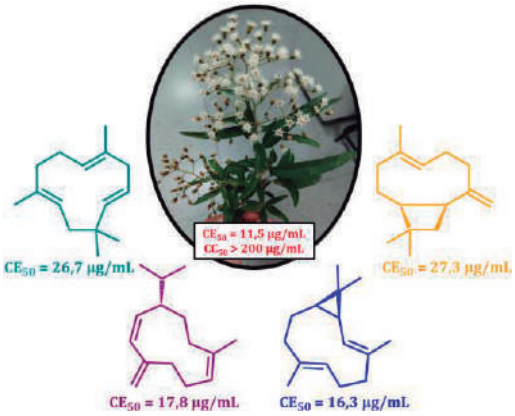


Tabela 1. Valores de CE_{50} para os sesquiterpenos majoritários de *V. polyanthes* e de misturas (1:1) frente a formas tripomastigotas de *T. cruzi*.

	CE_{50} (µg/mL)			
	β-cariofileno	*α-humuleno*	*germacreno D*	*biciclogermacreno*
β-cariofileno	**27,3 ± 0,8**	25,6 ± 2,6	16,3 ± 0,9	12,1 ± 3,6
α-humuleno	25,6 ± 2,6	**26,7 ± 3,6**	10,3 ± 1,9	15,1 ± 3,8
germacreneno D	16,3 ± 0,9	10,3 ± 1,9	**17,8 ± 4,3**	10,5 ± 1,8
biciclogermacreno	12,1 ± 3,6	15,1 ± 3,8	10,5 ± 1,8	**16,3 ± 2,3**

Em vermelho – destacam-se as misturas com valores de CE_{50} inferiores aqueles determinados para os sesquiterpenos puros, cujos valores estão em negrito.

Como observado, as atividades mais expressivas para essas séries foram observadas para as misturas de β-cariofileno + biciclogermacreno (CE_{50} = 12,1 µg/mL), germacreno D + biciclogermacreno (CE_{50} = 10,5 µg/mL) e α-humuleno + germacreno D (CE_{50} = 10,3 µg/mL) sugerindo um possível efeito sinérgico causado pela combinação desses compostos. Tais valores são similares ao obtido para o óleo essencial bruto (CE_{50} = 11,5 µg/mL). Adicionalmente, vale destacar que nenhum dos compostos isoladamente, nem suas misturas binárias, apresentaram citotoxicidade (CC_{50} > 200 µg/mL). Tais resultados permitem sugerir que a atividade anti-*T. cruzi* observada para o óleo essencial bruto de *V. polyanthes* não é proveniente de um único constituinte, mas sim da interação entre esses compostos.

Referências: [1]WHO, **Chagas disease**, 2021; [2]Galván, I. L. *et al*. **Exp. Ver. Anti Infect. Ther**. 2021, 19(5), 547-556; [3]Moreira R. R. D., *et al.*, **Nat. Prod. Res.** 2017, 31(24), 2905-2908.

Agradecimentos

CAPES; CNPq; FAPESP; IB; UFABC.

Área: QPN *(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)*

Avaliação do efeito citotóxico de alcaloides aporfínicos oriundos de *Ocotea puberula* (Lauraceae) em células de câncer de próstata

Daniela C. Tristão (PG)*,[1] Natalia M. Araujo (PG),[2] Ranyelison S. Machado (PG),[2] Rodrigo E. Tamura (PQ),[2] João H. G. Lago (PQ)[1]

daniela.tristao@ufabc.edu.br

[1] Centro de Ciências Naturais e Humanas, Universidade Federal do ABC (UFABC), Santo André, SP; [2] Laboratório de Biologia Molecular do Câncer, Universidade Federal de São Paulo (UNIFESP), São Paulo, SP

Palavras Chave: *dicentrina, N-óxidos, citotoxicidade, câncer de próstata, PC3, DU145*

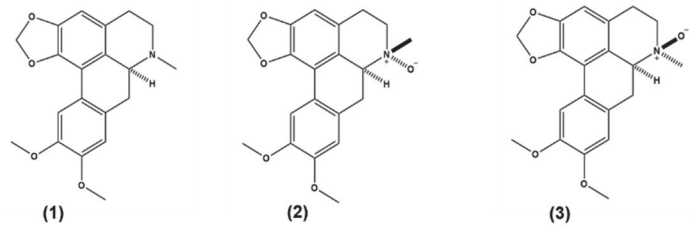
Highlights

Evaluation of cytotoxic effect of aporphinic alkaloids from *Ocotea puberula* (Lauraceae) on prostate cancer cells. In this work, the cytotoxic activities obtained for (*S*)-dicentrine and its *N*-oxide suggest an important role for the substituent and its stereochemistry on antitumor effect over prostate cancer model.

Resumo/Abstract

Considerando o potencial farmacológico da biodiversidade vegetal brasileira para a descoberta de novos protótipos antitumorais[1], o extrato alcaloídico das folhas de *Ocotea puberula* (Lauraceae) foi submetido a sucessivos fracionamentos cromatográficos, que levaram ao isolamento de seu composto majoritário (*S*)-dicentrina (**1**). Este foi avaliado pela primeira vez frente a linhagens celulares de câncer de próstata (PC3 e DU145), problema que corresponde à maior incidência global de câncer entre os homens[2,3]. Corroborando o potencial citotóxico descrito para alcaloides aporfínicos[4], a (*S*)-dicentrina (**1**) apresentou valores de CI_{50} de 22,5 µM (PC3) e 19,7 µM (DU145). Ainda, o composto (**1**) foi utilizado como material de partida para a preparação dos derivados diastereoméricos (6a*S*, 6*S*)-dicentrina *N*-óxido (**2**) e (6a*S*, 6*R*)-dicentrina *N*-óxido (**3**) que, após purificação via CLAE e caracterização por RMN e EM, foram avaliados frente às células PC3 e DU145. Como resultado, o alcaloide **3** mostrou potencial equivalente ao de seu precursor (**1**), com CI_{50} de 29,3 µM (PC3) e 37,9 µM (DU145), enquanto seu diastereômero (**2**) se mostrou totalmente inativo (CI_{50} > 50 µM) nas duas linhagens testadas. Adicionalmente, os três alcaloides foram também avaliados frente à linhagem não tumoral HEK293 e, como resultado, os compostos **1** e **3** apresentaram CI_{50} de 17,4 µM e 20,8 µM, respectivamente, enquanto o composto **2**, mais uma vez, não demonstrou ser citotóxico. Tais resultados sugerem que há um papel importante da porção heterocíclica das aporfinas estudadas no que tange a atividade citotóxica, principalmente referente à configuração do novo centro estereogênico gerado nos derivados *N*-óxidos.

Figura 1: Estruturas moleculares dos compostos 1-3



(1) (*S*)-dicentrina; (2) (6a*S*, 6*S*)-dicentrina *N*-óxido; (3) (6a*S*, 6*R*)-dicentrina *N*-óxido

Tabela 1: Citotoxicidade dos compostos 1-3

Compostos	Câncer de Próstata (PC3)	Câncer de Próstata (DU145)	Não tumoral (HEK293)
	CI_{50}, µM	CI_{50}, µM	CI_{50}, µM
1	22,5 ± 15,2	19,7 ± 6,4	17,4 ± 1,0
2	> 50	> 50	> 50
3	29,3 ± 1,2	37,9 ± 7,5	20,8 ± 4,3

Como parte essencial desse estudo, serão realizados ensaios de proliferação celular e de mecanismo de morte celular, com o objetivo de aprofundar a compreensão acerca do modo de ação dos alcaloides bioativos, obtidos em alta concentração na espécie estudada (**1**) e preparados via métodos simples e eficientes (**3**).

Referências: [1]Talib, W., H. *et al*., Molecules, **2020**. 25, 5319; [2]Sekhoaca, M. *et al*., Molecules, **2022**. 27 (17), 5730; World Health Organization. Cancer. **2024**. [4]Stévigny, C. *et al*., Curr. Med. Chem. – Anti-Cancer Agents, **2005**. 5, 173-182.

Agradecimentos/Acknowledgments

CAPES, CNPq, FAPESP, UFABC, UNIFESP

AVALIAÇÃO DO POTENCIAL ANTI-*Schistosoma mansoni in vitro* E *in vivo* DE SESQUITERPENOS DE *Drimys brasiliensis* (WINTERACEAE)

Eric Umehara[1] (PG), Rayssa A. Cajás[2] (PG), Josué de Moraes[2] (PQ) e João Henrique G. Lago[1] (PQ)

ericumehara@hotmail.com

[1]*Centro de Ciências Naturais e Humanas, Universidade Federal do ABC, Santo André – SP*
[2]*Centro de pesquisas de doenças negligenciadas, Universidade de Guarulhos, Guarulhos – SP*

Palavras-Chave: Drimys brasiliensis*, sesquiterpenos, atividade anti-helmíntico,* Schistosoma mansoni

Highlights

Evaluation of the anti-*Schistosoma mansoni* potential *in vitro* and *in vivo* of sesquiterpenes from *Drimys brasiliensis* (Winteraceae). In the present study, seven sesquiterpenes (**1 – 7**), including one new (**5**), were isolated from the branches of *Drimys brasiliensis*. After evaluation of anti-*S. mansoni* activity, compound **7** exhibited high potential *in vitro* and *in vivo*.

Resumo

O presente estudo teve como objetivo realizar a prospecção fitoquímica do extrato hexânico dos galhos da espécie vegetal *Drimys brasiliensis* (Winteraceae) a fim de se obter metabolitos especiais com potencial anti-*S. mansoni*. Após avaliação preliminar, foi observado que o extrato causou 100% de morte do parasita a 200 μg/mL, sugerindo a presença de compostos ativos. Por meio de técnicas de desreplicação molecular por RMN e EM foi possível observar que o mesmo se mostrou constituído majoritariamente por compostos terpênicos. Após processo de fracionamento cromatográfico, foi possível obter sete sesquiterpenos dos quais dois do tipo drimano: poligodial (**1**) e 9-deoximuzigadial (**2**), um de esqueleto sabinano: 7α-hidroxi-sesquisabinano (**3**) além de quatro de esqueleto bisabolano: 3α-hidroxi-2-oxo-bisabola-1,10-dieno (**4**), 2β,3α-diidroxi-bisabola-1,10-dieno (**5**), α-curcumeno (**6**) e 3β,6β-dioxi-bisabola-1,10-dieno (**7**). As estruturas dos compostos **1 – 7** foram definidas via RMN uni e bidimensionais. Este é o primeiro relato da presença dos compostos **2** - **7** na espécie *D. brasiliensis* enquanto que o sesquiterpeno **5** é inédito. Na sequência, os compostos **1 – 7** foram submetidos a avaliação frente a *S. mansoni* em modelo *in vitro* sendo que **7** foi o único que mostrou atividade (CE_{50} = 4,1 ± 1,2 μM), indicando a importância do grupo endoperóxido para observação desse potencial[1]. Frente a esse resultado, o composto **7** foi selecionado para a avaliação em modelo *in vivo* sendo observada, após tratamento, redução de 62% da carga parasitaria em vermes adultos, 98% da carga parasitaria de ovos imaturos no intestino e 99% de redução da oviposição nas fezes do modelo animal. Tais resultados indicam, portanto, que o sesquiterpeno **7** reduz parcialmente a carga parasitária dos vermes adultos e totalmente a carga oviparia, inibindo a reprodução e interrompendo o ciclo de vida do parasito tornando o composto **7** um produto natural promissor para o desenvolvimento de futuros fármacos visando o tratamento da esquistossomose.

Figura 1: Estrutura molecular dos sesquiterpenos de esqueletos drimano (**1-2**), sabinano (**3**) e bisabolano (**4-7**) isolados da espécie vegetal *D. brasiliensis*

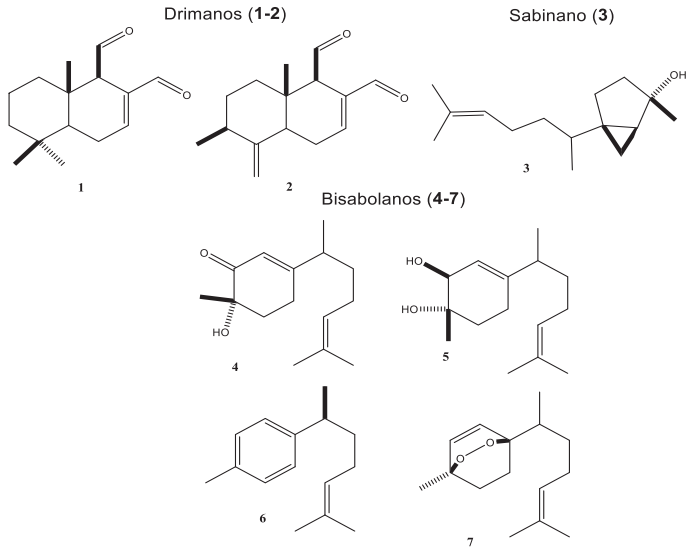
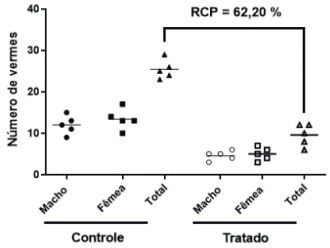
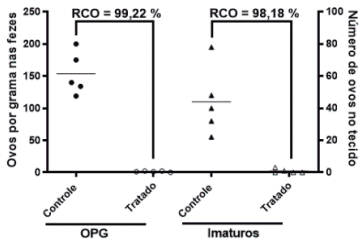


Figura 2: Efeito do composto **7** na carga parasitária de camundongos infectados por *S. mansoni* após 42 dias de infecção



RCP: Redução da carga parasitária

Figura 3: Efeito do composto **7** na carga de ovos nas fezes e no intestino nos camundongos infectados por *S. mansoni* em relação ao controle



RCO: Redução da carga oviparia

[1]Y. Pollack, R. Segal & J.Golenser. *Parasitology Research*, 76, p570-572, 1990

Agradecimentos

CAPES, CNPQ e FAPESP

Área: QPN

Bioactive compounds from *Humiria balsamifera* with cytotoxic potential

Julia Miho Tanaka (IC),[1] Ana Letícia P. Santos (PG),[1] Paula Rezende (PQ)[2], Leticia Veras Costa-Lotufo (PQ) [2] Antônio J. Cantanhede Filho (PQ)[3] and Vanderlan Bolzani (PQ).[1]

j.tanaka@unesp.br; vanderlan.bolzani@unesp.br

[1]Instituto de Química, Universidade Estadual Paulista – UNESP-IQ, Araraquara, SP, Brazil. [2] Institute of Biomedical Sciences, University of São Paulo, São Paulo, SP, Brazil. [3] Federal Institute of Education, Science and Technology of Maranhão, São Luís, MA, Brazil.

Keywords: Humiria balsamifera, Humiriaceae, cytotoxic activity

Highlights

Isolated compounds from the stems of *Humiria balsamifera* showed high cytotoxicity against HCT116 cells.

Resumo/Abstract

In conventional medicine, *Humiria balsamifera* var., popularly called Mirim, is known to ward against long-term illnesses like diabetes and obesity[1]. Although phytochemistry is a field with limited research, extracts from this plant have the potential to be antibacterial, anti-inflammatory, and antimalarial, among other effects[2]. The current study aimed to prepare extracts from the leaves and stems of the *Humiria balsamifera* species using different polar solvents. The bioactivity of the extracts and isolated compounds against HCT-116 colorectal cancer cells were evaluated. The stem and leaves were dried, and extracted with solvents of different polarities (Hexane, EtOAc, EtOH, and MeOH) and concentrated. The stem's EtOAc extract proved to be more straightforward to work with. The sample was eluted in column C_{18} with a gradient of 5–100% B for 40 minutes using the solvents A (H_2O/0.1% Formic Acid) and B (MeOH/0.1% Formic Acid). After isolation, three compounds were shown to have high cytotoxicity. Further isolation and characterization studies of compounds from other prepared extracts will be carried out, in addition, other activities that have not been explored will also be investigated.

Samples	MM (Da)	Inhibition (%)
C_Hex	-	6.40
C_MeOH	-	54.33
C_EtOH	-	53.52
C_EtOAc	-	59.33
C_ EtOAc _P1	329.13	97.60
C_ EtOAc _M3	481.13 / 503.12	82.14
C_ EtOAc _M4	465.12 / 487.12	74.19

Agradecimentos/Acknowledgments

CAPES, CNPq (INCT/BioNat), and FAPESP (Cepid/CibFar and INCT/BioNat) for research financial support.

Referências

(1) BARBOSA, K. B. F.; COSTA, N M. B.; ALFENAS, R. de C. G.; DE PAULA, S. O.; MINIM, V. P. R.; BRESSAN, J. Estresse oxidativo: conceito, implicações e fatores modulatórios. **Revista de Nutrição,** 4 (23), p.629-643. 2010.

(2) DIAS, E.d.J.S.; CANTANHEDE, A.J.F.; CARNEIRO, F.J.C; DA ROCHA, C.Q.; DA SILVA, L.C.N.; SANTOS, J.C.B.; BARROS, R.F.; SANTOS, D.M. Antimicrobial Activity of Extracts from the Humiria balsamifera (Aubl). **2021**, v.10, n. 7, p. 1479.

Área: QPN

Biological and Chemical Screening of Secondary Metabolites from Marine Sponges as Inhibitors of *Plasmodium falciparum*

Mariane M. Mendanha (IC), Karina F. Baraco (PQ), Kamila L. Macedo (PG), Giovana R. Mendes (PG), Rafael V. C. Guido (PQ), Roberto G. S. Berlinck (PQ)

marianemendanha@usp.br

[1]*Instituto de Química de São Carlos, Universidade de São Paulo, IQSC -USP;* 2Instituto de Física de São Carlos, Universidade de São Paulo, São Carlos, SP

Keywords: *marine sponges, antiplasmodial activity, Plasmodium falciparum, screening*

Highlights

Malaria affects mainly children in Africa, that needs novel drugs for treatment. This work is a screening of marine sponge extracts against *P. falciparum*, using chemical and biological analysis.

Abstract

Marine sponges are the oldest animals on Earth and are organisms of great pharmacological interest due to their ability to accumulate compounds with potent biological activities.[1] This work aimed at the screening of a variety of sponge extracts against *Plasmodium falciparum*, the species responsible for the most severe cases of malaria. Malaria causes millions deaths/year, particularly in African children up to 5 years old. In Brazil, the Amazon region is considered an endemic area for malaria in the country.[2] Furthermore, there are reports that *P. falciparum* is becoming resistant to current medications.[3] Therefore, there is a real urgency in finding new anti-plasmodial agents effective to treat malaria.

A collection of 15 sponge species were extracted with MeOH. The organic extract was defatted with n-hexane. The polar fraction was subjected to a solid-phase extraction on a cyanopropyl-bonded cartridge in normal elution mode. In total, 55 fractions were evaluated for their antiplasmodial activity against *P. falciparum* (3D7 strain, chloroquine-sensitive). Of these fractions, 32 showed inhibition of inhibition of the parasite growth higher than 90% at the concentration of 50 µg/mL, among which 18 showed inhibition equal to or higher than 95%. All active fractions were analyzed by HPLC-UV-MS on a C_{18} reversed-phase column with a mobile phase composed of MeCN with 0.1% formic acid + MeOH with 0.1% formic acid (eluent A) and H_2O with 0.1% formic acid (eluent B), in a gradient of increasing concentration of A in B. UV monitoring was carried out between 200 and 400 nm and the analysis by mass spectrometry were carried out using electrospray ionization in positive and negative modes, with detection between 120 and 1100 Da. Among the sponges investigated, a species coded BA07_ES87 was selected because it presented potent antiplasmodial activity for almost all SPE fractions. Moreover, its chromatographic profile indicated the presence of brominated compounds. The isolation of the active compounds is currently underway and results will be presented and discussed.

[1] Hai, Y., *et al*. *Nat. Prod. Rep.,* **2022***, 39,* 969-990. https://doi.org/10.1039/D1NP00075F
[2] White, N. J., Malaria J., **2022**, *21*, 284. https://doi.org/10.1186/s12936-022-04301-8
[3] Haldar, K.; Bhattacharjee, S.; Safeukui, I. *Nat. Rev. Microbiol*., **2018**, *16*, 156–170. https://doi.org/10.1038/nrmicro.2017.161

Acknowledgments

The authors thank CNPq and FAPESP for the financial support and scholarships.

Área: QPN

Brazoides E and F, Two New Alkaloids, and other compounds from *Justicia wasshauseniana* Profice *(JW)*, Acanthaceae.

Mário Geraldo de Carvalho (PQ),[1] Renata D. Fernandes (PQ),[1*] Raimundo Braz Filho (PQ),[1,3] Denise M.Braz (PQ),[2] Luciano R. Suzart (PQ),[1] Tatiane N. Tejero (PG),[1] Glauco F. Bauerfeldt (PQ),[1] Mariele R.S. Gonçalves (PG),[1]

mariogdecarvalho@gmail.com; renataduartef@googlemail.com

[1]Institute of Chemistry, Department of Organic Chemistry, Federal Rural University of Rio de Janeiro (UFRRJ), Rodovia BR 465, Km 07, 23890-000 Seropédica, RJ, Brazil; [2] Department of Botany, Federal Rural University of Rio de Janeiro (UFRRJ), Rodovia BR 465, Km 07, 23890-000 Seropédica, RJ, Brazi; [3] LCQUI-CCT- North Fluminense State University Darcy Ribeiro (UENF), 28013-600 Campos dos Goytacazes-RJ – Brazil

Palavras-Chave: *Justicia wasshauseniana, Acanthaceae, Alkaloids, Steroids, Brazoides, Stereochemistry*

Highlights

Discovered two new alkaloids and five other special metabolites in *Justicia wasshauseniana*. Structural similarity led to the naming of the alkaloids Brazoides E and F, honoring Raimundo Braz Filho.

Resumo/Abstract

The herbaceous plant *Justicia wasshauseniana* (Jw) Profice is endemic to Brazil, native to the Atlantic Forest in the states of Rio de Janeiro, Espírito Santo, and Bahia. *Justicia* is the largest genus of Acanthaceae, its species have significant popular indications. For instance, *J. gendarussa*, known as Anador, is used in folk medicine to treat fever, cough, canker sores, arthritis, headaches, facial paralysis, earache, bronchitis, liver diseases, chronic rheumatism, inflammation, vaginal discharge, dyspepsia, and ocular diseases.[1,2] Phytochemical studies of this species led to the identification of triterpenoids, steroids, flavonoids, and nitrogen compounds. Among the nitrogen compounds, four new alkaloids were named as Brazoides A-D in honor of the renowned researcher Raimundo Braz-Filho.[3] These narratives justify the interest of this study, which aims to conduct the chemical investigation of this plant (*Jw*).
Leaves and stems of *Jw* were collected in Parque Natural Municipal do Curió, Paracambi, RJ, in September 2009. The collected material was identified by Denise Monte Braz whose testimonial sample is deposited in the Herbarium of the Department of Botany at UFRRJ, D.M. Braz 274RBR. The botanical material, dried and pulverized, were separately extracted with dichloromethane and methanol. The solvent was then removed, and the respective extracts were obtained: JwCD (Jw, Stem Dichloromethane, 2.39 g); JwFD (Jw, Leaf Dichloromethane, 20.64 g); JwCM (Jw, Stem Methanol, 44.79 g) and JwFM (Jw, Leaf Methanol, 55.09 g). Phytochemical investigation of the leaf (**JwF**) and stem (**JwC**) extracts of *Justicia wasshausseniana* led to the isolation of five steroids and a carbohydrate known in the literature, and two new alkaloids. The steroidal saponins 3-O-β-D-glucopyranosylsitosterol and 3-O-β-D-glucopyranosylstgmasterol were isolated from the **JwCD**. The steroids mixture sitosterol, stigmasterol and campesterol were obtained from **JwFD**. The chromatographic fractionation of n-Butanol fraction, obtained from partition of **JwFM**, led to the isolation of two new alkaloids, Brazoide E and Brazoide F and the carbohydrate α-D-glucopyranosyl-(1→2)-β-D-fructofuranoside. Both alkaloids were named according to the article published in onor to the renowned researcher Raimundo Braz Filho.[3] Their structures were characterized by High-Resolution electrospray ionization mass spectrometry (HRESIMS, negative mode) and nuclear magnetic resonance (1D and 2D NMR), infra-red (IV) and comparison to literature data. Theoretical calculations including simulated circular dichroism (DC) combined with the experimental spectra analyzes were used to define the structures and the absolute stereochemistry of alkaloids, (3S,5S)N-(phenyl-o-methylene-O-5)-3hydroxy-5-carboxylic acid γ-lactam (**1**) and (3S,5S)N(phenyl-o-methylene-O-5)-3hydroxy-5-carbonil-(2,3-dihydroxypropanoate) γ-lactam (**2**). A biosynthetic proposal is made for alkaloids, including those already recorded in the literature.[3b] This is the first phytochemical study of *Justicia wasshausseniana.*Profice *(JW).*

References

1. Corrêa, G. M.; Alcântara, A. F. C. Chemical constituents and biological activities of species of *Justicia* - a review. *Braz. J. Pharmacog.* **2012**, *22*, 220-238. doi: 10.1590/S0102-695X2011005000196.
2. Braz, D. M. *Justicia paracambi*, a new Brazilian species of Acanthaceae. Phytotaxa 236, 184-190. **2015**. doi: 10.11646/phytotaxa.236.2.7.
3. a) Sonal, P.; Maitreyi, Z.; Pharmacognostic study of the root of *Justicia gendarussa*. Asian J. Tradit. Med. 6, 61, **2011**. b) Souza, L. G. S., et al..; Brazoides A-D, new alkaloids from *Justicia gendarussa* Burm. F. Species, *J. Braz. Chem. Soc.*, 28|7| 1281-1287, **2017**.

Agradecimentos/Acknowledgments

The CAPES, CNPq and FAPERJ for research support and granted scholarship.

Área: QPN

Cafestol roasting derivatives and *in silico* evaluation as potential human farnesoid X receptor ligands by docking simulations

Claudia Moraes de Rezende (PQ), Maria Alice Esteves da Silva * (PG), Magaly Girão Albuquerque (PQ)
crezende@iq.ufrj.br; m.aliceesteves@ufrj.br.
Instituto de Química (IQ) – Universidade Federal do Rio de Janeiro (UFRJ) – Brasil

Keywords: *Coffee diterpenes*, *Hypercholesterolemia*, *Unfiltered coffee*, *Molecular docking*, *Nuclear receptor*, *Ligand binding domain*

Highlights

15,16-Dehydrocafestol and regioisomers, roasting products from cafestol, were synthetized and evaluated in molecular docking approach as potential FXR ligands for hypercholesterolemic activity.

Abstract

Cafestol, one of the most potent hypercholesterolemic agents described in the human diet, is responsible for the relationship between unfiltered coffee consumption and the development of cardiovascular diseases.[1] *In vivo* and *in vitro* assays indicate that the hypercholesterolemic activity of cafestol is due to its agonist activity at the farnesoid X receptor (FXR), a bile acid activated nuclear receptor mainly expressed in the liver. During the roasting of coffee beans, cafestol undergoes thermal degradation due to dehydration of the tertiary hydroxyl group at C16, forming 15,16-dehydrocafestol among other isomers. Regarding these derivatives in coffee drinks, in which isolation from coffee beans is not viable, scarce information is known about their biological activities. Investigating whether these cafestol derivatives have hypercholesterolemic potential would expand knowledge about the relationship between unfiltered coffee consumption and dyslipidemia. Therefore, this work aims to obtain 15,16-dehydrocafestol and its regioisomers through a new three-step synthetic route, and also to investigate their potential binding modes on human FXR by computational (*in silico*) molecular docking approach. Cafestol, the starting material, was isolated from crude Arabica coffee beans using a method developed by our research group.[2] In the first step of the synthesis, the primary hydroxyl group of cafestol was protected using TBDMSCl (3.0 eq) and imidazole (4.5 eq) in anhydrous DMF (50°C, inert atmosphere, 24h), with 75% yield. In the 2nd step, the protected diterpene was dehydrated with methyl-*N*-(triethyl-ammonium-sulfonyl)-carbamate (1.5 eq) in anhydrous toluene (50°C, inert atmosphere, 48h), resulting in three regioisomers that were purified by semi-preparative HPLC, with 15% yield of each isomer. Finally, in the 3rd step, the protecting group was removed with TBAF (2.5 eq) (tetrabutylammonium fluoride) in anhydrous THF for 24h, resulting in the three cafestol derivatives. The intermediate and final products were characterized by 1D/2D ^{1}H and ^{13}C NMR spectroscopy.

The 3D structures of the ligands were constructed, and geometry optimized with the MMFF94 method, using the *PC Spartan Pro* (v.1.0.5) program (www.wavefun.com). The 3D structure of the target protein, the ligand binding domain (LBD) of human FXR (nuclear receptor subfamily-1 group-H member-4, NR1H4), is available in the Protein Data Bank (www.rcsb.org) under PBD ID: 1OSH (resolution: 1.80 Å) co-crystallized with fexaramine, a potent agonist, used as a reference compound for docking validation by redocking.[3] Docking of cafestol and its derivatives and redocking of fexaramine were carried out with the *DockThor* server (dockthor.lncc.br). Protein-ligand intermolecular interactions were analyzed with the BIOVIA *Discovery Studio Visualizer* (DSV) program (discover.3ds.com). In the LBD hydrophobic pocket, fexaramine shows interactions with several residues (Met269, Phe288, Ile290, Leu291, Thr292, Met294, Ala295, Met332, Ile339, Leu352, Arg355, Ile356, Met369, Tyr373, Met454, Leu455, Trp458, Phe465, and Trp473). 15,16-Dehydrocafestol showed greater affinity for the target than cafestol, interacting with a greater number of residues, including His298, Phe333, Ser336, Phe340, Ile361, Tyr365, His451, and those highlighted in bold for fexaramine (**Fig.1**). These preliminary results suggest that these cafestol derivatives formed during roasting possibly act synergistically to cafestol in raising serum cholesterol.

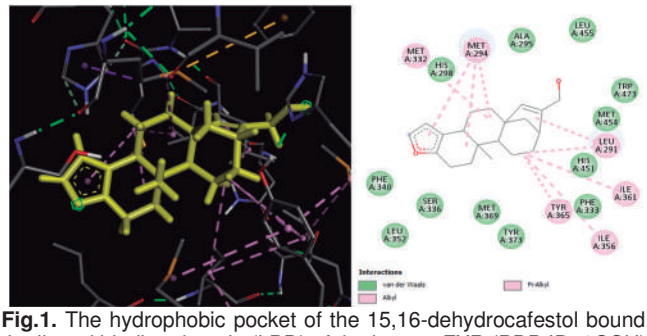


Fig.1. The hydrophobic pocket of the 15,16-dehydrocafestol bound to the ligand binding domain (LBD) of the human FXR (PDB ID: 1OSH).

1) Silva, M.A.E.; Brand, A.L.M.; Novaes, F.J.M.; Rezende, C.M (**2023**) Cafestol, kahweol and their acylated derivatives: antitumor potential, pharmacokinetics, and chemopreventive profile. *Food Reviews International*, 39(9):7048.
2) Novaes, F.J.M.; Lima, F.A.; Calado, V.; Marriott, P.J.; Aquino Neto, F.R.; Rezende, C.M. (**2020**) Isolating valuable coffee diterpenes by using an inexpensive procedure. *Industrial Crops and Products*, 152:112494.
3) Downes, M.; Verdecia, M.A.; Roecker, A.J.; Hughes, R.; Hogenesch, J.B.; Kast-Woelbern, H.R.; Bowman, M.E.; Ferrer, J.L.; Anisfeld, A.M.; Edwards, P.A.; Rosenfeld, J.M.; Alvarez, J.G.; Noel, J.P.; Nicolaou, K.C.; Evans, R.M. (**2003**) A chemical, genetic, and structural analysis of the nuclear bile acid receptor FXR. *Molecular Cell*, 11(4):1079.

Acknowledgments

PPGCAL Programa de Pós-Graduação em Ciência de Alimentos, CAPES, FAPERJ, CNPq, Embrapa Café

Área: QPN

Chemical composition and evaluation of the antitumor potential of methanolic extract from *Euphorbia tirucalli* against the strain of anaplastic thyroid cancer

Anndreisa Christiny Monteiro (PG),[1] Paloma R. Oliveira (PG),[2] Ileana G. S. de Rubió (PQ),[2] Rodrigo E. Tamura (IC),[2] Patricia Sartorelli (PQ).[1]*

anndreisa.monteiro@unifesp.br; psartorelli@unifesp.br

[1]Institute of Environmental, Chemical and Pharmaceutical Sciences, UNIFESP – Campus Diadema; [2]Cancer Molecular Biology Laboratory, UNIFESP.

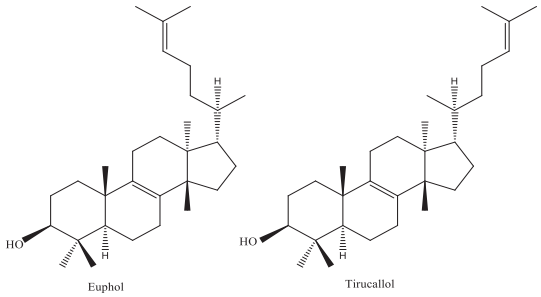
Key words: Antitumor activity, *Euphorbia tirucalli, Natural Products, Triterpenes.*

Highlights

In the study, two triterpenes were identified: eufol and tirucalol. The tests carried out to evaluate their anticancer potential showed activity against HTH83 anaplasic thyroid cancer cells.

Abstract

Cancer is a disease that can affect different organs of the human body. Among these neoplasms, thyroid cancer is the most common type of malignant tumor of the endocrine system, and its incidence has increased considerably in recent years, ranking fifth among the cancers that most affect women, with an estimated 8.2 million deaths per year worldwide[1]. In this respect, studies in search natural products that can act to prevent the development and proliferation of tumor cells are extremely important for humanity, and plants are a promising source of study. *Euphorbia tirucalli*, a plant belonging to the Euphorbiaceae family popularly known as “avelós”, is widely used in folk medicine to treat various ailments, mainly digestive, respiratory and skin disorders[2]. The aim of this study was therefore to isolate and identify the chemical constituents of *E. tirucalli*, as well as to evaluate their potential for antitumor activity against anaplastic thyroid cancer (HTH83 cell line). After obtaining the methanolic extract, a liquid-liquid partition (Hex/DCM/AcOEt) was carried out. The dichloromethane phase was chosen to start the fractionation and was subjected to silica column chromatography (CC) using DCM/AcOEt as the mobile phase, in an increasing polarity gradient, affording 248 fractions which were then regrouped into 14 sub-fractions according to the similarity profile of their chemical constituents in thin layer chromatography (TLC). Of these, fractions ET-C2 and ET-C3 were selected, due to their chromatographic profile suggesting the presence the terpenes, to carry out the Sephadex LH-20 chromatographic column, using the DCM/MeOH solvent as the mobile phase, with a gradient, and a total of 23 fractions were collected, which were finally regrouped into 5 sub-fractions according to their chromatographic profile. Of these, the ET-SF-3.4 subfraction was selected for ^{1}H and ^{13}C NMR spectroscopic analysis, which allowed identify the triterpenes eufol and tirucallol as the major compounds. Preliminary tests of antitumor activity in thyroid tumor cells (HTH83) were promising according to IC_{50} (inhibiotry concentration 50%) of 13,297 µg mL^{-1}, and eufol and tirucallol may be associated with these activities, since the scientific literature shows good recurrent anticancer activity in other types of cancers that affect humans. Given the lack of studies on thyroid cancer in the scientific literature, the results of this study show the great potential of the *E. tirucalli* species as a source of bioactive natural products for the development of anticancer prototypes.



BIBLIOGRAPHICAL REFERENCES

[1] TAN et al., Anaplastic carcinoma of the thyroid: a 24-year experience. Head & neck. 1995;17:8.

[2] SALEHI, B. et al. **Euphorbia-Derived Natural Products with Potential for Use in Health Maintenance** *Biomoléculas* **2019**, *9*(8), 337; https://doi.org/10.3390/biom9080337

Acknowledgments

This study was funded by CAPES, CNPQ and FAPESP.

Área: QPN

Chemical Modification of Softwood Kraft Lignin with Maleic Anhydride to Improve UV-Shielding Properties

Gabriel Moraes (PG),[1*] Felipe Souto (PQ),[1] Verônica Calado (PQ).[1]

gabrielrsm@eq.ufrj.br; gabrielrsm@eq.ufrj.br

[1]*Escola de Química, Universidade Federal do Rio de Janeiro (UFRJ)*

Keywords:*(Lignin, Chemical Modification, Maleic Anhydride, UV-Shielding).*

Highlights

Lignin is a natural, renewable, and low-cost UV-Shielding molecule. The interest for new sunscreen ingredients places lignin into evidence. This work aims at tunning lignin's UV-blocking properties.

Resumo/Abstract

Solar light is composed by ultraviolet (UV, 200-400 nm), visible (400-700 nm), and infrared (700-1000 nm) radiation. The ultraviolet region is subdivided into UVA (320-400 nm), UVB (290-320 nm), and UVC (200-290 nm) regions (Hudson *et al.*, 2020). The ozone layer absorbs 100% UVC radiation and 90% UVB in the stratosphere. However, the remaining percentage of UVB radiation and all incident UVA reaching the Earth's surface are associated with severe harm to the body, such as burns, premature aging, and skin cancer (Paiva, 2015). Sunscreen is recommended against exposures to ultraviolet rays, being composed by two types of ingredients for radiation protection. These ingredients are classified as physical and chemical agents. Physical agents act reflecting and dispersing UV radiation, often using inorganic compounds such as titanium dioxide (TiO2) and zinc oxide (ZnO). Chemical agents, aromatic organic molecules like avobenzone and benzophenone, act by absorbing UV radiation. However, these agents are associated with various health risks because of their photocatalytic activity, generating free radicals and, consequently, effects such as premature aging and skin cancer (Bhattacharya and Sherje, 2020). Therefore, the searching for natural ingredients with low cytotoxicity, photostability, and UV protection properties is promising. Lignin is a molecule present in the cell walls of plants and demands various functions, including providing rigidity, nutrient transport, and protection against external threats and UV radiation. Various chromophore groups, such as hydroxyls, ketones, and quinones, justify the UV protection property of lignin. Consequently, lignin is a promising substitute for conventional photoprotective agents. However, the structural complexity of the molecule, low absorption in the UVA region, and low dispersion in creams pose challenges in applying lignin in photoprotective systems (Tran *et al*, 2021). Therefore, the present study aims to chemically modify a softwood kraft lignin with maleic anhydride to enhance its UV-blocking properties and apply it as a renewable, green, and biocompatible photoprotective agent. Chemical reactions were conducted in a dimethyl sulfoxide solution with 2 g of lignin and 3. 12 g of maleic anhydride under magnetic stirring at 70ºC for 6 hours. The product was precipitated in a 5% sodium chloride solution, vacuum-filtered, and washed with deionized water until neutral pH. Subsequently, the sample was placed in an oven at 60ºC for 24 h and stored in a Scott flask. The modified lignin was characterized using Fourier-transform infrared spectroscopy (FTIR), hydrogen nuclear magnetic resonance (NMR-H), and ultraviolet-visible spectroscopy (UV-VIS). In the FTIR analysis, characteristic vibrations indicating the formation of ester groups in the molecule's structure were observed, such as acyl groups (COOR) around 1660 cm^{-1} and carbon-oxygen bonds (C-O) at 1212 cm^{-1}. The NMR-H results showed new signals in δ1.7–2.4 ppm associated with new acetyl groups in molecule structure and a signal shift in the region of aromatic protons (δ6.3–7.7 ppm). UV scanning indicated an increased absorption in the UVB and UVA regions in the modified samples. Thus, preliminary characterizations revealed the promising chemical modification of lignin with maleic anhydride for application in photoprotective systems.

Agradecimentos/Acknowledgments

This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – Brasil (CAPES) – Finance Code 001, and Fundação Carlos Chagas Filho de Amparo à Pesquisa do Estado do Rio de Janeiro – (FAPERJ) – Finance Code SEI-260003/000322/2024.

Área: QPN

Chemical profile by HPLC-ESI-qTOF-MS/MS from the leaves from *Annona dolabripetala* (Annonaceae)

Gabriela D. Leonardo (IC),[1*] Natyele R. Fonseca (IC),[1] Diogo F.G. Andrade (PG),[1,2] Adriana Quintella Lobão (PQ),[3] Leando M. Rocha (PQ),[2] Alessandra Leda Valverde (PQ),[4] Lucas Silva Abreu (PQ).

gabriela_dinis@id.uff.br;

[1] Laboratório de Química de Produtos Naturais, Universidade Federal Fluminense, Niterói, RJ, Brasil; [2] Laboratório de Tecnologia de Produtos Naturais, Universidade Federal Fluminense, Niterói, RJ, Brasil; [3]Instituto de Biologia, Departamento de Biologia Geral, Universidade Federal Fluminense, Niterói, RJ, Brasil; [4] LaProMAr, Universidade Federal Fluminense, Niterói, RJ, Brasil

Palavras Chave: *Annona dolabripetala, Chromatography, Phytochemistry, Nuclear magnetic resonance (NMR)*

Highlights

Phytochemical study of the *Annona dolabripetala* species using HPLC-ESI-qTOF-MS/MS analyzes focusing on the annotation of bioactive substances.

Resumo/Abstract

The Natural Products Chemistry is responsible for the study of secondary metabolites of natural species, normally with biological activity associated. These substances have played an important role in the production of drugs throughout history. In this context, studies on the Annonaceae family have a great importance in discovery of substances that have cytotoxic effects and other biological activities. The specie *Annona dolabripetala* is an endemic Brazilian plant and there are no chemical studies described in literature. Thus, the objective of this work is the characterization of the chemical profile of the *Annona dolabripetala* species based on the annotation of bioactive compounds able to promote the development of new drugs. An ethanolic crude extract of the collected leaves was prepared and subsequently extracted by liquid-liquid partition with solvents of different polarities (hexane, dichloromethane, de ethyl acetate and butanol). The fractions obtained were subjected to phytochemical screening and analysis by thin layer chromatography (TLC). After these analyses, the dichloromethane and ethyl acetate fractions were chosen to investigate by HPLC-ESI-qTOF-MS/MS. A manual dereplication was carried out and the presence of alkaloids, flavonoids-*O*-glycosides and chlorogenic acids were annotated. The presence of precursor and fragment ions were compatible with alkaloids such as asimilobine (*m*/*z* 268), liriodenine (*m*/*z* 276), coclaurine (*m*/*z* 286), coreximine or 10-demethyldiscretine (*m*/*z* 328), kikemanine (*m*/*z* 342), flavonoids-*O*-glycosides such as kaempferol-hexoside (*m*/*z* 447), quercetin-hexoside (*m*/*z* 463), kaempferol-pentoside-hexoside (*m*/*z* 579), kaempferol-rutinoside (*m*/*z* 593), quercetin-pentoside-hexoside (*m*/*z* 595), quercetin-rutinoside (*m*/*z* 609), and other phenolics such as chlorogenic acid (*m*/*z* 353). Manual dereplication were tentatively assigned by the interpretation of their fragmentation patterns obtained from mass spectra (MS2 experiments) and literature information was also employed for evaluation of the samples. These results show a similar chemical profile to those already reported for species of the genus *Annona* and the family. These preliminary results provide evidence of the metabolic potential of the species and encourage further research leading to the isolation and identification of substances with bioactive potential. So, it is necessary to continue the studies into the research of these compounds and in the analysis of the associated biological activity to contribute to phytochemical enrichment and the development of new drugs.

References:

MORAIS, Selene Maia de; VIEIRA, Ícaro Gusmão Pinto. Introdução a prospecção de produtos naturais. Belo Horizonte, Mg: Poisson, 2021.

TOMAZ, A.C.A; NOGUEIRA, R.B.S.S.; PINTO, D.S.; AGRA, M.F.; SOUZA, M.F.V.; DACUNHA, E.V.L. Chemical constiuents from *Richardia grandiflora* (Cham. & Schltdl.) Steud. (Rubiaceae). Revista Brasileira de Farmacognosia, v.18, n.1, p.47-52, 2008.

Agradecimentos/Acknowledgments

Fundação Carlos Chagas Filho de Amparo à Pesquisa do Estado do Rio de Janeiro (FAPERJ) and Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPQ).

Área: QPN

Chemical prospection of the bioactive polysaccharides from the *Brazilian Shitake* mushroom (*Lentinula raphanica)*

Ruberney da Silva de Oliveira (PQ),[1] Jullia Darc Silva (IC),[1] Dirce Leimi Komura (PQ)[2], Rubi Vargas-Isla (PQ),[3] Noemia K. Ishikawa (PQ)[3], Maria Carolina B. Di Medeiros Leal (PQ)[4], Elaine Rosechrer Carbonero (PQ),[1]

darcjullia@discente.ufcat.edu.br; elaine_carbonero@ufcat.edu.br

[1]Instituto de Química, Universidade Federal de Catalão (UFCAT); [2] Instituto Federal de Educação, Ciência e Tecnologia do Maranhão (IFMA), Campus São João dos Patos; [3] Instituto Nacional de Pesquisas da Amazônia (INPA); [4] Centro Universitário do Planalto Central Apparecido dos Santos (UNICEPLAC)

Keywords: *Lentinula raphanica; Brazilian shiitake; macrofungus; polysaccharides.*

Highlights

The polysaccharides of the *L. raphanica* mushroom were evaluated to confirm their similarity to those described for *L.edodes,* which is widely marketed for culinary and medicinal purposes.

Abstract

Lentinula raphanica, known as Brazilian shiitake, is one of the edible macrofungi found in the Amazon Rainforest, cultivated and marketed mainly by the Yanomami indigenous community (Sanöma). Of the eight species reported for this genus, three have been recognized as safe and suitable for human consumption; however, only *Lentinula edodes* have been commercialized on a large scale, being the second most consumed worldwide. Considering the lack of studies regarding the species under study and the therapeutic effects reported for *L. edodes*, the main objective of the present study is to identify polymers with biotechnological potential from *L. raphanica and* reinforce their health benefits. For this, the polysaccharide extracts obtained by aqueous and alkaline extractions were purified by the freeze/thaw and precipitation techniques with Fehling's solution and characterized by ^{13}C and ^{1}H NMR, GC-MS (monosaccharide composition and methylation), and HPLC-RI/LS. Based on the methodology employed, four polymers were purified, three of which were similar to those described for *L. edodes*, namely: 1) heterogalactan consisting of an α-D-Gal*p* (1→6)-linked main chain, partially substituted in O-2 by non-reducing terminals of α-L-Fuc*p* and β-D-Man*p*, called fucomanogalactan (*Lr*-PF_2AF fraction; *Lr*-FMG). 2) Branched β-Glucan formed by a main chain consisting of (1→3)-linked β-D-Glc*p* units, partially substituted in O-6 by non-reducing ends of β-D-Glc*p*, on average, 2 substitutions for every 5 residues of the main chain (*Lr*-PAQ and *Lr*-PK1 fraction; *Lr*-Glc 1), similar to *Lentinan*, previously isolated from *L. edodes*. 3) Branched β-glucan containing a main chain consisting of β-Glcp (1→6) units, which are partially replaced in O-3 with side chains of lengths different constituted by β-Glc*p* (1→3)-linked units (*Lr*-PF2K1 fraction; *Lr*-Glc 2). 4) Fully substituted β-Glucan formed by a main chain consisting of β-D-Glc*p* (1→3,6) linked units, with non-reducing ends of β-D-Glc*p* linked to O-6 (*Lr*-PF_2PAK_5 fraction; *Lr*-Glc 3). In general, it can be concluded that there is a similarity between the polymers, suggesting that *Brazilian shiitake* has high biotechnological potential, considering the numerous therapeutic properties and industrial applications of these carbohydrates.

Reference:

Sheng *et al*. Recent advances in polysaccharides from *Lentinus edodes* (Berk.): Isolation, structures and bioactivities. *Food Chemistry*, 358, 129883, 2021.

Agradecimentos/Acknowledgments

This study was supported by the Federal University of Catalão (UFCAT) and financed in part by the Fundação de Amparo à Pesquisa do Estado de Goiás (FAPEG). The authors acknowledge Prof. Dr. Antônio Gilberto Ferreira from the Federal University of São Carlos and Prof. Luciano M. Lião from the Federal University of Goias for supporting the NMR experiments.

Área: QPN

Clerodane diterpenes from leaves of *Echinodorus grandiflorus* (Alismataceae)

João Pedro V. Moriconi (IC)[1], Mariana M. Borges (PG)[1], João Henrique G. Lago (PQ)[2], Edgard A. Ferreira (PQ).[1]*

jp.valdomoriconi@gmail.com; edgard.ferreira@mackenzie.br*

[1]School of Engineering, Mackenzie Presbyterian University; [2]Center of Natural Sciences and Humanities, Federal University of ABC.

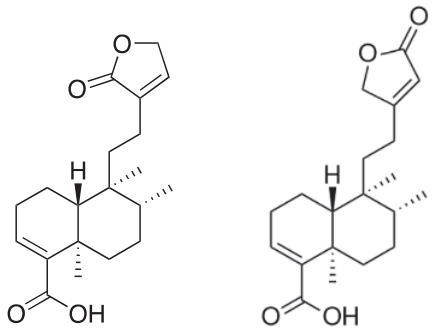
Keywords: *Echinodorus, Clerodane diterpene, Aquatic macrophyte.*

Highlights

A set of chromatographic procedures including column chromatography, gel permeation chromatography and semi-preparative HPLC of ethyl acetate extract obtained from leaves of *E. grandiflorus* afforded two clerodane diterpenes, Patagonic Acid (**1**) and Clerodermic Acid (**2**). This is the first report of Clerodermic Acid in the genus *Echinodorus*.

Abstract

Aquatic Macrophytes, usually know as aquatic plants, have been efficiently adapted to aquatic environment and can be found easily in rivers, lakes and even in soils covered or saturated by water[1]. Aquatic macrophytes are represented by approximately 2600 species among 450 genera[1]. The family Alismataceae comprises seventeen genera and approximately 120 species including the genus *Echinodorus*. In Brazil this genus counts with seventeen species in all regions and biomes. The *Echinodorus grandiflorus*, popularly known as “leather hat” in Brazil is a traditional plant with applications in folk medicine as anti-inflammatory, throat inflammation anti-arthritis, anti-hypertensive, among others.[2] Despite the substantial number of species, only two of them had the phytochemical study performed in which three classes of diterpenes were described: clerodane, *seco*-labdane and cembrane[3-5]. As part of a continuous study aiming to explore chemical diversity of aquatic macrophytes, the dried leaves *E. grandiflorus* were subjected to extraction by maceration in hexane and ethyl acetate, respectively. Thus, the ethyl acetate extract was subjected to a set of chromatographic procedures starting from silica gel column chromatography, followed by gel permeation chromatography, and finishing with semi-preparative HPLC to afford two structural related clerodane diterpene compounds, Patagonic Acid (**1**) and Clerodermic Acid (**2**). Their structures were defined by analysis of ^{1}H, ^{13}C NMR and HR-MS spectral data and comparison with data reported in the literature[6-7]. These results contribute with this genus in terms of chemotaxonomic aspects, whereas the compound **2** is reported for the first time in this genus.



1 **2**

References: [1]Irgang *et al*. Roessléria. 6, 395, 1984; [2]Marques *et al*. Food. Chem. Toxicol. 109, 1032, 2017; [3]Kobayashi *et al*., Tetrahedron Lett. 41, 2939, 2000; [4]Kobayashi *et al*., 2000; [5]Shigemori *et al*., J. Nat. Prod. 65, 82, 2002; [6]Pinto *et al*., J. Braz. Chem. Soc. 21, 1819, 2010; [7]Efdi *et al*., Bioorg. Med. Chem. 15, 3667, 2007.

Acknowledgments

This work was funded by grants of Fundo Mackenzie de Pesquisa (MackPesquisa - 231010). We also thank Sumiko Honda of São Paulo Municipal Herbarium (PMSP) for identification of plant species.

Área: QPN_____
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Co-culture exploration of some selected species of *Fusarium* and *Neofusicoccum* genera

Mustapha Ngaski Abubakar (PQ),[1]* Vitor de Souza Mazucato (PG),[1] Paulo Cezar Vieira (PQ).[1]

mngaskyii@usp.br; vitor.mazucato@usp.br; pcvieira@fcfrp.usp.br

[1]Faculdade de Ciências Farmacêuticas de Ribeirão Preto, USP - Avenida do Café s/n - 14040-903 - Ribeirão Preto, SP

Keywords: *Co-culture, Neofusicoccum, Fusarium, Metabolites, NMR*

Highlights

The co-cultures of an endophytic genus, Neofusicoccum (V6) with two phytopathogenic species of Fusarium (V15 & V18) afforded metabolites with marked antimicrobial and protease inhibitory activity.

Resumo/Abstract

Fungal infestation on agriculture particularly on protease-rich edible fruits such as papaya, pineapple, and persimmon results in huge economic losses annually. Therefore, the need to checkmate these species' activities as well as devise means/approach (co-cultivation) to utilize their resources cannot be over emphasized. Hence, co-cultivations involving the three species together as well as all the two possible (inter and intra) species combinations were carried out in rice media and subsequently extracted with EtOAc. Percentage yields of the axenic cultures showed 2:1 production ratios of triglyceride against other metabolites. Interestingly, reverse yields were observed in the co-culture permutations with the trio combination recording an even much higher yield. This scenario perhaps, suggests the activation of certain biosynthetic pathways that led to either conversion or blockage of the glycerides thereby enhancing the production of critically needed metabolites. The ^{1}H NMR spectra of the crude extracts showed distinct signals of promising/interesting metabolites. Particularly, the trio combination (***V6***:***V15***:***V18***) showed enhanced signal peaks which could be attributed to the induced interactions faced by the species within a confined space. Similarly, the co-cultures involving two species (***V6***:***V15***; ***V6***:***V18*** & ***V15***:***V18***) showed better yields when compared with their axenic environments. Bioassay-guided isolation is underway to identify and characterize the specialized metabolites with the view to gain insight into these species' chemo-diversity and potential bioactivity against certain strains of pathogens.

Agradecimentos/Acknowledgments

FAPESP - (Processo No: 2022/10835-1) for the financial sponsorship. FCFRP, CNPq and CAPES for providing the facilities & enabling environment to carry out this research. FCE(T) Gusau for the Postdoc leave of absence.

Área: QPN

Co-culture of *Penicillium setosum* and *Cryptococcus neoformans* reveals the production of antifungal diketopirerazine

Cláudia M. da S. C. de Oliveira (PG),[1*] Milena C. Bassicheto (PG),[2] Renan S. Barbosa (PG)[2], Renata C. Pascon (PQ)[2], Gilvan F. da Silva (PQ)[3], Thiago A. M. Veiga (PQ),[2] Lívia S. de Medeiros (PQ)[2].

coliveira08@unifesp.br; livia.soman@unifesp.br

[1]Programa de Pós-Graduação em Química - Ciência e Tecnologia da Sustentabilidade, UNIFESP; [2]Programa de Pós-graduação em Biologia Química, UNIFESP, [3]Embrapa Amazônia Ocidental.

Keywords*: Penicillium setosum*, diketopiperazines, dereplication, antimicrobials.

Highlights

A mixed fermentation strategy involving *P. setosum* and *C. neoformans* was employed to induce the production of secondary metabolites. The compound bisdethiobis(methylthio)acetylaranotine demonstrated antimicrobial activity against *C. neoformans*. This study focuses on the discovery of other dicetopiperazine compounds biosynthesized by this strain during mixed fermentation, aiming to identify compounds with therapeutic potential against pathogens such as *C. neoformans.*

Abstract

Co-cultures, also known as mixed fermentations, involves the growth of two or more microorganisms. This approach has emerged as an effective strategy to increase the production of natural products and to boost the activation of cryptic or silent gene clusters responsible for synthesizing new secondary metabolites. Many of these clusters are susceptible to biotic and/or abiotic environmental modifications what may further the production of bioactive compounds as a result of chemical and biological responses. The genus *Penicillium* represents one of the largest sources of fungal known chemodiversity, thus revealing a promising source for the discovery of new therapeutic agents through chemical and biological exploration of its secondary metabolome. In previous studies conducted by our research group (LaBiORG), with the *Penicillium setosum* CMLD 18 isolated from the *Swinglea glutinosa* plant, we identified the production of dicetopiperazines (DKPs) by the specie. These studies showed the detection of the compounds bisdethiobis(methylthio)acetylaranotine and fellutanine C. Their cytotoxic effects were confirmed, representing the first report of antileukemic activity of this dicetopiperazine to date[1]. Based on these findings, this work set out to investigate the interaction between the endophyte *P. setosum* and the pathogenic fungus *Cryptococcus neoformans*, seeking to determine whether this interaction could increase the production of other DKPs and trigger the expression of other silent biosynthetic pathways in *P. setosum*. Then, the cultivation *P. setosum* and *C. neoformans* was performed in a liquid Potato Dextrose (BD) culture environment, under static and agitated conditions. The extracts were analyzed by high-resolution liquid chromatography-mass spectrometry (HPLC-HRMS). Molecular dereplication is being performed through manual inspection, *in sillico* metabolomics tools, as well as data analysis on the GNPS platform. According to the obtained molecular annotations, it was possible to identify the induction of diketopiperazines in extracts from the co-culture, which were not detected in the axenic cultivation of *P. setosum* exposed under the same conditions. Bisdethiobis(methylthio)acetylaranotine was confirmed as one of the DKPs whose the production was induced by the applied co-culture. Interestingly, this class of compounds has antifungal activities described in the literature against *C. neoformans*[3,4]. Therefore, the compound bisdethiobis(methylthio)acetylaranotine (which had been previously isolated in our studies involving *P. setosum* and OSMAC approach[1,2]), was subjected to bioassays with *C. neoformans*, showing antifungal activity against the pathogen. This result highlights the potential of DKPs as candidates for the development of new antifungal agents to combat infections caused by *C. neoformans*.

References: 1. de Carvalho, A. C.; and Veiga, T. A. M.; Metabolites, 13., 1-19 (2022). **2.** Björn, B. H. and Zeeck, A.; ChemBioChem, 3., 619-627 (2002). **3.** Li, Yan and Bills, G. F.; Journal of Natural Products, 79., 2357–2363 (2016). **4.** Zhao, P. and Zu, S.; Biotechnol Lett, 41., 651–673 (2019).

Acknowledgments

Capes 88887.671409/2022-00; FAPESP Project 2020/08270-0

Área: QPN

Complete ^{1}H and ^{13}C-NMR data assignment for semi-synthetic derivatives of cinnamic acid from Brazilian green propolis by software-assisted methodology

Pedro Yuri Kovatch (PG),[1,2*] Alexsandro Euripedes Ferreira (PQ),[1] Julian Carlos da Silva Pavan (PG),[1] Fernando Soares de Lima (PQ),[2] Jairo Kenupp Bastos (PQ),[3] Vladimir Constantino Gomes Heleno (PQ).[1]

pedroyk@ipt.br.

[1]Núcleo de Pesquisa em Ciências Exatas e Tecnológicas da Universidade de Franca, UNIFRAN; [2]Instituto de Pesquisas Tecnológicas do Estado de São Paulo S.A., IPT. [3]Faculdade de Ciências Farmacêuticas de Ribeirão Preto – Universidade de São Paulo.

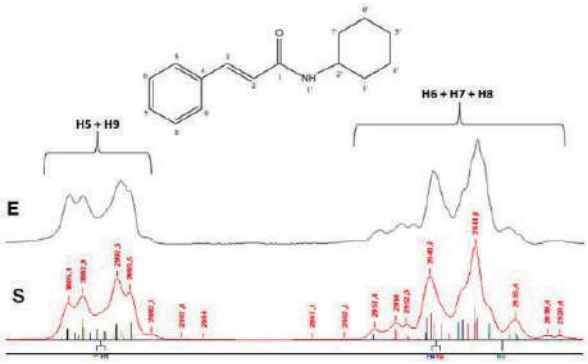
Keywords: *cinammic acid derivatives; NMR assignments; multiplicity clarifying; J-values measurement; NMR_MultSim.*

Highlights

Detailed assignments of 1H and 13C NMR data for several semi-synthetic derivatives of cinnamic acid were successfully completed. This was achieved using a software-assisted methodology with the programs FOMSC3_rm_NB and NMR_MultSim. The determination of all hydrogen coupling constants and clarification of all signal multiplicities demonstrate the effectiveness of this method.

Abstract

All derivatives presented in this study were obtained from research conducted on trans-cinnamic acid isolated from samples of Brazilian green propolis. The detailed investigation of the ^{1}H and ^{13}C NMR data of trans-cinnamic acid derivatives was planned to be accomplished due to their significant pharmacological properties documented in the literature, including antioxidant, anti-inflammatory[1], and antitumor[2] effects. Another factor motivating this study was the lack of detailed NMR data available for this particular class of compounds. Despite the utilization of advanced NMR equipment, there are instances where the complexity of a signal can pose challenges in interpretation, particularly when confirming proposed assignments based on experimental data[3]. To address this issue, 1H NMR signals were simulated to validate the experimental assignment data for all compounds. The simulations were performed using the FOMSC3_rm_NB (First Order Multiplet Simulator/Checker) and NMR_MultSim (Multiplet Simulator) programs, which account for distortions and interference from nearby chemical shifts. Both programs are accessible free of charge. The comparison between an experimental NMR signal (E) in CDCl3 and a simulated signal using these programs (S) is depicted in the figure. The resemblance between the experimental and calculated signals confirms the accuracy of the assigned data.



References:

[1] PONTIKI, E. et al. Design, synthesis and pharmacobiological evaluation of novel acrylic acid derivatives acting as lipoxygenase and cyclooxygenase-1 inhibitors with antioxidant and anti-inflammatory activities. European Journal of Medicinal Chemistry, v.46, n. 1, p. 191-200, 2011.

[2] PONTIKI, E. et al. Novel Cinnamic Acid Derivatives as Antioxidant and Anticancer Agents: Design, Synthesis and Modeling Studies. Molecules, v. 19, n. 7, p. 9655-9674, 2014.

[3] FERREIRA AE, ROCHA ACFS, BASTOS JK, HELENO VCG. Software-assisted methodology for complete assignment of ^{1}H and ^{13}C NMR data of poorly functionalized molecules: The case of the chemical marker diterpene *ent*-copalic acid. J Mol Struct [Internet]. 2021 Mar; 1228:129439.

Acknowledgments

The authors are grateful to the institutions UNIFRAN, IPT and CAPES for financial support.

Área: QPN

Comprehensive Revision of the Heliannuol Family: Ordering the Chaos Through an Integrated ANN-PRA/DP4+ Tandem Computational Approach

Lucas H. Martorano (PG),[1] Alessandra L. Valverde (PQ),[1] Carlos M. R. Ribeiro (PQ),[1] Ariel M. Sarotti (PQ),[2] Fernando M. S. Junior (PQ)[1*]

lucashm@id.uff.br; fernando_martins@id.uff.br

[1]*Department of Organic Chemistry, UFF;* [2]*Instituto de Química Rosario (CONICET), UNR.*

Palavras-Chave: *Natural products, Molecular modeling, DFT, NMR, Structural Revision.*

Highlights

In this study, we employed a protocol for theoretical calculations of ^{1}H and ^{13}C NMR chemical shifts using DFT, followed by the application of ANN-PRA and DP4+ tools to analyze all the structures of Heliannuols, natural sesquiterpenes mainly isolated from *Helianthus annuus*. Our results indicate that some originally proposed structures require revision, while others are supported by the initially proposed structure.

Abstract

Heliannuols, sesquiterpenes primarily isolated from H. annuus, are recognized for diverse biological activities, such as phytotoxic effects.[1] These secondary metabolites exhibit robust allelopathic potential, being considered as a natural herbicide. The carbon skeleton of these compounds features a benzene ring fused to a heterocyclic ring of 5, 6, 7, or 8 members (see figure 1a).[1-7] Despite an extensive study regarding the total synthesis of heliannuol in the literature, certain members lack proposed synthetic methodologies. Additionally, original structures were often elucidated based on correlations and similarity of NMR data, with limited stereochemical analysis. Consequently, structural reassignment is a common topic in the heliannuol family. Based on this, we conducted a comprehensive quantum chemical simulation of NMR parameters, utilizing an integrated ANN-PRA/DP4+ approach, to analyze the Heliannuol family.[8,9]

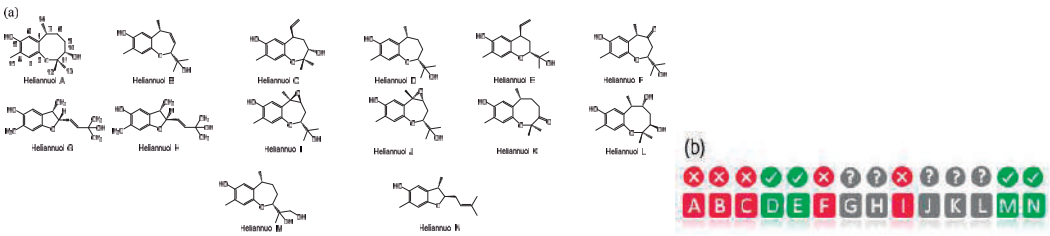


Figure 1: (a) Structures of heliannuols A-N. (b) Result obtained using the experimental data provided in the isolation papers.

The calculations of ^{1}H and ^{13}C NMR chemical shifts were conducted employing the Density Functional Theory coupled with the GIAO method (GIAO-HDFT) at the GIAO/mPW1PW91/6-31G(d)//mPW1PW91/6-31G(d) theory level, using the Gaussian 09 software package. The results obtained with all the members of the Heliannuol family using the experimental data provided in the isolation papers is provided in figure 1b.[10]

Acknowledgments

To the funding agencies CNPq, CAPES, and FAPERJ, we express our gratitude for their financial support.

References

[1]Macías *et al., Tetrahedron Lett.*, **1993**, 34, 1999–2002. [2]Macías *et al., J. Org. Chem.*, **1994**, *59*, 8261-8266. [3]Macías *et al.*, *Tetrahedron Lett.*, **1999**, 40, 4725-4728. [4]Macías *et al.*, *J. Nat. Prod.*, **1999**, 62, 1636-1639. [5]Macías *et al.*, *Phytochem.*, **2002**, 61, 687-692. 6Marsni *et al.*, *J. Agric. Food. Chem.*, **2015**, 63, 6410-6421. 7Georgantea *et al.*, *Tetrahedron*, **2016**, 72, 3262-3269. [8]Grimblat *et al.*, *J. Org. Chem.*, **2015**, 80, 12526–12534. [9]Sarotti, A. M. *Org. Biomol. Chem.*, **2013**, 11, 4847. [10]Frisch *et al.*, Gaussian 09; Gaussian Inc.: Wallingford, CT, **2009**.

Área: QPN

Constituintes químicos e atividades antioxidante e anti-inflamatória de *Miconia ligustroides* (Melastomataceae).

Gabriella Pereira Furio (PG)[1], Mirelli Bianchin (PG) [1]*, Sabrina Chinaglia Costermani (IC)[2],Eduardo Jorge Pilau (PQ)[2], Silvana Maria de Oliveira (PQ)[2].

gabriella.p.furio@gmail.com; bianchin.mirelli@gmail.com

[1]Departamento de Química, UEM;

Palavras Chave: Melastomataceae, Miconia Ligustroides, Antioxidante, Anti-inflamatória, HPLC-QTOF-MS/MS.

Highlights

Phytochemical study and biological activities of *Miconia ligustroides*

Belonging to the Melastomataceae family, the *Miconia ligustroides* species is little studied. It presents great potential for biological activities that could contribute in the future to the production of new medicines and herbal medicines.

Resumo/Abstract

A família Melastomataceae é composta por um grande número de espécies, no entanto, existem poucos estudos etnomedicinais, fitoquímicos e farmacológicos relatados na literatura. Desta família, as espécies do gênero *Miconia* são utilizadas na medicina popular brasileira para tratamento de doenças dermatológicas, reumáticas, inflamatórias e como analgésico. Estudos anteriores mostraram que tais atividades biológicas estão associadas a presença de metabólitos especializados principalmente da classe dos flavonoides e triterpenos. O presente trabalho relata o estudo químico e as avaliações do potencial antioxidante e anti-inflamatório das partes aéreas de *M. ligustroides*. O material vegetal foi coletado no Parque Estadual do Guartelá (Tibagi- PR, Brasil), foi seco e submetido a extração por macerações consecutivas com metanol a frio até a obtenção do extrato bruto (EB). A composição química do EB foi determinada por UHPLC-QTOF-MS/MS que resultou na identificação de 26 substâncias como sendo majoritariamente flavanonas, flavonóis derivados da mirecetina e triterpenos que são frequentemente associados as atividades biológicas. O potencial antioxidante dos extratos foi avaliado mediante a capacidade de redução de Folin-ciocalteu, redução ferro (FRAP), e atividades dos radicais DPPH, ABTS. Tais procedimentos revelaram um elevado teor de fenólicos totais no EB (66,80mg EAG/g), com potencial antioxidante nos métodos testados (ABTS=1055,31 µmol de Trolox/g; DPPH=278,93 µmol de Trolox/g; FRAP= 6,79 mmol de Fe^{2+}/g). A atividade anti-inflamatória *in vivo* foi realizada pelo método de edema de orelha, induzido pelo óleo de cróton, em camundongos e avaliação da atividade de mielopiroxidade (MPO). O EB de *M. ligustroides* inibiu significativamente o edema de orelha (13,55 ± 0,38 mg), apresentando resultado semelhante ($p>0,05$) ao tratamento com os anti-inflamatórios comuns, o extrato também provocou a redução da atividade de MPO em 88,90 % semelhante ao resultado encontrado pela indometacina. De modo geral, os resultados obtidos sugerem que a *M. ligustroides* produz metabólitos especializados que apresentam atividade anti-inflamatória e reforçam a importância em explorar as propriedades químicas e farmacológicas da família Melastomateceae.

Referencias: [1]CRUZ, A.V.D. et al. Uso medicinal de espécies das famílias Myrtaceae e Melastomataceae no Brasil. Floresta e Ambiente, v.11, p.47-52, 2004.; [2]GANDHI, S.R. et al. Health functions and related molecular mechanisms of Miconia genus: A systematic review. Heliyon, v.9, março de 2023.; [3]GOLDENBERG, R. O gênero Miconia (Melastomataceae) no Estado do Paraná, Brasil. Acta Botanica Brasilica, v.18, n.4. p.927-947, 2004. [4]CUNHA, G.O.S.; Da Cruz, D.C.; Menezes, A.C.S. An Overview of Miconia genus: chemical constituents and biological activities. Pharmacognosy and Natural Products, v.26, p.77-88, 2019.

Agradecimentos/Acknowledgments

CAPES, CNPq e Fundação Araucária.

Área: QPN

Dereplication of isoquinoline alkaloids from the stem of *Annona montana* Macfad. (Annonaceae) and biological activities of the extracts

Brenna Késia Ferreira da Silva (PG)[1], Ana Cristina da Silva Pinto (PG)[5], Rosemary Aparecida Roque (PG)[5], Adriana Dantas Gonzaga de Freitas (PG)[6], Emmanoel Vilaça Costa (PQ)[1], Felipe Moura Araújo da Silva (PQ) [4], Hector Henrique Ferreira Koolen (PQ)[3], Waldireny Rocha Gomes (PQ)[2].

*** brenna.silva@seducam.org.br / waldirenyrocha@ufam.edu.br**

[1]Departamento de Química, UFAM (DQ/UFAM), Manaus-AM; [2]Faculdade de Ciências Farmacêutica, UFAM (FCF/UFAM), Manaus-AM; [3]Escola Superior de Ciências da Saúde, UEA, Manaus-AM. [4]Central Analítica, UFAM (CA/UFAM), Manaus-AM, [5]Lab. de Malária e dengue, INPA, Manaus-AM; 6. Instituto de Ciências Biológicas. (ICB/UFAM), Manaus-AM

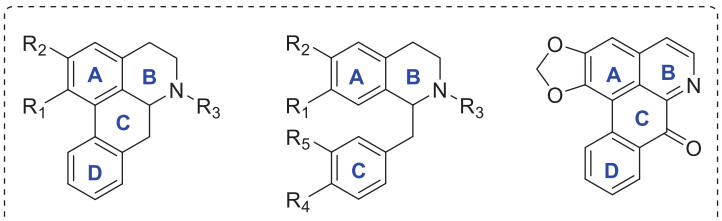
Palavras-Chave: *Falsa graviola, Perfil químico, Espectrometria, Antimicrobiano, Larvicida.*

Highlights

1. Extracts from *Annona montana* exhibit antimicrobial and larvicidal activity against *Aedes aegypti*; 2. Seven isoquinoline alkaloid derivatives were annotated from the alkaloid fraction of the stem, with three being described for the first time in this species.

Abstract

A. montana is a species belonging to the Annonaceae family, a native tree found in tropical forests. Popularly known as false soursop, araticum-cagão, and mountain soursop. Traditional populations often use it for treating snake bites, obesity, insomnia, flu, diabetes, and different types of cancer [1,2]. The plant material was collected, dried, pulverized, and subjected to static maceration assisted by ultrasonic bath with hexane and subsequently with methanol to obtain the extracts. Preliminary phytochemical analysis on TLC, with the Dragendorff reagent, indicated the presence of alkaloid compounds in the methanolic extract, which underwent the acid-base extraction process[3]. A portion of the alkaloid fraction was processed in a mass spectrometer where the major ions underwent sequential fragmentation (MSn). The crude extracts and the alkaloid fraction underwent antimicrobial[4] and larvicidal tests with *A. aegypti.* In the analysis of the total ion spectrum of the alkaloid fraction from the stem of *A. montana*, several peaks related to protonated substances with even *m/z* values attributed to alkaloids were observed. From the analysis of the mass spectra fragmentations(MS^n), three aporphinic alkaloids were annotated: annonaine (**1**), *N*-methyl annonaine (**2**), and *N*-methyl asimilobine (**3**); Three benzylisoquinoline alkaloids: coclaurine (**4**), *N*-methyl coclaurine (**5**), and reticuline (**6**); And one oxoaporphinic: liriodenine (**7**), of which three (**2**, **3**, and **5**) are described for this species for the first time. At a concentration of 250 µg/mL of the hexane extract, the *S. aureus* and *E. Coli* strains showed a translucent inhibition halo of 20 mm, and *C. albicans* showed a halo of 19.3 mm. The methanolic extract showed no antimicrobial activity. At a concentration of 400 µg/mL, the methanolic extract, alkaloid fraction, and neutral fraction showed larval mortality after 48h of 83%, 90%, and 100% for *A. aegypti*. The biological activities presented in *A. montana* extracts can be attributed to the structural variety of alkaloids produced by this species. Further tests are needed after isolating these metabolites to consolidate the information provided.



	R1	R2	R3	R4	R5
1	-O-CH2-O-				
2	-O-CH2-O-		-CH3		
3	-OCH3	-OH	H		
4	-OH	-OCH3	H	-OH	H
5	-OH	-OCH3	-CH3	-OH	H
6	-OH	-OCH3	-CH3	-OCH3	-OH

Figure 1. Annotated alkaloids from the stem extracts of *Annona montana*.

References

[1] Wu, Y., *et al*. Plat. Med., 61, 146−49, 1995; [2] Bailon-moscoso, N., *et al*. F. agricul. Immunol. 27, 4, 559–569, 2016; [3] Costa, E.V., *et al. J. Nat. Prod.*, 69, 292-296, 2006; [4] Bauer, A. W., *et al. J. A. J. Clin. Pathol., 45, 4, 493-496, 1966.*

Acknowledgments

The authors are grateful to CAPES, CNPq, FAPEAM, UEA and UFAM for financial support, and CA/CAM/UFAM for NMR and MS analysis.

Área: QPN

Desreplicação molecular de ácidos graxos acetilênicos com atividade anti-*Trypanosoma cruzi* das sementes de *Porcelia macrocarpa*

Ivanildo A. Brito (PG)[1], Erica V. Castro Levatti (PG)[2], Andre G. Tempone (PQ)[2], João Henrique G. Lago (PQ)[1].
ivanildo.brito@ufabc.edu.br

[1]*Centro de Ciências Naturais e Humanas, Universidade Federal do ABC, Santo André, SP;* [2]*Instituto Butantan, São Paulo, SP.*

Palavras Chave: *Compostos acetilênicos, Trypanosoma cruzi, Annonaceae.*

Highlights

Molecular dereplication of acetylenic fatty acids with anti-*Trypanosoma cruzi* activity from *Porcelia macrocarpa* seeds. This work reports the molecular dereplication of a bioactive fraction obtained from *Porcelia macrocarpa* seed extracts, leading to the characterization of ten chemically related fatty acids.

Resumo/Abstract

Os produtos naturais desempenham um papel crucial como fontes valiosas de moléculas a serem exploradas no processo de desenvolvimento de protótipos e medicamentos frente a diversas doenças. Neste contexto, a doença de Chagas, uma enfermidade parasitária provocada pelo protozoário *Trypanosoma cruzi*, emerge como um desafio significativo para a saúde, afetando mais de seis milhões de pessoas globalmente[1]. Em continuação aos nossos estudos visando a obtenção de metabólitos com ação anti-*T. cruzi,* nesse trabalho foi detectado que o extrato em CH_2Cl_2 das sementes de *Porcelia macrocarpa* apresentou atividade contra as formas tripomastigotas e amastigotas do parasita (100% de morte a 200 µg/mL). Após sucessivas etapas cromatográficas utilizando sílica gel, foi obtida uma fração bioativa com valores CE_{50} de 4,05 µg/mL (tripomastigotas) e de 0,48 µg/mL (amastigotas), potencial similar ao determinado para o fármaco padrão benznidazol (CE_{50} de 3,90 e 0,95 µg/mL). A análise de RMN de ^{1}H da fração bioativa mostrou sinais característicos de ácidos graxos acetilênicos, sendo estes um tripleto em δ 2,34 (J = 7,4 Hz, H-2) e um simpleto intenso em δ 1,25 referente aos hidrogênios da cadeia metilênica longa. Esse espectro apresentou ainda um tripleto em δ 2,24 (J = 7,0 Hz) atribuído aos hidrogênios H-12 e H-15, ligados a carbonos adjacentes a ligação tripla. Também, foram observados dois sinais característicos de uma ligação dupla terminal, sendo um duplo-duplo-tripleto em δ 5,80 (J = 16,9, 10,2 e 6,6 Hz) e um multipleto em δ 4,96. Além desses, o espectro de RMN de ^{1}H também mostrou um tripleto em δ 0,87 (J = 6,9 Hz), referente a hidrogênios de um grupo metílico na terminação da cadeia lateral. O espectro de RMN de ^{13}C mostrou um sinal em δ 172,6 atribuído ao carbono carbonílico (C-1) além de sinais atribuídos a carbonos sp em δ 80,4 (C-13) e 80,3 (C-14). Além desses, sinais referentes a carbonos sp^2 foram observados em δ 139,2 e em 114,3, referentes aos carbonos da ligação dupla terminal. Um sinal menos intenso em δ 14,1, atribuído a presença da metila terminal, foi também observado, confirmando a co-ocorrência de ácidos com e sem ligação dupla na terminação da cadeia lateral. Assim, visando a caracterização estrutural de tais compostos, a fração foi submetida a analise via CLAE/EM (modo negativo), o que permitiu inferir a presença de dez ácidos (**1** – **10**) com formulas moleculares definidas como $C_{20}H_{33}O_2$ ([M - H]$^-$ em *m/z* 305,2479, **1**), $C_{22}H_{37}O_2$ ([M - H]$^-$ em *m/z* 333,2790, **2**), $C_{24}H_{41}O_2$ ([M - H]$^-$ em *m/z* 361,3103, **3**), $C_{26}H_{45}O_2$ ([M - H]$^-$ em *m/z* 389,3417, **4**), $C_{28}H_{49}O_2$ ([M - H]$^-$ em *m/z* 417,3730, **5**), $C_{30}H_{53}O_2$ ([M - H]$^-$ em *m/z* 445,4043, **6**), $C_{20}H_{35}O_2$ ([M - H]$^-$ em *m/z* 307,2634, **7**), $C_{22}H_{39}O_2$ ([M - H]$^-$ em *m/z* 335,2948, **8**), $C_{24}H_{43}O_2$ ([M - H]$^-$ em *m/z* 363,3260, **9**) e $C_{26}H_{47}O_2$ ([M - H]$^-$ em *m/z* 391,3574, **10**). Adicionalmente, a análise do padrão fragmentação observado nos espectros de EM-EM permitiu posicionar a ligação tripla entre os carbonos 13 e 14 conforme ilustrado na **Figura 1**, devido à presença, em todos os espectros, de um sinal em *m/z* 249,1856, oriundo da fragmentação em C-16. Dentre essas substâncias, apenas o composto **2** foi descrito anteriomente[2], sendo os demais, portanto, inéditos na literatura.

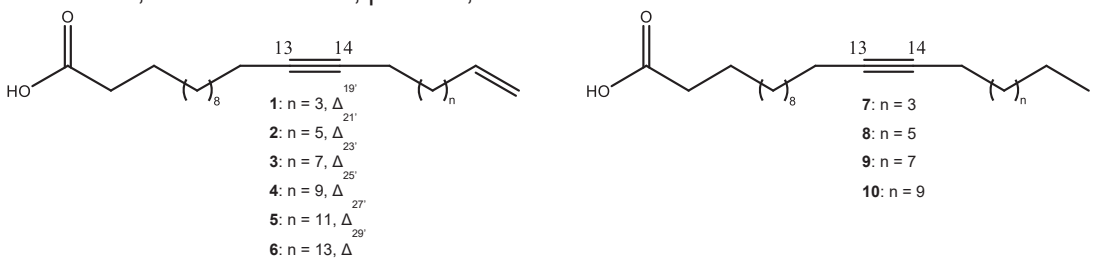


Figura 1. Estruturas químicas dos ácidos graxos bioativos **1** - **10** identificados nas sementes de *P. macrocarpa*

Agradecimentos/Acknowledgments

Agradecimentos: FAPESP, CNPq e CAPES. **Referências**: [1] DNDI, **2018**. [2] Brito, I. A. et al. *JBCS*, 1-7, **2020.**

Área: QPN

Determination of relative and absolute configuration of diterpenes isolated from *Medusantha martiusii* from computational spectroscopy.

Lucas H. Martorano (PG),[1] Edileuza Bezerra (PG),[2] Josean Tavares (PQ),[2] Marcelo S. Silva (PQ),[2] Lucas S. Abreu (PQ),[1] Fernando M. S. Junior (PQ)[1*]

lucashm@id.uff.br; fernando_martins@id.uff.br

[1]*Department of Organic Chemistry, UFF;* [2]*Department of Pharmaceutical Sciences, UFPB.*

Palavras-Chave: *Natural products, Stereochemical, DFT, NMR, ECD.*

Highlights

In this study, we utilized computational spectroscopy methodology to determine both the relative and absolute configurations of 9 diterpenes isolated from *Medusantha martiusii*. Our approach involved conducting ^{1}H and ^{13}C NMR calculations, employing the DP4+ tool, and simulating electronic circular dichroism (ECD) spectra. We further validated our findings by comparing the results with experimental data obtained from the isolated natural product. The application of this comprehensive protocol proved successful, leading to the accurate determination of the stereochemistry for all diterpenes.

Abstract

Medusantha martiusii is a native species in Brazil, commonly known as "cidreira-do-mato" and traditionally utilized in the treatment of intestinal and stomach ailments.[1] Nine diterpenes (some of them new structures) have been isolated from this species, and due to their intriguing activity and potential as a medication for gastrointestinal diseases, the accurate determination of the relative and absolute configurations of these substances is crucial. To achieve this, computational spectroscopy was employed. The calculations of ^{1}H and ^{13}C NMR chemical shifts were carried out using Density Functional Theory coupled with the GIAO method (GIAO-HDFT) at the GIAO/mPW1PW91/6-31+G(d,p)//B3LYP/6-31G(d) theory level. For the DP4+ method application, the magnetic shielding tensors for all candidates of each compound were added into the DP4+ Excel spreadsheet.[2] ECD simulations were conducted at the TD-DFT level of theory in acetonitrile, using a polarizable continuum model with the integral equation formalism, at the CAM-B3LYP/TZVP level. All quantum-mechanical calculations were executed using the Gaussian 09 software package.[3] After all simulations, the comparison with experimental data (NMR and ECD) were carried out. The very good agreement between observed and theoretical data allowed the unambiguous determination of both relative and absolute configuration of the isolated compounds.

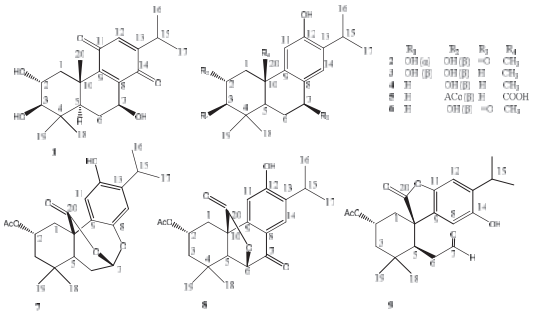


Figure 1: (a) Structures of diterpenes 1-9 isolated from *Medusantha martiusii*.

Acknowledgments

To the funding agencies CNPq, CAPES, and FAPERJ, we express our gratitude for their financial support.

References

[1]Agra *et al.*, *Revista Brasileira de Farmacognosia*, **2008**, *18*, 472-508. [8]Grimblat *et al.*, *J. Org. Chem.*, **2015**, 80, 12526–12534.

[10]Frisch *et al.*, Gaussian 09; Gaussian Inc.: Wallingford, CT, **2009**.

Área: QPN

DITERPENES PRODUCTION BY THE MARINE-DERIVED FUNGUS *Biatriospora* sp. CBMAI 1333

Lamonielli F. Michaliski (PG)[1,2]*, Menting Liu (PQ)[2], Yi Tang (PQ)[2], Roberto G. S. Berlinck (PQ)[1].

rgsberlinck1010@outlook.com; lamonielli.michaliski@usp.br

[1]Insituto de Química de São Carlos, Universidade de São Paulo, Brazil; [2]Department of Chemical and Biomolecular Engineering, University of California, Los Angeles, USA.

Key words: *Diterpene biosynthesis; Marine fungus; Biatriospora sp.*

Highlights

The fungal genus *Biatriospora* is of limited occurrence and yet poorly known[1]. Herein we present the biotechnological production of diterpenes by the fungus *Biatriospora* sp. CBMAI 1333. The final products of all canonical diterpene cyclases gene clusters were expressed in vivo, isolated and identified by NMR and GC-MS.

Resumo/Abstract

The marine fungal strain *Biatriospora* sp. CBMAI 1333 has shown the ability to produce several phomactin diterpenoids[2,3], related to the taxanes.[4] *Biatriospora* spp. strains are still underexploited. Little is known about the ecology and metabolism of these fungi[1]. Herein we report results of further investigations of the diterpene metabolism of *Biatriospora* sp. CBMAI 1333. Following whole gDNA sequencing, we identified four putative diterpene cyclase (DTC) and two geranylgeranyl pyrophosphate synthases (GGPPS) gene clusters (GC). The four putative DTCs were expressed in *Aspergillus nidulans* A1145 ΔEM along with one of the two GPPPSs identified, to supplement the GGPP precursor to the DTCs. Heterologous expression experiments were performed following a well-stablished pipeline.[5] The DTCs+GGPPSs transformant strains were cultured in CD-ST agar plates for five days, followed by hexane extraction. Metabolite production was investigated by GC-MS analysis. Four transformant strains, DTC1+GGPPS1, DTC2+GGPPS1, DTC3+GGPPS1 and DTC4+GGPPS1 were further investigated by large scale cultures. We purified the diterpene core precursors produced by DTC1-4, and identified the products by NMR and GC-MS analyses. Additionally, DTC2 was co-expressed with accessory oxido-reductase enzymes from its cluster, leading to the identification of an advanced biosynthetic product never before reported from fungal cultures.

[1] Kolařík, M., *et al*. *Plant Syst. Evol.*, **2017**, *303*, 35–50. http://doi.org/10.1007/s00606-016-1350-2
[2] Kuroda, Y., *et al*. (2018). *Nature Chem.*, **2018**, *10*, 938–945. https://doi.org/10.1038/s41557-018-0084-x
[3] da Silva Oliveira, L. *et al*. *J. Nat. Prod.*, **2023**, *86*, 2065–2072. https://doi.org/10.1021/acs.jnatprod.3c00383
[4] Tokiwano, T., *et al.* (2005). *Org. Biomol. Chem.*, **2005**, *3*, 2713–2722. https://doi.org/10.1039/b506411b
[5] Yee, D. A., & Tang, Y. (2022). *Meth. Mol. Biol.*, **2022**, *2489*, 41–52. https://doi.org/10.1007/978-1-0716-2273-5_3

Agradecimentos/Acknowledgments

LFM and RGSB thank the financial support by FAPESP (2013/50228-8, 2017/25100-9, 2019/07894-3, 2019/17721-9 and 2022/07831-4).

Enhancing Product Stability by Microencapsulation of a nanoemulsion of Plant Extracts

Ailane S. de Freitas (PG),[1] Ilza Maria de O. Sousa (PQ), Luan da S. D. Rabelo (PG), Pamela Bendel (IC)[1], Lorena Ribeiro (IC)[1], Mayra Biccigo (PG)[1], Ana Ruiz (PQ)[1], João E. Carvalho (PQ)[1], Mary Ann Foglio (PQ) [1]*

[1]Universidade Estadual de Campinas (UNICAMP), Faculty *of Pharmaceutical Sciences, Ph*ytochemistry, Pharmacology and Experimental Toxicology Laboratory, Cândido Portinari Str.,200, 13083-871 Campinas-SP, Brazil

Key words: *carajurin, HPLC, tocotrienois, stability, 6,7-dihydroxy-5,4'-dimetoxyflavilium*

Highlights

The microencapsulation of a nanoemulsion of plant extracts provided stable product at room temperature, overcoming environmental challeges.

Abstract

Our research group previously demonstrated *Fridericia chica*(Bonpl.) L.G. Lohmann (Sin. *Arrabidaea chica* Verlot), standardized extract's wound healing capacity in Phase I and II clinical trials of volunteers with head and neck cancer. The challenge for producing quality herbal medicines is in the standardization of plant input to guarantee the production of products that present reproducibility of effects and chemical constitution among different batches. The Anthocyanins, involved in the species pharmacological activity, are unstable under adverse environmental conditions; therefore, the preservation of thermolabile bioactive components of medicinal plants challenges the herbal industry. Hence, to minimize the loss of bioactive compounds, avoiding the need of cold production chain, herein we report the microencapsulation of a nanoemulsion containing the association of *F. chica* standardized extract with 5% of an enriched tocotrienol fraction, obtained from *Bixa orellana*, providing a stable product at room temperature. Extraction at -5°C with 70% ethanol + 0.3% citric acid under continuous stirring of *F. chica* leaves provided the standardized crudo extract. Paulo Roberto Carvalho from Institute of Food Technology (ITAL-Campinas_SP) provided 70% tocotrienol-enriched fraction. The project registration number at Brazilian Genetic Resources SisGen is under number #A5489C9. The nanoemulsion was prepared with high-energy method using a tip sonicator. This emulsion further microencapsulated, adding hydrolyzed collagen to the nanoemulsion, as wall material, provided a powder by spray drying. Carajurin (6,7-dihydroxy-5,4'-dimetoxyflavilium) and delta and gamma tocotrienol contents were evaluated by HPLC-UV/VIS, in triplicate, at 470nm and 295nm, respectively, during 120 days at room temperature (25^{0}C ± 2^{0}C), refrigerated (2-8^{0}C), and greenhouse (40^{0}C/75%). Standard for analytical curves for carajurina and tocols, were achieved by successive column chromatography with microcrystalline cellulose or silica, with further purification on a C-18E column provided standards. The tocol content remained stable throughout the period from 0 to 120 days (0.38%±0.01) in the three environmental conditions studied. The carajurina content showed differences in the time and type of storage. Compared to the original content (T0= 0.50% ± 0.01), storage at room temperature resulted in a loss of 14% of the carajurina content in 120 days. Storage in refrigerators and greenhouses resulted in a loss of 38% (0.31% ± 0.05) and 82% (0.09% ± 0.01) respectively during the same period, showing that these conservation conditions promote interactions between components of micro and nanoparticles, causing possible chemical degradation, protein denaturation and particle aggregation. The use of the nanoemulsion microencapsulation strategy demonstrated the ability to preserve carajurin, delta, and gamma tocotrienols throughout the 120 days at room temperature, providing an economically more suitable active plant pharmaceutical ingredient for use in various topical formulations for wound healing purposes.

Acknowledgments

Capes, CNPQ e FAPESP grant number 2021/01280-3

Área: QPN

Estudo fitoquímico e avaliação antibacteriana de *Hypericum brasiliense* Choisy (Hypericaceae)

Sofia T. M. da Silva (IC),[1*] Julia C. Scaffo (PG),[2,3] Diogo F.G. Andrade (PG),[1,2] Thais Pereira de Mello (PQ),[3] André Luís Souza dos Santos (PQ),[3] Lucas Silva Abreu (PQ),[1] Leandro Rocha (PQ).[2]

sofiamussi@id.uff.br;

[1] Laboratório de Química de Produtos Naturais, Universidade Federal Fluminense, Niterói, RJ, Brasil; [2] Laboratório de Tecnologia de Produtos Naturais, Universidade Federal Fluminense, Niterói, RJ, Brasil; [3]Laboratório de Estudos Avançados em Microrganismos Emergentes e Resistentes, Universidade Federal do Rio de Janeiro, Rio de Janeiro, RJ, Brasil.

Palavras Chave: *Metabólitos Secundários, Produtos Naturais, Espectrometria de Massas, Staphylococcus aureus*

Highlights

Phytochemical study and antibacterial evaluation of *Hypericum brasiliense* Choisy (Hypericaceae);

Perfil químico por HPLC-ESI-qTOF e atividade antibacteriana do extrato hexânico das partes aéreas.

Resumo/Abstract

As infecções bacterianas são um grande problema de saúde pública em escala mundial. A gravidade das infecções bacterianas pode variar de leves a potencialmente fatais, dependendo da virulência da bactéria envolvida e da resposta do sistema imunológico do hospedeiro. A resistência a antimicrobianos é uma preocupação global crescente devido os agentes terapêuticos antibacterianos tradicionais perderem eficácia ao longo do tempo de uso. Desta forma, produtos de origem natural são fontes ricas em metabólitos secundários possivelmente antibacterianos. A espécie vegetal *Hypericum brasiliense* foi descrita anteriormente com ação antibacteriana. O objetivo do estudo consiste na fitoquímica de novos metabólitos antibacterianos derivados do extrato de *Hypericum brasiliense*, utilizando técnicas analíticas para racionalizar o isolamento de substâncias bioativas. O extrato fração hexano das partes aéreas foi preparado por maceração e posteriormente concentrado por evaporação rotatória. O extrato foi submetido a análises cromatográficas por HPLC-ESI-qTOF para obtenção do perfil químico e concentração inibitória mínima (CIM) em cepas *Staphylococcus aureus* sensível (ATCC 29213) e resistentes (HU25, USA300) a meticilina pela metodologia de microdiluição seriada em caldo Muller-Hinton em placas de 96 poços seguida da concentração bactericida mínima (CBM) em placas de Petri com ágar Muller-Hinton. Foi anotado as substâncias como os floroglucinois japonicina A, uliginosina B e isouliginosina B. O extrato foi submetido a fracionamento utilizando cromatografia em coluna aberta e as substâncias isoladas estão sendo submetidas a análise por RMN. A fração em hexano de *H. brasiliense* apresentou CIM de 6,25 a 3,125 µg/mL e CBM de 12,5 a 6,25 µg/mL, e desta forma, pode ser considerado um extrato antimicrobiano promissor. Por fim, as substâncias isoladas serão avaliadas quanto o potencial antibacteriano que será realizado em microdiluição para determinação da CIM e CBM nas cepas bacterianas supracitadas. Esse trabalho demostra o potencial antibacteriano da fração hexano do extrato de *H. brasiliense,* bem como os florogucinóis como possíveis responsáveis pela atividade biológica.

Referências: FRANÇA, H. S. et al. **Química Nova**, v. 32, p. 1103-1106, 2009; ROCHA, L. et al. **Phytochemistry**, v. 40, n. 5, p. 1447-1452, 1995; Clinical and Laboratory Standards Institute (CLSI). Performance Standarts for Antimicrobial Susceptibility Testing. 33rd ed. CLSI supplement M100; ISBN 978-1-68440-171-0 [Eletronic]). Clinical and Laboratory Standarts Institute, USA, 2023

Agradecimentos/Acknowledgments

Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES), Fundação Carlos Chagas Filho de Amparo à Pesquisa do Estado do Rio de Janeiro (FAPERJ), and Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPQ).

Área: _____
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Evaluation of host plant consumption and virus-induced changes to the metabolome and immune response of a generalist insect

Marília E. Gallon (PG),[1] Nadya D. Muchoney (PG)[2]; Leonardo Gobbo-Neto (PQ)[1]; Angela M. Smilanich (PQ)[2].

mariliagallon@hotmail.com.br

[1] *Núcleo de Pesquisa em Produtos Naturais e Sintéticos, School of Pharmaceutical Sciences of Ribeirão Preto, University of São Paulo (USP), Av. do Café s/n°, Ribeirão Preto, SP 14040-903, Brazil*

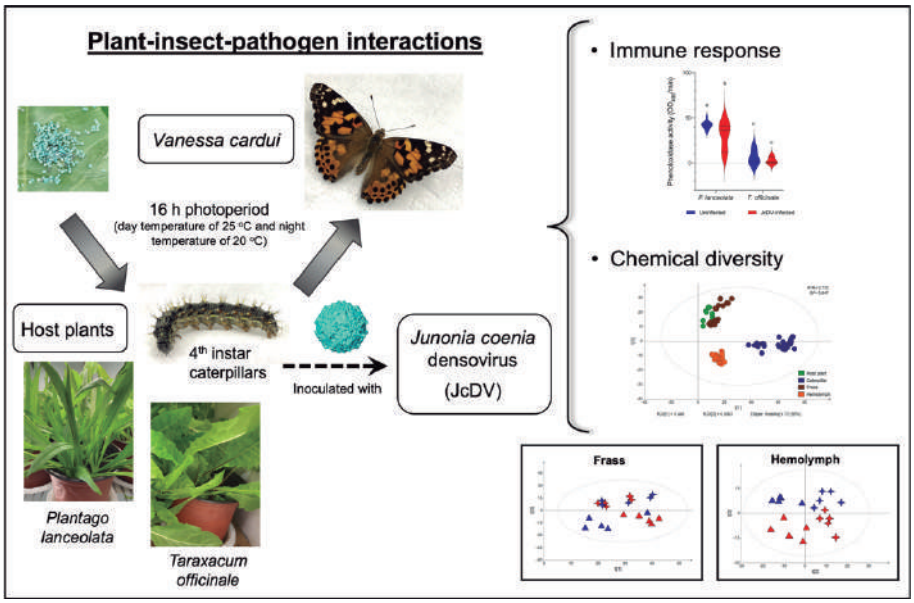
[2] *Department of Biology, University of Nevada, 1664 N. Virginia St., Reno, NV 89557, USA*

Keywords: Vanessa cardui, Plantago lanceolata, Taraxacum officinale, Junonia coenia densovirus, chemical diversity, LC-MS

Highlights

Infection by an entomopathogenic virus induced changes to insect metabolome and immune response. Insect chemical diversity was dependent upon host plant consumption and viral infection.

Abstract



Understanding the interactions between plants, insects and pathogens in a multitrophic context it is an evolving field in chemical ecology. In insects, viral infections have been commonly associated with differential expression of primary metabolites (e.g., carbohydrates, amino acids and lipids), which in turn may also influence secondary metabolite content. Herein, we investigate the changes in the metabolome of *Vanessa cardui* caterpillars subjected to a viral infection by Junonia coenia densovirus (JcDV) and reared on two host plants that vary in secondary metabolites, *Plantago lanceolata* L. (Plantaginaceae) and *Taraxacum officinale* L. (Asteraceae), by means of chemical diversity indices obtained by a liquid chromatography-mass spectrometry (LC-MS)-based metabolomic approach. Additionally, insect immune response was evaluated by phenoloxidase (PO) activity. Chemical diversity indices showed that viral infection induced changes to the chemical content of insect hemolymph and frass dependent upon host plant consumption. Overall, insect immune response was higher in individuals feeding on *P. lanceolata* compared with those feeding on *T. officinale*. Additionally, infection with JcDV caused suppression of PO activity, which was not host plant dependent. Therefore, we found that insect immunity was more strongly affected by host plant consumption than by JcDV infection, which corroborated the assumption that insect development is greatly influenced by the nutritional value and chemical content of the host plant. Nevertheless, JcDV infection induced changes to insect metabolome, which were dependent upon both viral infection and host plant consumption. Taken together, our findings showed that viral infection combined with host plant consumption creates a unique chemical environment, particularly within the insect hemolymph. Going forward, exploring how these metabolites contribute to defense against viral infection may benefit from the background gained herein and contribute to a more comprehensive understanding of plant-insect-pathogen interactions.

Acknowledgments

Authors are grateful to the São Paulo Research Foundation—FAPESP (grant#2021/07911-5 and #2017/17023-4) and Coordination for the Improvement of Higher Education Personnel—CAPES.

Área: QPN

Evaluation of phenolic compounds and antioxidant activity of *Melipona quadrifasciata* geopropolis extracts obtained with different solvents

Gabriel T.S. Ribeiro (IC), Rafael F. Santos (PG), Gabriel F. Santos (PG), Rosane N. Castro (PQ)

teles.gb217@gmail.com

Instituto de Química- Departamento de Química Orgânica – UFRRJ

Keywords: *Stingless bee, Phenolic compounds, Antioxidant capacity*

Highlights

The geopropolis of *M. quadrifasciata* has antioxidant activity and its chemical composition appears to be partially polar because its activities were concentrated in the acetate and ethanolic extracts.

Resumo/Abstract

The geopropolis of *stingless bee* has been presenting very interesting results in relation to biological activities, but there are still few studies related to the chemical composition of these natural products[1]. *Melipona quadrifasciata* anthidioides is a species of stingless bee popularly known in Brazil as “mandaçaia”. Products derived from bees for food and therapeutic uses, have stimulated the evaluation of the chemical composition of geopropolis. The interests of researching geopropolis and its properties is due to the presence of bioactive compounds and its pharmacological properties as antifungal[2], antiviral, antioxidant[3], among other activities. These biological activities are observed because of the presence of phenolic acids and flavonoid. Thus, this study aimed to investigate the phenolic profile and antioxidant activity of different geopropolis extracts from the stingless bee *Melipona quadrifasciata* (Mandaçaia), collected in the municipality of Santo Aleixo, Rio de Janeiro region, Brazil. In this work, extracts were prepared using 10g of geopropolis pulverized in a Soxhlet extractor for 6h using solvents of increasing polarity, obtaining extracts of hexane (EHGP), dichloromethane (EDGP), ethyl acetate (EAGP), ethanol (EEGP) and a hydroalcoholic (EHAGP), using 70% ethanol and 30% water. The determination of flavonoids and phenolic compounds was carried out by colorimetric tests, using the $AlCl_3$ complexation methods and the Folin-Cioucalteu reagent, respectively. Furthermore, the antioxidant capacity was detected by the 2,2-diphenyl-1-picrylhydrazyl (DPPH) radical capture method. Except for the EHGP which did not present significant values in the tests, the results obtained for each extract investigated for total phenolic content were: 8.6mg EAG.100mg^{-1} for EDGP; 18.61mg EAG.100mg^{-1} for EAGP; 27.98mg EAG.100mg^{-1} for EEGP; 16.28mg EAG.100mg^{-1} EHAGP. Furthermore, for the content of total flavonoids, EHGP and EDGP, however, the values obtained for the other extracts were good: 0,69mg EQE.100mg^{-1} for EAGP; 2.11mg EQE.100mg^{-1} for EEGP; 2.18mg EQE.100mg^{-1} for EHAGP. Regarding the antioxidant capacity expressed by IC_{50}, the extracts presented the following values: 76.57 µg.mL^{-1} for EDGP; 6.48µg.mL^{-1} for EAGP; 2.38µg.mL^{-1} for EEGP and 7.65µg.mL^{-1} for EHAGP. The results obtained demonstrated that the acetate (EAGP) and ethanolic (EEGP) extracts presented a higher concentration of phenolic compounds and more powerful antioxidant properties in the tests. It was also able to prove that the extractions made with different polarity solvents was a success, as it could be observed the separation of compounds according to its polarities. Preliminary chemical analysis indicates the presence of gallic acid and naringenin in geopropolis. The chemical composition of geopropolis appears to be partially polar because its activities were concentrated in the acetate and ethanolic extracts. Therefore, the results indicate the antioxidant potential of *M. quadrifasciata* geopropolis, being a promising source for identifying new molecules with therapeutic properties.

1. Santos, Cintia Miranda dos. Composição química e atividade antioxidante de geoprópolis de *Melipona quadrifasciata* anthidioides. Trabalho de Conclusão de Curso – Dourados, MS: UFGD, 2015. 39f.
2.DA SILVA, E. C. C.; MUNIZ, M. P.; NUNOMURA, R. C. S. Constituintes fenólicos e atividade antioxidante da geoprópolis de duas espécies de abelhas sem ferrão amazônicas. Quím. Nova, Vol. 36, No. 5, 628-633, 2013.
3. BRAND-WILLIAMS, W., CUVELIER, M. E., & BERSET, C. Use of a free radical method to evaluate antioxidant activity. *Lebens Wiss Technology* (LWT), 28(1), 25–30, 1995.

Agradecimentos/Acknowledgments

The authors appreciate the support from FAPERJ, CNPQ and CAPES for the fomentation.

Área: QPN

Evaluation of potential of β-Glucans from mushrooms as ingredients for cosmeceutical products

Ana Vitória Caetano Barbosa (IC),[1] Elaine Rosechrer Carbonero (PQ),[1] Dayane R. Brito (PQ)[1], Dirce Leimi Komura (PQ)[2] Maria Carolina B. Di Medeiros Leal (PQ)[3],

ana_barbosa@discente.ufcat.edu.br; elaine_carbonero@ufcat.edu.br

[1]Instituto de Química, Universidade Federal de Catalão (UFCAT); [2] Instituto Federal de Educação, Ciência e Tecnologia do Maranhão (IFMA), Campus São João dos Patos; [3] Centro Universitário do Planalto Central Aparecido dos Santos (UNICEPLAC)

Keywords: Macrofungi, Mushroom, β-Glucans, Triple helix, Skin-friendly products.

Highlights

Three-dimensional structures of β-Glucans, obtained from the mushrooms via aqueous extraction, were evaluated by Congo red assay, aiming to select bioactive ingredients for the cosmeceutical industry.

Abstract

Macrofungi has been recognized as a promising source of bioactive polysaccharides for various purposes. β-glucans have received particular attention, mainly for their antitumor and immunomodulatory effects, in response to their binding to specific receptors, such as Dectin 1, among the biomacromolecules produced by these organisms. In addition to their recognized ability to act in the immune response, these polymers have shown promising skin health promotion effects, including anti-wrinkle, wound healing, antioxidant activity, anti-ultraviolet (UV) effect and moisturizing effect. Given the above, the main objective of this research is to select fungal beta-glucans capable of promoting skin health for cosmeceutical applications. Firstly, the three-dimensional structure of different (1→3) and (1→6)-linked beta-glucans obtained from the mushrooms *Agrocybe aegerita, Cantharellus guyanensis, Hericium erinaceus, Hypsizigus marmoreus*, *Lentinula edodes,* and *Pleurotus eryngii, previously characterized by NMR, was* evaluated using the Congo Red assay. Briefly, the polysaccharide solution was mixed with the Congo red solution, and the NaOH solution was then added. The concentration of NaOH solution was adjusted gradually from 0 to 0.50 M. At the same time, Congo red solution without polysaccharide was used as the experimental control group. The maximum absorption wavelength (λ_{max}) at different concentrations was measured using a UV/Vis spectrophotometer (Kasvi) in the 400–600 nm range. By the data obtained, only the beta-glucans gel exhibited a triple-helical conformation due to redshift of $\lambda_{max,}$ in the presence of water or low NaOH concentration (< 0.15 M), followed by a decrease of λ_{max} with the increase in NaOH concentration. Other beta-glucans evaluated showed different λ_{max} behaviors, suggesting another conformation. These results reflect the influence of the parameters as the degree of branching, distribution, length of side chains, and molar mass in the three-dimensional conformation. Considering that carbohydrates with a triple-helix structure are more biologically effective, the evaluated glucan gel was shown to be a promising natural ingredient for skin-friendly products. Antioxidant activity, wound healing, and other experiments will be carried out in order to confirm these findings.

References:

Vetter J. The mushroom glucans: molecules of high biological and medicinal importance. *Foods*, 12*(5)*, 1009, 2023. https://doi.org/10.3390/foods12051009

Guo X, Kang J, Xu Z, Guo Q, Zhang L, Ning H, and Cui SW. Triple-helix polysaccharides: formation mechanisms and analytical methods. *Carbohydr. Polym.* 262, 117962, 2021. https://doi.org/10.1016/j.carbpol.2021.117962

Agradecimentos/Acknowledgments

This study was supported by the Federal University of Catalão (UFCAT) and financed in part by the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPQ) and Fundação de Amparo à Pesquisa do Estado de Goiás (FAPEG). The authors acknowledge Prof. Dr. Antônio Gilberto Ferreira from the Federal University of São Carlos and Prof. Luciano M. Lião from the Federal University of Goias for supporting the NMR experiments.

Área: QPN

Evaluation of the antifungal activity of geopropolis extracts produced by *Melipona quadrifasciata anthidioides* and *Melipona bicolor*

Gabriel F. dos Santos (PG),[1*] Gabriel T. S. Ribeiro (IC),[1] Aguida A. de Oliveira (PQ),[2] Rosane N. Castro (PQ).[1]

gabriel.fulgencio21@gmail.com

[1]Departamento de Química Orgânica-IQ – UFRRJ; [2]Departamento de Microbiologia e Imunologia Veterinária-IV - UFRRJ.

Keywords: Mandaçaia, *guarupu,* antifungal activity, *Sporothrix brasiliensis*.

Highlights

In this work, the ethanol extract of mandaçaia and guarupu geopropolis was evaluated for its antioxidant potential, total phenolic and flavonoid and against clinical strains of *Sporothrix brasiliensis*.

Resumo/Abstract

In Brazil there are several types of stingless bees (Tribo *Meliponini*), such as, *Melipona quadrifasciata* (mandaçaia) and *Melipona Bicolor* (guarupu), objects of this work and sources of the natural geopropolis matrix. This natural product is a resinous substance of complex chemical composition, collected by bees from different parts of the plant tissue, plus soil and/or clay[1]. Several biological activities of geopropolis have been evaluated, such as antibacterial, antifungal, antiviral and antioxidant. The genus *Sporothrix* includes important dimorphic fungi pathogens that cause sporotrichosis, a neglected endemic mycosis with worldwide distribution, and that affects humans and animals. Brazil has a high rate of sporotrichosis caused by fungi, and in particular, cats are the most infected by *S. brasiliensis*, and play an important role in zoonotic transmission[2]. Treatment options for sporotrichosis include itraconazole and amphotericin B, medications generally associated with adverse and deleterious reactions, in addition to the emergence of new fungal isolates resistant to medications already used. Thus, this work aimed to evaluate the profile of phenolic compounds and antioxidant capacity of different geopropolis extracts of mandaçaia and guarupu, and to investigate the *in vitro* antifungal activity against clinical isolates of *S. brasiliensis,* the major causative agents of sporotrichosis in Brazil. Mandaçaia geopropolis was collected from an apiary located in Bosque da Barra, while guarupu geopropolis was collected in São Conrado, both in Rio de Janeiro. The pulverized geopropolis samples (10 g) were extracted with 200 mL of 95% ethanol for two hours in an ultrasonic bath, the process was carried out three times, and then the extracts were evaporated in a rotary evaporator. The extracts were then combined to provide geopropolis ethanolic extract for mandaçaia (EEGP-M) and guarupu (EEGP-B). The ethanolic extracts were solubilized in methanol:water (7:3 v/v) and partitioned with *n*-hexane and dichloromethane, respectively, providing the following fractions for each geopropolis: FR-Hex, FR-DCM and FR-MeOH:H_2O. The qualitative chemical profile of each fraction was evaluated by analytical thin layer chromatography, revealed in an ultraviolet lamp at a length of 254 nm and in a sulfuric vanillin solution, and high-performance liquid chromatography coupled to a diode array detector. It was possible to observe that different polarity solvents helped to simplify the constituents of the complex geopropolis matrix. The total phenolic and flavonoid content were evaluated compared to gallic acid (GA) and quercetin (QE) standards, respectively. The FR-DCM fractions showed the highest results for phenolic and flavonoid for both species (18.9 mgEGA g^{-1} and 4.2 mgEQE g^{-1}, respectively) for mandaçaia and (0.53 mgEGA g^{-1} and 4.67 mgEQE g^{-1}) for guarupu. The DPPH (2,2-diphenyl-1-picrylhydrazyl) assay was used to determine the antioxidant capacity of the extracts and the fraction, the FR-DCM fractions presented the highest results (EC_{50}= 0.200 mg mL^{-1}) for mandaçaia and (0.102 mg mL^{-1}) for guarupu. The better result in *M. bicolor* is consistent with the results of total flavonoid content, making it possible to correlate antioxidant activity with the presence of flavonoids. The antifungal activity was investigated against clinical strains *S. brasiliensis* and the positive control was Itraconazole (MIC = 0.016 mg mL^{-1}). The best result in guarupu was observed in EEGP-B and FR-Hex (MIC = 0.281 mg mL^{-1} for both), and for mandaçaia FR-Hex was the one that demonstrated the best results (MIC = 0.281 mg mL^{-1}). However, EEGP-M and FR-DCM for both geopropolis exhibited the same values (MIC = 0.562 mg mL^{-1}). The FR-MeOH:H_2O only presented result in mandaçaia (MIC = 0.281 mg mL^{-1}). The antifungal activity showed the inhibition potential of mandaçaia and guarupu geopopolis and their fractions against *S. brasiliensis*. The results presented here showed greater antifungal activity of hexane extracts of gepropolis, when compared to other geopropolis extracts, demonstrating that these natural products are promising for the treatment of sporotrichosis and need to be further investigated.

1. CARDOSO, et al. *Revista Virtual de Química*. v. 7 (6), 2457-2474, 2015.
2. WALLER et al. *Science and Animal Health*. V.5 (2),151-165, 2017.

Agradecimentos/Acknowledgments

CAPES, FAPERJ, CNPq, UFRRJ

Área: QPN

Evaluation of the antimicrobial potential of alkaloids from *Duguetia lanceolata*: a combined approach of molecular networking, *in silico* and *in vitro* analysis

Jackson Monteiro (PG)[1], Erick Dantas (PG)[1], Marisi G. Soares (PQ)[2], Renata Pascon (PQ)[1], Marcelo Vallim (PQ)[1], Patricia Sartorelli (PQ)[1]*

jackson.monteiro@unifesp.br; psartorelli@unifesp.br

[1]Universidade Federal de São Paulo – UNIFESP; [2]Instituto de Química, Universidade Federal de Alfenas – UNIFAL;

Key-words: *Duguetia lanceolata, alkaloids, antimicrobial activity, molecular networking, in silico and in vitro analysis.*

Highlights

The alkaloid extract obtained from *D. lanceolata* was analyzed and a molecular network was created using GNPS. The annotated alkaloids evaluated *in silico* and *in vitro* against pathogenic organisms.

Resumo/Abstract

The discovery of antibiotics should have put an end to the problem of bacterial infections, but this has not been the case, as it has led to the evolution of bacterial resistance mechanisms against several class of antibiotics. Bacterial pathogens that are resistant to structurally distinct antimicrobial agents are microorganisms that cause infections and are therefore, a major concern in terms of public health, which is why research into antimicrobial activity using natural products is becoming increasingly important against pathogenic microorganisms.[1,2] In this way, the present study was aimed at a combined approach of molecular networking, *in silico* and *in vitro* analysis using LC-MS/MS data from the alkaloid extract obtained from the leaves of *D. lanceolata*, for the evaluation of the antimicrobial potential using GNPS (*Global Natural Products Social Molecular Networking*) platform, soit was possible to generate molecular networks to obtain chemical information about the alkaloids present in the extract. This database combines MS/MS spectra based on a similar mass fragmentation profile, with the underlying concept being that structurally related molecules fragment in a similar way, resulting in analogous patterns. This allowed the annotation of 35 alkaloids, including the major compound glaucine. The alkaloids annotated were then evaluated for their *in silico* antibacterial properties against pathogenic bacteria and fungi as well as against their target proteins in the present investigation using *PASS online* (*Prediction of Activity Spectra for Substances*)[3], a computer-based program, which was used to screen the biological activity of the compounds and *SwissDrugDesign*[4] to predict the molecular interactions that can occur between a target protein and a small molecule. Twenty-two of the annotated alkaloids were predicted to have antibacterial, bacterial efflux pump inhibitor and antifungal activity. We then selected glaucine (the main compound), which was also included in the *in silico* prediction list, to carry out *in vitro* assays. This alkaloid has been isolated and tested for its antimicrobial activity against Gram-positive and Gram-negative bacterial strains and yeasts, presenting *Minimum Inhibitory Concentrations 90%* (MIC) for the Gram-positive bacteria *S. aureus* (ATCC25923) 208 µg/ml (90.8%±0.4) and *E. faecium* (ATCC CCB076) 52µg/ml (90.0%±1.0) and for the fungal strains *C. gatti* (R265 - serotype B) 26µg/ml (91.3%±2.8), *C. gatti* (NIH312 - serotype C) 52µg/ml (92.0%±1.7). *In silico* docking studies on pathogenic organisms and their target proteins in this research may suggest a possible mechanism of action of glaucine against those microorganisms in which it was shown to be active. In development, we will also isolate other alkaloids to carry out in vitro assays. The results of this work have highlighted the relevance of evaluating the alkaloids present in the *D. lanceolata*, which may offer effective antimicrobial agents due to their new structural properties that can combat antimicrobial resistance.

[1]Morrison *et al*., Antimicrobial resistance; *Gastrointestinal Endoscopy Clinics* (2020): 619-635.
[2]Hobson *et al*., The antibiotic resistome: a guide for the discovery of natural products as antimicrobial agents; *Chemical Reviews* (2021): 3464-3494.
[3]Filimonov D.A., *et al*. Prediction of the biological activity spectra of organic compounds using the PASS online web resource. *Chemistry of Heterocyclic Compounds*, (2014): 50 (3), 444-457.
[4]Grosdidier A, *et al*.. SwissDock, a protein-small molecule docking web service based on EADock DSS. *Nucleic Acids Res.* 2011 Jul;39(Web Server issue):W270-7.

Agradecimentos/Acknowledgments

FAPESP, CAPES and CNPq

Área: ORG

Evaluation of the antiurolithic activity of medicinal plants

Daniele de Oliveira Silva (PG),[1*] Lara P. D' M. Costa (IC),[1] Paula P. O. Salem (PG),[1] Paulo R. S. da Silva (IC),[1] Ana H. M. Macedo (IC)[1], Patricia Sartorelli (PQ),[2] João H. G. Lago (PQ),[3] Daniela A. Chagas de Paula (PQ),[1] Danielle F. Dias (PQ),[1] Marisi G. Soares[1](PQ)[1]

marisi.soares@unifal-mg.edu.br; daniele.oliveira@sou.unifal-mg.edu.br

[1]*Institute of Chemistry, Federal University of Alfenas (UNIFAL – MG)*
[2]*Institute of Environmental, Chemical and Pharmaceutical Sciences, Federal University of São Paulo, São Paulo,SP.*
[3]*Center of Natural Sciences and Humanities, Federal University of ABC, Santo Andre, São Paulo, SP.*

Keywords: *Medicinal plants; Antiurolithic; Decoction; Infusion; Piper umbellatum; Solanum cernuum.*

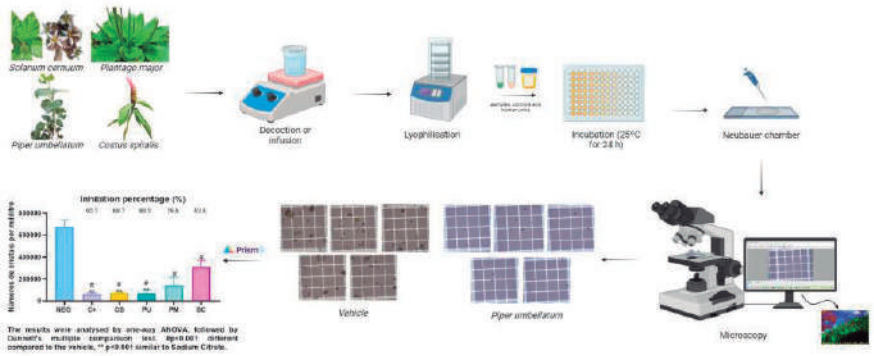
Highlights

The antiurolithic activity of *P. umbellatum* (89.3%) and *S. cernuum* (53.8%), the latter of which is endemic to Brazil, was investigated, revealing their potential for the first time in this study.

Abstract

Urolithiasis, or kidney stone disease, affects about 10% of the world's population, with 80% of cases being of calcium oxalate (CaOx), which can occur in dihydrate and monohydrate forms[1]. This multifactorial condition results in the formation of kidney stones, which can lead to renal dysfunction if left untreated[2]. At present, modern medicine lacks effective treatments for completely removing kidney stones and reducing their incidence. Therefore, the search for therapeutic and preventive alternatives is crucial. In this context, medicinal plants play a fundamental role in the discovery of new drugs[3]. In this study, the antiurolithic activity of plants with ethnopharmacological history in the treatment of kidney stones was investigated, including *Plantago major*, *Costus spiralis*, *Piper umbellatum*, and *Solanum cernuum*. The decoction of *C. spiralis* and the infusion of *P. major*, *P. umbellatum*, and *S. cernuum* were obtained according to popular reports described in the literature, with yields ranging from 10.31% to 26.68%. The antiurolithic activity of the medicinal plants was evaluated using urine containing CaOx crystals at a concentration of 2 mg/mL[4], compared to negative and positive controls, sodium citrate. All tested samples exhibited statistically significant differences compared to the negative control group ($p < 0.001$). *P. umbellatum* (89.3%) and *C. spiralis* (88.7%) demonstrated the most promising results, displaying significant dissolution in the size of CaOx crystals, including dihydrate and monohydrate varieties. The species *S. cernuum* (53.8%), an endemic species, also showed antiurolithic potential. This study reports for the first time the antiurolithic potential of *P. umbellatum* and *S. cernuum*, emphasizing the importance of medicinal plants in the treatment of urolithiasis and the search for pharmacologically active substances.

Figura 1 - Graphical abstract



Acknowledgments

CAPES – Financing Code 001 (no. 88887.805159/2023-00), FAPEMIG (APQ-02353-17, APQ-00207-18, APQ-05218-23, APQ-00544-23, and BPD-00760-22), CNPq (316204/2021-8, 406837/2021-0, 408115/2023-8), and FINEP.

[1]Singh, P., et al. Nat. Rev. Nephrol., **2022**, 18(4), 224-240.
[2]Tan, R. Y. P., et al. Int. Urol. Nephrol., **2023**, pp. 1-9.
[3]Barros, M. E. et al. Urol. Res., **2003**, 30, 374.
[4]Salem, P. P.O. et al. J. of Ethnopharmacology, **2020**, 23.

Área: QPN

EXTRACTION, ISOLATION AND CHARACTERIZATION OF MYCOSPORINE-LIKE AMINO ACIDS FROM *NAGANISHIA FRIEDMANNI* WITH POTENTIAL USE IN SUNSCREENS

Renan S. Barbosa* **(PG)[1] Gabriel M. da Silva (PG)[4], Marcelo A. Vallim (PQ),[2]Lívia S. de Medeiros (PQ)[3] Renata C. Pascon (PQ)[2]**

renan.santini@unifesp.br;

[1]Programa de Pós-Graduação em Biologia Química, Universidade Federal de São Paulo - UNIFESP; [2]Departamento Ciências Biológicas, UNIFESP; [3] Departamento de Química- UNIFESP; [4] Programa de Pós-graduação Interunidades em Biotecnologia – USP-IPT-Butantan

Palavras Chave: *HPLC-MS, Mycosporine, Naganishia Friedmanni,, biomolecule.*

Highlights

Biotechnological approach of mycosporine and mycosporine-like amino acids. Use of “greener” biomolecules in sunscreens, an alternative to synthetic compounds.

Resumo/Abstract

Ultraviolet radiation causes several harmful effects on living organisms, especially on the human epidermis, where lesions can lead to skin cancer. The existing alternatives to avoid or delay these impacts on the skin are artificial synthetic sunscreens, which are made of petroleum derivatives, a non-renewable source, and in many occasions are toxic from long term use, moreover it can endanger marine organisms, such as coral, causing the natural phenomenon known as coral bleaching. However, natural sunscreens replace some of these synthetic compounds for more “greener” molecules, derivatives from plants, algae and in our case from fungi, specifically *Naganishia Friedmanni*, making this a more biotechnological approach and very important research as an alternative for the petroleum derivates. Among the differences between synthetic and natural sunscreens we can list the long time for the decomposition of the petroleum derivatives. Therefore, it is worth to focused research on natural molecules production, such as mycosporine and mycosporine-like amino acids (MAAs). Those biomolecules are capable of converting UV radiation into heat, among their many properties. The Microbial Interactions Laboratory at the Federal University of São Paulo it is exploring a yeast collection, looking for those that have the ability to perform the mycosporine biosynthesis. In this work, a *Naganishia Friedmann*i isolated from our yeast collection was analyzed. The production of mycosporine by this isolate was confirmed by our previous data. The mass spectrometry results showed us the specific peak and the fragmentation pattern of one MAA. But we have many new approaches to improve not only production but also separation of those biomolecules. For the production of mycosporines we were exploring different types of induction, extraction and isolation parameters. Different types of induction as UV irradiation, osmotic induction, can influence in more biotechonogical approach.. Therefore, our goal is to develop specific analytical methods, better induction systems of the mycosporine produced by *N. Friedmanni*, comprising its extraction and isolation to its chemical characterization using mainly using chromatographic techniques such as Liquid Chromatography High Performance coupled to Mass Spectrometry (HPLC-MS).

Agradecimentos/Acknowledgments

- FAPESP
- CAPES/CNPq
- LIMIC

Área: QPN
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Fatty acid compositions of two strains of *Lentinula edodes* (Shiitake) under different spawn formulations

Gabriel Fernando Fuzzo (IC)[1], Isabel Arjonas Fernandes Avila (PG)[2], Lucas da Silva Alves (PG)[2], Lincoln L. Romualdo (PQ)[1], Diego Cunha Zied (PQ)[2], Elaine Rosechrer Carbonero (PQ) [1]

gabrielfuzzo@ufcat.edu.br; gabrielfuzzo@hotmail.com

[1] Institute of Chemistry, UFCAT; [2] Faculty of Agricultural and Technological Sciences, Campus Dracena (FCAT/ UNESP—Dracena)

Palavras-Chave: *Mushrooms, Lentinula edodes, Shiitake, Fatty acids, FAME, GC-MS*

Highlights

This study analyzed fatty acid profiles of two *Lentinula edodes* strains under different spawn formulations to evaluate their nutritional values.

Resumo/Abstract

Evidence indicates that mushrooms have been utilized for culinary and medicinal purposes since the dawn of humanity across various civilizations globally. Although approximately 2189 species are recognized as safe food, only about 100 species have been produced and consumed worldwide, with shiitake (*Lentinula edodes*) being the second species most commercialized for this purpose. Given the diversity of strains and substrates used for the cultivation of these fungi, it is necessary to evaluate their constituents to validate them as a healthy food. The main objective of this research was to evaluate the influence of different spawn formulations on the fatty acid composition of two *Lentinula edodes* strains (LED 19/11 and LED 20/06). Fatty acids profile of the *L. edodes* samples were identified, and their ratios were determined following saponifying fats with 0.5 N methanolic potassium and refluxing with a solution of ammonium chloride and sulphuric acid in methanol (Hartman and Lago, 1973). The resulting fatty acid methyl ester (FAME) was analyzed by gas chromatography-mass spectrometry (GC-MS) using an Agilent model 3300 gas chromatograph linked to a Finnigan Ion-Trap, Model 810-R12 mass spectrometer. An HP5-MS capillary column (30 m x 0.25 mm i.d) was used for qualitative and quantitative analysis of FAME. The FAMEs were identified by their typical retention times and electron impact profiles, which were confirmed by comparison with the spectral database found on the LIPID MAPS® website. The results are expressed in the relative percentage of each fatty acid, calculated by internal normalization of the chromatographic peak area. According to the data obtained, the samples analyzed presented a similar chromatographic profile, containing at least twelve compounds, with unsaturated fatty acids (UFAs; 59.1 to 79.9%) being more prevalent than saturated (SFAs; 18.3 to 28.9%) ones. The polyunsaturated fatty acid methyl linoleate (18:2, $\Delta^{9,12}$) is the highest fatty acid concentration, varying from 58.6 to 79.9, followed by saturated palmitic acid (16:0; 14.4 to 24.4%). In general, the strain and/or spawn formulation did not qualitatively affect the composition of the fatty acids, which are rich in essential fatty acids, especially 18:2, and therefore should be contained in the diet.

References:

Hartman L, Lago RC. Rapid preparation of fatty acid methyl esters from lipids. *Lab Pract*., 22(6):475, 1973.
LIPID MAPS®. Disponível em: https://www.lipidmaps.org/

Agradecimentos/Acknowledgments

This study was supported by the Federal University of Catalão (UFCAT) and financed in part by the Fundação de Amparo à Pesquisa do Estado de Goiás (FAPEG). The authors acknowledge Prof. Dr. Diego from the UNESP, *Campus* Dracena for donated the mushroom samples.

Área: QPN

Fungi in Confrontation: Production of Metabolites in the Co-culture between Citrus Phytopathogens and its Endophytic Fungi.

[1*] José R. F. Maciel (PG), [1] Eder V. Araujo (PG),[1] Mayra S. Pinheiro (PG),[1] Evandro Silva (PQ), [1]Rodolfo D. L. Junior(PG),[1,2] Taícia P. Fill (PQ).

jrfmaciel7828@gmail.com*

[1]State University of Campinas, Institute of Chemistry, CEP, 13083-970 Campinas, SP, Brazil.
[2]University of São Paulo, Institute of Chemistry, CEP 13566-590, São Carlos, SP, Brazil.

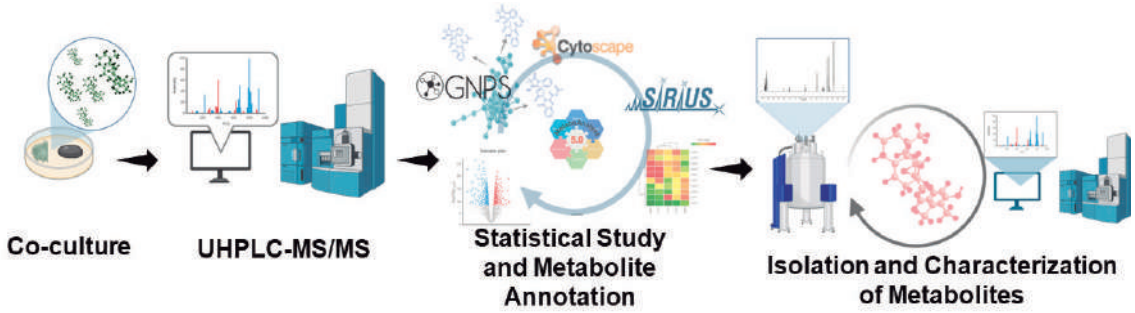
Keywords: Citriculture, Phytopathogen, Endophytic, Co-culture, Natural products, Metabolomics.

Highlights

This work aimed to study the co-culture between the endophytic fungus, *Colletotrichum* sp., and the citrus phytopathogens, *G. candidum* and *P. digitatum*.Inhibition rates of 67.8% and 73.4% were observed for *G. candidum* and *P. digitatum* respectively. Furthermore, macrolides were isolated from the co-culture between *Colletotrichum* sp.-*G. candidum* and structure characterized.

Abstract

Citriculture stands out as one of the most profitable and fundamental sectors in the global economy, with oranges being the most widely produced and consumed citrus fruit across the world. However, citrus phytopathogens are threatening the citrus sector, causing considerable economic losses due to the spread of diseases, including those related to the post-harvest period. Therefore, this study aimed to search for biocontrol strategies for diseases caused by citrus fungal phytopathogens. Endophytic fungi have been described as potential candidates for biocontrol, therefore in this study we isolated the endophytic community of healthy *Citrus sinensis* fruits in order to evaluate its potential against the two main problems in the post-harvest period, *Geotrichum candidum and Penicillium digitatum*. Metabolic evaluation by HPLC-MS/MS was carried out in the co-cultures between the endophytic fungus isolated from orange peel, *Colletotrichum* sp., and the two phytophatogens. The results obtained revealed the antagonistic activity of the endophytic fungus *Colletotrichum* sp. in relation to the phytopathogens during co-culture. Under cultivation ideal conditions, it was observed that *Geotrichum candidum* had a significant inhibition rate of 67.8% and for *P. digitatum* an inhibition rate of 73.4% was observed. UHPLC-MS/MS analyzes combined with the use of statistical tools such as MetaboAnalyst identified 12 differential ions in the coculture between *G. candidum* and *Colletotrichum* sp. The use of databases, including GNPS, and *in silico* tools, such as Sirius, resulted in the annotation of macrolides and sphingofungins during this interaction. Furthermore, through preparative HPLC, metabolites from the macrolide class were isolated from co-culture and structure characterized. A significant increase in the production of these metabolites was observed during the fungal interaction, compared to the monoculture of *Colletotrichum* sp. These results suggest that the metabolites produced by the endophyte are potentially involved as defense mechanisms against the citrus phytopathogen *Geotrichum candidum*. It is important to highlight that previous studies have not yet linked the production of macrolides and sphingofungins to *Colletotrichum* sp. and *G. candidum* during co-culture, making this research a fundamental basis for future investigations in the development of control strategies for citrus phytopathogens.



[1]COSTA, J.H., Wassano, C.I., Angolini, C.F.F. *et al.* Antifungal potential of secondary metabolites involved in the interaction between citrus pathogens. *Sci Rep* **9**, 18647 (2019).
[2] KNOWLES, S. L. et al. Fungal–fungal co-culture: a primer for generating chemical diversity. ***Nat. Prod. Rep.***, Greensboro, NC, US, v. 39, n. 8, p. 1557-1573, fev./2022.

Acknowledgments

CNPq, Capes and FAPESP

Área: QPN

Genome mining for Biosynthetic Gene Clusters of potential antimicrobial secondary metabolites from basidiomycetes fungi

Beatriz I. M. do Carmo (PG),[1*] Lhaís A. Caldas (PQ),[2] Patricia Sartorelli (PQ).[1]

beatriz.isabel@unifesp.br

[1]*Instituto de Ciências Ambientais, Químicas e Farmacêuticas, UNIFESP – Campus Diadema.*
[2]*Netherlands Institute of Ecology, NIOO-KNAW, Holanda.*

Keywords: *Basidiomycete Fungi, Biosynthetic Gene Clusters, Genome Mining, Antimicrobial Potential.*

Highlights

This work presents genome mining for biosynthetic gene clusters (BGC) of six basidiomycete fungi gifted for biosynthesis of antimicrobial secondary metabolites. Herein, it was observed that these basidiomycetes carried 717 BGCs in total, being most of them sesquiterpenes (TC), non-ribosomal peptides (NRPS-like), polyketides (PKSs) and hybrid clusters (PKS-NRPSs) synthases.

Abstract

The excessive and improper consumption of antibiotics have driven the evolution of antimicrobial resistance genes in bacteria. Consequently, the World Health Organization has promoted research aiming at prospecting new antibiotics against the “ESKAPE” multidrug-resistant bacteria using natural products. Basidiomycetes fungi are considered an important source of bioactive molecules, often effective against other fungi and/or bacteria [1]. In addition, secondary metabolites (SMs) are often biosynthesized by multi-enzyme pathways and proteins comprising one pathway tend to be encoded within a clustered set of genes, termed a biosynthetic gene cluster (BGC). Genome mining approach is responsible for identifying these candidate BGCs [2]. Moreover, fungi with a large BGC number per genome and high natural product variability are so-called “gifted” for SMs production and can encode much more SMs than was previously known from their expressed SMs [3]. In this study, we explored the biosynthetic potential for BGCs that encode for the production of potentially bioactive metabolites of gifted basidiomycete fungi, thus broadening the chances of identifying SMs with antimicrobial potential. For that, the genome sequence files of six potentially gifted basidiomycete fungi were retrieved from the Mycocosm repository: *Cyathus pallidus, Cyathus stercoreus, Dendrothele bispora, Favolaschia claudopus, Mycena latifolia, and Mycena capillaripes Frankland.* The BGCs of the basidiomycetes were predicted by FungiSMASH. These predictions were further analyzed with BGCLib, to annotate the BGCs according to their specific compound’s classes. Aiming to construct a phylogenetic tree to dereplicate metabolites, fungal biosynthetic sequences fully characterized were extracted from MiBIG repository. Afterward, the core sequences enzymes of interest were extracted from the genes predicted using BGClib [4]. IQ-Tree was used to construct the phylogeny analyses and iTOL to annotate the trees. According to the results obtained by the genome mining approach, it was possible to dereplicate 717 BGCs in total, being sesquitepene synthases as the most abundant BGCs (265), followed by NRPS-like (134), PKSs (43), and hybrid clusters (16). These preliminary results show that these fungi are a powerful source of SMs production, with a broad variety range of SMs classes, especially concerning the production of possible antimicrobial SMs, as non-ribosomal peptides and polyketides are known to be potentially active against different bacteria strains [5].

[1] Clericuzio, M.; et al., A Systematic Study of the Antibacterial Activity of Basidiomycota Crude Extracts. Antibiotics 2021, 10, 1424. https://doi.org/10.3390/antibiotics10111424
[2] Mosunova, O., et al., (2021). The biosynthesis of fungal secondary metabolites: From fundamentals to biotechnological applications. In Encyclopedia of Mycology (pp. 458–476). Elsevier. https://doi.org/10.1016/B978-0-12-809633-8.21072-8
[3] Richard H. Gifted microbes for genome mining and natural product discovery, Journal of Industrial Microbiology and Biotechnology, Volume 44, Issue 4-5, 1 May 2017, Pages 573–588, https://doi.org/10.1007/s10295-016-1815-x
[4] Blin et al., antiSMASH 7.0: new and improved predictions for detection, regulation, chemical structures and visualisation, Nucleic Acids Research, Volume 51, Issue W1, 5 July 2023, Pages W46–W50, https://doi.org/10.1093/nar/gkad344
[5] Dror, B. et la., State-of-the-art methodologies to identify antimicrobial secondary metabolites in soil bacterial communities-A review. Soil Biology And Biochemistry, [S.L.], v. 147, p. 107838, ago. 2020. Elsevier BV. http://dx.doi.org/10.1016/j.soilbio.2020.107838

Acknowledgments

CNPq Conselho Nacional de Desenvolvimento Científico e Tecnológico · CAPES · FAPESP Fundação de Amparo à Pesquisa do Estado de São Paulo · UNIFESP Universidade Federal de São Paulo · LaBiORG Laboratório de Química Bio-Orgânica Otto Richard Gottlieb

Área: QPN

Glycosides derivatites isolated from *Ouratea polygyna* Engl. leaves and *in silico* evaluation of it's Anti-SARS-COV-2 activity.

Aylla L. Haick* **(PG),[1] Mário G. de Carvalho (PQ),[1] Raimundo Braz Filho (PQ),[1] Carlos Maurício R. de Sant'anna (PQ)[1], Lisieux de S. Julião (PG)[2]**

ayllalopeshaick@gmail.com; mariogdecarvalho@gmail.com;

[1 2] Departamento de Química Orgânica, UFRRJ

Palavras Chave: *Ouratea polygyna Engl; Glycosides; 3CLPRO; SARS-COV-2; Molecular docking*

Highlights

Isolation and structural elucidation of a possibly new isoflavone glycoside and two known phenolic glycosides;

Evaluation of Anti-SARS-COV-2 activity using molecular docking of isolated compounds and it's acetilated derivatites

Abstract

Ouratea polygyna Engl. leaves were collected in Natural Park of Vale do Rio Doce – ES (SISGEN:A00B531). The leaves were cleaned, dried and powdered. The crude extract was prepared by maceration with methanol at room temperature untill saturation of the phase and partitioned with organic solvents – hexane (OPFH), dichloromethane (OPFD), ethyl acetate (OPFAC) and buthanol (OPFB). OPFAC was submitted to chromatographic procedures (Figure 1), leading to isolation of 1-*O*-benzoyl-β-D-glucopiranoside **(1)**, Lanceoloside A **(2)** and 5-hydroxy-6,7,4',5'-tetramethoxyisoflavone-3'-*O*-β-D-glucopiranoside **(3)**. The structures were elucidated by unidimensional and bidimensional ^{1}H and ^{13}C NMR, including NOESY experiment. Untill now, we did not find any registers of **(3)** in the literature.

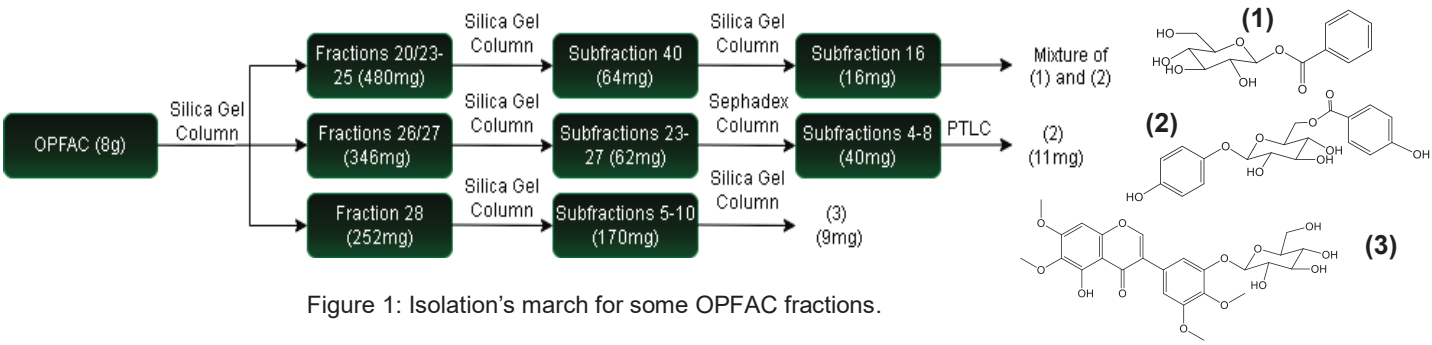


Figure 1: Isolation's march for some OPFAC fractions.

The isolated substances and it's acetilated derivatites were evaluated for inhibition of 3CL^{PRO}, the main protease of SARS-COV-2 virus, by molecular docking, using GOLD software. The crystalographic structure was obtained from Protein Data Bank (PDBid: 7END) with resolution of 1,99Å[1]. Redocking studies were performed and allowed to define GoldScore as fitness function. Between the analysed compounds, acetilated derivatite of **(1)** exhibited the highest Score (67,35) and interactions with HIS41 and CYS145 residues, a catalytic dyad responsible for the first step in the enzymatic mechanism. The predicted pose shows a possible interference in the dyad interaction by the 2-acetil group, disturbing the enzyme activity. We highlight that **(2)** already shown in vitro activity against 3CL^{PRO} [2] and this results can indicate new inhibitors candidates.

[1] HOU, N. *et al*. Development of Highly Potent Noncovalent Inhibitors of SARS-CoV-2 3CLpro. **ACS Cent. Sci**., 2023

[2] DE CARVALHO, M. G. *et al*. Biflavonoids and other Phenolics Compounds from Ouratea Polygyna and Their Activities Against 3CLpro of SARS-COV-2. in: **15th world congress on polyphenols applications**, 2022.

Acknowledgments

The authors acknowledge CAPES, CNPQ, FAPERJ and Vale do Rio Doce - ES

Área: QPN

Influence of bagasse sugarcane biochar on the metabolic profile of corn leaves

Marina C. Patrocínio (IC),[1] Erica P. Gonçalves (IC),[1] Bruna C. Pinto (PG),[2] Osania E. Ferreira (PG),[2] Mariana G. de Aguilar (PQ),[3] Lúcia P.S. Pimenta (PQ),[3*] Jaqueline C. L. Carvalho (PQ), [1] Alan R.T. Machado (PQ).[1]

lpimenta@qui.ufmg.br; alan.machado@uemg.br

[1]Departamento de Ciências Exatas, UEMG; [2]Programa de Pós-graduação em Ciências Ambientais, UEMG; [3]Departamento de Química, UFMG.

Keywords: Metabolomics, NMR, Carbon, Soil.

Highlights

- Soil conditioning with bagasse sugarcane biochar influences the metabolite production in corn leaves.
- The application of high doses (5 and 10% w/w) of bagasse sugarcane biochar stimulated the production of aconitic, chlorogenic, and formic acids in corn leaves.
- Soil conditioning with bagasse sugarcane biochar promoted greater efficiency in cellular respiration and energy production.

Abstract

The use of biochar is an innovative approach in agriculture to enhance crop productivity and soil quality, as well as to promote carbon sequestration. However, despite these benefits, there remains a gap in understanding the effects of biochar on the metabolic profile of plants. To address this issue, a greenhouse experiment was conducted to evaluate the response of corn seedlings to the application of biochar derived from sugarcane bagasse. Five treatments corresponding to doses of 0, 1, 3, 5, and 10% w/w of biochar applied to the soil were evaluated. Thirty days after sowing, the dry biomass of the leaves was extracted using a mixture of methanol-d_4 and a buffer solution (KH_2PO_4) in D_2O (pH 6.0), containing 0.01% (w/v) TSP-d_4. The extracts were then analyzed by ^{1}H NMR. The spectral data were grouped into 0.04 ppm windows (binning) and transformed into a data matrix using Chenomx 10.0 software. Subsequently, simple variance analysis (One-Way ANOVA) and Hierarchical Clustering Analysis (HCA) combined with a heatmap were performed on the MetaboAnalyst 6.0 platform. The results showed 55 bins with statistical differences between the treatments. Analysis of these bins allowed the identification of formic acid, acetic acid, 4-aminobutyric acid, chlorogenic acid, alanine, sucrose, isoleucine, valine, asparagine, glucose, and aconitic acid. The dendrogram combined with the heatmap revealed that soil conditioning with biochar resulted in a positive effect on the production of aconitic, chlorogenic, and formic acids and a negative effect on the other compounds identified. The increase in levels of these compounds indicates greater efficiency in cellular respiration and energy production in corn plants grown in soil conditioned with biochar.

Acknowledgments

The authors thank Fundação de Amparo à Pesquisa do Estado de Minas Gerais (FAPEMIG [grant number APQ-03110-22]) and Universidade do Estado de Minas Gerais (UEMG [Productivity Researcher of the UEMG – PQ/UEMG]) for their financial support and fellowships. The authors acknowledge the BioAnalytical Facility NEPS-DQ (https://ne.qui.ufmg.br) at the Universidade Federal de Minas Gerais, Belo Horizonte, MG, for the support with NMR analyses of this work.

Área: QPN

Investigation of *Baccharis trimera* for cosmetic application

Wéldion G. M. Júnior (PG),[1] Adriana P. M. G. Macedo (PQ),[1] Geisa F. Makishi (TC),[2] Romário P. da Costa (PG),[1] Quezia B. Cass (PQ),[3] Richele P. Severino (PQ),[1] Vanessa G. P. Severino (PQ),[4] Lorena R. F. de Sousa (PQ)[1*]

weldiongmjr@gmail.com; *lorennarf@ufcat.edu.br

[1]Instituto de Química, UFCAT; [2]Empresa parceira Livealoe; [3]Departamento de Química, UFSCar; [4]Departamento de Química, UFG.

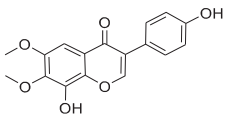
Palavras Chave: *medicinal plants*, *Carqueja*, *GNPS*, *Flavonoid*, *enzymes*.

Highlights

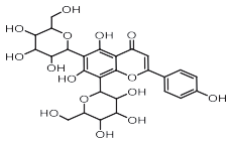
Carqueja is starting to be investigated in this work against elastase for cosmetic application. By using LC-HRMS and molecular networking compounds have been dereplicated from ethanolic extract from the leaves.

Resumo/Abstract

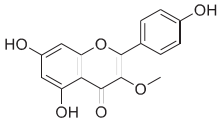
Natural products (NPs) are highly used as active ingredients in cosmetic formulations. Among the targets used to screen NPs, the search for elastase inhibitors can be a strategy to afford new anti-aging agents.[1] The *Baccharis trimera* (Less)DC. (Asteraceae), popular known as carqueja, has been reported with various biological activities such as antioxidant, anti-inflammatory and many others.[2] Therefore, in the search for Natural Products for phytocosmetic application this species was selected for chemical and biological study against elastase. The enzyme activity was measured by absorbance of the product after substrate cleavage, *N*-succinyl-Ala-Ala-Ala-*p*-nitroanilide (λ=410 nm).[3] The crude ethanolic extract from leaves of carqueja showed elastase inhibition of 38% and now we intend to fractionate the extract to investigate if it will increase activity. The crude extract was dereplicated using hyphenated LC-HRMS technique and for mass spectra analysis were used molecular networking (GNPS), DataAnalysis and Compound Crawler. In the GNPS data treatment was generated 452 nodes, 534 edges and 38 clusters, where 28 compounds were annotated, which five flavonoids were classified as gold. Comparing ion fragments with literature data[4-7] allowed us to identify the presence of this flavonoids in the extract, dihydroxy-dimethoxyisoflavone (*m/z* 315.0871) (**1**), apigenin-di-C-glucoside (*m/z* 595.1656) (**2**), isokaempferide (*m/z* 301.0707) (**3**), eupatorin (*m/z* 345.0975) (**4**) and isoschaftoside (*m/z* 565.1552) (**5**). Flavonoids are well known for their various biological properties.[8] As future perspectives, bioguided fractionation will be performed in order to improve elastase inhibitory potential and to isolate active compounds.



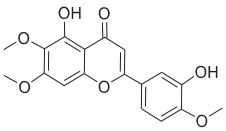
1



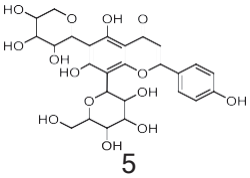
2



3



4



5

[1]Videira, I.F.D.S.; et al. *An. Bras. Dermatol*. 88: 76-83, 2013.
[2]Bobek, V.B.; et al. *Brazilian Journal of Pharmaceutical Sciences*. 58: e19118, 2022.
[3]Tiedermann, V. *Elastase and α-chymotrypsin inhibition studies. Uppsala University*.1-16, 2018.
[4]Lan, L.; et al. *Phytochemistry Letters*. 13: 156-159, 2015.
[5]Beelders, T.; et al. *Molecules.* 19(8): 11760-11790, 2014.[6]Tešević, V.; et al. *Journal of the Serbian Chemical Society*. 79(11): 1355-1362, 2014.[7]Colombo, R.; et al. *Journal of the Brazilian Chemical Society*. 19: 483-490, 2008. [8]Wang Z.L.; et al. *Pharm Biol*. 56: 465-484, 2018.

Agradecimentos/Acknowledgments

This research project received financial support from CAPES and FINEP (Reference: 0558/21) Brazil.

Área: QPN

Isolated Pentacyclic Triterpenoids and a Flavone from *Eremanthus erythropappus* DC. MacLeish (Asteraceae)

Leonardo Luiz Oliveira de Mello (PG),[1,2]* Ademar Alves da Silva Filho (PQ),[2] Giovanni Wilson Amarante (PQ),[1,2]

leonardo_Luiz_@outlook.com; leonardo_Luiz_@outlook.com

[1]Departamento de Química, Instituto de Ciências Exatas (ICE), UFJF; [2]Departamento de Ciências Farmacêuticas, Faculdade de Farmácia, UFJF

Keywords: *Triterpenoids, Flavones, Betulinic Acid, Friedelin, Acacetin, Eremanthus erythropappus*

Highlights

Betulinic acid and acacetin were newly isolated from *Eremanthus erythropappus*, in addition to friedelin, previously isolated for this species. Results lead to improved candeia phytochemical knowledge.

Resumo/Abstract

Eremanthus erythropappus (Asteraceae), known as candeia-da-serra, is commonly used in Brazilian folk medicine due to its activities, including antibacterial, antinociceptive and antiparasitic properties, which are often attributed to the presence of key metabolites, primarily terpenoids and flavonoids[1]. Apart from the α-bisabolol-rich essential oil derived from this plant, known for its various properties, including potent activity against *Staphylococcus aureus*[2], further exploration of the chemical composition of the extract is crucial for gaining a comprehensive understanding of this plant matrix as a valuable source of bioactive compounds for treatment of body malfunctions. Therefore, this work aimed to isolate and identify metabolites through fractionation of *E. erythropappus* aerial parts extract. The candeia extract was obtained by briefly immersing its aerial parts in a solution of dichloromethane/methanol (1:1, v/v), with subsequent concentration of the solvent under reduced pressure. The crude extract was fractionated through vacuum liquid chromatography (VLC), a low-pressure chromatographic technique, where the separation process involved a gradient of hexane/ethyl acetate. Resulting fractions were further purified, leading to isolation and identification of compounds after NMR analysis. Betulinic acid was isolated for the first time from this species among the isolated metabolites. After recrystallization in methanol/ethanol (1:1 v/v), it formed white needle crystals, and characteristic chemical shifts of this triterpenoid were identified. These included a low-field carboxyl hydrogen (12.00 ppm), exomethylenic protons of the allyl group (4.68 and 4.56 ppm), and a less shielded sp^3 carbon (54.8 ppm) bonded to the electron-withdrawing carboxyl group in the ^{1}H and ^{13}C NMR spectra respectively. In addition, the hydrogenated carbon pattern, consisting of six methyls, six methines, and eleven methylene groups, was assigned in the DEPT-135 NMR. Moreover, the fractionation of the extract resulted in yellowish-green crystals as one of the fractions, later identified as acacetin. This flavone, not previously reported for *E. erythropappus*, was confirmed by a characteristic substitution pattern in NMR spectra. This pattern included a low-field hydroxyl proton (12.92 ppm), deshielded due to hydrogen bonding with the C ring keto group (182.2 ppm), an α-carbonyl proton (6.84 ppm), and two ortho coupling constants (10 Hz) related to a disubstituted pattern due to a methoxy group (56.0 ppm) at C-4' in the B ring. Friedelin, previously identified in *E. erythropappus*[3], was also isolated as white crystals after ethyl acetate recrystallization. Structural confirmation of this triterpenoid was achieved through ^{1}H,^{13}C, DEPT-90 and DEPT 135 NMR analysis, further supported by literature comparison.

[1]Keles, L.C., Melo, N.I., Aguiar, G.P., Wakabayashi, K.A.L., Carvalho, C.E., Cunha, W.R., Crotti, E.M., **Quimica Nova**, 2260, 10, 2010

[2]Nascimento, A.M.A., Brandão, M.G.L., Oliveira, G.B., Fortes, I.C.P., Chartone-Souza, E. **Antonie van Leeuwenhoek** 92, 100, 2007

[3]Jorge, N.C., Guedes, L.M., Aguilera, N., Becerra, J., Isaias, R.M.S., **Biochemical Systematics and Ecology**, 104379, 100, 2022

Agradecimentos/Acknowledgments

We express our gratitude to FAPEMIG, CAPES (Finance Code 001), CNPQ, UFJF, and Rede Mineira de Química for their valuable financial support.

Área: QPN

ISOLATION AND CHARACTERIZATION OF A PHLOROGLUCINOL FROM THE LEAVES OF *Callistemon viminalis* (MYRTACEAE)

Ana Clara L.N. Silva (PG),[1*] Marisi G. Soares (PQ),[2] Gabriela V. Araujo Flores (PG),[4] Luiz Felipe D. Passero (PQ),[3] Patrícia Sartorelli (PQ).[1]

clara.nunes17@unifesp.br

[1]Programa de Pós-Graduação em Biologia Química, Instituto de Ciências Ambientais Químicas e Farmacêuticas, Universidade Federal de São Paulo – UNIFESP; [2] Institute of Chemistry, Federal University of Alfenas, Minas Gerais; [3] Paulista State University, São Vicente, SP; [4] Universidade de São Paulo – USP, SP.

Keywords: *Callistemon viminalis*, phloroglucinol, secondary metabolites, antileishmanial activity.

Highlights

From the leaves of *Callistemon viminalis* it was possible to isolate and characterize a compound belonging to the phloroglucinol class and test its activity on the amastigote form of *L. amazonensis*.

Abstract

Callistemon viminalis (CV), commonly known as "bottle brush" due to the shape of its flowers, belongs to the Myrtaceae family, and its use in traditional medicine for treating colds, gastroenteritis, diarrhea, and skin infections is documented in the literature. Phytochemical research on CV extracts has revealed its richness in various classes of triterpenoids, flavonoids, saponins, steroids, alkaloids, tannins, carbohydrates, and amino acids[1,2]. Notably, this plant stands out due to its chemical composition, which includes compounds from the phloroglucinols class. These secondary metabolites exhibit remarkable structural variation, allowing them to possess diverse biological activities[3,4]. The objective of this study was to isolate compounds present in CV leaves (SisGen-A20C5C) and evaluate their anti-leishmanial activity. Following the preparation of the methanolic extract from the leaves, partitioning was performed, followed by a biomonitoring test to assess the biological activity of the partitions (Hexane, Dichloromethane, and Ethyl Acetate) against the promastigote form of *Leishmania amazonensis*. The dichloromethane phase was selected due to its EC_{50} value of 35.7 µg/mL compared to the standard drug Miltefosine with 8.26 µg/mL, showing promise as a mixed sample. This partition was further fractionated, resulting in 17 fractions, four of which showed the best EC_{50} values for the promastigote form of *L. amazonensis* (CVFD-2, 3, 4 and 5). After biomonitoring with the fractions, the four best were analyzed by HPLC-EMAR-IES(+)-EM/EM, and based on the UV chromatogram and BPC, the CVFD-5 fraction was selected for isolation in HPLC-DAD. It was possible to isolate compound 1, which was subsequently characterized by one- and two-dimensional NMR, as well as HRMS. Based on the literature and the data acquired, it was possible to characterize this substance, which was identified as belonging to the class of phloroglucinols. As far as biological testing is concerned, the compound was subjected to a semi-quantitative evaluation of its anti-amastigote potential, where it proved to be not very active.

References

[1] WU, J. W., LI, B. L., TANG, C., et al. "Callistemonols A and B, Potent Antimicrobial Acylphloroglucinol Derivatives with Unusual Carbon Skeletons from *Callistemon viminalis*", Journal of Natural Products, v. 82, n. 7, p. 1917–1922, 2019. DOI: 10.1021/acs.jnatprod.9b00064.

[2] ABDELMALEK, E. M., RAMADAN, M. A., DARWISH, F. M., et al. "Callistemon genus- a review on phytochemistry and biological activities", Medicinal Chemistry Research, v. 30, n. 5, p. 1031–1055, 2021. DOI: 10.1007/s00044-021-02703-y. Disponível em: http://dx.doi.org/10.1007/s00044-021-02703-y.

[3] CELAJ, O., et al. Phloroglucinols from Myrtaceae: attractive targets for structural characterization, biological properties and synthetic procedures. Phytochem Rev 20, 259–299, 2021. https://doi-org.ez69.periodicos.capes.gov.br/10.1007/s11101-020 -09697-2

[4] PHANG, Y. L. et al. Recent advances in the synthesis of natural products containing the phloroglucinol motif. Natural Product Reports, v. 39, n. 9, p. 1766-1802, 2022.

Acknowledgments

FAPESP, CAPES and CNPq.

Área: QPN

Isolation and characterization of two phenolic substances from *Eleutherine bulbosa* (Mill.) Urb. (Iridaceae)

Igor Ramón de Sousa Graça (PG),[1]* Matheus Vinicius Natividade Belém (PG),[1] Weider Henrique Pinheiro Paz (PQ),[2] Felipe Moura Araújo da Silva (PQ),[3] Thalisson Amorim de Souza (PG),[4] Josean Fechine Tavares (PQ),[4] Hector Henrique Ferreira Koolen (PG),[2] Waldireny Rocha Gomes (PQ) [5].
ramonigor555@gmail.com

[1]Departamento de Química, (UFAM), Manaus-AM; [2]Universidade do Estado do Amazonas, (UEA), Manaus-AM; [3]Central Analítica, (CA/UFAM), Manaus-AM; [4]Laboratório Multiusuário de Caracterização e Análises, (UFPB), João Pessoa-PB; [5]Faculdade de Ciências Farmacêutica, (UFAM), Manaus-AM.

Palavras Chave: *Marupazinho, Marupari, Chemical profile, NMR, Anthraquinones, Naphthalenes derivatives.*

Highlights

1. Two phenolic compounds were isolated from the bulb of *Eleutherine bulbosa* (Mill.) Urb. **2.** They were identified as 4,8-dihydroxy-3-methoxy-1-methylanthraquinone-2-carboxylic acid methyl ester and eleutherol. **3.** The substances are described in the literature with antimicrobial activity.

Abstract

Eleutherine bulbosa (Mill.) Urb. is a herbaceous plant belonging to the Iridaceae family, popularly known as 'marupari' and 'marupazinho'(1). It is a native species in tropical countries in South America, also present in Africa and Asia. In Brazil, it is distributed in the Amazon, Cerrado, Atlantic Forest, Pantanal and Caatinga(2). In its composition, several subclasses of phenolic substances have already been reported, highlighting the isolation and identification of naphthoquinones, naphthalenes derivatives and anthraquinones in *E. bulbosa* and their synonyms(3). This finding motivated us to continue isolating substances of this species. In this context, the objective of this study was to investigate the chemical composition of the bulb using classic and modern phytochemical approaches. The dichloromethane and ethanolic extracts were obtained by maceration at room temperature, after drying and calculating the yields, they were subjected to chemical profile analysis and the dichloromethane extract (24.0 g) was subjected to analysis by Column Chromatography (CC), Thin Layer Chromatography (TLC) and Preparative Thin Layer Chromatography (PTLC). The structural elucidation of the isolated substances was carried out using the Nuclear Magnetic Resonance spectroscopy technique (^{1}H and ^{13}C NMR - 1D/2D) and Mass Spectrometry (MS). Two phenolic substances were isolated (figure 1), 4,8-dihydroxy-3-methoxy-1-methylanthraquinone-2-carboxylic acid methyl ester (**1**) and eleutherol (**2**), both already reported in the literature with antimicrobial activity(3,4). The results obtained are relevant to the chemotaxonomy of the genus *Eleutherine*, and in particular for the species under study.

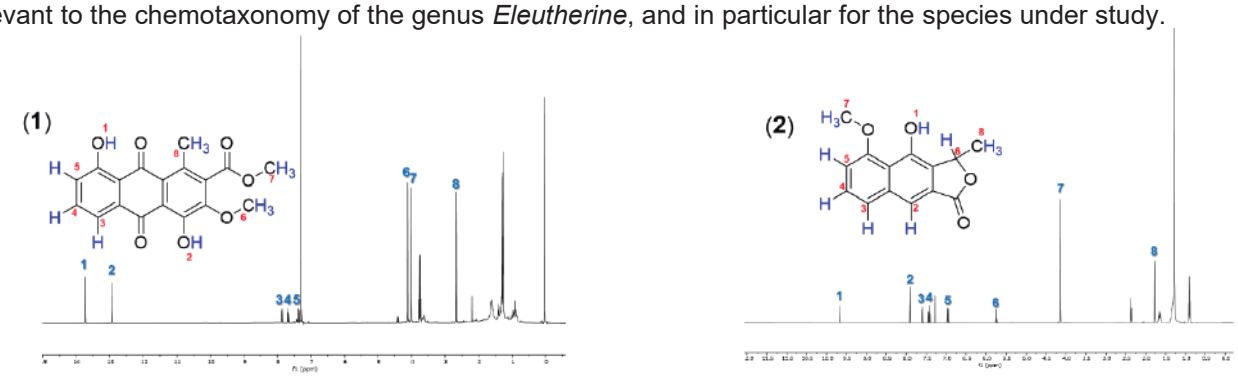


Figure 1: Isolated and identified substances from the bulb *Eleutherine bulbosa* (Mill.) Urb. and with their NMR spectra.

References

[1]LORENZI, H.; MATOS, F. **Plantas medicinais no Brasil: Nativas e exóticas**. 2 ed. SP: Instituto Plantarum de Estudos da Flora Ltda, 2008, p. 300-301. [2]EGGERS, L. *Eleutherine in* **Flora e Funga do Brasil.** Jardim Botânico do RJ. [3]MAHABUSARAKAM, W. et al. Naphthoquinones, anthraquinones and naphthalene derivatives from the bulbs of *Eleutherine americana*. **Planta medica**, p. 345-349, 2009. [4]CAMPOS, A. et al. Antifungal activity of pyranonaphthoquinones obtained from *Cipura paludosa* bulbs. **Natural Product Communications**, v. 10, n. 9, p. 1934578X1501000926, 2015.

Acknowledgments

The authors thank CAPES, CNPq, FAPEAM, FINEP for the financial support. As well as to UFAM, on behalf of the Analytical Center, for the NMR and Mass analyses, and to UEA, on behalf of the Postgraduate Program in Biotechnology and Natural Resources of the Amazon (MBT), for the physical support to carry out this study.

Isolation of a novel lathyrane-type diterpene from the roots of *Jatropha mollissima* (Pohl.) Baill.

Luiz Henrique de Amorim Pereira (PG)[1]*, Thalisson Amorim de Souza (PG)[1], Emille Wannick Reinaldo da Silva (PG)[1], Natanael Teles Ramos de Lima[1], Gabriela Ribeiro de Souza[1], Yuri Mangueira do Nascimento[4], Gilmário Moreira Lima[4]; Maria de Fátima Agra (PQ)[2], Raimundo Braz-Filho (PQ)[3], Marcelo Sobral da Silva (PQ)[1,5] e Josean Fechine Tavares (PQ)[1,5]

luizhenriqueap@ltf.ufpb.br; josean@ltf.ufpb.br

[1] Programa de Pós-Graduação em Produtos Naturais e Sintéticos Bioativos, UFPB; [2]Departamento de Biotecnologia, UFPB; [3] Departamento de Química, UFRRJ; [4] Laboratório Multiusuário de Caracterização e Análises, UFPB; [5] Departamento de Ciências Farmacêuticas, UFPB.

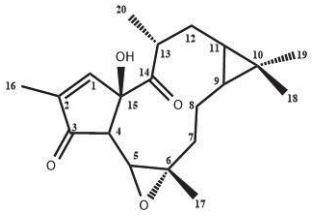
Keywords: Phytochemitry; Euphorbiaceae; Pinhão-Bravo; Lathyrane-type diterpene

Highlights

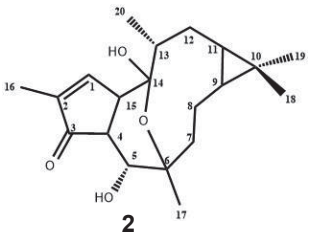
The phytochemical study of the species *Jatropha mollissima* (Pohl.) Baill. (Euphorbiaceae) led to the isolation of two compounds belonging to the class of lathyrane-type diterpenes, with one of them being a novel compound not previously reported in the literature..

Resumo/Abstract

The plant *Jatropha mollissima* Pohl. (Baill.) is a vegetal species endemic to the Caatinga biome, belonging to the Euphorbiaceae family, and is commonly known as "pinhão-bravo" or "pinhão-de-purga." In tradicional medicine, this species is utilized for various medicinal purposes due to its antiophidian, anti-inflammatory, anthelmintic, and antimicrobial activities. However, current literature lacks comprehensive studies exploring the phytochemical investigation and pharmacological potential of this plant. Therefore, this study aims to isolate and identify secondary metabolites present in the roots of *J. mollissima*.For the analyses, the hexane extract of the root powder (EHJM-R) was obtained by maceration for seven days, which was then defatted and subsequently fractionated by column chromatography using silica gel 60 (70 – 230 mesh) as the stationary phase and a mobile phase composed of hexane, ethyl acetate, and methanol, either in pure form or as binary mixtures. Thirty-seven fractions were obtained from the fractionation, which were monitored by thin-layer chromatography (TLC) followed by high-performance liquid chromatography with a diode array detector (HPLC-DAD) on an analytical scale (C-18 silica as the stationary phase and acetonitrile/water as the mobile phase).Fraction 23 (442mg) was chosen for compound isolation using preparative scale HPLC-DAD, leading to the isolation of two compounds (1 and 2). For structural determination, these compounds underwent high-resolution mass spectrometry and nuclear magnetic resonance techniques (uni- and bidimensional), in conjunction with comparisons to existing literature. Both isolated compounds belonged to the class of diterpenes with lathyrane-type skeletons. Compound 1 (Jatrogrossidion) had been previously reported in the literature, while Compound 2 was identified as a novel diterpene. Therefore, this study contributes to the phytochemical knowledge of *Jatropha mollissima*, emphasizing the remarkable chemical diversity of species present in the Brazilian semi-arid region.



1



2

References:

BRUM, R. L. *et al*. Jatrowediol, a lathyrane diterpene from *Jatropha weddelliana*. **Journal Of The BrazilianChemical Society**, v. 12, n. 2, p. 259-262, abr. 2001.

CASTELO, R.M. *et al*. Determinação de Fénois e Flavonoides Totais dos Galhos de *Jatropha mollissima* (Pohl) Baill. (pinhão-bravo). **Brazilian Journal Of Development**, [S.L.], v. 6, n. 7, p. 52147-52154, 2020. CAVALCANTE, N.B.; SANTOS, A.D.C.; ALMEIDA, J.R.G.S. The genus Jatropha (Euphorbiaceae): a review on secondary chemical metabolites and biological aspects. **Chemico-Biological Interactions**, v. 318, p.108976, fev. 2020.

SCHMEDA-HIRSCHMANN, G.; TSICHRITZIS, F.; JAKUPOVIC, J. Diterpenes and a lignan from *Jatropha grossidentata*. **Phytochemistry**, v. 31, n. 5, p. 1731-1735, maio 1992.

Agradecimentos/Acknowledgments

CAPES PgPNSB LMCA Finep

Área: QPN

Isolation of compounds from underexploited parts of pequi for possible industrial applications.

Carlos E. T. Rosa (IC)[1], Jullia D. Silva (IC)[1], Joyce L. Vieira (PG)[1], Elaine R. Carbonero (PQ)[1], Lorena R. F. de Sousa (PQ)[1], Richele P. Severino (PQ)[1]*.

carlosrosa@discente.ufcat.edu.br; richeleps@ufcat.edu.br

[1]*Laboratório de Bioquímica e Química Orgânica (LaBiOrg), Instituto de Química, Universidade Federal de Catalão, Avenida Dr. Lamartine Pinto de Avelar, 1120, Vila Chaud, Catalão/GO, 75704-020, Brasil.*

Palavras Chave: *Caryocar brasiliense, Pequi, Extractions, Pectin.*

Highlights

The study of *Caryocar brasiliens*e fruit ("Pequi") led to the isolation of pectin compounds from your external mesocarps and the identification of major fatty acids, aiming at industrial applications.

Abstract

Pequi (*Caryocar brasiliense - Caryocaraceae*), a characteristic fruit of the Brazilian cerrado, has applications in the food, cosmetic and pharmaceutical industries, because it has nutritional and medicinal properties (ALMEIDA & SILVA, 1994). An integrative bibliographic review (Scifinder, PubMed, SCIELO, and Web of Science) shows more than 200 compounds have already been described for this species, including flavonoids, carotenoids, fatty acids, saponins and terpenoids, in addition to various biological activities, such as antioxidants, anti-inflammatory, cholesterol reduction, among others. In this view, the research aimed to study the underexploited parts of the pequi as external mesocarps. The ethanolic extractions of the peel (EC) and unhealthy pulp (EP) were carried out three times, for 72 hours each. The crude ethanolic extracts were solubilized in methanol (7:3 - methanol/extract), and fractionation was performed by a liquid-liquid partition with hexane (PH) and ethyl acetate (PA). All extracts and partition fractions were analyzed by gas chromatography-mass spectrometry (GC-MS). The main compound in EC was palmitic acid methyl ester (69.1%), while in the EP was caproic acid (73.0%). The fraction PH-EP was shown to be composed mainly of 4-hydroxy-4-methyl 2-pentanone, while in the PA-EP was 2-methyl 2-cyclopenten-1-one. Aqueous pulp extraction was also carried out to obtain the fixed oil through maceration and heating (90 °C), followed by filtration and centrifugation (7000 rpm, 10 min, 28 °C). The supernatant (fixed oil) was subjected to derivatization using methanolic potassium (0.5 M) and analyzed by GC-MS. The fixed oil had a composition of esterified fatty acids as methyl ester: hexadecanoic acid (palmitic), 9,12-octadecadienoic acid (linoleic), and octadecanoic acid (stearic). The fruit peel was subjected to hot aqueous extraction (4 hours; 96 °C) three times, followed by ethanolic precipitation, centrifugation (4000 rpm, 10 min, 20 °C), dialysis (12-14 kDa), and freeze-drying. The polymer obtained (4.9%) was analyzed by GC-MS after derivatization (hydrolysis, reduction with $NaBH_4$ and acetylation) and Carbon Nuclear Magnetic Resonance (^{13}C NMR), being characterized as pectin, a heteropolysaccharide belonging to the soluble fiber family. Spectroscopic data in comparison with the literature (PROVIN, 2012) allowed determining its monosaccharide constitution as being predominantly galacturonic acid (α-D-GalAp), galactose (α-D-Gal), and arabinose (α-L-Ara). The isolated pectin shows an IC_{50} of ± 0.34 μM in antioxidant assay by DPPH. This set of results demonstrates that pequi can be a potential source for possible applications in the food, pharmaceutical, and cosmetic industries.

References:
ALMEIDA & SILVA. Pequi e Buriti - Importância alimentar para a população dos Cerrados. EMBRAPA. 1994.
PROVIN, L. Extração, caracterização química e propriedades reológicas de pectina da casca de *Caryocar brasiliense* Cambess (Pequi). Universidade Federal do Paraná. 2012.

Acknowledgments

This study was financed by the Fundação de Amparo à Pesquisa do Estado de Goiás (FAPEG) and the Federal University of Catalão (UFCAT) for the scholarship.

AREA: QPN

Isolation of oleanolic acid from *Galianthe matogrossiana* with potential activity against *Trypanosoma cruzi* amastigotes.

Mariele R.S. Gonçalves (PG),[1*] Mariana de C.C. Pinto (IC),[1] Mário G. de Carvalho (PQ),[1] Marco Edilson F. de Lima (PQ),[1] Afonso S. M.M Velez (PG),[1] Débora Decoté-Ricardo (PQ),[2] Raimundo Braz Filho (PQ).[1,3]
mariele.rondon@gmail.com

[1] Institute of Chemistry, Federal Rural University of Rio de Janeiro (UFRRJ), Seropédica, RJ, Brazil; [2] Veterinary Institute, Federal Rural University of Rio de Janeiro (UFRRJ), Seropédica, RJ, Brazi ;[3] LCQUI-CCT- North Fluminense State University Darcy Ribeiro (UENF), 28013-600 Campos dos Goytacazes-RJ – Brazil.

Keywords: *3-O-acetyl-oleanolic*, *Chagas Disease, Galianthe matogrossiana, Special metabolites, Cytotoxicity*

Highlights

Isolation of 3-*O*-acetyl-oleanolic acid from *Galianthe matogrossiana*: a natural product with promising antiparasitic activity against the amastigote forms of *T. cruzi* (Tulahuen C2C4-LacZ strain) with an IC_{50} of 11.06 µM.

Abstract

The class of pentacyclic triterpenes, notably oleanolic acid (OA) and its isomer, stands out as a subclass of terpenes abundantly biosynthesized in the plant kingdom, characterized by their diversity of biologically active molecules.[1] OA is frequently found in plants used in traditional medicine and has been the subject of extensive scientific studies, revealing a wide range of therapeutic activities, including antidiabetic, antioxidant, antiviral, hepatoprotective, anti-inflammatory, antimicrobial, antiproliferative, and anticancer properties.[2] The substitution of the hydroxyl group in AO to an acetyl lipophilic group (AOA) modified the physical and biological properties of the original compound, enhancing its action against *P. falciparum* in the derivative AOA compared to OA (IC_{50} AOA= 4.3 µg/ml, IC_{50} OA= 27.4 µg/ml), suggesting potent antimalarial activity.[3] In this study, we describe an ongoing unpublished study on the endemic species of Brazil, *Galianthe matogrossiana* (*GM*), as a promising natural source for obtaining AOA. A voucher specimen of the plant is deposited in the CGMS herbarium of the Federal University of Mato Grosso do Sul, under registration number 79574. The aerial parts of *GM* (2.72 kg) were processed and subjected to various extraction and purification steps, resulting in the isolation of a white crystalline needle-like precipitate (312.5 mg). The resulting fractions were analyzed by ^{1}H and ^{13}C nuclear magnetic resonance, involving comparison with literature data, and identified as 3-*O*-acetyl-oleanolic acid (Figure 1).[3] The tested compound showed promising antiparasitic activity against amastigotes of *T. cruzi* (Tulahuen C2C4-LacZ strain). AOA inhibited the growth of amastigotes after 120 hours of incubation, with a 50% inhibitory concentration (IC_{50}) of 11.06 µM. Additionally, the compound exhibited reasonable cytotoxicity to LLCMK2 cells (IC_{50} of AOA = 34.46 µM) at the concentrations used (Figure 2). The relevance of these results is highlighted, as there are no reports of previous studies on the antiparasitic activity of this compound. Our results indicate that AOA, an unmodified natural product, exhibited trypanocidal effects on the intracellular replicative form of greatest clinical relevance of *T. cruzi* (amastigotes) with a highly relevant IC_{50} for a natural product, as well as showing a reasonable selectivity index (SI= 3.11).

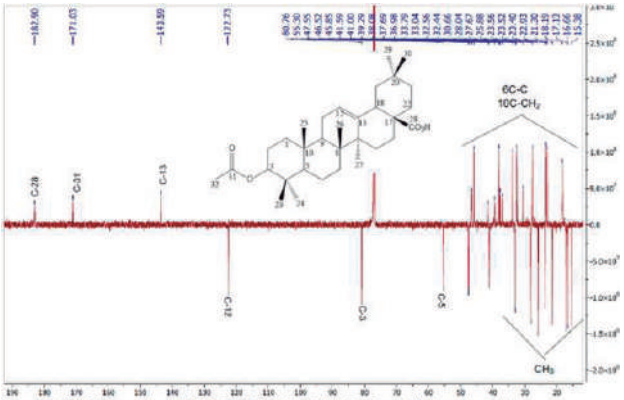


Figure 1: ^{13}C NMR spectrum (DEPT-Q; 125MHz, $CDCl_3$) of 3-*O*-acetyl-oleanolic acid.

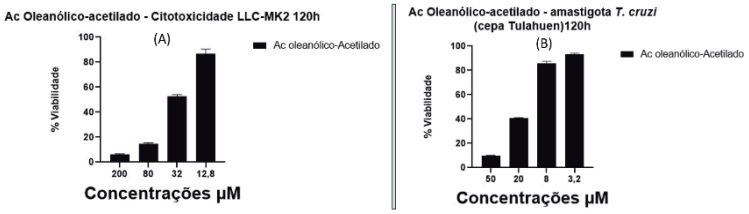


Figure 2: Cytotoxic effect of acetylated oleanolic acid on: (A) LLC-MK2 cells and (B) amastigote forms of T. cruzi (Tulahuen strain C2C4 LacZ).

[1]SILVA, F. C. O. *et al*. **Bioatividades de triterpenos isolados de plantas: Uma breve revisão**. *Revista Virtual de Química*, v. *12*, p. 234-247, 2020; [2]RASHEED, H. M. *et al*. **Isolation of oleanolic acid from Lavandula stoechas and its potent anticancer properties against MCF-7 cancer cells via induced apoptosis**. *Journal of King Saud University - Science,* v. *35*, n. 2, p. 102454, 2023; [3]FADIPE, V. *et al*. **Antimycobacterial, antiplasmodial studies and cytotoxicity of oleanolic acid and its derivative from Syzygium aromaticum Linn (Myrtaceae)**. *Journal Biomedical and Biopharmaceutical Research*, v. *17*, p. 1-12, 2020.

Acknowledgments

The **CAPES**, **CNPq** and **FAPERJ** for research support and granted scholarship.

Área: QPN
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Larvicidal activity of the Total Alkaloid Fraction of Prosopis juliflora (SW) D.C. leaves against Aedes aegypti (Linnaeus, 1762)

Jonatas T. Silva (PG)[1], Maria D.G. Lima (IC)[2], Plinio P.G. Junior (PQ)[3], Renato A. Silva (PQ)[4], Leandro R.R. Lucena (PQ)[5], Thiago Muniz de Souza (PQ)[6].

thiago.munizs@urfpe.br; jonatas.silva001.js@gmail.com

[1,2,3,4,5,6]*Universidade Federal Rural de Pernambuco.*

Key words: Aedes aegypti, Prosopis juliflora, piperidine alkaloids, biolarvicide.

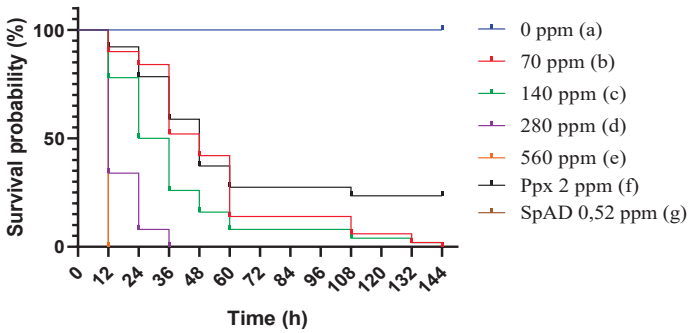
Highlights

This report presents the efficiency of the extract of piperidine alkaloids present in Prosopis juliflora as a larvicide against Aedes aegypti at the L3 stage.

Abstract

Aedes (Stegomyia) aegypti (Linnaeus, 1762) is the vector responsible for several epidemics, and vector control is the best way to combat the insect. This study aims to evaluate the effect of the total alkaloid fraction (TAF) extracted from Prosopis juliflora applied to A. aegypti larvae at the L3 stage. The total alkaloid fraction (TAF) was obtained using the methodology described by Tabosa et al[1]. The bioassays were conducted in a completely randomised design (DIC) following methodology adapted from the World Health Organisation[2] and Cruz et al[3], with seven treatment groups, consisting of: four test groups corresponding to a control group (***a***, as a blank), alkaloid extract at concentrations of 70 **(b)**, 140 **(c)**, 280 **(d)** and 560 ppm **(e)**, two reference standards formulated by commercial larvicides, Piriproxifen (***f***, 2.0 ppm), and NATULARTM DT ESPINOSADE® (***g***,0.52 ppm), as shown in figure 1. The results were evaluated using the Kaplan-Meier test with GranphPadPrism Software 8.0.1 for Windows. It was observed that the plant extracts significantly reduced the probability of survival and the lifespan of A. aegypti larvae when compared to the control (log-rank test, X^2= 292.4; df = 4; p < 0.0001), In addition to showing greater larvicidal activity in the first 60 hours of exposure, severe malnutrition, paralysis and convulsions were observed, which preceded death (Figure 1). The concentration of 560 ppm was the most lethal among the extracts and it did not differ statistically from the treatment with Espinosade® (SpAD) (X^2 = 0.000; df = 1; p > 0.9999). However, treatment with Piriproxifen showed a loss of larvicidal activity after 108 hours. In parallel with the neurotoxic effects observed, indicating that the alkaloids act on the central nervous system (CNS), the extracts also delayed the emergence of pupae for 144 hours.

Figure 1: Kaplan-Meier survival curves (in hours) of larves of *Ae. Aegypti* to different treatments.



Thus, it can be concluded that the alkaloids present in Prosopis julilfora show lethal toxic activity in vitro in various stages of Aedes aegypti with satisfactory results.

Acknowledgments

UFRPE · UAST
Sociedade Brasileira de Química

References

[1]Tabosa I. M. *et al*. **Rev. Bras. de Farm**. 9 (10): 11-22, 2000
[2]World Health Organization, *et al*. **Epidemic, & Pandemic Alert**. Genebra. 2009.
[3]Cruz I. L. S. *et al*. **Revista de Saúde**. 10 (1): 15-19, jan./jun., 2019.

Área: _____
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Ligand-fishing assay based on immobilized kallikrein enzyme for the identification of ligands in natural extracts.

Camila Loreta Rocha (PG)[1*], Anelize Bauermeister (PQ)[1], Ana Maria Soares Pereira (PQ)[2], Carmen Lúcia Cardoso[1]

ccardoso@ffclrp.usp.br; camila.loreta@usp.br

[1]*Grupo de Cromatografia de Bioafinidade e Produtos Naturais, Departamento de Química, Faculdade de Filosofia, Ciências e Letras de Ribeirão Preto, Universidade de São Paulo, Ribeirão Preto, Brazil..*

[2] *Departamento de Biotecnologia Vegetal da Universidade de Ribeirão Preto (UNAERP), Ribeirão Preto, SP, Brasil*

Keywords: *ligand fishing, kallikrein, enzyme immobilization, enzyme ligands, natural extract, GNPS.*

Highlights

Kallikrein (KLK) was covalently attached on magnetic beads (MBs). Affinity-based assay: compounds with affinity for the immobilized target is retained and can be further eluted for structural analysis.

Resumo/Abstract

Kallikreins (KLKs) are a group of serine protease enzymes that play a significant role in biological fluids and tissues.[1] The deregulated activity and expression of human kallikreins (KLKs) may be involved in various pathologies, [2] making these enzymes an attractive biological target for identifying molecules that can modulate KLK activity. Screening assay models can utilize an activity-based and/or affinity-based approach by using a ligand-fishing method. This approach involves an immobilization procedure, followed by sample incubation step (S0), washing to separate binders from non-binders (S1-2) and binder desorption and characterization (S3).[3] Analytical approaches based on LC–MS are typically employed to obtain the chemical profile of the ligands with affinity for the immobilized target protein. Herein, we present the ligand fishing assay using the KLK enzyme from porcine pancreas, which exhibits similarity to human KLK-1. The enzyme was immobilized on magnetic particles (MBs) through the amine-glutaraldehyde reaction resulting in KLK-MB. We evaluated the optimal conditions for enzyme concentration, pH, and incubation time. Qualification studies with inhibitors, binders and non-binders confirm that the screening assay can identify reference ligands. Ligands present in the desorption step, displaying an Affinity ratio (AR) > 1.0, are selected as strong binders. We investigate the extracts of *Psychotria. carthagenensis* (leaves fractions water **(A)**, CH_2Cl_2**(B)** and butanol **(C)**, as well as the crude extract EtOH of *Cupania vernalis, Stryphnodendron adstringens, Dilenia indica, Solanum lycocarpum*, and leaves crude extract MeOH of *Aloysia polystachya, and Serjania erec*ta, using the ligand fishing approach with KLK-MB. From S3 fractions the binder ions $[M+H]^+$ was identify. For P. *carthagenensis* **(A)** *m/z* 303.3 (AR= 1.1), 500.6 (AR= 1.2); P. *carthagenensis* **(B)** *m/z* 564.9 (AR= 1.4), 621.3 (RA= 5.0), P. *carthagenensis* (C) *m/z* 384.3 (AR= 3.8), 428.5 (AR=3.0). For *C. vernalis* (% KLK-Inhibition = 53.3 ± 4.4*) m/z 300.1 (AR= 1.0). for *S. adstringens* (% KLK-Inhibition= 62.4 ± 4.3*) *m/z* 380,1 (AR=6.9). For *D. indica m/z* 272.1 (RA= 1.9). For *S. lycocarpum* (% KLK-Inhibition 80.4 ± 3.4*) *m/z* 313.0 (RA= 1.2), 352.2 (RA=1.6). For *A. polystachya* (% KLK-Inhibition= 78.7 ± 6.4**) m/z 432.3 (RA= 1.1), 601.2(RA= 1.2), 528.9 (RA= 1.8), 553.2 (RA=2.0). For *S. erecta* (% KLK-Inhibition= 73.0 ± 1.3**) m/z 344.0 (RA= 1.3). The sample containing the ligands were analyzed by untargeted mass spectrometry and the LC-MS/MS data was searched against the spectral library from the Global Natural Products Molecular Networking (GNPS). In the samples *A. polystachya* and *P. carthagenensis* **(B)**, a mono and a di-C-glycosilated flavonoid were annotated respectively. Glycosylated flavonoids have been shown as potential compounds to interact with human proteins. [4]

* From Carvalho et al., 2021 https://doi.org/10.1016/j.jpba.2021.114026; ** Tested by GCBPN.

1. Costa-Neto CM, Dillenburg-Pilla P, Heinrich TA, et al. Int Immunopharmacol. 2008 Feb;8(2):135–42. doi: 10.1016/j.intimp.2007.08.003. 2. Kryza T, Silva ML, Loessner D, Heuzé-Vourc'h N, Clements JA. Biochimie. 2016 122:283–99. doi: 10.1016/j.biochi.2015.09.002 3. Zhuo, R., Liu, H., Liu, N., and Wang, Y. Molecules, 2016, 21:1516. doi: 10.3390/molecules21111516 4. Caruso, IP, Vilegas, W, de Souza, FP, Fossey, MA. 4, Cornélio, ML. J Pharm Biomed Anal. 2014 98:100-6. doi: 10.1016/j.jpba.2014.05.015.

Agradecimentos/Acknowledgments

The authors thank FAPESP (2022/00432-7; 2014/502995), CNPq (307108-2021-0) and CAPES (financial code 001) agencies for the financial support and fellowship.

Área: QPN
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

In vitro anti-*Schistosoma mansoni* activity of acetogenins and fatty acids from *Porcelia ponderosa* (Annonaceae)

Dalete Christine S. Souza* **(PG),[1] Rayssa A. Cajás (PG),[2] Thainá R. Teixeira (PG),[2] Emerson A. Oliveira (PQ),[1] Maria C. Souza (PQ),[3] Josué de Moraes (PQ),[2] João Henrique G. Lago (PQ)[1]**

christine.silva@ufabc.edu.br

[1]Center of Natural and Human Sciences, Federal University of ABC, SP; [2]Research Center on Neglected Diseases, University of Guarulhos, SP; [3]Forest Campus, Federal University of Acre, AC.

Palavras Chave: Porcelia ponderosa*, acetogenins, fatty acids, enediyne system,* Schistosoma mansoni.

Highlights

Two new enediyne γ-lactones (**1** and **2**) and their precursor fatty acids (**3** and **4**) were obtained from seeds of *Porcelia ponderosa* had their *in vitro* activity evaluated against the *Schistosoma mansoni* worm.

Abstract

Different bioactive natural products have been obtained from Annonaceae species, specifically alkaloids, flavonoids, acetogenins, and fatty acids[1]. As part of our continuous studies regarding the discovery of new anthelmintic prototypes based on natural products, in the present work, the anti-*Schistosoma mansoni* effects of acetogenins **1** and **2** and their biosynthetically related fatty acids **3** and **4**, obtained from *Porcelia ponderosa*, were evaluated *in vitro*. After chromatographic fractionation of crude CH_2Cl_2 extract from seeds of *P. ponderosa*, compounds **1 – 4** were chemically characterized by analysis of NMR and MS data, as indicated in Figure 1. Compounds **1** – **2** and **3** – **4** were incubated in 24-well plates with one adult male and one female worms (i.e., one worm pairs) in RPMI 1640 culture medium supplemented with 5% inactivated fetal bovine serum containing antibiotics (100 U/mL penicillin and 100 μg/mL streptomycin). Praziquantel was used as standard drug and untreated parasites were used as controls. Adult worm pairs were obtained from Swiss mice by perfusion 42 days after infection. The 24-well plate was kept for 72 h at 37ºC and 5% CO_2 and the viability of compounds **1** – **4** was monitored by microscope at 2, 24, 48 and 72 h. Parasites with any body movement were considered viable and parasites without body movement observed at least for 1 or 2 minutes, were considered dead[2]. After conduction of the antischistosomal assay, the obtained data were processed in the software GraphPad Prism 8.0.2 and it was possible to observe a time and concentration-dependent result of mortality induction. As results, compounds **1** – **2** displayed activities for male and female worms at 83.3 μg/mL, however, it has been observed that it affects the male worms first (48h) and then the female worms (72h). Differently of acetogenins **1 – 2**, the fatty acids **3** – **4** showed to be inactives at the maximum concentration tested (200 μg/mL), suggesting that the presence of the γ-lactone ring moiety is crucial for anthelmintic activity.

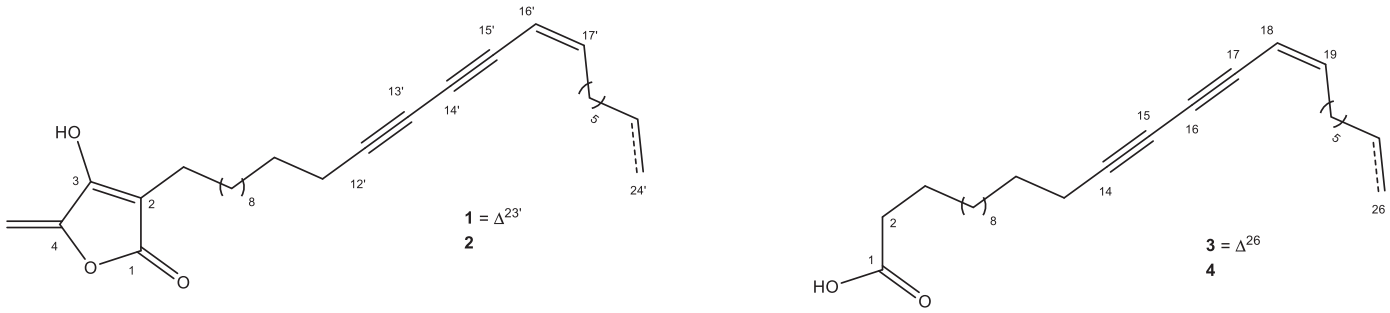


Figure 1 – Structures of enediyne acetogenins (**1** and **2**) and fatty acids (**3** and **4**) from seeds of *P. ponderosa*.

References [1]Brito, I. A. et al. *J. Braz. Chem. Soc.* **2021**, 32, 447-453. [2]Brito, J. R. et al. *Sci Rep*. **2022**. 12.

Acknowledgments

CAPES, CNPq and FAPESP

Área: __QPN_____

Penicillium digitatum mycotoxins: An occult risk in orange juices

Éder de Vilhena Araújo (PG)[1*], Franciele F. Souza Jesus (IC)[1], Beatriz Lederman Valente (PG)[3], Marcelo Cristianini (PQ)[3], Cassiana C. Montagner (PQ)[2], Taicia Pacheco Fill (PQ)[1]

***e164664@dac.unicamp.br**

[1]Microbial Chemistry Laboratory, Institute of Chemistry, University of Campinas, Build 118, Brazil; [2]Environmental Chemistry Laboratory, Institute of Chemistry, Build 155, Brazil; [3]Department of Food Technology, School of Food Engineering, University of Campinas, Build 80, Brazil

Keywords: Orange juices, *Penicillium digitatum*, Tryptoquialanines, Inactivation treatments, Fish Embryo Toxicity.

Highlights

Mycotoxins tryptoquialanine A and B were determined in commercial orange juices. Thermal and HPP treatments reduced only partially TA and TB contents. The FET assays in Zebra-fish indicated TA and TB toxicity.

Abstract

There has been a growing consumption of fresher and more nutritious food globally. Within this context, orange juice appears as a prominent choice among fruit-based beverages, appreciated for its rich nutritional content, taste, and minimal caloric intake. Nevertheless, challenges in post-harvest, including distribution logistics, storage, and processing techniques, can enhance the susceptibility of citrus fruits to colonization by various fungal pathogens. The fungus *P. digitatum*, emerges as the primary causative agent, triggering substantial losses estimated at 70% to 90%. In our studies, we were able to observe that upon colonization in the citrus host, P. digitatum biosynthesizes tremorgenic alkaloids, including not only tryptoquialanines A (TA) and B (TB) as illustrated in Fig.1, but also fumitremorgins, fumiquinazolines and tryptoquivalines that were purified and characterized. Since there is a huge concern about orange quality control, we validated an analytical method to detect TA and TB in different orange juice samples (homemade and industrial commercially available juices) employing QuEChERS and LC-MS/MS. Linearity was excellent over a broad concentration range (1–1000 µg kg^{-1} high range, 1-75 µg kg^{-1} low range) with $R^2 \geq 0.998$. LOD and LOQ were determined at 1 and 3 µg kg^{-1}, respectively, and recoveries ranged from 57 to 83% with RSD ≤ 13%. The analysis of the different orange juice models revealed a significant presence of the TA alkaloid in both fresh and industrially processed 100% orange juices. We also investigated thermal and HPP (High Pressure Processing) treatments to inactivate the mycotoxins, our data indicated reductions of TA and TB contents by ≤ 32%. The acute toxicity of mycotoxins was evaluated in zebrafish embryos. The hatching of zebrafish eggs was delayed in the presence of both 1 and 10 mg L^{-1} of TA and TB. However, the TA and TB exposure did not affect the growth of zebrafish larvae. Additionally, the levels of TA and TB observed in orange juice samples are in the range of values associated with tremorgenic mycotoxins capable of inducing neurological disorders in vertebrates and deserves attention. Consequently, our methodology could be applied into routine quality control analyses of orange juice beverages, given the notable threat posed by these tremorgenic alkaloids to human health.

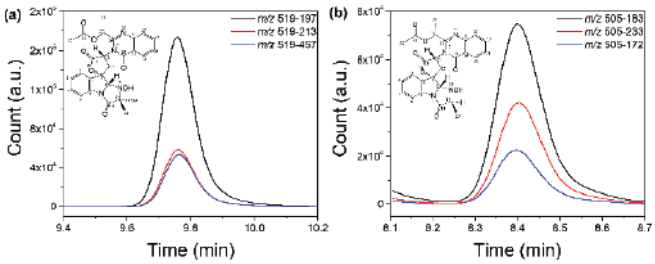


Fig. 1. The chemical structure of the *P. digitatum* mycotoxins (a) tryptoquialanine A $C_{27}H_{28}N_4O_7$ 518.1801 g mol^{-1}; (b) tryptoquialanine B $C_{25}H_{24}N_4O_6$ 504.1645 g mol^{-1}.

Acknowledgments

This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – Brasil (CAPES) #2015/18790-3 – Finance Code 001 | FAPESP #2021/00728-0

Machine learning techniques and the discovery of new hit compounds against *Trypanosoma cruzi* - a computational and experimental approach

Henrique Barbosa* (PG),[1] **Gabriel Z. Espinoza (IC),[2] Maiara Amaral (PQ),[3] Érica V. C. Levatti (PQ),[3] Mariana B. Abiuzi (PG),[3] Gabriel C. Veríssimo (PG),[4] Philipe O. Fernandes (PG),[4] Vinícius G. Maltarollo (PQ),[4] Andre G. Tempone (PQ),[3] Kathia M. Honorio (PQ),[1,2] João Henrique G. Lago (PQ).[1]**

barbosa.h@ufabc.edu.br;

[1]Center for Natural and Human Sciences, UFABC; [2]School of Arts, Sciences and Humanities, EACH/USP; [3]Laboratory of Pathophysiology, Butantan Institute; [4]Department of Pharmaceutical Products, UFMG.

Keywords: *Big Data, Machine Learning, Natural Product, American Trypanosomiasis, Andrographolide.*

Highlights

The present work proposes to train a machine learning model capable of predicting activity toward *T. cruzi* parasites. For this, a dataset of natural products was created using anti-*T. cruzi* data available in the literature. Subsequently, using this dataset to train machine learning models, andrographolide was selected as a hit compound. To prove this result, andrographolide was isolated from the *Cymbopogon schoenanthus* and evaluated against *T. cruzi* trypomastigote and amastigote forms showing IC_{50} values of 29.4 and 2.9 µM, respectively.

Abstract

Chagas disease, caused by the parasite *Trypanosoma cruzi*, is an illness that affects approximately 8 million people worldwide, for which the only treatment options are benznidazole and nifurtimox[1]. In this context, the use of machine learning procedures can help with the search for new drugs. This work created a dataset with *T. cruzi* molecules, including data such as IC_{50}, CC_{50}, and SMILES. Two machine learning models - Random Forest and k-Nearest Neighbors - were used to predict the biological activity of natural products against amastigote forms of the parasite. These models were applied to a virtual screening of an external natural product database, and the diterpene andrographolide was identified as a promising hit compound. To prove the model applicability, andrographolide was isolated from the leaves of *Cymbopogon schoenanthus* and tested toward *T. cruzi* trypomastigote and amastigote forms showing IC_{50} values of 29.4 and 2.9 µM, respectively. The standard drug, benznidazole, showed IC_{50} values of 17.7 and 5.0 µM. Andrographolide was also evaluated for cytotoxicity in mammalian cells showing reduced toxicity with CC_{50} value of 92.8 µM, representing a selectivity index of 32, similar to benznidazole (SI = 39). In addition, *in silico* analyses and literature information show that andrographolide fulfills many DNDi requirements to be a hit compound.[2] Therefore, this work successfully built a machine learning model capable of predicting biological activity for compounds against amastigotes of *T. cruzi*, which was proved through experimental approaches, as indicated in Figure 1.

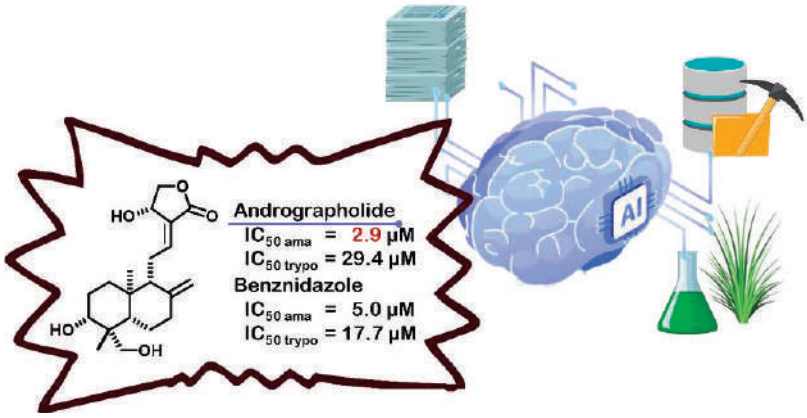


Figure 1 - Process of work from literature data to hit discovery.

Acknowledgments

UFABC, CAPES, FAPESP and CNPq.

References: [1]World Health Organization, **WHO**. 2 Katsuno, K. *et al*. Hit and Lead Criteria in Drug Discovery for Infectious Diseases of the Developing World. **Nat**. **Rev**. **Drug Discovery** 2015, 14, 751−758.

Área:
__QPN_____
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Mapping resveratrol in peanut (*Arachis hypogea* L.) agricultural waste

Mirella T. F. Ranzeti (IC),[1] Gabriela Cremasco (PG),[2] Ana C. F. Ferezin (IC),[1] Daniel Rinaldo (PQ),[1,2]

mirella.ferreira@unesp.br

[1]Departamento de Química, FC-UNESP, Bauru; [2]Instituto de Química, IQ-UNESP, Araraquara.

Palavras Chave: Residues; Waste reuse; Peanut roots; Peanut hull; Peanut stem; Resveratrol.

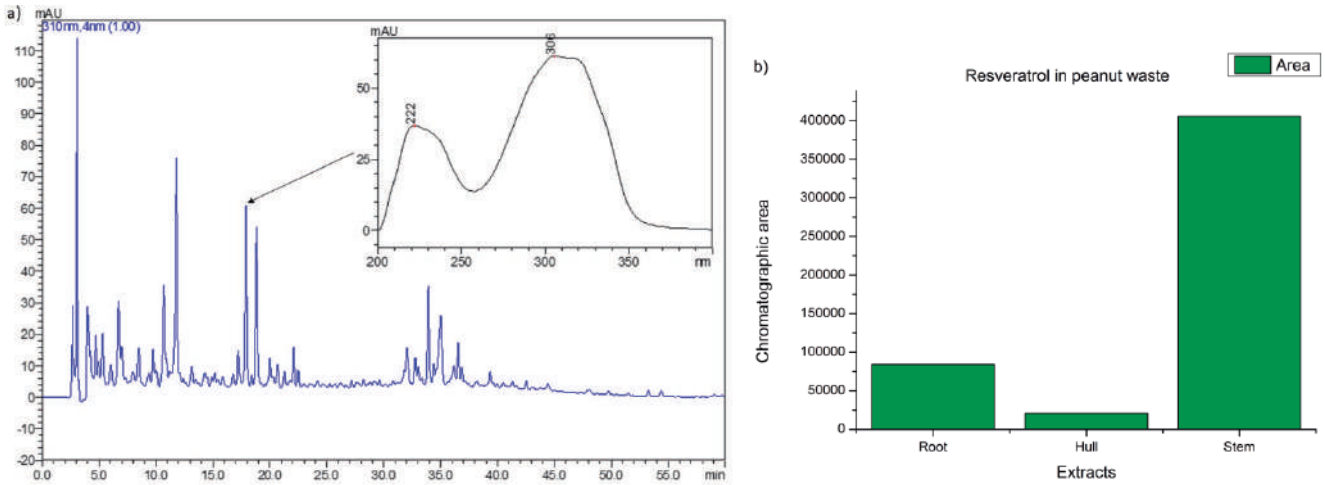
Highlights

Peanuts are a source of resveratrol. Use of agro-industrial waste. By-products extraction.

Resumo/Abstract

The cultivation of peanuts, *Arachis hypogea* L., is one of the agricultural activities that produces the most waste in Brazilian agriculture. The legume contains flavonoid compounds and stilbene polyphenols, highlighting resveratrol, which are of great importance to the pharmaceutical industry.[1] Looking for a way to obtain it from peanut waste, strategies for mapping the presence and quantity of resveratrol in different types of peanut waste are essential to maximize the efficiency of extractions. To guide this research, extractions were performed on different type of peanut waste to identify which part of the plant has the highest amount of resveratrol. Extractions were performed with a ratio of 1:15 (m/v) and extracting solution was 8:2 EtOH/H_2O.[2] The identification of resveratrol was by adding the standard, comparing the UV spectrum and retention time with that of the authentic standard. The relative amount was calculated by comparing area of the resveratrol peak in each type of waste. Among the waste study, the stem has the highest relative quantify of the compound, around 4,8 times greater than other part of the plant (Fig. 1).

Figure 1. (a) Chromatogram of the peanut stem extract and UV spectrum of resveratrol, analyzed at 310 nm; (b) Comparison between the resveratrol peak areas obtained in each chromatographic profile of the parts of the peanut waste.



References

[1] EMBRAPA, Empresa Brasileira de Pesquisa Agropecuária. **Amendoim. O produtor pergunta, a Embrapa responde**. Embrapa Informação Tecnológica. Brasília, DF. 2009.

[2] LOPES, Renata Miranda. **Determinação de resveratrol em folhas de amendoim silvestre (Arachis sp.)**. Universidade de Brasília - Faculdade de Ciências e da Saúde, Programa de Pós-graduação em Ciências da Saúde, Brasília, 2011.

Agradecimentos/Acknowledgments

The authors gratefully acknowledge financial support from the State of Sao Paulo Research Foundation (FAPESP, Fundação de Amparo à Pesquisa do Estado de São Paulo), grant # 2022/11628-0, grant # 18/50025-3 and grant # 2014/50926-0, and the National Institute of Science and Technology - INCT BioNat, grant # CNPq 465637/2014-0, Brazil.

Área: QPN

Metabólitos secundários das cascas do caule de *Poraqueiba sericea* Tulp.

Jader L. Tavares (FM),[1] Railda Neyva M. Araújo (FM),[2] Lúcio Flávio P. Santos (IC),[3] Joycelene Santos Alves (IC),[4] Ana Carolina M. de Oliveira (IC),[4] Haroldo S. Ripardo Filho (PQ),[5] Manoel L. Lopes Junior (PQ),[4] Marivaldo José C. Corrêa (PQ),[4] Giselle Skelding P. Guilhon (PQ),[4] Lourivaldo S. Santos (PQ).[4*]

lsslouri@gmail.com

[1]EE Manoel Joaquim Monteiro, SEDUC/PA; [2]EEEM Agostinho Morais de Oliveira, SEDUC/PA; [3]Instituto Federal do Pará, IFPA; [4] Universidade Federal do Pará, PPGQ; [5]Instituto Federal do Amapá, IFAP.

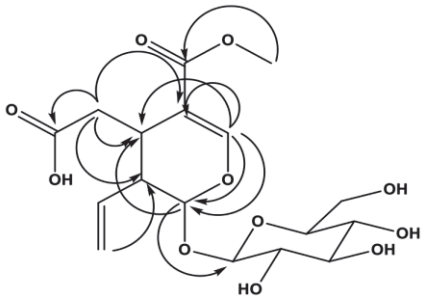
Palavras Chave:*Poraqueiba sericea, Icacinaceae, triterpenos, secoiridoide, secoxiloganina.*

Highlights

Secondary metabolites from the stem bark of *Poraqueiba sericea* Tulp. Nine compounds were isolated from *P. sericea* and identified as stigmasterol and sitosterol (in mixture), betulínic acid, ursolic acid, cafeoil betulínic acid, lupeol, betuline, oleanolic acid and the secoiridoide secoxyloganin (**1**).

Resumo

Poraqueiba sericea Tulp. é uma árvore de grande porte pertencente à familia Icacinaceae, que cresce exclusivamente na Amazônia. No Brasil, esta árvore é cultivada por seu fruto comestível (conhecido por “umari” e “mari”), de sabor agradável e característico, consumido puro ou com farinha de mandioca. O óleo extraído industrialmente do mesocarpo é utilizado em frituras, sendo rico em ácidos graxos[1]. Na indústria, a farinha de “umari” substitui a farinha de trigo. As folhas da planta são usadas por algumas tribos na Amazônia como infusão para tratamento contra disenteria[2]. É bastante apreciada no Peru por seu fruto ter sabor agradável e característico, onde é consumida *in natura* e também como ingrediente principal na composição de uma bebida local chamada "Cahuana" preparada com amido de tapioca[3]. Neste trabalho, as cascas do caule (2,5 kg) secas e trituradas de *P. Sericea* foram submetidas a extrações sequenciais a frio com os solventes hexano e acetato de etila, durante sete dias para cada solvente. Após filtração o solvente foi eliminado sob pressão reduzida para obtenção dos extratos brutos hexânico (4,05 g) e acetato de etila (34,95 g). Os extratos foram submetidos à cromatografia de coluna utilizando sílica gel e eluição com o sistema de solventes hexano:acetato de etila em polaridades crescentes. Do extrato bruto hexânico foram obtidos os esteróides estigmasterol e sitosterol (30 mg em mistura) e isolado o triterpeno ácido betulínico (14 mg). Do extrato bruto acetato de etila foram isolados os triterpenos ácido ursólico (4,1 mg), ácido cafeoil betulínico (41 mg), lupeol (29 mg), betulina (63 mg) e ácido oleanólico (114 mg), além do secoiridoide secoxiloganina (**1**) (30 mg). As estruturas dos compostos foram determinadas principalmente por meio de extensivas análises espectroscópicas, incluindo RMN 1D (^{1}H e ^{13}C), 2D (COSY, HSQC e HMBC) e por comparação com dados relatados na literatura.



Secoxiloganina (**1**)

Referencias:
[1]Silva, NAC.*Grasas Aceites*. 48:11-16 (1997). [2]Huamán, PRO, Vargas EBA, Garazatua JF. *Rev Amaz Invest Alim*. 1:30-37 (2001). [3]Zebiri, I. et. al. *Natural Product Research*, 1-6 (2016).

Agradecimentos

À CAPES e ao CNPq pelo auxílio financeiro, e à UFPA pela infraestrutura para a realização deste trabalho.

Área: __QPN___

Metabolomic analysis by PLS-DA of the genus *Banisteriopsis* e *Stigmaphyllon* (Malpighiaceae)

Jaqueline M. G. Silva* **(PG),[1] Helena Mannochio-Russo (PQ),[2] Rafael F. Almeida (PQ),[3] Maria L. Zeraik (PQ) [1]**

jaqueline.munise@uel.br

[1,4] Laboratory of Phytochemistry and Biomolecules (LabFitoBio), Department of Chemistry, UEL; [2] Skaggs School of Pharmacy and Pharmaceutical Sciences, University of California San Diego; [3] Department of Botanical, UEG.

Keywords: *LC-MS/MS, Metaboanalyst, PLS-DA.*

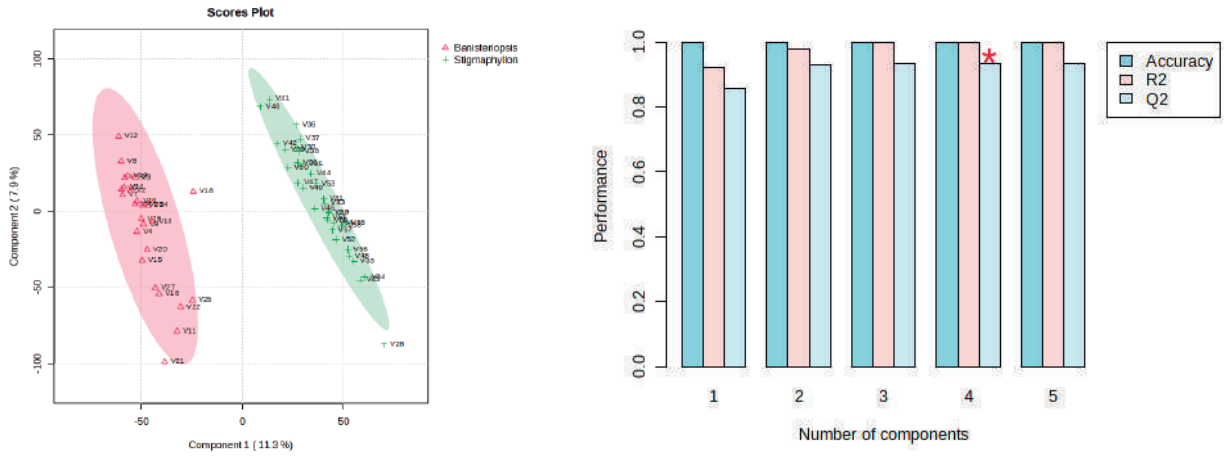
Highlights

- 54 samples were compared, 21 from *Banisteriopsis* and 33 from *Stigmaphyllon genera*.
- The PLS-DA analyses revealed that the metabolomic profiles for both genera are statistically different.

Abstract

Banisteriopsis and *Stigmaphyllon* are relevant genera of the botanical family Malpighiaceae with antioxidant, antifungal, and stimulant activities[1,2]. We report a chemometric analysis for the discrimination of these genera. Initially, 21 *Banisteriopsis* and 33 *Stigmaphyllon* samples comprising 16 and 26 species of each genera were separately extracted with EtOH:H_2O (4:1). Subsequently, the extracts were analyzed by Liquid Chromatography coupled with Mass Spectrometry[3]. The metabolomic profiles were organized in a matrix and subjected to Partial Least Squares Discriminant Analysis (PLS-DA). Two main groups were formed, reflecting the two genera in this study, with 95% confidence (Figure 1), and high accuracy, R and Q values were obtained. In the positive part of component 1, *Stigmaphyllon* samples were grouped. The loading values for the positive part of component 1 suggest that the structure of *m/z* 535,2683 and retention time (R_t) 6,3 min is relevant for *Stigmaphyllon*. The *Banisteriopsis* samples were grouped in the negative region of component 1. The loadings show that the most important structures for the separation of *Banisteriopsis* have *m/z* 838,641 (R_t = 8,08) and 807,5277 (R_t = 8,45), possibly aromatic molecules with alcohols. Therefore, we verified the structures that differentiate *Banisteriopsis* and *Stigmaphyllon*.

Figure 1 – Comparison of *Banisteriopsis* x *Stigmaphyllon* by PLS-DA and accuracy, R and Q values.



References

[1]Nunes, B. C. *et al.,* **Industrial Crops and Products**, v. 92, n. 15, p. 277-289, 2016.
[2]Quaresma, D. M. O. *et al.,* **Bioorganic Chemistry**, v. 105, 2020
[3] Mannochio-Russo, *et al.,* **Front. Plant Sci**. v. 13, 2022.

Acknowledgments

We thank CAPES, CNPq and UEL.

Área: QPN

Metabolomic Approach to the Pathogen-Host Interaction of a New Emerging Citrus Pathogen Isolated in Brazil

Mayra Pinheiro,[1*] José R. F. Maciel,[1] Evandro Silva,[1,2] Taicia Fill.[1]

m234915@dac.unicamp.br

[1]State University of Campinas, Institute of Chemistry, CEP, 13083-970 Campinas, SP, Brazil
2University of São Paulo, Institute of Chemistry, CEP 13566-590, São Carlos, SP, Brazil

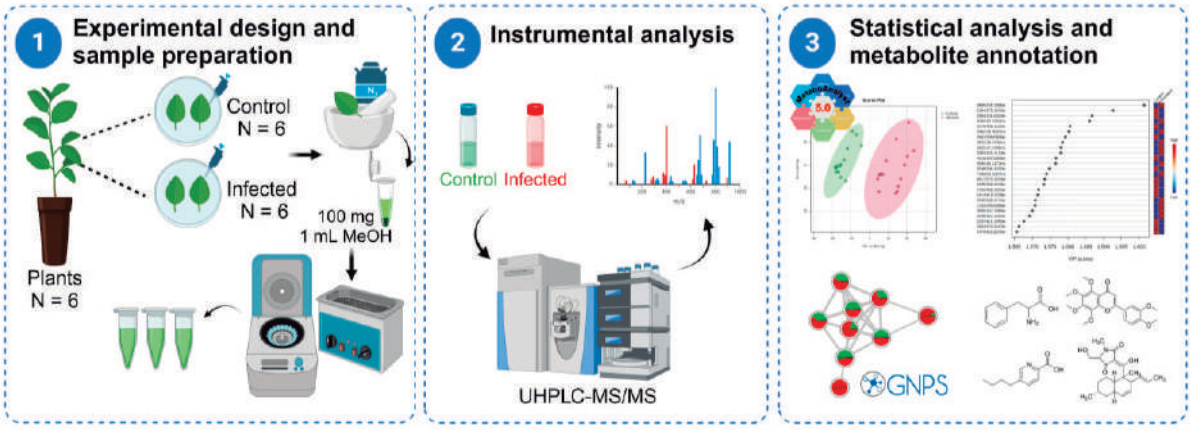
Keywords: Metabolomics, Phytopathogen, Mass spectrometry, metabolites, Citrus sinensis.

Highlights

This work applied an untargeted metabolomics LC-MS/MS approach to investigate the host-pathogen interaction of a new Citrus phytopathogen. We were able to identify plant defense metabolites and fungal metabolites that may play a role in its pathogenicity.

Abstract

Brazil is the world's largest producer and exporter of citrus fruits[1]. However, the Brazilian citrus industry faces significant economic challenges due to losses in orange production, primarily associated with diseases caused by phytopathogens[2]. In this study, we applied an untargeted metabolomics workflow based on mass spectrometry to investigate the metabolites involved in the interaction between the phytopathogen (LaBioQuiMi01) and its citrus host. Two groups were evaluated: infected leaves and healthy leaves at different time points after inoculation (5, 10, and 15 dpi). Through multivariate analyses PCA and PLS-DA, it was possible to observe discrimination between control plants and infected plants, indicating metabolic differences between the groups. In the infected group, alterations in the biological system were observed, particularly at elevated levels of aminoacids including phenylalanine ($[M+H]^+$ *m/z* 166.0865), flavanones, such as nobiletin ($[M+H]^+$ *m/z* 403.1388), hesperidin ($[M+H]^+$ *m/z* 611.1968), tangeretin ($[M+H]^+$ *m/z* 373.1287) and Gardenin B ($[M+H]^+$ *m/z* 359.1130). These flavonoids are likely involved as naturals defense or resistance mechanisms in this Citrus species[3]. Other compounds were also observed only in the infected samples, including peptides (*m/z* 295.1291), organic acids ($[M+H]^+$ *m/z* 190.0953), and mycotoxins. The latter are produced by the microorganism when cultivated in vitro. The results obtained so far give us insights concerning the metabolism of the fungus LaBioQuiMi 01 and potential phytotoxic compounds that may be involved in the pathogenicity of LaBioQuimiMi 01, acting as virulence factors. Therefore, the results provide insights for further investigations into the interaction of the fungus LaBioQuiMi01 with its citrus host.



References
[1] Fao (2020) FAO. http://www.fao.org/faostat/en/#home. Acesso 10 de fevereiro de 2024.
[2]Kanashiro, A.M. et al., 2020. *Penicillium italicum*: An underexplored postharvest pathogen. Front. Microbiol. 11, 606852
[3]de Moraes Pontes, Joao Guilherme, et al. "Mass spectrometry imaging as a potential technique for diagnostic of Huanglongbing disease using fast and simple sample preparation." *Scientific Reports* 10.1 (2020): 13457.

Acknowledgments

To the National Council for Scientific and Technological Development (CNPq, Brazil), grant number 142600/2021-0, and the São Paulo Research Foundation (FAPESP), for their financial support.

Área: QPN

Metabolomics and chemometrics to discover metabolites from Brazilian flora with neuroprotective and anti-inflammatory properties

Ana Claudia Chagas de Paula Ladvocat (PQ),[1] Marisi Gomes Soares (PQ),[2] Danielle Ferreira Dias (PQ),[2] Daniela Aparecida Chagas-Paula (PQ),[2,*].

daniela.chagas@unifal-mg.edu.br

[1]*Department of Pharmaceutical Sciences, Federal University of Juiz de Fora (UFJF), 36036-900, Juiz de Fora, Minas Gerais, Brazil;* [2]*Institute of Chemistry, Federal University of Alfenas (UNIFAL-MG), 37130-001, Alfenas, Minas Gerais, Brazil.*

Palavras Chave: *Parkinson disease, Mass spectrometry, Dereplication, Prediction, Artificial intelligence.*

Highlights

Neuroprotective compounds in an experimental model of Parkinson's disease and compounds with differential anti-inflammatory mechanism of action were discovered. Prediction models were also validated.

Resumo/Abstract

Metabolic strategies based on ultra-performance liquid chromatography coupled with high-resolution mass spectrometry (UPLC-HRMS) have been used to determine biomarkers of pharmacological properties in complex samples of extracts from plant species. They allow the characterization of the chemical composition in a comprehensive manner, without necessarily requiring time-consuming isolation and purification steps.[1-4] A minimum amount of sample needed for metabolomics studies, on average 20 mg of the pulverized plant species, is a relevant advantage in comparison to the classical studies. Especially when the study is regarding plant species that are faced in risk of extinction or are from areas of difficult access. Multivariate and univariate statistical analyses with chemometric studies are usually associated for adequate analysis and treatment of metabolomic data.[2-4] In this way, combining such methodologies, the study of hydroethanolic extracts of several species of Brazilian flora was carried out. Through these studies, it was possible to discover several markers of neuroprotective activity in an experimental model of Parkinson's disease[2] and of anti-inflammatory activity with innovative mechanism of action of dual protection of the main inflammation pathways (cyclooxygenase and lipoxygenase).[3] It was also possible the detection of hundreds of new substances that should be further investigated.[2-4] Additionally, the use of chemometric, statistical and artificial analyses has allowed the construction of prediction models of pharmacological activity based on the metabolomic data.[4]

[1] Katchborian-Neto A. *et al.*; Integrative open workflow for confident annotation and molecular networking of metabolomics MSE/DIA data. ***Briefings in Bioinformatics***, **2024**, 25, bbae013. https://doi.org/10.1093/bib/bbae013
[2] Katchborian-Neto A. *et al.*; Neuroprotective potential of Ayahuasca and untargeted metabolomics analyses: applicability to Parkinson's disease. ***J. Ethnopharmacol.***, **2020**, 255, 112743. https://doi.org/10.1016/j.jep.2020.112743
[3] Domingos O.S. *et al.*; Anti-Inflammatory derivatives with dual mechanism of action from the metabolomic screening of *Poincianella pluviosa*. ***Molecules***, **2019**, 24, 43775. https://doi.org/10.3390/molecules24234375
[4] Alcântara B.G.V. *et al.*; Anti-Inflammatory activity of Lauraceae plant species and prediction models based on their metabolomics profiling data. ***Chemistry & Biodiversity***, **2023**, 20, e202300650. https://doi.org/10.1002/cbdv.202300650

Agradecimentos/Acknowledgments

The authors extend their gratitude to the José Badini OUPR herbarium (UFOP - Federal University of Ouro Preto) and II-Leopoldo Krieger CESJ herbarium (UFJF - Federal University of Juiz de Fora) for providing the plant material; and to the financial support from the following agencies: CAPES (finance code 001); FAPEMIG (finances codes APQ-05218-23, APQ-00544-23, APQ-02353-17, APQ-00207-18, BPD-00760-22, and RED-00213-23); and CNPq (finances codes 408115/2023-8, 316204/2021-8, and 406837/2021-0).

Área: QPN

Molecular dereplication strategies guided the isolation of new cytotoxic isoflavonoids from the roots of *Vicia faba* (FABACEAE)

Victor M. Sipoloni (PG),[1]* Elthon G. Ferreira (PQ),[2] Eric Yoshitaka Lee (IC),[3] João Marcos Batista Jr (PQ),[3] Letícia V. Costa-Lotufo (PQ),[2] Paula C. Jimenez (PQ),[4] Miriam Uemi (PQ),[2] Lívia S. de Medeiros (PQ),[2] Thiago A. M. Veiga (PQ).[1]

victor.sipoloni@unifesp.br

[1] Instituto de Ciências Ambientais, Químicas e Farmacêuticas, Universidade Federal de São Paulo, Diadema, Brasil; [2]Instituto de Ciências Biomédicas, Universidade de São Paulo, São Paulo, Brasil; [3] Instituto de Ciência e Tecnologia, Universidade Federal de São Paulo, São José dos Campos, Brasil; [4]Instituto do Mar, Universidade Federal de São Paulo, Santos, Brasil.

Palavras Chave: *Vicia faba, Isoflavonoids, Dereplication, Cytotoxic potential, Colorectal carcinoma.*

Highlights

Utilizing dereplication strategies for constructing a feature-based molecular network, we successfully isolated two novel isoflavonoids exhibiting cytotoxic potential from *Vicia faba*.

Abstract

The occurrence and isolation of isoflavonoids within the *Vicia* genus have not been previously reported in the literature, despite various authors detecting such flavonoids through metabolomic approaches [1,2]. In light of this, we employed modern approaches for dereplicating compounds from crude extracts of *Vicia faba*, a species belonging to the Fabaceae family. Fractions obtained from the roots underwent cytotoxic assays against HCT-116 cells (colorectal carcinoma) and were further analyzed by LC-MS/MS. To guide our chemical study, we incorporated cytotoxic activity data into a feature-based molecular networking constructed using the GNPS database (Fig. 1A). Notably, clusters belonging to the flavonoid class were observed, with only one feature present in a cytotoxic fraction. Subsequent semi-preparative HPLC purification steps facilitated the isolation of a mixture of two diastereoisomeric isoflavanones (Fig. 1B). Their structures were elucidated through 1 and 2D NMR experiments, HRMS data, and a proposed fragmentation mechanism (Fig. 1C). Following an extensive search across various databases, we suggest that both compounds are novel in the literature. Circular dichroism experiments are underway to complete the unequivocal structural elucidation of these compounds. Cytotoxic assays revealed an IC_{50} = 7.1 µM against HCT-116 cells. Our findings highlight the significance of dereplication approaches in expanding the chemodiversity of *Vicia* genus. Along with, from the same fraction we also isolated two known isoflavones: alfalone and 8-*O*-retusin.

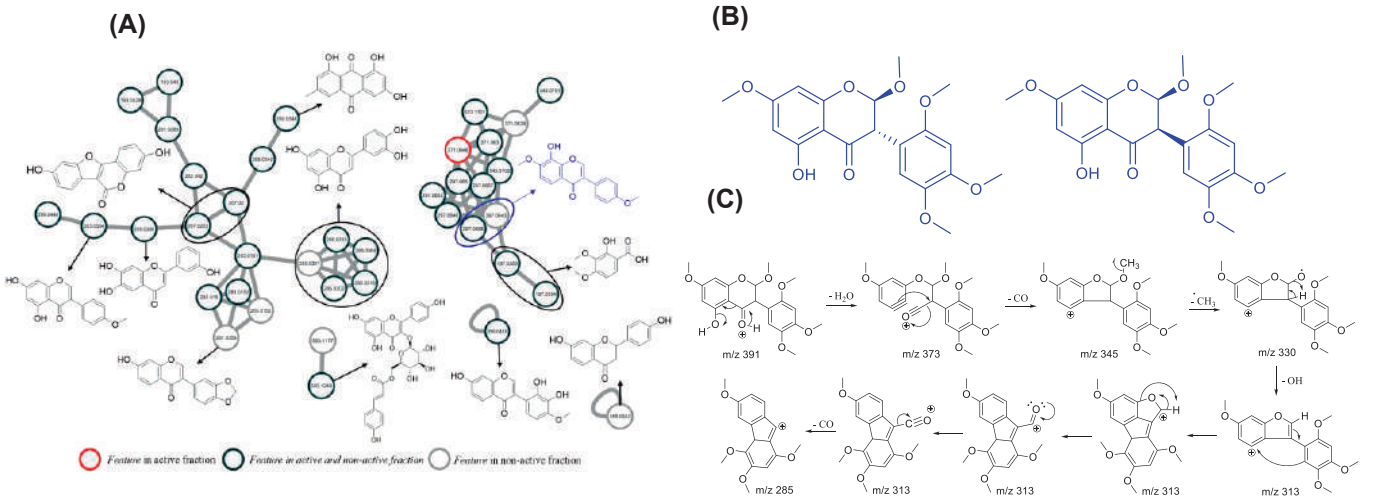


Figure 1. (A) Feature-based Molecular Networking constructed on the GNPS platform; **(B)** Structures of the diastereoisomeric isoflavanones; **(C)** Proposed fragmentation mechanism for the isoflavanones.

1- FAYEK, N. M. et al. **Journal of Agricultural and Food Chemistry**, v. 69, n. 17, p. 5252–5266, 2021.
2- VALENTE, I. M. et al. **Food Research International**, v. 116, p. 888–896, 2019.

Acknowledgments

CAPES: 88887.684866/2022-00; FAPESP: 2018/04095-0 e 2020/08270-0; LaBiORG; UNIFESP

Área: QNP

Molecular networking of the marine fungus *Penicillium citrinum*-4A14 extract and antifungal activity of citrinin associated with red LED light

Wanderson Z. Cosme (PG)[1*], Maria L. F. R. de Melo (IC)[1], Gustavo M. Dias (PQ)[2], Marcos A. Soares (PQ)[3], Regina H. Pires (PQ)[1], Marcio L. A. Silva (PQ)[1], Wilson R. Cunha (PQ)[1], Patrícia M. Pauletti (PQ)[1], Ana H. Januario (PQ)[1].

wanderson_cosme@outlook.com

[1]University of Franca, UNIFRAN; [2]Federal University of ABC, UFABC. [3]Federal University of Mato Grosso, UFMT.

Keywords: *Dereplication, Didemnum perlucidum, GNPS, Metabolomics, Phototherapy.*

Highlights

The chemical profile of the extract from *Penicillium citrinum*-4A14 was analyzed by UPLC-MS, and in parallel, the antifungal activity of citrinin against *Candida* strains was assessed with and without the association of LED light.

Abstract

Microorganisms derived from marine environment exhibit morphological characteristics, survival strategies, and metabolites remarkably distinct from their terrestrial counterparts, especially due to contrasting environmental conditions such as high pressure and salinity[1]. In this study, we address investigations here regarding the biological potential of *Candida* species with and without the incorporation of red LED, as well as the dereplication of chemical constituents by UPLC-MS and molecular networking of the extract from *Penicillium citrinum*-4A14 associated with the ascidian *Didemnum perlucidum*. The UPLC-ESI/Q-TOF, MS/MS equipment from Waters™, was employed in the analysis of the EtOAc extract from the fungus *P. citrinum*-4A14, cultivated in malt medium. Analyses were conducted in both positive and negative modes. The MS-Convert software (version 3.4.16) was used to convert ESI-MS/MS data to mzXML format, and the GNPS platform was employed to organize the data into molecular networks. The extract was subjected to reverse phase chromatographic purifications using a flash chromatography system, Buchi Pure 850®, allowing the isolation of citrinin. The antifungal activity of the citrinin, ranging from 15.62 to 2.000 µg/mL, was tested against Candida species, including *C. albicans* ATCC 90028, *C. glabrata* ATCC 2001, and *C. parapsilosis* ATCC 90018. Biofilms were formed in 96-well microplates, exposed to PA-2F, and irradiated with red LED (590 nm, 3.000 mW-3.0 J/cm^2) continuously for 10 minutes[2]. The biofilm inhibitory concentration (CBIM) was determined using the total plate count method. The experiments were performed in triplicate. The ESI-MS/MS analysis of the *P. citrinum*-4A14 extract led to the annotation of compounds: citrinin $C_{13}H_{13}O_5$, $[M-H]^-$ *m/z* 249.095, along with its analogs, decarboxycitrinin $C_{12}H_{13}O_3$, $[M-H]^-$ *m/z* 205.096, esclerotinin C $C_{12}H_{13}O_4$, $[M-H]^-$ *m/z* 221.093, citrinin hydrate $C_{13}H_{15}O_6$, $[M-H]^-$ *m/z* 267.111, citrinolactone B $C_{13}H_{13}O_4$, $[M+H]^+$ *m/z* 233.034, quinolactacin B1/B2 $C_{15}H_{17}N_2O_3$, $[M+H]^+$ *m/z* 273.022, the dipeptide threonylphenylalanine $C_{13}H_{17}N_2O_4$, $[M-H]^-$ *m/z* 265.094, and the chromones emodin $C_{15}H_9O_5$, $[M-H]^-$ *m/z* 269.069, and endocrocin $C_{16}H_9O_7$, $[M-H]^-$ *m/z* 313.069. Regarding the antifungal evaluation, citrinin without LED incorporation showed minimum inhibitory concentration (MIC) values above 2.000 µg/mL for the three selected *Candida* species. In contrast, the combination of citrinin with red LED light enabled a logarithmic reduction of CFU/mL of 3.26±0.16 for *C. albicans*, 2.90±0.09 for *C. glabrata*, and 2.50±0.05 for *C. parapsilosis*. Our results indicate that phototherapy using LED technology in combination with natural products can be a viable alternative for antimicrobial efficacy.

References

[1] Li, X. *et al*. Molecules, 28(17), 6371, 2023.

[2] Sanitá, P.V, *et al*. Lasers in Medical Science. 33, 709-717, 2018.

Acknowledgments

This research was supported by CAPES, CNPq and FAPESP.

Área: _____QPN_____

New acetogenins from *Porcelia macrocarpa* (Warm.) R.E. Fries fruit peels

Fernanda Thevenard (PG),[1] Ivanildo A. Brito (PG),[1] Érica Valadares de C. Levatti,[2] Andre G. Tempone (PQ),[2] João Henrique G. Lago (PQ).[1]

fernanda.thevenard@ufabc.edu.br

[1]*Centro de Ciências Naturais e Humanas, UFABC - SP;* [2]*Laboratório de Patofisiologia, Instituto Butantan - SP*

Palavras Chave: Porcelia macrocarpa, *Acetogeninas, Enyne, Enedyne,* Trypanosoma cruzi

Highlights

Thirteen acetogenins were isolated from *P. macrocarpa* fruit peel MeOH extract. ^{1}H and ^{13}C NMR analysis, along with LC/ESI-HRMS, allowed to identify four acetylenic compounds (**1-4**), four enyne conjugated compounds (**5-8**), three enedyne conjugated compounds (**11-13**) and two diyne compounds (**9** and **10**).

Abstract

Natural products and their derivatives are used in drug development, offering diverse scaffolds and presenting multitudes of biological activity.[1,2] The protozoan *Trypanosoma cruzi* causes Chagas disease, which although can be fatal, only possesses two pharmaceuticals for treatment: nifurtimox and benznidazole.[3] Fractionation of the MeOH extract of *P. macrocarpa* fruit peels led to an acetogenin-rich fraction. NMR data associated with LC/ESI-HRMS analysis showed that this fraction consisted of acetogenins **1** – **13** (Figure 1). Its ^{1}H NMR spectrum displayed signals at δ_H 1.43 (d, *J* = 6.5 Hz, H-5), 2.58 (dt, *J* = 10.0 and 4.8 Hz, H-2), 4.31 (dd, *J* = 4.8 and 3.0 Hz, H-3) and 4.44 (dq, *J* = 6.5 and 3.0 Hz, H-4), characteristic of a γ-lactone system. Additional signals at δ_H 5.82 (ddt, *J* = 16.9, 9.9 and 6.8 Hz) and 4.97 (m) were assigned to a terminal double bond and those at δ_H 6.04 (dt, *J* = 10.7 and 7.6 Hz) and 5.48 (t, *J* = 10.7 Hz) were indicative of an internal conjugated double bond. The ^{13}C NMR spectrum confirmed the proposal structure presenting signals referring to the lactone ring at δ_C 177.5 (C-1), 47.6 (C-2), 71.3 (C-3), 78.7 (C-4) and 13.7 (C-5) as well as those related to a terminal double bond at δ_C 139.2 and 114.5, terminal methyl group at δ_C 14.1, internal conjugated double bond at δ_C 137.6 (C-16') and 115.2 (C-15'), and triple bonds at δ_C 65.2 – 84.8. ESI-HRMS data allowed for identification of acetylenic compounds **1** ($C_{21}H_{35}O_3$, $[M+H]^+$ *m/z* 335.2583), **2** ($C_{21}H_{37}O_3$, $[M+H]^+$ *m/z* 337.2741), **3** ($C_{25}H_{39}O_3$, $[M+H]^+$ *m/z* 391.3228) and **4** ($C_{25}H_{41}O_3$, $[M+H]^+$ *m/z* 393.3361), where **1** and **3** possess the terminal double bond in the side chain. ESI-HRMS also allowed to confirm the structures of enyne conjugated compounds **5** ($C_{23}H_{36}O_3$, $[M+H]^+$ *m/z* 361.2740), **6** ($C_{23}H_{38}O_3$, $[M+H]^+$ *m/z* 363.2893), **7** ($C_{25}H_{40}O_3$, $[M+H]^+$ *m/z* 389.3054) and **8** ($C_{25}H_{42}O_3$, $[M+H]^+$ *m/z* 391.3210). Furthermore, compounds with two conjugated triple bonds were identified as **9** ($C_{21}H_3O_3$, $[M+H]^+$ *m/z* 349.2376) and **10** ($C_{23}H_{35}O_3$, $[M+H]^+$ *m/z* 359.2581). Enedyne conjugated compounds **11** ($C_{23}H_{41}O_3$, $[M+H]^+$ *m/z* 361.2744). **12** ($C_{25}H_{36}O_3$, $[M+H]^+$ *m/z* 385.2742) and **13** ($C_{25}H_{38}O_3$, $[M+H]^+$ *m/z* 387.2897) were also identified. All compounds displayed fragmentation at *m/z* 255.1968, indicating the position of the triple bond at C-11' of the side chain, similar to related acetogenins.[4] This is the first occurrence of compounds **1, 2, 9 – 11**.

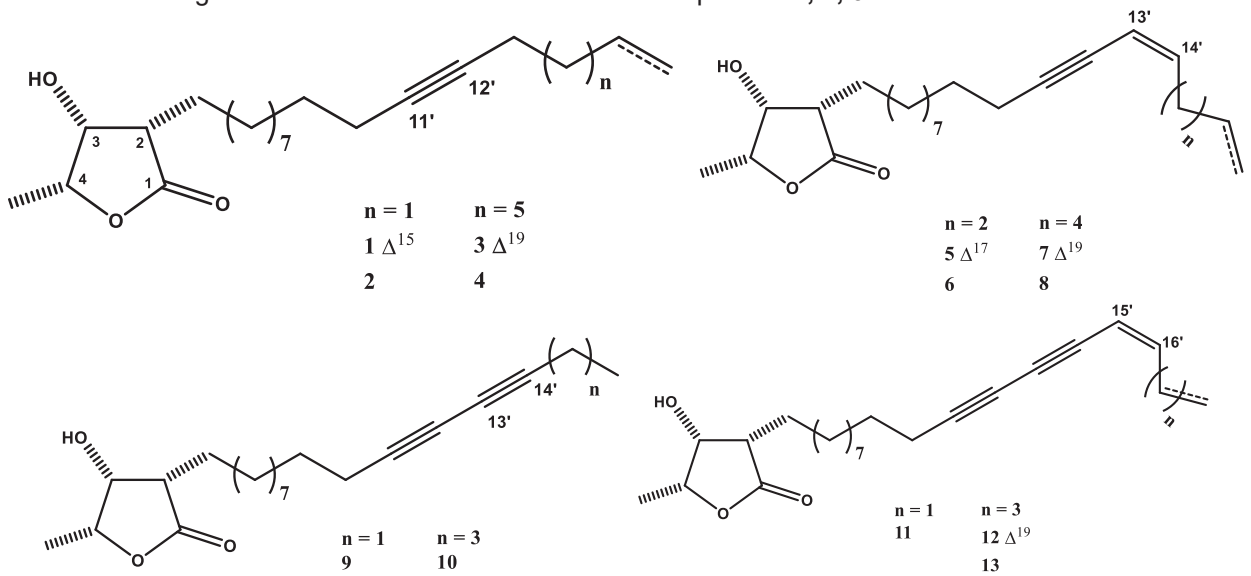


Figure 1 – Structures of acetogenins **1** - **13** from *Porcelia macrocarpa* fruit peels

References: 1.Calixto, J. B. *An. Acad. Bras. Ciênc.* **91** (2019). 2. Najmi, A. et al. *Molecules* **27**, 349 (2022). 3. Soeiro, M. D. N. C. *Mem. Inst. Oswaldo Cruz* **117** (2022). 4.Oliveira, E. A. *et al. J. Nat. Prod.* **82**, 1177–1182 (2019).

Acknowledgments

FAPESP (Process 2020/01221-4), CAPES, CNPq, CEM-UFABC, Instituto Butantan

Área: QPN

New iridoids from *Himatanthus articulatus* and disposable electrochemical biosensors of acetylcholinesterase to insect control.

João B. Fernandes (PQ),[1*] Artur da S. Cruz (PG),[1] Sean dos S. Araújo (PG),[1] Gabriele F. da Silva(IC),[1] Lulliana T. Franco (IC),[1] Isabelle Mercaldi (IC),[1] Dorai C. Periotto (PQ),[1] Ronaldo C. Faria (PQ),[1] Maria Fátima G. F. da Silva (PQ),[1] Moacir R. Forim (PQ).[1]

*djbf@ufscar.br

[1]Chemistry department, Federal University of Sao Carlos - UFSCar

Key words: Insect control, disposable biosensors, acetylcholinesterase, Iridoids.

Highlights

Extract of *H. articulatus* presented activity against *L. gongylophorus* and it presented three inedited iridoids. Electrochemical biosensors for acetylcholinesterase from leaf-cutter ants were developed.

Abstract

This communication presents the study of plant to control insect plague and the development of methodology to determine the insecticide action of natural products using biosensor of Acetylcholinesterase from *Atta sexdens.*

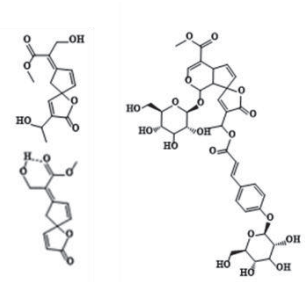


Figure 1. Iridoids isolated from *Himatanthus articulatus*.

Himatanthus articulatus is recognized in ethnobotany for its traditional use in combating diseases in the Amazon population. The antimicrobial capacity of the extract and compounds isolated from this plant was explored. The results revealed the effectiveness of the extract in controlling the fungus *Leucoagaricus gongylophorus*, culminating in the isolation of three structures previously undescribed in the literature for this species (Figure 1). The structures were determined using spectroscopic data, NMR, MS, IR and UV.

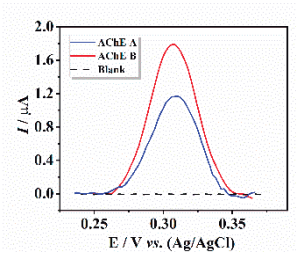


Figure 2 SWV response in the absence (dash line) and presence of 3.35 μmol L–1of ATChI using the Bio-AChE A (—) and B (—) in 10 mmol L–1 PBS solution pH 7.4.

Disposable electrochemical biosensors for acetylcholinesterase (AChE) from leaf-cutter ants was developed using printed carbon-based microelectrodes (SPCE) by screen printing, and then modified with some reaction steps such as the addition of polydiallyldimethylammonium (PDDA) and gold nanoparticles (AuNP) for the immobilization of acetylcholinesterase enzymes by covalent bonding. The identification of immobilization efficacy was detected through enzymatic activity, namely, the oxidation of the product thiocholine (TCh), which is the product of the reaction between the AChE enzyme and the substrate acetylthiocholine iodide (ATChI). The oxidation potential of the product is at Epa = +300 mV vs. Ag/AgCl, according to other studies (Cinti et al., 2017; Fiore et al., 2023). Figure 2 shows the peak currents for leafcutter ant enzymes recorded by Square Wave Voltammetry (SWV). This result confirms the effectiveness of enzymatic immobilization of both enzymes that are expressed by leaf-cutter ant organisms. These biosensors are potential tools for identifying natural compounds that can be applied as insecticides for insects plague control.

REFERENCES

Cinti, S., et al. (2017). Biosensors and Bioelectronics, 93, 46–51.
Fiore, L., et al. (2023). Sensors and Actuators B: Chemical, 379, 133258.

Acknowledgments

FAPESP, 2012/25299-6, CAPES, CNPq, 312366/2018-3.

Área: QPN

Nova γ-lactona com potencial anti-helmíntico de *Nectandra membranacea*

Vinicius C. Rocha* **(PG),[1,2] Rayssa A. Cajas (PG),[3] Josué de Moraes (PQ),[3] João Henrique G. Lago (PQ).[2]**

vc.rocha@unifesp.br

[1]Department of Chemistry, Federal University of São Paulo – UNIFESP; [2]Center of Natural and Human Sciences, Federal University of ABC; [3]Research Center for Neglected Diseases, University of Guarulhos – UnG.

Key-Words: *Schistosomiasis,* Schistosoma mansoni, Nectandra membranacea, *γ- lactone.*

Highlights

The hexane extract from branches of *Nectandra membranacea* afforded a fraction with potent anthelmintic activity, which showed to be composed by one new γ-lactone named membranaceolide.

Resumo

A esquistossomose é uma doença parasitária que afeta cerca de 250 milhões de pessoas, em especial em países subdesenvolvidos. Apesar do impacto social, existe um único fármaco disponível para o tratamento dessa doença, o praziquantel cuja eficácia é limitada às infecções iniciais. Desta forma, a busca de novos compostos com ação anti-helmíntica se faz necessária, sendo a biodiversidade florística brasileira uma fonte inesgotável de derivados bioativos. Assim, para realização do presente estudo, foi selecionada a espécie vegetal *Nectandra membranacea* (Lauraceae), cuja ação antiparasitária de extratos dos galhos foi descrita previamente na literatura[1], contudo sem o conhecimento do perfil fitoquímico. Assim, partindo de uma pequena quantidade de material vegetal (1 g) foi preparado o extrato hexânico dos galhos da espécie (100 mg), o qual mostrou atividade frente ao parasita *Schistosoma mansoni* em ensaios *in vitro*. Após fracionamento cromatográfico de parte do material (20 mg), foi obtida uma fração (5 mg) que causou 100% de morte de casais de vermes na fase adulta a 100 µg/mL nas primeiras 24 h do período de incubação. Em um período de 48 h de incubação, foi observado 100% de morte dos vermes a 50 e a 25 µg/mL para machos e fêmeas, respectivamente. Frente a esses resultados, a identificação estrutural dos compostos presentes na fração bioativa foi realizada via analise espectroscópica/espectrométrica. No espectro de RMN de ^{1}H, foram observados, dentre outros sinais, um simpleto largo em δ 5,24, atribuído à um hidrogênio ligado a carbono carbinólico (H-3), dois duplos-dupletos acoplados em δ 4,71 (*J* = 2,8 e 1,3 Hz) e 4,92 (*J* = 2,8 e 1,6 Hz), ambos atribuídos aos hidrogênios do grupo metilênico exocíclico (H-5) e de um triplo-dupleto em δ 7,06 (*J* = 7,9 e 2,2 Hz), atribuído ao hidrogênio metínico conjugado à carbonila (H-6), sugerindo a presença de um sistema β-hidróxi-γ-metileno-γ-lactônico. Além disso, foi sugerida a presença de uma ligação dupla na cadeia lateral alifática devido à presença de um multipleto em δ 5,33. A análise dos espectros de RMN de ^{13}C e de DEPT permitiu observar sinais atribuídos a C-3 em δ 66,2, aos carbonos do grupo metilênico exocíclico em δ 157,8 (C-4) e 91,1 (C-5), além de dois sinais referentes a carbonos sp^{2} em δ 127,4 (C-2) e 149,9 (C-6). Finalmente, foi possível observar a presença de um sinal referente ao carbono C-1 em δ 166,9, confirmando a presença da unidade γ-lactônica. Além disso, nesse espectro foram observados, além de um sinal intenso em δ 29,2, dois picos em δ 129,7 e 130,2 relativos a carbonos olefínicos, confirmando a presença de uma ligação dupla na cadeia lateral alifática. Visando determinar a extensão da cadeia lateral, a fração foi analisada por EM onde foram observados os íons $[M+H]^{+}$, $[M+Na]^{+}$, $[2M+H]^{+}$ em *m/z* 391, 413 e 781, respectivamente, compatíveis com a fórmula molecular $C_{25}H_{42}O_{3}$. Ainda nesse espectro, foi observado um fragmento em *m/z* 363, sugerindo que a ligação dupla se encontra entre C-22/C-23, de forma similar ao tambouranolóideo, uma γ-lactona isolada previamente de *Tambousissa* sp[2]. Desta forma, a estrutura do composto foi determinada como mebranaceolídeo (figura 1), inédito na literatura. Os resultados obtidos podem ser considerados promissores no que tange a ação anti-helmíntica desta substância visando realização de ensaios futuros para determinar a ação *in vivo*.

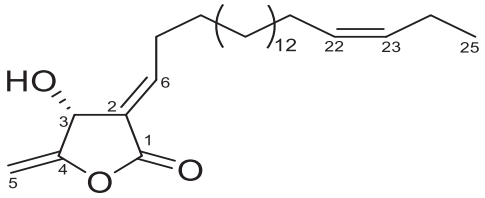


Figura 1: Formula estrutural do membranaceolídeo, uma nova γ-lactona de *N. membranacea* com ação anti-*S. mansoni*.

References: [1]Chinchilla, M. et al. *Rev Biol Trop*. **2012**, 60(2), 881-91. [2]Yoder, B.J. et al. *Nat. Prod. Res*. **2007** 21(1), 37-41

Agradecimentos

FAPESP, CNPq, CAPES, UFABC, UNIFESP, UnG

Área: QPN

Novos eudesmanolídeos isolados de *Mikania nummularia* DC.

Marina de Monroe Gonçalves (PG),[1*] Érica V. de Castro (PQ),[2] Rayssa A. Cajás (PG),[3] Roberto Baptista P. Almeida (PG),[4] André G. Tempone (PQ),[2] Josué de Moraes (PQ),[3] João Henrique G. Lago (PQ).[1]

marina.monroe@ufabc.edu.br

[1]Centro de Ciências Humanas e Naturais, UFABC; [2]Instituto Butantan; [3]Núcleo de Pesquisa em Doenças Negligenciadas, UNG ;[4]Departamento de Botânica – Instituto de Biociências, USP.

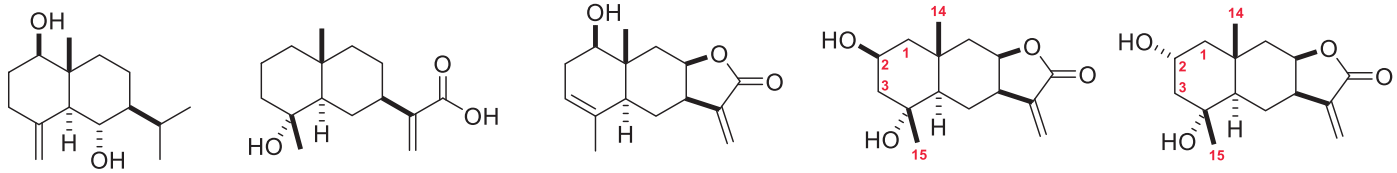
Palavras Chave: *Mikania nummularia, Sesquiterpenos, Eudesmanolídeo, Atividade antiparasitária.*

Highlights

New eudesmanolides isolated from *Mikania nummularia* DC. The hexane extract from *M. nummularia* showed activity against *T. cruzi* and *S. mansoni*. Chromatographic procedures resulted in the isolation of five sesquiterpenes, including two novel eudesmanolides.

Resumo

Visando a busca de novos protótipos naturais bioativos para doença de Chagas e para a esquistossomose, o extrato hexânico das partes aéreas de *Mikania nummularia* DC. (Asteraceae), até então inédita no ponto de vista fitoquímico, causou 100% de morte (a 200 μg/mL) das formas tripomastigotas de *Trypanosoma cruzi* e de vermes adultos de *Schistosoma mansoni*. Frente a esse resultado, tal extrato foi submetido a fracionamento cromatográfico biomonitorado o que resultou, até o momento, no isolamento de cinco compostos (**1** – **5**). Após análises de espectros de RMN, incluindo técnicas 2D e EM de alta resolução, foi possível a identificação de três sesquiterpenos de esqueleto eudesmano conhecidos: 4(15)-eudesmano-1β,6α-diol (**1**)[1], ácido ilícico (**2**)[2] e isoivangustina (**3**)[3]. Análises comparativas entre os espectros de RMN de ^{1}H, ^{13}C e HSQC dos compostos **4** e **5** evidenciaram a presença sinais característicos comuns para ambos, tais como sinais indicativos da presença de carbonos sp^{2} (δ 142,0/120,5 e 141,8/120,7), uma carbonila (δ 170,7 e 170,6), três carbonos carbinólicos (δ 76,8/ 71,3/68,0 e 76,7/72,5/64,9), dois grupos metílicos (δ 25,1/21,8 e 23,8/20,8), quatro carbonos metilênicos (δ 48,5/ 46,5/45,3/24,7 e 52,3/50,5/45,0/24,7), dois carbonos metínicos (δ 51,1/41,3 e 50,8/41,3) e um carbono quaternário (δ 33,3 e 33,2), sugerindo a ocorrência de eudesmanolídeos[3]. A diferença fundamental entre os espectros de RMN de ^{1}H de ambos os compostos foi observada para os sinais dos hidrogênios H-2 em δ 4,30 (quint, *J* = 3,4 Hz) para **4** e em δ 3,82 (tt,*J* = 11,5 e 4,1 Hz) para **5.** Tal variação foi também observada nos espectros de RMN de ^{13}C, onde os sinais referentes a C-2 foram detectados em δ 68,0 e em δ 64,9 para os compostos **4** e **5**, respectivamente, o que permitiu inferir que os compostos são diastereoisômeros. A análise dos espectros NOESY dos compostos **4** e **5** contribuiu para definição da estereoquímica relativa. Como principal diferença, foi possível observar a correlação entre os sinais de H-2 com H-15, H-14, H-3 e H-1 para o composto **5**, enquanto para o composto **4** foi observado somente a correlação entre H-3 e H-1. Finalmente, os dados de EM de alta resolução confirmaram a fórmula molecular $C_{15}H_{22}O_4$ para ambos compostos devido a presença de íons $[M + Na]^+$ em *m/z* 289,1453 e 289,1421 para **4** e **5**, respectivamente. Frente ao exposto, as estruturas dos compostos **4** e **5** foram elucidadas e os mesmos nomeados nummulariolídeo A e B, respectivamente.



1 **2** **3** **4** **5**

[1]ALBARRACIN, L. T. et al., **Biochemical Systematics and Ecology**, 74, 60 – 62, 2017. [2]GUILHON, MÜLLER. **Phytochemistry,** 47, 227-229, 1998. [3]NAGASAMPAGI, B. A. et al., **Phytochemistry**, 20, 2034-2036, 1981.

Agradecimentos

UFABC, FAPESP, CNPq e CAPES

Área: QPN

Optimization of ultrasound assisted extraction of bioactive compounds from *Psidium guineense* fruits using response surface methodology

Dayenne A. A. de Souza (PG)[1]*, Camila F. B. Albuquerque (PG)[2], Pablo Luis B. Figueiredo (PQ)[3], Claudia Quintino Rocha (PQ)[4], Massuo Kato (PQ)[5], Renan Campos Chisté (PQ)[2], Joyce Kelly R. da Silva (PQ)[1,2]

joycekellys@ufpa.br; dayenne@ufpa.br

[1]Programa de Pós-Graduação em Química, UFPA; [2] Programa de Pós-Graduação em Biotecnologia, UFPA; [3] Programa de Pós-Graduação em Ciências Farmacêuticas, UFPA; [4] Programa de Pós-Graduação em Química, UFMA; [5] Instituto de Química, USP.

Keywords: *Myrtaceae; phenolic compounds; antioxidant activity; process optimization; caffeoyl-quinic acid.*

Highlights

The experimental design made it possible to obtain an extract from araçá fruits (*Psidium guineense* Sw.) rich in total phenolic compounds and with high antioxidant activity. The results show the viability of the use in the industrial process for producing bioactive compounds with cosmetic applications.

Resumo/Abstract

The Araçá (*Psidium guineense* Sw.) is a non-native Myrtaceae species in Brazil that is commonly found in the Pará state. It is an important fruit for the local economy and traditional medicine as it possesses medicinal properties and is used to treat inflammation and gastric disorders[1]. The fruit contains phenolic compounds that have several applications in different sectors, particularly in cosmetics. The fruits were collected in Belém, cleaned, cut and frozen, and were subsequently freeze-dried for 72 hours. In this study, the ultrasound-assisted extraction method was optimized using the central composite design 2^3 to extract these bioactive compounds from the fruit (pulp, peel, and seeds). The study evaluated the effect of different factors, including ethanol concentration (%), solid-liquid ratio (SLR), and extraction time (min), on the total phenolics content (TPC) and antioxidant activity (DPPH, % radical inhibition) according to matrix of table 1. A polynomial model was obtained from linear regression, considered predictive and significant at 95% of confidence ($p< 0.05$). The optimized parameters were found to be EtOH 25%, SLR 1:5, and 10 min extraction time, resulting in 304.6 ±7.7 mg EAG/g of TPC and 59.5 ±1.7% of DPPH inhibition. The optimized extract also displayed inhibition of β-carotene lipid peroxidation, with an IC_{50} value of 20.9 µg/mL and a good sun protection factor (SPF 16.0 ± 1.0). Furthermore, the optimized extract contained total flavonoids and carotenoids, with values of 309.2 ± 17.7 mg QE/g, 108.2 ± 11.1 µg/g, and 20.9 µg/mL, respectively. The analysis of the optimized extract by HPLC-DAD-MS identified several bioactive compounds, including quinic acid, ellagic acid, valoneic acid dilactone, and caffeoyl-quinic acid. The significant antioxidant activity was found to be correlated with these bioactive compounds[2], revealing the potential of Araçá fruits for use in cosmetics.

Table 1- CCD matrix and average values TPC and % DPPH inhibition of the *Psidium guineense* extract

Experiment	EtOH (%)	RSL	T (min)	TPC (mg GAE.g^{-1})	DPPH (%I)
1	3:4 (+1)	1:5 (-1)	10 (-1)	270.28 ±6.07^{a}	58.74 ±2.34^{a,b}
2	1:4 (-1)	1:5 (-1)	10 (-1)	262.18 ±11.43^{a,b}	74.42 ±1.70^{c}
3	3:4 (+1)	1:15 (+1)	10 (-1)	108.85 ±7.19^{c}	43.87 ±1.46^{d,e,f}
4	1:4 (-1)	1:15 (+1)	10 (-1)	113.79 ±9.85^{c}	39.77 ±3.58^{d,f}
5	3:4 (+1)	1:5 (-1)	30 (+1)	304.56 ±7.71^{d}	59.49 ±1.69^{a,g}
6	1:4 (-1)	1:5 (-1)	30 (+1)	237.75 ±8.25^{b}	64.80 ±5.72^{a,c}
7	3:4 (+1)	1:15 (+1)	30 (+1)	79.63 ±4.61^{e}	34.03 ±2.45^{f}
8	1:4 (-1)	1:15 (+1)	30 (+1)	134.35 ±10.28^{c}	47.69 ±2.35^{b,d,e}
9	1:1 (0)	1:10 (0)	20 (0)	200.00 ±10.17^{f}	52.31 ±2.03^{b,e,g}
10	1:1 (0)	1:10 (0)	20 (0)	175.29 ±13.54^{f}	53.76 ±3.39^{a,b}
11	1:1 (0)	1:10 (0)	20 (0)	226.12 ±10.61^{a,b}	55.34 ±9.49^{a,e}

[1]Nascimento, K. F., et al. Antioxidant, anti-inflammatory, antiproliferative and antimycobacterial activities of the essential oil of *Psidium guineense* Sw. and spathulenol. Journal of Ethnopharmacology, 210, 351–358. 2018.
[2]Senanayake, C. M., et al. Phenolic extracts of the leaves of *Psidium guineense* Sw. improve the shelf life of sunflower oil and baked cake and antioxidant status of Wistar rats. Journal of Food Biochemistry, e12632. 2018.

Agradecimentos/Acknowledgments

FAPESPA for the financial support.

Área: QPN

Other Compounds and Antinociceptive Activity of *Galianthe matogrossiana*

Mariana de C.C. Pinto (IC),[1] Mariele R.S. Gonçalves (PG),[1*] Mário G. de Carvalho (PQ),[1] Bruno G. Marinho (PQ),[2] Isabela M. da Costa (IC),[2] Raimundo Braz Filho (PQ).[1,3]

marianacarvalhocosta.trabalhos@gmail.com; mariele.rondon@gmail.com

[1]Institute of Chemistry, Department of Organic Chemistry, Federal Rural University of Rio de Janeiro (UFRRJ), Rodovia BR 465, Km 07, 23890-000 Seropédica, RJ, Brazil; [2] Department of Physiological Sciences, Federal Rural University of Rio de Janeiro (UFRRJ), Rodovia BR 465, Km 07, 23890-000 Seropédica, RJ, Brazi; [3] LCQUI-CCT- North Fluminense State University Darcy Ribeiro (UENF), 28013-600 Campos dos Goytacazes-RJ – Brazil

Palavras-Chave: *Galianthe matogrossiana, Rubiaceae, Antinociceptive activity, Special metabolites.*

Highlights

The roots and aerial parts of Galianthe matogrossiana demonstrate remarkable antinociceptive activity, with some fractions standing out, composed of relevant triterpenoids.

Resumo/Abstract

The roots and aerial parts of *Galianthe matogrossiana* (GM), an endemic species in Brazil, were collected at Mirante do Geodésico in Chapada dos Guimarães-MT.[1] Identification was carried out by Vali Joana Pott (UFMS), with confirmation by specialist Elza L. Cabral (UNNE), and the voucher specimen was deposited in the CGMS herbarium at the Federal University of Mato Grosso do Sul, under registration 79574. The botanical material, after drying and pulverization, underwent methanol extraction followed by liquid-liquid partition, resulting in hexane (FH), dichloromethane (FD), ethyl acetate (FA), and hydroalcoholic residue (RH) fractions from each part of the plant. The antinociceptive activity of FH, FD, FA, RH fractions, and the methanolic extract was evaluated through the abdominal writhing test in mice induced by acetic acid. In the experimental model, one hour before intraperitoneal administration of 0.8% (v/v) acetic acid in saline solution, the animals were orally treated with the samples to be evaluated. After 30 minutes of acetic acid injection, the total number of writhes was recorded, quantifying the effectiveness of the samples in reducing such behaviors. According to the data described in Figure 1, it is highlighted that, except for FH from roots, all tested fractions and extracts exhibited low numbers of writhes, indicating a notable antinociceptive effect. FD from roots and aerial parts of GM stood out as a more effective alternative in acute pain models in mice, showing fewer numbers of writhes compared to other samples. The phytochemical study of FH and FD from roots resulted in the isolation and identification of ten constituents, including steroids, triterpene acids, vanillic acid, *p*-hydroxybenzoic acid, scopoletin, and umbellata H.[2] In this summary, we disclose other metabolites, isolated from these respective fractions, which were characterized by ^{1}H and ^{13}C NMR, as well as MS. These metabolites were determined as a mixture of glycosylated steroids, *β*-sitosterol and stigmasterol, the triterpene 3-*O*-acetyl-ursolic acid in combination with acetylated oleanolic acid, a mixture of triterpenes, with the main one being pomolic acid 3*β*-acetate, a lupeol, along with a mixture of triterpenoids derived *α*- and *β*-amyrin. Emphasis is placed on the presence of pentacyclic triterpenes ursanes and oleananes in FD from roots, which may justify the significant activity observed in this fraction, as well as in other GM samples, given their known antitumor and anti-inflammatory activities.[3,4] These unprecedented findings for the species, whose study is ongoing, underscore the continued need for biochemical research. Additionally contribute to the chemical and medicinal potential attributed to species in the genus.[2,5]

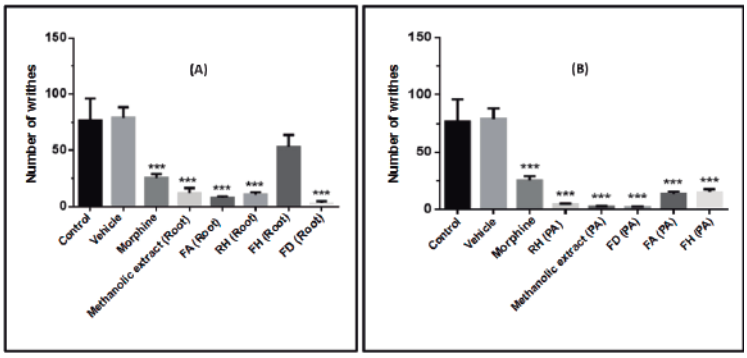


FIGURE 1. Effect of extracts and fractions from the roots (**A**) and aerial parts (**B**) of *Galianthe matogrossiana* on acetic acid-induced abdominal writhing in mice.

References

1. Cabral, E.L. of new species of *Galianthe* (rubiaceae) for brazil. Bonplandia. 13, 15-19, 2004.
2. Gonçalves, M.R. S., et al. Chemical Study of *Galiante matogrossiana: Prospection of total phenols and Flavonoids, and Some compounds identifiation. 9th BCNP, Fed. Univ. of Bahia, october 24 to 27, 2023.*
3. Dalla Vechia L, et al. Derivados oleananos e ursanos e sua importância na descoberta de novos fármacos com atividade antitumoral, anti-inflamatória e antioxidante. Quím Nova.;32(5):1245–52, 2009.
4. Tsai, S.-J.; Yin, M.-C.; J. Food Sci. 2008, 73, 174.
5. Mentz, L.A.; et al. On the medicinal flora of Rio Grande do Sul: notes on the work of D'Avila (1910). Pharmacy Notebook. v. 13, no. 1, p. 25-48, 1997.

Agradecimentos/Acknowledgments

The CAPES, CNPq and FAPERJ for research support and granted scholarship.

Área: QPN

Phytochemical Investigation of Zanthoxylum rhoifolium (Rutaceae): Isolation and Characterization of Dihydrochelerythrine and Lupeol

Matheus Vinicius Natividade Belém (PG),[1*] Igor Ramón de Souza Graça (PG),[1] Felipe Moura Araujo da Silva (PQ),[2] Weider Henrique Pinheiro Paz (PQ),[3] Thalisson Amorin de Souza (PG),[4] Josean Fechine Tavares (PQ),[4] Hector Henrique Ferreira Koolen (PQ)[3], Waldireny Rocha Gomes (PQ)[5].
matheusbelem248@gmail.com

[1]Departamento de Química, (UFAM), Manaus-Am; [2] Central Analítica, (UFAM), Manaus-AM; [3]Universidade do Estado do Amazonas, (UEA), Manaus-Am; [4]Laboratório Multiusuário de Caracterização e analises, (UFPB), João Pessoa-PB; [5]Faculdade de Ciências Farmacêutica, (UFAM), Manaus-AM

Palavras Chave:*(Tinguaciba, Metabolites, Isolation, Alkaloid, Triterpene).*

Highlights

1. The study aimed to isolate and identify Z. rhoifolium metabolites. **2.** Dihydrochelerythrine and lupeol were isolated from hexanic root extract. **3.** Pharmacological properties include antimicrobial, antinociceptive, and anti-inflammatory activities. **4.** Further research necessary to fully explore the pharmacological potential of these metabolites.

Resumo/Abstract

Zanthoxylum rhoifolium Lam (Rutaceae) is a species popularly known as mamica-de-cadela, limãozinho or tinguaciba[1] and its distribution covers the whole of South America, mainly found in the cerrado, Atlantic Forest and Amazon regions of Brazil[1]. The species of the genus *Zanthoxylum* contain alkaloids, phenolic compounds (lignans, coumarins and flavonoids), steroids and terpenes distributed in roots, stems, branches and leaves[2]. In this context, the importance of carrying out phytochemical investigations to isolate new metabolites is evident, considering the extensive exploitation of the species from both a chemical and pharmacological point of view. The aim of this study was to isolate and identify the metabolites of *Z. rhoifolium*. The hexanic extract of roots (11.5 g) obtained by cold maceration was subjected to fractionation by Column Chromatography (CC) and Preparative Thin Layer Chromatography (PTLC). The structural elucidation of isolated substances was carried out using Nuclear Magnetic Resonance spectroscopy (NMR ^{1}H and ^{13}C-1D/2D) and Mass Spectrometry (MS). Two substances were isolated: dihydrochelerythrine (**1**), a Benzophenanthridine alkaloid, and the triterpene lupeol (**2**) (Figure 1), which have already been reported in the species. The pharmacological properties of both metabolites are described, highlighting the antimicrobial and antinociceptive activity[3 e 4], for dihydrochelerythrine, and the antiprotozoal, anti-inflammatory, antitumor and antimicrobial activity[5] for lupeol. Therefore, there is a need to continue the research to explore these metabolites in greater depth, with a view to their pharmacological properties.

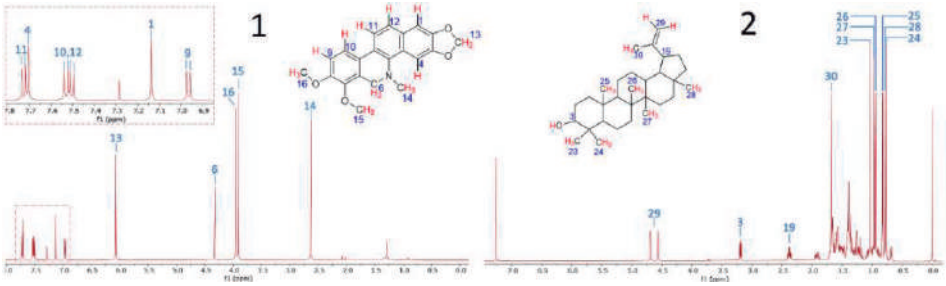


Figure 1. Isolated and identified compounds from root of *Zanthoxylum rhoifolium* present in hexane extract.

References

[1] CARVALHO, P.E.R. **Espécies arbóreas brasileiras**. 2014.; **[2]** DIÉGUEZ, R. et al**. Potencialidad del género Zanthoxylum como fuente de agentes con actividad biológica**. Acta Farmacéutica Bonaerense, v. 23, n. 2, p. 243-251, 2004.; **[3]** WEI, W. et al. **A review on classification and biological activities of alkaloids from the genus Zanthoxylum species**. Mini reviews in medicinal chemistry, v. 21, n. 3, p. 336-361, 2021.; **[4]** YAO, J. et al. **Antiparasitic efficacy of dihydrosanguinarine and dihydrochelerythrine from Macleaya microcarpa against Ichthyophthirius multifiliis in richadsin (Squaliobarbus curriculus).** Veterinary Parasitology, v. 183, n. 1-2, p. 8-13, 2011.; **[5]** GALLO, M. et al. **biological activities of lupeol**. Int. J. Biomed. Pharm. Sci, v. 3, n. 1, p. 46-66, 2009.

Agradecimentos/Acknowledgments

The authors are grateful to CAPES, CNPq, FAPEAM, FINEP for financial support, CA/CAM/UFAM for NMR and MS analysis and Graduate Program in Biotechnology and Natural Resources of the Amazon (MBT-UEA) for physical support.

Área: QPN

Phytochemical Study of *Annona Squamosa* L. and Biological Activities of its constituints.

Dianne D. Formoso (PG)[1*], Chrystiaine H. C. de Matos (PG)[1]; Jessica C. Amaral (PG)[1], Danielle Fernandes da Silva (PG)[1], Maria F. F. G. da Silva (PQ)[1], João B. Fernandes (PQ)[1].

chrystiainecampos@gmail.com; didianne459@gmail.com

[1] *Laboratório de Produtos Naturais, Departamento de Química, UFSCar.*

Palavras Chave: *Annonaceous acetogenins, RMN, Annonaceae, Antitumor agent.*

Highlights

The text describes the research on the phytochemical composition of extracts of the plant *Annona squamosa* L. of the Annonaceae family, which is recognized as a promising source of metabolites with potential therapeutic and medicinal functions. In 1982, it was reported the discovery of a new class of secondary metabolites in plants, known as Annonaceae acetogenins (ACGs), which currently comprises about 430 naturally occurring compounds found mainly in plants of this family.

Resumo/Abstract

Annona squamosa L. belongs to the Annonaceae family, which is a promising natural source of metabolites with potential therapeutic and medicinal functions. In 1982, the first member of a new class of secondary metabolites in plants was reported, which currently comprises a group of 430 natural compounds found almost exclusively in plants of the Annonaceae, called Annonaceae acetogenins (ACGs). The present work aimed to investigate the phytochemical composition of *A. squamosa* leaf extracts through bioguided studies in the search for biologically active substances. Ethyl acetate extracts were obtained from dried leaves by percolation. To evaluate the insecticidal potential, the extract was incorporated into the insects diet at a concentration of 1.0 %. In addition, negative controls were performed, in which the extracts were not present, and a positive control (Corteva). Each treatment was conducted with a total of 50 caterpillars in quintuplicates, that is, 10 caterpillars per replicate, kept in screw test tubes. The tubes were then stored at a temperature of 25 ± 2 °C, relative humidity of 60 ± 5 % and a 12-hour photophase. Assessments were carried out every 24 hours throughout the insect's development until the emergence of adults, evaluating mortality (%). In this study, three acetogenins were isolated from the leaves of *A. squamosa* L. 1D and 2D NMR analyzes carried out confirmed the presence of three isomers acetogenins called Squamostins[1]; containing a smaller carbon chain between the lactone and the first tetrahydrofuran ring. Isomers are differentiated by the position and stereochemistry of their hydroxyl groups. The results showed a monoisotopic mass of m/z 639.4818 $[M+H]^+$, corresponding to a molecular formula $C_{37}H_{67}O_8^+$ and a mass error of 1.02 ppm for the acetogenin isomers. The insecticidal activities of ethyl acetate extracts from *A. squamosa* leaves against *Spodoptera frugiperda* were highly lethal for early-stage caterpillars, resulting in almost 100.0% mortality in the first 24 hours after application of the treatments.

Agradecimentos/Acknowledgments

This work was supported by grants from Capes /INCT.

[1]FUJIMOTO, Yoshinori et al. Annonaceous acetogenins from the seeds of *Annona squamosa*. Non-adjacent bis-tetrahydrofuranic acetogenins. **Chemical and Pharmaceutical Bulletin**, v. 42, n. 6, p. 1175-1184, 1994.

Área: QPN

Phytochemical study of the aerial parts from *Trigynaea axiliflora* (ANNONACEAE)

Natyele R. Fonseca (IC)[1], Victória S. Mafra (IC)[1], Diogo F. G. Andrade (PG)[2], Adriana Q. Lobão (PQ)[3], Alessandra L. Valverde (PQ)[4], Leandro M. Rocha (PQ)[2], Lucas S. Abreu (PQ)[1]
natyelerodrigues@id.uff.br

[1]*Laboratório de Química de Produtos Naturais, Universidade Federal Fluminense, Niterói, RJ, Brasil.*
[2] *Laboratório de Tecnologia de Produtos Naturais, Universidade Federal Fluminense, Niterói, RJ, Brasil.*
[3] *Instituto de Biologia, Departamento de Biologia Geral, Universidade Federal Fluminense, Niterói, RJ, Brasil.*
[4] *LaproMar, Universidade Federal Fluminense, Niterói, RJ, Brasil.*

Key words*: Chromatograpy, Natural Products, Alkaloids, Nuclear Magnetic Resonance (NMR), Trigynea axiliflora*

Highlights

The ethanolic extract of the leaves from *T. axiliflora* was subjected to a classic phytochemical study and led to the isolation of xylopine, which is being described for the first time in the species.

Resumo/Abstract

Natural products, including those from plants, offer a wide range of chemical structures that may be used for drug development. In this context, where Brazil has a rich biodiversity, this study searches for natural products with a focus on secondary metabolites, including alkaloids, terpenoids, flavonoids and others, which have pharmacological potential and a wide range of applications.[1] Therefore, the focus was directed towards the Annonaceae family, which comprises numerous species found in various brazilian biomes, such as the Atlantic Forest.[2] Thus, the objective of this work is the classic phytochemical study of the leaves from *Trigyneae axiliflora.* The species *T. axiliflora* was chosen as the object of study due to the absence of phytochemical studies reported in the literature. The leaves of this species were subjected to ethanolic extraction and the extract was partitioned with the following solvents: hexane, chloroform, ethyl acetate and butanol. A phytochemical screening was conducted, and a positive indication for the presence of alkaloids was observed in the chloroform and butanol partitions, followed by analysis through thin-layer chromatography. The chloroform fraction was selected for fractionation due to its fluorescence and positive test for dragendorff. It was subjected to vacuum liquid chromatography (VLC) and separation by open column chromatography. This process led to the detection of yellowish crystals, which were purified by solvent washing and analyzed using Nuclear Magnetic Resonance (NMR) ^{1}H. The chemical shifts obtained in the spectrum confirmed the isolation of an aporphinic alkaloid identified as xylopine(1). Despite identifying a previously reported substance with biological potential, it was noted that this was the first chemotaxonomic study of the compound.[3] In view of the results obtained, it is important to continue this study in order to contribute to the enrichment of the chemistry of the genus *Trigyneae* and the search for new bioactive substances.

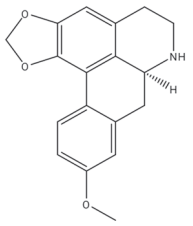


Figure 1: Xylopine's chemical structure

[1]QUEIROZ, Emerson et al. Princípios ativos de plantas superiores. 2. ed. São Carlos: Edufscar, 2015.232 p.
[2]LOPES, J. D. C., & Mello-Silva, R. (2014). Diversidade e caracterização das Annonaceae do Brasil. *Revista Brasileira de Fruticultura*, *36*, 125-131.
[3]Figueiredo, F. F. (2019). Constituintes químicos e avaliação da atividade biológica de Xylopia frutescens Aubl.(Annonaceae).

Agradecimentos/Acknowledgments

We deeply thank the Programa Institucional de Bolsas de Iniciação Científica (PIBIC-UFF), do Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPQ) e da Fundação Carlos Chagas Filho de Amparo à Pesquisa do Estado do Rio de Janeiro (FAPERJ).

Área: QPN

Piperine as potential bioinsecticide in the *Dalbulus maidis* control

André Vaz de Souza (IC)[1], Ian Raffaello Gallo Godoi (PG)[2], Aniele Beatriz Dias (PG)[2], Leonardo Garcia Biazotti (IC)[3], Rodrigo Neves Marques (PQ)[3], Tatiana Santana Ribeiro (PQ)[1].

ian.gallo@estudante.ufscar.br

[1]Departamento de Ciências da Natureza, Matemática e Educação - DCNME, UFSCar - campus Araras; [2]Programa de Pós-Graduação em Ciência dos Materiais - PPGCM, UFSCar - campus Sorocaba; [3]Departamento de Biotecnologia e Produção Vegetal e Animal, UFSCar - campus Araras

Keywords: *"Dalbulus maidis", Piperine, Bioinsecticide, Maize, Soxhlet extraction.*

Highlights

Piperina showed positive results in the control of the *Dalbulus maidis*, revealing potential application as a natural insecticide, minimizing environmental impacts.

Abstract

The agribusiness is one of the major activities of the national economy. Maize is the second most cultivated grain, being used mainly in food and biofuels, however corn cultivation faces problems of pests that affect its production and quality, among them is the corn leafhopper (*Dalbulus maidis*)(DeLong & Wolcott) [1]. Insecticides are used to prevent the proliferation of this insect, these products are chemical substances used to kill, attract and repel insects from monocultures [2]. Currently, the main insecticides used for pest control in maize plantations are of synthetic origin, their use is growing with the development of new monocultures with consumption reaching amounts in the order of billions of dollars [2; 3]. This fact is worrying, since the chemical compounds present in synthetic insecticides can cause irreparable damage to the environment [2]. To minimize environmental impacts natural compounds can be used as an alternative to synthetic pesticides, due to their lower toxicity [3]. One of this substances is piperine, an alkaloid with amide function that has several biological activities described in the literature, among them, bioinsecticidal action, which makes it an interesting candidate for the development of natural insecticides [4].The objective of this project was to evaluate the bioinsecticidal action of piperine on the corn leafhopper (*Dalbulus maidis*). The Soxhlet method was used to extract piperine from black pepper (*Piper nigrum*), which was supplied by INCAPER-ES. The pepper stayed in reflux for 8 hours in ethanolic solution. To purify the substance, a recrystallization process was carried out in ethanol and the sample was characterized by FT-IR, M.P. and ^{1}H NMR. For the biological tests, maize seedlings (V2-V3) were sprayed with 2 mL of four different solutions: i) 99.8% ethanol, ii) 1.0% (w/v) piperine , iii) 2.5% (w/v) piperine, and iv) 5.0% (w/v) piperine, and subsequently, after the evaporation of ethanol, the seedlings were placed in traps and 5 corn leafhopper adults (7-9 days) were transferred to each bottle. The experiment included a control (untreated) without the bioinsecticide and three treatments with the bioinsecticide and a total of five replicates each. The tests were monitored every 24 hours during 5 days. After the monitoring period, a total of 11 corn leafhoppers were found dead, 7 for the 5.0% (w/v) solution and 4 leafhoppers for the 2.5% (w/v) solution. Piperine showed bioinsecticidal effect for corn leafhopper control, furthermore, no adverse effects were observed on plant development. Thus, this compound presents potential for corn leafhopper control and can be applied in future field tests.

References:

[1] GUARALDO, M. C. Brasil pode superar a Índia na produção de grãos em 2023. **EMBRAPA**. Disponível em:<https://www.embrapa.br/busca-de-noticias/-/noticia/73611968/brasil-pode-superar-a-india-em-2023-na-producao-de-graos>. Acesso em: 01 de jul. 2023.

[2] DE MOURA, V. M.; SCHLICHTING, C. L. R. Alcalóides, Piretróides e Rotenóides: inseticidas naturais como uma alternativa ecológica sustentável. **Revista UNINGÁ**, Maringá – PR, n.13, p.37- 44, jul./set. 2007.

[3] RAMOS, A**. Efeito de Maize Bush Stunt Phytoplasma na sobrevivência de Dalbulus maidis (DeLong & Wolcott) (Hemiptera: Cicadellidae) sobre o milho e plantas infestantes**. Dissertação de Mestrado. ESALQ, Piracicaba. 2016.

[4] OKWUTE, S. K.; EGHAREVBA, H. O.. Piperine-type amides: review of the chemical and biological characteristics. **International Journal of Chemistry**, v. 5, n. 3, p. 99, 2013.

Acknowledgments

PPGCM Programa de Pós-Graduação Ciência dos Materiais · FAPESP · UFSCar Araras Lab.COMAM · CNPq · CAPES

Área: QPN

Potential of microemulsion of essential oil of *Pectis brevipedunculata* (Gardner) Sch.Bip. against *L.* (L.) *amazonensis* promastigotes and RAW 264.7 cells

Auxiliadora C. C. Barata Lopes (PG),[1*] Marcos B. P. Camara (PQ),[1] Gláucia L. N. Lopes (PG),[4] Matheus O. do Nascimento (PG),[4] Júlia K. A. M. Xavier (PQ),[3] Cáritas de J. S. Mendonça (PQ),[3] André L. M. Carvalho (PQ),[4] Cláudia Q. da Rocha (PQ),[1,3]

rocha.claudia@ufma.br; auxiliadora.lopes@discente.ufma.br

[1]Programa de Pós-Graduação em Biodiversidade e Biotecnologia da Rede BIONORTE, UFMA; [3]Programa de Pós-Graduação em Química, UFMA; [4]Programa de Pós-Graduação em Ciências Farmacêuticas, UFPI

Keywords: *Asteraceae, Biotechnology, Formulation, L. (L.) amazonensis, Macrophages, Promastigote.*

Highlights

Pectis brevipedunculata EO is active against *L.* (L.) *amazonensis*;
Pectis brevipedunculata EO microemulsion (IC_{50}:0.93µg/mL) is more efficient than the drug used (Pentamidine, IC_{50}:4µg/mL).

Resumo/Abstract

Pectis brevipedunculata (Gardner) Sch.Bip., popularly known in Brazil as alecrim do campo, is an herb from the Asteraceae family frequently consumed in the form of tea because it has a calming effect. This species contains components, such as neral and geranial, which have diverse biological activities, such as leishmanicidal. The goal of this study was to chemically characterize the essential oil (EO) obtained from *P. brevipedunculata* (EO-PB) through hydrodistillation and microemulsion formulated with EO (ME-PB), Tween 80 and Transcutol P, in addition to evaluating the leishmanicidal potential against *Leishmania* (L.) *amazonensis* promastigotes and cytotoxicity against RAW 264.7 cells. EO-PB and ME-PB were analyzed by gas chromatography coupled to a mass spectrometer (GC/MS). Among the compounds identified, monoterpene hydrocarbons stand out. α-pinene and limonene, followed by neral and geranial, are the major compounds of EO-PB and ME-PB. EO-PB presented an inhibitory concentration (IC_{50}) of 20 µg/mL and ME PB of 0.93 µg/mL, indicating that the leishmanicidal activity of ME-PB is approximately 20 times greater compared to EO-PB. This indicated that the incorporation of EO into the microemulsion resulted in the optimization of biological activity. ME-PB was also more efficient compared to Pentamidine, the reference drug used as a positive control (IC_{50}: 4 µg/mL). EO and ME-PB are considered active against the investigated parasite, as they have IC_{50} values below 100 µg/mL. Selectivity indices indicate that ME-PB is more selective for parasite inhibition. Thus, ME-PB may constitute an alternative for the treatment of leishmaniasis, since the inhibitory concentration (IC_{50}) for promastigotes was lower than that considered toxic for cells (CC_{50}).

Referências:

Adams, R.P. *Identification of Essential Oil Components by Gas Chromatography/Mass Spectrometry*, 4th ed.; Allured Publishing Corporation: Carol Stream, IL, USA, 2007.
Mota, E.F.; Rosario, D.M.; Veiga, A.S.S.; Brasil, D.D.S.B.; Silveira, F.T.; Dolabela, M.F. Biological activities of Croton palanostigma Klotzsch. *Pharmacogn. Mag.* **2016**, 12, S96–S101. https://doi.org/10.4103/0973-1296.176109.
Reis, A.S.; Rios, C.E.P.; Melo, L.P.; Costa, G.C.; Silva, L.A.; Patrício, F.J.B.; Amaral, F.M.M.; Nascimento, F.R.F. Atividade leishmanicida in vitro de frações do extrato hidroalcoólico das folhas de *Chenopodium ambrosioides* L. *Rev. Ciênc. Saúde* **2012**, *14*, 119–126.
Tempone, A.G.; Borborema, S.E.T.; Andrade, H.F.; Gualda, N.C.A.; Yogi, Á.; Carvalho, C.S.; Bachiega, D.; Lupo, F.N.; Bonotto, S.V.; Fischer, D.C.H. Antiprotozoal activity of Brazilian plant extracts from isoquinoline alkaloid-producing families. *Phytomedicine* **2005**, *12*, 382–390. https://doi.org/10.1016/j.phymed.2003.10.007.

Agradecimentos/Acknowledgments

CAPES
FAPEMA Fundação de Amparo à Pesquisa e ao Desenvolvimento Científico e Tecnológico do Maranhão
CNPq

Área: QPN

Preliminary Assessment of the Chemical Profile and activity against *Sporothrix brasiliensis* of Green Propolis Ethanol Extract

Andressa A. Barros (IC)[1*], Lucas O. Pires (PG)[1], Rafael F. dos Santos (PG)[1], Águida A. de Oliveira (PG)[2], Rosane N. Castro (PQ)[1*] barros.andressaandrade@hotmail.com

[1]Instituto de Química - Departamento de Química Orgânica, UFRRJ; [2]Instituto de Veterinária - Laboratório de Micologia e Micotoxinas, UFRRJ

Keywords: *Propolis, Artepillin C, Antigungal properties*

Highlights

Evaluation of the chemical profile, antioxidant and antifungal activity of ethanolic extract of green propolis.

Abstract

Green propolis (GP) is produced by *Apis Mellifera* L. using resinous substances collected from different plant species in the Southeast region of Brazil, mainly *Baccharis dracunculifolia* DC (BD)[1]. The chemical profile of GP is shown to be very similar to its botanical source, and Artepillin C is highlighted as the biomarker and main bioactive compound with different biological properties, such as antioxidant, antitumor and antifungal[1]. (**Figure 1**)

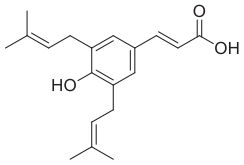


Figure 1: Chemical strutucte of Artepillin C

Sporotrichosis is a zoonosis caused by fungi of the genus *Sporothrix* (*S. schenckii* or *S. brasiliensis*) that mainly affects felines and can be transmissible to humans through contact with infected areas, bites or scratches from affected animals. Natural products emerge as an important tool for discovering new active compounds against resistant strains that are often not affected by traditional patented fungicides on the market[4]. This work aims to investigate the chemical profile, the antioxidant capacity (DPPH) and antifungal activity of ethanolic extracts from GP (Paracambi – RJ, 2012) and of Artepillin C (compound isolated from GP)[3]. The extract (EEP) was prepared in a Soxhlet extractor from 3.00 g of pulverized sample and 150 mL of ethanol (6 h). The determination of phenolic (TP) and flavonoid (TF) content was carried out using the Folin-Ciocalteau and $AlCl_3$ complexation methods. The analysis of antioxidant capacity was carried out using the DPPH radical. The evaluation of the chemical profile was carried out by HPLC-DAD. The antifungal activity was carried out against strains of *S. brasiliensis* at 28 ºC, with the drugs itraconazole and amphotericin B as controls[2].The EEP presented a yield of 44.90% m/m. The TP and TF content was 4.05 mg EAG.100 mg^{-1} and 3.82 mg EQ.100 mg^{-1} of extract, respectively and the antioxidant capacity was 27.75 mg/mL. The results presented demonstrated the presence of antioxidant species, highlighted by the high content of phenolic compounds and flavonoids. When evaluating the chemical profile by HPLC-DAD, the presence of constituents such as caffeic, *p*-coumaric acids and prenylated compounds such as Artepillin C can be observed. Both EEP and Artepillin C showed activity against *S. brasiliensis* with an MIC of 0.56 mg/mL and 0.187 mg/mL, respectively. The results demonstrated suggest that the presence of prenylated compounds such as Artepillin C, may be responsible for the antifungal property. GP stands out for its high content of bioactive substances with therapeutic activity. This study showed the promising use of EEP from Brazilian GP as an antifungal for the treatment of sporotrichosis caused by *S. brasiliensis*. The results encourage further studies with this beekeeping product to evaluate its use and understand its effectiveness.

1.Lima et al; Revista Tecnologia e Tendências10, 93-110, 2019.
2.Peter, C. M. et al. *Arq. Bras. Med. Vet. Zootec*., 71, 819-827. 2019.
3.Pires, L. O.; Castro, R. N. *Rev. Virt. Quim*., 3, 1984-6835; 2023.
4.Waller, S. B. et al. *Sci. Anim. Health*., 5, 151-165. 2017.

Acknowledgments

The authors would like to thank the support and funding provided by CAPES, CNPQ and FAPERJ.

Área: QPN

Preparation of Semisynthetic Derivatives of Kaurenoic Acid from *Mikania glomerata*, Mainly Through Amidation Reactions.

Ana Carolina F. S. Rocha (PG)[1*], Julian C.S. Pavan (PG)[1], Jairo K. Bastos (PQ)[2], Vladimir C.G. Heleno[1] (PQ).**

*carol_gu.soares@hotmail.com, **julian.c.s.pavan@hotmail.com

[1]*Research Nucleus in Exact and Technological Sciences - University of Franca, Franca, SP.*
[2]*Ribeirão Preto School of Pharmaceutical Sciences - University of São Paulo, USP.*

Keywords: *Kaurenoic acid, Mikania glomerata, diterpenes, structural modification.*

Highlights

Kaurenoic acid was isolated from *Mikania glomerata* and subjected to structural modifications. Methoxylation, catalytic hydrogenation, and amidation reactions were onducted resulting in 21 derivatives.

Abstract

The plant *Mikania glomerata* is a native Brazilian species, commonly known as guaco, which was included in the first edition of the Brazilian Pharmacopoeia in 1929[1]. This species contains several specialized metabolites from different classes. A major compound found in guaco is kaurenoic acid (KA), a terpenoid of the diterpene class that has been extensively studied for its biological properties[2]. To expand de range of semisynthetic compounds of the kaurane class and use the olefinic carbons in the structure, methoxylation and catalytic hydrogenation of the double bond were primarily performed. With three different carboxylic acids in hand, they were subjected to a series of amidation reactions with various amines to produce a significant group of analogs. The isolation of KA began with the grinding of dried aerial parts of guaco, followed by conditioning in a vessel with dichloromethane and ultrasound treatment for 15 minutes. The dichloromethane was filtered, and the extract was concentrated by rotary evaporation, yielding the dichloromethane extract. Subsequently, a hydroalcoholic suspension of the extract was prepared with ethanol and water (9:1) and washed with hexane (5 x 600 mL). The hexane phase was evaporated using rotary evaporation. Vacuum liquid chromatography (VLC) was performed with silica gel 60 (230-400 mesh); and silica gel 60 H (70-230 mesh), in a 1:1 ratio, using mobile phases with increasing polarity gradient, furnishing 12 fractions. Column chromatography (CC) was then carried out to isolate pure KA. A portion of KA underwent methoxylation[3] to produce methoxylated kaurenoic acid (KAOMe), while another portion underwent catalytic hydrogenation to yield hydrogenated kaurenoic acid (KAH). The two pre-modified compounds were identified by comparing their nuclear magnetic resonance (NMR) spectra with that of KA. These three compounds served as starting materials for a series of reactions with seven different amines, following previously described methodology[4]. Twenty-one amide derivatives were synthesized, purified by CC and identified by NMR. Product Yields ranged from 15% to 94%. The reactions were monitored by thin-layer chromatography (TLC) to determine reaction times, which varied from 20 to 90 minutes. By obtaining two pre-modified compounds from KA, and subjecting them to amidation reactions, 21 analogs of the kaurane skeleton, were produced, with 14 being previously unpublished substances. All compounds will undergo biological assays to assess their cytotoxicity against healthy and cancerous cells.

References

[1]SILVA, R. A. D. Pharmacopeia dos Estados Unidos do Brasil. São Paulo: Companhia Editora Nacional, p. 1147, 1926. [2]COUTINHO, L. A.; GONÇALVES, C. P.; MARCUCCI, M. C. Composição química, atividade biológica e segurança de uso de plantas do gênero *Mikania*. Revista Fitos, v. 14, n. 1, p. 118-144, 2020. [3]BOECK, P. et al. A simple synthesis of kaurenoic esters and other derivatives and evaluation of their antifungal activity. Journal of the Brazilian Chemistry Society, v. 16, p. 1360-1366, 2005. [4]BANDGAR, R. P.; BETTIGERI, S. V. Communications. Vol. 34, p. 2917-2924, 2004.

Acknowledgments

This research was financed by CAPES, CNPq, and FAPESP.

Área: QPN

Process for obtaining polymeric nanoparticles of ethanolic extract of *Passiflora edulis* seeds and evaluation of antioxidant capacity

[1]Messias de Oliveira Silva (PG),[1] Marilene Brandão Tenório Fragoso (PQ), [2] Arthur Luy Tavares Ferreira Borges (PG),[2] João Victor Lessa de Oliveira (PG),[2] Ticiano Gomes do Nascimento (PQ),[2] Jadriane de Almeida Xavier (PQ),[1] Marília Oliveira Fonseca Goulart (PQ),[1*]

messias.silva@iqb.ufal.br; mofg@qui.ufal.br

[1] *Institute of Chemistry and Biotechnology, Federal University of Alagoas;* [2] *Institute of Pharmaceutical Sciences, Federal University of Alagoas;*

Key Words: Sour passion fruit, Nanoparticles, Use of waste, Antioxidant capacity.

Highlights

EEPE did not reduce cell viability and showed good antioxidant capacity. Microencapsulated 70% EEPE captured 83.3 ±3.1% of the DPPH• radical, higher than the 56.0 ±3.1% of non-microencapsulated EEPE.

Abstract

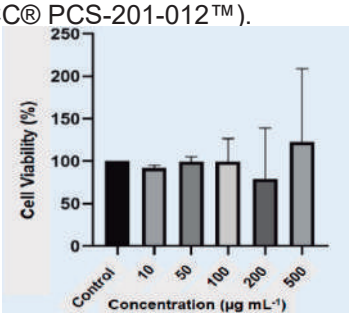
The search for natural products with multiple biological properties, effective and non-toxic has grown significantly in recent years. Brazil is currently the largest producer and consumer of sour passion fruit (*Passiflora edulis),* with 90% destined for industrial processing, generating tons of waste, several biological activities already attributed to passion fruit seed extracts, due to the presence of bioactive compounds such as piceatanol , resveratrol, and naringenin[1]. Since the beginning of the 1990s, nanoparticles have been studied and used as nanocarriers. Polymeric nanoparticles are the most accepted drug delivery vehicles with clinical applications, due to factors such as biocompatibility, non-toxicity, biodegradability, stability, controlled release, targeted delivery, thus being an effective therapeutic alternative[2]. In view of the above, the present work aims to prepare nanoparticles loaded with ethanolic extract of *Passiflora edulis* seeds (EEPE) and evaluate the antioxidant activity. EEPE was obtained by continuous extraction in a Soxlhet apparatus, it was subjected to cell viability tests (MTT), polymeric nanoparticles loaded with EEPE were prepared with a combination of poly-ε-caprolactone and pluronic by the nanoprecipitation method, obtaining polymeric nanoparticles in concentrations of 30, 50 and 70% of extract in its composition and subsequently the antioxidant capacity of the extract and microencapsulated products was evaluated. We can observe the results of antioxidant capacity (Table 1) and cell viability (Figure 1).

Table 1. Total Phenolic Compound Content (CTF), radical anion capture Superoxide ($O_2^{\bullet-}$) and hypochlorous acid (HOCl).

Sample	CTF (mg EAG/g of dry extract)	DPPH IC_{50} (µg mL^{-1})	HOCl IC_{50} (µg mL^{-1})	$O_2^{\bullet-}$ IC_{50} (µg mL^{-1})
EESPE	227± 3,9	20,4 ± 2,1	1,7 ± 0,3	38,2 ± 0,5
Quercetin	-	4,8 ± 1,0	1,9 ± 0,3	8,8 ± 0,3

EEPE= Ethanolic Extract of *P. edulis* Seeds; EAG= Equivalent of gallic acid; IC_{50}=50% inhibitory concentration (µg mL^{-1}). Values expressed as average + deviation (n=3).

Figure 1. Analysis of cell viability against the HDF-A primary human dermal fibroblast cell line (ATCC® PCS-201-012™).



The results showed that EEPE did not reduce cell viability against the tested cell line. It showed good antioxidant capacity in the methods tested, including the capture of reactive species of biological importance. The nanoparticles incorporated with EESPE (30, 50 and 70%) were tested at concentrations of 10 and 50 µg mL^{-1} against the capture of the DPPH• radical. Among the microencapsulated products produced, the nanoparticle that has 70% in its composition showed a greater potential for capturing the DPPH• radical (83.3 ± 3.1%), compared to EESPE, which obtained 56.0 ± 3.1%, both at a concentration of 50 µg mL^{-1}. The release profile of the compounds is being evaluated.

1 Dos Santos et al. Molecules. (2022) 24;27(13):4064.;
2 do Nascimento et al. Nanoscale Research Letters (2016) 11:301.

Acknowledgments

CAPES, CNPQ and FAPEAL.

Área: QNP

Quinones isolated from the root extract of *Pleonotoma jasminifolia* (Bignoniaceae)

Leandro T. Anselmo ***(PG),[1*]*** **Thallisson A. de Souza (PQ),[2] Weider H. P. Paz (PQ),[1] Thiago A. M. Brito (PQ),[2] Eldrinei G. Peres (PG),[1] Felipe M. A. da Silva (PQ),[3] Emmanoel V. Costa (PQ),[3] Victor M. Sipoloni (PQ),[4] Marcelo S. da Silva (PQ),[2] Josean F. Tavares (PQ),[2] Hector H. F. Koolen (PQ),[1] Waldireny R. Gomes (PQ).[5]**

leandro.anselmo@ufam.edu.br

[1]Superior School of Health Sciences, Amazonas State University; [2] Multi-user Laboratory for Characterization and Analysis, Program of Natural and Synthetic Bioactive Products, Health Sciences Center, Federal University of Paraiba, João Pessoa; [3]Department of Chemistry, Federal University of Amazonas; [4]Department of Chemistry, Federal University of São Paulo; [5]Faculty of Pharmaceutical Sciences, Federal University of Amazonas.

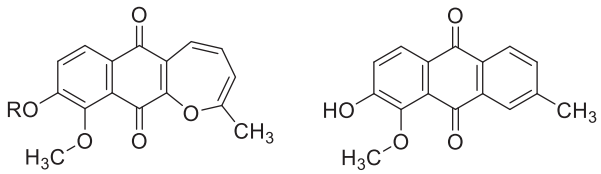
Palavras Chave: Quinones; oxepines; Pleonotoma.

Highlights

The phytochemical study of the roots of *Pleonotoma jasminifolia* resulted in the isolation of four quinones, with two of them being novel compounds.

Resumo/Abstract

Pleonotoma jasminifolia (Kunth) Mier (Bignoniaceae) is a species commonly known as 'cipó-quira,' found in South American countries such as Brazil.[1] There are no records regarding the chemical composition and pharmacological properties of this species. Therefore, the objective of this study was to investigate the chemical composition of the root extract of *P. jasminifolia*. Metabolites present in the ethyl acetate extract were analyzed using Medium-Pressure Liquid Chromatography (MPLC) and purified by semi-preparative High-Performance Liquid Chromatography (HPLC). The structures of the isolated substances were elucidated through Nuclear Magnetic Resonance (NMR) spectroscopy of ^{1}H and ^{13}C (1D/2D) and Mass Spectrometry (MS).



(**1**) R= H
(**2**) R = CH_3
(**3**) R= H
(**4**) R = CH_3

Figure 1. Structures of chemical compounds isolated from the root *Pleonotoma jasminifolia.*

Four substances were isolated from the root extract of *P. jasminifolia* (Figure 1), including two novel naphthoquinones: pleonotoquinone A (**1**) and pleonotoquinone B (**2**), and two known anthraquinones: 7-hydroxy-8-methoxy-2-methyl anthraquinone (**3**)[2] and 7,8-dimethoxy-2-methyl anthraquinone (**4**)[3]. Substances **1** and **2** constitute the first report of quinones of the 2-methyl-oxepin type, representing a novel skeleton in the literature. The results obtained provide a significant chemotaxonomic contribution to the Bignoniaceae family, with emphasis on the species *P. jasminifolia* from the Amazon region.

Agradecimentos/Acknowledgments

The authors would like to thank the funding agencies (CAPES – Finance code 001), (CNPq), (FAPEAM) and (FAPESP).

REFERENCES

[1] Gomes, B. M. Revisão de Pleonotoma Miers (Gignonieae, Bignoniaceae). 2006.

[2] Kiiubchandani, M. L.; Srivastava, S. K. Curr. Sci. **1989,** 58, 138-139.

[3] Primus, P. S.; Wu, C. H. Y.; Kao, C. L.; Choo, Y. M. Nat. Prod. Res. **2022**, in press.

Área: QPN

Semi-Síntese de análogos de chalcona e Biotransformação pelo fungo *Exserohilum rostratum*

Patrícia S.B Marinho (PQ),[1,3] Hartmann de J. da S. Brito Jr. (PG),[1] Victoria L. Ribeiro (IC),[2] Heriberto R. Bitencourt (PQ),[2] Viviane V. Garcia (PQ),[3] Andrey M. do R. Marinho (PQ),[1,3] Joselina de A. Carvalho (PG)[3]*.

pat@ufpa.br; joselinaaraujocarvalho@gmail.com

[1]Programa de Pós-Graduação em Química, UFPA; [2]Faculdade de Química, UFPA; [3]Programa de Pós-Graduação em Química, UNIFESSPA

Palavras Chave: *Síntese, Análogos de chalconas, Biotransformação, Exserohilum rostratum, Atividade antimicrobiana*

Highlights

Semi-Synthesis of chalcone analogues and Biotransformation by the fungus *Exserohilum rostratum*. Chalcone analogues were synthesized and used as substrates in the biotransformation reaction with the fungus *Exserohilum rostratum*. Antimicrobial activity was evaluated against bacteria of interest to human health and agriculture.

Resumo/Abstract

A busca por substâncias de potencial terapêutico de baixo custo e a eficiência farmacológica oriunda da extração de produtos naturais tem culminado no desenvolvimento de novos fármacos de grande relevância para a criação de medicamentos contra inúmeras doenças. Nessa perspectiva, a síntese de estruturas biologicamente ativas com intuito de utilização no desenvolvimento de novos agentes terapêuticos tem-se destacado, principalmente a síntese de chalconas, uma vez que possuem alta diversidade de atividades farmacológicas. Além das sínteses orgânicas, as reações de biotransformação permitem que sistemas biológicos enzimáticos sejam capazes de alterar estruturas e produzirem moléculas semelhantes com potencial biológico. Diante disso, o presente estudo teve como objetivo sintetizar análogos de chalcona e realizar reações de biotransformação utilizando o fungo *Exserohilum rostratum.* Foram sintetizados quatro análogos de chalcona (*E*)-3-fenil-1-(piridina-3-il)prop-2-en-1-ona **(JA-01)**, (*E*)-1-(piridina-3-il)-3-(2,3,4-trimetoxifenil)prop-2-en-1-ona **(JA-02)**, (*E*)-3-(2-metoxifenil)-1-(piridin-3-il)prop-2-en-1-ona **(JA-03)** e (*E*)-3-(4-metoxifenil)-1-(piridin-3-il)prop-2-en-1-ona **(JA-04)** via reação de condensação do tipo Claisen-Schmidt. Os compostos sintetizados foram os substratos nas reações de biotransformação juntamente com o fungo *E. rostratum*. Para identificação dos substratos e dos produtos formados utilizou-se a técnica de RMN. Os análogos de chalcona foram obtidos com bons rendimentos: **JA-01** (59,1%), **JA-02** (64,6%), **JA-03** (90,2%) e **JA-04** (76,1%) e o fungo demonstrou ser um excelente biocatalisador, uma vez que o mesmo foi capaz de realizar as reações de biotransformação nos quatro substratos, levando a redução das ligações duplas C=C e C=O. Os resultados da atividade antimicrobiana foram promissores para as substâncias **JA-01** e **JA-03**, onde **JA-01** exibiu atividade bactericida com valor de CIM 62,5 µg/mL e atividade bacteriostático até a menor concentração testada de 3,91 µg/mL frente à *Xanthomonas axonopodis* pv. *passiflorae* e a **JA-03** mostrou-se favorável em impedir o crescimento bacteriano, com valor de CIM 250 µg/mL e bacteriostático até a concentração de 3,91 µg/mL para *Escherichia coli*.

Agradecimentos/Acknowledgments

UFPA, FAPESPA, CAPES, CNPq (Processo 308631/2021-8)

Área: QPN

Simplex centroid mixture design and chemometric analysis-guided isolation of new compound from a native Amazonian species

Ingrity S. C. Sá (PQ),[1,2*] Felipe M. A. Silva (PQ),[2] André C. Oliveira (PG),[2] Brenda R. C. Leocádio (PG),[2] Marcos T. Silva (PQ),[1] Rita C.S. Nunomura (PQ).[2,3]

ingrity.sa@ufam.edu.br

[1] *Instituto de Saúde e Biotecnologia (ISB), Universidade Federal do Amazonas (UFAM), Coari, AM;*
[2] *Central Analítica (CA), Centro de Apoio Multidisciplinar – (CAM/ UFAM), Manaus, AM;*
[3] *Departamento de Química (DQ/ UFAM), Manaus, AM.*

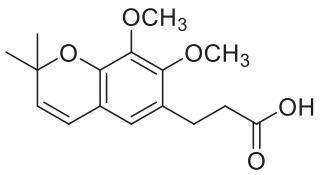
keywords: Amazon region, *B. parinarioides*, Hydroxycinnamic acids derivatives, Parinarioidins A-C, Phenolic profile, Phytochemical.

Highlights

- Integrative approach in phytochemical investigation of the bark from *B. parinarioides.*
- One new compound was isolated named parinarioidin C.
- Nine phenolic compounds were identified based on the MS and NMR analysis.
- Simplex centroid mixture is effective model to guide the isolation of new natural products.

Abstract

Brosimum parinarioides (Moraceae family), a plant species native to the Amazonian region, is known as “Amapá” or “Amapá-doce”, used in folk medicine for the treatment of several diseases. However, the knowledge regarding its phytochemical content is almost unexplored. To investigate the phytochemical composition of *B. parinarioides*, an integrative approach based on simplex-centroid design and chemometric analysis was adopted. According to simplex-centroid design, dichloromethane (DCM), ethyl acetate (AcOEt), and ethanol-based (EtOH) extracts were prepared and analyzed by DI-ESI-MS, and their chemical profile submitted to principal component analysis (PCA) and hierarchical cluster analysis (HCA). The AcOEt extract (500 mg) was subjected to liquid-liquid partition with Hex/AcOEt/MeOH/H_2O (9:1:9:1 v/v/v/v), yielding a two-phase system Hex/AcOEt (upper phase, UP) and MeOH/H_2O (lower phase, LP). The phase LP (180 mg) was purified by semi-preparative HPLC, using the gradient system of elution with water (A) and methanol (B): 50 –100 % B (v:v), at a flow rate of 3.7 mL/min for the time of 0-35 min, C18 column (250 mm × 10 mm, 5 µm), monitored by UV at 280 and 350 nm. The multivariate analysis pointed to the formation of three groups that highlighted *isoliquiritigenin*, *licoagrochalcone A*, *caffeic acid glucoside*, *epicatechin-glycoside*, *caffeic acid*, and an unknown compound as responsible for the segregation of these groups. The purification by HPLC resulted in the isolation of a new compound, characterized by NMR (1D and 2D) and HR-MS analysis, named *parinarioidin C* (Figure 1). In addition, *parinarioidin A*, *parinarioidin B*, *3-O-caffeoylquinic acid*, and *kanzonol C* were tentatively identified based on the interpretation of MS/MS spectra and internal standards comparison. The integrative approach proposed provided a simple and effective model to dereplicate known compounds and guide the isolation of a new compound from a native Amazon species, improving the knowledge regarding the phytochemical content of *B. parinarioides*.



Parinarioidin C

Figure 1. New compound from the bark of *B. parinarioides*.

Acknowledgments

The authors are grateful to CA/UFAM, ISB/UFAM, PPGQ-DQ/UFAM, CAPES, CNPq, FINEP, and FAPEAM for all support and scholarships.

Área: QPN

Steroidal Saponins of *Solanum jabrense* Agra and M.Nee

Anauara Lima e Silva* **(PG),[1] Thiago A. de M. Brito (PG),[1] Gilmário Moreira Lima (TM),[1] Maria de Fátima Agra (PQ),[2] Marcelo Sobral da Silva (PQ),[1] Josean Fechine Tavares (PQ)[1]**

anauaralima@ltf.ufpb.br

[1]*Postgraduate Program in Natural and Synthetic Bioactive Products, Health Sciences Center, Federal University of Paraíba, PB, Brazil;* [2] *Department of Biotechnology, Biotechnology Center, Federal University of Paraíba, PB, Brazil.*

Palavras Chave: Solanaceae, Clado Lepstostemonum, Natural Products, Glycosides

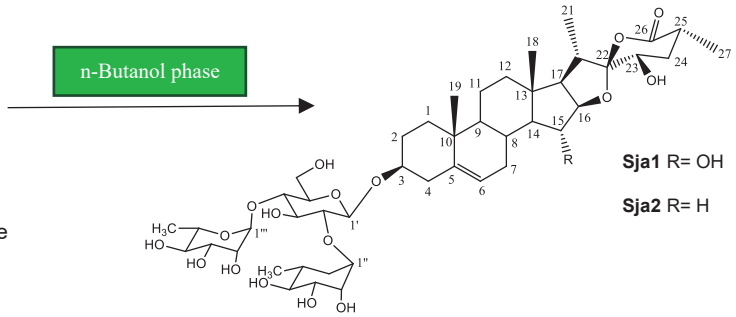
Highlights

- Two steroidal saponins were isolated from *Solanum jabrense* Agra and M. Nee.
- These steroidal saponins were first isolated from *Solanum jabrense* Agra and M. Nee.

Resumo/Abstract

Solanum jabrense belongs to *Solanum* subg. *Leptostemonum* (Solanaceae) is a species endemic to Brazil, occurring in northeastern altitude swamp, above 500 m, associated with rocky environments, exclusively in the States of Ceará, Paraíba, Pernambuco and Bahia. In previous studies, its pharmacological potential was demonstrated due to the presence of flavanoids and steroidal glycosides. In this work, the aerial parts of *S. jabrense* were dried and pulverized, then extracted in an ultrasonic bath with 80% MeOH, filtered, concentrated and partitioned using the solvents hexane, chloroform, ethyl acetate and n-Butanol. The n-Butanol phase was subjected to column chromatography, using silica gel as the stationary phase and hexane, ethyl acetate and methanol as the mobile phase, obtaining 35 fractions, which, after analysis by High Efficiency Liquid Chromatography coupled to the Diode Array detector (HPLC-DAD). Fraction 11 and 12 were subjected to column chromatography, using sephadex and methanol as the mobile phase, obtaining 14 and 16 fractions, respectively. Fraction 07 obtained from the fractionation of fraction 12 was analyzed by HPLC-DAD and subjected to preparative HPLC, using C-18 and acetonitrile and ultra-pure water, acidified with 0.1% formic acid, obtaining the substance coded as Sja1. Fraction 02 obtained from the sephadex fractionation of fraction 11 was analyzed by HPLC-DAD obtaining the substance coded as Sja2. After ^{1}H, ^{13}C and two-dimensional Nuclear Magnetic Resonance analyses (NMR), the substances were identified with an aglycone structure similar to foliumin (3,15,23-trihydroxyspirost-5-en-26-one 3-*O*-(rhamnopyranosyl-1-2) glucopyranoside), however with a glycosylated chain similar to solamargine (3-*O*-β-chacotrioside) (Sja1). Sja2 showed chemical shifts similar to Sja1, however signals related to C-14, C-15, C-16 and C-17 were similar to solamargine chemical shifts suggesting the absence of the hydroxyl group in C-15. From the phytochemical study of the n-Butanol phase of aerial parts of *S. jabrense*, it was possible to identify and isolate two new glycosylated saponins, this being the first record of these structures.

Solanum jabrense Agra & M. Nee



Agradecimentos/Acknowledgments

We are grateful to the CNPq; CAPES; UFPB; LMCA; IPeFarM and INCT-RENNOFITO.

Área: Produtos Naturais - (QPN)

Study of *Citrus aurantium* L. decoct, using LC-HRMS/MS to analyze bioactive compounds against the fungus *Fusarium jinanense*

Maria D. de Freitas[1] (PG), Rodolfo D. L. Junior[2] (PG), Taicia P. Fill[2] (PQ), Francisco E. F. da Silva[1] (PG), Davila Zampieri[1] (PQ), Cristiano S. Lima[3] (PQ), Eliane M. Inokuti[3] (PG), Andréia H. Oster[3] (TC), Telma L. G. Lemos[1*] (PQ).

*tlemos@dqoi.ufc.br

[1]Departamento de Química Orgânica e Inorgânica, Universidade Federal do Ceará, Campus do Pici, 60021-940, Fortaleza, Ceará, Brasil; [2]Instituto de Química, Universidade de Campinas, CP 6154, 13083-970, Campinas, SP, Brasil; [3]Departamento de Fitotecnia, Universidade Federal do Ceará, Campus do Pici, 60440-554, Fortaleza, Ceará, Brasil.

Keywords: *Citrus aurantium, Dereplication, Antifungal activity, Equiseti clade.*

Highlights

Annotation of secondary metabolites using LC-HRMS/MS.
Antimicrobial activity of industrial waste against the fungus (*Fusarium jinanense*) that causes yellow melon rot.

Abstract

Citrus aurantium, or bitter orange, is one of the many species of the *Citrus* genus, which is of little economic value compared to edible varieties due to its bitter taste. Many studies have described the benefits of using its essential oil in different applications, but little is known about the chemical composition and biological potential of the peel decoction obtained as a by-product. In the present work, the chemical composition and antimicrobial potential of the decoction and fractions against the phytopathogen *Fusarium jinanense* were evaluated using solid phase extraction (SPE) and liquid chromatography coupled with mass spectrometry (LC-MS/MS) and feature-based molecular networking (FBMN) based on characteristics of the fractions. In general, secondary metabolites from different classes such as flavonoids, coumarins, terpenes, limonoids and nitrogen compounds were annotated in the fractions and compared with the ethyl acetate extract from the bark decoction. The putative identification and visualization of the FBMN made it possible to annotate 57 compounds in the positive mode of analysis and 8 compounds in the negative mode. The bioactive fractions with high antifungal activity (up to 60.97% mycelial inhibition) against the causal agent of melon rot were found to contain polymethoxyflavones and coumarins, including nobiletin, 5-demethylnobiletin, ostenol and bergapten, which are reported in the literature to have antifungal activity against fungi of the genus *Fusarium*, *Candida* and *Aspergillus*. This approach could help to detect compounds or fractions enriched with high biological potential in little-exploited food sources, giving added value to this residue and helping to control different plant diseases caused by fungi.

Acknowledgments

CNPq Conselho Nacional de Desenvolvimento Científico e Tecnológico
CAPES
PGQUIM
LBPN
Laboratório de Biotecnologia e Produtos Naturais
LaBioQuiMi
bioMASS

Study of the Chemical Composition of *Klotzschia glaziovii* Leaves (Apiaceae)

Jalles Fernandes Queiroz[1], Emiret Otoni de Faria[1], Vanessa G. P. Severino[1], Lorena Ramos Freitas de Sousa[3], Tanja Schirmeister[2], Lucilia Kato[1].

Natural Products Laboratory and Institute of Organic Synthesis Chemistry, Federal University of Goiás, Brazil[1]
Institute of Pharmaceutical and Biomedical Sciences, Johannes Gutenberg University Mainz, Germany[2]
Institute of Chemistry, Federal University of Catalão - UFCAT Catalão-GO, Brazil[3]

jallesfernandes@discente.ufg.br; emiret@discente.ufg.br; vanessapasqualotto@ufg.br; lorennarf@ufcat.edu.br; schirmei@uni-mainz.de; lucilia@ufg.br

Keywords: Apiaceae, K. glaziovii, alkaloids and flavonoids

Highlights

Metabolites from *Klotzschia glaziovii* (Apiaceae) as potential treatments for neglected tropical diseases (NTDs).
Isolation and structural elucidation of unveil bioactive compounds.

Abstract

The Apiaceae family, prominent among angiosperms, especially in Brazil and Goiás, contains several species, including the poorly studied genus *Klotzschia*. Although *Klotzschia* is recognised as monophyletic, its taxonomy remains uncertain. In parallel, bioactivity assays were conducted on the extract with the aim of contributing to the global targets set by the World Health Organization (WHO) for the eradication of neglected tropical diseases (NTDs) by 2030, which affect millions of people worldwide. Dengue and Human African Trypanosomiasis (HAT or sleeping sickness) affect people who have been bitten by the vector. The molecular study will improve understanding of botanical taxonomy and suggest new treatments for specific neglected tropical diseases (NTDs). Leaves of *K. glaziovii* collected in Pirenópolis, Goiás, showed a composition rich in alkaloids, lipids, resin acids and essential oils. The characterization of the isolated metabolites was carried out by chromatographic analyses and nuclear magnetic resonance of ^{1}H, δ ^{1}H; 3.14, s; 6.18 d (J=2.0 Hz); 7.73 d (J=2.0 Hz); 6.88 d (J=8.5 Hz); 7.63 dd (J=2.15 and 8.46 Hz); 7.43 dd (J=2.15 and 8.8 Hz), δ ^{13}C 147.3; 137.2; 176.1; 161.0; 99.2; 165.7; 94.0; 156.4; 103.6; 123.0; 116.2; 145.5; 146.2; 116.6; 121.0. Comparative analysis with existing literature facilitated the identification of the flavonoid quercetin. In addition, LC/MS/MS analyses showed that the main compound corresponds to quercetin glycoside derivatives. For Fluorometric assays a sample of *K. glaziovii* was evaluated in inhibitory activity assays against the NS2B/NS3 serine protease from dengue virus and the Rhodesian cysteine protease from trypanosomes. To screen the extract, DENV-2 assays were performed using 100 µM of the fluorogenic substrate Boc-Gly-Arg-Arg-7-amino-4-methylcoumarin (AMC). Ludewing. et al. 2010. In the rhodesain inhibition assays, the release of the hydrolysis product from the substrate (Cbz-Phe-Arg-AMC, 10 µM) was determined continuously over a period of 10 min. Screening was performed in 50 mM sodium acetate, pH 5.5 containing 10 mM DTT with Cbz-Phe-Arg-AMC (10 µM) as substrate. For both screening assays, inhibitor solutions (ethanol extract) 73µg/mL were prepared from stocks in DMSO. Each assay was performed in duplicate in 96-well plates in a total volume of 200 µL. Fluorescence of the AMC product of substrate hydrolysis was measured using an Infinite 200 PRO microplate reader (Tecan) at room temperature with a 380 nm excitation filter and a 460 nm emission filter. The inhibitory activity against DENV-2 and Rhodesain was 27.6% and 60.75% for the *K. glaziovii* extract, respectively. This findings contributing to the understanding of the medicinal potential of plants of the Apiaceae family in the search for new treatments for neglected tropical diseases (NTDs).

Alen, M. M. F.; Schols, D. (2012). Dengue Virus Entry as Target for Antiviral Therapy. *Journal of Tropical Medicine*, 1-13.

Ludewig, S. et al. (2010). Enzyme kinetics and hit validation in fluorimetric protease assays. *Current Topics in Medicinal Chemistry*, 10(3), 368-382.

Newman, D. J., & Cragg, G. M. Natural Products as Sources of New Drugs over the Nearly Four Decades from 01/1981 to 09/2019. Journal of Natural Products,

Primikyri, A. et al. (2015). Understanding Zinc(II) Chelation with Quercetin and Luteolin: A Combined NMR and Theoretical Study.

Sampath, A.; Padmanabhan, R. (2009). Molecular targets for flavivirus drug discovery. *Antiviral Research*, 81, 6-15.

Acknowledgments

To Nuclear Magnetic Resonance Laboratory of the Multi-user Analytical Center (LaRCAM) of the Chemistry Institute and Regional Center for Technological Development and Inovation (CRTI) of the Federal University of Goiás (UFG). To AK Schirmeiter group of Institute of Pharmaceutical and Biomedical Sciences, Johannes Gutenberg University Mainz, Germany. CNPq, Finep, Capes and Fapeg for financial support.

Área: QPN

Two new glycosylated compounds from *Ruehssia caatingae* (Morillo) F. Esp. Santo & Rapini.

Yuri Mangueira do Nascimento (TC)[1], Jociano da Silva Lins (PG)[1]*, José Iranildo M. de Melo (PQ)[2], Gilmario Moreira Lima (TM)[1], José Maria Barbosa Filho (PQ)[1], Josean Fechine Tavares (PQ)[1], Marcelo Sobral da Silva (PQ).[1]

yurimangueira@ltf.ufpb.br; jociano.lins@ltf.ufpb.br

[1]*Drugs and Medicines Research Institute, Postgraduate Program in Natural and Synthetic Bioactive Products, Federal University of Paraíba, PB, Brazil.*

[2]*Postgraduate Program in Ecology and Conservation, State University of Paraíba, PB, Brazil.*

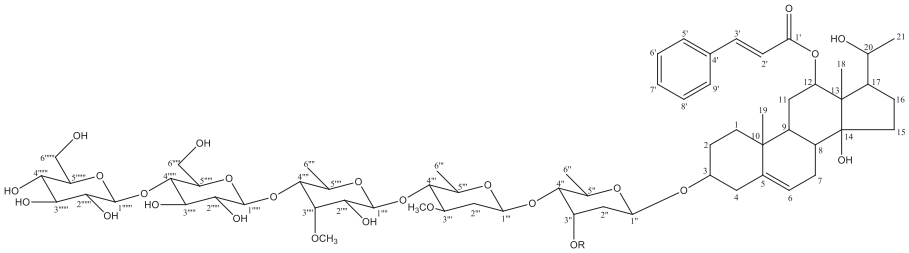
Keywords: *Saponin, Sesquiterpenoid spirovetivane-type, Apocynaceae, Ruehssia*

Highlights

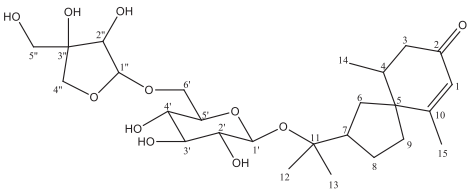
In this work, a new pregnane glycoside and a new spirovetivane-type sesquiterpene were isolated from the chloroform phase of the crude ethanolic extract of the species *Ruehssia caatingae*.

Resumo/Abstract

Ruehssia caatingae belongs to the Apocynaceae family, one of the ten largest families of Angiosperms. This species appears in nature as a shrub, widely distributed in the Brazilian semi-arid region, occurring in several rocky outcrops spread across the Caatinga. In view of the lack of chemical knowledge about the species.[1,2] In this work, the roots of *R. caatingae* were dried and pulverized, then extracted by maceration with 95% EtOH, filtered and concentrated. A part of the EEB was partitioned using the solvents hexane, chloroform, ethyl acetate and n-Butanol. The chloroform phase was subjected to column chromatography, using sephadex as the stationary phase and methanol as the mobile phase, obtaining 40 fractions, which, after analysis by High Efficiency Liquid Chromatography coupled to the Diode Array detector (HPLC-DAD), were gathered. Fractions 9 to 18 were subjected to column chromatography, using silica gel stationary phase and Hex, EtOAc and MeOH, obtaining 14 fractions, which, after analysis by HPLC-DAD, were combined. Fractions 9 and 10 were subjected to preparative HPLC-DAD, using C-18 and acetonitrile and ultra pure water, acidified with 0.1% formic acid, obtaining the substances coded as Rc-1 and Rc-2. After ^{1}H, ^{13}C and two-dimensional Nuclear Magnetic Resonance analyses, the substances were identified as: 3-*O*-*β*-cymaropyranosyl-(1→4)-*β*-oleandropyranosyl-(1→4)-6-deoxy-3-*O*-methyl-*β*-allopyranosyl-(1→4)-*β*-glucopyranosyl-(1→4)-*β*-glucopyranosyl-12-cinnamoyl-8-deoxy-17-hydrosarconstin (Rc-1) and hinesolone-11-*O*-*β*-*D*-apiofuranosyl-(1→6)-*β*-*D*-glucopyranoside (Rc-2). From the phytochemical study of the chloroform phase of *R. caatingae*, it was possible to identify and isolate a new pregnane glycoside and a new sesquiterpenoid of the spirovetivane type. Thus, contributing to the phytochemical knowledge of the Apocynacea family and the *Ruehssia* genus.



Rc-1



Rc-2

References

[1]ENDRESS, M. E. et al. **Springer: Cham**, p. 207–411, 2018.

[2]ESPÍRITO SANTO, F. S. et al. **Kew Bulletin**, v. 74, p. 1-79, 2019.

Agradecimentos/Acknowledgments

CNPq / CAPES /FAPESQ / UFPB / LMCA / IPeFarM / INCT

Área: QPN

Understanding the chemistry and ecological roles of metabolites produced by fungi associated with Brazilian stingless bees

Jullio Kennedy C. Soares (PG) [1, 2, *], Giordanno Di G. Silva (PG) [1, 2], Thiago A. Veiga (PQ) [1, 2], Michelle M. Morais (PQ) [1], Lívia S. de Medeiros (PQ) [1, 2]

jullio.kennedy@unifesp.br; livia.soman@unifesp.br

[1] Instituto de Ciências Ambientais, Químicas e Farmacêuticas, UNIFESP; [2] Laboratório de Química Bio-Orgânica Otto Richard Gottlieb (LaBiORG)

Keywords: Antimicrobials, Bees, Chemical Ecology, Fungi, Symbiosis.

Highlights

Metabolic extracts of fungi (*Penicillium exudans*, *Talaromyces wortmannii*, *Trichoderma atroviride*) isolated from stingless bees showed prominent antifungal activities against bee entomopathogens.

Abstract

Beehives, as well as wild colonies, are frequently affected by fungal infections caused by specialized (*Ascosphaera apis*) or opportunistic (*Aspergillus flavus*) pathogens able of killing the larval stages of bees. Additionally, the exposure to fungal biocontrol agents (such as *Beauveria bassiana*, *Metarhizium anisopliae*, and *Isaria fumosorosea*) used in agricultural systems are also potential threats to bee survival. Thus, this study aimed to evaluate the antifungal activity of extracts of filamentous fungi isolated from different parts of Brazilian stingless bee colonies called manduri (*Melipona marginata*) and mandaçaia (*Melipona quadrifasciata*) against these entomopathogens. From the sixty strains isolated until the moment, only eighteen were chosen for a metabolomic screening. Through the analysis of data obtained via UHPLC-DAD-QTOF-MS/MS combined with the chemical dereplication approach, three final strains demonstrated the secondary metabolism focused on the production of promising antimicrobial natural products. Organic extracts from the exudates and the mycelium of the fungal growth in different media culture were testes in antifungal susceptibility assays (poison plate) against five entomopathogens (*A. apis* CMLD 131, *A. flavus* CMLD 132, *B. bassiana* IBCB 66, *M. anisopliae* IBCB 425, *I. javanica* IBCB 638) at concentration of 1 mg/mL. Analyzing the poisoned plates with extracts in relation to the negative control, it was observed that all extracts had the potential to inhibit each of the five pathogens in some degree. Highlights the mycelial extracts of *Penicillium exudans* CMLD 72 and *Talaromyces wortmannii* CMLD 83 showing inhibition of the growth of entomopathogens ranging from 7% to 92% (**Figure 1**). In both symbionts, azaphilones were annotated. This class of polyketides were previously associated with bees and termites, which may therefore be related to the protection of these eusocial insects. The extracts of the third symbiont, *Trichoderma atroviride* CMLD 34, characterized by the presence of 2-pyrone derivatives, showed inhibitions ranging from 16% to 62%, and represent the first description of this specie and chemical compounds for the bee system. Finally, it is expected to evaluate the antifungal potential of each of these compounds to confirm their ecological role in the protection of bees mediated by symbionts.

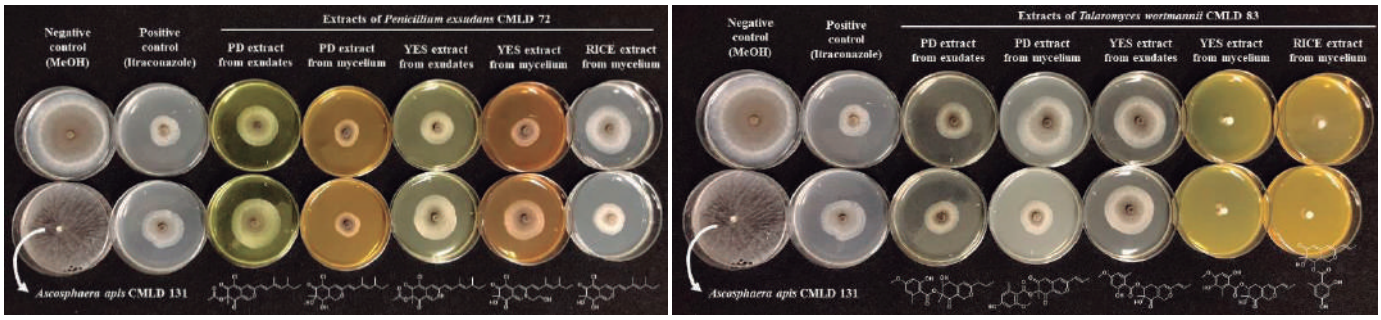


Figure 1. Poison plate assays of *P. exudans* CMLD 72 (left) and *T. wortmannii* CMLD 83 (right) strains against *A. apis* CMLD 131.

Acknowledgments

The authors thank the CAPES (88887.798945/2022-00) and the FAPESP (2020/08270-0, 2022/14896-5) for financial support.

Área: QPN

Usage of hyphenated technique in the search for potential elastase inhibitors from *Chomelia ribesioides* Benth.

Kyuri Ribeiro (PG),[1] Adriana P. M. G. Macedo (PQ),[1] Romário Pereira da Costa (PG),[1] Richele P. Severino (PQ),[1] Quezia B. Cass (PQ),[2] Lorena R. F. de Sousa (PQ)[1*]

kyuri.ribeiro@discente.ufcat.edu.br; *lorennarf@ufcat.edu.br

[1]Instituto de Química, UFCAT; [2]Departamento de Química, UFSCar.

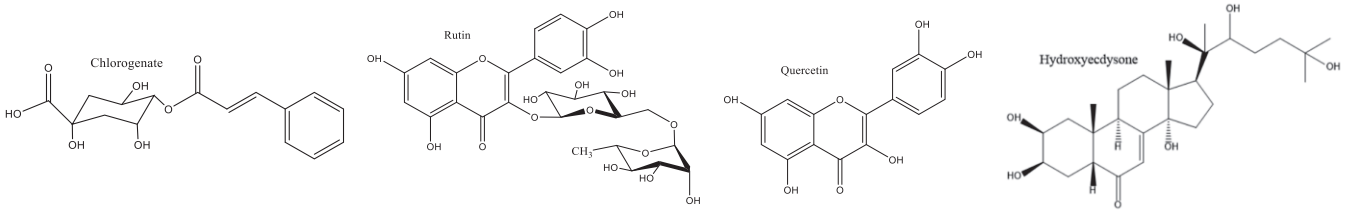
Palavras Chave: *Biological activities, chemical profile, enzymatic assay, LC-HRMS.*

Highlights

Fruits and leaf of *Chomelia ribesioides* showed inhibitory activity against elastase and chemical study of crude ethanolic extracts revealed the presence of flavonoids, a class of compounds known as elastase inhibitors.

Resumo/Abstract

Elastase is a serine protease of chymotrypsin family, which cleave peptide bonds of elastin, collagen, and fibronectin, and when elastase is overexpressed, the skin loses elasticity.[1]In the search of elastase inhibitors, Natural Products (NPs) from plants have been investigated.[3] The *Chomelia* is a genus from Rubiaceae family which secondary metabolites have been highly studied. Highlighting the species *Chomelia asiatica* and *Chomelia obtusa*, widely cited in the literature, their chemical profile revealed alkaloids, steroids, phenols, flavonoids and terpenes.[2,3] Some species of this genus have been shown biological activities such as healing, antimicrobial, antioxidant and anti-inflammatory potential.[2] However, there is no much knowledge about chemical profile of the species *Chomelia ribesioides* and its application. In this view, the aim of this research was to investigate *C. ribesioides* chemically and using enzymatic assay against elastase. The ethanolic extracts of leaf and fruits were tested using spectrophotometric measurements by cleavage of substrate *N*-succinyl-Ala-Ala-Ala-*p*-nitroanilide (wavelength of 410 nm) in spectrophotometer[4] and results showed 58.6% and 58.7% of inhibition respectively. The chemical profile was determined using LC-HRMS technique in positive mode and results were analyzed using the DataAnalysis and CompoundCrawler software and the GNPS platform. The dereplication of the compounds by GNPS resulted in the annotation of 38 compounds. Using the software mentioned above and comparing spectra data to literature[5-8] it was possible to identify four compounds up to now, chlorogenate, quercetin, rutin and hydroxyecdysone. Compounds identification and fractionation of active extract will be performed in order to understand the biological activity.



REFERÊNCIAS:

[1]TIEDERMANN, V. Elastase and α-chymotrypsin inhibition studies. *Uppsala University*,1-16, 2018.
[2]PESSOA, M.C.R. RI UFPE: Disponível em: https://repositorio.ufpe.br/handle/123456789/27096., 40-40, 2016.
[3]MANOJJ, D. *et al. South African Journal of Botany*, 128: 54-61, 2020.
[4]VIDEIRA, I.F. dos S. *et al. An. Bras. Dermatol*. 88: 76-83, 2013.
[5]WILLEMS, J.L. *et al. Analytica Chimica Acta*, 933: 164-174, 2016.
[6]JAHAN, N. *et al. Chemical Papers*, 6-7, 2022.
[7]SATHEESHKUMAR, N. SHANTIKUMAR, S; KOMALI, M. *Chromatography Research International*, 2014: 1-8, 2014.
[8]ROSTANDY, B.; GAO, X. *Metabolomics*, 15: 8-10, 2019.

Agradecimentos/Acknowledgments

This research project received financial support from CAPES and CNPq (Processo: 403611/2020-2, Programa MAI/DAI - UFCAT), Brazil.

Área:_____QPN_____

Using tandem mass spectrometry for chemical profile of flowers of *Qualea grandiflora*

Isadora Gonzaga da Silva (IC),[1] Léia C. Mendes (PG),[1] Andressa O. Rosa (PG),[1] Romário Pereira da Costa (PG),[2] Richele P. Severino(PQ),[1] Quezia Bezerra Cass (PQ),[2] Lorena R. F. de Sousa (PQ)[1*]

Isadora.gonzaga@discente.ufcat.edu.br; *lorennarf@ufcat.edu.br

[1]*Instituto de Química, UFCAT*
[2]*Departamento de Química, UFSCar*

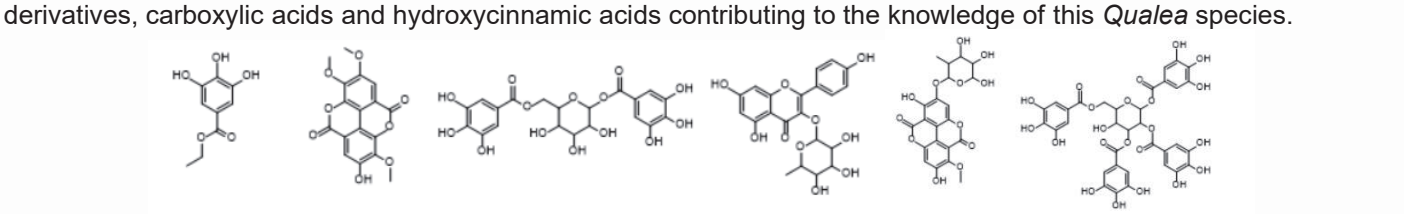
Palavras Chave: *Qualea grandiflora, flowers, chemical profile.*

Highlights

Q. grandiflora (pau-terra) is a medicinal plant and not much are known about the flowers of this plant. In this work we investigated the chemical profile of ethyl acetate fraction of flowers using LC-HRMS allowing to identify nineteen compounds.

Abstract

Qualea grandiflora Mart. (Vochysiaceae), known as “pau-terra” or “pau-terra-do-cerrado”, is known for its usage against inflammatory diseases and gastrointestinal disorders.[1] *Qualea* species have been shown many biological potential sucha as antiulcerogenic, antibacterial and antiparasitic activities.[2,3] Our research group have been investigated *Q. grandiflora* species and chemical studies of fruits, stems bark and leaves have been reported, revealing gallotannins, ellagic acid derivatives and flavonoids.[4] In this view, the aim of the research was to perform the chemical profile of the flowers, since there is no study in literature up to now. Starting from 746 g of fresh flowers, 118 g of crude ethanolic extract (QgFIE) was obtained, resulting in a yield of 15.8% from this ethanol extraction process. Fractionation was performed and ethyl acetate extract was investigated using experiment of liquid chromatography-high resolution quadrupole-time of flight mass spectrometry (LC-HRMS). For the analysis, a CortecsTM C18+ (2.7 µm particle size; 10 × 0.21 cm) (Waters, Milford, MA, USA) analytical column was used with a mobile phase composed of water (A), acetonitrile (B), and 0.1% v/v of formic acid was added to both solvents. A linear gradient of 5 to 100% B in 20 min was used at a flow rate of 0.2 mL min^{-1}, with temperature of 40 °C. The ionization experiments were carried out at negative $[M - H]^-$ mode. The Data Analysis 4.0 software and Bruker Smart Formula (Bruker Daltonics, Bremen, Germany) were used as tools for compounds identification. In addition, MS/MS data were compared to literature data.[5-7] From the flowers study was possible to identify nineteen compounds belonging to the class of flavonoids, gallotannins, ellagic acid derivatives, carboxylic acids and hydroxycinnamic acids contributing to the knowledge of this *Qualea* species.



[1]Neto, FC, Pilon, AC, Silva, DH, Da Silva, VB. *Phytochem. Ver.* **2011**, 10: 413.
[2]Ayres, MCCA, Escórcio, SP, Da Costa, DA, Chaves, MH, Vieira Júnior, GM, Cavalheiro, AJ. *Quím. Nova.* **2008**, 31: 1481.
[3]Cordeiro, T de M, Borghetti, F, Charneau, S. *Pharmacogn. Mag.* **2017**, 52: 668.
[4]Neto, GSG, da Costa RP, Zanini CL, Aguiar, AC, Souza, JO, de Souza GE, Severino, RP, Cass, QB, Cruz, FC, Oliva G, Guido, RVC, de Sousa, LRF. *J. Braz. Chem. Soc.* **2020**,31: 1475-1484.
[5]Singh, A, Bajpai, V, Kumar, S,Sharma, K. R, Kumar, B. *Natural Product Communications* **2016**, 11: 239-244.
[6]Muccilli, V,Cardullo, N, Spatafora, C, Cunsolo, V, Tringali, C. *Food Chemistry* **2017**, 215: 50–60.
[7]Kumar, S, Chandra, P, Bajpai, V, Singh, A, Srivastava, M, Mishra, DK, Kumar, B. *Ind. Crops and prod*. **2015**, 69: 143-152.

Acknowledgments

This study was financed in part by the CAPES (Coordenação de Aperfeiçoamento de Pessoal de Nível Superior, Brazil), Finance Code 001, and by CNPq.

Área: QPN

Volatile organic compounds from *Melipona quadrifasciata anthidioides* Lepeletier, 1836 (Apidae, Meliponini) sacrificed in hygienic behavior test

Jossimara N. de Jesus* (PQ),[1, 2] Paulo Roberto R. Mesquita (PQ),[2] Kelly B. da Silva (PQ),[2] Frederico de M. Rodrigues (PQ),[2] Carlos Alfredo L. de Carvalho (PQ),[1] João G. da Costa (PQ),[3] Cândida Maria L. Aguiar (PQ)[4]

prrmesquita@gmail.com; jjneiva21@gmail.com

[1]Insecta Research Laboratory, UFRB; [2]Agricultural Technological Center of the State of Bahia, Cetab/SEAGRI; [3]Embrapa Alimentos e Territórios, EMBRAPA; [4]Department of Biological Sciences, UEFS

Keywords: *Bee health, Dead brood removal behavior, GC-MS, Headspace, Stingless bees*

Highlights

VOCs from larvae were characterized by HS-SPME/GC-MS. Multivariate analysis showed that there was a separation in the compound profiles between the different treatments used in bee colonies.

Abstract

Losses of bee populations, mainly related to the synergistic effects between the occurrence of pests, pathogens, and contaminations from different origins, have raised concerns about the level of health of the colonies. Hygienic bees detect dead larvae through chemical signals and remove them from the colony. This study shows the profile of volatile organic compounds (VOCs) from larvae of *M. q. anthidioides* subjected to three death induction techniques for hygienic behavior (HB) studies: freezing in liquid nitrogen (LN2), freezing in a freezer (FRZ) and piercing of offspring with an entomological pin (PIN). The VOCs of 18 samples were obtained by HS-SPME and characterized using GC-MS and identified 42 VOCs from the following chemical classes: hydrocarbons, terpenes, esters, carboxylic acids, ketones, alcohols, and aldehydes. The relative abundance values of the compounds were processed and applied in Sparse Partial Least Squares Discriminant Analysis. Fig. 1A shows the VOCs profile of each technique and Fig. 1B shows contribution of the main VOCs in separating these profiles, with the three most discriminating compounds shown in Fig. 1C. The results obtained suggest that the variability in the chemical composition and relative abundance of VOCs is associated with the treatment used in HB studies, showing that the choice of method for inducing brood mortality can influence the speed of brood removal, and in the classification of the colony as hygienic or unhygienic.

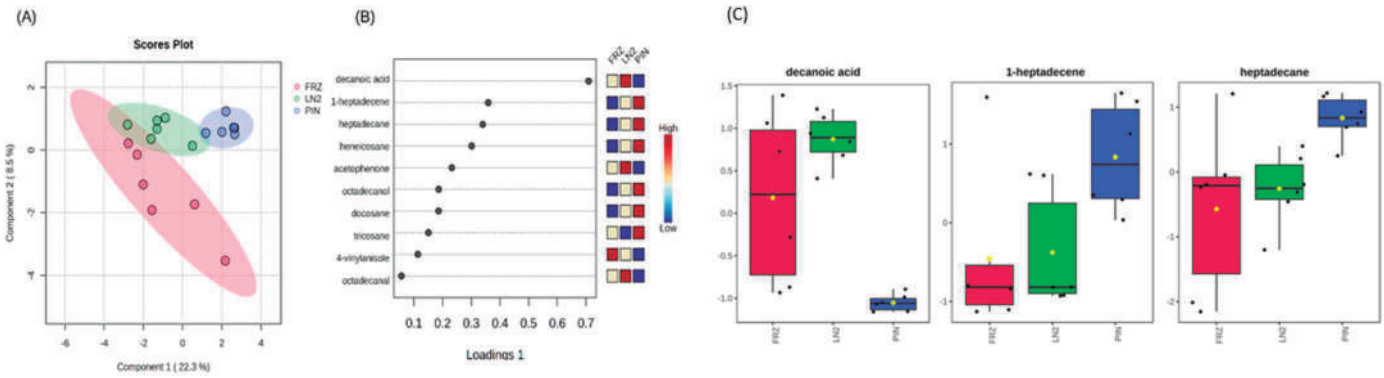


Fig. 1. Sparse partial least squares discriminant analysis (sPLS-DA) of volatile compounds from *Melipona quadrifasciata anthidioides* larvae subjected to three treatments (freezer-FRZ, liquid nitrogen-LN2, drilling-PIN) identified by GC-MS (A); Most discriminating VOCs in component 1 of sPLS-DA in decreasing order of contribution (B); Three most discriminating compounds between techniques (C).

Acknowledgments

This work was carried out with the support of the CAPES – Financing Code 001, linked to the Postgraduate Program in Agricultural Sciences at the Federal University of Recôncavo da Bahia (Scholarship for Jossimara N. Jesus).

Área: QPN

Would natural products be important for fungal endophytic association? A chemical ecology study of *Penicillium brasilianum* endophytism.

Daniel Yuri Akiyama (PG),[1] Marina Ferreira Maximo (PG),[1] Maria Eduarda Radavelli Santos,[2] Adriana Aparecida Lopes (PQ),[2] Taicia Pacheco Fill (PQ).[1]*

d195888@dac.unicamp.br; taicia@unicamp.br.

[1]Instituto de Química, UNICAMP; [2]Unidade de Biotecnologia, UNAERP.

Key-words: *Chemical Ecology, Biosynthesis, Endophyte-host interaction*.

Highlights

Investigation of the natural products involved in *P. brasilianum* – *M. azedarach* L. endophytic association. Among the produced fungal metabolites, JBIR-113 had its biosynthetic origin discovered.

Abstract

The chemistry involved in fungal-plant interactions has been under constant evolutionary pressure to optimize the production of small molecules that mediate communication, pathogenicity, defense responses and adaptation to the environment. Although chemical ecologists and natural products chemists have mainly focused on studying microbes' virulence factors in many pathosystems, little is known about the role of fungal secondary metabolism in non-pathogenic endophytic associations with the plant host. To shed light upon endophytic colonization mechanisms, we established a study system based on the in vitro growth of *Melia azedarach* L. and *Penicillium brasilianum*. We were able to successfully colonize not only the roots but the whole plantlets with two genomic and metabolic distinct *P. brasilianum* strains (LaBioMMi 136, a known root endophyte from *M. azedarach* L. and MG11, a soil isolate). Endophyte recovery assays indicated a lower colonization on leaves by the MG11 strain. Mass spectrometry-based chemical dereplication of the extracts from fungal-colonized plants led to the annotation of previously reported natural products from *P. brasilianum* such as brasiliamides, verruculogen, austin-related meroterpenes and the cyclodepsipeptide JBIR-113. Both the meroterpenes and cyclodepsipeptides are only produced by the LaBioMMi-136 strain, which might be related to the different observed colonization rates. Interestingly, JBIR-113 harbors a pipecolic acid moiety in its structure, a rare non-proteinogenic amino acid mainly found in marine natural products. We then decided to investigate the biosynthetic origin of JBIR-113. Genome mining revealed a nonribosomal peptide synthethase (NRPS) with a modularity corresponding to the structure JBIR-133. The knock-out of the NRPS, a phenylalanine ammonia-lyase, responsible for the first step in benzoic acid formation, and a monoamine oxidase, responsible for the conversion of lysine into pipecolic acid, was carried out through PEG-mediated protoplast transformation. Gene knock-out cassettes were constructed through in vivo recombination in yeast. Phenotypic characterization of the obtained mutant strains confirmed the biosynthetic origin of JBIR-113. Overall, our work offers insights into how the endophytic association between *M. azedarach* L. and *P. brasilianum* occurs, how distinct fungal metabolic backgrounds might be related to different colonization rates and provides a connection between the natural product JBIR-113 and its biosynthetic gene cluster.

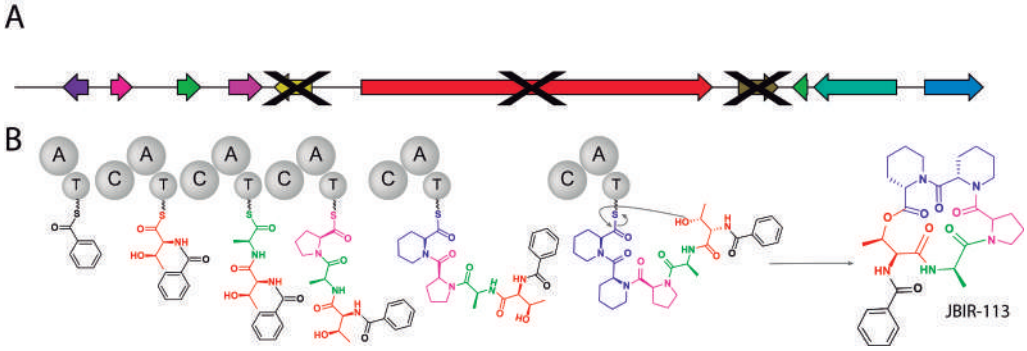


Figure 1. Biosynthetic gene cluster for the production of JBIR-113 and the genes knocked-out in this work (A). Proposed biosynthetic assembly of JBIR-113 (B).

Acknowledgments

CNPq CAPES serrapilheira FAPESP

QVE

Química Verde

Sociedade Brasileira de Química

Área: _____
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Aplicação de solventes ambientalmente adequados na selenilação de núcleos naftólicos

João Pedro Vargas Jesuino (IC)[1], Mylena Mendes Gularte (PG)[1], Antonio L. Braga (PQ)[2], Juliano Alex Roehrs (PQ)[3] e Juliano Braun Azeredo (PQ)[1]

joaojesuino.aluno@unipampa.edu.br; jbraunquimico@gmail.com

[1]Programa de pós-graduação em ciências farmacêuticas, PPGCF, Universidade Federal do Pampa – UNIPAMPA campus Uruguaiana; [3]Departamento de Química – Universidade Federal de Santa Catarina; [3] Instituto Federal de Educação Ciência e Tecnologia Sul-riograndense – IFSUL campus Pelotas

Palavras Chave: *Naftol, Selenilação, Solventes verdes, Polissorbato-80, Química verde*

Highlights

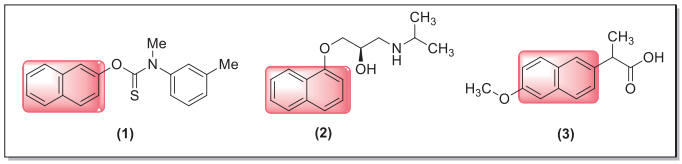
Title: Use of green solventes in the selenylation of naftols.

Development of a new methodology for the selenylation of napholic systems. Variation of several greener solvents for the selenylation of 2-naftol with diphenyl diselenide. Polisorbate-80 was found as the best result among the solvents tested.

Resumo/Abstract

O núcleo naftalênico é composto por dois anéis benzênicos fundidos entre si. Esse composto demonstra propriedades químicas estritamente relacionadas a sua aromaticidade, e pelo fato de ser uma espécie rica em elétrons. O naftaleno possui destaque a respeito das suas atividades biológicas evidenciadas em alguns fármacos, como por exemplo o antifúngico tolnaftato **(1),** o anti-hipertensivo propranolol **(2)** e o anti-inflamatório naproxeno **(3)** (Figura 1).[1]

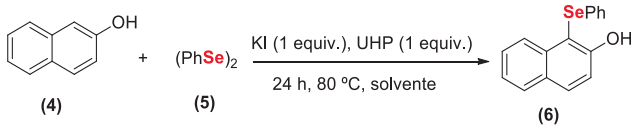
Figura 1. Fármaco com núcleo naftalênico



A introdução de um átomo de selênio nesse núcleo é de extrema relevância, haja visto que moléculas orgânicas de selênio possuem grande apelo, especialmente pela propriedade antioxidante a elas atribuídas.[2] Nesse contexto, a otimização das condições reacionais para realizar esse processo necessita constantemente ser aprimorada, especialmente no que se refere à adequação desses métodos aos princípios de química verde. No que se refere a isso, um dos parâmetros importantes de serem observados é a escolha do solvente mais adequado para que essa transformação ocorra. Assim, escolher solventes que minimizem de alguma forma o impacto no meio-ambiente se faz necessário projetando que esse processo seja utilizado em escala industrial.

Dessa forma, nosso trabalho estudou a variação dos solventes na selenilação do 2-naftol **(3)**, empregado disseleneto de difenila **(4)** como substrato padrão, na presença de KI e peróxido de hidrogênio-uréia (UHP). Dentre os solventes com caráter ambientalmente adequados testados, o melhor resultado foi obtido utilizando-se o surfactante polissorbato-80, onde o produto selenilado **(5)** foi sintetizado em 83% de rendimento (Tabela 1, Entrada 4).

Tabela 1. Variação dos solventes



Entrada	Solvente	Rendimento (%)
1	2-Me-THF	45
2	PEG-400	70
3	PEG-200	67
4	Polissorbato-80	83
5	lactato de etila	15
6	etanol	47

Com os resultados obtidos até o momento, pode-se concluir que o método de selenilação em polissorbato-80 possui grande eficácia do ponto de vista de rendimento e do ponto de vista ambiental, visto que esse solvente pode ser reciclado e reutilizado. Estudos adicionais estão em andamento em nosso laboratório.

[1]*Eur. J. Org. Chem* **2017**,4740. [2]*Chem. Rev.* **2004**, *12*, 6255

Agradecimentos/Acknowledgments

PPGCF- Universidade Federal do Pampa

Área: QVE

Avaliação da qualidade das misturas de biodieseis de óleos de milho, de girassol e de licuri (*Syagrus coronate).*

Acacia Adriana Salomão (PG),[1] Isabelly C. B. Gonçalves (IC),[1] Arnaldo G. de Oliveira Júnior (PG),[2] Gildo Girotto Júnior (PQ),[1*] Matthieu Tubino (PQ),[1]

acacia@unicamp.br; ggirotto@unicamp.br; tubino@unicamp.br

[1]*Departamento de Química Analítica, IQ-UNICAMP,* [2]*Departamento de Química Orgânica, IQ- UNICAMP*

Palavras Chave: *Biodiesel, Óleo de licuri, Estabilidade oxidativa, Ponto de entupimento de filtro a frio, Blendas.*

Highlights

Evaluation of the quality of biodiesel blends from oils of corn, sunflower and licuri *(Syagrus coronate).*
Evaluation of oxidative stability and cold filter plugging point (CFPP) of blends of biodiesels prepared from licuri, corn and sunflower oils.

Resumo/Abstract

Biodiesel é uma mistura de monoalquilesteres proveniente da reação de transesterificação de óleos vegetais, sendo os de soja e canola os mais usados mundialmente. Porém, a utilização desses óleos aumenta a competição entre a produção de alimentos e do biocombustível. O uso de fontes alternativas, como o óleo de licuri, pode beneficiar comunidades locais por explorar espécies nativas, proporcionando emprego e renda em regiões economicamente menos favorecidas. Neste trabalho foram avaliados alguns parâmetros de qualidade, como a estabilidade à oxidação expressa pelo período de indução (PI) e o ponto de entupimento de filtro a frio (PEFF) das blendas de biodieseis de óleos de milho, girassol e licuri, em diferentes proporções. A Agência Nacional de Petróleo, Gás Natural e Biocombustíveis (ANP) estabelece que o PI seja de no mínimo 13 h e o PEFF esteja entre 0 a 19 °C, dependendo do mês e região/UF de destino do produto. Os biodieseis de óleo de milho e de girassol foram preparados por reação de transesterificação em duas etapas, com metanol na presença de metóxido de sódio como catalisador, sob agitação e aquecimento à 60 ˚C por uma hora, seguido do processo de purificação com lavagem com água, secagem em estufa a 100 ˚C, por 1 hora, e tratamento com resina de troca iônica. A preparação de biodiesel do óleo de licuri seguiu o mesmo procedimento, com uma etapa prévia de esterificação com metanol, usando ácido sulfúrico concentrado como catalisador. O PI foi determinado pelo método Rancimat (873 Biodiesel Rancimat Metrohm). O PEFF foi determinado segundo a norma ASTM 6371. Todas as determinações foram realizadas em triplicata. Determinou-se o índice de acidez do óleo de licuri que, inicialmente, apresentou o valor 2,21±2,10 mg KOH g^{-1}. Após realizar a etapa de esterificação o índice de acidez do óleo diminuiu para 0,41±0,02 mg KOH g^{-1}, viabilizando a síntese do biodiesel de licuri, por transformar os ácidos graxos livres, responsáveis pela acidez, em ésteres, com consequente diminuição da acidez. A tabela abaixo ilustra os valores de PI e PEFF dos biodieseis obtidos a partir dos óleos de milho, de girassol, de licuri e de blendas destes biodieseis.

Licuri:Milho	PI (h)	PEFF (ºC)	Licuri:Girassol	PI (h)	PEFF (ºC)
100:0	69,8±4,2	9,0±0,6	100:0	69,8±4,2	9,0±0,6
80:20	37,3±2,9	5,7±0,6	80:20	23,6±2,6	6,3±0,6
70:30	15,1 ±0,1	2,7 ±0,6	70:30	14,7±0,6	5,0±0,6
50:50	8,6±0,3	1,7 ±0,6	50:50	8,4±3,3	1,7±0,6
30:70	3,1 ±0,1	-2,3 ±0,6	30:70	3,1±0,1	-2,3±0,6
20:80	6,8 ±0,1	-3,7 ± 0,6	20:80	3,7±0,4	-3,3±1,2
0:100	7,7± 0,1	-8,0±1,0	0:100	2,8±0,3	-9,7±0,6

Um dos principais problemas dos biodieseis de milho e de girassol é a baixa estabilidade à oxidação. A adição do biodiesel de licuri aos biodieseis de milho e girassol favorece o aumento do PI, enquadrando-o à especificação da ANP, mantendo-se o PEFF abaixo do limite máximo admitido. Biodieseis provenientes de óleos saturados apresentam valores elevados de PEFF, prejudicando a qualidade do biocombustível. Os resultados obtidos no presente trabalho indicam que, com o uso biodiesel de licuri nas blendas, este parâmetro enquadra-se nas normas para algumas misturas. Considerando, também, a sua estabilidade à oxidação, considera-se promissora a utilização do biodiesel de licuri em blendas, visando obter produto final de boa qualidade.

Agradecimentos/Acknowledgments

Ao CNPq pelo financiamento e ao IQ-UNICAMP pela infraestrutura oferecida.

Ferrari, R. A. e Souza, W. L. *Quim. Nova* **2009**, *32*, 106; Silva, P. R. e Freitas, T. F. S. *Ciência Rural* **2008**, *38*, 843; Araújo, P. H. M; Maia, A. S; Cordeiro, A. M. T. M; Gondin, A. D; e Santos, N.A. *ACS Omega* **2019**, 4, 15849- 15855. Serrano, M.; Oliveros, R.; Sánchez, M.; Moraschini, A.; Martínez, M; Aracil, J. *Energy* **2014**,*65*, 109.

Área: QVE

Beyond Benign and the Green Chemistry Commitment Program: Empowering a Systemic Change in Chemistry Education

Juliana L. Vidal,[1] Natalie J. O'Neil,[1] Amy S. Cannon[1]*

juliana_vidal@beyondbenign.org; amy_cannon@beyondbenign.org

[1]*Beyond Benign Inc., 18 Church Street, P.O. Box 1016, Wilmington, MA, 01887, United States.*

Keywords: *Green Chemistry, Sustainability, Education*

Highlights

The Green Chemistry Commitment is a program created by Beyond Benign to catalyze the adoption of green chemistry in higher education, providing systemic and lasting change toward a sustainable future.

Resumo/Abstract

Green chemistry education is critical for providing scientists and citizens with the required tools to assess, choose, and further design more benign processes and products for our society and our environment. To host and empower a whole community dedicated to implementing green chemistry teaching and practices across the education continuum, Dr. John Warner and Dr. Amy Cannon founded Beyond Benign in 2007. One of its programs, the Green Chemistry Commitment (GCC), is a signal of intent provided by universities, colleges, institutes, and centers to begin or continue incorporating green chemistry in their curricula.

10 years after its launch, the GCC program supports more than 150 higher education institutions in over 15 countries through a diverse, accessible, and inspiring community that acts as a collective voice to inspire the broader adoption of green chemistry. In this presentation, an overview of the Commitment program and its impact on transforming chemistry education in Brazil and beyond will be performed. The benefits of incorporating green chemistry principles and practices in research, teaching, and service will also be discussed, thus highlighting the important role of collaboration between individuals, sectors, and organizations in providing students with the skills and abilities to create a sustainable planet.

Agradecimentos/Acknowledgments

Beyond Benign, the American Chemical Society Green Chemistry Institute (ACS GCI), and the Green Chemistry Commitment participating institutions.

Área: QVE

Design and Green Synthesis of a Novel Tripeptide for Sebum Control and In vitro and Clinical Studies.

Vinícius Kuchenbecker (IC),[1] Cleverson R. Princival (PQ),[1] Brasil, M. C. O. A. (PG),[2] Cilli, E. M (PQ),[2] Giovana Padovani (PQ),[1] Lilian Mussi (PQ),[1] Flávio B. Camargo (PQ),[1] Rafael V. C. Guido (PQ),[3] Wagner V. Magalhães (PQ),[1] Edson Katekawa (PQ).[1]*

vinicius.kuchenbecker@chemyunion.com; edson.katekawa@chemyunion.com

[1]Research, Development & Innovation Department, Chemyunion Ltda., São Paulo, Brazil; [2]Department of Biochemistry and Organic Chemistry, IQ, UNESP; [3]São Carlos Institute of Physics, University of São Paulo.

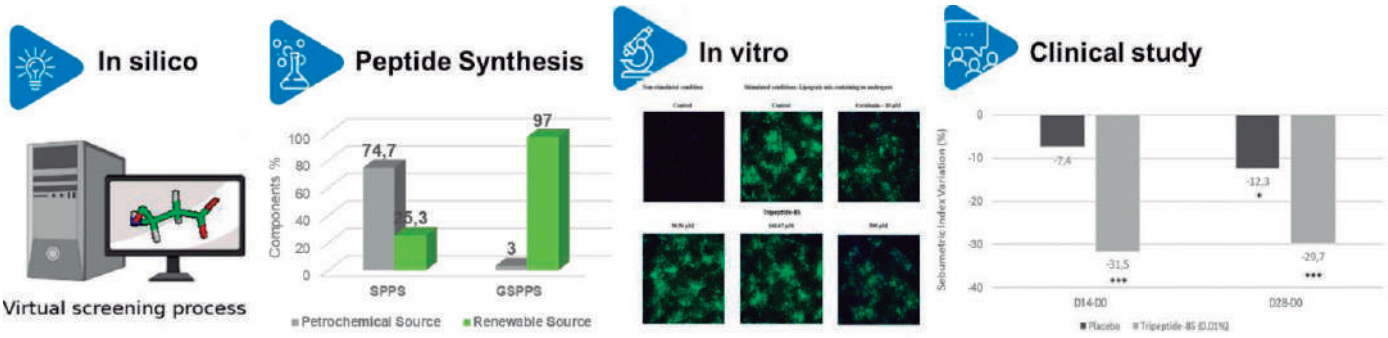
Palavras Chave:*(Green Chemistry, In Silico, Clinical Study, GSPPS, Peptide, MC5R Receptor, Sebum Control)*

Highlights

Greener synthesis of peptide for cosmetic applications. Virtual screening process for design of unprecedented tripeptide for sebum control in skin. New MC5R receptor antagonist tripeptide with action in the reduction of sebum production through *in vitro* and clinical studies. Large-scale peptide synthesis.

Resumo/Abstract

Sebaceous glands are multi-lobular glandular structures associated with hair follicles constituting the pilosebaceous units of the skin, whose main function is the production of sebum. Alterations in these glands can cause pathological processes such as hyperseborrhea and disseborrhea. These changes may favor *Cutibacterium acnes* (*C. acnes*) growth and biofilm formation, disrupt follicular barrier function, induce comedogenesis, and promote subsequent inflammation. In light of this, the aim of this study was to identify a new MC5R antagonist peptide and evaluate *in vitro* and *in vivo* its efficacy on sebum production control. The MC5R model was built using homology modelling, and a structure-based virtual screening process was performed. A tripeptide was selected based on its high affinity for the receptor, determined by the free binding energy. The new tripeptide was obtained by green solid phase peptide synthesis (GSPPS) methodologies, utilizing renewable solvents in the synthesis and purification process. The evolution of the synthesis and purification process made it possible to achieve a reduction of the use of raw materials and reagents from petrochemical sources (from initial 74,7% of petro-derived components, to only 3%) and an increase of more than 380% in the use of raw materials and reagents from renewable sources, thus allowing the process to reach naturalness index of 97%, which consists on high standards when it comes to peptide production. *In vitro* and clinical studies were performed to evaluate the tripeptide efficacy. Both experimental models showed significant effects on sebum levels decrease. In the clinical study, a significant reduction in sebumetric levels was observed after 14 days of treatment with a cosmetic formulation containing 100-ppm of tripeptide. In this work, we report the discovery of a new active cosmetic ingredient capable of reducing sebum production, and synthesized using an industrial process that strongly leans towards the principles of green chemistry.



Agradecimentos/Acknowledgments

CHEMYUNION LASEBio IFSC USP Finep FAPESP CNPq CAPES

Área: QVE

From plastic to soap: a proposal for scientific divulgation about the science contribution for plastic waste management

Thays A. N. Lopes (IC), Victor Hugo O. Cavalcanti (PG), Cíntia D. F. Milagre (PQ)*

thays.lopes@unesp.br; cintia.milagre@unesp.br

Institute of Chemistry, São Paulo State University (UNESP), Araraquara.

Keywords: *Green Chemistry; Sustainability; Plastics; PET, PLA, organic hydrolysis reaction*

Highlights

PET and PLA alcaline degradation were compared. Soap was made from PLA degradation. A hands-on activity to promote awareness of green and sustainable chemistry was carried out.

Abstract

Millions of tons of plastics are produced annually to meet society's demands. The inappropriate methods of plastic waste management result in a global environmental issue. Therefore, it is crucial to have strategies to minimize the environmental impacts caused by plastic excess.[1] In this regard, this work aims to spark curiosity and raise young students awareness about sustainable consumption (Sustainable Development Goals - SDG #12, Agenda 2030) and the processes of plastic degradation through a hands-on activity. Two polymers, the biobased biodegradable polylactic acid PLA and the recalcitrant petroleum-based polyethylene terephthalate PET were subjected to degradation by basic hydrolysis. The target audience was high school students and their science teachers from two public high schools at Araraquara- SP participants of the project "Futuras Divulgadoras Científicas de Museus: educação museal para o desenvolvimento sustentável". This two-hour activity, divided into three parts, was adapted from the educational material available at the Green Chemistry Teaching and Learning Community (GCTLC) and developed at the Araraquara Science Centre.[2] The first part consisted of brainstorming about the student's previous knowledge of green chemistry, sustainability, plastic usage, production, and degradation, followed by experimental activity (PLA and PET basic hydrolysis and comparison of the soap produced from PLA degradation with commercial soaps) and the fulfillment report. According to the students' reports, they understood the concepts of sustainability and the necessity for greener chemistry. Moreover, they conducted a chemical reaction – saponification - that transformed PLA into lactic acid, a "greener" active ingredient of many household cleaners. They used this new product - a cleaning solution - to clean dirty surfaces with oil, catchup, and mustard. As expected, the PET cups were not degraded under the experimental conditions used herein, and the students could learn what variables and controls are in science experiments. Besides the success of this hands-on activity, we strongly suggest 4 hours: 2 hours for background reading and discussions plus 2 hours laboratory.

Figure 1.
Experimental Activities

Reference: [1] Atlas do plástico: Fatos e números sobre o mundo dos polímeros sintéticos. Fundação Heinrich Böll (2020) available at https://br.boell.org/pt-br/2020/11/29/atlas-do-plastico access February 2024. [2] GCTLC Beyond Benign - Green Chemistry Education available at https://gctlc.org/, access February 2024.

Acknowledgments

The authors acknowledge the financial support of CTPetro (CNPq – FNDCT) grant no. 408711 / 2022-1 project "Processes Intensification at the Service of the Environment: Biocatalytic Degradation of PET", and the fellowships from Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) - Finance Code 001 and CNPq PIBIC RT/UNESP. The authors express their gratitude to prof. José Murayama, coordinator of the project "Futuras Divulgadoras Científicas de Museus: educação museal para o desenvolvimento sustentável" and prof. Camila Silveira for the invitation to develop this scientific divulgation activity within their project.

Área: QVE

Renewable polymers from carbonated macaw palm oil and polyphenols

Rafael T. Alarcon (PD),[1] Caroline Gaglieri (PD),[2] Gilbert Bannach (PQ),[2] Éder T.G. Cavalheiro (PQ),[1]

rafael.alarcon@usp.br ; caroline.gaglieri@unesp.br; gilbert.bannach@unesp.br; cavalheiro@iqsc.usp.br

[1] Universidade de São Paulo-USP, Instituto de Química de São Carlos, São Carlos, SP, Brazil; [2] Universidade Estadual Paulista "Júlio de Mesquita Filho" - UNESP, Faculdade de Ciências, Bauru, SP, Brazil

Keywords: *Renewable material, vitrimer, Carbon dioxide, Green Chemistry*

Highlights

The macaw palm oil was reacted with Tris(2-aminoethyl)amine to give a fatty amide, which was epoxidated and further carbonated providing a renewable monomer. This monomer was reacted with polyphenols.

Abstract

The macaw palm oil (MPO) is obtained from a palm tree found in Brazil and has been cultivated for technological and scientific purposes. The MPO is categorized as a semi-dry oil containing 79% of the unsaturated fatty chain. This oil has already been used as a monomer for poly-hydroxyuretanes, acrylic and ester polymers. However, for the first time, MPO was reacted with Tris(2-aminoethyl)amine to synthesize fatty acid amides (FAA). The FAA was then reacted by Prilezhaev reaction to form an epoxide derivative, which was further reacted with CO_2 to give a carbonate derivative (AMPO-C). After that, the AMPO-C was reacted with 4 different polyphenols (curcumin, quercetin, tannic acid and gallic acid) for 48 h at 120 °C to produce poly-hydroxycarbonates. The FAA, its derivatives and poly-hydroxycarbonates were characterized by spectroscopic analysis (e.g., FTIR and ^{1}H-NMR) and thermal analysis (TG-DTA and DSC). These poly-hydroxycarbonates have thermal stability up to 200 °C by TG and present glass transitions as confirmed by DSC. All polymers presented vitrimeric properties (e.g. self-healing features). Figure 1 shows the self-healing process under red light (660 nm) for the poly-hydroxycarbonates using curcumin as a cross-linker. The polymer can be ground and recovered after this process.

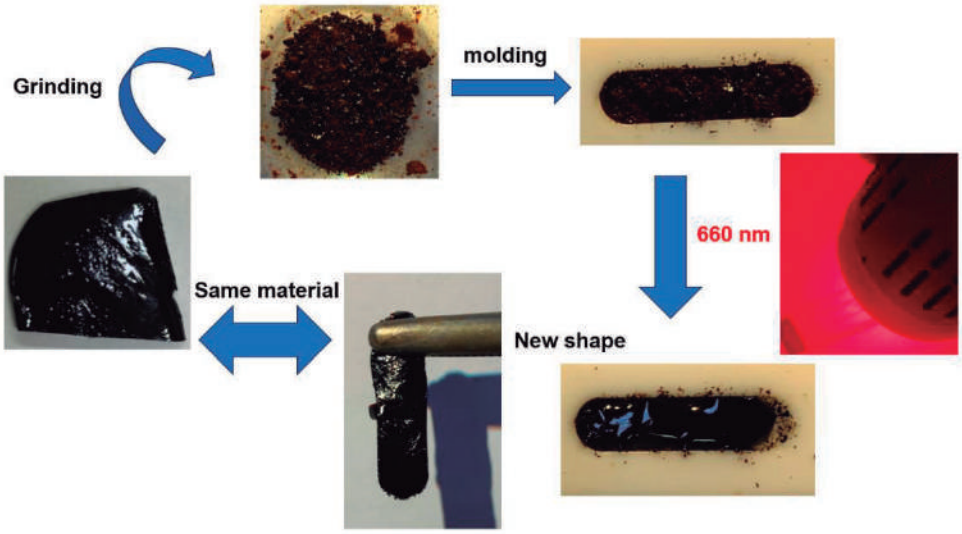


Figure 1. Reshaping of poly-hydroxycarbonate/curcumin under red light (660 nm)

Acknowledgments

The authors wish to thank the São Paulo Research Foundation-FAPESP (grant 2021/14879-0, 2021/02152-9 and 2022/15211-6), CAPES (grants 024/2012 and 011/2009 Pro-equipment), and CNPq (grant 303247/2021-5, 150233/2021-1) for financial support.

Área: QVE

SUSTAINABLE DEVELOPMENT OF ANTIOXIDANTS ADDITIVES FOR BIOFUELS FROM CRUSTACEAN WASTE

Francisco Leonardo Moreno Martins (IC),[1] Francisco E. A. Rodrigues (PQ),[1] Tathilene B. M. G. Arruda (PQ).[2] Emanuelle P.H. Alencar (PG)[1], Rebeca Teobaldo Pinto (PG)[1],

francisco.leonardo.moreno06@aluno.ifce.edu.br ; francisco.eduardo@ifce.edu.br

1 *Department of Chemistry, Federal Institute of Ceará;* 2 *Department of Chemistry, Federal University of Ceará.*

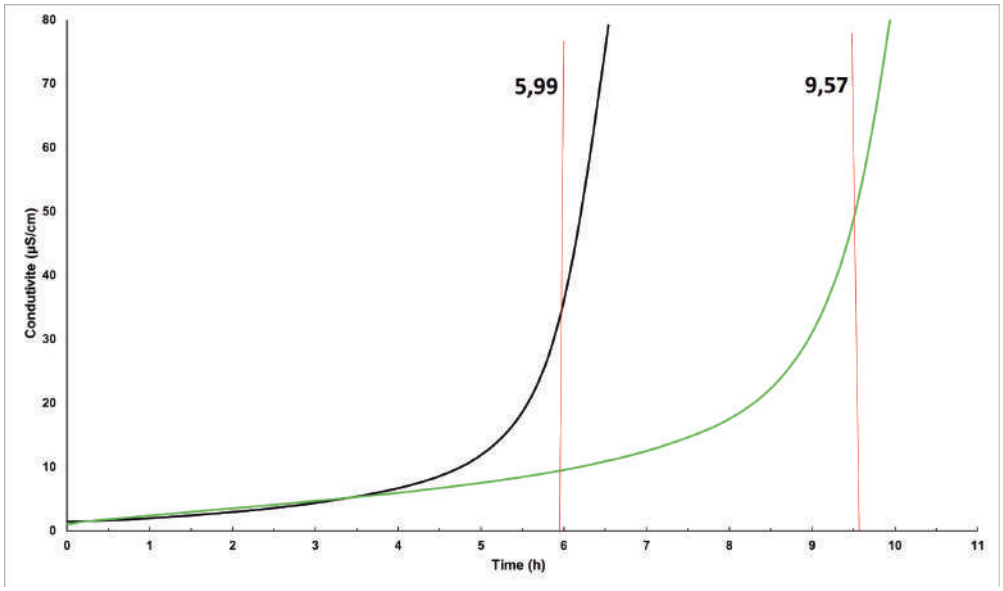
Keywords: *Sustainable, Antioxidants, Crustacean Waste, Biodiesel.*

Highlights

- Crustacean waste has potential as an additive antioxidant.
- The Biodiesel was characterized using thermogravimetry and oxidative stability tests.
- Concentration of 1% to biodiesel showed the most significant results.

Resumo/Abstract

The accentuated dumping of organic material along with other solid waste causes the appearance of vectors that bring diseases and contaminate the environment with the generation of manure and gases. One of these discarded materials is the residue from the fishing industry: the cephalothorax and shrimp shells. The extract, in addition to coming from a renewable source, being biodegradable, can be obtained using low-cost solvents that can also be recovered to be used again, they are ethyl alcohol and hexane. In this sense, the present work evaluated the shrimp hexane extract as an enhancer of oxidative stability in biodiesel. The thermal characterization of the extract obtained by thermogravimetry. In an oxidative stability test by Rancimat method, the most significant results were observed at a concentration of 1% to biodiesel (Fig. 1), which generated an increase of 3h in the induction period in relation to biodiesel without the additive.



(Figure 1 - — sample without the additive antioxidant / — sample with 1% EHCC.)

Agradecimentos/Acknowledgments

PPGER/ IFCE, CAPES, CNPQ.

Área: QVE

Synthesis of Composites of Lignin from cashew apple bagasse with photoprotective properties

Vanessa Moreira Frota (PG),[1]* Stefanny Freitas de Oliveira (IC),[1] Tigressa Helena Soares Rodrigues (PQ),[2] Maria Valderez Ponte Rocha (PQ).[1]

vanessa-frota1@hotmail.com; valderez.rocha@ufc.br

[1]*Departamento de Engenharia Química, Centro de Tecnologia, Universidade Federal do Ceará – UFC;*
[2]*Departamento do Curso de Química, Centro de Ciências Exatas e Tecnologia, Universidade Estadual Vale do Acaraú – UVA*

Keywords: *Lignin, Quaternization, Titanium Oxide, Zinc Oxide, Photoprotective Properties.*

Highlights

- Use of an agro-industrial residue (cashew apple bagasse) for lignin recovery;
- Modification and conjugation of lignin with titanium and zinc oxides for photoprotective enhancement.

Abstract

Natural substances with radiation-protective qualities such as lignin have attracted great interest, and the use of agro-industrial residues such as cashew apple bagasse (CAB), appears as an economic and alternative source to obtain this biomolecule. As a natural resource of renewable biomass, lignin is non-toxic, biodegradable, cheap, easy to obtain, and the richness in aromatic rings with photoprotective potential. Besides this, hybrid composites of lignin-metal oxide with excellent absorption properties and UV stability have promising applications when considering photoprotection[1,2,3]. In this context, the objective of this work was to produce and characterize the quaternized lignin and its conjugation with titanium and zinc oxides to improve its stability and photoprotective properties. The production of quaternized lignin was carried out with 3-chloro-2-hydroxypropyltrimethyl ammonium chloride at 85 °C and 1000 rpm for 4 h. The lignin hybrid composites were synthesized using zinc and titanium oxides during 4 and 6 h, respectively, at 85 °C, under mechanical stirring of 1000 rpm and dark conditions. After, the dispersion was homogenized at 15000 rpm for 20 min and yields were calculated for each process. The quaternization of lignin from CAB was identified by FTIR analysis in the band at 1470 cm^{-1}, and the bands of ZnO and TiO_2 conjugated with quaternized lignin were observed in the 400 - 450 cm^{-1} e 500 - 600 cm^{-1}, respectively. The yields were 56.6% of quaternized lignin (QLig), 48.1% of QLig-TiO_2 and 35.9% of QLig-ZnO composites. When compared with non-quaternized lignin (Lig), the yields of composites were 38.92% of Lig-TiO_2 and 22.84% of Lig-ZnO. The zeta potential of the composites synthesized using the QLig increased, from + 5.77 ± 0.1 mV (Lig-TiO_2) to + 12.2 ± 0.4 mV (QLig-TiO_2) for titanium composites, and - 41.0 ± 0.1 mV (Lig-ZnO) to - 44.5 ± 0.5 mV (QLig-ZnO) for zinc composites, indicating that quaternization allowed improving the stability of the composites in relation to non-quaternized lignin, analyzing the results in modulus. Therefore, quaternized lignin composites, especially the composites formulated with zinc, showed higher stability than lignin composites, with a promising photoprotective potential for application in sunscreens.

[1] ANUSHIKHA; GAIKWAD, K. K. **Biomass Conversion and Biorefinery**, p. 1-13, 2023.
[2] WANG, H., WANG, Y., FU, F., QIAN, Y., XIAO, Y., YANG, D., & QIU, X. **International journal of biological macromolecules**, v. 150, p. 371-379, 2020.
[3] KAUR, R., BHARDWAJ, S. K., CHANDNA, S., KIM, K. H., & BHAUMIK, J. **Journal of Cleaner Production**, v. 317, p. 128300, 2021.

Acknowledgments

Embrapa Agroindústria Tropical
CAPES
CNPq Conselho Nacional de Desenvolvimento Científico e Tecnológico
FUNCAP

Área: QVE

THE BRAZILIAN SCENARIO FOR BIOLUBRICANTS RESEARCH – A CRITICAL REVIEW OF THE YEARS FROM 2011 TO 2023.

Rebeca Teobaldo Pinto (PG)[1], Tathilene B. M. G. Arruda (PQ)[2]*, Francisco E. A. Rodrigues (PQ)[3], Emanuelle P. H. Alencar (PQ)[3], Francisco L. M. Martins (IC)[3]

rebecateobaldo@outlook.com; tathilene@gmail.com

[1]Federal Institute of Ceará, Campus Maracanaú; [2]Federal University of Ceará, Department of Organic and Inorganic Chemistry; [3] Federal Institute of Ceará, Campus Caucaia.

Keywords: *Biolubricants, Brazil, Biodiversity.*

Highlights

- The low consumption of Biolubricants in Brazil.
- The focus of Brazilian research in just two states.
- Industrial support mainly to research using enzymatic catalysis.

Resumo/Abstract

In order to understand the scenario of Brazilian research about biolubricants, improving cognition about the field of knowledge of environmentally friendly lubricants and how Brazilian researchers could contribute to the popularization of biolubricants by Brazilian lubricant consumers, this critical review explores the scientific works about the topic. The main criteria of selection of the papers were articles developed in Brazilian Universities and Institutes or with the presence of Brazilian researchers. The increase in researches about biolubricants in the last 3 years in the country (Fig.1) presents different contributions to knowledge about the synthesis, characterization and application of biolubricants. The objective of this review is to point out the diversity in the chemical routes used in the articles, the variety of botanical species used in the different experiments whose objective was the development of biolubricants (Fig. 2). In this way, the quality of the work produced by Brazilian researchers in the area of biolubricants, combined with the important and considerable diversity of oilseed species that can be found in Brazil, demonstrate the potential to enrich cognition in the field of knowledge not only for the Brazilian public, but for the entire world.

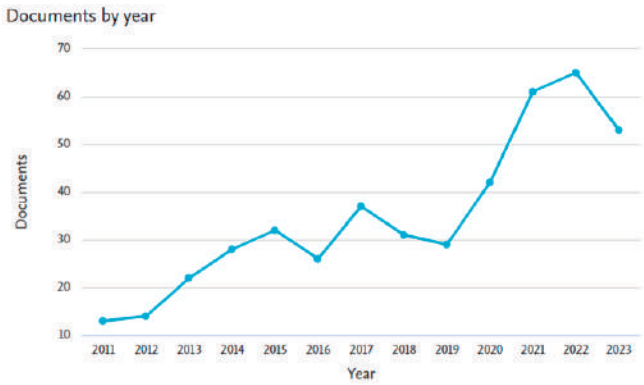


Figure 1- Number of articles published in the last years, using SCOPUS database

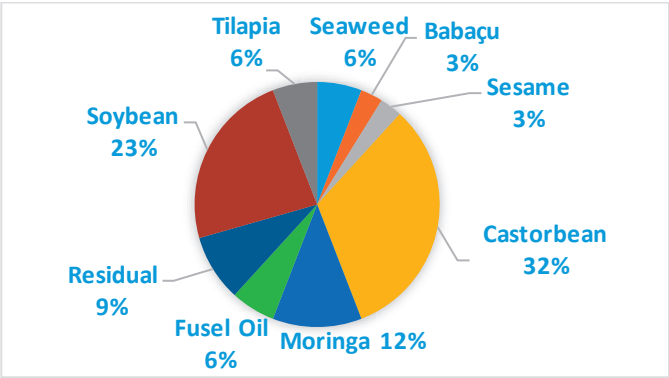


Figure 2- Main feedstock used by Brazilian researches in the production of biolubricants

Agradecimentos/Acknowledgments

PPGER/ IFCE, CAPES, CNPQ.

TEC

Química Tecnológica

Sociedade Brasileira de Química

Área: TEC

ACELERAÇÃO DE TECNOLOGIAS DAS UNIVERSIDADES PARA O MERCADO: ESCALAB CENTRO DE ESCALONAMENTO E MODELAGEM DE NEGÓCIOS

Thamires L. B. Alves (PG),[1*] Ana Paula De C. Teixeira (PQ),[1] Rochel Montero Lago (PQ),[1] Breno G. De F. Oliveira (PG),[1] Luísa C. A. Barbosa (PG),[1] Maria D. De Oliveira.[1] thamires.braz@escalab.com.br.

[1]Departamento de Química, Universidade Federal de Minas Gerais (UFMG). Av. Pres. Antônio Carlos, 6627 – Pampulha, Belo Horizonte - MG – 31270-901

Palavras Chave: *INOVAÇÃO, ESCALAB, TECNOLOGIAS QUÍMICAS, ESCALONAMENTO.*

Highlights

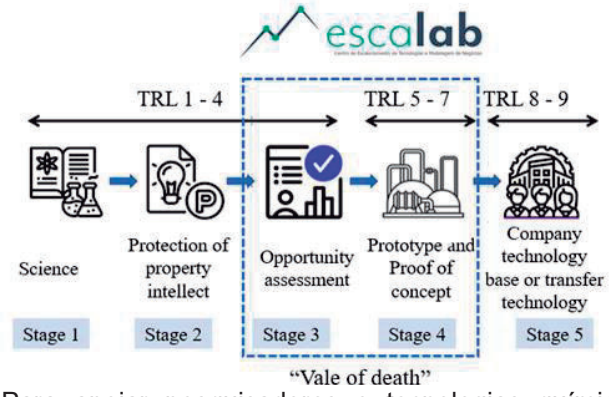
Accelerating university technologies to the market: Escalab center for scaling and business modeling

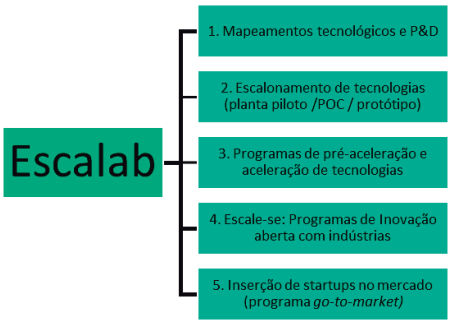
Escalab is a chemical technology and innovation lab at UFMG structured to take technologies to the market and connect academy-industry focused on scale up, business modeling and startup creation.

Resumo/Abstract

Esse trabalho tem como intuito descrever o processo de inovação, com foco em levar tecnologias químicas nascidas nas universidades ao mercado.

O processo de inovação pode ser pensado em cinco etapas, mostradas na figura ao lado. As pesquisas em universidades avançam bem durante as duas primeiras etapas, mas tem enormes dificuldades para avançar nas etapas 3 e 4, que são conhecidas como o "Vale da Morte", onde a imensa maioria das tecnologias perece. Desse modo, o conhecimento de como realizar essas etapas é fundamental para melhorar o processo de transferência de tecnologias da universidade para o mercado e sociedade[1].





Para apoiar pesquisadores e tecnologias químicas nas Etapas 3 e 4, foi criado o Escalab (Centro de Escalonamento de Tecnologias e Modelagem de Negócios), um laboratório da UFMG (Universidade Federal de Minas Gerais), que tem como objetivo fomentar o processo de inovação, levando tecnologias da bancada até a escala piloto e ao mercado. Para isso, o Escalab atua na realização de diferentes atividades mostradas na figura ao lado[2].

O Escalab possui toda a infraestrutura, *know-how* e mão de obra qualificada necessários para a realização do escalonamento da tecnologia e modelagem de negócios.

Agradecimentos/Acknowledgments

INCT Midas, FAPEMIG, CNPq, CAPES.

1. Alves, T. L. B.; Teixeira, A. P. C.; Oliveira, B. G. D. F.; Barbosa, L. C. A.; Oliveira, M. P. D. De; Lago, R. M.; *Quim. Nova* **2023 (*in press*).**

2. Comunicação; **2023**, https://escalab.com.br/

Área: TEC

Application of alcoholic extract of coffee leaves as an antioxidant additive in biodiesel.

Nathan F.Silva (IC),[1] Eduardo G. de Sousa (IC),[1] Júlia W. Campos (IC),[1] José Gonçales Filho (PG); Isadora G. Branco (PG); Érica S. Romagnoli (PQ) ; Karina A. B. Angilelli (PQ);[1] Dionisio Borsato (PQ).[1]

Nathansilva1905@yahoo.com; dborsato@uel.br
[1]*Departamento de Química, UEL*

Palavras Chave: Biofuel, Induction period; Oxidation reaction, Rate constant, degradation

Highlights

Biodiesel oxidation was investigated using alcoholic extract from coffee leaves as an additive with antioxidant properties. The extract exhibited a good result retarding the oxidation reaction

Resumo/Abstract

Fossil fuels currently are the most used energy source and have a significant impact on the environment, being one of the main contributors to the emission of greenhouse gases. In light of this ecological challenge, researchers have begun efforts to identify a suitable alternative to fossil fuels. Among the various alternatives, biodiesel, produced from renewable raw materials such as vegetable oils and animal fats, appears as a promising substitute for petroleum diesel. Biodiesel offers a series of advantages, including local supply, reduction of aromatic and sulfur oxide emissions into the atmosphere, mitigation of greenhouse gas emissions and potential reuse of glycerin, a product generated during the transesterification process in biodiesel production. Despite its significant environmental benefits, biodiesel has reduced oxidative stability compared to conventional diesel due to the presence of fatty acid esters and double bonds in the carbon chain, these attribute could render biodiesel less suitable for utilization in automotive engines, potentially leading to heightened viscosity, increased acidity, and the formation of gum-like substances and solid compounds. In addition, during the production, transportation, and storage phases, biodiesel is susceptible to exposure to moisture and transition metal ions, such as copper and iron which can potentially originate from the equipment involved in its production and the storage tanks, thereby hastening the oxidative process and potentially rendering it unsuitable for certain applications. Therefore, for the appropriate commercialization of biodiesel, antioxidants are used to increase the induction period (IP), reduce the rate constant of oxidation reactions (k) and prolong storage. The use of synthetic antioxidants is one of the ways to control the biodiesel oxidation process, however natural extracts with antioxidant properties have gained importance due to their easy obtainment, in comparison with the complex and expensive synthesis of synthetic antioxidants, becoming a great alternative for retarding oxidation reactions and reducing the ultimate production cost of the biofuel. The triglyceride transesterification reaction was conducted with 50% of palm oil and 50% of soybean oil), along with absolute methanol and potassium hydroxide as the reaction catalyst. For extract preparation, 10 g of dried and crushed samples of coffee leaves were carefully weighed and mixed in a beaker containing 250 mL of absolute ethyl alcohol.The concentrations of methyl esters, present in the biodiesel was measured with chromatographic analysis (GC-MS) and the quantification of phenolic compounds present in the prepared natural alcoholic extract was carried out according to the Folin-Ciocalteu method. The chromatographic analysis (GC-MS) presented a proportion of saturated fatty acid methyl esters in the biodiesel sample was found to be 33.86% w/w, whereas unsaturated constituted 62.99% w/w. The alcoholic extracts derived of coffee leaves, presented 21.89 mg of GAE g^{-1} dry mass. The induction period of biodiesel, with natural antioxidant extract, was analyzed using a Rancimat model 743, Metrohm Instruments equipment according to EN 14112. The rate constant was obtained with the adjusted data of the natural logarithm (ln) of the electrical conductivity vs time, provided by the accelerated oxidative stability assay (EN 14112) at 110 °C. To carry out oxidative stability tests at 110°C using Rancimat and obtain IP and k, the biodiesel sample was prepared by adding 10.0 mL of coffee leaf extract to 100 g of biodiesel and kept at rest for 24 hours. The biodiesel sample containing the extract presented IP of 12.42 h and k of 0.2296 h^{-1} and the control sample IP of 2.35 h and k 1.3323 h^{-1}. These data indicate that the alcoholic extract of coffee leaves can be used to reduce the oxidative degradation of biodiesel, thus increasing its storage time.

Agradecimentos/Acknowledgments

To UEL, CNPq and CAPES

Área: TEC

AQUEOUS DRILLING FLUID: STUDY OF THE EFFECTS OF CALCIUM HYDROXIDE CONTAMINATION

Jéssica Magalhaes dos Santos Xavier (IC)[1], Roberto de Souza Silva (PG)[2], Mário Sérgio Schultz (PQ)[2], Cid Pereira (PQ),[1]

cid.pereira@gmail.com

[1]*Instituto Multidisciplinar de Química – Centro Multidisciplinar UFRJ Macaé Universidade Federal do Rio de Janeiro UFRJ*
[2] *Instituto de Biodiversidade e Sustentabilidade – NUPEM – UFRJ Macaé*
Palavras Chave: *Drilling Fluid, Oil Platform.*

Highlights

In petroleum activities, drilling fluids are of fundamental importance as a tool that enables progress in drilling. This work aims to address the effects of contamination of the aqueous drilling fluid with Calcium Hydroxide ($Ca(OH)_2$).

Resumo/Abstract

In petroleum activities, drilling fluids are of fundamental importance as a tool that enables progress in drilling. During drilling, several problems can arise, including contamination of the aqueous fluid by cement during casing cementing operations and cement plugs. Calcium hydroxide, $Ca(OH)_2$, present in the cement composition can cause serious problems to the properties of the fluid, causing loss of circulation and completely interrupting the drilling process. This work consists of analyzing the effects of contamination of aqueous drilling fluid by calcium hydroxide, focusing on evaluating changes in rheological properties, pH, alkalinity and volume of filtrate resulting from this contamination. Aqueous drilling fluids are those that have water as the continuous phase, their definition is based primarily on the nature of the water and the chemical additives used in the preparation of the fluid. The ratio between the fundamental components and their interactions results in significant changes in the physical and chemical properties of the fluid. Therefore, the composition is the main element to be considered in controlling its properties. This work aims to address the effects of contamination of the aqueous drilling fluid with Calcium Hydroxide ($Ca(OH)_2$), and to present the physical and chemical methods for analyzing contaminated aqueous drilling fluid. The results comparing the base fluids and the contaminated fluids will be presented, analyzing how contamination by $Ca(OH)_2$ modifies the main properties of the aqueous drilling fluid, namely rheology, pH, alkalinity, and filtrate. For a better understanding, below is how the fluids were named: Base fluids without contaminants: 1a and 1b Fluids contaminated with 1 lb/bbl of $Ca(OH)_2$: 2a and 2b Fluids contaminated with 1.5 lb/bbl of $Ca(OH)_2$: 3a and 3b.

		Fluids without contaminants			Fluids contaminated		
Properties	**Units**	**Fluid 1a**	**Fluid 2a**	**Fluid 3a**	**Fluid 1b**	**Fluid 2b**	**Fluid 3b**
Visc. Plast. (VP)	lb/100ft^2	15	15	16	15	14	8
Limit of es. (LE)	lb/100ft^2	39	45	47	44	10	8
Visc. Apar.(VA)	lb/100ft^2	34	35.5	39.5	37	19	12
G_0	lb/100ft^2	15	17	18	16	5	3
G_{10}	lb/100ft^2	19	20	20	19	5	3
Mass Espec.	lb/gal	9.1	9.1	9.1	9.1	9.1	9.1
Filtered API	mL	4	4	4.8	4.1	4.8	6.2
pH	-	7	11	13	7	11	13
Pm	mL	0.3	1.2	1.5	0.1	0.6	1.2
Pf	mL	0.1	0.5	0.8	0.1	0.3	0.6
Mf	mL	0.1	0.5	0.8	0.1	0.3	0.6

It was found that their rheological properties, filtrate alkalinity, and pH showed higher values compared to the uncontaminated fluid. This higher alkalinity and pH changes have a significant impact on polymer fluids, as they are quite sensitive to these changes. As a result of this contamination, there was increased flocculation in the system, intensified by the temperature increase resulting from the aging of the fluid. This combined effect led to a complete destabilization of the system, exacerbated by the activation of starch and the loss of effectiveness of the anionic polymer (xanthan gum) in a highly alkaline medium. The treatment of this fluid should be done preventively with the use of sodium bicarbonate, where Ca2+ precipitation will occur, dispersing the flocs and maintaining the stability of the fluid.

Agradecimentos/Acknowledgments

Instituto Multidisciplinar de Química (IMQ) – UFRJ Macaé.

Área: TEC

Bioleaching of fluorescent lamp waste containing rare earth elements

Beatriz S. Gonçalves (IC),[1*] Warley P. de Sá (IC),[1] Ailton G. R. Toledo (PQ),[1] Elias P. F. Neto (PQ),[2] Sidney J. L. Ribeiro (PQ),[1] Eduardo S. Chaves (PQ),[2] Klaiani B. Fontana (PQ),[2] Denise Bevilaqua (PQ).[1]

bs.goncalves@unesp.br

[1]Departamento de Bioquímica e Química Orgânica, IQ-UNESP; [2]Departamento de Química, UFSC.

Palavras Chave: *Bioleaching, Fluorescent powder, Rare earth elements, Acidithiobacillus thiooxidans, Recycling.*

Highlights

Acidithiobacillus thiooxidans was able to leach REE from fluorescent powder.

Two-step bioleaching showed better recovery efficiency of rare earth elements.

The residues generated were analyzed by SEM-EDS, and XRD.

Resumo/Abstract

Currently, rare earth elements (REEs) hold extreme strategic importance for technological development and national sovereignty. This significance arises from the fact that these elements are essential for the production of high-tech electroelectronic products and the development of strategic materials in the energy sector. In this context, the need for investment in scientific and technological research to enable the extraction, isolation, purification, and recovery of REEs is evident. This includes not only the exploration of high-grade ores but also of waste and recycled materials. For instance, the disposal of fluorescent lamps, widely used for public and domestic lighting, is underexplored for REE recovery. Fluorescent lamp waste contains a significant amount of REEs in its composition, especially Eu, Y, Tb, Ce, and La. Compared to conventional chemical methods, routes based on biological processes may be more economical and environmentally sustainable for recovering metals from primary sources (mineral deposits) and secondary sources (end-of-life products, industrial waste). The extraction of metals from solid sources can be facilitated through bioleaching, a process that involves biologically catalyzed reactions capable of releasing microbial leaching agents, including acids (organic and inorganic). Generally, the extraction of valuable substances from waste requires the dissolution or partial destruction of oxides, hydroxides, phosphates, carbonates, or silicates that contain the desired metals. This dissolution occurs through secondary processes, such as microbial acid production (dissolution promoted by protons or acidolysis), complexing agents (dissolution promoted by complexation or complexolysis), and reducers or oxidizers (dissolution promoted by redox processes or redoxolysis). Among the various types of microorganisms capable of dissolving waste containing REEs, this study employed *Acidithiobacillus thiooxidans*, a chemolithoautotrophic bacterium that tolerates acidic environments, the presence of high concentrations of heavy metals, and can utilize sulfur as an energy source, secreting sulfuric acid as a metabolite. Despite its enormous potential, few studies have evaluated the use of this microorganism for the recovery of REEs from secondary sources. Thus, this study explored the use of *A. thiooxidans* in the bioleaching of fluorescent lamp waste, aiming to solubilize REEs that can be utilized in higher value-added products. Bioleaching experiments were performed in batch cultures at a 2% pulp density. The concentration of REE were measured using an ICP-OES, the residues generated were analyzed by Scanning Electron Microscopy coupled with Energy Dispersive X-ray Spectroscopy (SEM-EDS), and X-ray diffraction (XRD), revealing a significant solubilization of REEs.

Agradecimentos/Acknowledgments

The authors gratefully acknowledge the funding provided by the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) – Processo 407747/2022-2. The authors would also like to thank GFQM-IQ (XRD analysis), and LMA-IQ (FEG-SEM analyses).

Área: TEC

Comunicando o Programa QUI+S: Inovação Sustentável ao seu alcance!

Valeska P. da S. R. Pardi (PQ)[1], Maryna M. Barros (PG)[1], Thais A. Silva (FM)[1], Germano M. C. Fagundes (IC)[1], Izabella C. N. P. Andrade (PG)[1], Rochel M. Lago (PQ)[1], Ana Paula C. Teixeira (PQ)[1]*
valeskaperorp@gmail.com; anapct@ufmg.br

[1]*Departamento de Química, ICEx, UFMG*
Palavras-Chave: *Sustentabilidade, inovação, Qui+S*

Highlights

Communicating the QUI+S Program: Sustainable Innovation at Your Fingertips!

The QUI+S Program employs a comprehensive communication strategy across various platforms to reach diverse audiences interested in sustainability. It customizes its message to resonate with educators, industrial leaders, and others, aiming to build a more sustainable Brazil.

Resumo/Abstract

A estratégia de comunicação do Programa QUI+S é um esforço dedicado a estabelecer vínculos significativos com todos os interessados em sustentabilidade e inovação sustentável.

Utilizamos o Instagram para destacar atividades, eventos e narrativas inspiradoras, o LinkedIn para estabelecer conexões profundas com profissionais comprometidos com a transformação sustentável, o WhatsApp para comunicação instantânea e fornecimento de atualizações imediatas, nosso site como *hub* informativo completo com recursos detalhados, e o Facebook para construir uma comunidade vibrante compartilhando conteúdos envolventes e conectando pessoas alinhadas com nossa visão.

O que nos distingue é nossa adaptabilidade. Personalizamos nossa comunicação para atingir públicos diversos, desde educadores até líderes industriais, garantindo que a mensagem do QUI+S ressoe em cada segmento. Em termos de resultados, a projeção de alunos para o Programa aumentou de 160 para 211, atingindo 33% da meta de 500 alunos no mês de lançamento. Na esfera da divulgação virtual, com foco no Instagram como a principal plataforma, o programa conquistou 522 seguidores em 4 meses, alcançando uma média mensal de 130,5 seguidores. Em janeiro de 2024, esse número aumentou para 602 seguidores, com alcances superiores a 8 mil contas, considerando interações, seguidores, comentários e impressões. Esses resultados destacam o impacto positivo e o crescimento consistente do Programa QUI+S.

Figura 1 - Métricas das redes sociais e curso Qui+S

Agradecimentos/Acknowledgments

Capes, CNPq, FAPEMIG, INCT Midas, SBQ, CFQ e UFMG.

Área: TEC

Desenvolvimento de protótipos de suporte inerte para a produção de enzimas fúngicas em biofilmes

Yves Cassiano Zuchini (IC)[1], Ian Castro-Gamboa (PQ)[1], Kelly Johana Dussán Medina (PQ)[1] e Daniela Alonso Bocchini (PQ)[1].

yves.zuchini@unesp.br; ian.castro@unesp.br

[1] *Instituto de Química, Universidade Estadual Paulista – UNESP-IQ, Araraquara, SP, Brasil.*

Palavras-Chave: *biofilme, impressão 3D, fungos filamentosos*

Highlights

Development of inert support prototypes for the production of fungal enzymes in biofilms. An inert support printed on a 3D printer was developed with sustainable material that can be used for the growth of filamentous fungal biofilm.

Resumo/Abstract

Biofilmes naturais ocorrem quando crescimentos microbianos se associam com uma superfície, formando um agregado de células [1]. Esse conceito foi originalmente desenvolvido para bactérias, entretanto se sabe que fungos filamentosos também são capazes de formarem biofilmes [2]. As células que formam um biofilme são capazes de apresentar uma alta taxa metabólica [3], tal como uma intensa produção de enzimas [4] Além disso, os biofilmes que são desenvolvidos em matrizes poliméricas permitem uma organização estrutural da morfologia dos organismos [5]. Em vista disso, esse trabalho teve como objetivo desenvolver um protótipo de suporte para crescimento de biofilme fúngico de forma a maximizar a produção de enzimas, em específico celulases e lacases. O suporte consiste em 3 peças encaixáveis, na primeira ocorre o crescimento do biofilme, a segunda serve de ligação entre a primeira e a terceira, e a terceira tem a função de ajustara altura do suporte como um todo, essas foram desenvolvidas a partir de um procedimento: **I** design e desenho da peça; **II** fatiamento e configurações de impressão; **III** impressão; **IV** teste para análise de falhas e reinício do processo. Na etapa I, a peça foi desenhada no programa AutoCAD visando um design que proporcione alta superfície de contato para que o fungo consiga se fixar bem, mantendo o contato com o oxigênio e com o meio líquido. Na etapa II, são feitas adequações para adaptar a impressão para as especificações da peça, como alterar altura de cada camada, velocidade de impressão, entre muitas outras. Na etapa III, foram feitas impressões em diferentes materiais O material escolhido foi o PLA (ácido poliáctico) feito a partir de dextrose extraída de materiais de fontes renováveis, de fácil uso em impressões, e quimicamente verde. A etapa IV consistiu em testes para averiguar se as interações entre as peças de suporte, uma vez montadas dentro do sistema de cultivo fúngico, estariam apropriadas para a proliferação de células na superfície desejada. Dessa forma, foi desenvolvido um suporte protótipo que atende a teoria para melhor produção enzimática, de fácil desenho e impressão, e com materiais renováveis, de forma que o processo se enquadra no que é preconizado pela filosofia da Química Verde. Estão em andamento testes com uma linhagem do fungo *Penicillium javanicum* para a produção de celulases para investigar a afinidade e a eficiência do suporte.

Agradecimentos/Acknowledgments

CNPq (INCT/BioNat), and FAPESP (Cepid/CibFar and INCT/BioNat) for research financial support.

Referências/References

1. REYNOLDS, T. B.; FINK, G. R. **Science**, v. 291, n. 5505, 2001. 878 - 881.
2. HARDING, M. W. et al.**Trends in Microbiology**, v. 17, n. 11, p. 475– 480, 2009.
3. RAMAGE, G. et al. **Critical Reviews in Microbiology**, v. 35, n. 4, p. 340- 355, 2009.
4. SAUER, K. et al. **Journal of Bacteriology**, v. 184, n. 4, p. 1140-1154, 2002.
5. SATO, V. S. et al. **Applied Biochemistry and Biotechnology**, , v. 174, p. 610–624, 2016.

Área: TEC

Estudo da adsorção do corante laranja reativo 3R MR utilizando microesferas de quitosana como adsorvente.

Késia K. V. Castro (PQ),[1] Amanda Gabriely M. Costa (IC),[2*] Francisco Medeiros de Andrade Neto (IC),[2] Zilvam Melo do Santos (PQ),[2] Izabelly Larissa Lucena (PQ),[2] Mônica Rodrigues de Oliveira (PQ) [2].

kesia.castro@ufersa.edu.br; amanda.costa84483@alunos.ufersa.edu.br.

[1]Departamento de Ciências Naturais, Matemática e Estatística, UFERSA; [2]Centro de Engenharias, UFERSA.

Palavras Chave: Quitosana, Adsorção, Corante reativo, Planejamento Experimental.

Highlights

Study of the adsorption of reactive orange dye 3R MR using chitosan microspheres as adsorbent. The objective of this study is to reduce the toxic effects of textile industries on the environment by removing dyes from their effluents to enable water reuse, using adsorption with chitosan.

Resumo/Abstract

A indústria têxtil é uma das mais poluentes devido aos corantes em seus efluentes. Buscando soluções ecológicas, a adsorção é um método eficaz para remover corantes. A quitosana, derivada de crustáceos, é um adsorvente natural promissor. Este estudo propõe microesferas de quitosana para melhorar sua eficácia na remoção de corantes, visando reduzir a poluição da indústria têxtil. Para o desenvolvimento do experimento foram realizadas análises espectrofotométricas, bem como planejamento experimental. Na execução produziu-se microesferas a partir da quitosana em pó, onde foram avaliados em cenários que variou-se o pH, concentração de corante e proporção de quitosana. Após as análises realizadas conclui-se que os experimentos que apresentaram uma maior porcentagem de remoção foram realizados no pH ácido (pH 4), isso acontece porque o meio ácido possibilita uma maior dissociação, acarretando a presença de cargas elétricas tanto no adsorvente quanto no adsorvato, isso causa maior atração entre eles, bem como uma maior massa de absorvente, o que acarreta uma remoção mais eficiente. As variáveis pH, proporção de quitosana e concentração de corante foram estatisticamente significativas para um intervalo de confiança de 95%. O pH exerceu a maior influência, com efeito negativo indicando que a adsorção é favorecida em pH ácido. O modelo estatístico ajustou-se bem, sendo preditivo para os valores das variáveis estudadas. Assim, as microesferas de quitosana demonstraram eficiência na adsorção do corante laranja reativo 3R MR, aproveitando sua vantagem como polímero natural e de fácil obtenção.

Agradecimentos/Acknowledgments

Departamento de Engenharia e Tecnologia, Departamento de Ciências Naturais, Matemática e Estatística, Centro de Engenharia, Centro de Ciências Exatas e Naturais, UFERSA.

Área: TEC

Estudo do processo de organofilização de uma argila proveniente da região sudeste do estado de São Paulo

Alessandra Stevanato (PQ)[1], Otávio Mesquita Vilaça (PQ)[2]*, Delia do Carmo Vieira (PQ)[2]

stevanato@utfpr.edu.br; otavio-1910@hotmail.com

[1]Departamento Acadêmico de Química, UTFPR – Campus Londrina; [2]Departamento Acadêmico de Engenharia de Materiais, UTFPR – Campus Londrina.

Palavras Chave: *Argilas, Argilominerais, Hidrofobicidade, Brometo de Cetiltrimetilamônio (CTAB), Caracterização Microestrutural.*

Highlights

Study of the organophilization process of a clay from the Southeast region of the state of São Paulo. Potential applications of hydrophobic materials: self-cleaning, anti-corrosion, oil-water separation and others. Properties and characterizations of these materials will be presented at this congress.

Resumo/Abstract

As argilas encontram-se amplamente distribuídas na crosta terrestre e apresentam propriedades peculiares devido aos argilominerais presentes, tais como: habilidade de trocar íons, estrutura em camada, área superficial alta, reatividade e biocompatibilidade. Estas características permitem uma facilidade para modificar a superfície e obter materiais hidrofóbicos e/ou superhidrofóbicos, que ampliam as aplicações tecnológicas destes materiais. Este trabalho apresenta um estudo do processo de organofilização de uma argila proveniente da região sudeste do estado de São Paulo. Duas concentrações do surfactante brometo de cetiltrimetilamônio (CTAB) foram investigadas, sendo acima e abaixo da sua concentração micelar crítica (CMC). O caráter hidrofóbico foi evidenciado quando os materiais foram colocados em contato com a água (inspeção visual), e as imagens fotográficas também mostraram uma mudança notável no ângulo de contato das argilas organofílicas em relação as argilas *in natura* e na forma sódica. Na concentração do CTAB abaixo da sua concentração micelar crítica, o material apresentou um maior ângulo de contato, ou seja, nesta concentração obteve-se um material de maior hidrofobicidade nas condições investigadas. A Figura 1 ilustra o caráter hidrofóbico quando uma gota de água foi depositada na superfície dos respectivos filmes: argila *in natura* (A); argila na forma sódica (B); argila organofílica abaixo da CMC (C) e argila organofílica acima da CMC (D).

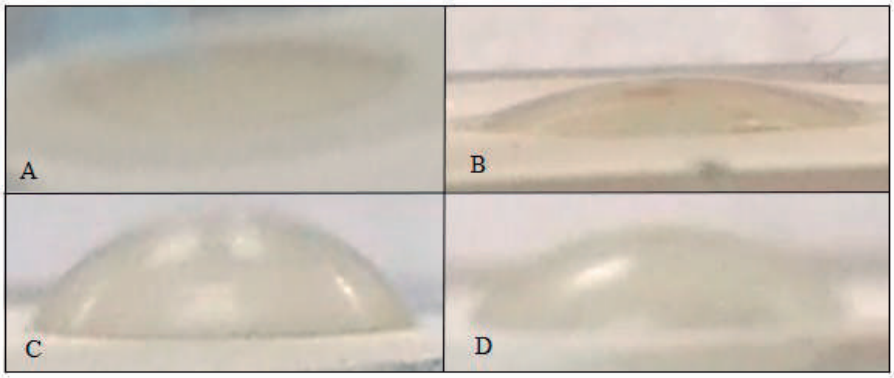


Figura 1. Ângulo de contato formado com os filmes: argila in natura (A); argila na forma sódica (B); argila organofílica abaixo da CMC (C); argila organofílica acima da CMC (D).

Os resultados de espectroscopia vibracional na região do infravermelho e a composição química (EDS) corroboram que houve a formação de materiais hidrofóbicos por uma metodologia simples.

Agradecimentos/Acknowledgments

Aos Departamentos Acadêmicos de Engenharia de Materiais (DAEMA) e de Química (DAQUI) da Universidade Tecnológica Federal do Paraná (UTFPR) do campus Londrina.

Área: TEC

Introduction of bioenergy in education with a focus on household waste as a source of biomass

Fernanda M. R. Cariello (PG),[1] Esther O. S. Santos (PG), [1] Mateus C. C. Silva (PG), [1] Mauro R. D. Jota (PG), [1] Erica D. Silva (FM), [2] Wilma A. Gonzalez (PQ). [1]*

melo.fernanda@ime.eb.br; d5wilma@ime.eb.br

[1]Seção de Engenharia Química, Programa de Pós- Graduação em Química, IME; [2] Universidade Federal do Rio de Janeiro, UFRJ

Keywords: *Biogas, Organic Waste, Bioenergy, Solid Waste, Environmental Education*

Highlights

Generation of biofuels from household solid waste. Environmental education in the propagation of sustainability. Playful activities to raise awareness of alternative energy sources.

Abstract

The use of residual biomass production chain of biodiesel from palm oil (fibers, shells and empty bunches) using thermal conversion processes such as pyrolysis at differentt emperatures, you can add great economic value.The fibers of empty oil palm bunches, after dry, crushed and classified granules, was characterized by different techniques and then temperatures on steel reactor type batch bench scale. By the physico-chemical and fuel products generated, the process employed may be a solution for the disposalof these materials, which improves the quality of the environment because much of the waste will no longer pass, for example, by incineration processes and/or direct combustion, minimizing the percentage of CO2 released into the atmosphere. Another promising source of raw material is urban solid waste. According to data from the Brazilian Association of Public Cleaning Companies and Special Waste (ABRELPE), Brazil generated 76.8 million tons of these wastes in 2020, of which 51% are organic waste[1]. In 2022, this same Association verified that 381 kg of garbage per person were produced in the country[2]. Considering this amount, the process to be chosen for the use of solid waste for bioenergy generation depends on the type of solid material existing in dumping ground: such as tires, plastic, paper, wood, glass, and organic waste, among others. Regardless of the process to be used for bioenergy generation, the main difficulty lies in the separation, collection, and specification of these wastes. Their use as raw material depends not only on technology and catalysis, but mainly on environmental education aimed at perpetuating sustainability. In this context, during the bioenergy discipline at the Military Institute of Engineering, the geopolitic of fossil and renewable fuels in the world was presented and debated, highlighting that the use of domestic waste for renewable energy generation is a promising reality. However, despite the potential for the use of solid waste, dumping ground are still a reality in the country, even with current legislation, which led us to think about specific educational activities that could inform and motivate children, young people, and adults in search for sustainability in the home environment, even in low HDI locations as a form of social inclusion. Education transmitted in a playful way would be a way of raising awareness and multiplying knowledge in the family. The proposed activities are presented in figure 1, as a way of stimulate and guiding the use of waste as a source of raw material for the production of biofuels, in addition to contributing significantly to reducing the environmental impact resulting from the inappropriate disposal of this material.

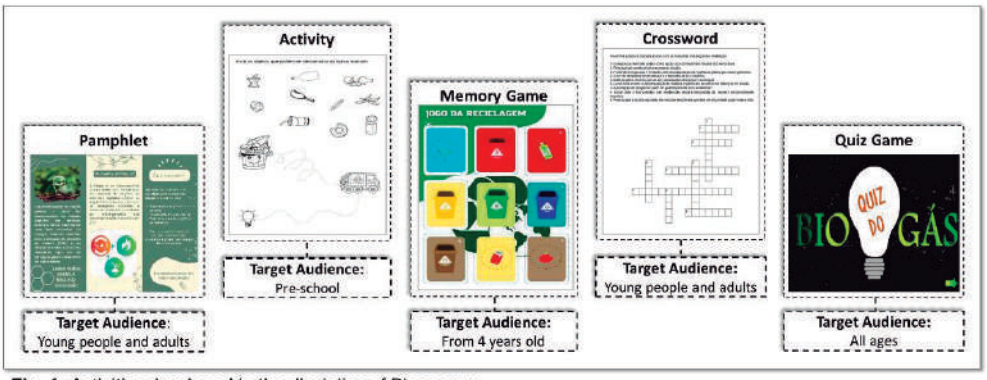


Fig. 1: Activities developed in the discipline of Bioenergy

[1]ABRELPE, 2020. Panorama dos Resíduos Sólidos. https://abrelpe.org.br/panorama/
[2] ABRELPE, 2022. Panorama dos Resíduos Sólidos. https://abrelpe.org.br/panorama/

Acknowledgments

CAPES, FAPERJ e IME.

Área: TEC

New tecnology for removal of oil spills: vegetable loofah (*Luffa aegyptiaca*) with hydrophobic surface coated with magnetic nanoparticles

Georgiana F. da Cruz (PQ),[1*] Luana C. M. Cantagesso (PG),[1] Gustavo E. P. Mendes (PG),[1] Aryane Tofanello (PQ).[2]

georgiana@lenep.uenf.br

[1]Laboratory of Petroleum Engineering and Exploration (LENEP), UENF; [2]Center for Natural and Human Sciences (CCNH), UFABC

Keywords: *Oil Spill, Magnetic Nanoparticle, Marine Environment Remediation, Sustainability.*

Highlights

Magneto-sorbent composite superhydrophobic and superoleophilic
Matrix based on vegetable loofah with an association of Fe_3O_4 nanoparticles
Technology developed to remove crude oil from environmental

Abstract

Oil spills can occur in different water bodies, such as oceans, rivers and bays, leading to significant environmental damage, especially to marine wildlife. In this study we developed a new technology, using low-cost material (vegetable loofah, *Luffa aegyptiaca*) functionalized with magnetite (Fe_3O_4) nanoparticles, which can be used both as a containment barrier and to remove the remaining oil droplets without carrying water during the cleaning phase. The oil-in-water spill simulation was conducted with a NaCl solution and with two Brazilian different oils (oil 1, API 25, Total Acid Number, TAN, 0,5 mg KOH/g oil; and oil 2, API 20, TAN 1.4 mg KOH/g oil). The vegetable loofahs (VL) were coated with two configurations of nanoparticles, pure magnetite (Fe_3O_4, VLnano-A) and magnetite functionalized with CTAB (cationic surfactant cetyltrimethylammonium bromide, VLnano-B). In addition, the loofah surface was treated with stearic acid to make it hydrophobic (it´s super repellent of water) (HVL). The results showed that the loofah with and without hydrophobic treatment was able to adsorb the oil (light, oil 1, and heavy, oil 2), reaching values from 78% (untreated loofah, Fig. 1a) to over 98% and without carrying water (hydrophobic loofah, Fig. 1b). The scanning electron microscopy images (SEM, Fig. 1c) depict that the loofah is composed of interwoven fibers that form non-rough lamellar structures. When modified with nanoparticles, the reticular structure remains intact, indicating that the fibers were not damaged during the process. This study highlighted the potential of a vegetable loofah, cheap and scalable, coated with Fe_3O_4 nanoparticles and with hydrophobic surface for effective oil spill removal for oils with different API, which is crucial for minimizing the environmental impact of such incidents. The findings suggest that this material may also be used for oil remediation in conjugation with other available technologies.

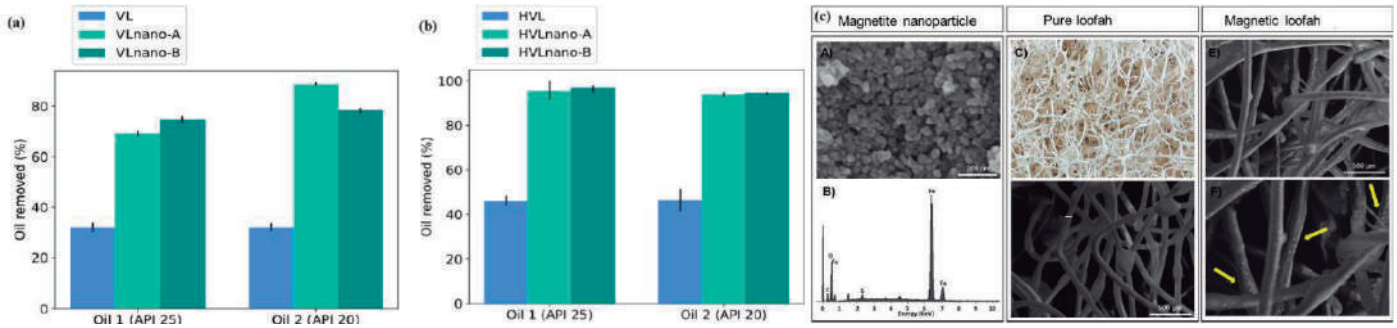


Figure 1. (a) Remediation capabilities of vegetable loofah (VL) coated with different types of nanoparticles; (b) Remediation capabilities of hydrophobic vegetable loofah (HVL) coated with different types of nanoparticles; (c) SEM of the magnetite nanoparticle, pure loofah and magnetic loofah.

Acknowledgments

The authors are grateful to FAPERJ (E-26/210.163/2021) and CAPES (Finance Code 001) for providing the resources needed to conduct this research and CNPq (DT II for Cruz, G. F.; 307480/2020-8). We also thank the support of LENEP/UENF and UFABC Multiuser Central (CEM) facilities in the experimental characterizations.

Área: TEC

Programa Qui+S: criação de *startups* em sustentabilidade

Maryna M. Barros (PG)[1], Valeska P. da S. R. Pardi (PQ)[1], Thais A. Silva (FM)[1], Germano M. C. Fagundes (IC)[1], Izabella C. N. P. Andrade (PG)[1], Rochel M. Lago (PQ)[1], Ana Paula de C. Teixeira (PQ)[1]*
maryna.moreira@hotmail.com; anapct@ufmg.br

[1]*Departamento de Química, ICEx, UFMG*
Palavras Chave: *Sustentabilidade, Startups, Qui+S, tecnologias*

Highlights

Qui+S Program: creation of sustainability startups

In one of the Qui+S projects, the Escale-se Summit program, technologies in hard science and sustainability are being accelerated and scaled to be available in 2024.

Resumo/Abstract

A SBQ está trabalhando no Programa Qui+S, que tem como objetivo principal impactar a sustentabilidade no país por meio da química.[1] Este é formado por dois Objetivos de Química para o Desenvolvimento Sustentável (OQDS) e respectivos eixos de ação, além de cinco desafios direcionadores, os quais norteiam todos os projetos e ações executados dentro do Qui+S.[2] Dentro do OQDS 2, uma importante inciativa em execução é o programa Escale-se Summit. Assim, este trabalho tem como objetivo apresentar as tecnologias finalistas do Escale-se Summit.

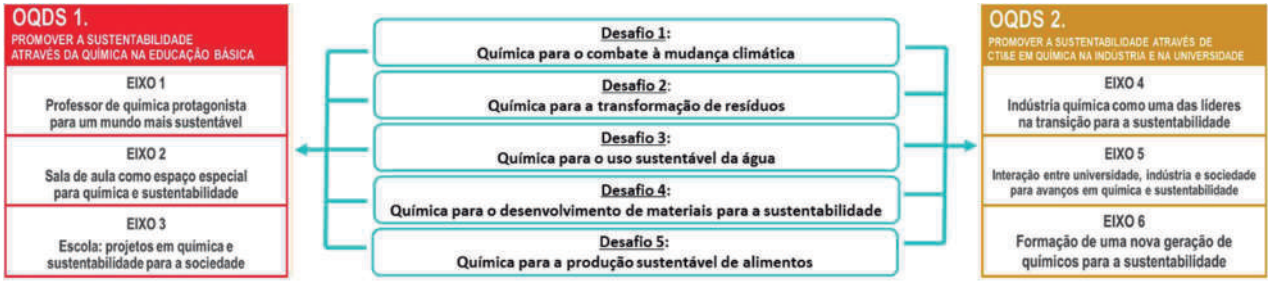


Figura 1 –OQDS, eixos de ação e desafios direcionadores do Programa Qui+S

O programa Escale-se Summit foi desenvolvido em parceria com o Escalab, um centro de escalonamento de tecnologias e modelagem de negócios do INCT MIDAS-UFMG, CFQ, FAPEMIG e empresas parceiras e teve como objetivo mapear tecnologias maduras em universidades dentro dos temas dos cinco desafios que direcionam o Qui+S. Para tal, ele foi dividido em quatro etapas:

Figura *2* – Etapas Programa Escale-se Summit

Na primeira etapa, o programa recebeu inscrições de 72 tecnologias de todo o país. Entre estas, dez foram selecionadas para etapa de diagnóstico. Posteriormente, quatro passaram para fase de aceleração e, então, se selecionou a FePREM e a Delta Entech para receberem o aporte de até R$100.000,00 na fase final de escalonamento.

A FePREM possui uma tecnologia para valorização de rejeitos de mineração, a qual permite produzir imãs permanentes a partir da síntese da ferrita. Já a Delta Entech desenvolveu uma tecnologia voltada para obtenção de um catalisador heterogêneo objetivando a produção de biodiesel. Ao fim da etapa 3, duas startups, referentes à essas tecnologias foram criadas e nesse momento começaram a fase de escalonamento.

Espera-se que a partir de todo o trabalho desenvolvido dentro do Escale-se Summit, as tecnologias selecionadas possam ser inseridas no mercado, gerando impactos positivos, na área de sustentabilidade, para toda a sociedade ainda no ano de 2024.

Referências:

1- SBQ. Movimento química pós 2022. Disponível em: http://www.sbq.org.br/mqp2022/
2- Silva, I. F.; *et al.* Movimento Química pós 2022: construção de um Plano de Ação para que a química e seus atores impactem a sustentabilidade e soberania no Brasil. Química Nova, Vol. 45, No. 4, 497-505, 2022

Agradecimentos/Acknowledgments

Capes, CNPq, FAPEMIG, INCT Midas, SBQ, CFQ, Escalab e UFMG

Área: _____TEC_____
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Strategic Connections through RD&I Networks to promote University-Industry Interaction in Sustainability

Leonardo Silva Assunção (IC),[1] Izabella Cristinna Nogueira Passos Andrade (PG),[2] Rochel Montero Lago (PQ),[2] Ana Paula de Carvalho Teixeira (PQ),[2]

Leo.9463@gmail.com; izabella.cnpandrade@gmail.com; rochellago@gmail.com; anapct@ufmg.br

[1] Departamento de Química, UFMG; [2] Centro de Escalonamento de Tecnologias e Modelagem de Negócios, ESCALAB.

Palavras Chave: *Inovação sustentável, Conexão academia-indústria, ESCALAB, Redes de pesquisa, Colaboração estratégica*

Highlights

STRATEGIC CONNECTIONS THROUGH RD&I NETWORKS TO PROMOTE UNIVERSITY-INDUSTRY INTERACTION IN SUSTAINABILITY

Escalab promotes connections between various innovation, education and sustainability networks through Rede Hub: Rede Escalab Mineral, INCT Midas, Qui+S, and GRUTAM.

Resumo/Abstract

Contemporary scenarios demand innovative and sustainable approaches to address global challenges in the environment, natural resource scarcity, and quality of life. In this context, strategic connections promote economic development while addressing crucial issues for planetary preservation. One of the most effective strategies for driving sustainable innovation is establishing connections between universities and the industry. Escalab promotes this collaboration, this initiative highlighted by strategic partnerships with SENAI and UFMG, acts as a vital bridge between academic research and market demands (OLIVEIRA & FRANCO, 2019).

Students involved in industry-related projects demonstrate enhanced decision-making and leadership skills compared to those not engaged in such projects (MICHAUDEL, Quentin et al, 2015). Escalab stands out for its ability to overcome this challenge, bridging academic knowledge with industry needs. This collaboration not only promotes interest and discussion across various scientific and sustainability fields but also attracts resources through strategic partnerships with companies.

Economic and business studies emphasize the significance of university-industry relations in driving economic growth (FURMAN & MACGARVIE, 2009). To further strengthen this connection, Escalab established the Rede Hub Sector, aiming to optimize communication and strategies between the university and the industry as an interface. This structure serves as a direct facilitator, connecting academic institutions like UFMG to industry partners and networkers, generating innovative technological solutions with positive impacts on the market and society. This research aims to transform environmental and social challenges into opportunities, generating economic, environmental, and social benefits.

For example, the Rede Escalab Mineral faces specific challenges related to mining waste, demonstrating an interdisciplinary and collaborative approach to solving complex problems. Similarly, INCT Midas emphasizes the importance of applied research and underscores the need to train professionals capable of catalyzing sustainable changes. Moreover, programs like Qui+S and Rede de Educação, shaping education from early stages, popularize science to the future generations. GRUTAM, with its advanced infrastructure and industrial collaborations, illustrates how academic research can translate into practical and sustainable solutions.

Furthermore, these collaborations create a broad knowledge network, establishing an environment where innovation and sustainability are interdependent. The effectiveness of these partnerships in promoting sustainable practices underscores the ongoing need for collaborative approaches to address the complex challenges the future presents.

Agradecimentos/Acknowledgments

We express our gratitude to ESCALAB, its networks and partners. We thank the public funding agencies, CNPq and FAPEMIG, for their financial support. To the researchers and professionals involved in the networks presented.

Área: TEC

Sulfation of β-glucan produced by *Lasiodiplodia theobromae* MMPI promotes increased antioxidant, antimicrobial, and antiviral potential against the respiratory syncytial virus (RSV)

Alaor Martins da Silva (PG),[1] André Luiz Dyna (PG),[2] Ligia Carla Faccin Galhardi (PQ),[2] Tamires Pereira Rosa (PG),[1] Mário Antônio Alves da Cunha (PQ).[1]*

alaormartins16@gmail.com; mcunha@utfpr.edu.br

[1]Laboratório de Biotecnologia e Bioprocessos, Departamento de Química, UTFPR, campus Pato Branco/PR; [2]Laboratório de Virologia Básica e Aplicada, Departamento de Microbiologia, UEL

Palavras Chave: *Exopolysaccharides, Lasiodiplodia, Sulfonate groups, Antiviral capacity, Respiratory disease.*

Highlights

The sulfation of β-glucans is a strategy for enhancing or inducing new biological properties in polysaccharide macromolecules. Sulfated derivatives of these biomacromolecules have shown various biological functionalities, including antiviral activity.

Abstract

A β-glucan produced by the ascomycete Lasiodiplodia theobromae was subjected to sulfation derivatization. Two derivatives with different degrees of substitution (DS) were obtained: LAS-S1 (DS 0.11) and LAS-S2 (DS 0.51). The derivatives were characterized by Fourier-transform infrared spectroscopy (FTIR), thermal analysis (TGA/DTG and DTA), X-ray diffraction (XRD), and scanning electron microscopy (SEM). The antimicrobial, antioxidant, and antiviral potential against respiratory syncytial virus (RSV) were also evaluated.

Bands in 1200 cm^{-1} and 800 cm^{-1} regions are attributed to the asymmetric stretching vibration of S=O and the bending vibration of C-O-S (associated with the C-O-SO3 group), respectively (Figure 1) and demonstrate the sulfation of the macromolecule, especially the LAS-S2 derivative. The low degree of substitution of the LAS-S1 sample could explain the low intensity of the specific signals of *O*-sulfonation in the LAS-S1 derivative.

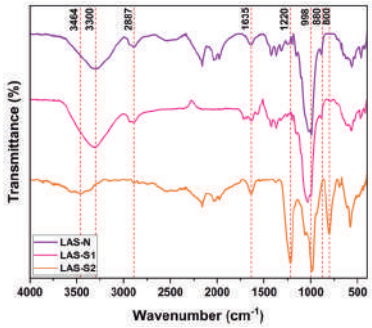


Figure 1. FT-IR spectrum of LAS-N (native β-glucan), LAS-S1 (DS 0.11) e LAS-S2 (DS 0.51).

The sample with a low degree of sulfation (LAS-S1) exhibited the best potential for antioxidant activity, with a 50% removal capacity of hydroxyl radicals and 44.5% removal of hydrogen peroxide (15 mg/L) in antioxidant activity assays. The LAS-S1 sample showed fungicidal action against *Candida tropicalis* ATCC 13813 (MIC 0.03125 µg/mL), while LAS-S2 demonstrated bacteriostatic efficacy against *Listeria monocytogenes* ATCC 10111 (MIC 0.25 µg/mL). However, none of the tested compounds inhibited *Staphylococcus aureus* ATCC 25923.

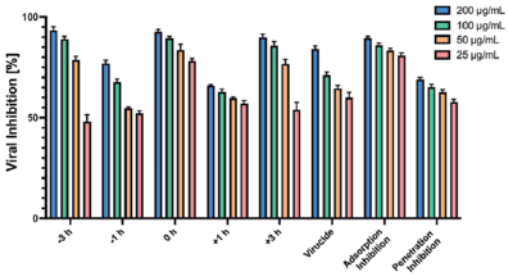


Figure 2. Antiviral assay on HEp-2 cells: Evaluation of LAS-S2 against RSV.

Cytotoxicity assays (MTT) with HEp-2 cells showed that samples LAS-N, LAS-S1, and LAS-S2 exhibit low cellular cytotoxicity (CC_{50} > 1000 µg/mL), even at the highest tested concentration. The results are promising compared to Ribavirin (CC_{50} > 230.6 µg/mL), a positive and inhibitory control for RSV. LAS-S2 (IC_{50}: 1.38 µg/mL) exerts a more potent inhibitory concentration compared to LAS-N (IC_{50} > 200 µg/mL) and LAS-S1 (IC_{50}: 34.5 µg/mL), and its efficacy is close to the IC_{50} of Ribavirin (IC_{50}: 1.38 µg/mL). This discovery demonstrates the relevance of LAS-S2 in future biological and pharmacological applications as a promising virucide against Respiratory Syncytial Virus (RSV).

Acknowledgments

Central de Análises – UTFPR, campus Pato Branco/PR; Laboratório de Virologia Básica e Aplicada – UEL, Londrina/PR, CNPQ e Fundação Araucária.

Área: TEC

Technical perspective for re-refining used and contaminated lubricating oils from Wind turbines using flash point x density

[1]Michelle S. G. Dantas (PQ),[2] Heron B. Cabral (IC),[3] Samara D. S. Silva (T),[3] Izaak B. de LIma (FM), [3] Jessica M. de Matos (FM).

michelle.dantas@ifrn.edu.br; heron.b@escolar.ifrn.edu.br

[1,2]Departamento de Engenharia de energia, IFRN; [3]Departamento de Petróleo & Gás, IFRN

Palavras Chave: *Re-refinig, Lubrificants, Flash point, Wind turbines.*

Highlights

RN has been standing out as one of the main hubs for wind energy generation in Brazil. This work evaluated the potencial of AER-11, after re-refing processes was evaluated for flash point and density tests.

Abstract

The growth of the wind farm in Rio Grande do Norte has been significant over the years, making the state one of the main hubs for wind energy generation in Brazil. Exploring the enviromental aspects and impacts related to the use of aeroturbine lubrication oils is importante because these oils are essential for the proper functioning of Wind turbines, but they can also present environmental challenges, especially when not managed properly and can pose risks of contamination of the soil and water. Re-refining is a processo f recycling and regenerating used and contaminated lubricating oils (UCOLs), which can help mitigate environmental impacts – it involves purifying and removing impurities from used oils, making them suitable for reuse. The lubricating oil used in aeroturbines, when dumped inappropriately, causes pollution to the environment and can reach groundwater; when burned incorrectly, it generates significant emissions of metal oxides, as well as toxic gases, such as dioxin and sulfur oxides. This work aims to evaluate the potential os a possible new experimental substance LUB_AER 11 that was subjected to new reaction routes for re-refining UCOLs – the starting material was obtained from na aeroturbine in a Wind farm in RN. Susbtance was subjected to re-refining processes and evaluated physicochemically for flash point tests (parameter indicates the minimum temperature at which a flammable liquid begins to release vapors that can ignite in contact with ignition source), as well as related to density tests, among other tests.

To determine flash point, according to ASTM D93, seventy mililiters of sample were transferred to the test cup equipped with na electronic temperature sensor, heated and shaken at intervals of 5 to 6°C min^{-1} and 99°C to 120 rpm, respectively. An ignition source was applied to the test cup at regular intervals of 1°C from temperature between 23 and 28°C below the expected flash point. The interruption of the agitation in the system only occurred after the detection of a “flash”. LUB_AER 11 has been tested with a compatibility of pH 6, therefore, a neutral pH and ideal for lubricant function. The results are shown in the following table, wich evaluates the influence of flash point versus LUB_AER 11 samples obtained at diferente temperatures.

	Flash point (°C)	Density (g/mL)
LUB_AER 35°C	70	0,82
LUB_AER 65°C	65	0,82
LUB_AER 95°C	110	0,78
Oxidized aeroturbine sample	91	0,86

This work examined a lubricant sample, focusing on the importance of high temperature for stability and noted that turbine samples have a higher density due possible impurities. Highlight for the re-refined sample _ LUB_AER 11 – 95°C, which stands out for its lower density, indicating better quality.

Acknowledgments

To UFRN for the analyzes to complete this study.

TEO

Química Teórica

Sociedade Brasileira de Química

Área: TEO
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Analysis of commercial nanoparticle effect in gasoline combustion using artificial neural network

Rita C. O. Sebastião (PQ),[1*] Natália R. S. Araujo (PG),[1] Fabrício J.P. Pujatti (PQ),[2] Augusto C. T. Malaquias, José G. C. Baeta[2]

ritacos@ufmg.br

[1]Departamento de Química, UFMG; [2]Departamento de Engenharia Mecânica, UFMG.

Keywords: *gasoline combustion, kinetic of combustion, artificial neural network*

Highlights

- Combustion analysis of Brazilian gasoline and nanoparticles effect

- Determination of combustion kinetic using artificial neural network

-Correlation between combustion kinetic and engine performance

Resumo/Abstract

Recent directives to encourage the use of cleaner energy sources are key to controlling environmental pollution. But fossil fuels remain as the leading source of energy for transport sector in the forthcoming years. Considering energy transition, it is necessary to develop reasonable initiatives that improves energy efficiency, mainly in automotive engines. In this sense, one of the possible alternatives for making gasoline-fueled internal combustion engines spark ignited (ICE-SI) more attractive is the addition of catalyst nanoparticles as additives to conventional fossil fuels. The aim of this work is to study the combustion process of a commercial regular Brazilian gasoline, with and without the addition of nanoparticles in a Single Cylinder Research Engine (SCRE). All the tests were done at a fixed indicated mean effective pressure (IMEP) of 7 bar, at three different speeds: 1900, 2200 and 3000 rpm. These operating points were selected because they represent typical conditions for vehicle commercial engines subjected to urban driving cycles. The chemical kinetics was studied from the Mass Burned Fraction (MBF) data as a function of the crank angle position. The study was based on the determination of the kinetic triplet: activation energy (Ea), frequency factor (A) and mechanism of reaction throughout the combustion process using artificial neural network.

At the beginning of the process, it was verified that activation energy for the gasoline combustion with commercial nanoparticles is greater than that for regular gasoline combustion. This result can be related to an increase in intermolecular forces between gasoline molecules and nanoparticles, which requires more energy to break the interaction, vaporization, and subsequent burning. After 60% conversion, the Ea of the gasoline combustion process with the nanoparticle is lower than of regular gasoline combustion process. It is then suggested that the nanoparticle can act as a local heat source, contributing to combustion by reducing the Ea. Although the initial combustion process presented superior Ea for the gasoline with nanoparticles, it is verified an enhanced molecularity, (A), which consequently results in a superior rate constant to the process, compared to regular gasoline. In the final stages of combustion, it is observed that the activation energy of gasoline with nanoparticles remains almost constant until the end of the process.

The rate constant parameter is one of the most important combustion parameters, which determines engine performance. It is calculated based on Ea, A and mechanism. A fuel with superior rate constant is favorable because it reduces the combustion duration, preventing heat loss to the cylinder walls. According to the results, it was determined that the rate constant is higher for the combustion of gasoline system with nanoparticles compared to regular gasoline. The rate constant can be related to engine performance and consume; however, this analysis will be carried out in the future work.

AMPAH, Jeffrey Dankwa et al. Progress and recent trends in the application of nanoparticles as low carbon fuel additives—a state of the art review. **Nanomaterials**, v. 12, n. 9, p. 1515, 2022.

Agradecimentos/Acknowledgments

The authors would like to thank CNPq, EMBRAPII, HOREB BRASIL, FAPEMIG and UFMG/PRPq for the financial support.

Área: TEO

Análise conformacional do poli (fluoreto de vinilideno) (PVDF) e efeitos de estabilização

Kenzo T. Miyake (IC),[1] Rodrigo A. Cormanich (PQ).[2*]

K219172@dac.unicamp.br; cormanich@unicamp.br

[1] Universidade Estadual de Campinas (UNICAMP), Faculdade de Engenharia Química, Av. Albert Einstein, 500 Campinas, São Paulo 13083-862, Brasil.
[2] Universidade Estadual de Campinas (UNICAMP), Instituto de Química, rua Monteiro Lobato, Campinas, São Paulo 13083-852, Brasil.

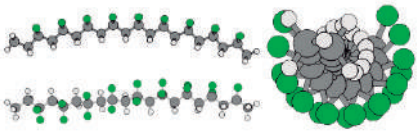
Palavras Chave:*Análise Conformacional; Química Computacional; Fluoroalcanos*

Highlights

Poly (vinylidene fluoride) (PVDF) comformational analysis and stabillization effects. PVDF has two stable helical conformers. Investigation of its local minimum revealed eletrostatic forces between vicinal hydrogen and fluorine atoms to be the cause of helicity.

Resumo/Abstract

PVDF is a fluoroalcane with applications and physico-chemical properties similar to polytetrafluoroethylene[1]. Based on previous studies that reported stable helical conformations due to hyperconjugative for fluorohydrocarbon polymers[2], well established computational analysis techniques were utilized to study the conformers of PVDF. In spite of local maximization, zigzag conformers were found not to be relevant to any transition state whereas helical strucutures of approx. 165° dihedrals where identified as local minima. In lieu of true transition states, energetic barriers were studied through the simultaneous variation of multiple geometric parameters, allowing for single coordinate mapping of the energy levels between both relevant conformers. Comparative Natural Bond Order, Natural Coulomb Energy and Natural Steric Analysis calculations between aforementioned local maxima and minima revealed the stabilization of helical structures by electrostatic interactions primarily between 1,3 fluorine-hydrogen as well as 1,5 fluorine-hydrogen atoms.



Side views of both zigzag and helical PVDF conformations on the left and helical PVDF conformer front view on the right

[1]LEMAL, D. M. Perspective on Fluorocarbon Chemistry. The Journal of Organic Chemistry, v. 69, n. 1, p. 1–11, jan. 2004. [2]CORMANICH, R. A.; O'HAGAN, D.; BÜHL, M. Hyperconjugation Is the Source of Helicity in Perfluorinated n-Alkanes. Angewandte Chemie, v. 129, n. 27, p. 7975–7978, 31 maio 2017.

Agradecimentos/Acknowledgments

The authors are grateful to FAPESP and FAEPEX for the financial support of this research. The authors also thank FAPESP for a Young Researcher Award to RAC (#2018/03910-1) and a scholarship to KTM (#2023/05418-5) and FAEPEX for a grant (#2380/23). CNPq is acknowledged for a fellowship to RAC (#306912/2023-6). CENAPAD-SP and CESUP computational resources are also gratefully acknowledged.

Área: TEO

Análise teórica da diminuição da barreira de energia de inversão nos fluoroBCBs

Caio E. V. P. Nascimento (IC),[1] Rodrigo A. Cormanich (PQ)[2*]

c204441@dac.unicamp.br; cormanich@unicamp.br

[1]*Universidade Estadual de Campinas (UNICAMP), Instituto de Química, rua Monteiro Lobato, Campinas, São Paulo 13083-852, Brasil.*

Palavras Chave: Biciclos, Química Computacional, Fluoroalcanos

Highlights

Theoretical Analysis of the lowering of the inversion energy barrier for fluoroBCBs. When substituting a hydrogen in BCB for a fluorine atom, the inversion energy barrier lowers significantly. A theoretical analysis revealed that this is due to an interaction between the antibonding orbital of the bridgehead carbons' bond and a lone pair orbital from the fluorine atom in the transition state (TS).

Resumo/Abstract

The inversion of a BCB has been experimentally observed only once[1]. In a later study it was observed that the substitution of a hydrogen with a fluorine atom in bicycles can lower the inversion energy barrier; this was also calculated to apply to BCBs[2]. Energy calculations and Natural Bond Orbital (NBO) analysis with a B3LYP/6-311+G** theoretical level of several fluoroBCBs revealed that the most dramatic energy differences were due to an optimal orbital alignment of the antibonding orbital from the bond between the bridgehead carbons and one of the lone pair orbital of the fluorine atom in the transition state (TS) of the inversion. This causes the inversion energy barrier to drop from $\Delta G^{\ddagger}$ = 71.4 kcal/mol in the non-substituted BCB to $\Delta G^{\ddagger}$ = 4.6 kcal/mol in the hexafluoroBCB.

Side view of the antibonding orbital for the bridgehead carbons' bond and the lone pair orbital from the fluorine for the 1-fluoroBCB and its transition state (TS)

[1]Woodward, R. B.; Dalrymple, D. L. J. Am. Chem. Soc. **1969**, 91, 4612; [2]Lemal, D. M. The Effect of Fluorine Substitution on Ring Inversion in Bicyclo[1.1.0]butanes. The Journal of Organic Chemistry **2009**, 74 (6), 2413-2416. https://doi.org/10.1021/jo802693v

Agradecimentos/Acknowledgments

The authors are grateful to FAPESP and FAEPEX for the financial support of this research. The authors also thank PIBIC for a scholarship to CEVPN and FAEPEX for a grant (#2380/23). CNPq is acknowledged for a fellowship to RAC (#306912/2023-6). CENAPAD-SP and CESUP computational resources are also gratefully acknowledged.

Área: TEO

Assessment of a computational protocol for predicting standard reduction potential of Osmium(III) complexes

Gabriel de S. Martins (IC)[1*], Diego F. S. Paschoal (PQ)[2]

gabrielmartins1102@gmail.com; diegopaschoal01@gmail.com

[1]*Núcleo de Química Teórica e Computacional de Macaé, Polo Ajuda, Instituto Multidisciplinar de Química, Centro Multidisciplinar UFRJ-Macaé, Universidade Federal do Rio de Janeiro, Macaé, RJ, Brazil.*

Keywords: *Osmium complexes; Redox potential; DFT; Basis sets; Solvent effects; Relativistic effects.*

Highlights

The role of the DFT functionals, dispersion, basis sets, solvent models, and relativistic effects were assessed for predicting the reduction potential of Os(III/II) complexes.

Mean relative deviation of only 15% were obtained considering $[Os(NH_3)_6]^{+3/+2}$ and $[Os(bipy)_3]^{+3/+2}$.

Resumo/Abstract

Osmium (Os) complexes have attracted great interest due to their large number of applications, such as homogeneous catalysis, photophysics, and as promising anticancer agents. Considering the biological applications of Os complexes, Considering the biological applications of Os(III) complexes, the reduction potential is an important property to be evaluated, since the potential mechanism of action of these complexes involves reduction to Os(II). Then, the present study aims to build a computational protocol for predicting the standard reduction potential (ε^0) of Os(III/II). Initially, the redox systems $[Os(NH_3)_6]^{+3/+2}$ and $[Os(bipy)_3]^{+3/+2}$, which have experimental data for the ε^0 of -0.749 V and 0.800 V, respectively, were selected (Fig. 1). The experimental data, in water, were measured by cyclic voltammetry in relation to the standard hydrogen electrode (SHE). The ε^0 was calculated according to equation: $\varepsilon^0\ (V) = 27.2114 \times (G_{ox} - G_{red}) - \varepsilon^0_{abs}(SHE)$, with the ΔG values obtained from the construction of a thermodynamic cycle, with the optimized structures and thermal corrections obtained in the gas phase. For the construction of the computational protocol, the role of the solvent effects - implicit solvent model (IEF-PCM and SMD) and cavities (UFF, Bondi, and Pauling), DFT functional and dispersion effects, osmium basis sets (OSBS), ligands basis sets (LBS), and relativistic effects were assessed. The calculations were performed in GAUSSIAN 16 Rev. C.01 program, except for relativistic calculations that were carried out in ORCA 5.0.4 program (*quasi* relativistic) and ReSpect 5.1.0 program (4-components). First, solvent effects were evaluated at the B3LYP/def2-SVP/def2-SVP level, considering the implicit solvation models IEF-PCM (with the Radii set from UFF, Bondi, and Pauling) and SMD. The calculated results show that the inclusion of solvent effects is of fundamental importance for the prediction of ε^0, with the values obtained with the IEF-PCM(Bondi) presenting the smallest mean relative deviation (MRD) – 44%, being of 55% with the NH_3 ligands and 33% with the bipy ligands (Fig. 1). When the dispersion effects are included considering the def2-TZVP basis set for Os atom, the obtained MRD of 15% is an improvement over the MRD of 35.8% at M06-L/def2-TZVP//SMD protocol obtained by Rulisek [2]. In the next steps, the ligands basis sets and relativistic effects will also be evaluated.

B3LYP/def2-SVP	$[Os(NH_3)_6]^{+3/+2}$	$[Os(bipy)_3]^{+3/+2}$	
	RD	RD	MRD
Gas phase	1431%	845%	1138%
IEF-PCM(UFF)	167%	42%	105%
IEF-PCM(Bondi)	55%	33%	44%
IEF-PCM(Pauling)	45%	69%	57%
SMD	67%	26%	46%

Fig. 1. Os(III/II) studied and calculated results considering the solvent effects.

[1] Céron-Camacho, R. et al. *Molecules* **26**, 1563 (2021). [2] Rulísek, L. *J. Phys. Chem. A* **117**, 16871-16877 (2013).

Agradecimentos/Acknowledgments

The authors would like to thank the Brazilian agency FAPERJ (E-26/201.336/2022 – BOLSA and E-26/210.070/2022 – DCTR).

Área: TEO

Atomistic Simulation Insights into Non-Flammable Electrolytes

Alexandre Moni Pereira (PG),[1,2*] Wessel van Ekeren (PG),[3] Daniel Brandell (PQ),[3] Reza Younesi (PQ),[3] Luciano T Costa (PQ)[1]

***amoni@id.uff.br;**

[1]*MolMod-CS, Physical Chemistry Department, Institute of Chemistry, Fluminense Federal University, Brazil*
[2]*Centre for Mineral Technology (CETEM),Molecular Modeling Laboratory, Rio de Janeiro, RJ, Brazil*
[3]*Department of Chemistry-Ångström Laboratory, Uppsala University, Box 538, Uppsala SE-751 21, Sweden*

Palavras Chave:*Density Functional Theory (DFT), Molecular Dynamics (MD), Non-Flammable Electrolytes.*

Highlights

- Non-flammable liquid electrolytes enhance the safety of alkaline metal ion-based batteries.

-Atomistic simulations can predict and elucidate molecular structural and dynamical properties.

Resumo/Abstract

Alkaline metal ion-based (Li, Na and K) batteries have been used in a wide range of applications such as energy storage for electric vehicles and other devices. The demand for energy grows daily and, with it, the demand for better and safer batteries. Trimetyl phosphate (TMP) and Triethyl phosphate (TEP) are known for reducing electrolyte flammability, but they may hinder cyclability[1]. On the other hand, diglyme (2G) and tetraglyme (4G) can enhance this property but the former presents lower thermal stability[1]. In order to understand how different mixtures affect the electrolyte properties, molecular dynamics (MD) simulations were employed. Through this technique, we can calculate density, viscosity, investigate the ions solvation, and also obtain the conductivity as a measure of the ion mobility. The systems were built by packmol and comprised of two ions ($[BF_4]^-$ and $[PF_6]^-$) with five different compositions of mixtures containing either TMP or TEP and either 2G or 4G, investigated over a temperature range spanning from 283.15K to 373.15K. OPLS-AA force field[2] was employed to describe the systems. Only the atomic partial charges were refined based on DFT calculations using B3LYP[3,4] and def2-TZVP[5] as basis set. RESP fitted charges derived from DFT calculations significantly improved theoretical outcomes, while other MD results closely aligned with the experimental data, enabling correlations between solvent structure and the studied properties. Figure 1 illustrates the potential energy landscape derived from the computed charges.

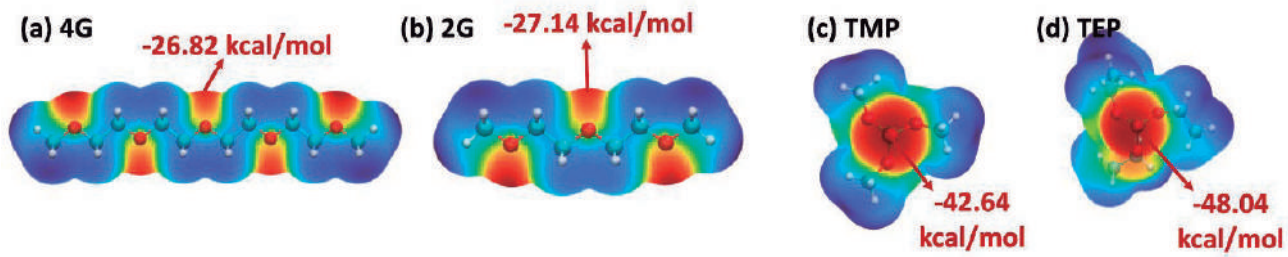


Figure 1 -Potential energy landscape derived from the computed charges.

[1]R. Gond, W. van Ekeren, R. Mogensen, A. J. Naylor and R. Younesi, Mater. Horiz., 2021, 8, 2913–2928
[2]W. L. Jorgensen, D. S. Maxwell and J. Tirado-Rives, Journal of the American Chem-ical Society, 1996, 118, 11225–11236
[3] A.D. Becke, J.Chem.Phys. 98 (1993) 5648-5652
[4]C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785-789
[5]F. Weigend and R. Ahlrichs, Phys. Chem. Chem. Phys., 2005, 7, 3297.

Agradecimentos/Acknowledgments

We acknowledge CNPQ for the scholarship and also the Joint Brazilian–Sweden Collaboration facilitated by CAPES/STINT.

Área: TEO
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Avaliação, *in silico*, da interface de interação entre um fragmento de anticorpo e o CD22, para aplicação em CAR-T *Cell.*

Alice Soares de Queiroz* **(PG)** [1], **Axel Jhonantam Oliveira Lima (IC)** [2], **Marcos Roberto Lourenzoni (PQ)**[1]
alice.queiroz@fiocruz.br*

[1]*Biotecnologia de Recursos Naturais, UFC;* [2]*Graduação em Biotecnologia, UFC*

Palavras Chave: CARs anti-CD22, scFvs de M971, Dinâmica Molecular, MM/PBSA.

Highlights

In silico evaluation of the interaction interface between an antibody fragment and CD22, for application in CAR-T Cell.

Resumo/Abstract

A Leucemia Linfoide Aguda é um dos tipos mais agressivos de câncer. O antígeno CD22 é uma das glicoproteínas expressas por células B leucêmicas. A terapia por células CAR-T é um exemplo de uma das imunoterapias desenvolvidas a fim de alcançar a remissão dessa malignidade e baseia-se na expressão de um Receptor Quimérico de Antígeno (CAR), o qual possui a função de redimensionar a ação da célula T, tornando-a capaz de reconhecer antígenos específicos na superfície de células tumorais. A estrutura do CAR responsável pelo reconhecimento antigênico é o fragmento variável de cadeia única (scFv), o qual é formado pelos domínios VL e VH de um anticorpo monoclonal e o *linker,* que conecta os dois domínios. Recentemente, começaram a ser publicados resultados de ensaios clínicos de dois CARs anti-CD22 denominados de CARs de scFv de *linker* curto e longo ambos usando o scFv de M971, com o scFv de *linker* curto tendo maior afinidade ao CD22 que o scFv de linker longo. Diante desse contexto, o objetivo deste trabalho é compreender as diferenças estruturais na interface scFv/CD22 curto e longo que levam a diferença de afinidade e efetuar um protocolo seguro que possa ser a ser utilizado na proposição de mutações nesses scFvs para melhorar a eficiência de células CAR-T. Experimentos usando simulações de Dinâmica Molecular (DM) foram executados em triplicata, tendo a trajetória analisada por método de Mecânica Molecular de *Poisson-Boltzmann* com Solvatação da Área de Superfície (MM/PBSA), para investigar a energia livre de ligação (ΔGligação) entre o CD22 e os scFvs. A estrutura do fragmento Fab de M971 e dos domínios D6-D7 do CD22 está depositada no PDB, cód. 7O52. Os complexos scFv/CD22, com CD22 inserido em modelo de membrana lipídica, foram construídos a partir da estrutura cristalográfica, com coordenadas atômicas preservadas e complementadas com regões faltantes (alças) e submetidos à protocolos de minimização e termalização para produção de trajetórias por DM em triplicata de 400 ns. Como resultado, foi observado que os complexos scFv/CD22 curto e longo tiveram estabilidade estrutural semelhantes. Os scFvs se mostraram estruturalmente diferentes o que os diferenciou quanto a estabilidade na interface scFv/CD22. Através da análise de MM/PBSA para os complexos observou-se que ΔGligação médios dos sistemas scFv/CD22 estão próximos do ΔGligação experimental (-12,45 para scFv curto e -11,65 para scFv longo). O uso do modelo de membrana nas simulações influenciou positivamente no resultado ΔGligação com maior acurácia. Os resultados alcançados geraram um protocolo confiável que pode ser usado para

proposição de mutações, *in silico* e *in vitro*, nos scFvs para realçar a afinidade ao CD22 e propor CARs mais efetivos para terapia celular *CAR-T Cell*.

Agradecimentos/Acknowledgment

Universidade Federal do Ceará. Fundação Oswaldo Cruz (Ceará). Fundação Cearense de Apoio ao Desenvolvimento Científico e Tecnológico (FUNCAP).

Área: TEO

Born-Oppenheimer Molecular Dynamics (BOMD) Study of the Chiral Sensitivity of Choline Chloride Sugar Based Deep Eutectic Solvents

Flávia Pirola Rosselli (PQ),[1] Manoel Gustavo Petrucelli Homem (PQ),[2] Quezia Bezerra Cass (PQ),[2] Luiz Carlos Gomide Freitas (PQ),[2*]

gomide@ufscar.br

[1]Departamento de Bioquímica, UNOESTE-Jaú; [2]Departamento de Química, UFSCar-São Carlos

Palavras Chave: *Eutectic Liquids, Cuiral Sensitivity, Quantum Dynamics, Amoxicillin, Glucose, Trehalose*

Highlights

Born-Oppenheimer Molecular Dynamics was used to calculate the interaction energy of chiral molecules, Amoxicillin 1 and 2, with chiral eutectic liquids obtained from the mixture of choline chloride salt with glucose and trehalose.

Resumo/Abstract

Abbott's publication [1] reported the production of an eutectic liquid mixing the solids choline chloride and urea at room temperature. Since then, various eutectic liquids have been obtained by mixing choline chloride with hydrogen bond donor compounds [2]. In this work, we report the theoretical investigation of chiral properties of two eutectic liquids obtained from an equimolar mixture of choline chloride with, respectively, glucose or trehalose, whose structures were obtained from the PubChem database [3]. Absorption spectra (Figs.1-2) calculated with the Zindo-CI method [4] implemented in the ORCA program [5], show the close agreement between the CD spectra of glucose and trehalose molecules before and after interaction with choline chloride. Therefore, the chirality of the sugar molecules is preserved in the eutectic liquid. Next, the interaction of the chiral molecule (antibiotic) Amoxicillin with these eutectic liquids was studied. Amoxicillin 1 corresponds to the structure obtained in the PubChem database. The enantiomer, Amoxicillin 2, was obtained by inverting the original atomic coordinates of Amoxicillin 1. In Figs.3-4, results for the total solute-solvent cluster energies, obtained along trajectories calculated with BOMD methodology, at T=300K and integration step of 2.0 fs, using the XTB program [6] are presented. The calculations were performed using initial cluster geometries shown in Figs.5-6. One observes appreciable differences between the interaction energies of both Amoxicillin enantiomers with the solvents. In both cases, Amoxicillin 1 presents greater stability, showing the influence of chirality on the solvation energy. Simulations results obtained using cluster sizes ranging from 2 to 12 eutectic liquid unites show the same energy pattern. These results indicate the potential use of these eutectic liquids as chiral solvation media.

Figure 1

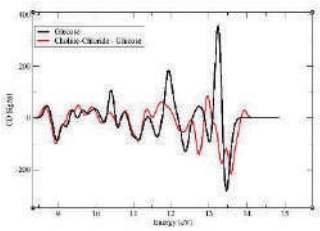


Figure 2

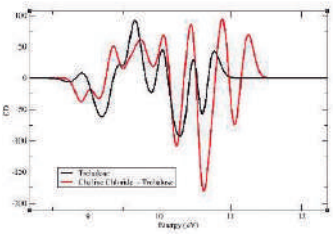


Figure 3

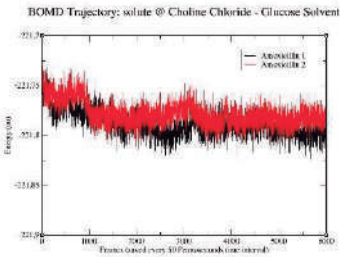


Figure 4

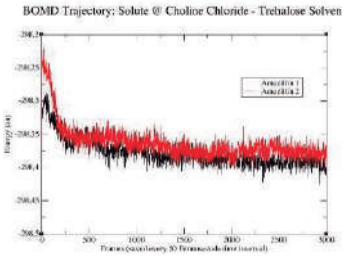


Figura 5-Glucose

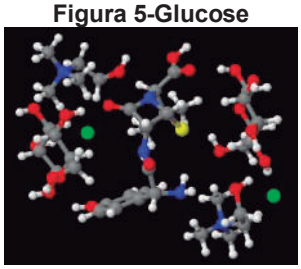
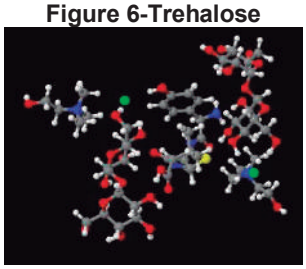


Figure 6-Trehalose



1- Abbott, A. P.; Capper, G.; Davies, D. L.; Rasheed, R. K.; Tambyrajah, V. Novel Solvent Properties of Choline Chloride Urea Mixtures. Chem. Commun. 2003, 0, 70−71.
2- Deep Eutectic Solvents: A Review of Fundamentals and Applications Benworth B. Hansen et all, *Chemical Reviews* **2021** *121* (3), 1232-1285.
3- PubChem Data Base, https://pubchem.ncbi.nlm.nih.gov/
4- Zindo - Ridley, J.; Zerner, M. Theor. Chim. Acta. 1973, 32, 111.
5- Orca version 5.0.4, Frank Neese, Max Planck Institute fuer Kohlenforschung.
6 – C. Bannwarth, E. Caldeweyher, S. Ehlert, A. Hansen, P. Pracht, J. Seibert, S. Spicher, S. Grimme, WIREs Comput. Mol. Sci., 2020, 11, e01493. DOI: 10.1002/wcms.14.

Área: TEO

Characterization of the UV-Vis spectra and akamptisomerism for aza-analogues of *push-pull* diboron porphyrinoid complexes

Patrick L. L. Rocha (PG),[1] Isabela S. de Almeida (IC),[1] Natalia M. Raffaeli (IC),[1] Karine N. de Andrade (PG),[1] Rodolfo G. Fiorot (PQ).[1]*

patrickllr@id.uff.br; rodolfofiorot@id.uff.br

[1]*Departamento de Química Orgânica, UFF;*

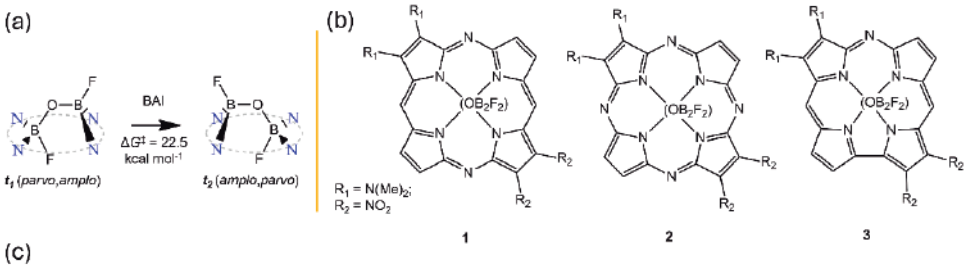
Palavras Chave: *Td-dft calculations, Molecular Modeling, Aza-porphyrins, Coordination chemistry, Stereochemistry.*

Highlights

The TD-DFT (CAM-B3LYP/6-31+G(d,p) UV-Vis spectra for *push-pull* corrolazine, diazoporphyrin and porphyrazines are reported. Energy barriers (B3LYP-D3/def2-TZVP) for akamptisomerization are assessed.

Resumo/Abstract

Novel diboron porphyrinoid complexes reveal a plethora of structure-dependent photophysical and chiroptical properties for potential applications as optoelectronic devices. Notably, properties such as the absorption spectra of such complexes can be finely tuned, whether by the modification of the conjugated ring or through peripheral functionalization, such as the addition of *push-pull* moities.[1,2] Moreover, such complexes present an unique coordination chemistry, where the restricted *bond-angle inversion* (BAI) of the central oxygem atom of asymmetric *transoid* diboron complexes characterizes two isolable conformational isomers, named *akamptisomers* (**Fig. 1a**).[3] Herein, we employ *time-dependent density functional theory* (TD-DFT) calculations for the characterization of the photophysical profile of interconvertible *transoid* akamptisomers of novel *di-* and *tetra-* azo analogues of porphyrinoid complexes (**Fig. 1b**). Additionally, B3LYP-D3/def2-TZVP energy barriers for BAI are reported.



(c)

I	HOMO-LUMO gap (ev)	$\lambda_{max\,(S_0\rightarrow S_1)}$ (nm)	Molar absorption coefficient ε (10^4 M^{-1} cm^{-1})	Oscillator strength *f*		II	ΔG‡ ($t_1\rightarrow t_2$) (kcal mol-1)	ΔG_{rel} (t_2-t_1) (10^{-3} kcal mol-1)
1-t_1	- 1.88	592	2.4	0.25		**1**	30.4	1.2
1-t_2	- 2.19	586	2.5	0.10				
2-t_1	- 2.10	572	3.1	0.39		**2**	32.8	0.2
2-t_2	- 1.84	579	2.7	0.33				
3-t_1	- 2.06	558	1.0	0.11		**3**	43.4	0.2
3-t_2	- 2.18	537	1.5	0.13				

Fig 1. (a) - *Bond-angle inversion* (BAI) scheme and expected energy barrier for the *transoid* akamptisomerization; (b) – Evaluated diboron porphyrinoid complexes; (c) – I. CAM-B3LYP/6-31+G(d,p) simulated absorption spectra, II. B3LYP-D3/def2-TZVP thermodynamic profile of akamptisomerization through direct *bond-angle inversion* (BAI).

Complexes containing more azomethine nitrogens (**1**,**2**) yielded more intense absorption bands in the visible light region. For (**2**), the monoconfigurational charge transfer (CT) S_1 state was characterized by H→L electronic transitions. All evaluated energy barriers for the restricted $t_1\rightarrow t_2$ interconversion satisfied the prerequisites for akamptisomerism.

References: [1] - Angewandtechemie - International Edition, v. 62, n. 8, 13 fev. 2023. [2] - Tetrahedron Letters, v. 133, 19 dez. 2023. [3] - Nature Chemistry, v. 10, n. 6, p. 615–624, 1 jun. 2018.

Agradecimentos/Acknowledgments

CNPq, CAPES, FAPERJ, and LoboC-UFRJ (NACAD).

Área: TEO
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Computational modeling of glyphosate detection on proline containing lipopeptide micelles: MD and DFT modeling of weak acids.

Pedro T. Sodré (PG)*[1], Bárbara Bianca Gerbelli (PQ)[1], Wendel Andrade Alves (PQ)[1], Maurício Domingues Coutinho Neto (PQ)[1]

mauricio.neto@ufabc.edu.br;t.sodre@ufabc.edu.br.

[1]*CCNH, Universidade Federal do ABC.*

Palavras Chave: Glyphosate, Biosensor, Molecular Dynamics, DFT, Self-Assembly, MMPBSA.

Highlights

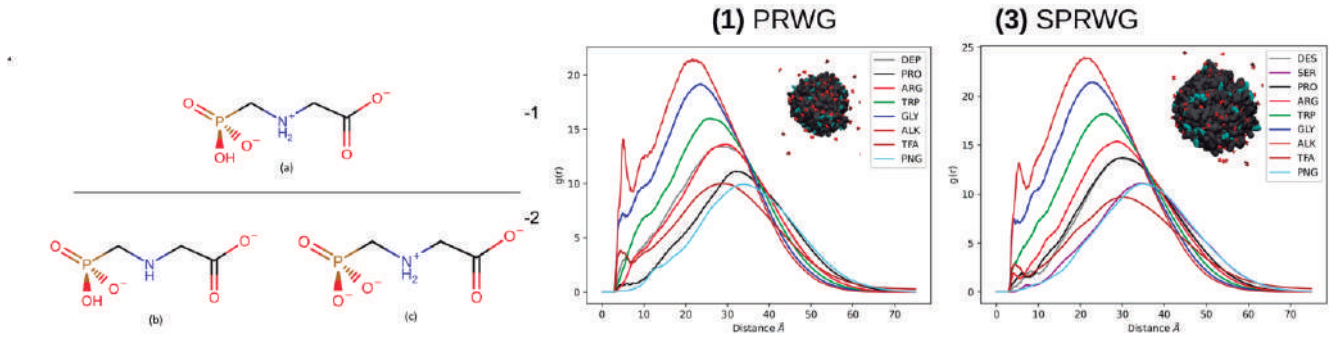
The interaction of proline-containing lipopeptide self-assembly aggregates with glyphosate was investigated computationally using molecular dynamics, density functional theory and MMPBSA calculations.
The complex weak acid equilibrium in the aggregate influences glyphosate detection by altering the electrostatic interactions and protonation states.

Resumo/Abstract

PRWGC$_{18}$ and SPRWGC$_{18}$ micelles partially ionize in water upon aggregation (solution pH being 3.5 and 3.0 for a concentration of 0.3 mg/ml respectively) and have been used for aldol catalysis and glyphosate detection. Glyphosate, also known as N-(phosphonomethyl)glycine, is an organophosphorus herbicide that is extensively utilized globally and has been the subject of numerous debates. The resulting biosensor depends on glyphosate equilibria with important pKa values being 2.27 and 5.57.

In this work, we investigate the interaction between proline-containing lipopeptide self-assembly aggregates and glyphosate molecules utilizing molecular dynamics, density functional theory, and MMPBSA calculation. DFT pKa calculations suggest that the N-terminal residue in micellar systems acts as a weak acid due to a large pKa shift upon aggregation. This finding suggests a potential picture of interactions between glyphosate and the micelles, where the PRWGC$_{18}$ and SPRWGC$_{18}$ micelles are partially charged at the pH relevant for pesticide detection.

We used MD simulations employing the AMBER suite of codes and force fields to study lipopeptide assembly structures. Results from MD simulations revealed a Stern-like layer organization with ions glyphosate, trifluoroacetic acid (TFA), and N-terminal cations at the ionic interface. Chemical structures of glyphosate (left) and radial distribution function of the micelle (right) depict their layered structure. Using MMPBSA, we compute glyphosate-micelle binding free energy for different micelle charges (100% and 50% protonated) and glyphosate charges (-1 and -2) contemplating distinct pH regimes. Our results suggest that for the pH afforded by the micellar environment, glyphosate should interact in its -1 charged state with partially protonated micellar systems. However, due to its stronger acidity, the SPRWGC$_{18}$ micellar system can interact in its partially charged state at lower pHs, enabling the stabilization of glyphosate in its -2 charged state at larger pesticide concentrations.



Acknowledgments

This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – Brasil (CAPES) – Finance Code 001. FAPESP 17/02317-2.

Área: TEO

Computational Study of Enantioselective Iminium Ion Catalysis in the Synthesis of Pyrroloindolines

Felipe S. Cardoso (PG),[1*] **Bruno M. Paz** (PQ),[1] **Ataualpa A. C. Braga** (PQ).[1]

felipe_schoma@usp.br

[1]*Instituto de Química USP.*

Key words: *Pyrroloinolines, Iminium Ion, Asymmetric Catalysis, Computational Chemistry, Non-covalent Interactions.*

Highlights

The results show that the interactions leading to catalytic selectivity differ from expectations. This new information may pave the way for modifications that enhance both selectivity and yield.

Abstract

Pyrroloindolines constitute an organic group serving as the structural foundation for drugs such as Physostigmine. Other molecules within this group exhibit potential as novel drugs for cancer treatment. The asymmetrical synthesis of pyrroloindolines, catalyzed by an iminium ion, occurs through the activation of the catalyst with an aldehyde that reacts with tryptamine (Fig. 1). The selectivity arises from the asymmetrical structure of the catalyst, which creates distinct non-covalent interactions between tryptamine and the catalyst, depending on which enantiomer is formed. Initially, the assumption was that only the substrate would change position relative to the catalyst. However, after a conformer analysis with the CREST program and confirmation through DFT calculations with B3lYP-GD3BJ/def2-svpp functional and base, the results present a different perspective. The reaction intermediate reveals that bond formation may occur in a manner previously deemed inaccessible due to steric effects. Further analysis could provide explanations for these results and offer insights for improvement. Another noteworthy aspect of the catalytic cycle is the significance of the cocatalyst, in this case, an acid. Transition state calculations indicate energy barriers higher than 36 kcal/mol, suggesting that the cocatalyst may participate in areas of the catalytic cycle beyond the formation of the iminium ion. This implies that enhancements to the cocatalyst could potentially increase the reaction yield.

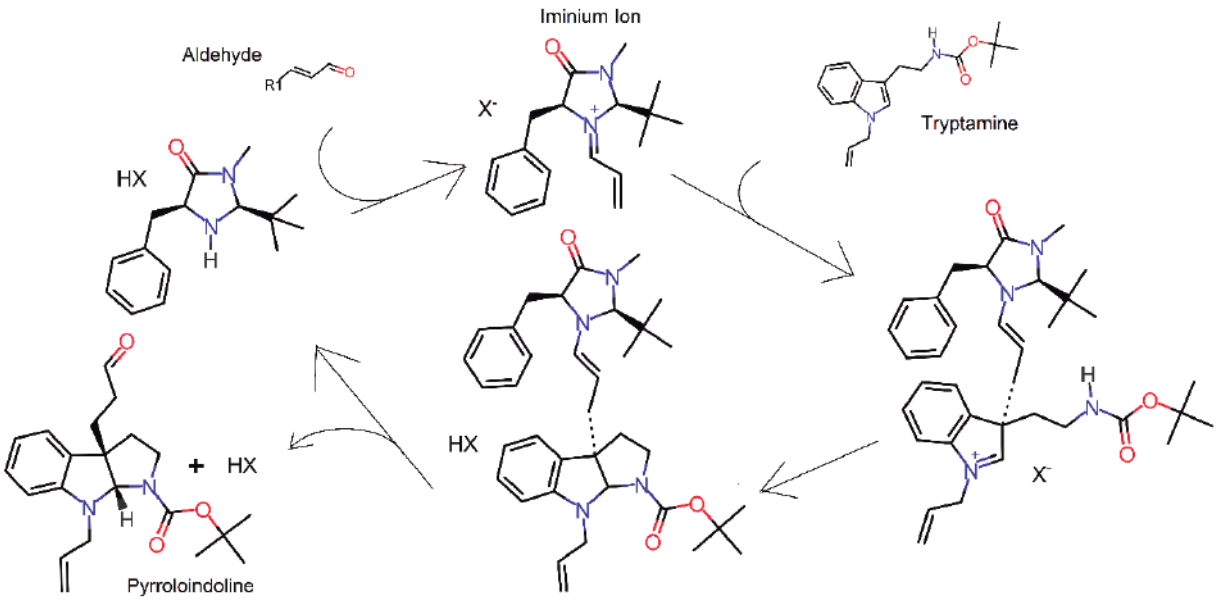


Figure 1. Catalytic cycle of pyrroloindoline synthesis

Acknowledgments

Felipe S. Cardoso thanks CNPq for Masters scholarship (Grant #131711/2023-7). A.A.C.B. acknowledges the financial support of FAPESP and CNPq (Grant #313720/2023-1).

Área: TEO

Computational study of ionic surfactants self-assembly in mixtures of deep eutectic solvents with water

Rafaela Eliasquevici (IC),[1] Kalil Bernardino (PQ)[1]

rafaela.eliasquevici@estudante.ufscar.br; kalilb@ufscar.br

[1]*Departamento de Química, UFSCar*

Palavras Chave: Molecular dynamics, Self-assembly, Surfactant, Solvophobic effect, Micelles, Hydrogen bonds.

Highlights

Molecular dynamics simulations of sodium dodecyl sulfate micelles in mixtures of water and the deep eutectic solvent reline showing a preference for the later at micelle surface.

Resumo/Abstract

Surfactants have a hydrophilic head and a hydrophobic tail. Above the critical micellar concentration, they aggregate, exposing heads to the solvent and keeping tails inside due to the balance between the solvophobic effect and the polarity or charge of their heads. Deep eutectic solvents (DES) are innovative solvents that differ from traditional ones because of their physical and chemical properties. They are formed by a eutectic mixture of acids and bases with a lower melting point than their components, allowing them to be in a liquid state at room temperature. The SDS was studied in pure water and mixtures of water and reline, a DES formed by a binary mixture of urea and choline with water molar fractions of 0.40, 0.57, and 0.73. For the first simulation, 60 monomers of SDS were packed with the heads pointing outward and the tails remaining inside a sphere. Subsequently, water molecules and 60 counter-ions filled the simulation box. This micelle formed in water was used as the starting point for the preparation of the simulations with water and reline mixtures. During the 240 ns of simulation, there was no dissociation in any of the structures - the final structure of the micelle in the system with a water molar fraction of 0.57 can be seen in Figure 1 a. It was noticed that in the systems with reline, there are almost no molecules of water and no counterions on the micelle surface (Figure 1b). An analysis of the average number of hydrogen bonds between the head of the dodecyl sulfate and the water confirmed that. For the system of the micelle in pure water, this number is high, but for the mixtures of reline and water, these numbers decrease substantially as long the molar fraction of water gets smaller. The radial distribution function of sodium around the micelle center shows the disappearance of the sodium peak at the micelle surface when adding reline to the solution while choline has a peak at ca. 2 nm (Figure 1 c and d). Those results demonstrated that the DES outcompeted water for interaction with the micelle.

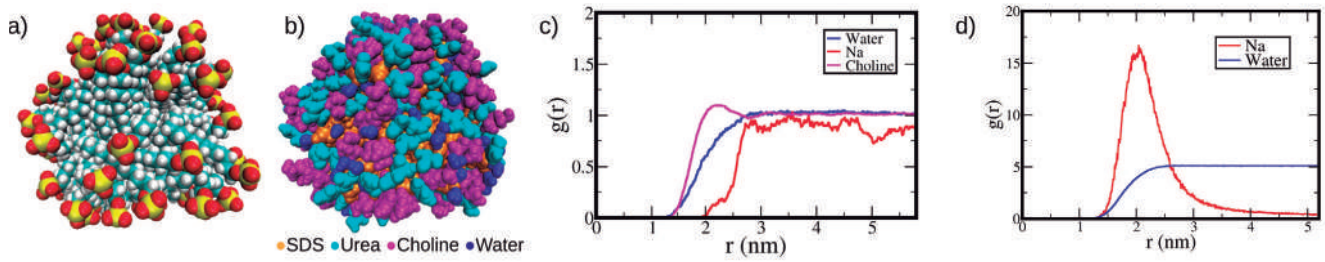


Figure 1 - representation of the **a)** final structure and **b)** first interaction shell of the micelle in system with water molar fraction of 0.57 and radial distribution function in systems **c)** water molar fraction of 0.57 and **d)** pure water.

Agradecimentos/Acknowledgments

We thank FAPESP for financial support and scholarship (grants 2023/09350-6 and 2022/15862-7) and the "Laboratório Nacional de Computação Científica (LNCC/MCTI, Brazil)" for the use of the supercomputer SDumont (https://sdumont.lncc.br)

Área: TEO

Computational study of the hydrolysis mechanism of merocyanine in a basic medium

Selma Fabiana Bazan (PQ),[1] Juliana Fedoce Lopes (PQ)[1]

sfbazan@gmail.com

[1]*Laboratório de Química Computacional, Instituto de Física e Química, UNIFEI*

Merocyanine, DFT, Hydrolysis mechanism, Decomposition.

Highlights

Merocyanine's decomposition was studied with DFT in basic pH.
The reaction studied is thermodynamically unfavorable.
Other paths and the kinetics of the process are being explored.

Abstract

Chromism, a phenomenon present in certain chemical substances, is characterized by reversible transformations, often accompanied by variations in coloration. These substances find wide application in various sectors, such as in the manufacture of cosmetics, temperature indicators, ophthalmic lenses, dyes, thermometers, and sensors.[1,2] A notable example is the class of chromophoric substances known as spiropyran (SP), which is composed of an indole group, a pyran ring, and a chiral carbon. Under exposure to ultraviolet light, SP undergoes a break, forming the open configuration called merocyanine (MC). The stability of merocyanine is crucial for its practical application, being influenced by factors such as pH and solvent polarity. Although studies on the mechanism of merocyanine decomposition are not yet fully elucidated, our work aims to investigate this process in a basic medium through computational simulations using Gaussian 09 software, employing the DFT approach with m062x exchange-correlation functional, 6-31g(d,p) basis set, and the IEFPCM model to consider the effect of the implicit solvent. Abeyrathna *et al.*[3] propose a mechanism for the decomposition of merocyanine, as illustrated in Figure 1.

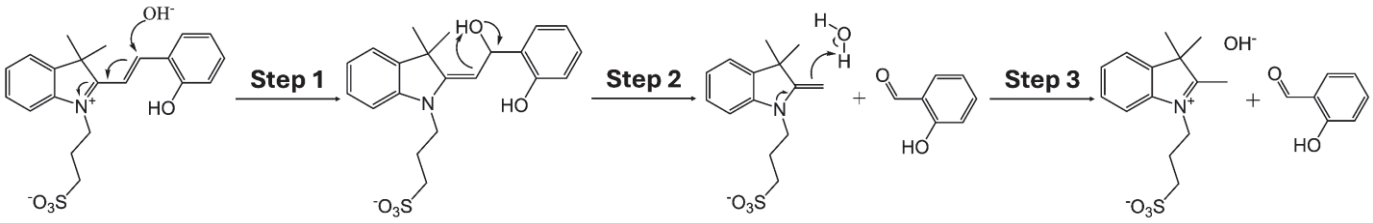


Figure 1. Proposed mechanism by Abeyrathna *et al.*[2] from the decomposition of merocyanine in a basic medium

Our study investigates this proposed mechanism, and our results indicate that steps 1 and 2 are thermodynamically favorable, with the ΔG values of -55.18 and -1.71 kcal mol^{-1}, respectively. However, in step 3, we observe an unfavorable thermodynamic tendency, with the ΔG value of +58.13 kcal mol^{-1}. We are currently exploring other mechanism proposals and investigating the process's kinetics. Understanding this mechanism is essential to produce stable molecules and for the consequent practical application of these chromophoric substances.

References

[1] Morsümbül, S. and Akçakoca Kumbasar, E. P. IOP Conf. Ser.: Mater. Sci. Eng., 2018, 459, <https://doi.org/10.1088/1757-899X/459/1/012053>.
[2] Shiraishi, Y., Itoh, M. and Hirai, T. Phys. Chem. Chem. Phys., 2010, 12, <https://doi.org/10.1039/C0CP00140F>.
[3] Abeyrathna, N and Liao, Y. J Phys Org Chem 2016; 1–5 <https://doi.org/10.1002/poc.3664>.

Acknowledgments

The authors acknowledge the funding agencies FAPEMIG, CAPES, and CNPq for their support.

Área: TEO

DFT Investigation on the Antioxidant Capacity of Culinary Spice Polyphenols

Heitor Avelino De Abreu (PQ),[1] André M. Oliveira (PQ),[2] Mithun Rudrapal (PQ)[3].

heitorabreu@ufmg.br

[1]*Departamento de Química, Instituto de Ciências Exatas, UFMG;* [2]*Departamento de Controle Ambiental e Química, CEFET-MG (Campus Contagem);* [3]*Departament of Pharmaceutical Sciences, Vignan´s Foundation for Science (India).*

Palavras Chave: *polyphenols, rosmarinic acid, ellagic acid, antioxidant.*

Highlights

DFT calculations were employed to estimate the antioxidant potential of some polyphenol species.

Rosmarinic and Ellagic acids are polyphenols extracted from culinary spices.

Thermodynamic properties point out ellagic acid as a better antioxidant agent then rosmarinic acid.

Resumo/Abstract

This study investigates the antioxidant potential of two culinary spices polyphenols, rosmarinic acid (**RA**) and ellagic acid (**ELA**), which inhibit key enzymes involved in inflammatory pathways. The antioxidant capacity of **ELA** and **RA** was assessed using DFT calculations, employing M06-2X/6-311G(2d,2p) and B3LYP/6-311G(2d,2p). Enthalpies were determined for non-ionized phenol (ArOH), ionized (ArO^-), radical (ArO•), and cation radical ($ArOH^+$•) forms. The scavenging activity was correlated with phenolic O-H bond dissociation enthalpy (BDE), adiabatic ionization potential (IP), proton dissociation enthalpy (PDE), proton affinity (PA), and electron transfer enthalpy (ETE)[1], considering the various OH groups and the protonation state of **RA**´s carboxylate group at physiological pH (Figure 1).

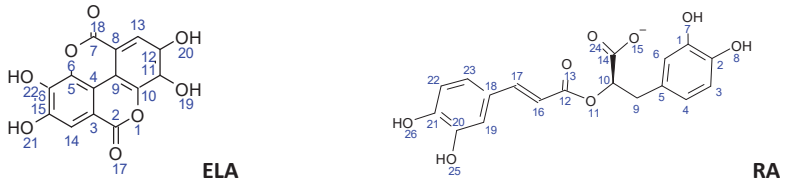


Figure 1. Numbering pattern of OH groups in **ELA** and **RA**.

Functional M06-2X displayed overestimated values when compared to B3LYP. The smaller BDE indicates a greater propensity for hydrogen atom transfer mechanisms, with the results favouring **RA** over **ELA**. In **ELA**, the 7-OH group is less reactive, possibly due to the proximity to the negative carboxylate group. Electron-donating groups such as OH decrease the BDE of phenols, increasing antioxidant activity[2]. A lower value of IP suggests a stronger electron-donating ability. Discrepancies arise when different functionals are used to calculate cation radicals, affecting the IP calculation of the 2-OH group in **ELA**, and M06-2X exhibiting better reproducibility. **ELA**'s OH groups demonstrate a higher tendency to act as electron donors compared to **RA**, due to the planar, fused rings of **ELA**, more effective at dispersing the positive charge of the cation radical than **RA**´s open chain. BDE is influenced by the local environment induced by substituents, while the IP value is affected by extended delocalization and conjugation of π-electrons. Higher PDE values result in slower acidity due to smaller OH dissociation via proton liberation, a behaviour observed more prominently in **ELA**. Lower PA values indicate easier formation of ArO^-, a profile exhibited similarly by both. **RA** demonstrates superior electron-transfer capabilities.

[1] Molski, M. Heliyon (2023) 9, e12806; Xue, Y. et al. Food Chemistry (2014) 151 , 198–206. [2] Bordwell, F.G.; Cheng, J.P. J. Am. Chem. Soc. (1991) 113, 1736–1743; De Heer, M.I. et al. J. Org. Chem. (1999) 64, 6969–6975; Najafi, M. et al. Bull. Chem. Soc. Jpn. (2013) 86, 497–509

Agradecimentos/Acknowledgments

CEFET-MG, UFMG, Vignan´s Foundation for Science, FAPEMIG, CNPq, CAPES

Área: TEO

Dispersion-corrected DFT-D4 effects on the geometry of a tetragonal iron complex.

Fernanda Milanez Brugnari (IC),[1] Ana Paula de Lima Batista (PQ)[1*].

fernandamilanez@estudante.ufscar.br; aplbatista@ufscar.br

[1]*Departamento de Química, UFSCar.*

Keywords: *Iron (II) complex, DFT-D4 methods, reliable geometries.*

Highlights

Iron-based photosensitizer for sustainable processes. The improvements in geometry calculations using the DFT-D4 approach depend on the selected functional.

Abstract

Using photosensitizers to harness light as a reactant in various transformations represents an approach to make industrial processes more sustainable. However, most current photosensitizers are based on 4d or 5d metal complexes, which are more expensive and less versatile.[1,2] A promising alternative is the use of the $Fe(HMTI)(CN)_2$ (HMTI = 5,5,7,12,12,14-hexametil-1,4,8,11-tetraazaciclotetradeca-1,3,8,10-tetraeno) complex, the first-known tetragonal Fe (II) complex as a potential photosensitizer.[2] In this study, we investigated the influence of the DFT-D4[3] correction for obtaining the iron complex geometry. All calculations were performed using ORCA.[4] For this purpose, a comparison was made between DFT and X-ray geometries and DFT-D4 and X-ray geometries, Figure 1. Lower RMSD (root mean square error), MUD (mean unsigned error), and MSD (mean signed error) were obtained with the B2PLYP-D4 density functional. Hence, this B2PLYP-D4 geometry can be chosen as a starting point for further calculations towards developing new photosensitizers.

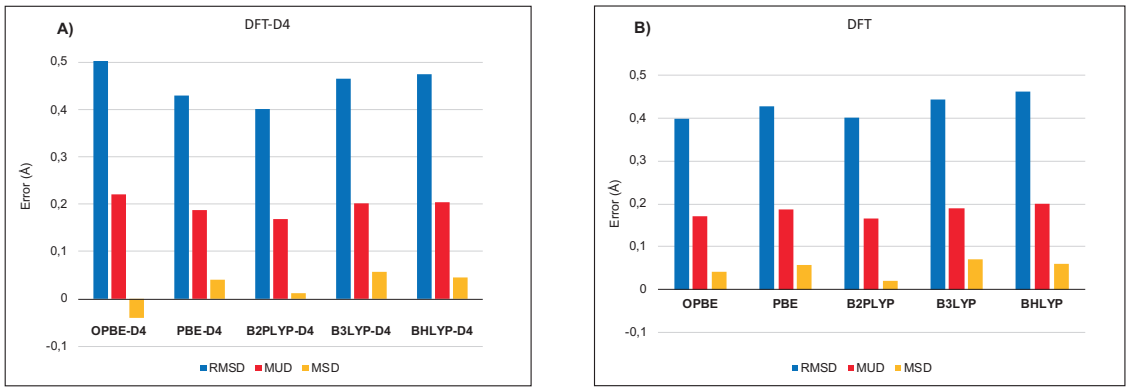


Figure 1. Explored density functionals for the study of the geometry of the $Fe(HMTI)(CN)_2$ complex **(A)** with D4 dispersion correction **(B)** and without D4 dispersion correction.

[1]H. Takeda, K. Ohashi, A. Sekine, and O. Ishitani, *J. Am. Chem. Soc.* **138**, 4354 (2016).
[2]J. T. Malme, R. A. Clendening, R. Ash, T. Curry, T. Ren, and J. Vura-Weis, *J. Am. Chem. Soc.* **145**, 6029 (2023).
[3]E. Caldeweyher, S. Ehlert, A. Hansen, H. Neugebauer, S. Spicher, C. Bannwarth, and S. Grimme, J. Chem. Phys. 150 (2019).
[4]Nesse, F. The ORCA program system. *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2**, 73-78 (2012).

Acknowledgments

FAPESP (2022/12043-5) and CAPES (001).

Área: TEO

Dissecting Methanol Adsorption on H-ZSM-5: A Multiscale Exploration using QM/QM

Thiago M. Mizumoto (PG),[1*] **Leonardo J. Duarte (PD),[1] Ataualpa A. C. Braga (PQ)[1]**

tzumizumoto@usp.br

[1] *Instituto de Química, Departamento de Química Fundamental, Universidade de São Paulo, São Paulo-SP, Brazil.*

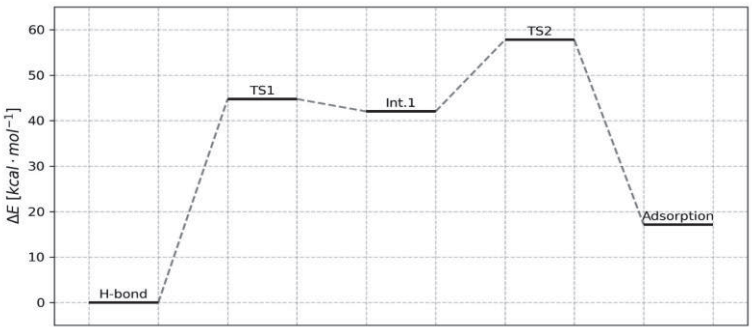
Keywords: *DFT, Heterogenous catalysis, Zeolites, Reaction mechanism, Cluster.*

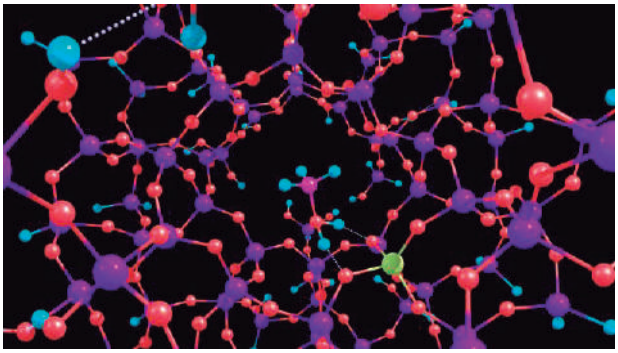
Highlights

A cluster approach using hybrid methodologies. The chemisorption of methanol occurs in three steps: hydrogen bond physisorption and proton transfer, dehydration via nucleophilic substitution and methyl cation migration.

Abstract

Zeolites are solids which have periodic structures arranged into ordered channels on the molecular scale. The variety of channel shapes and accessibility to molecules and macromolecules is what made this class of material be referenced as “molecular sieves”. These channels have been proposed to have key effects due to its spatial arrangement, as observed in catalysis. The confinement effect is believed to enable reaction paths through the stabilization of highly energetic transition states or through shape selection. In this present work, the mechanism by which methanol adsorbs on the zeolite is studied through the use of hybrid QM1/QM2 methodologies in a cluster approach that divides the structure of the zeolite into two regions: active and peripherical. The results, as depicted in Figures A and B, using PBE-D4/def2-SVP to the active region and XTB2 to the rest of the system, show that the employed methodology properly describes adsorption energy when compared to the literature. In order to shed light on the mechanism, this work makes use of the NEB-TS method to find the minimum energy path connecting two minima while minimizing the saddlepoint.





Figures: A) Electronic energy obtained for the adsorption process of Methanol over HZSM5. B)H-Bond van der Waals complex of methanol adsorbed over HZSM5.

Acknowledgments

TMM thanks Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – Brasil (CAPES) for a PhD scholarship (grant number 88887.827174/2023-00). LJD thanks Fundação de Amparo à Pesquisa do Estado de São Paulo, FAPESP, for a postdoctoral fellowship (grant number 2022/09269–1). A.A.C.B. acknowledges the financial support of FAPESP (Grant 2015/01491-3), the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) of Brazil for academic support (Grant 313720/2023-1), and CAPES that partially supported this work (Finance Code 001).

Área: TEO

Effects caused by fluoride on the physical and chemical properties of amino acids and proteins

Davi Medeiros Fortunato Cantanhede (IC),[1] Rodrigo A. Cormanich (PQ).[2*]

d232776@dac.unicamp.br; cormanich@unicamp.br

[1]*Instituto de Química, Univerisdade de Campinas;* [2]*Instituto de Química, Univerisdade de Campinas.*

Palavras Chave:*Biomoléculas; Química Computacional; Docking Molecular*

Highlights

Conformational and electronic effects caused by the presence of the fluorine atom in the molecules of 4-Fluoro-Threonine, 4S(R)-Fluoro-Proline, 5-Fluoro-Tryptophan. Thermodynamic stability of secondary structures (α-helix and β-Sheet) of tetrapeptides containing fluorinated units. Mechanistic investigation of isomerizations performed by PIN1 protein.

Resumo/Abstract

Fluorinated amino acids are compounds of great value that are constantly applied in various fields of biosciences. However, only one fluoroamino acid of natural origin has been discovered so far. To understand the stereoelectronic modifications caused by the fluorine atom in these molecules, DFT calculations were performed at the theoretical B3LYP level. For the amino acids 4-fluoro-threonine and 5-fluoro-tryptophan, fluoride did not exert a significant influence. For proline, however, a direct influence on the *endo-exo* conformational equilibrium was found for both the R and S configurations. *Keq(endo-exo)* values were compared to the amino acid of natural origin, 4-Hydroxy-Proline. Fluorinated analogs showed a more pronounced effect. Afterward, the determination of the relative thermodynamic stability between the α-helix and β-Sheet structures in tetrapeptides was done. Only marginal changes in $\Delta\Delta G$(α-helix⇌β-Sheet) were found. Finally, the PIN1 protein mechanism was mimicked for a Ser-Pro dipeptide and a Gly-Ser-Pro-Gly tetrapeptide. The aim was to determine a possible mechanism for the Cis-Trans interconversion done by the Prolyl Isomerase PIN1. A transition state formed by cyclic phosphate was found (Figure 1).

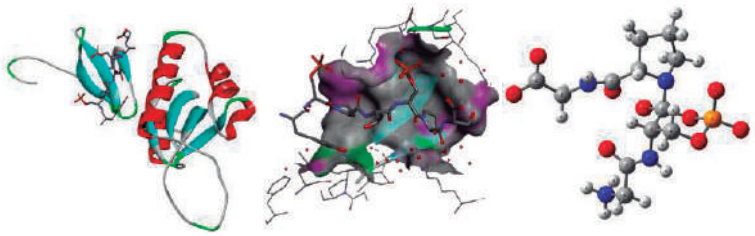


Figure 1: WW motif of PIN1 interacting with phosphoserine and the cyclic phosphate as the proposed transition state

Agradecimentos/Acknowledgments

The authors are grateful to FAPESP. The authors also thank FAPESP for a Young Researcher Award to RAC (#2018/03910-1) and a scholarship to KTM (#2023/15485-1). CNPq is acknowledged for a fellowship to RAC (#306912/2023-6). CENAPAD-SP and CESUP computational resources are also gratefully acknowledged.

Evaluation of the Performance of Density Functionals for Molecular Geometries of Iron Complexes

Renan R. Bertoloni (PG),[1] Ana Paula de Lima Batista (PQ),[2] Antonio G. S. de Oliveira Filho (PQ).[1*]

renanrbert@usp.br

[1] *Departamento de Química – Faculdade de Filosofia, Ciências e Letras de Ribeirão Preto (FFCLRP – USP)*
[2] *Departamento de Química – Universidade Federal de São Carlos (UFSCar)*
Keywords: *Catalysis, Sustainability, Coordination Compounds, Electronic Structure*

Highlights

Geometric optimization of 20 iron complexes was carried out utilizing the xTB, OPBE and BP86-D4 methods.
The xTB method, due to its lower computational cost, is very promising for iron complexes.

Abstract

With the advancement of research in chemistry, coordination complexes have been gaining increasing importance, both in the materials field and in healthcare.[1,2] Among all the metals studied, those with higher abundances in the Earth's crust, especially iron, stand out because of their significantly lower costs. With the advancements in computing and computational models available to the scientific community, computational chemistry has been increasingly used in the scientific discovery process. For the application of these models, it is necessary to quantify the deviations between calculated properties and those observed experimentally, aiming to optimize the balance between computational cost and accuracy in the obtained results. In this context, this work aimed to study 20 structures of mononuclear Fe complexes (especially organometallic or with polypyridine ligands) with widely used computational approaches, by comparing the results obtained by calculations with XRD data obtained in the literature. The methods used were xTB, OPBE, and BP86-D4 with the def2-TZVP basis set for the latter two. The values of root mean square error (RMSE), mean unsigned error (MUE) and mean signed error (MSE) were calculated for all the complexes. Taking the $[Fe(bpy)_3]^{2+}$ complex (**2**) as an example, similar deviations were obtained between the three methods used (**Figure 1a**). However, the xTB method has the advantage of being a much faster method, indicating that it is an excellent alternative for determining the molecular geometry of iron complexes, especially when compared with the BP86 method which, for diatomic molecules of transition metals, was one of the best functionals for equilibrium distances when compared with experimental results.[3] For some of the studied complexes (**1**, **3**, **5**, **16**), xTB showed large deviations, mainly due to spin-crossover properties and free rotation of ligands (**Figure 1b**). Therefore, that the xTB method is a promising tool but should be used with caution, preferably in conjunction with more robust methodologies or validated against experimental data.

[1]*Polyhedron* (2023), *241*, 116485; [2]*Appl. Sci.* (2022), *12*, 3442; [3]*J. Chem. Theory Comput.* (2017), *13*, 5291–5316.

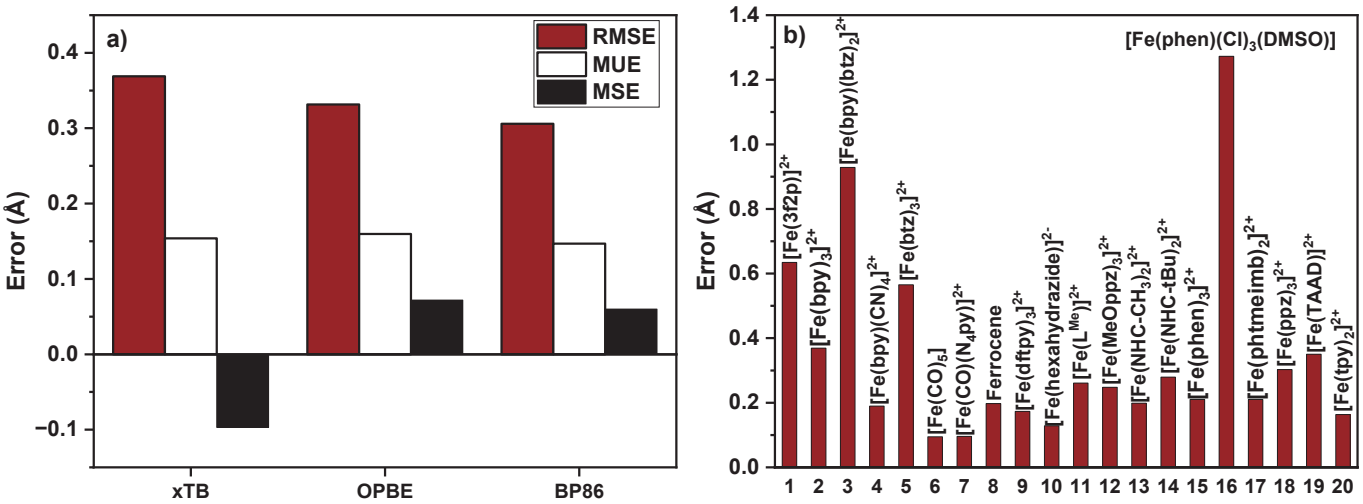


Figure 1: Comparison of the errors obtained for the molecule $[Fe(bpy)_3]^{2+}$ (**a**) and comparison of the RMSEs obtained for the series of molecules studied using the xTB method (**b**).

Acknowledgments

The authors would like to thank the Brazilian agencies CNPq, Fapesp and CAPES for their financial support of this work.

Área: TEO

Excited-State Bond Angle Inversion: (F)B–O–B(F)-Porphyrins as Potential Molecular Photoswitches

Karine N. de Andrade (PG)[1], Natalia Marques Rafaelli (IC)[1], Jhonathan R. Souza (PQ)[2], Paula Homem-de-Mello (PQ)[2], Rodolfo G. Fiorot (PQ)[1,*]

karineandrade@id.uff.br; rodolfofiorot@id.uff.br

[1]Departamento de Química Orgânica, UFF; [2]Centro de Ciências Naturais e Humanas, UFABC

Keywords: akamptisomerism, boron complex, DFT, TD-DFT

Highlights

(F)B–O–B(F)-porphyrins as promising photoswitches: the energy barrier for the bond angle inversion that separates distinct isomers with difference in low-intensity Q bands is reduced from the ground to the first excited state.

Abstract

Thermal bond angle inversion (BAI) in porphyrins with a (F)B–O–B(F) anchored bridge can give rise to diastereoisomers (***t*₁** → ***t*₂**), named akamptisomers[1]. This process induces distortion in the pseudo-plane of the porphyrin (Figure 1a, bold), potentially influencing their electronic structure and making these compounds molecular photoswitches candidates. A photoswitching compound must exhibit *i*. isomerization promoted by light, and *ii*. distinct energy profiles for the individual compounds[2]. Herein, we conducted DFT and TD-DFT calculations at CAM-B3LYP/6-31+G(d,p) level with G09 software to investigate thermal and excited-state (ES)-BAI, respectively, in a push-pull system (Figure 1a). This system proved to be promising as photoswitches in our previous work[3]. Our results revealed that in the ground state (S_0), the thermal BAI occurs with a barrier of $\Delta E^{\ddagger}$=21.3 kcal mol^{-1}, leading to isomers ***t*₁** and ***t*₂** with a small energy difference, ΔE=–2.6 kcal mol^{-1}. The ESBAI, preliminary explored through single-point calculations, showed a lowering of $\Delta\Delta E^{\ddagger}$ = 2.9 kcal mol^{-1} in the S_1 compared to S_0, indicating that isomerization is favored in the excited state (Figure 1b). This makes BAI an intriguing isomerization process to be explored in the excited state. The absorption profile, simulated in both gas-phase and implicit (IEFPCM) water media (Figure 1c), exhibited a more significant difference in solvent media, particularly for low-intensity Q bands: $|\Delta\lambda|(S_1)$ = 12 nm in the gas phase, while $|\Delta\lambda|(S_1)$ = 24 nm in solvent. This difference is attributed to the increased charge separation in polar media, favoring intramolecular charge transfer (ICT) in the push-pull system, assessed by molecular orbitals evaluations (Figure 1c). In the BAI, the electron-donor and the electron-withdrawing groups connected to the pseudo-planes are distorted in ***t*₁** and ***t*₂**, thus affecting the ICT in each akamptisomer and increasing the distinction between the absorption profiles. This work is in progress, and our expectations include evaluating the full ESBAI by exploring geometry optimization at the S_1 level, and examining possible contributions of the triplet state through intersystem crossover evaluations.

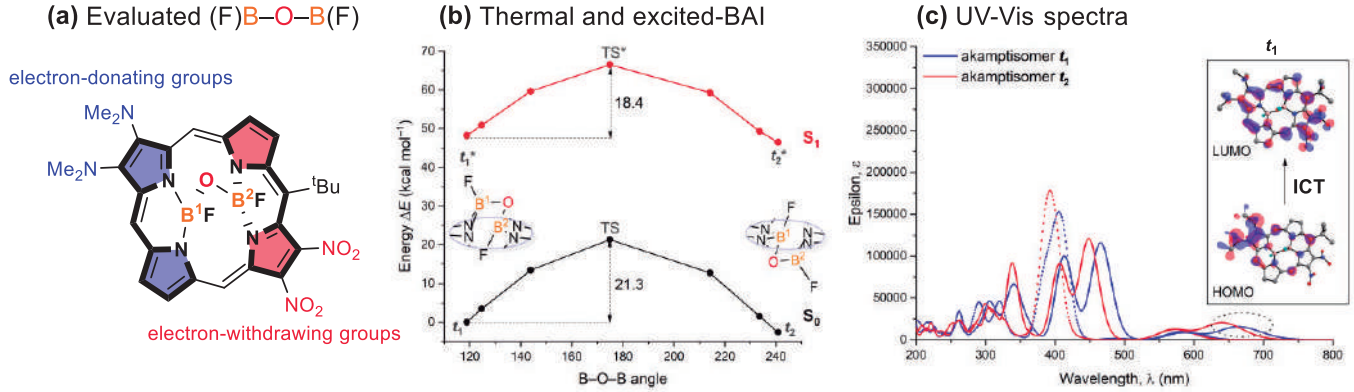


Figure 1: (a) (F)B–O–B(F)-porphyrin push-pull structure. Pseudo-planes highlighted in blue (electron-donating group) and red (electron-withdrawing group); **(b)** Thermal (black) and excited-state (red) BAI profiles obtained from single-point calculations along the B–O–B reaction coordinate; **(c)** UV-Vis spectra in gas-phase (dashed) and solvent (solid) for ***t*₁** (blue) and ***t*₂** (red). Lowest energy electronic transition (HOMO→LUMO) of akampisomer ***t*₁** highlighted.

References: [1.] Canfield, P. J. et al. *Nat Chem* 10, **2018**, p. 615; [2.] Wang, Z. *et al*. Chem Soc Rev 51, **2022**, p. 7313. [3.] Unpublished results.

Acknowledgments

CNPq, CAPES, FAPERJ, NACAD - Lobo C (id = a20006), FINEP & UFABC.

Área: _____TEO**_____**

Exploring machine learning algorithms for the prediction of CO_2 and N_2 isotherm on nanoporous materials

João Matheus Chagas Sousa (IC),[1] Felipe L. Oliveira (PG),[1] Pierre M. Esteves (PQ).[1*]

joaosousa.chagas@gradu.iq.ufrj.br; pesteves@iq.ufrj.br

[1]*Departamento de Química Orgânica, Instituto de Química, UFRJ*

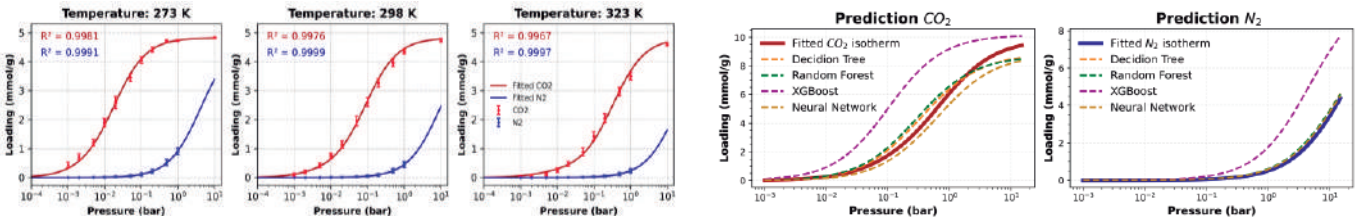
Palavras Chave: M*achine learning, Nanoporous materials, Adsorption, CO_2* capture.

Highlights

We apply machine learning algorithms and evaluate their ability to predict CO2 and N2 adsorption isotherms in Nanoporous materials.

Abstract

The increasing emissions of greenhouse gases, specially as CO_2, are directly linked to the growing environmental impacts caused by climate change.[1] One promising strategy to address this issue is the usage of nanoporous materials for the capture and storage of CO_2. Reticular nanoporous materials such as MOFs and COFs have a great potential for CO_2 capture.[2] However, due to the large number of possible structures and its structural diversity their experimental exploration can be challenging. Computational techniques, including machine learning, offer a valuable tool for exploring these materials. Here, we investigate the application of several machine learning methodologies for the prediction of adsorption isotherms of gases such as CO_2 and N_2 on nanoporous materials. Additionally, the impact of several dimensionality reduction techniques and feature selection methods on the predictive performance of the machine learning models was evaluated. For a set of porous materials taken from the CRAFTED[3] database, we fitted a Dual-site Langmuir (DSL) isotherm model to the CO_2 and N_2 isotherms. Four predictive models were evaluated: Decision Tree, Random Forest, xGBoost, and Neural Networks. The fit of the DLS model on the adsorption data of the 1340 materials from CRAFTED presented a good fit (R^2>0.9) for 1223, as exemplified in Figure 1(a). This fitted parameters were used to train the four different machine learning models. Among this models, at least three of them (Random Forest, xGBoost and Neural networks) presented good results (R^2>0.8), as exemplified in Figure 1(b). The Neural Network model presented the best result among the evaluated models. The combination of textural properties with RAC descriptors resulted in models with better predictive capabilities, followed by the versions with dimensionality reduction and textural and chemical descriptors individually.



(a) **(b)**

Figure 1: (a) Isotherms fitted with the DSL model for CO_2 and N_2 at temperatures 273K, 298K, and 323K**. (b)** DSL models for CO_2 and N_2 isotherms at the temperature of 273K and the prediction with the evaluated ML models.

REFERENCES:

[1] STEFFEN et al. Philos. Trans. Royal Soc. A PHILOS T R SOC A, 2011, 369(1938), 842-867.
[2] Yaghi, O. M. ACS Cent. Sci, 2019, 5(8), 1295-1300.
[3] Oliveira et al. Sci Data, 2023, 10, 230.
[4] Janet, J. P. et al. J. Phys. Chem, 2017, A121, 8939–8954.

Acknowledgments

CNPq, CAPES, FAPERJ, FINEP-ANP.

Área: TEO

iLEGO: A Python Tool for Building 3D Arrangements for Ionic Liquids Structures

Jonathan B. Brum (PG),[1]* Cauê T. O. G. Costa (PQ),[1] Luciano T. Costa (PQ).[1]

jonathanbrito@id.uff.br

[1]*MolMod-CS, Department of Physical Chemistry, Institute of Chemistry, UFF.*
Keywords: Ionic liquids, Python tool, Ion pair, molecular modeling.

Highlights

- Development of a new software for calculating chemical environments of ionic liquids;

- Spatial description of ionic liquids consistent with the literature;

- Low computational cost with coherent accuracy.

Resumo/Abstract

Ionic liquids (ILs) are highly sought-after in the literature due to their unique physicochemical properties, such as low vapor pressure and reduced volatility[1]. Primarily composed of anions of various natures and bulky organic cations, theses ionic pairs can be combined in order to form more than 10^8 species which is a large chemical space. However, due to the high computational cost, fewer than 10^3 of these species have been investigated to date. This work introduces the iLEGO Building software, a program developed in Python language, which uses rotation matrices of rigid bodies[2] and optimized translation vectors combined with the semiempirical GFN0-xTB and GFN2-xTB methods[3,4] for the geometry optimization. The application has a small computational cost compared to robust quantum calculations and can be used as a pre-optimization step for molecular dynamics (MD) or density-functional theory (DFT) calculations. Figure 1 shows the iLEGO results for a combination of different anions and imidazolium based ILs.

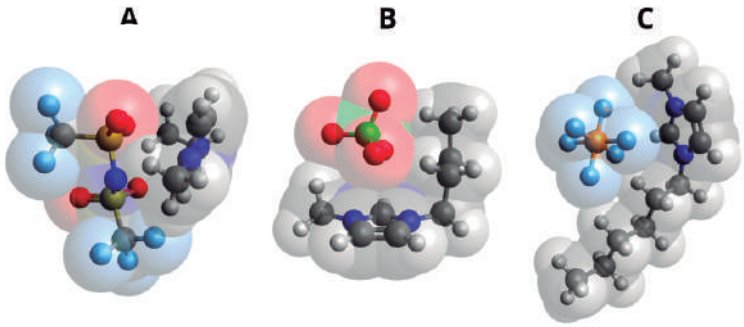


Figura 1: In A, the combination between the TFSI anion and the C2MIM cation. In B, the combination between the ClO_4 anion and the C4MIM cation. In C, the combination between the PF_6 anion and the C6MIM cation.

These structures were selected from 314 so that the entire conformational space was studied in intervals of 8 degrees. iLEGO is also able to be a tool for generating topologies for MD simulations based on GAFF and OPLS force field, which is under development.

[1] R. Vekariya, Journal of Molecular Liquids, 2016, 227. 44-60.

[2] LaValle S; M. Cambridge University Press; 2006. 81-100.

[3] P. Pracht, E. Caldeweyher, S. Ehlert, S. Grimme, ChemRxiv, 2019, preprint.

[4] C. Bannwarth, S. Ehlert and S. Grimme., J. Chem. Theory Comput., 2019,15, 1652-1671.

Agradecimentos/Acknowledgments

The authors would like to thank the support from CAPES, FAPERJ and CNPq, and also the facilities resources from CENAPAD, DIRAC and LNCC.

Área: TEO

Interaction of ionic liquids with active pharmacological ingredient with lipid bilayers by molecular dynamics simulation.

Leticia R. Dias (IC),[1] Kalil Bernardino (PQ).[1]

leticiarldias@gmail.com

[1]*Departamento de Química, UFSCar.* [2]

Palavras Chave: Ionic Liquids, Lipid Bilayer, Drugs, Molecular Dynamics Simulations, Pmf Calculation.

Highlights

Molecular dynamics simulations to compute the free energy of penetration of ibuprofen and biocompatible ionic liquids with its conjugated anion into lipid bilayers and characterize the structure.

Resumo/Abstract

Topical medicines have the advantage of less damage to the digestive system, but they present as a challenge the difficulty in penetrating the vast majority of active pharmacological ingredients through the epidermis, since to do so they must present both good water solubility and affinity with the hydrophobic interior of lipid bilayers. An alternative that has attracted attention to facilitate the penetration of potential drugs through the epidermis consists of converting the drug into a cation or anion of an ionic liquid, which are defined as salts with melting point inferior to 100ºC. Such modification also improves its solubility in water and eliminates problems associated with crystallization. Using classical molecular dynamics simulations, it is possible to compare the penetration of the anti-inflammatory ibuprofen in its neutral form into POPC lipid bilayers (Figure 1) with its penetration in the deprotonated (anionic) form in biocompatible ionic liquids. As models of ionic liquids, the study was carried out with the biocompatible cations choline and decyl-choline. Such simulations were carried out with the Gromacs program, and calculations of potential of mean force (pmf) for the penetration of drugs into the bilayer using the umbrella sampling method were made to evaluate the effects that the incorporation of the drug and the cation of the ionic liquid influence the structure and dynamics of the bilayer. This study aims to understand the interaction of drugs with biological membranes which may help in the development of new formulations for topical use that have better penetration through the epidermis.

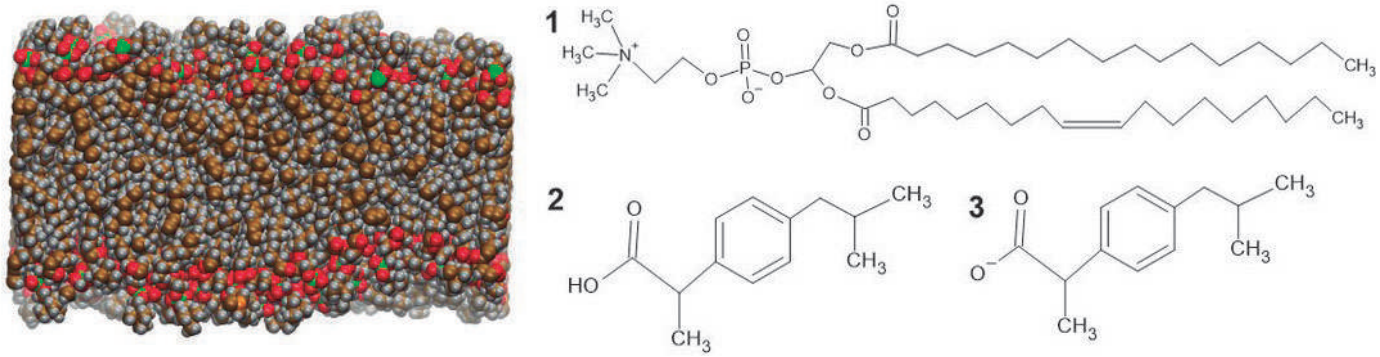


Figure 1: (Left) POPC lipid bilayers in the Van der Waals representation. (Right) 1: 1-palmitoyl-2-oleoyl-glycero-3-phosphocholine lipid. 2: Ibuprofen molecule. 3: Ibuprofenate ion.

Agradecimentos/Acknowledgments

"We thank FAPESP for financial support and schoolarship (grants 2023/15437-7 and 2023/09350-6) and and the "Laboratório Nacional de Computação Científica (LNCC/MCTI, Brazil)" for the use of the supercomputer SDumont (https://sdumont.lncc.br)"

Área: TEO

Investigation of the properties of pyrrhotite and troilite through DFT calculations

Tercio Paulo Felix Xisto (PG).[1]* Hélio A. Duarte (PQ)[1].

terciofelixxisto@gmail.com

[1]*Department of Chemistry, UFMG*

Keywords: *DFT, density of states, Hubbard.*

Highlights

Pyrrhotite (Fe_7S_8) and troilite (FeS) were calculated using GGA-U PBE/PW. The optimized structures are in agreement with the experimental data. Pyrrhotite is ferromagnetic and troilite is diamagnetic. Troilite is a semiconductor with a band gap of 0,12 eV and pyrrhotite is estimated to be a conductor.

Resumo/Abstract

Sulfide minerals are those in which the sulfide anion is bonded to metallic cations. This class of minerals stands out as a primary and crucial source of nonferrous metals, contributing significantly to industries and the economy. The iron-sulfides, which are the most abundant group of sulfide minerals, are usually found with some valuable metal ions, such as Cu, Pb, Zn, Au, Pt, and Ag. Recently, it was observed that pyrrhotite is not floated, in gold mining, contributing to the acidification of the tailing dams due to the acid rock drainage.

Sulfide minerals are categorized into groups based on the structure that represents them. Two important minerals of the sulfide class are pyrrhotite (Fe_7S_8) and troilite (FeS). Both minerals are derived from the nickeline (NiAs) structure. Troilite is the initial derivative of the nickeline structure. The presence of Fe vacancies in the troilite structure lead to the formation of pyrrhotite.

Plane-wave Density Functional calculations have been performed as implemented in the Quantum Espresso Package. Ultrasoft pseudopotentials and the GGA PBE XC functional together with the Hubbard correction (GGA+U) have been used. Initially, we conducted calculations to evaluate the convergence of the cutoff energy and the K-points grid to obtain an accurate description of the electronic structure of the crystalline systems. Afterwards, we adjusted the magnetization to identify a more stable magnetic configuration. To ensure energy accuracy of 10^{-3} Ry, Troilite cut-off energy was set to 50 Ry with 221 K-points, while pyrrhotite employed a cut-off energy of 90 Ry with 121 K-points. A Hubbard parameter (U) equal to 1 eV was applied for troilite and pyrrhotite structure, achieving optimal agreement with the experimental geometry for both structures. The optimized lattice parameters ratio c/a are 1,96 and 1,07 for troilite and pyrrhotite, respectively. These values must be compared to the experimental values of 1,97 and 1,08 for troilite and pyrrhotite respectively. Troilite is spin compensated, with absolute magnetization of 37.23 μ_B, which corresponds approximately to 3.1μ_B for each Fe center. Pyrrhotite is ferromagnetic with total and absolute magnetization of 4.44 e 76.19μ_B, respectively. The density of states of both structures indicates that troilite is semiconductor with a band gap of 0,12 eV and pyrrhotite is conductor. The nature of the bonding in troilite and pyrrhotite will be discussed in detail based on topological analysis of the electron density, band structure and thermodynamics.

References

1. VAUGHAN, David J.; CORKHILL, Claire L. Mineralogy of sulfides. **Elements**, v. 13, n. 2, p. 81-87, 2017.
2. BELZILE, Nelson et al. A review on pyrrhotite oxidation. **Journal of geochemical exploration**, v. 84, n. 2, p. 65-76, 2004.

Agradecimentos/Acknowledgments

CNPq. Based Mineral High-Performance Materials and Processes Network–RENOVAMin (Proc. RED-00102-16)

Área: TEO

Kinects and Thermochemistry of the Propagation Stages of Primary Radicals of Trimethoxymethane and the Implications for its Use as an Alternative Fuel

Caio F. G. Oliveira (IC),[1] Glauco F. Bauerfeldt (PQ).[1*]

caiofab@ufrrj.br; bauerfeldt@ufrrj.br

[1]*Departamento de Química Fundamental, UFRRJ.*

Keywords: *Reaction mechanisms, Oxymethylene ethers, Trimethoxymethane, Alternative fuel,* Transition state theory.

Highlights

Oxymethylene ethers produce little NOx and soot. Trimethoxymethane, as it is branched, will have better properties. The energies of the transition state, reactants and products were obtained.

Abstract

Trimethoxymethane (TMM) $(H_3CO)_3CH$ is a compound that belongs to the family of oxymethylene ethers, which has been considered as an alternative fuel, or additive for diesel, produced from renewable sources [1-3]. The theoretical study of the combustion of this compound will provide its profile in relation to the fragments released after its burning, contributing to the identification of its impact on the environment and its characteristics as an alternative fuel or additive that reduces the environmental impact of diesel. The energy values of the fragments and transition states were obtained by the computational method M062X/aug-cc-pVTZ, DFT level of theory. The geometries of all species involved were optimized, including the saddle points, with the aim of finding the energy minima. The identification of the stationary points located was carried out through calculations of vibrational frequencies. Rate coefficients were determined by the conventional transition state method, through the KINPRO[4] program, which was developed in our own laboratory. Demethylation, with the concomitant formation of the dimethoxymethyl oxidanyl radical ($PdissCH_3$), is the main reaction in high temperature and pressure regimes. The investigated steps (**Figure 1**) of intermediate (**I**) were: **I** → $C(O)(OCH_3)_2$ + H (R1a), **I** → $C(OH)(OCH_3)_2$ (R1b), **I** → $OCOCH_3$ + CH_3OH (R1c), **I** → $CH(O)OCH_3$ + OCH_3 (R1d), the third being the one with the lowest total relative barrier, because even though it initially has a slightly higher third energy barrier, as the reaction path continues, this becomes shows more energetically favorable (considering the entire reaction path). The speed constant results (**Figure 2**) corroborate this finding, as R1c has the highest constant values. In the future, other TMM intermediate radicals will be studied.

Figure 1: Power diagram of $PdissCH_3$ combustion mechanism

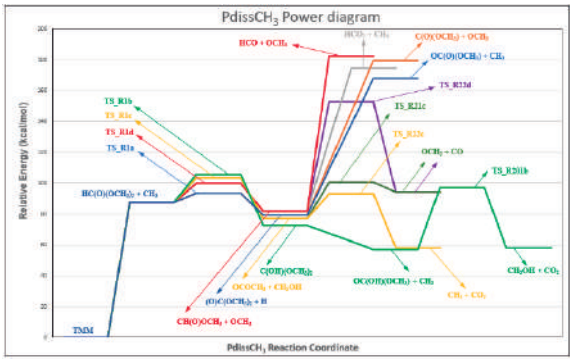
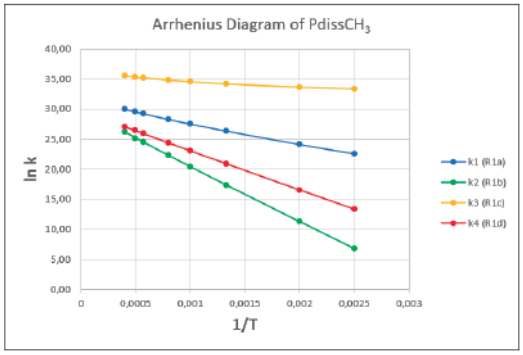


Figure 2: Arrhenius diagram of $PdissCH_3$



References: [1]Härtl, M. et al. Fuel 2015. 153, 328–335. [2]Döntgen, M. et al. Combust Flame 2022. 242, 112186. [3]Döntgen, M. et al. Proc. Combust. Inst. 2023. 39, 305–314. [4]Vieira, G. S. S. et al. Assessment of Uni and Bimolecular Reaction Kinetics of Dimethoxymethane with the KINPRO Package. In: 10th European Combustion Meeting, 2021, Virtual Edition. Proc European Combust Meeting, 2021

Acknowledgments

CNPq Conselho Nacional de Desenvolvimento Científico e Tecnológico
UFRRJ
CIMOL
UFRRJ LCQ LABORATÓRIO DE CINÉTICA QUÍMICA

Área: TEO

Kinetic stability of nanoparticles dispersions in ionic liquids with domain segregation – a molecular dynamics simulation study

Kalil Bernardino (PQ).[1]*

kalilb@ufscar.br

[1]*Departamento de Química, UFSCar*

keywords: Nanoparticles, ionic liquids, potential of mean force, aggregation free energy, molecular dynamics simulations, stability

Highlights

- Potential of mean force for the formation of hydrophobic and hydrophilic NPs in two ionic liquids
- Multiple energy barriers observed for the aggregation due to domain segregation in the solvent

Resumo/Abstract

Ionic liquids (ILs) are defined as salts with melting point below 100ºC and have attracted great attention in synthesis and extraction processes due to their unique properties like an essentially null vapor pressure and the capacity to solubilize both organic and inorganic species. Regarding the synthesis of nanomaterials, in addition to those properties, many ILs can also stabilize nanoparticles (NPs) dispersions without additives like surfactants. This is usually attributed to the segregation between hydrophobic and hydrophilic domains inside the IL. In this work, the potential of mean force (PMF) was computed between pairs of both hydrophilic and hydrophobic NPs in two different ILs: 1-butyl-3-methylimidazolium tetrafluoroborate (C4) and 1-octyl-3-methylimidazolium tetrafluoroborate (Figure 1 a) in order to quantify this effect. Only the C8 displays significant domain segregation, resulting in alternating hydrophilic and hydrophobic shells around NPs (Figure 1 b). Simulations were performed at 300 K using the Martini 3.0 force field and Gromacs software. Besides the aggregation still being thermodynamically favorable, as seen by the global minimum of the PMF at the contact distance, the domain segregation in the IL results in not only one, but several barriers for the aggregation, rendering a kinetic stability that was confirmed by simulations of concentrated NPs dispersions (Figure 1 c), which showed that in C4 all the particles were clustered together after 2500 ns while in C8 only the formation of a few dimers were observed.

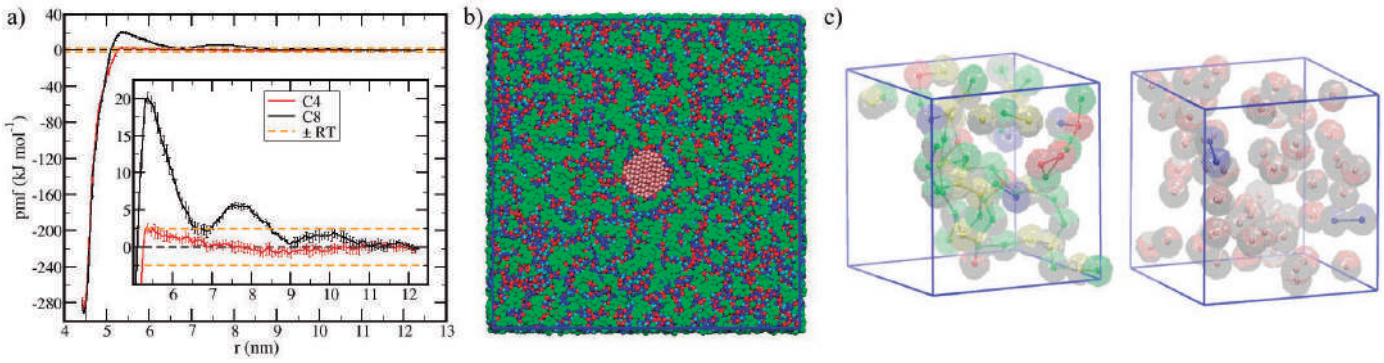


Figure 1 – a) PMF for the aggregation of a pair of hydrophilic NPs in the two ILs. **b)** Structure showing the segregation between hydrophobic (green) and hydrophilic (blue and red) domains around the hydrophilic NP in C8. **c)** Structures observed after 2500 ns simulation of NPs in C4 (left) and C8 (right) ILs, with lines connecting NPs that are in contact with each other.

Agradecimentos/Acknowledgments

FAPESP for financial support (grant 2023/09350-6) and the "Laboratório Nacional de Computação Científica" (LNCC/MCTI, Brazil) for the use of the supercomputer SDumont (https://sdumont.lncc.br).

Área: _____TEO_____

Kinetic study using artificial neural network for combustion process in spark ignition engines - A comparative with Brazilian commercial gasolines.

Natália R. S. Araujo (PG),[1] Rita C. O. Sebastião (PQ),[1] Felipe S. Carvalho (PG),[1] João Pedro Braga (PQ),[1] Fabrício J.P. Pujatti (PQ),[2] Lucimar V. Amaral (PG)[2]

nataliarsaraujo@ufmg.com; ritacos@ufmg.br

[1]Departamento de Química, UFMG; [2]Departamento de Engenharia Mecânica, UFMG.

Keywords: *Kinetic of combustion, Internal combustion engines, Mass Burned Fraction, Ignition Delay.*

Highlights

Kinetics of fuel combustion in internal combustion engines.

Comparison between regular and premium commercial gasolines in Brazil.

Simplified kinetics using Multi-Layer Perceptron.

Abstract

Combustion processes in internal combustion engines can be described and compared through their kinetic properties. Through the comparison of combustion kinetics of air/fuel mixtures, it is possible to optimize the process and create solutions to increase its fuel conversion efficiency [1]. However, defining the right mechanism is not a simple task. The number of species and reaction steps grows almost exponentially with the number of carbon atoms in the fuel; making it impractical to grasp the physical meaning from such large mechanisms. A simplified description of chemical kinetics is, therefore, extremely useful for practical applications of combustion sciences to engineering problems, as engineers seek to know the behavior of practical systems and the actual fuel. The aim of the present study is to develop and explore a methodology using Artificial Neural Network (ANN) that uses the Mass Burned Fraction (MBF) data as a function of the crankshaft angle (°CA) to determine the combustion kinetics in engines. The kinetic triplet will be determined, consisting of Activation Energy (Ea), Frequency Factor (A) and Reaction Model throughout the combustion process. The kinetic triplet will be used to explore the combustion characteristics of different gasoline formulations and engine operation. The experimental data were obtained in a single cylinder research engine (SCRE) operating with two gasoline formulations commercialized in Brazil, regular (R) and premium (P). The SCRE was tested in steady-state, and stoichiometric (λ=1.00) conditions at 11 bar IMEP and speed engine of 4000, 4500 and 5000 rpm. The kinetic methodology follows the combustion along the process and recover the values of Ea and A without resort to mechanisms that describe each reaction individually but describing the global contribution of physical models [2]. The kinetic study showed a significant change in the flame evolution, and consequently the reaction model, at 40% of conversion for R, and 20% for P. Therefore, the mechanism for both samples can be divided in two events. For event 1, R had a high contribution of the Avrami-Erofeev (Amn) model with order n=2, and P followed the Am3 model. For event 2, both samples present similar physical mechanisms with higher contribution of Am2. R presented the highest values of Ea and A in comparison with P. The values are coherent with the results of ignition delay (the angular interval of the engine shaft between the moment of the spark and the start of the combustion process). The higher the value of Ea, the higher the ignition delay [3]. In conclusion, the present methodology allows one to characterize the combustion process in different stages through the °CA and the kinetic parameters help us to explain significant parameters in the engine performance, as ignition delay.

[1] Amaral, L. V., et al. (2021). Effects of gasoline composition on engine performance, exhaust gases and operational costs. Renewable and Sustainable Energy Reviews, 135, 110196.

[2] Araújo, N. R. S., et al. (2022). Kinetic study of domestic sewage sludge combustion using Hopfield neural network. Journal of Thermal Analysis and Calorimetry, 147(24), 14371–14380.

[3] Cancino, L. R., et al. (2020). A six-compound, high performance gasoline surrogate for internal combustion engines: Experimental and numerical study of autoignition using high-pressure shock tubes. Fuel, 261, 116439.

Acknowledgments

The authors would like to thank CNPq, FAPEMIG and UFMG/PRPq for the financial support.

Área: _TEO_____

Metastable merocyanine derivative conformers: A description from a scalar and vector-based topological approach

Asdrubal Lozada-Blanco (PQ),[1]* Juliana Fedoce Lopes (PQ).[1]

aslozada@gmail.com

[1] *Laboratório de Química Computacional - LaQC - Instituto de Física e Química, UNIFEI*

Keywords:*Structural stability, Metadynamics, QTAIM, Rotamer, Chromism, Merocyanine.*

Highlights

Metadynamics obtains hundreds of rotamers
Torsions α, β, and γ induce structurally unstable conformations
Coalescence of critical points explained metastable and unstable rotamers

Resumo/Abstract

The phenomenon of chromism is understood as the reversible change of color in substances, is the result of the variation of the electronic structure and of the configuration in molecules under the effects of external factors such as temperature, pressure, electromagnetic field, solvents, etc. [1]. Notably, among these reversible changes are mechanisms involving the conversion between the closed form of spiropyrans and the open form of merocyanines [2]. To assess the set of rotational forms in the open form of merocyanine, a conformational ensemble and a scalar and vector-based topological analysis were employed to describe the structural stability, according to the Palis-Smale criteria [3], of the derivative merocyanine rotamers. For each selected conformer (CCT, CTC, TCC, CTT, TCT, TTC and TTT) a conformer-rotamer ensemble was obtained using the iterative metadynamic protocol (iMTD), implemented in CREST [4]. Applying the topological approach within the QTAIM framework to explain the effects of torsions α, β, and γ on the formation of structurally unstable or metastable conformations of merocyanine derivatives. The analysis showed that torsion induces the division of the nuclear configuration space into three separate structurally stable regions and the formation of an unstable set of rotamers related to the coalescence of critical points (3,-1) and (3,+1).

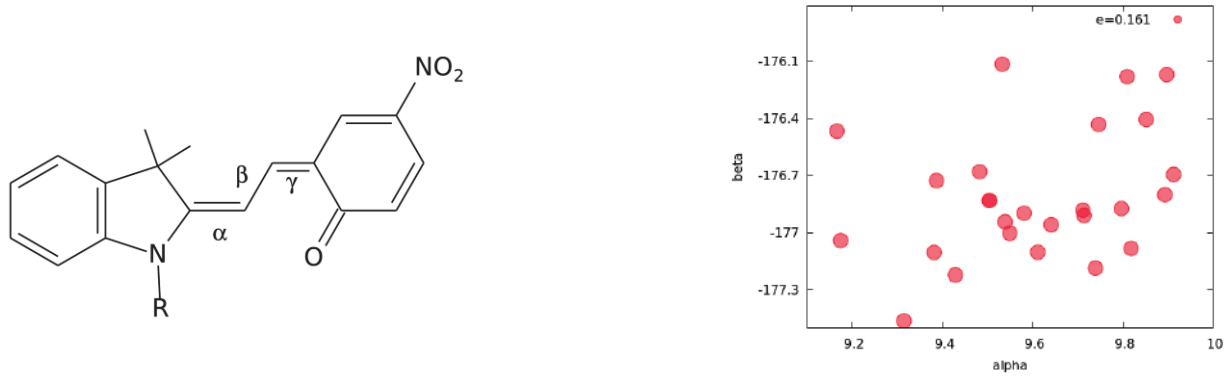


Figure 1. i) Scheme of the derivative merocyanine showing torsions α, β, and γ, and ii) Ellipticity values for a set of rotamers in the CTT conformation.

[1] PAPADAKIS, R. Dyes and pigments: Novel applications and waste treatment. IntechOpen, 2021.
[2] KORTEKAAS L. and BROWNE W. R. Chem. Soc. Rev., 2019, 48, 3406
[3] SHUB M., FATHI A. and LANGEVIN R. Global Stability of Dynamical Systems. Springer-Verlat, 1987
[4] PRACHT P., BOHLE F. and GRIMME S. *Phys. Chem. Chem. Phys.*, 2020, *22*, 7169-7192

Agradecimentos/Acknowledgments

We acknowledge financial support from the National Council for Scientific and Technological Development (CNPq - Brazil, grant 150836/2023-6) and Minas Gerais State Agency for Research and Development (Fapemig - Brazil). We also thank the Physics and Chemistry Institute of the Federal University of Itajubá.

Área: TEO

Molecular docking studies of Mn(II), Co(II), and Ni(II) complexes containing phenanthroline and maleate ligands on DNA/BSA

Jailton R. Viana (TM),[1] Francisco W. S. Rodrigues (PG),[1] Antonio D. S. G. Lima (PG),[1] João G. Oliveira Neto (PQ),[1] Adenilson O. dos Santos (PQ),[1] Mateus R. Lage (PQ).[1]

jailton.viana@ufma.br;

[1]*Programa de Pós graduação em Ciência dos Materiais (PPGCM), Centro de Ciências de Imperatriz (CCIm), Universidade Federal do Maranhão (UFMA), Imperatriz-MA, Brazil.*

Palavras Chave: *Molecular Docking, DNA/BSA, Coordination complex*

Highlights

The theoretical study revealed the main sites of interactions, with lower energetic parameters, of DNA/BSA with the coordination complexes of the transition metal ions Mn(II), Co(II), and Ni(II) with the ligands 1,10- phenanthroline and maleate. The study results suggest the stronger binding of the Co(II) complex to the DNA/BSA.

Abstract

Coordination complexes constituted of metal cations and bidentate ligands have interesting biological properties. Complexes containing 1,10-phenanthroline have the ability to bind to DNA and RNA through non-covalent interactions or intercalation [1]. Molecular docking is a very efficient technique for discovering the details of molecular interactions with biomolecules, such as non-covalent interactions, indicating the best binding position and the binding free energy. Similarly, the low values of inhibition constant (Ki) indicate good stability of the complexes (inhibitor + protein). The in silico experiments to evaluate the interaction mode and binding affinity of the complexes of Mn(II), Co(II), and Ni(II) (MnPhenMale, CoPhenMale, and NiPhenMale) to DNA/BSA were performed by molecular docking and redocking using the AutoDock Vina software. The structure of the macromolecule of B-DNA dodecamer d(CGCGAATTCGCG)2 (PDB ID: 1BNA) [2] and BSA (PDB ID: 4F5S) was downloaded from the Protein Data Bank (http://www.rcsb.org./pdb) and then retrieved. Polar hydrogens and Kollman charges were added to prepare the PDB files using the AutoDock Tools software (version 1.5.7). The file was then saved in PDBQT format using MGL Tools-1.5.7. The lattice coordinates for the BSA binding sites were set according to their respective binding site (subdomain IIA), and chain B was selected to perform independent simulations. The inhibition constant Ki (μM), the binding free energy, the estimated total energy of VdW + Hbond + desolv (kcal/mol), and the total intermolecular energy parameters were calculated to evaluate the binding of each of the complexes to DNA/BSA [3]. In our studies, the docking of metal complexes, protein-ligand (Figure 1), was limited to the effective interaction. Polar residues among these amino acids enable easy interaction between the complex and BSA via van der Waals forces and hydrogen bonding. The results (Table 1) reveal that all the synthesized complexes showed binding energy ranging from -5.80 to -6.67 kcal.mol^{-1} towards the target DNA and BSA protein. Then, docking of all the complexes tested at the interaction site of the macromolecules is favorable. Both non-polar and polar sites in the complexes facilitated its binding with DNA. Therefore, the complexes can bind to the sites of interaction of BSA and DNA, with stronger binding of the Co(II) complex.

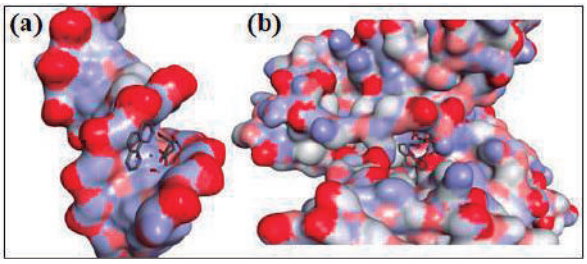


Figure 1. Docked model of the interaction of the complexes on (a) DNA and (b) BSA.

Table 1. Parameters calculated for the interactions.

Macromolecule	Ligand	Est. inhibition constant (Ki)(μM)	Binding energy (kcal.mol^{-1})	VdW+bond+desolv energy (kcal.mol^{-1})	Total intercooled energy (kcal.mol^{-1})
DNA	MnPhenMale	15.09	-6.58	-9.32	-4.30
	CoPhenMale	12.86	-6.67	-9.42	-3.92
	NiPhenMale	28.08	-6.21	-8.95	-5.24
BSA	MnPhenMale	56.50	-5.80	-8.54	-6.30
	CoPhenMale	15.82	-6.55	-9.29	-4.41
	NiPhenMale	43.73	-5.95	-8.69	-6.03

[1] P. Hazarika, B. Bezbaruah, P. Das, O. K. Medhi, *et. al.*, *J. Biophys. Chem.*, **2011**, *2*, 152.
[2] M. Bashir, I. Yousuf, C. P. Prasad, *Spectrochim Acta A Mol Biomol Spectrosc,* **2022**, *271,* 120910.
[3] R. D. Thanoon, E. A. Ibadi, I. Ahmad, H. T. Alamir, *et. al.*, *Front Chem* **2023**, *11*, 1266520.

Agradecimentos/Acknowledgments

CNPq, CAPES; FAPEMA.

Área: TEO

Performance of different density functionals in the geometry optimization of a tetragonal Fe (II) complex

Bruno C. Severino (IC),[1] Ana Paula de Lima Batista (PQ)[2]*.

brunocampana@estudante.ufscar.br; aplbatista@ufscar.br

[1]*Departamento de Química, UFSCar*

Keywords*: Iron (II) complex, DFT functionals, photosensitizers.*

Highlights

The investigation of different density functionals' performance in determining the geometry of the $Fe(HMTI)(CN)_2$ complex. Sustainable energy conversion using iron (II) complexes. The B3LYP-G functional provides a suitable geometry for further calculations.

Abstract

Light-driven processes have an essential role in more sustainable global economies.[1,2] In this context, iron-based photosensitizers such as the $Fe(HMTI)(CN)_2$ (HMTI = 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene) are of great importance since iron is a more abundant metal.[1,3] A meaningful step during DFT calculation is to select the most appropriate functional. Given that the X-ray structure is available for the $Fe(HMTI)(CN)_2$ complex, a comparison between theoretical and experimental structures was conducted, Figure 1. The def2-TZVP basis set was tested in all geometry optimizations in the ORCA program.[4]

Figure 1 (a) presents the data obtained for RMSD (root mean square error), MUD (mean unsigned error), and MSD (mean signed error) analyses between DFT and X-ray structures, while Figure 1 (b) displays the corresponding results for errors when employing DFT and X-ray structures excluding H atoms. As expected, the highest errors were observed in the dataset shown in Figure 1 (a). In this scenario, the PBE0 functional performs the best, providing the lowest average errors. PBE is the functional with the poorest performance. In Figure 1(b), the B3LYP-G functional was considered the most suitable.

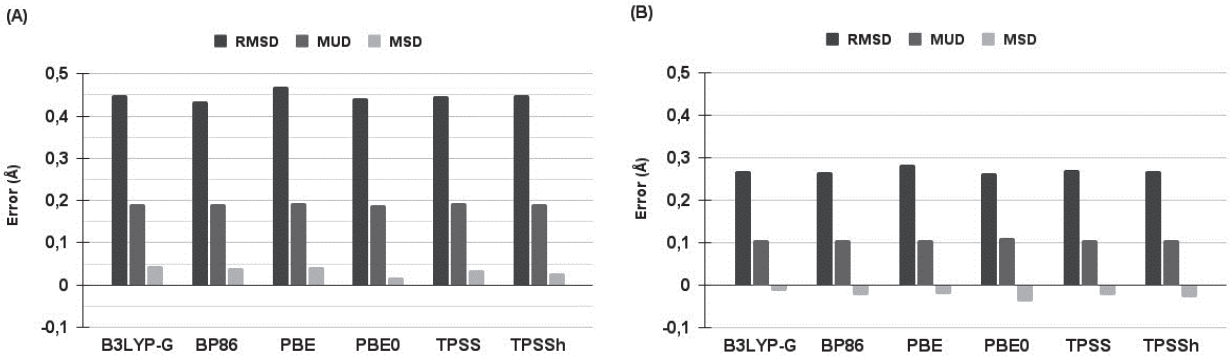


Figure 1. RMSD, MUD and MSD error analyses between each DFT complex and X-ray structure with all atoms (A) and without H atoms (B).

[1]Y. Liu, P. Persson, V. Sundström and K. Wärnmark, *Acc. Chem. Res.* **49**, 1477 (2016).
[2]P. Dierks, Y. Vukadinovic and M. Bauer, *Inorg. Chem. Front.* **9**, 206 (2022).
[3]O. S. Wenger, *Chem. - Eur. J.* **25**, 6043 (2019).
[4]Neese, F. The ORCA program system. *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2**, 73–78 (2012).

Acknowledgments

FAPESP (2022/12043-5), CNPq and CAPES (001).

Predicting the Ruthenium-99 NMR chemical shift in Ru(II) complexes using the NMR-DKH basis sets

Júlio de P. C. Oliveira (PG),[1] Diego F. S. Paschoal (PQ).[1]*

julio.pco@hotmail.com; diegopaschoal01@gmail.com

[1]*Núcleo de Química Teórica e Computacional de Macaé, Polo Ajuda, Instituto Multidisciplinar de Química, Centro Multidisciplinar UFRJ-Macaé, Universidade Federal do Rio de Janeiro, Macaé, RJ, Brazil.*

Keywords: *NMR, NMR-DKH, Ruthenium Complexes, DFT, Basis Set, Chemical Shift.*

Highlights

The new TZ2P all-electron basis set named as NMR-DKH for the ruthenium atom was proposed.
The PBE0/NMR-DKH/IEF-PCM(UFF)//B3LYP/LANL2TZ(f)/def2-SVP/IEF-PCM(UFF) protocol presents a MRD of 9.3 %.

Abstract

Recent research has demonstrated that ruthenium (Ru) complexes are effective in treating cancer and are less toxic compared to platinum complexes used in chemotherapy. The interest in Ru complexes stems from their different oxidation states, molecular geometry, and the wide variety of ligands that can be attached to the Ru ion, resulting in different electronic and steric properties. Ruthenium nucleus is highly sensitive to changes in the chemical environment, making them useful in nuclear magnetic resonance (NMR) spectroscopy. Therefore, the development and application of computational methods for the characterization of these compounds are of fundamental importance, mainly using chemical shift (δ) in NMR spectroscopy to develop new candidates for anticancer drugs. In the present study, a computational protocol for predicting the δ^{99}Ru in Ru(II) complexes using the new NMR-DKH basis set was proposed. The NMR-DKH basis set was developed according to the methodology proposed by Paschoal et al. [1-3]. Furthermore, a set of 25 Ru(II) complexes with δ^{99}Ru experimental data in the range of 18000 ppm were selected. The geometries were optimized and characterized as minimum point on the potential energy surface through harmonic frequency calculations at B3LYP/LANL2TZ(f)(Ru)/def2-SVP(ligands)/IEF-PCM(UFF) level. The δ^{99}Ru were calculated from the proposed linear regression model between the $\sigma^{99}Ru_{calc}$ and $\delta^{99}Ru_{expt}$, where a set of 11 DFT functionals were evaluated at GIAO-*DFT-Functional*/NMR-DKH/IEF-PCM(UFF) level. All calculations were carried out in Gaussian 16 Rev. C.01 program. The proposed models presented mean relative deviation (MRD) between 9.3 % (DFT-PBE0) and 15.9 (DFT-revTPSS) (Fig. 1). DFT functionals constructed with higher order density gradients exhibit the largest MRD (TPSS, revTPSS, and TPSSh). The smallest MAD are observed in hybrid GGA functionals, PBE - MRD=10.4 %, and PBE0 - MRD=9.3 %. The model δ_{calc}=-0.8893σ_{calc}-1515.3, obtained from the computational protocol PBE0/NMR-DKH/IEF-PCM(UFF)//B3LYP/LANL2TZ(f)(Ru)/def2-SVP(ligands)/IEF-PCM(UFF) presented the lowest MRD and determination coefficient R^2=0.9868. Subsequently, new Ru(II) complexes will be included to build and validate the proposed model for calculating the δ^{99}Ru.

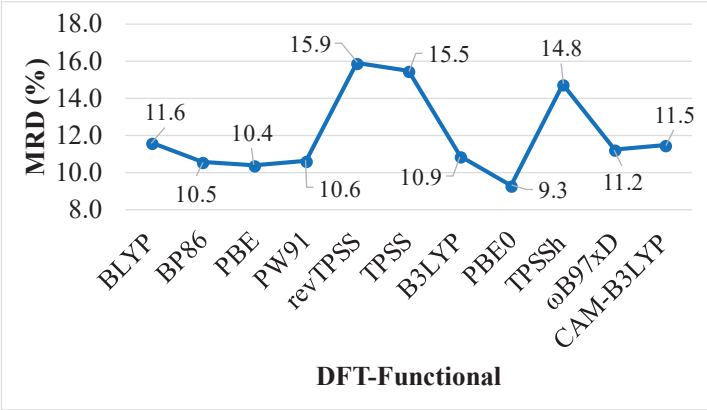


Figure 1. Mean relative deviation calculated for the empirical linear model in the present work.

[1] Paschoal, D. F. S. et. al. *J. Comput. Chem.* **37**, 2360-2373 (2016); [2] de Andrade, T. F. C. B. et. al. *J. Phys. Chem. A*. **126**, 5434-5448 (2022); [3] Gomes, M. G. R. et. al. *Magnetochemistry*. **9**, 172 (2023).

Acknowledgments

The authors would like to thank the Brazilian agency FAPERJ (E-26/201.336/2022 – BOLSA and E-26/210.070/2022 – DCTR) and CAPES (Finance Code 001) for the financial support.

Área:TEO

Prediction of hydrolysis of Rare Earth elements: A theoretical approach

Pedro A. A. Novaes (PG).[1]* Alexandre C. Bertol (PQ),[2] Hélio A. Duarte (PQ)[1].

pedroaugusto29@hotmail.com

[1]Departamento de Química, UFMG; [2]Departamento de Química UFRJ

Palavras Chave: *DFT, Hydrolysis, Rare Earths.*

Highlights

The 1st, 2nd and 3rd hydrolysis of REE were evaluated. The coordination number of the hexaaqua complexes are important to evaluate the hydrolysis. Light REE (La-Gd), coordinated 9 H_2O molecules, and heavy REE (Tb-Lu, Sc and Y) coordinated 8 H_2O molecules.

Abstract

The rare earth elements (REE) are a set of elements composed of fifteen lanthanides from ^{57}La to ^{71}Lu in addition to ^{21}Sc and ^{39}Y. Mastering the process of extracting and separating ETRs is strategic for national sovereignty and the development of Brazil's high-tech industry due to its importance as a basic input in the production of magnets, catalytic cracking, battery alloys, polishing powders, among others applications[1].The simple fact of knowing how many water molecules are coordinated around the metal ion and how the hydrolysis process occurs is an important challenge for computational description.

The geometries were optimized using the PBE, PBE0 and M06 XC functional, employing the def2-TZVP basis sets. For rare earth elements (REE), the inner core electrons have been replaced by effective potentials (ECP). Vibrational frequencies, calculated in the harmonic approximation, were incorporated to ensure that the optimized geometries in the gas phase represent true minima on the potential energy surface. The influence of the solvent environment, specifically in the aqueous phase, was also considered, using the Implicit Solvation Model (SMD). All calculations were performed using ORCA 5.0.4.[2]

We assessed the hydrolysis of Rare Earth Elements (REE), examining the 1st, 2nd, and 3rd hydrolysis steps. Light REEs (La-Gd) with 9 H2O molecules and heavy REEs (Tb-Lu, Sc, and Y) with 8 H2O molecules coordinated are the most stable aqua complexes and in accordance with the literature[3].

Predicting the hydrolysis constant of REE is still a difficult task for the state-of-the-art of the theoretical methods. The chemical model used with explicit water molecules in the first solvation shell and the implicit solvation method to describe the long range interactions are not enough to permit reliable hydrolysis constant predictions. The liability of the water molecules requires that the dynamics of the system must be considered. The different method of estimating the hydrolysis constant will be discussed in detail.

References

[1] OPARE, E.O.; STRUHS, E.; MIRKOUEI, A. A comparative state-of-technology review and future directions for rare earth element separation. Renewable and Sustainable Energy Reviews, v. 143, p. 110917, 1 jun. 2021.
[2] NEESE, F. Software update: The ORCA program system—Version 5.0. Wiley Interdisciplinary Reviews: Computational Molecular Science, v. 12, n. 5, 1 set. 2022.
[3] Duvail M, Spezia R, Vitorge P. A dynamic model to explain hydration behaviour along the lanthanide series. Chemphyschem. 2008 Apr 4;9(5):693-6.

Acknowledgments

CNPq. Based Mineral High-Performance Materials and Processes Network–RENOVAMin (Proc. RED-00102-16)

The impact of different basis sets on the geometry of a tetragonal iron (II) complex: A DFT approach

Lívia L. Conceição (IC),[1] Ana Paula de Lima Batista (PQ)[1*].

livialima@estudante.ufscar.br; aplbatista@ufscar.br

[1]*Departamento de Química, UFSCAR.*

Keywords: Sustainability, iron (II) photosensitizers, basis set.

Highlights

Computational studies on iron (II) photosensitizer for sustainable energy conversion. The def2-TZVPP basis set is a good trade-off between accuracy and computational time.

Abstract

The sustainable synthesis of fuels and chemicals using sunlight as a driving force provides a potential and viable path to mitigate rising CO_2 emissions and transition to a greener chemical industry.[1,2] In this context, computational quantum chemistry calculations were used to obtain structural information about the tetragonal $Fe(HMTI)(CN)_2$ complex, Figure 1(a), a photosensitizer with multiple applicability. Using def2-SVP, def2-TZVP, def2-TZVPP, def2-QZVP basis set and fixing the OPBE functional, optimized geometries of this ferric complex were generated. All calculations were carried out using the ORCA program.[3] The difference between each theoretical geometry and the X-ray one was analyzed. According to Figure 1 (b), the best basis sets applied were def2-TZVPP and def2-QZVP, as they present more similarity in cartesian coordinates of atoms (minor RMSD – root mean square errors) and slightest interatomic distances differences (MSD – mean signed error and MUD – mean unsigned error). However, as the def2-QZVP database takes about six times longer to deliver the data, the def2-TZVPP can be chosen to provide equally reliable and faster results.

(a) **(b)**

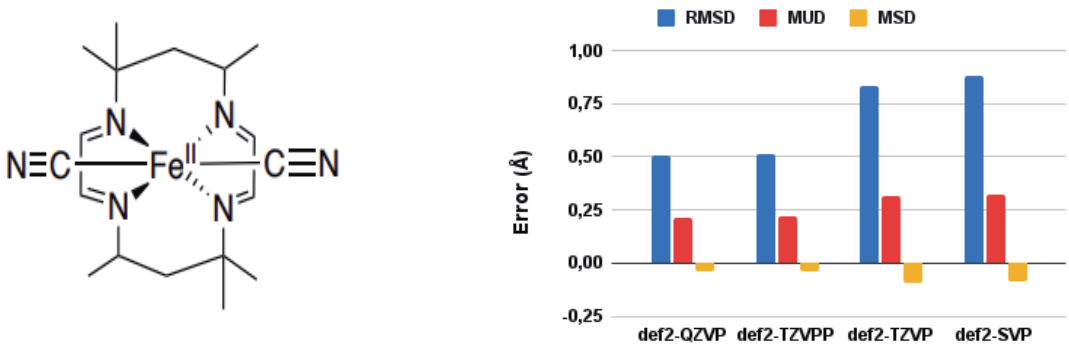


Figure 1. $Fe(HMTI)(CN)_2$ **(a)** and the comparison of the errors obtained for $Fe(HMTI)(CN)_2$ **(b)**.

[1]W. Wang, S. Wang, X. Ma e J. Gong, *Chem. Soc. Rev.* **40**, 3703 (2011).
[2]J. M. Kolle, M. Fayaz e A. Sayari, *Chem. Rev.* **121**, 7280 (2021).
[3]Neese, F. The ORCA program system. *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2**, 73–78 (2012).

Acknowledgments

FAPESP (2022/12043-5) and CAPES (001).

Área: TEO

Theoretical evaluation of BORANIL dyes for DSSC application

Bruna H. Cortes (IC),[1] Ana Julia F. Souza (IC),[1] Nicole A. Camargo (IC),[1] Richard S. Araujo (IC),[1] Paulo A. C. Duque (IC),[1] Samara R. Amorim (IC),[1] Paula Romanhi (PG),[2] Julliane Yoneda (PQ),[1] Leandro F. Pedrosa (PQ).[1,2*]

brunahonorato@id.uff.br; leandropedrosa@id.uff.br

[1] Instituto de Ciências Exatas, Departamento de Química, UFF; [2] Programa de Pós-Graduação em Química, Instituto de Química, UFF.

Palavras Chave: *BORANIL, DSSC, Fluorophores, TD-DFT.*

Highlights

On the basis of density functional theory (DFT) and time-dependent DFT (TD-DFT), we provide the opto-electronic properties of BORANILs dyes to see their applicability in organic DSSC.

Abstract

BORANIL dyes are promising in the field of biomarking, in organic light-emitting diodes (OLED) and in dye-sensitized solar cells (DSSC).[1] The geometrical structures, optical properties, and the performance of these dyes are investigated by DFT and TD-DFT calculations aiming to understand the relationship of structure and property for BORANIL-based sensitizers and to develop excellent photoelectric materials.[2] The structures of ground state and ionic state were optimized at B3LYP/6-31G(+d,p) level and frequency calculations were performed to make sure the stability of the obtained structures using the Gaussian 16W. Figure 1 illustrates small band gaps for compounds **1a-c**, which result in easier excitation of electrons and facilitation of absorption of longer wavelength light. As the LUMO energy levels of **1a-c** are not higher than those of the conduction band of TiO_2 (-4.0 eV), which is favorable for the injection of electrons from the dye into the conduction band of TiO_2. The HOMO levels are enough lower than the redox potential of the I^-/I_3^- electrolyte (-4.7 eV), which means that the designed dyes have potential to obtain electrons from electrode to regenerate the dye molecules. Therefore, we consider that BORANIL **1a-c** sensitizers exhibit good photophysical properties for application in DSSCs.

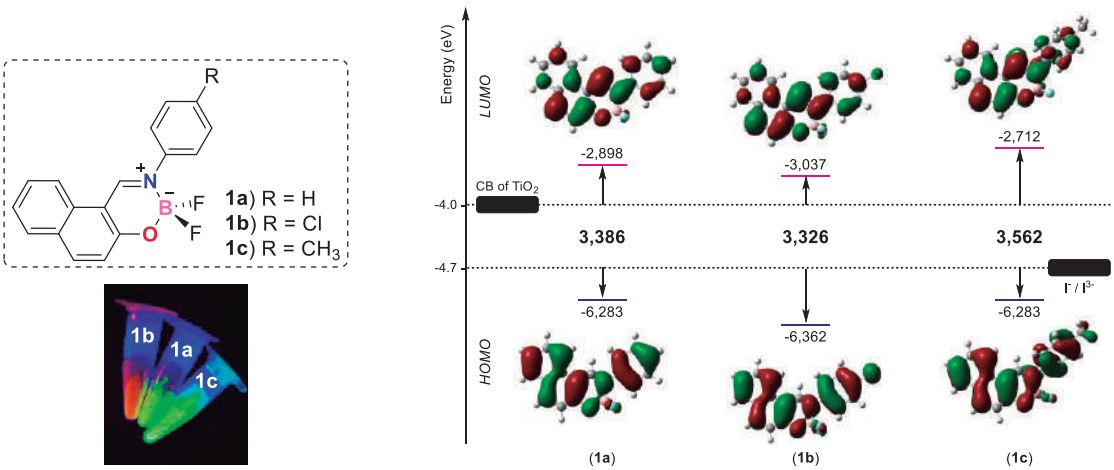


Figure 1: FMOs and the orbital energies for BORANILs (**1a-c**).

Acknowledgments

CAPES, CNPq, FAPERJ, UFF.

[1] Nandi, R. P.; et al. *Chem. Eur. J.*, **2020**, *26*, 16306.
[2] Liu, H.; et al. *J. Chem. Inf. Model.*, **2019**, *59*, 2248.
[3] Arooj, Q.; et al. *Materials*, **2019**, *12*, 4024.

Área: INO

Theoretical Studies of electronic properties of the $[Ru(bpy)_2(L)(NO)]^n$ complex, where L = isonicotinamide, sulfite or imidazole

Artur Vasconcelos Lima (IC), **Gustavo S. Bezerra (IC), Izaura C. N. Diógenes (PQ), Tércio de F. Paulo (PG)***

arturvasc@alu.ufc.br

Departamento de Química Orgânica e Inorgânica, UFC

Keywords: Nitrosyl complexes; nitric oxide; DFT;

Highlights

- Nitrosyl complexes can be used as NO donor.
- DFT studies are needed for understand nitrosyl complexes electronic properties.
- A ligand exchange can affect the pH equilibrium of NO_2^-/NO by 10 units.

Abstract

The scientific interest in the coordination chemistry of nitrosyl complexes arises from their capacity to donate nitric oxide (NO), a molecule that has shown multiple protectives and deleterious physiological functions.[1] However, nitrite (NO_2^-) and nitric oxide (NO) interconversion is crucial for maintaining optimum NO flux in mammalian physiology. The interconversion into nitrosyl complexes is significantly influenced by the chemical properties of the metal and the other ligands. According to literature,[2] the pH value at which nitrite and NO have equal concentrations may shift 10 pH units when just one of the ligands is exchanged. Hence, computational calculations employing density functional theory (DFT) can be crucial in comprehending the electronic properties of nitrosyl complexes and their impact on the nitrite/nitrosyl interconversion. In this study, DFT and its time-dependent extension (TD-DFT) were employed to investigate the electronic properties of the $[Ru(bpy)_2(L)(NO)]^n$ and $[Ru(bpy)_2(L)(NO_2)]^n$ complexes (Figure 1), where L = isonicotinamide (ina), imidazole (imz), or sulfite (SO_3^{2-}). All calculations were performed with the Gaussian 09 program using the B3LYP hybrid functional. The 6-311++g(d,p) basis set was used to characterize the non-metallic atoms, whereas the LANL2DZ basis set was applied for Ru. The optimized geometries in a potential energy minimum were confirmed by the absence of any imaginary frequency in vibrational analysis calculations. TD-DFT calculations were carried out using the polarizable continuum (PCM) model. The molecular orbital composition and FTIR, UV-Vis spectra, molecular orbitals, and the assignment of principal transitions were extracted from the output files by the Multiwfn and GaussSum 3.0 programs, respectively. For the studied complexes, the pH values at which nitrite and NO have equal concentrations are 1.5, 5.6, and 10.3 for L = ina, imz, and sulfite, respectively. Thus, we present here a preliminary study that evaluates the electronic properties of the complexes and their impact on the interconversion reaction. Additionally, an attempt to calculate the equilibrium constant of the interconversion reaction is presented as well.

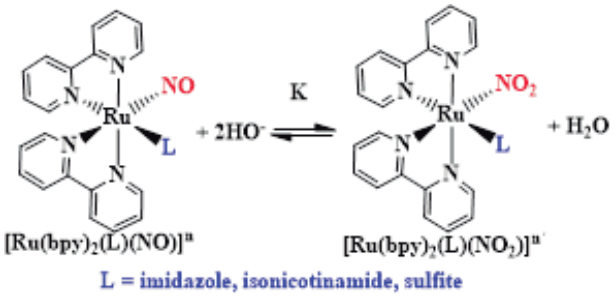


Figure 1. Interconversion reaction of nitrosyl/nitrite reaction in the studied complexes.

1 J. A. McCleverty. Chemical Reviews 104, 403-418 (2004)
2 E. M. Carvalho et. al. European Journal of Inorganic Chemistry 42, 4316-4348 (2021)

Acknowledgments

UFC, CAPES, CNPq, FUNCAP, FINEP, and CENAPAD-SP