# ANAIS DA

# 45ª REUNIÃO ANUAL DA SBQ

MACEIÓ, AL

31 de maio a
3 de junho de 2022

## Química Para o Desenvolvimento Sustentável e Soberano

Realização

Sociedade
Brasileira
de Química

*FERNANDO DE CARVALHO DA SILVA*

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# PREFÁCIO

No período de 31 de maio a 3 de junho de 2022, a comunidade química brasileira esteve reunida em Maceió-AL na 45ª Reunião Anual da Sociedade Brasileira de Química (45ª RASBQ). A Reunião Anual da SBQ pode ser considerada o evento mais importante e tradicional da química brasileira congregando um grande número de estudantes, entre alunos de graduação e pós-graduação, professores e pesquisadores (jovens e sêniores) de química e áreas afins. Nos últimos quinze anos, a RASBQ atraiu, anualmente, entre 2000 e 4500 participantes, inscritos e convidados, nacionais e internacionais consolidando, cada vez mais, seu forte caráter científico e interdisciplinar voltados para temas na fronteira do conhecimento.

Após as duas últimas RASBQ (43ª RASBQ, em 2020 e 44ª RASBQ, em 2021) serem realizadas no modo virtual devido ao cenário de insegurança sanitária decorrente da pandemia da Covid-19, a 45ª RASBQ retornou ao modo presencial e ao Nordeste brasileiro, após 8 anos, e pela primeira vez na cidade de Maceió-AL. Esta escolha da cidade decorre da grande importância desta região para a SBQ, pois abriga muitos químicos que atuam em instituições de ensino e pesquisa, além da densa representatividade de associados nordestinos. Assim, a 45ª RASBQ movimentou mais de 1550 participantes, representantes de 27 estados do Brasil, subdivididos principalmente em 45% de pesquisadores, 31% de estudantes de pós-graduação e 16% de alunos de iniciação científica das mais diversas áreas de química e afins de todo Brasil e do exterior.

Este ano, o tema da 45ª RASBQ foi “Química Para o Desenvolvimento Sustentável e Soberano” e, como o ápice do *Movimento Química Pós 2022 – Sustentabilidade e Soberania*, teve como objetivo de promover reflexões sobre como a Química pode contribuir para a sustentabilidade e a soberania do Brasil. Tal movimento foi concebido tendo em conta três pontos: a comemoração em 2022 do bicentenário da independência do Brasil; a promulgação pela Assembleia Geral da ONU de 2022 como o Ano Internacional das Ciências Básicas para o Desenvolvimento Sustentável (sigla IYBSSD 2022); a dependência de nosso país de insumos químicos importados, bem como de itens e equipamentos diversos, caracterizando flagrante falta de soberania nessas questões, como claramente escancarado pela emergência sanitária causada pela pandemia de Covid-19. O Movimento, que é parte das atividades do IYBSSD 2022 e das comemorações Brasil 200 Anos, Rumo às Independências (coordenadas pela Sociedade Brasileira para o Progresso da Ciência – SBPC), é composto por diversas frentes, as quais estão sendo supervisionadas pela diretoria da SBQ. Uma dessas frentes é a produção de um documento de ações bem definidas e metas para promover a sustentabilidade e a soberania brasileira através da Química até 2050, levando em conta marcos da ONU para o desenvolvimento sustentável (2030) e para a emissão zero de carbono (2050). Este documento, está publicado na *Química Nova*[1,2] e foi apresentado e discutido no simpósio temático[3] da 45ª RASBQ.

A 45ª RASBQ, além da tradicional estrutura do evento com intercâmbio de ideias a partir de palestras, simpósios, sessões temáticas e apresentações de trabalho, também realizou um grande movimento junto à comunidade local, a partir do evento SBQ na Escola, envolvendo a participação de cerca de 960 alunos de escolas públicas e privadas e com exposições ao público de conhecimentos e experimentos científicos informando quanto a Química é importante para o desenvolvimento sustentável e quanto ela contribui continuamente para melhorar a vida das pessoas.

A abertura da 45ª RASBQ contou com a atração cultural do grupo musical "Tambor ou Bola" e a conferência de abertura foi proferida pelo prof. Claudio José de Araujo Mota (UFRJ) com título *"Do Fóssil ao Renovável: Química para o Desenvolvimento Sustentável"*. Adicionalmente, a programação da 45ª RASBQ contou com 5 workshops multidisciplinares, 4 minicursos, 2 simpósios, 3 sessões temáticas, 16 conferências convidadas, 16 sessões coordenadas, 2 sessões de painéis com a apresentação de mais de 800 trabalhos, assembleias regionais e divisionais, assembleia geral, além de sessões específicas, premiações e lançamentos de livros.

Um dos pontos altos do evento foram os simpósios onde um deles foi a respeito do tema da RA, Química Para o Desenvolvimento Sustentável e Soberano, e o outro com o título "Por que mulheres cientistas devem se importar com visibilidade nas mídias?" que discutiu como aumentar ainda mais a exposição da importância feminina na ciência através das mídias sociais e digitais.

A intensa programação científica e de alto nível apresentada na 45ª RASBQ promoveu a máxima integração entre estudantes de graduação e pós-graduação, pesquisadores e professores, incentivando a colaboração e fomentando a discussão sobre os avanços e desafios da química contemporânea.

Por fim, mais uma vez a comunidade química brasileira mostrou sua força que, mesmo diante das dificuldades e adversidades, a participação de mais de 1550 pessoas mostrou que a comunidade científica da SBQ está empenhada, unida e comprometida em torno do objetivo de fortalecer a química brasileira, em reverter este quadro político caótico da C&T&I do Brasil e combater cada vez mais os movimentos negacionistas e anticiências, consequência do distanciamento com a sociedade em geral. O próximo encontro será em Águas de Lindóia-SP (28-31 de maio de 2023) e representará mais uma vez a oportunidade de nos fazermos cada vez mais fortes e unidos.

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# SUMÁRIO

# AMB

# Química Ambiental

**Área: AMB** **Nº de Inscrição: 01082**

# A METHOD FOR THE EXTRACTION OF ANTIEMETIC DRUG RESIDUES FROM SEDIMENT SAMPLES FOR THE DETERMINATION USING LIQUID CHROMATOGRAPHY MASS SPECTROMETRY

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Keywords: Pharmaceutical drugs, Microextraction, Sediment, LC-MS.

## Highlights

- ✓ Development, optimization and validation of a liquid-liquid microextraction method for the analysis of sediment samples by LC-MS
- ✓ Antiemetic drugs: ondansetron; metoclopramide and bromopride
- ✓ Use of factorial design for optimization

## Abstract

In recent years the occurrence of pharmaceuticals in the environment has been a matter of growing concern. Methods for the analysis of pharmaceuticals in water, particularly in effluents from sewage treatment plants, have been reported. In contrast, analytical methods for pharmaceuticals in solid matrices, as sludge and sediment, are scarce, impairing the evaluation of polluted areas. The aim of this study was to develop a time and cost-effective multi-residue method to extract and determine three antiemetic drugs in polluted sediment. The superficial sediment was collected in the stream in which the effluent from the University Hospital of Santa Maria (at UFSM Campus) is released, after microbiological treatment. Target analytes were ondansetron, metoclopramide and bromopride. The quantification was performed with liquid chromatography quadrupole mass spectrometry – LC-MS (Shimadzu, Kyoto). The instrumental conditions for LC-MS were as follows: Shim-pack CLC-OSD column (5 µm, 150 x 4.6 mm); column oven temperature at 35 ° C; injection volume of 10 µL; gradient elution mode for mobile phase (0.8 ml min$^{-1}$ constant flow) composed by (i): eluent A - 5 mmol L$^{-1}$ of ammonium formate containing 0.1% formic acid and (ii) eluent B - acetonitrile containing 0.1% formic acid; total running time of 16 min; electrospray ionization in positive mode. The general procedure consisted of using 0.5 g of dry sediment, to which 5 ml of water were added followed by stirring for 2 min, with posterior addition of 1.3 mL of solvent for extraction, 2 g of salt and a final step of 2 min of agitation, plus 7 min for centrifugation. The supernatant was removed, evaporated under nitrogen flow at 40 ° C and resuspended in 1 ml of acetonitrile for analyzis by LC-MS. As extraction solvent, acetone, acetonitrile, ethyl acetate, isopropyl alcohol, methanol, ethanol and a mixture of these in a 1: 1 (v/v) ratio, were evaluated. The best recoveries were obtained using a mixture of ethyl acetate and acetone. As the salt, anhydrous magnesium sulfate, magnesium sulfate heptahydrate, ammonium chloride, potassium phosphate, ammonium formate, sodium chloride, ammonium sulfate, anhydrous sodium sulfate, calcium carbonate, potassium bicarbonate, dihydrate calcium chloride were studied to improve extraction. Anhydrous sodium sulfate provided the best results for all substances. The quantitative factors that significantly affect the extraction were identified using Plackett-Burman design containing 16 experiments and 3 central points. In this way, the amount of sample, the proportion of the extraction solvent mixture, the pH of the water, the amount of water, the amount of salt, the stirring time in both stages and the centrifugation time were optimized. Finally, method was optimized through a central rotational composite design. The developed method was suitable for the extraction of the three pharmaceutical drugs and the method showed to be adequate for the quantification of the three antiemetic pharmaceuticals in complex matrices, as sediment.

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## Acknowledgments

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**Área: AMB**

# A multi-geochemical characterization of sedimentary organic matter from Port of Suape, Northeast of Brazil

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*Keywords: Environmental Biomarkers, Organic Matter, Hydrocarbons, Heavy metal, Sediments, Port of Suape.*

## Highlights

- Results pointed to inputs of organic matter from biogenic and anthropic sources;
- A moderate to a high level of contamination by petroleum due to the influence of port and shipyard.

## Resumo/Abstract

The Suape Industrial Port Complex is one of the most important of Brazil and its intense human activities demand a greater understanding of the possible impacts on the environment. Thus, the present study aimed to carry out the geochemical characterization of sedimentary organic matter (OM) from Port of Suape, to assess the level of anthropic contamination. Five superficial sediments (0-10 cm) were collected in the Port and were preliminary treatment for homogenization of granulometry. Then, samples were submitted to the procedure of organic compounds extraction, as proposed by Frena et al. (2016)[1] and also submitted to multi-geochemical characterization for the determination of environmental biomarkers, such as Aliphatic Hydrocarbons (AHs) by Flame Ionization Detection Chromatography (GC-FID), Polycyclic Aromatic Hydrocarbons (PAH) by Gas Chromatography/Mass Spectrometry (GC/MS) and Heavy Metals by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). The concentrations of total *n*-alkanes ranged from 3.8 to 25.5 μg $g^{-1}$, and their diagnostic ratios indicated that all sediments were contaminated by petroleum at an early stage of biodegradation. The total concentrations of PAH (range from 236.3 to 644.9 ng $g^{-1}$) and their diagnostic ratios pointed to a mixture of contributions to the formation of OM, such as petrogenic and pyrolytic sources. The concentrations of some elements obtained by ICP-OES (Ag, As, Cd, Cr, Co, Cu, Ni, Pb, Sn, V, and Zn) were compared with the limit values established by the Canadian Guidelines for the Quality of Interim Sediments[3] and resolution 454/2012 of National Council for the Environment (CONAMA)[4], and we have found that all sampling points were not contaminated. In addition, the multivariate statistical analyses from principal components analysis and hierarchical cluster analysis (HCA) with heatmap reinforced the level of contamination indicators, which was revealed that the region close to one of the shipyards was the most affected by anthropic contamination by mainly petroleum. These results enable a better understanding of the level of contamination in an important Brazilian port and the need to develop remediation policies.

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**Área: AMB**

# Analysis of air quality in the city of Itabuna - BA through the determination of PAHs, nitro-PAHs and quinones.

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*Key words: Environmental health, particulate matter, air pollutants, polycyclic aromatic compounds*

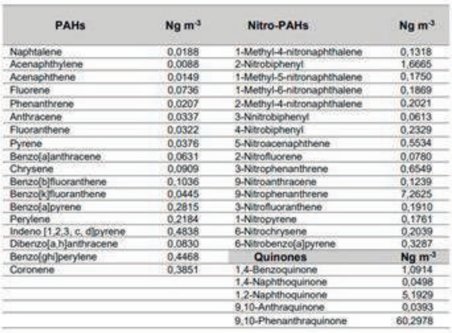
## Highlights

Determination of concentrations of 18 PAHs, 16 nitro-PAHs and 5 quinones in particulate matter collected in rural, residential and urban areas of the municipality of Itabuna - BA.

## Resumo/Abstract

PAHs and their nitrogenous (Nitro-PAH) and oxygenated (Oxy-PAH) derivatives are ubiquitous environmental contaminants, formed chiefly during the incomplete combustion of organic matter, being the main responsible for the introduction of these compounds into the environment, they are priority pollutants due to their threat to the environment and human health, which can cause several problems due to its mutagenic and carcinogenic potential [1]. Itabuna is part of the group of Brazilian municipalities that do not monitor and control air quality. The objective of this work was to simultaneously determine 39 organic compounds (PAHs, nitro-PAHs and quinones) among particulate material samples and to analyze the air quality of Itabuna - BA. Data were collected in 3 previously defined locations, within 21 days, using a Large Volume Sampler (LVS) for PM 2.5. Subsequently, chemical analysis was performed using the method developed by Santos et. al (2016) [2] for microextraction and GC-MS for determination of chemical compounds. Method validation was performed following the criteria suggested by the International Union of Pure and Applied Chemistry (IUPAC). Analyses of the particulate matter showed concentrations below the daily limits of PM 2.5 concentration established by the EU, WHO, US EPA, CONAMA and CETESB at all sampled points. Of the 39 compounds determined, 29 are above the limit of quantification (LQ). The concentrations in the PM 2.5 samples (Table 1) ranged from 0.0088 to 0.48348 ng $m^{-3}$ for PAHs, 0.0613 to 7.2625 ng $m^{-3}$ for nitro-PAHs and from 0.0393 to 60.2978 ng $m^{-3}$ for quinones.

Table 1. Mean concentrations of PAHs, nitro-PAHs and quinones



| PAHs | Ng $m^{-3}$ | Nitro-PAHs | Ng $m^{-3}$ |
|---|---|---|---|
| Naphtalene | 0.0188 | 1-Methyl-4-nitronaphthalene | 0,1318 |
| Acenaphthylene | 0.0088 | 2-Nitrobiphenyl | 1,6665 |
| Acenaphthene | 0.0149 | 1-Methyl-5-nitronaphthalene | 0,1750 |
| Fluorene | 0.0736 | 1-Methyl-6-nitronaphthalene | 0,1869 |
| Phenanthrene | 0,0207 | 2-Methyl-4-nitronaphthalene | 0,2021 |
| Anthracene | 0.0337 | 3-Nnitrobiphenyl | 0,0613 |
| Fluoranthene | 0.0322 | 4-Nitrobiphenyl | 0,2329 |
| Pyrene | 0,0376 | 5-Nitroacenaphthene | 0,5534 |
| Benzo[a]anthracene | 0,0631 | 2-Nitrofluorene | 0,0780 |
| Chrysene | 0.0909 | 3-Nitrophenanthrene | 0,6549 |
| Benzo[b]fluoranthene | 0,1036 | 9-Nitroanthracene | 0,1239 |
| Benzo[k]fluoranthene | 0,0445 | 9-Nitrophenanthrene | 7,2625 |
| Benzo[a]pyrene | 0,2815 | 3-Nitrofluoranthene | 0,1910 |
| Perylene | 0,2184 | 1-Nitropyrene | 0,1761 |
| Indeno [1,2,3, c, d]pyrene | 0,4838 | 6-Nitrochrysene | 0,2039 |
| Dibenzo[a,h]anthracene | 0.0830 | 6-Nitrobenzo[a]pyrene | 0,3287 |
| Benzo[ghi]perylene | 0,4468 | **Quinones** | **Ng $m^{-3}$** |
| Coronene | 0,3851 | 1,4-Benzoquinone | 1,0914 |
|  |  | 1,4-Naphthoquinone | 0,0498 |
|  |  | 1,2-Naphthoquinone | 5,1929 |
|  |  | 9,10-Anthraquinone | 0,0393 |
|  |  | 9,10-Phenanthraquinone | 60,2978 |

The results showed the daily health risk of the population exposed to chemical compounds present in the air, mainly due to the presence of benzo[a]pyrene in all samples.

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## Agradecimentos/Acknowledgments

**Área: AMB**

# A new binding agent for sampling atenolol with diffusive gradients in thin-film devices

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Keywords: *DGT, Graphene, Emerging Contaminants, In-situ Sampling, Passive Sampling.*

## Highlights

- Atenolol was adsorbed by 3D-graphene;
- Adsorptive capacity found was 188.8 mg L$^{-1}$;
- Elution efficiency is 57.6% using acetonitrile;
- The material has potential for application in DGT samplers.

## Abstract

The presence of emerging contaminants in the environment has been increasingly reported, and there is a need to sample different compounds that may be present in aquatic ecosystems. One possible way of sampling is through in-situ sampling devices based on diffusive gradients in thin-film (DGT). Many studies have reported the replacement of binding agents in these devices, where the adsorption of contaminants occurs, by materials that allow sampling optimization. So far, no work has reported using three-dimensional graphene-based materials in this application, despite the excellent adsorptive properties already reported for this type of material. In this sense, this work aimed to conduct preliminary tests to develop a DGT device with a modified binding layer, using a material based on three-dimensional graphene, to sample the drug atenolol (ATL) in water. Material synthesis was performed through an environmentally friendly and low-cost route, according to Jauris et al. (2020). The atenolol adsorption studies were conducted from the performance of kinetic and equilibrium studies. For the kinetic study, results were plotted as time *vs* $q_t$ and pseudo second order, and Avrami models were applied. Equilibrium isotherms were performed for 5 h, and concentrations between 25 and 1000 mg L$^{-1}$ were used. The $C_e$ *vs* $Q_e$ plots were constructed, and Langmuir, Freundlich, and Sips isothermal models were tested. Elution efficiency was performed using the eluents ethanol, acetonitrile, ethanol/acetonitrile (2:1, v/v), and acetonitrile/ethanol (2:1, v/v). Elution consisted of adding 3 mL of eluent to flasks with adsorbent, which were then taken to the ultrasound bath for 3 min and centrifuged (5 min, 3000 rpm). The solution was removed to another flask, this process was repeated 3 times, with the union of elution solutions at the end of the process. All experiments were performed in triplicate using an adsorbent/adsorbate ratio of approximately 1.3 g L$^{-1}$, and the samples were read in a fluorescence spectrophotometer ($\lambda_{exc}$ = 223 nm, $\lambda_{em}$ = 300 nm). The kinetic results showed an adsorption equilibrium time of 180 min, better fitting to the Avrami kinetic model. For the equilibrium isotherms, the best fit was the Sips model, presenting an adsorptive capacity ($Q_{max}$) of 188.8 mg g$^{-1}$. This model, at high concentrations, predicts monolayer adsorption with a limited number of sites on the surface of the adsorbent. The elution tests showed that the higher the amount of acetonitrile, the greater the amount of ATL removed from the material, that is, the better the elution, with efficiencies of 8.9, 30.3, 52.7, and 57.6% for ethanol, ethanol/acetonitrile 2:1, acetonitrile/ethanol 2:1, and acetonitrile, respectively. Thus, the previous results showed excellent interaction results between the material based on three-dimensional graphene and the drug atenolol, with a high adsorptive capacity that can be obtained quickly. In addition, the atenolol elution showed very satisfactory results, indicating that the material tested has great potential for application as a binding agent in diffusive gradient in thin-film devices. This unprecedented modification in the binding layer of DGT devices may expand the samplers measurement capacity, bringing new understandings about the presence of trace contaminants in different ecosystems.

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**Área: AMB**

# A novel report on toxic metals in the bile of two endangered Elasmobranchs, the Brazilian guitarfish and groovebelly stingray, from Southeastern Brazil

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Palavras-chave: *Biliary fluid, Conservation, Ecotoxicology, Selachii, Environmental contamination, Metals.*

## Highlights

Elasmobranchs (sharks and rays) are endangered worldwide. Biliary contaminant excretion is an excellent metal exposure biomarker. This is the first report on biliary metal excretion in Elasmobranchs.

## Resumo/Abstract

Anthropogenic activities are the main source of pollutants released into the environment. Some pollutants, such as metals, are of extreme concern due to their ability to bioaccumulate and, in some cases, biomagnify along the trophic chain, which can lead to deleterious effects in living beings, affecting metabolism, development and reproduction, even leading to death.[1] Elasmobranchs, a taxonomic group that includes rays and sharks, are greatly affected by these contaminants, as they are mostly top predators and display certain characteristics such as slow maturation and low fecundity. In addition, most species in this group are currently threatened with extinction.[2,3] Ecotoxicological studies on this group are, however, scarce. In this context, biliary metal excretion in fish is important to assess the levels of these pollutants in the aquatic environment, reflecting recent exposure, as this fluid is excreted from the body following each feeding episode in fish. However, no studies on elasmobranch bile as an environmental biomarker for exposure to metals are available to date.[3,4] In this context, this study evaluated the toxic elements arsenic (As), cadmium (Cd), mercury (Hg) and lead (Pb) for the first time in bile from rays captured by artisanal fisheries from different areas in the state of Rio de Janeiro, southeastern Brazil, using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). A total of 53 bile samples from two species were analyzed, the Brazilian guitarfish (*Pseudobatos horkelii*) and the groovebelly stingray (*Dasyatis hypostigma*) categorized as critically endangered and data deficient by the International Union for Conservation of Nature, respectively. The limits of detection and quantification were 0.003 and 0.01 mg $L^{-1}$ for As, 0.0007 and 0.0025 mg $L^{-1}$ for Cd, 0.002 and 0.004 mg $L^{-1}$ for Hg and 0.001 and 0.004 mg $L^{-1}$ for Pb. All four investigated metals were detected in the bile samples of both species. In *P. horkelii* (n=39) As ranged from 1.2 to 68 mg $L^{-1}$ (11 ± 12 mg $L^{-1}$), Cd from 0.07 to 1.3 mg $L^{-1}$ (0.4 ± 0.3 mg $L^{-1}$), Hg from 0.04 to 0,1 mg $L^{-1}$ (0.07 ± 0.02 mg $L^{-1}$) and Pb, from 0,02 to 0,1 mg $L^{-1}$ (0.05 ± 0.04 mg $L^{-1}$). In *D. hypostigma* (n=14) As ranged from 0.98 to 9.2 mg $L^{-1}$ (4 ± 2 mg $L^{-1}$), Cd from 0,001 to 0,8 mg $L^{-1}$ (0.3 ± 0.2 mg $L^{-1}$), Hg from 0.04 to 0.2 mg $L^{-1}$ (0.06 ± 0.05 mg $L^{-1}$) and Pb, from 0.02 to 0.1 mg $L^{-1}$ (0.04 ± 0.03 mg $L^{-1}$). Both rays are benthic, highly exposed to metals, as they feed on organisms associated with the substrate, a preferential compartment for the deposition of these pollutants. Arsenic was detected at higher concentrations compared to Cd, Hg and Pb, higher in Brazilian guitarfish, indicating that the Natural Monument of the Cagarras Islands (Copacabana) is more contaminated than the other collection sites (Barra da Tijuca and Recreio).

## Acknowledgments

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**Área: AMB**

# Anthocyanin eco-friendly colorant and its content in pH-responsive color change

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Kyewords: *Green Chemistry, Sustentability, pH Indicator, Dye, Chemistry Equilibrium.*

## Highlights

Anthocyanin contents greater than 2.8 % have potential to be used as eco-friendly colorants. Anthocyanin can be used in intelligent films showing good pH response.

## Abstract

The use of anthocyanins as a constituent of polymeric films has been the object of study because of their ability to antimicrobial and antioxidant in the films improving benefits for human health.[1] A support and a pH-responsive dye define the two parts that consist a pH indicator.[2] The aim of this study was to investigate the anthocyanin content in different samples. The anthocyanins content (AC) is calculated in percentage (%) in relation to cyanidin-3-glycosidic through the equation: $AC = \left[\frac{(A \times DF)}{(772 \times m)}\right] * 100\,\%$, using methanol acidulated with 1% HCl (MeOH/HCl, 1%) as extracting solvent,[3] where A is the absorbance value measured at 528 nm, DF is the dilution factor, 772 is the specific absorbance of cyanidin-3-glycosidic in the sample mass (g). Extraction was performed using 0.1000 ± 0.0030 g of plant material and 5.0 mL MeOH/HCl, 1%. The extract was filtered and adjusted to 10 mL with MeOH/HCl, 1% (w/w). The extractions were performed in triplicate. Absorbance was collected shortly after extraction to minimize photodegradation effects. This method allows the complete extraction of anthocyanins.[4] Anthocyanin content (Table 1) was calculated for samples of Blue *Agapanthus* (B-AG), White *Agapanthus* (W-AG), Lilac *Ipomea* (L-IP), Blue *Hydrangea* (B-HY), Pink *Hydrangea* (P-HY), Orange Lily (O-LY), Yellow Lily (Y-LY)~~)~~, Burnt Yellow Lily (B-LY), Red Rose (R-RO), Pink Rose (P-RO). The data indicate that anthocyanin contents greater than 2.8% have the potential to be used as eco-friendly colorants in smart polymer films[5] capable of exhibiting excellent pH responses in plastic packaging, contributing to sustainability and the environment, which is one of the principles of Green Chemistry.

**Table 1.** Anthocianin content (AC, %)

| Sample | B-AG | W-AG | L-IP | B-HY | P-HY | O-LY | Y-LY | B-LY | R-RO | P-RO |
|---|---|---|---|---|---|---|---|---|---|---|
| **AC (%)** | 1.72 | 0.21 | 3.75 | 1.83 | 1.50 | 2.87 | 0.07 | 9.55 | 30.79 | 3.37 |
| **SD** | 0.13 | 0.03 | 0.28 | 0.47 | 0.52 | 0.52 | 0.03 | 0.46 | 0.02 | 0.42 |

## Acknowledgments

LACOPPI, IFPR, PIBIS-FA, CNPq

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**Área: AMB**

# Application of melamine, thiourea and formaldehyde based adsorbent resin for removal of inorganic and organic mercury species from aquatic environment

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Palavras-chave: *Adsorção; Hg(II); Metil-Hg(I); Fenil-Hg(I); Isoterma; Reutilização.*

## Highlights

The MTF resin adsorbed, in pH=7.0, up to 90, 85 and 96% of Hg(II), Methyl-Hg(I) and Phenyl-Hg(I), respectively;
The ionic strength affects the adsorbent capacity of MTF resin for the evaluated Hg species.

## Resumo

O Complexo Estuarino Lagunar Mundaú-Manguaba (CELMM), ecossistema de grande relevância ambiental e socioeconômica para o estado de Alagoas, Brasil, tem despertado preocupação devido às elevadasconcentrações de Hg na água, especialmente na laguna Mundaú[1].Assim, o desenvolvimento de estratégias e materiais para remoção de Hg dos ecossistemas aquáticos se caracteriza como uma demanda ambiental, com foco na realidade local do CELMM. Este trabalho avaliou a capacidade de adsorção e reutilização de uma resina à base de melamina, tioureiae formaldeído (MTF) para remoção de espécies de Hg inorgânico e orgânico em amostras de água do CELMM(Alagoas, Brasil). Para os experimentos de isoterma de adsorção utilizou-se um sistema com 30 mg de resina e 50 mL de solução de Hg(II), Metil-Hg(I) ou Fenil-Hg(I), nas faixas de concentração de 1 a 210 mg $L^{-1}$; 1 a 90 mg $L^{-1}$; 1 a 220 mg $L^{-1}$,respectivamente. Para os experimentos de reutilização, a concentração de Hg era de 2 µg $L^{-1}$, com base no limite estabelecido pelo CONAMA 357/05 para águas salobras de classe 1[2]. O sistema foi agitado a 400 rpm, 25 ºC, durante 90 min e, em seguida, as alíquotas foram filtradas e analisadas por espectrometria de fluorescência atômica por vapor frio (CVAFS). A partir dos experimentos de adsorção verificou-se que a resina apresenta alta capacidade adsorvente para Hg(II), Metil-Hg(I) e Fenil-Hg(I)com índices de 197,7 mg $g^{-1}$, 19,1 mg $g^{-1}$ e 279,8 mg $g^{-1}$, respectivamente (Figura 1). Entretanto, não apresentou seletividade entre as espécies estudadas. O estudo de reutilização da resina MTF para íons Hg(II) revelou uma perda progressiva da eficiência de adsorção em função do uso (Figura 2). Os percentuais de remoção variaram de 90% a 0,5% entre o 1º e o 7º ciclo, havendo perda total da eficiência a partir do 5º ciclo. Entretanto, a capacidade de reutilização relativamente baixa é compensada pela reduzida massa de resina (30 mg) empregada na etapa de remoção da espécie de Hg na amostra de água. Aplicando a resina para adsorção de 2 µg $L^{-1}$ de Hg(II) adicionado a amostras de água salobras com salinidade de 11,59 g $L^{-1}$ e 0,102 g $L^{-1}$, coletadas no CELMM, foi possível observar que a eficiência da resina MTF na adsorção de Hg(II) diminui com o aumento da força iônica do meio uma vez que esta variou entre 67,4 e 43,1% para água de maior e menor salinidade, respectivamente. Esta alteração pode estar relacionada à atividade dos íons livres decorrente da formação de pares iônicos e do efeito de força iônica sobre o pH; à competição entre o metal e os eletrólitos presentes no meio pelos sítios de adsorção e/ou à ocorrência de mudanças no potencial eletrostático no plano de adsorção.

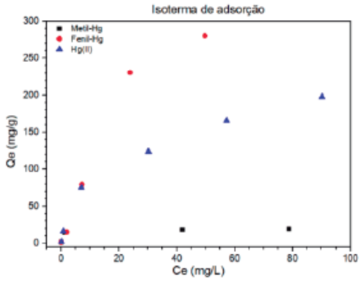

**Figura 1.** Isotermas de adsorção de Hg(II), Metil-Hg(I) e Fenil-Hg(I) pela resina MTF. (Ce = concentração de Hg(II), metil-Hg(I) e fenil-Hg(I) em solução; Qe = a quantidade de Hg(II), metil-Hg(I) e fenil-Hg(I) adsorvida por g de resina MTF)

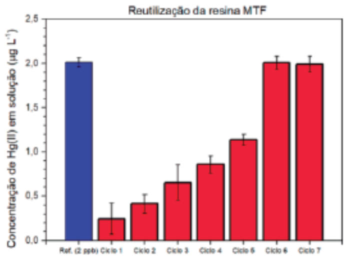

**Figura 2.** Experimento de reutilização da resina MTF na adsorção de Hg(II).

De modo geral, a resina MTF mostrou-se eficiente para remoção das espécies de Hg nas amostras de água da Laguna Mundaú, com elevada capacidade adsorvente para Hg(II), Metil-Hg(I) e Fenil-Hg(I). Dessa forma, a estratégia de remoção dessas espécies de Hg de amostras ambientais de água utilizando a resina MTF se mostrou satisfatória e com potencial aplicação em modelos para remediação de ambientes aquáticos contaminados com Hg.

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## Agradecimentos/Acknowledgments

**[CNPq, PPGQB-IQB-UFAL, CAPES, FAPEAL-FAPESP, SBQ]**

**Área: AMB**

# Assessment of the health impact of individuals exposed to particulate matter emitted by vehicle exhaust

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Palavras-Chave*: Deposition; respiratory tract; vehicular exhaust; MPPD*

## Highlights

The use of additives in the fuel blend tends to reduce the impact on the human respiratory tract.

Public transport users are more vulnerable to PM exposure in places where the flow of vehicles is more intense.

## Resumo/Abstract

This study aimed to evaluate the impact on the health of individuals exposed to PM emitted from vehicular exhaust, using the MPPD model (Multiple-path Particle Model). Sites were selected based on an inventory of PM data, consisting of: (i) Diesel cycle engine system, which the studied fuels were pure diesel (D), binary mixture of pure diesel with 11% biodiesel (B11) and ternary mixture of pure diesel, with 11% biodiesel and with the biocatalyst Xmile additive (B11X); (ii) daily $PM_{10}$ and $PM_{2.5}$ data from the CETESB platform (company responsible for monitoring the air in the metropolitan region of São Paulo (RMSP); and (iii) daily $PM_{10}$ data from Salvador's air monitoring stations (SSA), provided by CETREL (the company responsible for monitoring the city's pollutants). Both collected and inventoried data were mathematically modeled in the MPPD software, with the goal of simulate the deposition of particles in the human respiratory tract, according to the variation of the PM size and the exposure time in a scenario of a public transport user at a bus stop. The results obtained showed the efficiency of the use of additives in the fuel, promoting the reduction of both PM incidence and the impact of the deposition on human health, over the years (Figure 1). The analysis between cities RMSP and SSA showed the places with the highest and lowest incidence of PM, considering the flow of vehicles in each city, and how vulnerable a public transport user can be to the daily inhalation of these particles (Figure 2). Therefore, it was possible to highlight that individual from the RMSP suffer a lower impact on health, highlighting that the Barros Reis station (SSA) emits more PM than the Grajaú-Parelheiros station (RMSP), considering that it is located on a road, which has a high flow of vehicles in the region. Although the RMSP has a much larger bus fleet (13,883 bus fleet) than SSA (2,595 bus fleet), the city of Salvador has a greater tendency to circulate vehicles due to the high incidence of PM in certain regions, in addition to having a higher ratio of bus users (1,119 inhabitants/bus) than the RMSP (857 inhabitants/bus), leaving individuals more exposed to the emission of PM.

Figure 1. Deposition of PM in the alveolar region over 10 years.

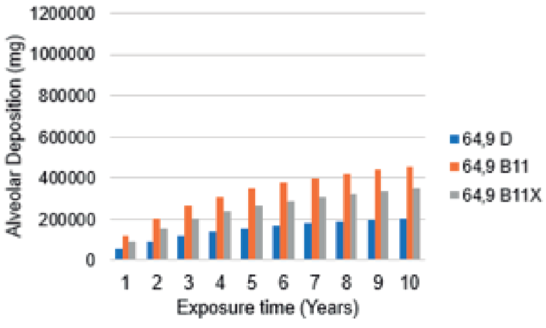
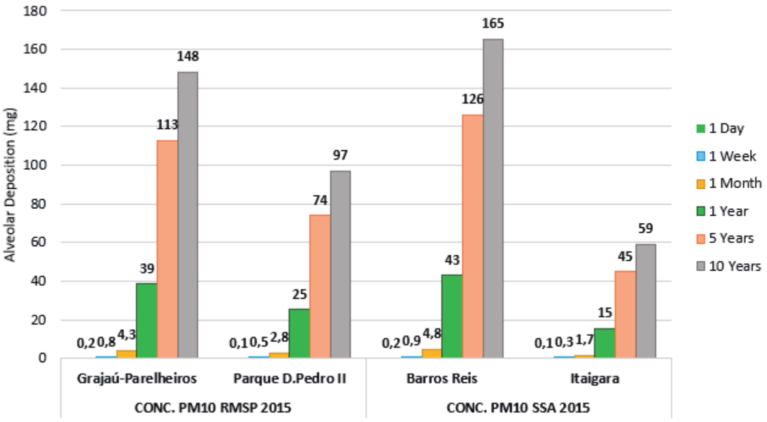


Figure 2. Deposition of PM in the alveolar region over 10 years.



**Área: AMB**

# Avaliação da Aplicação do Biochar de Casca de Pinhão e de seu Compósitos com Hidrogel em Estudos Ambientais com Cromo

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Palavras Chave: *Biochar, Cr (III), Cr (VI), DGT, Carvão Ativado, Águas naturais.*

## Highlights

Evaluation of the application of Biochar prepared from Brazilian-pine fruit shell and its hydrogel composites in environmental studies with chromium. Preparation of biochar from Brazilian-pine fruit and its hydrogel composites. Studies of the selective sorption of Cr. Use as a sorbent agent in DGT devices for speciation of metals.

## Resumo/Abstract

Biochar ou biocarvão é um material preparado pela pirólise de uma biomassa rica em carbono, sob condições reduzidas de oxigênio[1]. Esse material apresenta elevada área superficial, estrutura porosa, diferentes grupamentos químicos, baixo custo e, é ambientalmente amigável. Devido a diversidade de biomassa, condições de pirólise e uso de modificadores, biocarvões com diferentes características podem ser preparados e aplicados. Um dos usos desses materiais é na resolução de problemas ambientais, tais como no sequestro de carbono, como suplemento de nutrientes para solos, adsorvente, etc. Neste trabalho, propõe-se o preparo de biochar a partir de um resíduo gerado após consumo do pinhão, parte comestível da pinha da *Araucaria augustifolia*. A escolha se justifica pela casca do pinhão ser um resíduo recalcitrante e pelo amplo consumo do pinhão na região Sul do Brasil. Além disso, estudos vem sendo realizados com esse tipo de biochar para uso como substituto ao carvão ativado, e para fins analíticos, como pré-concentrador de espécies metálicas. Inicialmente foram preparados biocarvões da casca de pinhão com pirólise, sob baixa concentração de oxigênio, com temperaturas na faixa entre 600 a 800 ºC, na ausência e presença $ZnCl_2$ usado como modificador. Os materiais obtidos foram caracterizados por diversas técnicas como DRX, FTIR, Potencial Zeta, BET, MEV, entre outros. De modo geral, a pirólise da biomassa à 800ºC aumentou a porosidade e área superficial do material, a biomassa apresentou 0,8 $m^2 g^{-1}$ de área superficial, e o biochar preparado com 800º na ausência e presença de $ZnCl_2$ apresentou valores de 7,9 e 10,9 $m^2 g^{-1}$, respectivamente. A capacidade sortiva dos materiais foram avaliadas com teste de sorção em batelada realizado ensaios com até 50 µg $L^{-1}$ de Cr(III) e Cr(VI) em diferentes valores de pH. Observou-se uma capacidade seletiva para sorção de espécies de Cr em função do pH do meio. Em pH 7, o biochar sem modificação apresentou na sua superfície a presença de cargas negativas (potencial zeta: -32 mV) o que favoreceu a sorção de Cr(III). A sorção foi 76±3% e 0,1±0,1% para Cr(III) e Cr(VI), respectivamente. Já para o biochar com modificação a sorção da espécie aniônica foi favorecida (potencial zeta: +10 mV). Para pH 2, a sorção pelo biochar modificado com $ZnCl_2$ foi 2±1% e 79±7% para Cr(III) e Cr(VI), respectivamente. Devido ao seu comportamento diferenciado frente a especiação química do Cr, avaliou-se a aplicabilidade do material como agente sorvente para análise de especiação de Cr empregando a técnica de Difusão em Filmes Finos por Gradiente de Concentração, do inglês DGT. Para tal, um compósito preparado com o biochar de casca de pinhão imobilizado com hidrogel na forma de filme fino vem sendo estudado. Optou-se por utilizar a agarose, pela possibilidade de se obter um material ecologicamente correto, atóxico, sem cor e odor e de baixo custo. Os compósitos vêm sendo preparados com biochar e agarose na proporção de 2,0 e 3,3%. Os testes inicias em pH 7 com o compósito indicam a sorção de 43±3 e 57±3 % para Cr(III) e Cr(VI), respectivamente. A dessorção das espécies de Cr foi realizada com $HNO_3$ e variaram entre 40% e 100%. Mais estudos vêm sendo conduzidos buscando a sorção seletiva e caracterização dos compósitos. Dessa forma o biochar de casca de pinhão e imobilizado com agarose apresentou potencial para ser empregados em dispositivo DGT para detecção de cromo em águas naturais.

## Agradecimentos/Acknowledgments

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**Área: Química Ambiental**
*(ABM)*

# Avaliação da atividade larvicida por óleos não convencionais da Amazônia.

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Palavras Chave: *óleos amazônicos, Aedes aegypti; controle de vetores;*

## Highlights

Mosquito control is usually formulated with synthetic compounds such as pyrethroids, but most of these synthetic substances have side effects. Since the Amazon region is an important source of plants that produce various vegetable oils, and these are used by the local population for the treatment of diseases and are low cost and easily accessible. Soon after, different concentrations (80, 40 and 20 µg/mL) solubilized in DMSO (0.5%) were applied in the bioassay, containing 10 larvae under controlled conditions (25 ± 2 °C). Among the oils tested, mucajá oil showed the best activity against Aedes aegypti larvae, with a rate of 23, 16 and 13% at 80, 40 and 20 µg/mL respectively.

## Resumo/Abstract

A região Amazônica é uma fonte importante de oleaginosas (quantitativa e qualitativa), que produzem diferentes óleos vegetais, que são utilizadas pela população local para tratar diferentes doenças (Sarquis et al., 2021). Entre esses óleos, o óleo a partir das sementes de andiroba já foi relatado como repelente contra o *Aedes aegypti* (De Mendonça et al., 2005). Prophiro et al., (2012) descobriu que o efeito larvicida residual do óleo de andiroba em 72 h mostrou 100% de mortalidade para *Aedes aegypti*. Neste sentido, ampliar o estudo da ação de outros óleos não convencionais da região Amazônica, tais como, *Acrocomia* sp., Astrocaryum sp., *Mauritia* sp. (mucajá, tucumã e buriti, respectivamente). Os frutos foram coletados no Campus Marco Zero do Equador da Universidade Federal do Amapá, entre fevereiro e maio de 2020. Em seguida os frutos foram lavados com água corrente e secos em estufas (50ºC por 5 dias) e retirados os mesocarpos para extração dos óleos que foi realizada por meio de soxhlet, utilizando hexano como solvente, por 3h de extração, em seguida o excesso de solvente foi rotaevaporado. A partir dos óleos extraídos realizou-se a reações de transesterificação e amidação para obtenção de amidas graxas e ésteres graxos na aplicação larvicida. A análise dos óleos foi realizada por cromatografia gasosa acoplado a um espectrômetro de massa (CG/EM). As larvas do *Ae. aegypti*, da colônia Rokeffeller, foram utilizadas do 3º estágio larval. Foi preparada uma solução estoque de 1000 µg/mL a partir de cada óleo extraído. Logo em seguida diferentes concentrações (80, 40 e 20 µg/mL) solubilizadas em DMSO (0,5%) foram aplicado no bioensaio, contendo 10 larvas em condições controladas (25 ± 2 °C). A porcentagem de mortalidade das larvas foi realizada em período de 48 h após exposição às soluções larvas. Entre os óleos testados, o óleo de mucajá apresentou melhor atividade contra as larvas de *Aedes aegypti,* com taxa de 23, 16 e 13% em 80, 40 e 20 µg/mL respectivamente. Os demais óleos não apresentaram viabilidade larvicida nem na mais alta concentração (80 µg/mL). Vale destacar que a ação larvicida está diretamente relacionada com a composição química dos óleos testados, o óleo de mucajá apresentou majoritariamente o ácido palmítico com 20%, enquanto o óleo de buriti, apresenta o ácido oleico com 64% e o óleo extraído dos frutos de tucumã apresentou majoritariamente na sua composição química o ácido oleico com72%. Neste sentido a partir da reação de esterificação com (butanol) e amidação (butanolamina) com o óleo de mucajá, buscou-se modifica-lo quimicamente para potencializar seu efeito larvicida. Na maior concentração testada, a mistura de ésteres apresentou taxa 50% de mortalidade, enquanto a mistura de amidas graxas somente 26%. Estes resultados, preliminares demostram que pode ocorrer viabilidade larvicida em *Aedes aegypti* a partir do óleo de mucajá, e a forma de ésteres butílicos favorece a ação larvicida quando comprado ao triglicerídeo e butilamidas graxas. Outros estudos estão sendo realizados para potencializar a ação larvicida a partir do óleo de mucajá, pois este óleo é de fácil acesso e aquisição na região Amazônica.

## Agradecimentos/Acknowledgments

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**Área: AMB**

# Avaliação da capacidade de sorção de materiais naturais do Estado de Alagoas para remediação de derramamentos de óleo.

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Keywords: sorption, natural materials, kinetics, spillage.

## Highlights

Evaluation of the sorption capacity of natural materials from the State of Alagoas for oil spills remediation.

This work evaluated natural materials to oil spill application;

The average sorption for viscous oil ranged from 1.9 to 22.3 g/g;

The porous structure proved to be determinant for the sorption process.

## Resumo/Abstract

Industrial processes involving oily fluids cause destruction and alteration of entire communities of living organisms through toxic effects, such as the event that occurred in August 2019 that hit the northeast coast. The use of natural sorbents has been the focus of research in oil spill scenarios, as they are low-cost, biodegradable materials and have a reduced environmental impact. The fibers of kapok (Ceiba pentandra), coconut straw (Cocos nucifera) and loofah (Luffa cylindrica L.) were used in this study to evaluate their sorption capacity. Lubrax 20w50 Carro Sl Mineral Essential oil was used in contact and drip tests, studying the sorption kinetics with a contact time of 30 min followed by a capture stability test under agitation of 5 and 10 min, aiming at the understanding of how much oil the material can hold without easy detachment. The methodology of Oliveira et al (2020) was considered. The materials were characterized in optical microscopy with the samples dried and saturated with oil. Tests to identify the dripping time were performed at 30 sec intervals for 15 min. The sorption curve (g/g) versus dripping time (min) was constructed and it was possible to verify that the materials stop dripping in 7.5 min for coconut straw and in 5 min for vegetable loofah. On the other hand, in the case of kapok the drip equilibrium was reached only after 11 min. In the contact kinetics tests, the sorptions were established at 1 min, 5 min, 10 min, 15 min and 30 min, and when analyzing the sorption curves (g/g) versus contact time (min) it was found that the straw reached its maximum sorption value, 1.892±0.136 g/g, in 1 min, the loofah, 6.065±0.477 g/g, in 10 min, and the kapok, 22.281±0.920 g/g, in 1 min. It was observed, in turn, that both straw and kapok stand out due to the rapid sorption process. The stability tests showed that the kapok lost 2.69% of the oil sorbed after 5 min of agitation and 4.15% after 10 min of agitation; straw 72.67% and 37.21%; the loofah 44.22% and 40.25%, after 5 and 10 min of agitation, respectively. In response to the microscopic analysis, the porous structure of the loofah and the presence of lumens of the kapok justify the sorption values found, whereas the coconut straw has a rough surface, but without the presence of pores. In view of the above, the materials evaluated proved to be efficient, especially the kapok, in all the tests performed, attending the necessary requirements for use in spill scenarios.

Oliveira, L.M.T.M. et al. Ultrafast diesel oil spill removal by fibers from silk-cotton tree: Characterization and sorption potential evaluation. Journal of Cleaner Production, 263 (1), 121448, 2020.

## Agradecimentos/Acknowledgments

The Authors thanks for the financial support of Fundação de Amparo à Pesquisa do Estado de Alagoas (FAPEAL) and to Federal University of Alagoas (UFAL).

**Área: AMB**

# Avaliação da contaminação ambiental por hidrocarbonetos alifáticos (HAs) e policíclicos aromáticos (HPAs) em sedimentos do Rio Capibaribe, Pernambuco, Brasil.

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Palavras Chave*: Contaminação, Hidrocarbonetos, Rio Capibaribe, Espectrometria de massas, Sedimentos.*

## Highlights

**Assessment of environmental contamination by aliphatic (AH) and polycyclic aromatic (PAH) hydrocarbons in sediments of the Capibaribe River, Pernambuco, Brazil.**

- Assessment of contamination in areas near the textile pole and urban center of Capibaribe River;
- We have found high contamination from HAs and HPAs results due to anthropic actions around the river.

## Resumo/Abstract

As atividades antrópicas podem gerar um aumento na contaminação de sistemas aquáticos por meio de descargas urbanas e industriais, atividades relacionadas ao petróleo e tráfego de navegações. Desse modo, estudos que avaliem a contaminação nesses ecossistemas são necessários para se ter uma visão química mais detalhada dos ambientes aquáticos. Na análise da matéria orgânica (MO) sedimentar, os hidrocarbonetos alifáticos (HAs) e policíclicos aromáticos (HPAs) são comumente quantificados e usados para indicar as fontes de origem da MO, podendo elas serem biogênicas, pirogênicas ou petrogênicas. O objetivo do presente estudo, foi realizar uma investigação do nível de contaminação ambiental do Rio Capibaribe, nos municípios de Santa Cruz do Capibaribe e Toritama, Pernambuco, baseada na análise de sedimentos com foco na determinação de HAs e HPAs. Foram coletados 11 sedimentos superficiais (códigos de ST1 a ST11) em regiões com atividades industriais do polo têxtil e alta densidade populacional entre os municípios. As amostras foram secas em estufa a 60 ºC/48 h e peneiradas (2 mm), em seguida, 5 g do sedimento seco foi submetido ao processo de extração da fração orgânica com diclorometano/metanol em sistema de ultra-som. O extrato orgânico foi fracionado em coluna de vidro aberta utilizando hexano para obtenção da fração contendo os HAs e hexano/diclorometano para a fração dos HPAs. As frações de HAs e HPAs foram analisadas por cromatografia gasosa com detector de ionização por chama (GC-FID) e por cromatografia acoplada à espectrometria de massas (GC/MS), respectivamente. Para verificação das fontes de contaminação, utilizou-se os parâmetros: índice preferencial de carbono (CPI), as razões diagnósticas Pristano/Fitano, Benzo(a)antraceno/Benzo(a)antraceno+Criseno (BaA/BaA+Cri) e Indeno(1,2,3-cd)Pireno/Indeno(1,2,3-cd)Pireno+Benzo(ghi)perileno (IP/IP+Bghi). Para o CPI, a maioria das amostras tiveram valores de CPI>1, sendo classificadas como contaminadas por hidrocarbonetos de petróleo. Para Pristano/Fitano, as amostras ST2, ST4 ST8 e ST10 apresentaram valores > 1, caracterizando sedimentos contaminados com fonte petrogênica, sendo essas amostras coletadas em regiões onde há atividades do setor têxtil e alta densidade populacional dos municípios. Quanto a razão BaA/BaA+Cri, a MO da maioria das amostras apresentaram ser de fonte petrogênica. Para a razão IP/IP+Bghi, os resultados apresentaram amostras com MO característica de fonte pirogênica. Por fim, as análises estatísticas multivariadas por componentes principais (PCA) aplicada à análise de sedimentos permitiu identificar como principais contaminantes os HAs petrogênicos (Fitano) e HPAs pirogênicos (fluoranteno, benzo(a)antraceno e pireno), com maior contaminação nos sedimentos ST2, ST4 e ST10 que estão em regiões urbanas com alta densidade populacional, além de estarem também próximos às indústrias do polo têxtil no entorno do Rio Capibaribe. Dessa maneira, os resultados sugerem a existência de regiões no sistema aquático do Rio Capibaribe impactadas por ação antrópica devido à alta contaminação por hidrocarbonetos, sendo este o primeiro trabalho na região envolvendo o referido sistema aquático, cujos resultados enfatizam a necessidade de estudos contínuos de monitoramento ambiental.

## Agradecimentos/Acknowledgments

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**Área: AMB**

# AVALIAÇÃO DA TOXICIDADE E DESENVOLVIMENTO DE MÉTODO ANALÍTICO PARA DETECÇÃO E QUANTIFICAÇÃO DE ANTIVIRAIS EM ÁGUA

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*Palavras Chave: antirretrovirais, cromatografia a líquido, ecotoxicologia*

## Highlights

**EVALUATION OF TOXICITY AND DEVELOPMENT OF ANALYTICAL METHOD FOR DETECTION AND QUANTIFICATION OF ANTIVIRALS IN WATER**

Lack of studies about behavior of antiviral drugs in Brazilians water bodies. HPLC-DAD method to determining these drugs in aquatic environment and determination of LOEC with ecotoxicity tests

## Resumo/Abstract

Antivirais são fármacos utilizados especificamente no tratamento de infecções virais. Dentre eles, podem-se destacar os antirretrovirais que são usados para o tratamento de infecções por retrovírus, principalmente o HIV. Alguns antivirais são altamente bioativos, podendo afetar negativamente organismos não-alvo e persistir em ambientes aquáticos.[1] Esses compostos representam uma classe farmacológica pouco conhecida do ponto de vista ambiental, com poucos estudos que determinam concentrações desses fármacos em afluentes e efluentes de rios no mundo, sendo que, no Brasil, não há ainda estudos publicados. Nesse sentido, esse trabalho descreve o desenvolvimento de metodologia capaz de determinar a presença do antiviral aciclovir (ACV) e dos antirretrovirais lamivudina (LMV), zidovudina (AZT) e efavirenz (EFZ), em amostras de água. O método foi desenvolvido em sistema de cromatografia a líquido de alta eficiência (CLAE) com detector de arranjo diodo (DAD) nos comprimentos de onda máximos de absorção de cada um dos analitos: ACV (λ 254 nm), LMV (λ 266 nm), AZT (λ 270 nm) e EFZ (λ 245 nm) para análise deles em amostras de água coletadas no Rio Guandu. Essas amostras foram preparadas utilizando a extração em fase solida (EFS) como etapa de limpeza e concentração. Os melhores resultados foram obtidos com gradiente binário de eluição composto de acetonitrila e acetato de amônio (5 mM, v/v) em coluna Zorbax SQ-aq 2,1 x 150 mm; 3,5 mm (Agilent) a 35 ºC e vazão de 0,2 mL.min-$^{1}$ . O volume de injeção foi de 5 μL e o tempo de análise foi de 15 minutos. Curvas analíticas foram preparadas na faixa de 8 a 150 mg.L$^{-1}$ para cada um dos fármacos diluídos em MeOH e $CH_3COONH_4$ (5mM). Todas as análises foram realizadas em triplicata resultando em DPR < 2% e coeficientes de correlação ($r^2$ ) > 0,999. E os limites de detecção e quantificação em mg.mL$^{-1}$, foram respectivamente: ACV (0,078 e 0,261); EFV (0,155 e 0,518), 3TC (0,057 e 0,189) e para o AZT (0,282 e 0,942). Os ensaios de toxicidade foram realizados com os fármacos diluídos no meio de cultivo[2] dos organismos avaliados (Raphidocelis subcapitata, Ceriodaphnia dúbia e Daphnia similis). Raphidocelis subcapitata e Ceriodaphnia dúbia foram utilizados em ensaios de toxicidade crônica, no qual foi avaliada a resposta reprodutiva ou morte desses organismos quando expostos a concentrações de 0,01 a 20 mg.L$^{-1}$ dos fármacos. Daphnia similis foi utilizada em ensaio de embriotoxicidade no qual foi observada a presença de má formações em neonatos quando seus ovos foram expostos a concentrações de 0,02 a 5 mg.L$^{-1}$ de cada um dos fármacos. As concentrações de efeito observado (CEO) em todos os ensaios foram menores que 4,16 mg.L$^{-1}$ (ACV); 1,25 mg.L-1 (LMV); 2,5 mg.L-1 (AZT) e 0,03 mg.L-1 (EFZ). O EFZ foi o antiviral que apresentou maior toxicidade em todos os ensaios realizados. Nossos resultados apontam para necessidade de estudos de remoção destes compostos em ambientes aquáticos, no Brasil, visto que as concentrações tóxicas encontradas são menores do que a dose administrada durante os tratamentos. O método analítico otimizado associado a adequado processo de limpeza e concentração de amostras mostra-se adequado à determinação dos antivirais selecionados em amostras de água.

[1] Nannou, C. et al., Science of the Total Environment, 2020, 699, 134322.
[2] ABNT WBr 12648; 13373; 12713.

## Agradecimentos/Acknowledgments

FAPERJ e CNPQ.

**Área: AMB**

# Avaliação dos hidrocarbonetos presentes em fragmentos de óleo coletados na costa brasileira.

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Palavras Chave: *Derramamento de óleo; Hidrocarbonetos de Petróleo; HPAs ; Contaminantes persistentes; PARAFAC.*

## Highlights

**Evaluation of hydrocarbons present in oil fragments collected off the Brazilian coast after the oil spill accident.** Oil samples collected across 430 km for 1 year in the Brazilian coast after the oil spill event of 2019. PAHs were identified as perylene, chrysene and fluorene.

## Resumo/Abstract

O derramamento de óleo que atingiu o Brasil no ano de 2019 é o maior desastre ambiental ocorrido no litoral brasileiro. Dados da marinha brasileira demonstram que mais de 5.000 toneladas de óleo foram coletadas. Mesmo após 2 anos do avistamento inicial fragmentos de óleo continuam aparecendo, como observado no litoral norte paraibano em janeiro de 2022. Hidrocarbonetos de Petróleo Totais (TPH) são lixiviados no meio aquático em casos de derramamento de óleo e são contaminantes persistentes. Este trabalho teve o objetivo de avaliar as variações dos perfis de TPH em diversos fragmentos de óleo coletados ao longo de 1 ano e em diferentes condições. Considerando que na origem todas as amostras são provenientes do mesmo óleo, as diferenças de composição observadas entre as amostras coletadas podem trazer informações sobre os diferentes processos de lixiviação e degradação que cada amostra sofreu em função das diferentes correntes, temperatura e demais fatores ambientais a que foram submetidas. As amostras foram coletadas no decorrer 430 Km da costa dos estados Rio Grande do Norte, Paraíba, Pernambuco e Alagoas. Os fragmentos de óleo foram inseridos em água marinha sintética com o intuito de solubilizar os TPH possíveis, os extratos foram analisados por espectroscopia de fluorescência e os dados foram modelados por Análise de Fatores Paralelos (PARAFAC). Uma Análise de Componentes Principais (PCA) foi realizada, utilizando o modo A PARAFAC, para observar as dispersões das amostras de acordo com os TPH identificados. 6 TPH foram observados, sendo 3 derivados Hidrocarbonetos Policíclicos Aromáticos (HPAs) os tipos-Perileno, Criseno e Fluoreno. Os demais foram identificados como derivados de Dibenzotiofeno e *p*-Xileno, um outro TPH segue sem identificação até o presente momento. As atribuições foram feitas a partir dos perfis espectrais recuperados pelo PARAFAC [1-2]. O gráfico da PCA pode ser observado na figura 1. Observa-se que compostos do tipo-perileno são predominantes em amostras de óleo mais intemperizadas, como as coletadas em rochas na costa, com maior exposição ao sol. Isso implica numa maior persistência desses compostos com relação aos demais. As amostras coletadas no estado do Alagoas possuem uma maior concentração dos componentes tipo-fluoreno e tipo-p-xileno, respectivamente.

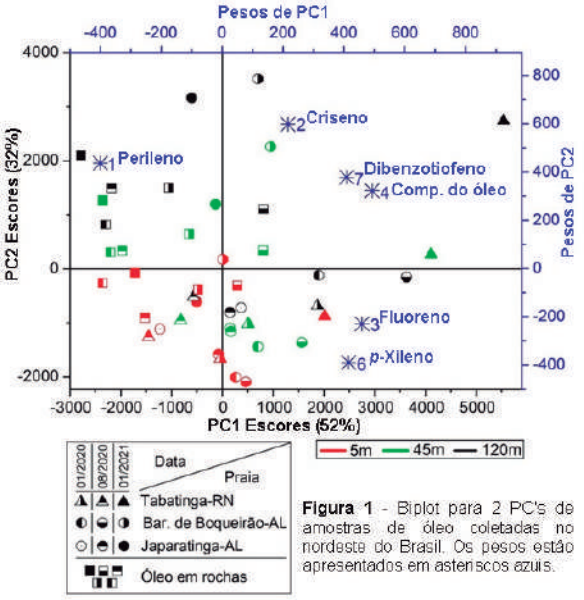

**Figura 1** - Biplot para 2 PC's de amostras de óleo coletadas no nordeste do Brasil. Os pesos estão apresentados em asteriscos azuis.

[1] J.H. Christensen, A.B. Hansen, J. Mortensen, O. Andersen, Characterization and matching of oil samples using fluorescence spectroscopy and parallel factor analysis., Anal. Chem. 77 (2005) 2210–2217.

[2] M.F.S. Khan, J. Wu, B. Liu, C. Cheng, M. Akbar, Y. Chai, A. Memon, Fluorescence and photophysical properties of xylene isomers in water: with experimental and theoretical approaches, R. Soc. Open Sci. 5 (2018) 171719.

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**Área: AMB**

# AVALIAÇÃO PONTUAL DE IVERMECTINA EM AMOSTRAS DE ÁGUAS SUPERFICIAIS DO RIO GUANDU POR CLAE

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*Palavras Chave: Ivermectina, Contaminação, COVID, HPLC.*

## Highlights

**SPOT EVALUATION OF IVERMECTIN IN SAMPLES OF SURFACE WATER FROM THE RIVER GUANDU BY CLAE**

Indiscriminate use of the drug ivermectin due to the COVID pandemic scenario. HPLC-DAD methods for determining pharmacological water samples.

## Resumo/Abstract

A destinação incorreta de medicamentos pode trazer como consequência a alteração dessas substâncias químicas pela exposição a fatores extrínsecos (umidade, temperatura e luz), contaminação de águas superficiais, subterrâneas, lençóis freáticos.[1] Tais modificações podem afetar diretamente e trazer impactos negativos para o meio ambiente, teias e cadeias tróficas. Exemplo prático disso é o surgimento de resistência bacteriana, no caso de resíduos de antibióticos. [2] Devido ao surgimento da variante do vírus SARS COV 19 que deu origem a pandemia do COVID 19 e a falta de informações que se tinham para o combate ao vírus muitas hipóteses de tratamentos que poderiam ser eficientes surgiram. O fato é, que em meio a esse processo de construção e considerando que os estudos ainda estão em andamento, a existência de artigos que busquem explicar a eficiência de algum fármaco que possa ser um aliado ao combate da covid-19, apresenta-se de uma maneira muito instável, uma vez, que a discussão apresentada se baseia em procedimentos que ainda estão em curso, que podem funcionar ou não.[3] Nesse aspecto, em meio a uma gama de estudos desenvolvidos, a comunidade cientifica analisa a Ivermectina como possível forma de tratamento. Dando origem ao uso indiscriminado de ivermectina pela população para combate ao vírus. Levando em consideração os efeitos tóxicos já conhecidos desse medicamento se faz necessário a investigação das concentrações dele no meio ambiente, uma vez que no Brasil temos um tratamento de esgoto deficiente. Nesse sentido, esse trabalho descreve o desenvolvimento de uma metodologia analítica capaz de determinar a presença de ivermectina em amostras de água do Rio Guandu em um momento pontual, foram coletados 20L de amostra do rio em um ponto antes da captação pela estação de tratamento. Os experimentos foram realizados em sistema de cromatografia a líquido de alta eficiência (CLAE) com detector de arranjo diodo (DAD) no comprimento de onda máximos de absorção do analito: IVM ($\lambda$ 254 nm). Melhores resultados foram obtidos com gradiente binário de eluição composto de metanol e água (v/v) em coluna Zorbax SQ-aq 2,1 x 150 mm; 3,5 mm (Agilent) a 40 ºC e vazão de 1 mL.min$^{-1}$ . O volume de injeção foi de 10 µL e o tempo de análise foi de 20 minutos. Curvas analíticas foram preparadas na faixa de 10 a 300 mg.L-1 do analito diluído em MeOH e H2O. Todas as análises foram realizadas em triplicata resultando em DPR < 2% e coeficientes de correlação (r2 ) > 0,999. Foi possível detectar e quantificar uma concentração média de 12,44µg.L$^{-1}$ de IVM no Rio Guandu em amostras de aguas superficiais de um ponto de coleta do Rio Guandu. Ainda que a presença da IVM seja relativamente breve em corpos d’água, devido a sua estrutura lipofílica, fazendo com que apresente alta afinidade a compostos orgânicos, podendo estar presente em maiores concentrações em solo, devido às suas características de sorção o método otimizado associado a adequado processo de limpeza e concentração de amostras mostra-se adequado à determinação da IVM em amostras de água

[1] EICKHOFF; HEINECK; SEIXAS, 2009

[2] PINTO, 2014

[3]PONTES, 2021

## Agradecimentos/Acknowledgments

INT e UCL.

**Área: AMB** **Nº de Inscrição: 00236**

# Avaliação de fibras de amianto em material particulado atmosférico

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Palavras Chave: *Material particulado, Amianto; Poluição indoor*

## Highlights

**Evaluation of asbestos fibers in atmospheric particulate matter**

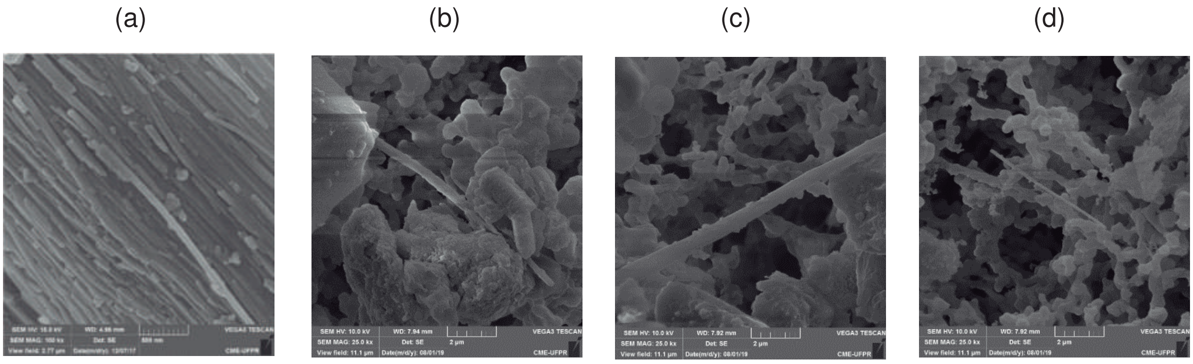
The use of asbestos in roof tiles can be a source of indoor pollution;

Scanning electron microscopy as an important tool to assess the presence of asbestos fibers in different types of samples.

## Resumo/Abstract

O amianto ou asbesto foi largamente utilizado no passado, devido as características de suas fibras, que possuem alta resistência mecânica, flexibilidade, estabilidade, afinidade com cimento e resinas, boa capacidade de isolamentos térmico e acústico, dentre outras. Por outro lado, existem estudos demonstrando os danos que a inalação desse material pode trazer para os seres humanos. O objetivo deste trabalho é verificar a presença ou não de fibras de amianto crisotila em ambientes internos que possuem telhas de amianto (dois barracões para estocagem de material e um banheiro), e em um ambiente externo. Em cada ponto as coletas foram em duplicata, totalizando 8 amostras, usando bombas de sucção, cassetes de plástico e membranas de éster de celulose (37 mm de diâmetro e porosidade de 0,45 μm). Depois das coletas, as amostras foram colocadas em placas de Petri e armazenadas em dessecador até as análises. As medidas de microscopia eletrônica de varredura (MEV) foram realizadas em um equipamento JEOL JSM 6360 LV, operando em vácuo de $10^{-4}$ Pa, a uma potência de feixe de 3 a 20 keV. A Avaliação química foi realizada através do Sistema de análise química tipo EDS (Oxiford), com software AZ Tech (Advanced) e detetor tipo SDD de 80 mm². As amostras foram depositadas em suportes de alumínio (31,8 mm de diâmetro e 10 mm de altura), fixadas com auxílio de fita dupla-face, recobertas e metalizadas com ouro. Os resultados mostraram que não foram verificadas fibras no ambiente externo, enquanto nos ambientes internos foi possível verificar sua presença, conforme Figura 1.

Figura 1: Micrografias obtidas por Microscopia Eletrônica de Varredura. (a) Padrão de amianto crisotila; b) Amostra coletada no barracão 1; (c) e (d) Amostras coletadas no banheiro.


(a) (b) (c) (d)

Para o ambiente externo, não foram verificadas fibras, enquanto nos ambientes internos foi possível verificar sua presença, principalmente no banheiro, que é um local com pouca ventilação e que permanecia fechado a maior parte do tempo. No entanto, os espectros de EDS indicaram a presença majoritária de carbono e oxigênio e menores teores de silício e de magnésio, o que indica a possível presença de material biológico. Assim, serão necessários estudos posteriores que envolvam mais coletas em locais que ainda possuem materiais contendo amianto, a fim de confirmar se é possível seu desprendimento e posterior contaminação do ambiente.

## Agradecimentos/Acknowledgments

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**Área: AMB**

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

# Benzene removal from gas stream combining adsorption and electrochemical oxidation in methanol medium

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Palavras Chave: *volatile organic compounds; gas stream treatment; adsorption; electrochemical oxidation; benzene.*

## Highlights

Benzene can be mineralized electrochemically in methanol medium.
GAC can be recovery with fresh methanol.
Value-added by-products were produced.
Electro-refinery can be used as treatment technology.

## Resumo/Abstract

Benzene is a volatile organic compound (VOC) very harmful to humans and the environment because its proven carcinogenicity. Coal combustion is one of the main sources of benzene release. Adsorption technology has shown promise for VOC decontamination from gas streams due to its high efficiency, low cost, simplicity, and low energy consumption [1]. This work aims to evaluate the combination of adsorption technology and electrochemical oxidation to improve the removal of benzene from gas stream and to argue about electro-refinery as treatment technology. For this purpose, granular activated carbon (GAC) was used as adsorbent material, and, in a first step, to adsorb the benzene from the gas stream. Afterwards, methanol desorbs the contaminant, recovering the GAC. Finally, the obtained high concentrated solution is treated electrochemically using a boron-doped diamond anode. Seven cycles were performed to verify the GAC recovery: three using fresh methanol (FM) and four using the methanol solutions post treated (MSPT). Using FM to desorb the benzene, GAC is completely recovery and the same amount of benzene is adsorbed step by step. On the other hand, when MSPT was used, there was a decrease in the GAC adsorption capacity. It means that the amount of benzene desorbed after each step of desorption using this kind of methanol decreases. This can be related with the deactivation of the active sites of GAC. Considering the maximum adsorption on each cycle, the reduction was 4.6, 12.4 and 42.8% for the second, third and fourth cycle, respectively, with the desorption performed with the MSPT. During the electrochemical oxidation, benzene removal showed a pseudo-first order behavior with a kinetic constant of 0.0017 $min^{-1}$. It is very important to note that during the electrooxidation of benzene in methanol, some value-added by-products can be generated. Anisole is one of the main by-products that are produced, reaching a maximum concentration of 1,200 mg $L^{-1}$. The formation of value-added by-products opens the possibility of explore the electro-refinery concept as treatment technology.

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## Agradecimentos/Acknowledgments

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**Área:** AMB

# BIODEGRADAÇÃO DO HERBICIDA ATRAZINA POR *SACCHAROMYCES CEREVISIAE*

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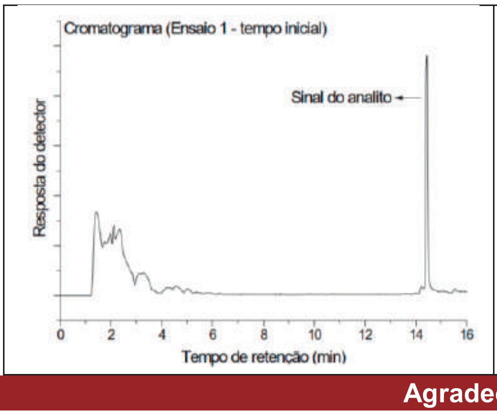
*Palavras Chave: Agrotóxicos, Bioaumento, Respiração basal do solo, Taxa de degradação*

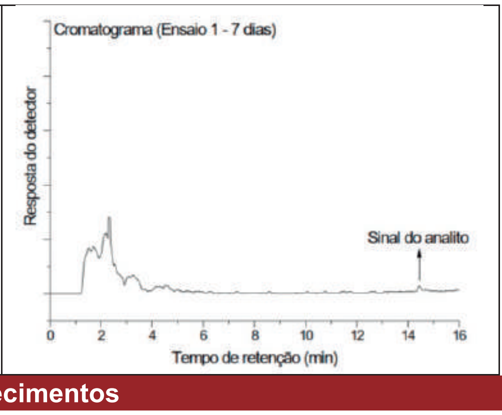
## Biodegradation of the atrazine herbicide by *saccharomyces cerevisiae*

Considering of the various environmental and health problems that the increasing use of pesticides has been causing, it is necessary to optimize techniques that aim at their rapid degradation. Atrazine is a herbicide used to control weeds, especially in corn and sugarcane crops. Thus, objective of this study was to verify the efficiency of the yeast Saccharomyces cerevisiae in the degradation of atrazine in soil contaminated with different concentrations of the commercial product. In order to determine the amount of carbon dioxide ($CO_2$) released during the tests was determined, which reflects the activity of the soil microbiota responsible for the degradation of organic compounds, using the technique of basal soil respiration. By gas chromatography coupled to a mass spectrometer (GC-MS), the concentration of atrazine was verified throughout the experiment (initial time, at 7, 14 and 64 days). Through statistical analysis of basal respiration data, the bioincrease factor with yeast was the most significant, followed by the addition of corn husk. The decline in atrazine concentration was verified by means of chromatographic analyses. Thus, it is suggested that bioremediation with *Sacharomyces cerevisiae* has the potential to increase herbicide degradation rates in the soil.

## Resumo

Atualmente, a busca pela maior produção de alimentos em espaços cada vez menores vem causando sérios impactos ambientais no solo pela intensa utilização de agroquímicos no controle de pragas e doenças. A atrazina (2-cloro-4-etilamina-6-isopropilamina-s-triazina) é um dos herbicidas mais utilizados em função de seu amplo espectro para o controle de ervas daninhas de folhas largas e pelo baixo custo. Uma alternativa para transformar contaminantes do solo em produtos menos tóxicos ou completamente convertidos em matéria inorgânica, água, dióxido de carbono e amônia é a biorremediação. A levedura *Saccharomyces cerevisiae* em razão de sua capacidade metabólica, apresenta papel importante na biorremediação ambiental, além de apresentar baixa toxidade. A levedura *S. cerevisiae* é um microrganismo aeróbio facultativo, não patogênico e muito utilizado na produção de cerveja, vinho e na panificação, o qual apresenta boa tolerância ao estresse osmótico e ao etanol. Assim, o presente trabalho teve como objetivo verificar a degradação do herbicida atrazina, utilizando a técnica de bioaumento com *S. cerevisiae*, proveniente do resíduo de levedura do processo de produção de cerveja, e adição de palha de milho. Para verificar a capacidade de degradação da atrazina pela levedura *S. cerevisiae*, preparou-se 50 mL de meio de cultura líquido para leveduras (YW) e adicionou-se 5 mL da levedura residual de cervejaria. As análises de CG-MS do solo revelam a diminuição da concentração do herbicida ao longo do experimento. Em todos os ensaios, obteve-se redução de mais de 55% dos níveis de atrazina nos primeiros sete dias, em oito dos ensaios, essa redução chegou a mais de 72%. Através dos cromatogramas (Fig. 1 e 2) verificou-se a alta atividade metabólica da levedura até o sétimo dia do experimento, não sendo mais detectada em oito ensaios a partir do 14º dia, restando apenas pequena concentração para dois ensaios. Assim, sugere-se que a biorremediação com *Saccharomyces cerevisiae* tem potencial para degradar o herbicida atrazina no solo.





## Agradecimentos

Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – Brasil — CAPES

**Área: ANA** **Nº de Inscrição: 00961**

# Biomass pretreatment: An intelligent system for obtaining pyrolysis products.

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Keywords: *biomass; grape seed; pyrolysis; microwave.*

## Highlights

Influence of the microwave for the pretreatment of lignocellulosic biomass;
To evaluate the pretreatment of biomass with microwave in bio-oil enriched with phenols;
Operation conditions and kinetic are shown as key of the pretreatment;
The use of the microwave demonstrated to have impacts hydrolysate (phenols and sugar) from lignocellulosic biomass.

## Abstract

Lignocellulosic biomasses are of great interest to the scientific community in terms of studies on the development of sustainable technologies in the chemical and fuel industries. To obtain a better efficiency in the process to be carried out, many biomasses undergo a pretreatment process. Pretreatment is a way to change the structure of lignocellulosic biomass (cellulose, hemicellulose, and lignin), thus facilitating macroscopic and microscopic changes in sample[1]. Microwave pretreatment is used as simple operation and energy efficiency, besides contributing to increase the accessibility and reactivity of cellulose[2]. Thus, the present work aims to develop pre-treatment processes for biomass as an alternative technology to increase the conversion of pyrolysis products for use in the chemical industry and energy. The residue of the wine industry (grape seed) was used as biomass. The pretreatment experiments developed in this work were carried out following a Box-Behnken experimental design with a study in 3 variables and 3 levels. A kinetic curve was performed to define how long the biomass would be stored in the microwave device (Mars 5 Xpress model) using the central planning point (120 ° C, pH 7 and 600 W). In general, 6 mL of liquid phase (buffer solution) and 2 g of biomass were used per reaction tube, with 20 tubes per batch. After pre-treatment, the biomass and the aqueous fraction were separated by filtration, the biomass was dried in an oven at 80 ° C for 24 h and the liquid fraction frozen for further analysis. The best result was that which presented a higher sugar content in the liquid phase and an intermediate value of phenolic compounds in that same fraction. According to the developed kinetic curve, the best time for performing the pre-treatments was 20 minutes, since there was a higher concentration of sugars in the liquid fraction, 0.8042 g / L, thus denoting a more effective attack on cellulose and hemicellulose from biomass. Besides, in this time, a phenolic content of 0.1006 g / L was obtained showing that microwave radiation attacked lignin to reduce its recalcitrance, that is, decreasing its resistance, making it more susceptible to reactions pyrolytic.

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## Acknowledgments

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**Área: AMB** **Nº de Inscrição: 1362**

# Biosorption Kinetics of Organic Dye in Crustaceans Residues Found in the State of Sergipe

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Palavras Chave: *Biosorption. Crustaceans. Methylene blue. Kinetics.*

## Highlights

Removal of the organic dye of effluents with crustaceans residues. Fast kinetics of biosorption of methylene blue in crustacean residues adjusted well to the pseudo-second order model.

## Abstract

The process of degradation of water resources has been accentuated due to the growing number of industrial activities, which release their effluents containing contaminants such as heavy metals and organic dyes; without proper treatment, in water bodies. The adsorption technique is widely used in the treatment of these liquid effluents, however, traditional adsorbents such as activated carbon have a high cost. In the context of the use of biosorption using cheap and alternative adsorbents, this research work aimed to study sorption kinetics of methylene blue in crustacean biomass found in Sergipe state, such as crab (*Ucides cordatus*), soft crab (*Callinectes exasperatus*), guaiamum (*Cardisoma guanhumi*) and oyster (*Crassostrea brasiliana*). The crustacean residues collected in the pub of the Aracaju-SE coast were washed and ground, then characterized by the zero loading point (PZC), and the influence of pH on the removal efficiency of the methylene blue by the biomasses of the plants was also evaluated. Then, kinetic data were obtained through batch experiments and modeling was performed. The biomasses showed slightly basic to basic PCZ: crab (7.75), crab (9.25), guaiamum (9.75) and oyster (8.25). Thus, they had higher removal efficiency at pH=11, and the guaiamum biomass presented the highest removal efficiency, 82%, followed by oyster with 78%, crab, 77% and crab with 63%. However, the biomasses presented moderate removal efficiency in the pH range from 3 to 7. The kinetics were fast, reaching equilibrium between 10 and 20 minutes and the kinetic data adjusted well to the pseudo-second order model. The biomasses presented as promising adsorbents and can be used in conjunction with traditional adsorbents, without the need to adjust the effluent pH, and due to their fast sorption kinetics of methylene blue, they can be used in both batch and column systems.

## Acknowledgments

CNPq, CAPES, FAPITEC, Laboratório de Biotecnologia Ambiental (LABAM/UFS), Laboratório de Tecnologias Ambientais (LATAM/NUPEG), Centro de Laboratórios de Química Multiusuários (CLQM/UFS), Laboratório de Corrosão e Nanotecnologia (LCNT), Associação Sergipana de Ciência (ASCi).

**Área: AMB**

# Chemical composition of bio-oil from the thermochemical conversion of lignocellulosic biomass

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Key words: *Pyrolysis, bio-oil, GC/MS.*

## Highlights

- Evaluate biomass weight and residence time to production of bio-oil by micropyrolysis
- Gas chromatography coupled with mass spectroscopy (GC/MS) was used to identify and quantify the compounds present in the bio-oil.

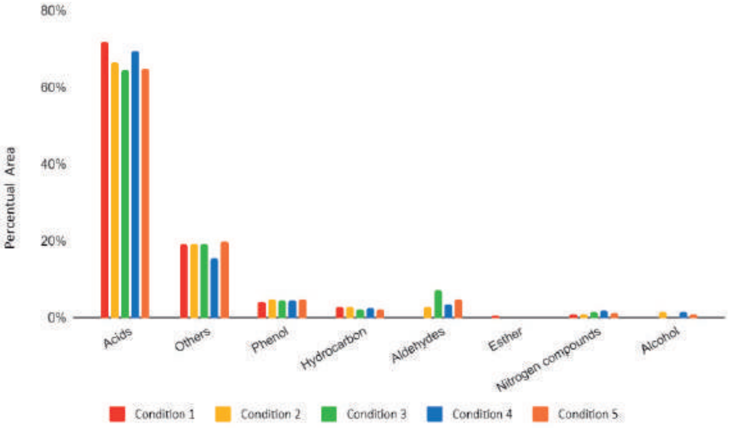
## Abstract

The use of agroindustrial waste for bio-oil production through thermochemical conversion processes of biomass, such as rapid micropyrolysis, besides being an alternative and sustainable strategy, is promising in the generation of products with high added value and can be applied in various segments depending on its composition, such as in the production of resins, biofuels, pharmaceutical industries, among others. In this context, the pyrolysis of an agro-industrial residue, the guava seed, was performed under different experimental conditions at a fixed temperature of 600 °C, where the bio-oil obtained was submitted to chromatography to calculate the percentage of organic functions present. Table 1 presents the information for each condition and Figure 1 represents the graph of the percentage of the compounds.

**Table 1:** Operational parameters of the micropyrolysis

| Reaction Conditions | Time (s) | Mass (mg) |
|---|---|---|
| **1** | 30 | 100 |
| **2** | 90 | 100 |
| **3** | 30 | 200 |
| **4** | 90 | 200 |
| **5** | 60 | 150 |

**Figure 1:** Distribution of compounds in bio-oil in different experimental conditions



The carboxylic acids were the compounds found in the highest amount in all conditions studied (65~75%), the phenomenon can be explained by the pyrolysis of a triglyceride biomass. The parameters showed that in low weight biomass 30 s of the residence time pyrolysis is effective to production of acids compounds.

This such substances cause negative impacts to bio-oil such as low calorific value, in addition to corrosiveness, but may be precursors of hydrocarbons used in the biofuels synthesis. The present work showed the need to use catalysts for the biomass conversion in products economical manufactured.

## Acknowledgment

**Área: AMB**

# Chemometric evaluation of aromatics VOCs in indoor/outdoor environments in Campos dos Goytacazes-RJ

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Palavras Chave: *Aromatics VOCs, Air Quality, Chemometrics, ATD-GC/MS*

## Highlights

Benzene and 1,2,3-trimethylbenzene were the most significant variables for separating samples between indoor and outdoor environments. The VOCs emission increased with the vehicle traffic in outdoor sampling.

## Resumo/Abstract

Volatile Organic Compounds (VOCs) are atmospheric pollutants that represent a significant risk to human health and the environment. Among them, the class of aromatics is highlighted as they can cause mutagenic and carcinogenic effects on human health. In this way, understanding their emission sources and behaviors in the environment is fundamental for developing strategies to reduce these pollutants in the atmosphere. However, the large number of data generated during their monitoring and the number of variables that can interfere in the environment make the evaluation and comprehension of these results harder. In this sense, the Principal Component Analysis (PCA) is an efficient multivariate statistical approach to reducing the dimension of the data, facilitating the interpretation of these results. In this context, this work aimed at monitoring ten aromatics VOCs present in the atmosphere of two environments, indoor (Laboratory of Chemistry – UENF) and outdoor (UENF main entrance gate), in the city of Campos dos Goytacazes – RJ. Sampling was performed actively in glass tubes filled with Tenax ®, using a suction pump with a flow of 200 mL $min^{-1}$. These tubes were heated in thermal desorption equipment (TD-20, Shimadzu), transferring the adsorbed compounds to the Gas Chromatograph column coupled to Mass Spectrometer (GCMS-QP2010 Plus, Shimadzu). Then, the generated data were evaluated in an unsupervised way using the PCA as an exploratory statistical tool. From the graphics scores, it was possible to observe the tendency to form two distinct groups that corresponded to the evaluated environments. In the loadings graph, it was possible to observe that benzene and 1,2,3-trimethylbenzene were the most significant variables for the separation of samples between indoor and outdoor environments, these two compounds being the majority in the outdoor environment. These compounds are emitted by fossil fuels, possibly derived from motor vehicles and/or by the gas station near the sampling point. In addition, there is an increase in the concentration of these two compounds due to the increased flow of vehicles in this environment during the vaccination period (started on March 27, 2020). The calculation of the toluene/benzene ratio below 2 corroborates these results, demonstrating the predominance of vehicular sources in this location. There is also a tendency to separate the indoor environment due to the concentrations of butylbenzene in this environment. The indoor environment is also characterized by high concentrations of most of the compounds evaluated, indicating the predominance of indoor emission sources within the closed environment or the accumulation of these pollutants in that location. As the indoor environment studied in this case is a chemistry laboratory that works with these compounds, the possibility that the emission of these compounds is derived from an indoor source is the most accepted hypothesis. Therefore, contamination of this environment can come from solvents used in the laboratory itself and poor ventilation. Finally, this study makes it possible to understand the VOC's composition in environments and their potential emission sources.

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**Área: AMB**

# Comparative study of bio-oils produced from different biomasses

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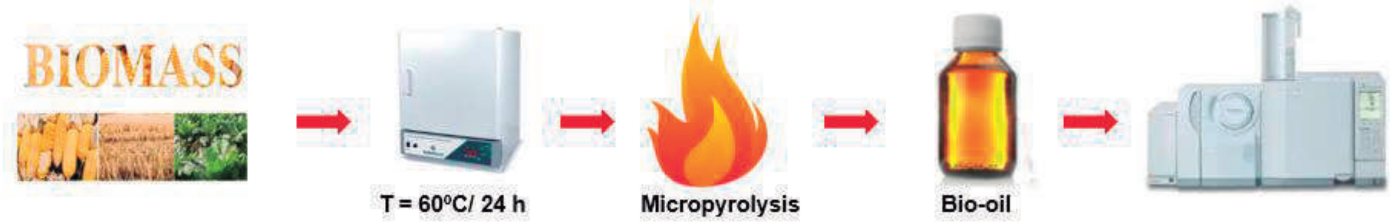
*Keywords: bio-oil, biomass, organic compound, micropyrolysis, GC/MS*

## Highlights

Use of agroindustry residues for production of bio-oil;
Comparison of bio-oils obtained by different biomasses (acerola seed, grape seed, guava seed and bean pods);
Statistical analysis of organic compounds obtained in different bio-oil by GC/MS.

## Abstract

The use the residues serve as source for chemical and energy industry. The composition of bio-oil is dependent of the biomass used in pyrolysis process. The different biomass structure of biomass can modify the concentration and major compounds present content in the bio-oil, the route to produce by-products with added value in the industry is different. The compounds distinction is of great value for the industrial sector that intends to use different raw materials for the production of inputs. The production of phenols, aromatic compounds and hydrocarbons, for example, through renewable sources and can to reduce the consumption of petroleum derivatives. The methodology applied is described below.



The compounds were identified by comparing the spectra using the NIST and WILEY library database, through retention time. In this way, the following results were obtained.

Table 1: Classification of the main constituents of bio-oil in different biomasses

| Biomass | % Functional Groups | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Others | Hydrocarbon | Ketone | Phenol | Ester | Alcohol | Ether | Amide | Aldehyde | Amine | Carboxylic Acid | Furan | Anhydride |
| Grape seed | 16,30% | 32,61% | 2,17% | 10,87% | 4,35% | 7,61% | 3,26% | 2,17% | 3,26% | 1,09% | 16,30% | - | - |
| Acerola seed | 19,35% | 6,45% | 22,58% | 25,81% | 3,23% | 3,23% | 3,23% | 3,23% | 6,45% | 3,13% | 6,45% | - | - |
| Guava seed | 14,49% | 27,54% | 1,45% | 8,70% | 7,25% | 5,80% | 1,45% | 1,45% | 5,80% | 1,45% | 23,19% | - | - |
| Bean pod | 31,43% | 14,29% | 22,86% | 11,43% | 2,86% | 2,86% | - | 2,86% | - | 2,86% | 2,86% | 2,86% | 2,86% |

pyrolysis bio-oils presented a mixture of compounds where ketones, acids, phenols, nitrogenous, alcohols, compounds with mixed functions etc.

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Área: AMB

# Comparison of formaldehyde atmospheric columns in São Paulo State using TROPOMI satellite instrument

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Keywords: *Atlantic forest, HCHO, Megacity, Remote sensing, Vertical column*.

## Highlights

Satellite-monitored formaldehyde showed high seasonality throughout 2020.

Significant statistical differences were found in HCHO concentrations over urban and forested areas.

## Abstract

The major sources of atmospheric formaldehyde (HCHO) are oxidation of volatile organic compounds (VOC), biomass burning and vehicular and industrial emissions; while HCHO removal processes are oxidation by OH radicals, photolysis and wet deposition. In our study, we evaluated the HCHO vertical columns recorded by the TROPOMI sensor (TROPOspheric Monitoring Instrument, Sentinel-5 Precursor satellite), over São Paulo State during 2020. A total of 19 specific areas were evaluated in four regions: two Atlantic forest areas (PETAR and PEMD); one sugarcane cultivation; and the Metropolitan Area of São Paulo (MASP), including densely urbanized areas and a third preserved Atlantic forest near the megacity (Morro Grande Reserve). A total of 3677 validated data were analyzed, corresponding to an average of 193 days of satellite passage for each area. The highest values of the HCHO columns were observed in the densely urbanized region, with averages between 1.98±1.13 and 2.20±1.31 x $10^{-4}$ mol/$m^2$, while in the forested or agricultural areas they ranged between 1.51±1.03 and 1.73±1.07 x $10^{-4}$ mol/$m^2$. Analysis of variance (ANOVA) and Tukey's test showed that the HCHO concentrations in the atmosphere of Morro Grande were more similar to those identified over the other forests or agricultural regions than to those over MASP, demonstrating that the reserve suffered little influence from urban emissions. The results presented high seasonality, with low densities during summer (rainy) and high ones during winter (dry) and spring (Figure 1). These results indicate a predominance of removal processes by wet deposition and photolysis, despite high photochemical activity with potential for HCHO formation during the summer.

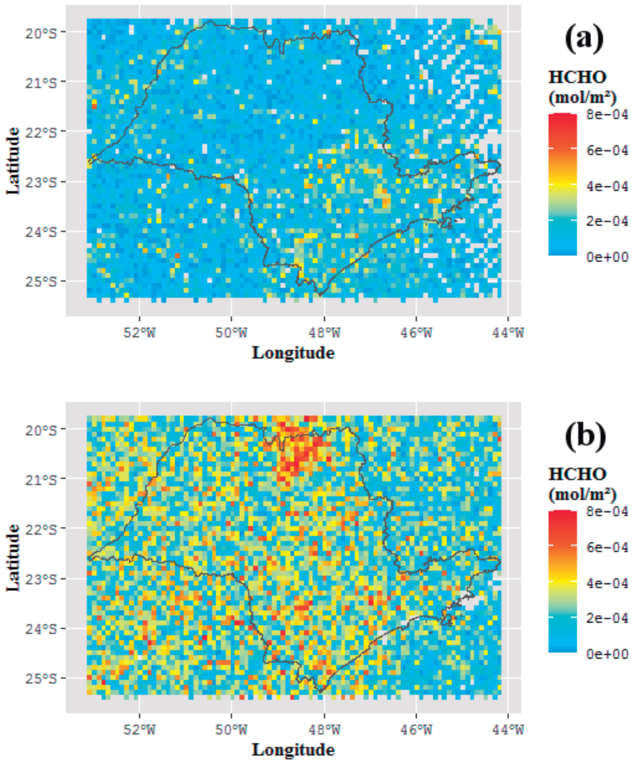

**Figure 1.** Satellite HCHO data in São Paulo State: (a) 01/26/2020 (summer) and (b) 09/13/2020 (winter-spring).

## Acknowledgments

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**Área: ELE**

# DEGRADATION OF SULFANILAMIDE BY ULTRAVIOLET AND ULTRASOUND IRRADIATION

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*Palavras Chave: Processos Oxidativos Avançados; fotodegradação, fotoquímica.*

## Highlights

Advanced Oxidative Processes (AOPs) are applied to the degradation of emerging contaminants of pharmacological origin. Ultraviolet (UV) radiation combined with ultrasound. Photodegradation ($C_6H_8N_2O_2S$).

## Abstract

Currently, UV radiation and Advanced Oxidative Processes are suitable for their potential use in treating some wastewater, as conventional methods are suitable for some recalcitrant treatments.[1] Because of this, the present work aimed to evaluate the efficiency of UV radiation and ultrasound, associated with advanced oxidative processes, in the degradation of sulfanilamide. Degradation monitoring was performed in a spectrophotometer with absorption readings taken at wavelengths of 257 nm, for sulfanilamide, and 313 nm, in which absorption followed by drug degradation was observed, indicating the formation of product(s). Initially, the techniques were studied separately (US and then UV) and then in combination (US + UV). Subsequently, hydrogen peroxide and atmospheric air were used as an oxidant for their effects on sulfanilamide degradation in combination with the US + UV technique. To verify the catalytic potential of some metals in the degradation of the drug, tests were carried out with the presence of the following metal ions: $Al^{3+}$, $Cu^{2+}$, $Mg^{2+}$, $Zn^{2+}$, $Co^{2+}$ e $Na^{+}$. Absorption at 313 nm was related to the possible formation of the product(s) formed, therefore, the monitoring of this band was carried out under all reaction conditions studied. The results showed that the combined techniques are efficient in the degradation of the drug, however, it was also observed that UV radiation alone already presents a satisfactory degradation (Fig. 1). The use of oxidizing reagents potentiated the degradation process, among them, the one that presented the best performance was hydrogen peroxide. ($H_2O_2$). Regarding the tests with metal ions, it was found that their presence did not improve the degradation of the studied drug.

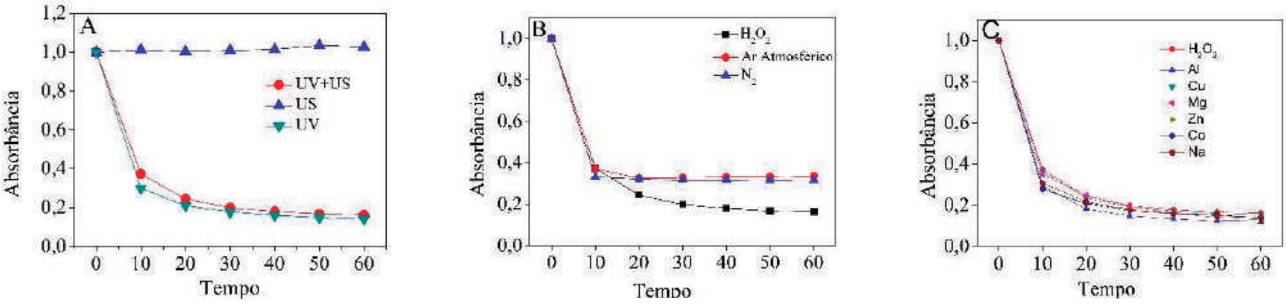

**Fig.1**. Condições reacionais estudadas para degradação: (a) UV, Ultrassom, UV + Ultrassom (b) ar atmosférico, $H_2O_2$, atmosfera inerte com $N_2$ (c) $Al^{3+}$, $Cu^{2+}$, $Mg^{2+}$, $Zn^{2+}$, $Co^{2+}$ e $Na^{+}$.

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## Agradecimentos/Acknowledgments

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**Área: AMB** **Nº de Inscrição: 1158**

# Determinação de material particulado e dióxido de nitrogênio na pirólise de madeira para a produção de carvão vegetal: Estudo de caso

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Palavras Chave: *Material particulado, Dióxido de nitrogênio, Carvão vegetal, Pirólises, Amostragem ativa.*

## Highlights

**Determination of particulate matter and nitrogen dioxide in wood pyrolysis for charcoal production: Case study**

A large quantity of particles and nitrogen oxides is released from wood combustion;

Roasting is the phase of highest PMs emission and carbonization of nitrogen dioxide in wood pyrolysis.

## Resumo/Abstract

A produção de carvão vegetal abrange 8,5% da matriz energética do Brasil. Para obtenção deste produto utiliza-se a pirólise da madeira pelo método de combustão parcial controlada em fornos circulares. O processo ocorre em quatro fases: secagem, torrefação, carbonização e fixação do carbono. Esta tecnologia representa 65% da produção de carvão vegetal do país, por isso a importância do seu estudo. Não obstante, as condições de produção são rudimentares e sem aproveitamento dos gases do processo que liberam no meio ambiente compostos orgânicos voláteis (COV), sobretudo hidrocarbonetos, monóxido de carbono (CO), óxidos de nitrogênio ($NO_x$) e material particulado (MP). Diante do exposto, o objetivo do trabalho é avaliar a concentração de material particulado e dióxido de nitrogênio ($NO_2$) no ar próximos aos fornos circulares convencionais sem queima de gases, em uma unidade produtiva de carvão vegetal localizada na região dos campos gerais do Paraná. Para isso, foram feitas coletas de MP em diferentes períodos para cada umas das fases da pirólise da madeira: torrefação, carbonização e fixação e descarregamento do carvão do forno. As amostras foram coletadas em triplicata usando cassetes e filtros de éster de celulose (37 mm de diâmetro e 0,8 µm de porosidade), por meio de bomba portátil, a vazões de 2 L min$^{-1}$ e tempos de amostragem variando de 70 min, 140 mim e 210 min. Antes e após as coletas, os filtros foram colocados em dessecador por 24h, para condicionamento e a massa do MP coletado foi obtida por análise gravimétrica, realizando pesagem dos filtros em uma balança analítica com resolução de 0,0001 g. Os resultados mostraram que a fase com maior material particulado foi torrefação, com uma concentração média de 37,14 mg·m$^{-3}$, o que foi 1.3, 3.1 e 1.1 vezes maior do que as fases de carbonização, fixação e descarregamento, respectivamente. Para as coletas de $NO_2$, foram usados filtros de celulose impregnados com trietanolamina 11%, etilenoglicol 3,6% e acetona 25%, nas etapas de torrefação e carbonização. Após coleta, os filtros foram extraídos com água ultrapura e analisados através da reação colorimétrica de Griess-Saltzman, em 540 nm. Os valores médios de concentração foram de 2,7 µg m$^{-3}$ na torrefação e de 15,5 µg m$^{-3}$ na carbonização, ressaltando a importância do aumento da temperatura e a injeção de ar controlado na formação de óxido de nitrogênio (NO) e sua posterior oxidação a $NO_2$ na atmosfera. Assim, é possível afirmar que a produção de carvão vegetal sem queima de gases é uma fonte importante de poluição do ar e representa uma ameaça para a saúde da população circundante e trabalhadores, portanto, é relevante implementar tecnologias mais limpas e efetivar leis mais eficazes para ajudar a reduzir e tornar o processo mais sustentável.

## Agradecimentos/Acknowledgments

CNPq, UTFPR, LEMA, LAMAQ, MPT, APREA e ao produtor de carvão vegetal da região dos Campos Gerais, Paraná.

**Área: AMB** **Nº de Inscrição: 248**

# Determination of metallic species in agricultural soils in agroecological and conventional environments

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Keywords: *Soil, Metallic Species, Conventional and Agroecological Environment*

## Highlights

Soil is an extremely important natural resource, it is a source of food for plants and where activities that are essential for the food of living beings are developed. In addition to the metallic species normally found in the soil, some metals originate from anthropic contamination. One of the possible sources are pesticides, widely used in agriculture in order to reduce or eliminate pests in plantations. Due to its persistence and easy absorption by plants, metal pollution in the soil is a major concern, as they can compromise human health through the food chain. In this context, the objective of this work is to determine metallic species in soil from agroecological and conventional environments, in order to relate the amount of metal found in the two environments. The results show that there is no significant difference between the concentrations of metals found in the agroecological environment and in the conventional environment, indicating a high concentration of Fe due to the constitution of the soil. Thus, it is concluded that the applied methodology was effective for the analyzed metals.

## Abstract

Soil is an extremely important natural resource, it is a source of food for plants and where agriculture, livestock and forestry are developed, activities that are essential for the food of living beings. In addition to the metallic species normally found in the soil, such as aluminum, manganese, iron, among others, some metals can originate from anthropic contamination, due to residues that are frequently introduced into the soil [1]. One of the possible sources of metals are pesticides, widely used in agriculture in order to reduce or eliminate pests in plantations. Due to its persistence and easy absorption by plants, metal pollution in the soil is of concern, as they can compromise human health through the food chain [1]. In this context, the objective of this work was to determine metallic species in soil from agroecological and conventional environments, in order to relate the amount of metal found in the two environments. The samples were collected in the Contested Settlement in the city of Lapa / PR, in 10 different points, 5 in an agroecological environment and 5 in a conventional environment. For preparation, the samples were taken to the oven for 48 hours at 50ºC, sieved in a 53 µm mesh and subjected to the burning of organic matter according to EMBRAPA 1979. The extraction was carried out based on the EPA 3050B protocol. The procedure was done in triplicate and with the addition of different concentrations of metals to verify the recoveries. The analytical curve was constructed in the range of 0 to 10 mg $L^{-1}$ for Mn, Zn and Cu and 0 to 20 mg $L^{-1}$ for Fe, obtaining $y = 0.00531 + 0.17186x$ for Mn; $y = -0.01983 + 0.3497x$ for Zn; $y = -0.02071 + 0.13775x$ for Cu and $y = 0.00197 + 0.08304x$ for Fe. The concentrations found vary from 105 to 141 µg $g^{-1}$ for Mn; 21 to 50 µg $g^{-1}$ for Zn; 22 to 54 µg $g^{-1}$ for Cu and 11 to 73 mg $g^{-1}$ for Fe. With the values of the concentrations found, the calculations of recoveries were performed, obtaining recoveries greater than 90%. The results show that there is no significant difference between the concentrations of metals found in the agroecological environment and in the conventional environment, indicating a high concentration of Fe and Mn due to the constitution of the soil. Thus, it is concluded that the applied methodology was effective for the analyzed metals.

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## Acknowledgments

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**Área: AMB** **Nº de Inscrição: 00693**

# Development of a protocol for simultaneous determination of microplastics and metals in fish tissue: an efficient way for monitoring environmental impact

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Palavras Chave: *Microplastics, Diluted acids, Environmental monitoring.*

## Highlights

The use of diluted acid allows simultaneous determination of microplastics and metals content in fish tissue. It allows to estimate the environmental impact, as well as the human exposure.

## Abstract

The life style adopted by humans in last decades have resulted in the production of huge amounts of plastic-based materials. When such residue is not properly exposed, it starts to accumulate in landfills or oceans. In both cases plastics starts to be part of animal food chain, thus impacting ecosystems. However, because of such irresponsible plastic disposal, animals and humans have been severely exposed to microplastics (MP, plastics with size lower to 5 mm). Such exposure results in humans ingestion of about 120 thousand particles of MP annually, which came from air, water, and food (fish has been considered the most significant). The potential problem is the transport of anthropogenic contaminants as organic compounds or metals and the leaching of chemical additives from MP to human organism. For the MP determination in animal tissues, it is required a step of organic matter digestion/solubilization, which is considered as an analytical challenge because minimum or no degradation of MP have to be obtained, even when using acid digestion for sample preparation. As a result, it is normally reported a non-efficient digestion of organic matter, or the MP degradation. In this sense, the aim of this work is the simultaneous determination of MP and metals in fish tissue using diluted nitric acid, with hydrogen peroxide as auxiliary reagent, looking for a condition where organic sample is fully digested and the MP content is maintained not degraded. In view of this, microwave-assisted wet digestion based on single reaction chamber technology (MAWD-SRC, UltrawaveTM, Milestone, Italy) was used for fish tissue digestion. Nine plastic samples were used for method optimization: polyethylene terephthalate (PET), polystyrene (PS), expanded polystyrene (EPS), polypropylene (PP), high-density polyethylene (HDPE), low-density polyethylene (LDPE), polycarbonate (PC), polyvinyl chloride (PVC) and polyurethane (PU). Plastic samples were ground in order to behave as MP. Panga fish (*Pangasius bocourti*) was used as an example of fish tissue (freshly used). After drying, the sample was mixed with known amount of MP. For all the experiments, 100 mg of MP sample were used with different sample masses (up to 2 g), which was digested with 6 mL of diluted $HNO_3$. After, the digests were filtered in filter paper and dried at 120 °C by 1 h in an oven. The remaining solid was weighted and the amount of MP was then determined. The resultant solution from sample digestion was used for metals determination (Al, As, Ca, Cd, Co, Cu, La, Mg, Mo, Pb and Zn). After optimization of $HNO_3$ concentration, digestion temperature, and the heating time, all the MP evaluated presented resistance to degradation (over than 90% recovery, except for PU). Metal recovery higher than 90% was obtained, which was evaluated by digesting a CRM of fish tissue (DORM-2, dogfish tissue). Results showed this a valuable method for environmental monitoring of human impact, as well as human exposure, to MP and metals.

## Acknowledgments

UFSM, CAPES, CNPq and FAPERGS

**Área:** ***AMB***

# Diagnóstico dos Resíduos Produzidos no Laboratório de Botânica da Embrapa Amazônia Oriental.

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Palavras Chave: *Resíduos, Resíduos de Laboratórios, Gerenciamento de Resíduos.*

## Highlights

Diagnosis of waste produced in the Botany Laboratory of Embrapa Eastern Amazon.

Keywords: Waste, Laboratory Waste, Waste Management.

## Resumo/Abstract

O Programa de Gerenciamento de Resíduos de Laboratórios (PGRL) consiste em implantar normas e procedimentos para reduzir, tratar e dispor adequadamente os resíduos laboratoriais. Para a implementação do PGRL o diagnóstico é uma das etapas mais importantes, e consiste em fazer o levantamento, classificação e caracterização dos resíduos produzidos em cada área laboratorial. Este trabalho apresenta o levantamento e classificação dos resíduos produzidos no Laboratório de Botânica da Embrapa Amazônia Oriental. O trabalho foi desenvolvido no Laboratório de Gerenciamento de Resíduos - GERELAB da Embrapa Amazônia Oriental, Belém - Pará. Para o diagnóstico dos resíduos produzidos foi realizada a análise de documentos originais do PGRL, do período de 2017 a 2021, referente ao Lab. de Botânica. Foi feita uma abordagem qualitativa dos dados, incluindo a identificação, descrição e classificação. A partir dos resíduos coletados foi feita uma avaliação quantitativa referentes ao percentual de cada tipo de resíduo produzido no Laboratório. Resultados: Os resíduos foram classificados em passivo: composto por todos os produtos químicos vencidos (reagentes e soluções) e materiais que não possuem mais serventia (vidrarias antigas ou quebradas, frascos de reagentes vazios, etc.); e ativo: produzidos em análises e roteiros de procedimentos realizados nos laboratórios, sendo estes classificados de acordo com o Documento 384 (SILVEIRA NETA & PARACAMPO, 2012) em 9 Grupos: G1) Perfurocortantes; G2) Sais Inorgânicos; G3) Solventes halogenados; G4) Solventes não halogenados; G5) Mistura de solventes e solução aquosa; G6) Solução aquosa; G7) Solução aquosa com metais pesados; G8) Óleos com produtos químicos e G9) Resíduos sólidos contaminados. Foram produzidos um total de 446,198kg de resíduos em 5 anos, sendo 368,158 Kg de resíduos passivos (82,51 %) e 78,04 kg (17,49%) de resíduos ativos. Foram coletados 56 tipos diferentes de produtos químicos vencidos do Laboratório de Botânica, somando 187 Kg (41,90%). Dos 9 Grupos que classificam os resíduos ativos, o laboratório de Botânica possui apenas: G1; G5; G6 e G9. Dos resíduos de análises, a maioria são resíduos alcoólicos, ou de solventes com baixo grau de periculosidade e em baixa quantidade. Entretanto, foi identificado o resíduo R- BOT -01 – G6 - Resíduo da Maceração do tecido do lenho, composto por 3ml de Ácido Acético P.A, 3ml de Peróxido de Hidrogênio 30% 1:1 (v/v), 5 gotas de sol. safranina 1%, que resulta na formação de perácido (ácido peracético), pela oxidação do ácido acético por peróxido de hidrogênio conforme a equação: $CH_3COOH + H_2O_2 \rightleftarrows CH_3COOOH + H_2O$, sendo um resíduo tóxico e corrosivo.

## Referência/Reference

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**Área: AMB** **Nº de Inscrição: 00234**

# Employment of an agro-industrial waste as a biossorbent for $Pb^{2+}$ e $Cd^{2+}$

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Palavras Chave: *Maracujá, Chumbo, Cádmio, Biossorção, Reaproveitamento.*

## Highlights

Lead and Cadmium represent 21% of the contamination in the Minas Gerais state according a government agency.

Kinetics was adjusted for pseudo-second order for Pb and pseudo-first order for Cd.

Langmuir isotherm model was adjusted for both metals, showing $Q_{max}$= 62,7±1,7 L $mg^{-1}$ for Pb and $Q_{max}$= 69,2±7,5 L $mg^{-1}$ for Cd.

## Resumo/Abstract

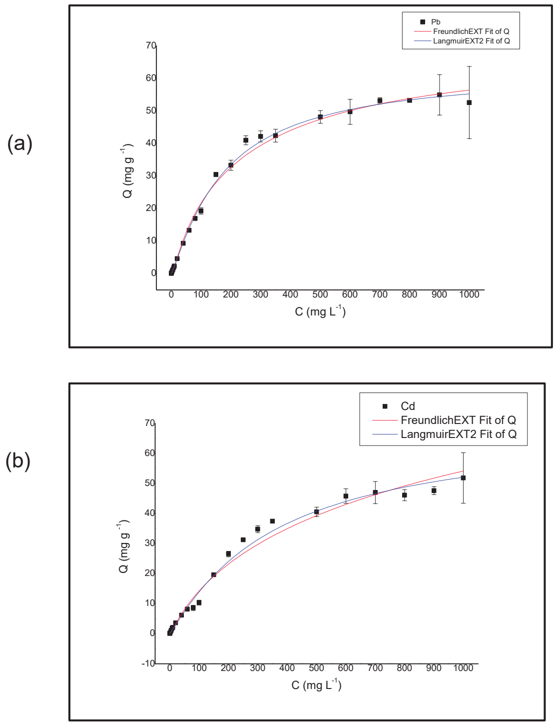

Figura 1. Isoterma de adsorção para (a) Chumbo e (b) Cádmio

Por definição, um contaminante é aquela substância ou elemento encontrado em concentrações anômalas, podendo causar algum efeito deletério ao meio ambiente. Um banco de dados do período de 2007 a 2017, mantido pela Fundação Estadual do Meio Ambiente de Minas Gerais (FEAM), apresentou um percentual de contaminação de Pb e Cd de 21% nas áreas registradas. Vários estudos em busca de estratégias e processos de descontaminação que minimizem os danos causados vêm sendo realizados ao longo dos anos.

O emprego de biomassa vegetal tem ganhado destaque especialmente por ser biodegradável, um recurso natural renovável e ser geralmente de baixo custo, por se tratar muitas vezes de um resíduo agroindustrial. Esse trabalho tem como proposta a utilização da farinha da casca do maracujá (PFPF) como biossorvente para a remoção de $Pb^{2+}$ e $Cd^{2+}$ de efluentes. Foram realizados estudos de cinética, a isoterma e estudos de dessorção. Para os estudos de cinética, foi avaliada a capacidade de adsorção em diferentes tempos, sendo que para Pb a cinética ajustou-se melhor à um modelo de pseudo-segunda ordem e para Cd à um modelo de pseudo-primeira ordem (adj-r² 0,8394 e 0,9096 respectivamente), ambos apresentando saturação a partir de 30 minutos. Para os estudos de isoterma, para ambos os metais foram ajustados tanto os modelos de Freundlich e Langmuir, sendo escolhido o modelo de Langmuir, que para Pb e Cd apresentaram maior valor de adj-R²= 0,9978 e 0,9886 e $Q_{max}$= 62,7±1,7 L $mg^{-1}$ e 69,2±7,5 L $mg^{-1}$ , respectivamente. Foi desenvolvido um planejamento de misturas contendo as principais soluções utilizadas para dessorção de metais: $HNO_3$ 0,1 M; $NaNO_3$ 0,1 M e $H_2O$ deionizada e posteriormente, com a melhor solução, foi avaliado o melhor tempo para dessorção. Para Pb, a condição de 100% de $HNO_3$ 0,1M foi a melhor solução de dessorção, removendo 60,5±7,7 % do metal presente em 120 minutos. Para Cd, uma mistura contendo 57% de $HNO_3$ 0,1 M, 21% de $NaNO_3$ 0,1M e 27% de $H_2O$ deionizada, foi a melhor solução de dessorção removendo 79,5±7,4 % do metal presente. Não houve diferença significativa (segundo teste T) entre os tempos de remoção, podendo ser utilizado um período mínimo de 30 minutos.

## Agradecimentos/Acknowledgments

Às instituições e agências de fomento: UFOP, PROPP, PPGQuim-UFOP, FAPEMIG, Rede Mineira de Química, CNPQ, CAPES, e à equipe LEAT.

**Área: AMB**

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

# Environmental and Social Relevance of Scientific Research of Usage, Stock and Disposal of Medicines and Medicinal Plants

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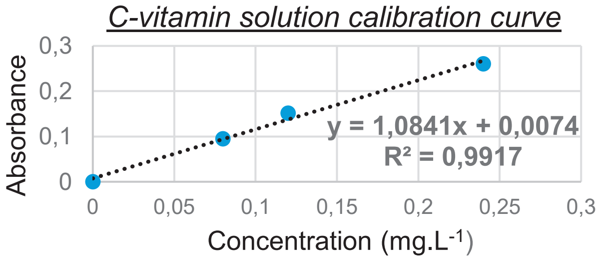
Keywords: *Sustainable, Environment, Scientific-Alphabetization, High-School research, Medicines, Medicinal-Plants*

## Highlights

Environmental and Social Relevance of Scientific Research of Usage, Stock and Disposal of Medicines and Medicinal Plants. The scientific investigations since the high school may improve the knowledge and perception of the students to the relevance of sustainable practices in several aspects. Since the professional application of medicinal plants until the disposal of industrial medicines, which can truly impact the nature, contaminating water and soil, promoting processes of environmental imbalance.

## Resumo/Abstract

This presentation unites two research developed with high-school students, supported by UNIFESO. One titled as "Awareness of the population about the correct usage, storage and proper disposal of medicines" and the second one, named "Biodiversity, chemical and medicinal aspects of the endemic and common flora from mountain region of Rio de Janeiro state". Both works discuss the proper handling with extracts of plants and industrial pharmaceuticals, by medical recommendation. Even with government guidelines about this subject, consulting the population through online forms, this research reveals low knowledge of the people (29,2% of respondents) about the correct disposal of those products. Still understanding their elimination in common waste can be harmful, people do not realize the real relevance of environmental imbalances, such as eutrophication, forced natural selection processes. Was also checked there are difficulties regarding proper storage of medicines and natural extracts (83,3% of respondents), recommended by health professionals. To illustrate the need of this properly storage, were made experiments using *Peumus boldus* extract and effervescent commercial C-vitamin, measuring their different aqueous solution concentration, using the Lambert-Beer law. Having not a spectrophotometer, these experiments were made taking pictures of the solutions and getting their RGB values at controlled ambience, obtaining the experimental constants by analytical lines. Two different conditions were runed: (i) sheltered from the sun, and (ii) exposed to the sun. Was verified the sun exposure produces rapid and intense degradation of all measured solution, as expected. All experiments were made with students. This approach aims increase the students, and their families', environmental consciences on this subject.



| Condition | (i) sheltered from the sun | | | (ii) exposed to the sun | | |
|---|---|---|---|---|---|---|
| Time (h) | 0 | 6 | 12 | 0 | 6 | 12 |
| C (mg/L) | **0,142** | **0,089** | **0,047** | **0,151** | **0,067** | **0,029** |
| Red (of RGB) | 176 | 201 | 223 | 172 | 212 | 233 |
| Transmittance | 0,690 | 0,788 | 0,875 | 0,675 | 0,831 | 0,914 |
| Absorbance | 0,161 | 0,103 | 0,058 | 0,171 | 0,080 | 0,039 |

Evaluation of concentration variation due to solution degradation under different conditions.

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## Agradecimentos/Acknowledgments

PICPq, UNIFESO, UFRJ, FAPERJ

**Área: AMB**

# Equilibrium isotherms and pH influence evaluation in atrazine adsorption process using activated carbon

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Palavras Chave: *Adsorção, agrotóxicos, isotermas de adsorção, atrazina, pH.*

## Highlights

This study is about a strategy to remove atrazine contaminated water using activated carbon. Also, it intends to evaluate the pH influence in the process and study the equilibrium isotherms.

## Resumo/Abstract

It is notable that research activities increased in the country not only for the significant portion of the economic contribution, but due to the fact that Brazil is considered the world's largest consumer of pesticides since 2009.Although the application of pesticides increases productivity, its intensive use and above the recommended doses often generates a set of negative consequences, such as impacts on human beings that go from simple nausea, headaches and skin irritations to chronic problems, as diabetes, congenital bad formations, changes in the endocrine system and several types of cancer. [1] Environmental impacts too are several, including contamination of water, plants and soil, decrease in the number of living organisms and increased pest resistance. Among the common abrasives found in Brazil, there is atrazine, and one technology to remove this contaminant in water bodies is adsorption.[2] Among the possible adsorbents to be used is powdered or granular activated carbon (AC). The AC isa porous material obtained from different raw and organic materials. In addition, it has a large surface area containing a variety of functional groups, responsible for its adsorption power. In this context, the objective of this work was to carry out adsorption experiments to remove atrazine from water bodies using activated carbon. In addition to carrying out equilibrium studies and evaluating the influence of different pH ranges on the process. The laboratorial experiments were done in several batches. A 1000mg/L atrazine solution was made to carry out all the following experiments: different concentrations (0,5; 1,0; 1,5; 2,0; 2,5; 3,0; 4,0; 5,0; 6,0 and 7,0 mg/L) tested in four different temperatures (20, 25, 35 and 45 °C). Also, five pH ranges were tested (4, 6, 7, 8 e 9). All the tests were developed with the same activated carbon weight: 0,038 g. The reactors were taken to the Dubnoff Bath SL-157, with agitation of 80 rpm for each one of the temperatures. After 12 hours of agitation, aliquots of each solution were filtered with a 0.45 µm pore syringe filter and conditioned and analyzed on LC-ESI-MS.About the pH tests, was observed that pH 4 had the best adsorption capacity (6,97 mg/g), followed by pH 6 (5,94 mg/g), pH 7 (5,9 mg/g), pH 8 (5,6 mg/g) and pH 9 showing the worst adsorption capacity (4,75 mg/g). The atrazine concentrations were monitored using LC-ESI-MS (LC 2020, Shimadzu®). Separation was carried out on a C18 VDSpher column (50 x 4.6mm x 5µm), mobile phase methanol and water (70:30). The monitored ion has a m/z ratio equal to 216 in positive mode. The analysis time was 7 min, and the method presented LOQ equal to 5 µg L-1, and linearity greater than 0.99. Having the results after this process was possible to make the equilibrium isotherms in two different models: Langmuir and Freundlich. Both models adjusted well to describe the isotherms but Langmuir model showed better results comparing the two models, with the respective values for $R^2$ for each one of the temperatures (20, 25, 35 and 45 °C): 0.92; 0.87; 0.91 and 0.97. Values for $R^2$ of Freundlich model were the following ones: 0.93; 0.86; 0.9 and 0,97. Considering these results, it's possible to attest that activated carbon is a successful alternative to remove atrazine from water bodies and for future tests, the pH 4,0 could be considered to carry out experiments, seeing that presented better adsorption capacity, as well the highest temperatures.

## Agradecimentos/Acknowledgments

Thanks to Universidade Federal da Fronteira Sul (UFFS) and Postgraduate Program of Environmental and Sustainable Technologies

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**Área: AMB** **Nº de Inscrição: 00340**

# Estrogenic hormones removal in a wastewater treatment plant (WWTP) using membrane bioreactor (MBR)

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Keywords: *Emerging Contaminants, Hormones, MBR.*

## Highlights

Quantification of estrogens in sewage
Removal rate and behavior of estrogens in a WWTP using MBR

## Resumo/Abstract

The presence of endocrine disruptors in the aquatic environment, especially natural and synthetic estrogens, has attracted the attention of researchers due to the impacts caused to organisms, such as damage to the reproductive system. In this context, the objective of the present study was to evaluate the occurrence, removal and space-temporal distribution of the estrogens at the Reuse Water Production Plant – RWPP Capivari II, (Campinas – SP) using a bioreactor coupled to membrane filtration (MBR). Samples collected monthly were filtered and the extraction of the analytes was performed using a solid phase extraction system. Estrogens were quantified using gas chromatography-mass spectrometry (GC-MS) and standard addition method. Estrogens concentrations (ng $L^{-1}$) in the raw sewage ranged from 157.90 to 1,502.80 for estrone (E1), 46.44 to 1,419.78 for 17-β-estradiol (E2) and 83.56 to 132.52 for 17-α-ethinylestradiol (EE2). The removal rate of the target compounds was calculated considering their concentrations in the raw sewage and in the effluent of the MBR. Average removals of 72.5%, 33.7% and 28.7% were found for compounds E2, EE2 and E1 respectively. In relation to the behavior of estrogens throughout the sewage treatment, it was possible to observe an increase in the concentration of the compounds in some biological tanks (Figure 1). In general, a large part of the estrogens excreted by humans are originally present in conjugated forms (glucuronides and sulfates), however, they are deconjugated by microorganisms during biological treatment and this may explain the increase in the concentration observed in some tanks. Another point to be noted is the behavior of estrone at the end of biological treatment. According to Alvarino *et al.* (2014), the increase in estrone concentration may be a consequence of the partial oxidation of other estrogenic hormones to estrone[1].

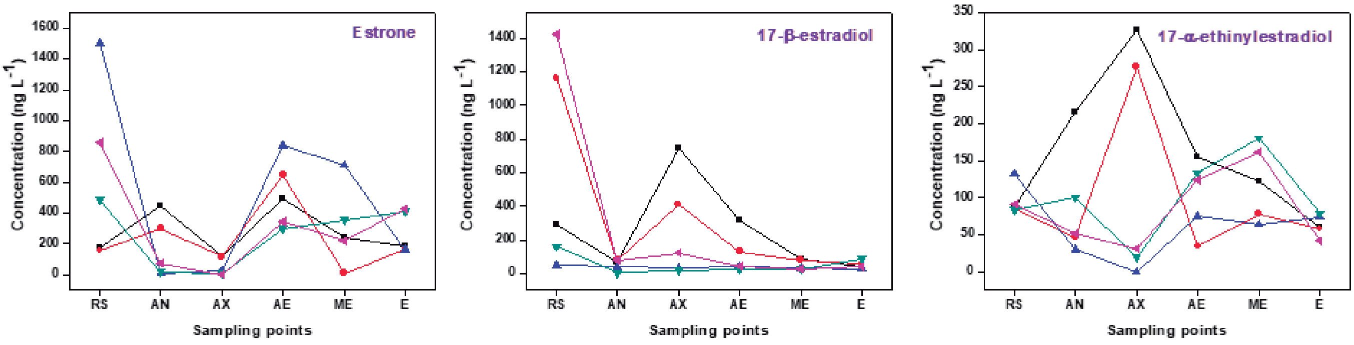

Figure 1- Behavior of estrogens during sewage treatment. RS: Raw Sewage; AN: Anaerobic Tank, AX: Anoxic Tank; AE: Aeration Tank; ME: Membrane Bioreactor; E: Effluent.

[1] Alvarino, T.; Suarez, S.; Lema, J. M.; Omil, F. Journal of Hazardous Materials, 278, 506–513, 2014.

## Agradecimentos/Acknowledgments

CAPES (1772630), CNPq (404086/2016-0, 305627/2018-0), FAPESP (2018/04820-6), INCTAA (CNPq 465768/2018-8 and FAPESP 2014/50951-4), Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES – Finance Code 001).

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

# Estudo dos principais íons solúveis em água presentes em material particulado (MP10) coletado na região urbana de Campos dos Goytacazes - RJ.

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Palavras Chave:*Poluição atmosférica, material particulado, cromatografia de íons, íons solúveis.*

## Highlights

Study of the main water-soluble ions present in particulate matter (PM10) collected in the urban region of Campos dos Goytacazes - RJ.
The characterization of the soluble ions associated with the particulate material was carried out
The identification of ions was performed by ion exchange chromatography.
There is evidence that fires cause an increase in the concentration of particulate matter when ions are present in the atmosphere.
This study enabled the identification of emission sources of the investigated ions.

## Resumo/Abstract

The municipality of Campos dos Goytacazes is characterized by the expressive cultivation of sugar cane, a culture that is still predominantly used here, the burning of its foliage to facilitate its harvest. Biomass burning is an important source of emission of atmospheric pollutants, such as particulate matter (PM), contributing thus to the increase of atmospheric pollutants. Therefore, the present work aims to evaluate the composition of the main water-soluble ions present in particulate matter ($PM_{10}$), collected in external atmospheres in the urban area of Campos dos Goytacazes-RJ, during harvest and off-season periods. of sugarcane. Samples were collected using a large volume sampler (HI-VOL). 27 samples were collected between June 2020 and October 2021 in which MP and ion gravimetric analyzes were performed. Analysis of ions (sodium, ammonium, potassium, magnesium, calcium, fluoride, chloride, nitrite, bromide, nitrate, phosphate and sulfate) were performed using an ion chromatograph. The general mean concentration of $PM_{10}$ was found to be 30 µg $m^{-3}$. Analyzing the harvest and off-season periods, higher average values were found in the harvest (31 µg $m^{-3}$ ) in relation to the off-season (25 µg $m^{-3}$ ). Between the 2020 and 2021 harvests, mean concentrations of 26 µg $m^{-3}$ and 36 µg $m^{-3}$ were found, respectively. The difference in PM concentrations was attributed to the increase in production in the 2021 crop compared to 2020, and to the lockdown carried out in 2020 due to the pandemic caused by the SARS-CoV-02 virus (Covid 19). In relation to ions, sodium and chloride showed significant concentrations in practically all samples, indicating a contribution of aerosols of marine origin throughout the analyzed period. Potassium, ammonium, nitrate and calcium ions showed a significant increase in the harvest period, the biomass burning in this period was indicated as the main source of these ions. Calcium was also associated with soil resuspension. The results of the calculations sulfate of non-marine origin and the ratio between nitrate and sulfate pointed the sulfate to its origin related to vehicle traffic. Pearson correlations and multivariate analysis using principal component analysis (PCA) indicated a good correlation between ammonium, sulfate and nitrate ions. Such correlation may be associated with secondary sources. The results obtained in this work were not sufficient for an in-depth statistical analysis. However, it was possible to identify the relationship between the harvest and off-season period and the soluble ionic composition of the $PM_{10}$ analyzed, demonstrating the impact on air quality caused by the burning carried out during the sugarcane harvest and other sources..

## Agradecimentos/Acknowledgments

CAPES, CNPq e FAPERJ

# Etanol, acetaldeído e metanol na água de chuva de diferentes cidades brasileiras

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Palavras Chave: *Emissão veicular, políticas públicas, queima de biomassa, produção de etanol*

## Highlights

**Ethanol, acetaldehyde and methanol in rainwater from different Brazilian cities**. The main source of ethanol, acetaldehyde and methanol in São Paulo and Curitiba appeared to be vehicular, while in Ribeirão Preto, ethanol distilleries and biomass burning can also be important sources. Forests can be an important source of methanol emission.

## Resumo/Abstract

Tabela 1: Média ponderada pelo volume (MPV) em μmol L$^{-1}$ de etanol, acetaldeído e metanol na água de chuva de diferentes cidades do Brasil

| Local | Etanol | Acetaldeído | Metanol |
|---|---|---|---|
| Ribeirão Preto<br>(n= 154) | 3,51 ± 0,17 | 0,65 ± 0,03 | 7,25 ± 0,18 |
| São Paulo<br>(n= 36 ) | 4,64 ± 0,38 | 0,74 ± 0,07 | 6,57 ± 0,39 |
| Curitiba<br>(n= 31) | 3,03 ± 0,23 | 0,42 ± 0,07 | 5,11 ± 0,24 |
| Cunha<br>(n= 5) | 1,35 ± 0,24 | 0,14 ± 0,10 | 6,50 ± 0,27 |
| Peruíbe<br>(n= 1) | 1,86 | 0,21 | 5,57 |

O uso e produção de etanol combustível tendem a aumentar no Brasil e no mundo, provocando um aumento na emissão de compostos oxigenados de baixa massa molar para atmosfera, incluindo aldeídos de elevada toxidade. O objetivo deste trabalho foi avaliar a concentração de etanol, acetaldeído e metanol na água de chuva de diferentes localidades do Brasil a fim de melhor compreender suas principais fontes. As amostras de chuva foram coletadas, com base em eventos, e analisadas por CG-FID - *Headspace* [1]. Na cidade São Paulo (SP) a MPV de etanol foi 32% maior do que em Ribeirão Preto (RP), e a de metanol 10% menor. A frota veicular de SP é cerca de 13 vezes maior do que a de RP, indicando que as emissões evaporativas das usinas de cana-de-açúcar da região são uma importante fonte de álcoois para atmosfera. Em Curitiba, as MPV de etanol e metanol na chuva foram significativamente menores (teste-t, $p < 0,05$) do que as concentrações de RP e SP, sendo a principal fonte regional, a emissão veicular. Em Cunha a amostragem foi feita a 1.019 m acima do nível do mar, em área de floresta, sem emissão veicular próxima, e a 20 km em linha reta do litoral, caracterizando as fontes biogênicas. A concentração de metanol em Cunha não diferiu dos grandes centros urbanos, demonstrando a importância da fonte biogênica desse álcool. Em Peruíbe, no momento da chuva, as trajetórias das massas de ar foram de origem marinha, minimizando as emissões veiculares locais. As concentrações de etanol e acetaldeído nas chuvas próximas da costa foram marcadamente menores do que em cidades mais urbanizadas. A série temporal de etanol na água de chuva de RP mostrou que nos últimos 10 anos, a MPV anual diminuiu em 0,35 μmol L$^{-1}$ ano$^{-1}$, apesar de ter havido um aumento de 20% na frota veicular da região metropolitana. Isso indica que a melhora no processo tecnológico de combustão pode ser responsável por tal redução. A emissão de etanol durante a queima de biomassa e a produção industrial podem ser as causas das maiores concentrações médias dessa espécie nas chuvas do período seco em RP, quando também ocorrem o maior número de focos de incêndio.

[1] GIUBBINA, F.F. et al. **Analytical Methods**, 9, 2915–2922, 2017.

[2] CETESB, dados de frota veicular 2021.

## Agradecimentos/Acknowledgments

Agradecemos à Fapesp (2018/16554-9; 2018/17931-0) e à CAPES.

# Etanol e acetaldeído na atmosfera de São Paulo e Ribeirão Preto

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Palavras-chave:*potencial de formação de ozônio, emissão veicular, oxidação fotoquímica, produção de etanol*

## Highlights

**Ethanol and acetaldehyde in the atmosphere of São Paulo and Ribeirão Preto.** Concentrations of atmospheric ethanol and acetaldehyde in Ribeirão Preto were greater than in São Paulo, despite the discrepancy on the size of the vehicular fleet. These results demonstrated the importance of theemissionsby the sugarcane industry and biomass burning. Photochemical oxidation is an important sink of ethanol and source of acetaldehyde, leading to an increase on the ozone potential formation.

## Resumo/Abstract

As consequências do uso de etanol combustível para a saúde humana ainda são desconhecidas, tendo em vista a produção de aldeídos de elevada toxicidade, a formação de ozônio e nitrato de peroxiacetila.O objetivo deste trabalho foi investigar a concentração e o comportamento diurno do etanol e acetaldeído na atmosfera de Ribeirão Preto (RP) e de São Paulo (SP). As amostras na fase gasosa foram coletadas nos anos de 2019 e 2020 nos*campi* da USP de Ribeirão Preto ede São Paulo, utilizando o método do condensado[1]. As análises foram realizadas por CG-FID-*Headspace*[2].Os perfis diurnos observados nas cidades de SP e de RP foram semelhantes (Figura 1), demonstrandoque houve formação fotoquímica de acetaldeído pela oxidação do etanol, que foi corroborada pelo perfil da intensidade da radiação solar em RP. Elevadas concentrações de etanol foram observadas em dias com intensa queima biomassa na região de RP. Embora a frota automotiva de SP seja ~ 13 vezes maior do que a de RP, as concentrações médias de etanol e acetaldeído na atmosfera de RP foram maiores (Tabela 1), demonstrando que as emissões evaporativas das usinas de cana-de-açúcar da região e a queima de biomassa podem ser importantes fontes dessas espécies para atmosfera.Opotencial de formação de ozônio (PFO) em RP foi até 3x maior do que em SP, revelando a importância dese conhecer principalmente a concentração de acetaldeído na atmosfera urbana para inferir a qualidade do ar e consequências para a saúde humana.

Figura 1: Etanol (EtOH) e acetaldeído (AA) na fase gasosa (ppbv) nas cidades de SP e RP

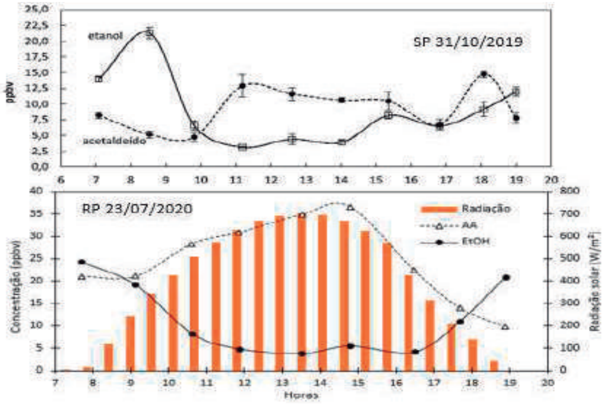
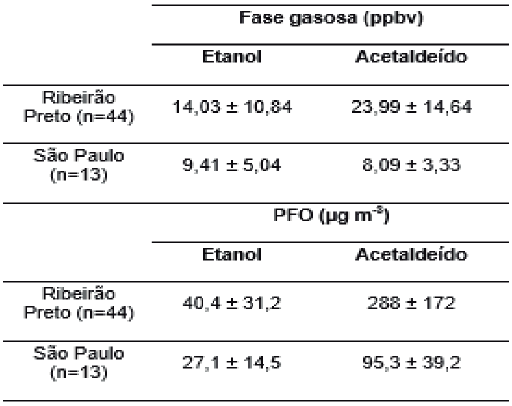


Tabela 1: Concentração média de etanol e acetaldeído na fase gasosa de SP e RP (ppbv) e potencial de formação de ozônio



| | Fase gasosa (ppbv) | |
|---|---|---|
| | Etanol | Acetaldeído |
| Ribeirão Preto (n=44) | 14,03 ± 10,84 | 23,99 ± 14,64 |
| São Paulo (n=13) | 9,41 ± 5,04 | 8,09 ± 3,33 |
| | PFO (μg m$^{-3}$) | |
| | Etanol | Acetaldeído |
| Ribeirão Preto (n=44) | 40,4 ± 31,2 | 288 ± 172 |
| São Paulo (n=13) | 27,1 ± 14,5 | 95,3 ± 39,2 |

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[2] GIUBBINA, F.F. et al. **Analytical Methods**, 9, 2915–2922, 2017.

## Agradecimentos/Acknowledgments

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**Área: Química Ambiental**
*SBQ*

# Evaluation of larvicidal potential of fatty acids obtained from palm oil deodorization distillate residue.

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Palavras Chave: *Óleo de palma, atividade larvicida, resíduo agroquímico.*

## Highlights

Organic compounds with larvicidal activity to control mosquitoes are generally formulated using synthetic compounds such as pyrethroids. However, most of these synthetic substances have adverse effects. The Amazon region is an important source of plants that produce different vegetable oils, and these are used by the local population to treat diseases. Among these oils, palm oil and its residues during the extraction process, DDPO (palm oil deodorizing distillate), has been gaining attention because it is easy to obtain, cheap and highly available in the region. DDPO is a bioproduct obtained during the physical refining of crude palm oil, rich in compounds with high added value. Samples of esters of DDOP, DDOP and standard fatty acids (myristic and stearic) were prepared with 100 µg/mL concentrations for larvicidal tests in A. aegypti. Five replications were performed, with ten larvae each. The larval mortality rate was determined after 24 h and 48 h of incubation. From the larvicidal test in Ae. aegypti, it was found that DDOP and its fatty esters, as well as standard fatty acids (myristic and lauric) showed high larvicidal action at 24 and 48 h at 100 µg/mL.

## Resumo/Abstract

Aedes aegypti is the vector that causes several diseases such as yellow fever, chikungunya, dengue and Zika, and for this reason it has been a public health problem in recent decades, especially in Brazilian urban centers [1]. The remaining method of controlling the propagation of this vector is the use of synthetic insecticides such as organophosphates, organochlorines and others [2]. However, the frequent use of these products has shown problems such as damage to the environment and human health, in addition to the emergence of populations of mosquito larvae resistant to these insecticides. In this context, in the search for low-cost natural products that can be used as larvicides against Aedes aegypti to control dengue transmission, as well as its potential use, distilled palm oil (DDPO) was tested under laboratory conditions on larvae. of this mosquito. This raw material was chosen because it is highly available and Brazil is among the largest palm oil producers in the world.

Larvicidal activity was performed from fatty acids and fatty amides a from DDOP. Thus, samples of DDOP ethyl esters, DDOP residue and standard fatty acids (myristic, lauric, oleic and palmitic) were prepared with 100 µg/mL concentrations for larvicidal tests in A. aegypti. They were performed in quintuplicate, with ten larvae in each experiment. Water and DMSO were used as negative controls. The larval mortality rate was determined after 24 h and 48 h of incubation (25 °C and 75% humidity). Larvae were considered dead when they did not respond to stimuli or did not rise to the surface of the solution, unlike those observed in the control. The experiments were conducted in accordance with the 2005 WHO guidelines

From the larvicidal test in Ae. aegypti, it was found that DDOP and its fatty esters, as well as standard fatty acids (myristic and lauric) showed high larvicidal activity at 24 and 48 h at 100 µg/mL. The DDOP presented mortality of 80% after 24 h and after 48 h, it was observed that the mortality reached 100%. Myristic fatty acid and lauric fatty acid presented 85% and 100%, respectively, of larvicidal mortality in Ae. aegypti in 24h. In contrast, a negative control consisting of water only showed no larvicidal action.

Such preliminary results demonstrate that DDOP residue can be an economically viable alternative for larvicidal action in Ae. aegypti, due to its low cost and good larvicidal action.

## Agradecimentos/Acknowledgments

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**Área: AMB**

# Evaluation of the environmental availability of potentially toxic metals in Zn-C batteries wastes using the sequential extraction scheme

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*Keywords: Batteries wastes, Potentially toxic metals, Sequential extraction scheme.*

## Highlights

The improper waste disposal may bring about health hazard. Zinc presented the highest mobility under acid conditions. Thermal treatment considerably reduced zinc availability in acid-soluble fraction.

## Resumo/Abstract

According to the Brazilian Association of Electrolytic Industry (ABINEE), the production of batteries increased more than 11% in 2021.[1] Nevertheless, these products contain potentially toxic metals and their incorrect discard could lead to contamination of the air, water tables, soils and in the end, reach the food chain resulting in risks to human health.[2] Aiming to raise citizen awareness and to minimize these negative impacts, CONAMA has published the 401/2008 resolution that established limits for Cadmium, Lead, Mercury and their compounds. However, even in accordance with the resolution, the batteries have potentially toxic metals, some of them not covered by the legislation, which can cause environmental impacts and health damage. Therefore, it is still important to develop recycling programs and to raise awareness of the appropriate discard of these objects. The sequential extraction schemes (SES) are used to evaluate the environmental availability of metals, since studying only the total concentration of the metals does not give information about in which form they are presented and how they are linked to the matrix. A protocol recognized internationally is the Community Bureau of Reference (BCR) that has four steps: Acid-soluble ($CH_3CO_2H$), Reducible ($NH_2OH.HCl$), Oxidizable ($H_2O_2$ + $NH_4CH_3CO_2$) and Residual ($HNO_3$ + HF), simulating environmental conditions increasingly drastic.[3] The objective of the present study is to understand the availability of potentially toxic metals in batteries wastes using the sequential extraction method BCR (adapted) with further quantification in inductively coupled plasma optic emission spectrometry (ICP OES). A thermal treatment was also applied to understand how this could affect the availability studied. Zn-C AA batteries of cylindrical format were used in the study because they are the most common. In the sequential extraction scheme, the concentrations of Lead were below the first analytical curve point (0.001 mg $L^{-1}$). The concentrations of Cadmium were below the first analytical curve point (0.001 mg $L^{-1}$) in the total digestion step and, then, in all the sequential steps too. Figures 1 and 2 showed that Zn presented the highest mobility and availability to be extracted under natural soil conditions (acid-soluble) while the other elements require more drastic conditions. This study reinforces the importance of the correct destination of battery wastes which are discarded in regular trash.

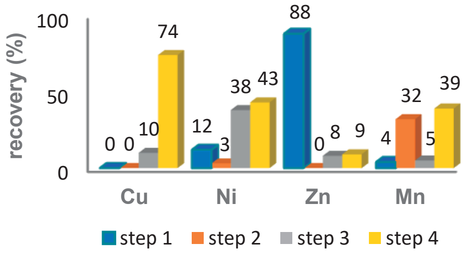

Figure 1. Recovery of each metal in each step for the battery without thermal treatment.

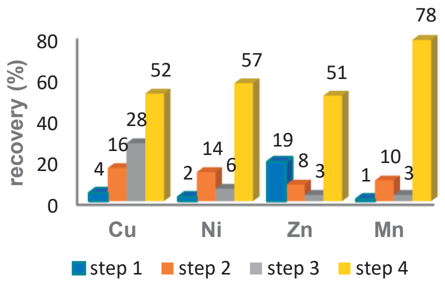

Figure 2. Recovery of each metal in each step for the battery with thermal treatment.

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3. MARIN et al. Analytica Chimica Acta, v. 342, p. 91-112, 1997.

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**Área: AMB** **Nº de Inscrição: 00512**

# EVALUATION OF ULTRAFILTRATION SYSTEMS FOR NATURAL WATERS IN AMAZON: SOLID PARTICLES, ORGANIC AND BIOLOGICAL CONTAMINATION

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Keywords: ultrafiltration system, biological contamination, coagulation, Amazon.

## Highlights

The inorganic and organic coagulants used with ultrafiltration membrane were efficient in removing turbidity and suspended solids in natural waters in Amazon. Organic coagulation + ultrafiltration was efficient in removing organic compounds. The studied system can be used by "riverside communities" along the banks of the Amazon River.

## Resumo/Abstract

Na região Norte, a população convive com uma realidade onde 67 % dos domicílios não têm rede de esgoto e 45 % não têm rede de abastecimento de água. Parte desta população, denominadas "comunidades ribeirinhas", estão estabelecidas ao longo das margens do rio Amazonas (Rio AM) ou de seus afluentes. A região amazônica no geral, vive em um contraste onde existe uma enorme disponibilidade hídrica, porém com carência de água para consumo humano, em especial para as comunidades que estão a grandes distâncias, considerando as dimensões amazônicas. Nesse sentido, o presente trabalho tem um papel importante ao avaliar a eficiência de sistemas alternativos para tratamento de águas naturais com elevada carga de sólidos, tal como no Rio AM. Inicialmente, montou-se o protótipo do sistema de tratamento de água com duas etapas, coagulação seguida de ultrafiltração, no laboratório da Universidade Federal do Amazonas, no Instituto de Ciências Exatas. O estudo deu-se com dois tipos de coagulantes (inorgânico/$Al_2(SO_4)_3$ e orgânico natural/Tanfloc-SG), seguida de filtração em uma membrana de ultrafiltração modelo RX-3001.5 UFC. Antes da avaliação dos parâmetros químicos e biológicos, foram realizados testes de jarros em amostras de água do Rio AM para definição da quantidade de coagulante, agitação e tempo de sedimentação. Fez-se também o ajuste de vazão e rendimento de água tratada. Após a obtenção das melhores condições de trabalho do sistema, deu-se os testes de eficiência usando os seguintes parâmetros: pH, condutividade elétrica, turbidez, oxigênio dissolvido, salinidade, sólidos em suspensão total (SST), remoção de bactérias termotolerantes (*E. Coli*) e remoção de substâncias orgânicas (adicionou-se cafeína e o pesticida diuron nas amostras). As condições de trabalho, bem como alguns resultados dos parâmetros estudados nas águas antes e depois de passar no sistema proposto, estão dispostos nas Tabelas 1 e 2.

**Tabela 1: Condições de funcionamento do sistema.**

| Dados Q das bombas | | Condições de coagulação |
|---|---|---|
| **Q** entrada (sensor 1) (L/h) | 421 | ≅10 mL de $Al_2(SO_4)_3$) / L<br>≅ 8 mL de C.ORG. / L<br>+ agitação rápida + agitação lenta + 40 – 60 min (floculação/decantação) |
| **Q** saída (sensor 2) (L/h) | 372 | |
| **Q** filtração (L/h) | 78,9 | |
| **Tempo** filtração (min.) | 10 | |

* Q = vazão

O sistema de ultrafiltração+coagulante natural à base de tanino, apresentou 100 % de remoção da turbidez, SST, microrganismo e remoção 84 % do pesticida.

**Tabela 2: Resultados dos testes de eficiência (E%) do sistema de ultrafiltração com coagulante natural [(A)] e inorgânico [(B)] em águas do Rio AM.**

| Parâmetros | Rio AM (Antes)[(A)] | Rio AM (Depois) [(A)] | E % | Rio AM (Antes) [(B)] | Rio AM (Depois) [(B)] | E % |
|---|---|---|---|---|---|---|
| Condutividade (µS) | 34,2 ± 0,1 | 45,6 ± 0,1 | + 33 | 62,8 ± 01 | 109,7 ± 1,3 | + 75 |
| Turbidez (NTU) | 28,8 ± 1,3 | 0,0 ± 0,0 | 100 | 202,7 ± 7,5 | 0 ± 0 | 100 |
| pH | 7,53 ± 0,06 | 7,53 ± 0,12 | NA | 7,45 ± 0,11 | 5,10 ± 0,26 | - 31 |
| Microbiológicos NMP/100 mL | 5<13<38 | < LQ < 2 | > 95 | 16<34<80 | < LQ < 2 | > 95 |
| Sólidos em Susp. Totais (mg/L) | 19,83 ± 0,01 | 0 ± 0 | 100 | 15 ± 0 | 4 ± 2,8 | 73 |
| Subs. Orgânica ng L | **43,19 ± 0,79 | 6,70 ± 0,1 | 84 | *19,06 ± 0,37 | *17,38 ±0,18 | 9 |

* cafeína, ** diuron

## Agradecimentos/Acknowledgments

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**Área: AMB**

# APLICAÇÃO DE RESÍDUOS DE CRIAÇÃO DE CAMARÃO EM FORMULAÇÕES DE FERTILIZANTES DE LIBERAÇÃO LENTA

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Palavras-Chave: *Fertilizante de liberação lenta, Montmorilonita, Ureia, Solo, Sustentabilidade ambiental*

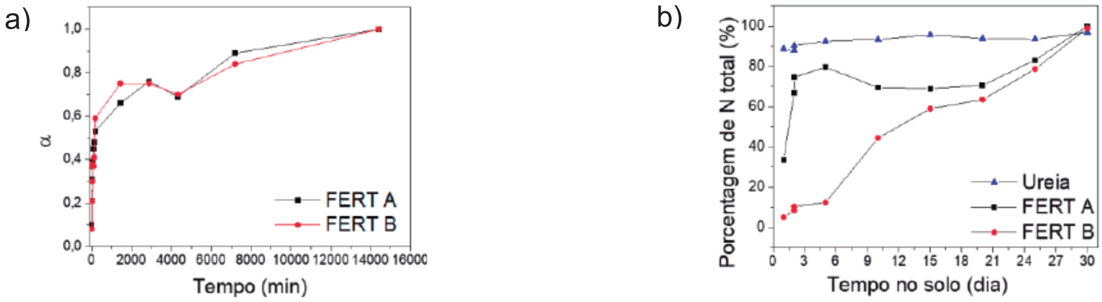
## Highlights

FEASIBILITY OF WASTES FROM SHRIMP PONDS IN SLOW RELEASE FERTILIZER FORMULATIONS
Fertilizers produced with waste from shrimp ponds;
Slow-release profiles of the fertilizers in water and soil.

## Resumo

A carcinicultura é um dos setores produtivos que mais cresce e contribui com o abastecimento mundial de pescado. Seus resíduos sólido e líquido são ricos em nutrientes e materiais orgânicos provenientes da ração, excreções do camarão e fragmentos de animais.[1] O descarte desses resíduos gera danos ambientais, tais como eutrofização e degradação dos solos produzindo problemas econômicos. Logo, é de grande importância desenvolver técnicas capazes de reinserir os resíduos na cadeia produtiva, fortalecendo a premissa do desenvolvimento sustentável da carcinicultura, por conta da sua importância econômica e social. Assim, neste trabalho foi sintetizado diferentes fertilizantes de liberação lenta empregando o resíduo sólido da carcinicultura com quitosana, montmorilonita e ureia como estratégia para uma agricultura sustentável. As esferas de fertilizantes (FERT A e FERT B) foram produzidos seguindo o método de gotejamento em uma solução de KOH 1 mol $L^{-1}$. A ureia foi utilizada como fonte de nitrogênio em todos os fertilizantes. As esferas de fertilizantes foram caracterizadas por análise elementar (CHN), obtendo-se 14,4 - 18,4 % de C, 5,6 - 6,9% de H e 12,3 - 19,3 % de N. Os fertilizantes apresentaram razões C/N baixas de 1,0-1,50, todavia, os valores obtidos são semelhantes ao do fertilizante mais utilizado na agricultura brasileira, a ureia (C/N 0,87).

Fig. 1: a) Perfis de liberação lenta da ureia nos fertilizantes FERT A e FERT B em água destilada; b) Porcentagem de liberação de N total no solo pelos fertilizantes FERT A, FERT B e ureia em 30 dias de incubação.



Os testes de liberação na água (Fig. 1*a*) mostraram que os fertilizantes liberam ureia de forma lenta, atingindo o máximo após 5 dias (95-97%). Os dados cinéticos da liberação de ureia em água, ajustaram-se ao modelo de cinético de Higuchi, indicando que o mecanismo de liberação ocorreu por difusão Fickiana. No estudo de liberação no solo (Fig. 1*b*) observa-se que os primeiros três dias de incubação no solo, a liberação de N foi menor que 32% e 10% para o FERT A e FERT B, respectivamente. E ainda, com 25 dias de incubação os fertilizantes apresentaram uma liberação de N inferior a 78%, corroborando para a afirmação de liberação lenta dos nutrientes pelos fertilizantes produzidos. Os fertilizantes FERT A e FERT B podem ser vistos como potenciais fertilizantes de liberação lenta de nitrogênio no solo, contribuindo para a minimização de problemas econômicos e ambientais. Além disso, foi mostrado que é possível a aplicação de resíduos da carcinicultura na formulação de fertilizantes de liberação lenta, se constituindo numa proposta real de reaproveitamento do setor industrial da carcinicultura, para liberação de nutrientes para as plantas.

## Agradecimentos

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

# From biomass to fuels: a novo carbon-efficient route

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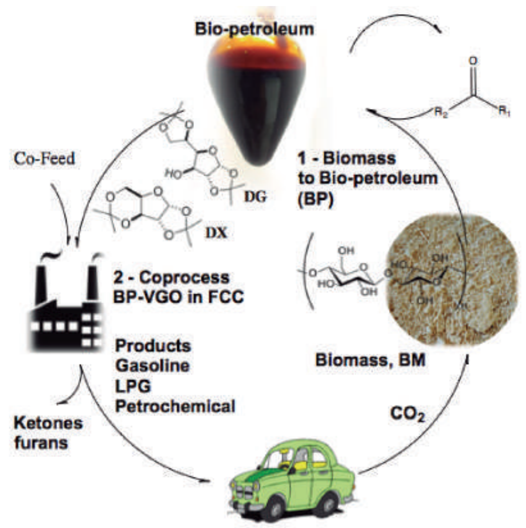
key-words: *Carbon-footprint, Refinery, Biomass, Green-fuel, Sugar, Ketal*

## Highlights

Biomass introduction into a refinery. Green products like GLP, gasoline, jet fuel, diesel, light olefin, and BTX. High efficiency (green carbon efficiency >70%) and low-cost route.

## Abstract

One of the greatest challenges to Science is to balance energy production with the carbon footprint. Beyond avoiding climate change, only renewable energy sources can provide energy for our and future generations[1]. The amount of second-generation biomass can support the entire production of green-fuel and petrochemical inputs [2] as fuel consumes ≈¼ of worldwide energy. Our proposed circular technology, figure 1, initiates with a mild ketalization of second-generation biomass to give a liquid product BP which shows feasible physical-chemical properties for subsequent transformation (density 1.2 g.cm$^{-3}$, viscosity 200 cp (60 °C), specific heat 1.8 J g.°C$^{-1}$). As detailed in our publications, it is composed mainly of ketal-sugar derivatives, composition $\approx C_{2n}H_{3n}O_n$ (ranges $C_{1.4-2}H_{2.2-2.9}O_1N_{0.007}$) [3]. BP and representative compounds like DG and DX (fig 1) can be transformed into aromatics [4-6], paraffins, isoparaffins, and cycloalcanes[7-9] with high yields and low coke amount. The flexibility to be converted in typical refinery processes to various products strongly suggests that BP could progressively substitute mineral oil. Hence, the oil refinery can benefit from reducing its carbon footprint. Further research and developments to approach zero net-carbon fuels will have great impacts and demands in advances in chemistry and especially in heterogeneous catalysis. In conclusion, our approach can be a secure transition in the structure of the matrix of energy to reduce carbon footprint and circumvent oil depletion. **Figure 1:** Circular economy of biomass to fuel in two steps. **Step 1**- BP production in mild condition (temperature from 90-140$^{o}$C, mineral acid from 0.1-0.4 wt.%, flexible to carbonylate type, like acetone and 2,5-hexadione for example, pressure varies in function of temperature and type of carbonylate, from room to 7 atm). **Step 2** – BP and example of representative compounds **DG**; 1,2:5,6-di-O-isopropylidene-α-D-glucofuranose and **DX**; 1,2:3,5-di-O-isopropylidene-α-D-xylofuranose are converted to value products. For instance, BP mixture with vacuum gasoil (VGO) in a typical fluid catalytic cracking process conditions gives drop-in fraction in gasoline and liquefied petroleum gas (LPG), petrochemicals, and oxygenates (ketones can be recycled to prepare BP, furans derivatives used as gasoline booster).



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To FAPERJ, CAPES and CNPq

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**Área: AMB**

# IDENTIFICAÇÃO DE FONTES E AVALIAÇÃO DE RISCO DE ESPÉCIES ORGÂNICAS NO MATERIAL PARTICULADO FINO EM ATMOSFERA URBANA

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*Palavras-Chave: Poluição atmosférica, Material particulado, Hidrocarbonetos Policíclicos Aromáticos, Emissões veiculares.*

## Highlights

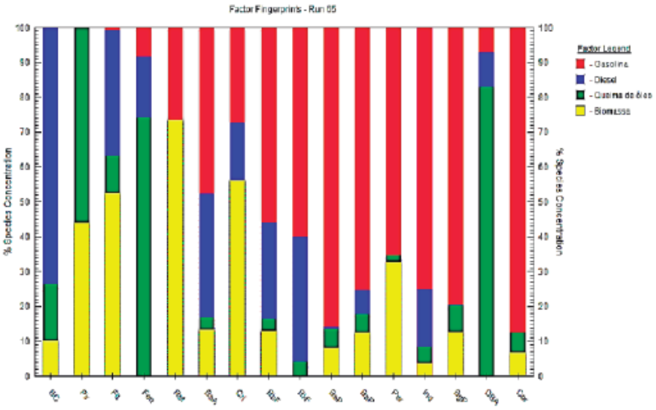
### Source identification and risk assessment of organic species in fine particulate matter in an urban atmosphere.

PAHs, Nitro-PAH and Oxy-PAH were determined in an urban area.
High molecular weight PAHs indicated influence on vehicular emissions.
The estimated risk of lung cancer was estimated at 1 ng m$^{-3}$.

## Resumo/Abstract

As atividades antrópicas, por meio de diversas ações tornam a atmosfera receptora de mistura complexa de substâncias orgânicas e inorgânicas. O presente estudo teve como objetivo investigar as concentrações de material particulado, *Black Carbon*, hidrocarbonetos policíclicos aromáticos (HPA), incluindo derivados nitrados e oxigenados. As amostragens ocorreram às margens da rodovia PR 445, próxima à área urbana de Londrina, no período de maio de 2017 a agosto de 2018, utilizando amostradores de alto volume. Dispositivos de extração miniaturizados foram utilizados para a extração de HPA e derivados, seguida de análise por CG / EM, que identificou 41 compostos. A variabilidade sazonal mostrou concentrações mais elevadas no período de baixa precipitação pluviométrica. Observou-se que as concentrações de *black carbon* apresentou redução de até duas vezes em relação a estudos anteriores realizados em diferentes pontos de Londrina. As concentrações médias de HPA variaram de 0,2 ng m$^{-3}$ (Antraceno) a 2,5 ng m$^{-3}$ (coroneno), os nitro-HPA variaram (0,3 a 3,6 ng m$^{-3}$) para 4-nitrobifenil e 2-nitrofentreno respectivamente. Os oxi-HPA (quinonas) encontradas foram 1,4-Naftoquinona, 9-Fluorenona, 9,10-Antraquinona, 2-Metilantraquinona e Benzo(a)antraquinona, com variação entre 0,3 ng m$^{-3}$ (1,4-NQ) a 4 ng m$^{-3}$ (9,10-AQ), sendo as mais abundantes. Valores esses iguais ou superiores aos observados em grandes centros, evidenciando a necessidade de estudos abrangentes e implicações na qualidade do ar. Aplicando o cálculo de razões diagnósticas (RD), os resultados demonstraram indicação de diferentes fontes de emissão de HPA e derivados. Nota-se, de maneira geral, que o local analisado apresenta predomínio de fontes pirogênicas em relação às fontes petrogênicas de HPA.

**Figura 1 -** Contribuição quantitativa das fontes identificadas por fatoração de matriz positiva - PMF



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**Área: AMB**

# Indoor air distribution of organic compounds from library in Rio de Janeiro, Brazil

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Palavras Chave: *library, indoor air, VOC, furfural,air, pollution*

## Highlights

Indoor air distribution of organic compounds from library in Rio de Janeiro, Brazil, alert managers of libraries in advance about the impact that indoor air quality.

## Resumo/Abstract

Libraries are specific environments that have controlled parameters such as relative humidity to prevent the proliferation of fungi and conserve works of art. In these environments, it is also necessary to control pests such as termites, cockroaches, rats and others, consequently generating the use of chemical products (organic compounds). In addition, books, theses and documents are made with different materials, paints, preservatives, etc. All of these conditions affect emissions of gases and particles into the atmosphere, as well as secondary reactions. Degradation of cellulose-based materials, such as paper, emits a variety of organic compounds (Lattuati-Derieux et al.2006; Dupont et al. 2007). Although there are many libraries in the world frequented by thousands of people, few studies assess air quality in these environments. The objectives of this study are to identify and quantify organic compounds present in the air indoor and outdoor and trace the profile of pollutants and their possible sources. Organic aerosol samples of indoor and outdoor air samples in nine sites in a library in Rio de Janeiro, Brazil. The compounds were analyzed by Gas Chromatography with Flame Ionization Detector (GC-FID) and Gas Chromatography–Mass Spectrometry (GC-MS). *n*-alkanes from C$_{15}$ to C$_{36}$ were quantified with C$_{max}$ varying between C$_{22}$, C$_{24}$ and C$_{29}$, presenting a bimodality that indicates anthropogenic and biogenic source ranging from 4.12– 44.55 ng / m$^3$. Aromatic fraction such as a series of phthalates (markers of plastics) ranging from 0.09–712.0 ng / m$^3$, polycyclic aromatic hydrocarbons (PAHs) ranging from 0.03-1.20 ng / m$^3$ and Dichlorodiphenyldichlorethylene (DDE), 1-Chlorine-2,2-bis (4-chlorophenyl) ethylene (DDMU), dichlorodiphenyltrichloroethane (DDD) and Dichlorodiphenyltrichloroethane (DDT) were found to range from 0.03-0.41ng / m$^3$. Pesticide was common in libraries to combat pests that degraded paper, the so-called bibliophage insects (Sacramento et al., 2015). In the fraction of polar compounds, a homologous series of aldehydes ranging from C$_7$ to C$_{17}$ (0.01–1.79ng / m$^3$), and vanillin (0.01-0.65 ng/m$^3$). Acids that are substances that can oxidize books and other exposed objects were identified at concentrations ranging between 0.01 and 30.26 ng m$^{-3}$, while furfural, that is a recognized marker of paper degradation, was regularly present at concentrations that ranged from 0.5 to 3.6 g m$^{-3}$. Compounds such as furfural, hexanal, benzaldeyde, vanillin were detected only indoor, which are originated from lignin degradation processes. It was interesting the presence of 1,1,1-trichloro-2,2-bischlorophenylethane (DDT) and its derivatives. Pesticides were used in libraries to combat paper-degrading pests. Therefore, DDT and other chemicals remain undegraded polluting the library rooms. This work shows the relevance of monitoring indoor air quality in libraries and the pollutants that can affect the well-being of the occupants

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**Área: AMB**

# Influence of the nanotube size grown on Ti-0.5W (wt.%) alloy on the mineralization of the fungicide carbendazim by photoelectrocatalysis

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Key Words: *Carbendazim degradation, nanotubes size, pollutant mineralization, Ti-O-W nanotubes, Ti-W alloy*

## Highlights

The CBZ mineralization is influenced by nanotube dimensions.

The wall thickness decreased with the increase of the anodization time.

NT/Ti-0.5W–6.0 μm showed higher mineralization efficiency for CBZ.

## Resumo/Abstract

The composition and dimension of the nanotubular oxides (lenght and wall thickness) may influence the efficiency of the photocatalytic processes on the degradation and mineralization of organic emerging pollutants. Then, the aim of this work was evaluate the relation between the dimensions of the self-organized nanotubes grown on Ti-0.5W (wt.%), such as length, inner diameter and wall thickness, and the degradation / mineralization of fungicide carbendazim (CBZ). Ti-0.5W (wt.%) alloy, with 54 $cm^2$ exposed area, was submitted to anodization process in order to obtain nanostructured Ti– O – W films using an organic electrolyte of ethylene glycol containing 0.2 mol $L^{-1}$ HF + 10 % $H_2O$. For this process, it was applied a constant potential at 120 V during a time that varied between 5 and 25 min to produce nanotubes with different sizes. The substrate anodized for 5 min produced nanotubes with a shorter length (1.0 μm) and thicker walls than the one anodized for 25 min. For long anodization time, the length of the nanotubes reached 6.0 μm. After the anodization process, the nanotubular oxide layers were submitted to heat treatment at 450 ºC for 150 min to obtain crystalline phases of $TiO_2$ (anatase and rutile) and tungsten oxides. The photoanode morphologies and crystalline phases were investigated by scanning electron microscope and X ray diffraction, respectively, and the nanostructures were measured using a software for processing images. Electrochemistry techniques (chronoamperometry and linear voltammetry) were applied to measure of electrode stability and photocurrent, using a solution containing 0.1 mol $L^{-1}$ $Na_2SO_4$, under a potential range from -0.025 to – 1,0 V vs. Ag/AgCl/Cl (3M). Finally, the photocatalytic/photoelectrocatalytic experiments of CBZ degradation were carried out in a tubular reactor with recirculation of the solution under UV-Vis irradiation of 1 sun (100 mW $cm^{-2}$). The mineralization and degradation rates were monitored by Total Organic Carbon and High Performance Liquid Chromatography, respectively. The NT/Ti-0.5W-1.0 μm presented a higher photocurrent than NT/Ti-0.5W-6.0 μm due to its greater photoactive mass in relation to thinner nanotubes. However, on the CBZ degradation, both nanotubes exhibited similar photocatalytic performances, reaching CBZ total degradation after 120 min. But, the NT/Ti-0.5W-6.0 μm presented high mineralization percentage when compared to NT/Ti-0.5W-1.0 μm due to its better interaction with the by-products in function the larger inner diameter that facilitated the entrance of bigger molecules and consequently their degradation/mineralization.

## Agradecimentos/Acknowledgments

**Área: AMB** **Nº de Inscrição: 00465**

# It's raining emerging contaminants!

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Keywords: *Pesticides, Dry and Wet Deposition, Rainwater, Microplastics.*

## Highlights

Few studies about contaminants in rainwater are found in the literature. Emerging contaminants can be transported in the atmosphere for long distances. Microplastics are ubiquitous in the environment.

## Abstract

Four samplers were installed in different cities in the state of São Paulo (Brotas, Campinas, São Paulo, and Ubatuba). Rainwater samples were collected between August/2019 and December/2019 into glass funnel placed above a 1 L amber glass bottle (Figure 1). Overall, 17 samples were collected through dry and wet deposition sampling. The samples were filtered through cellulose acetate membranes of 0.22-0.45 µm pore size. A solid phase extraction (SPE) method of the emerging contaminants compounds was applied. The SPE used 500 mL of sample, Oasis HLB cartridges, 5 mL of methanol and 5 mL of water for the conditioning followed by elution with 4 mL of methanol and 4 mL of acetonitrile. The eluate was concentrated until dryness with nitrogen and reconstituted with 500 µL of mobile phase. Nineteen compounds were quantified by liquid chromatography (LC) coupled to a mass spectrometer in tandem (MS/MS). Laboratory blanks were performed to verify that no cross-contamination are added to the samples during the laboratory procedures. Internal standards (Atrazine-d5, Fipronil-C13 and 2,4-D-C13) were used to quantify the analytes. The limits of quantification (LOQ) ranged from 0.5 ng $L^{-1}$ to 5 ng $L^{-1}$. Frequency of detection were higher than 82% for most compounds. For Imidacloprid and Simazine these frequencies were 29% and 6%, respectively. Emerging contaminants concentrations ranged from 1 to 223 ng $L^{-1}$ (Figure 2). For microplastic analysis, cellulose acetate membranes were visually inspected for presence of microplastics. Particles higher than 40 µm (smallest particle visible to the bare eye) were not observed. These samples will be analyzed by other analytical techniques, such as micro-ATR and micro-Raman.

Figure 1. Rainwater sampler.

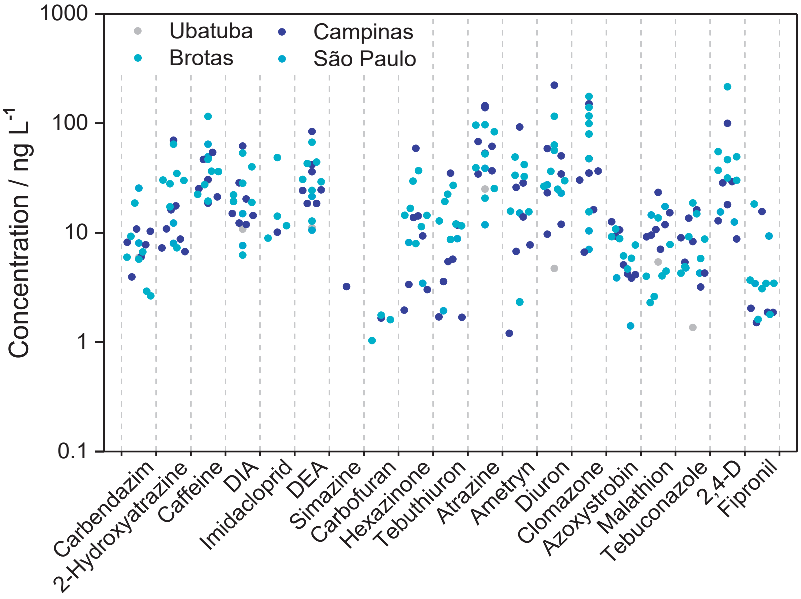

Figure 2. Emerging contaminants concentrations in rainwater.

## Acknowledgments

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2018/21733-0

**Área: ________AMB_______**

# kapok pod as a green adsorbent for removal of rhodamine b from water

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Keywords: *Biosorption, low-cost adsorbent, persistent pollutants, treatment of colored effluents.*

## Highlights

- Morphological structure of the material suggests high adsorptive potential; - Functional groups characteristic of lignocellulosic materials; - Rhodamine B adsorptive removal up to 93%.

## Abstract

The irregular disposal of residues and tailings from human activities has caused several environmental problems, before that, there has been a strong trend in the development of research and processes that minimize impacts. Adsorptive methods have gained prominence in the treatment of effluents since this technique has high efficiency in the removal of harmful pollutants to the environment. The use of biomass as adsorbent material tends to reduce the costs of the adsorptive process due to its availability, abundance, and low cost. Among the persistent pollutants, there is the compound Rhodamine B, which is a cationic dye, which, in addition to being difficult to remove, presents a health risk. From the biomasses from agricultural activities, we can mention the kapok pod, which is considered one of the few residues originating from kapok, since the fruit capsule is one of the only items that do not have an application described in the literature and, therefore, make use of it. as an adsorbent material, it provides the valorization of a material that was previously seen only as waste. In this context, the objective was to evaluate the kapok pod as an adsorbent material for the removal of Rhodamine B in aqueous solutions. Through the characterization analyzes with SEM (Scanning Electron Microscopy), FTIR (Fourier Transform Infrared Spectroscopy), XRD (X-Ray Diffractometry) and TGA/DTG (Thermogravimetric Analysis), the structural characteristics of the adsorbent were analyzed. Also, the adsorption kinetics, variations in adsorbent mass (Fig. 1B) and adsorbate concentration (Fig. 1C), influence of pH (Fig. 1A) and application in real waters. The functional groups observed were characteristic of lignocellulosic materials and indicated the possibility of interaction from hydrogen and/or dipole-dipole bonds. In the affinity tests, it was possible to observe a strong interaction in all pH ranges studied, in natural pH, the removal was greater than 89% against 5 mg.L$^{-1}$ of dye concentration and about 71% at 100 mg. L$^{-1}$. In the test using real water, the non-selectivity of the material was observed, due to the reduction of the adsorptive capacity in salt water, but still showing a removal percentage above 59%, under more severe conditions. In the kinetic study, it was observed that in 240 min about 80% of the material's adsorptive capacity was reached. Such results corroborate the use of this material as an environmentally friendly alternative in a dual carriageway, both in terms of the recovery of solid waste and its potential in processes of removing pollutants from water.

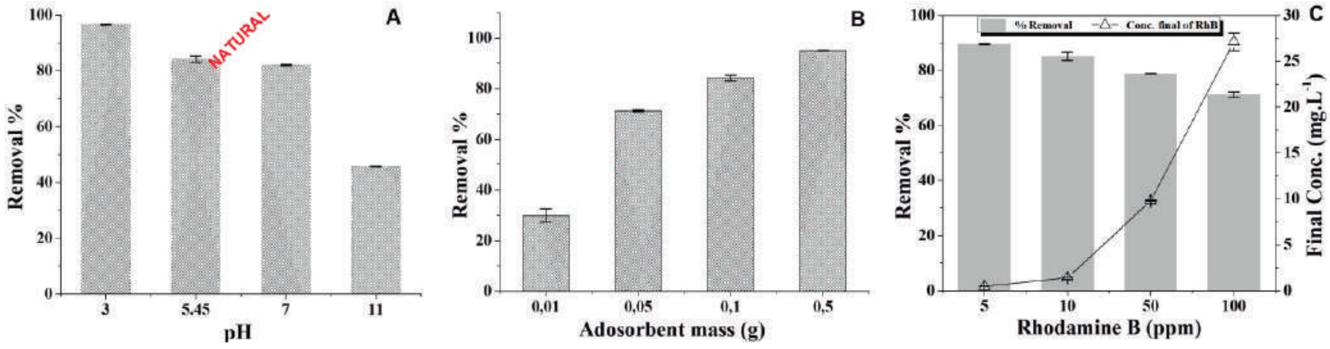

**Figure 1**: A – pH study; B - Adsorbent loading; C – Pollutant initial concentration.

## Acknowledgments

PPGEQ-UFAL, CAPES, FAPEAL, CNPQ.

**Área: AMB**

# Larvicidal and ecotoxicological analyzes of ethyl *p*-chlorocinnamate against *Aedes aegypti* larvae, vegetables and legumes

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Keywords: *Insecticide, Phytotoxicity, Bioavailability, Cinnamic acid.*

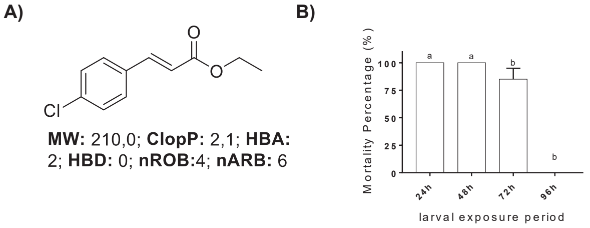
## Highlights

Ethyl *p*-chlorocinnamate proved to be a good larvicide, with a bioavailability of 72h. This compound showed low phytotoxicity, and promoted root growth of some plant species.

## Resumo/Abstract

Pharmacokinetic studies applied to insecticides are inherent to the discovery of new candidates with biological activity and low toxicity to the environment, such as the ecotoxicological investigation of insecticide molecules targeting the development of a product, including ethyl *p*-chlorocinnamate against *Ae. Aegypti* larvae.[1] Tests toward *Lactuca sativa*, *Allium cepa*, and *Solanum lycopersicum* are recent and highly efficient tools for determining the phytotoxicity of compounds.[2] This work describes physicochemical parameters, phytotoxicity, and bioavailability of ethyl *p*-chlorocinnamate. The larvicidal activity of ethyl *p*-chlorocinnamate ($LC_{50}$ = 8.3 μg/mL) is related to the cinnamoyl portion and ester function, as established by Hao and co-workers (2017)[3] (**Fig 1A**), mainly associated with the lipophilicity (ClogP) parameter observed in interaction study of insecticides. The larvicidal action of this compound in the environment is 72h, in which the first 48h being the most effective (**Fig 1B**).

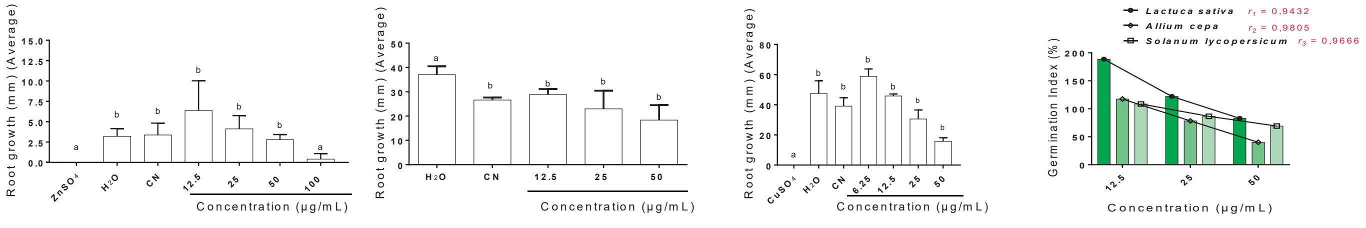
**Fig 1.** Pharmacokinetic properties and bioavailability of ethyl *p*-chlorocinnamate.



**MW:** 210,0; **ClopP:** 2,1; **HBA:** 2; **HBD:** 0; **nROB:**4; **nARB:** 6

a- Averages with the same letter as the standard composite did not differ by Dunnett's multiple comparison method; b- Averages that differed showed low significant difference ($p < 0.05$).

**Fig 2.** Ecotoxicological results of ethyl *p*-chlorocinnamate against *Lactuca sativa*, *Allium cepa* and *Solanum lycopersicum*.



Furthermore, this cinnamate showed low toxicity against *Lactuca sativa* (**Fig. 2A**), *Solanum lycopersicum* (**Fig. 2B**) and *Allium cepa* (**Fig. 2C**), being even a good regulator of root growth when compared to negative controls (0, 33% v/v $CH_3CN$) and blank (distilled water) (**Fig. 2A-C**). *Lactuca sativa*, despite its high sensitivity, stood out as the most resistant species in this study when compared to *Allium cepa* and *Solanum lycopersicum*(**Fig. 2D**). Fanilly, this compound can be considered as a good candidate for insecticide against *Ae. aegypti* and a root growth regulator for some plant species.

## Agradecimentos/Acknowledgments

CAPES, CNPq, FAPEAL, UFAL, LMC e LEAp.

**References:** [1] FRANÇA S. B. et al, *Bioor. Med. Chem*, 44, 2021; [2] YOUNG B. J. et al, *Ecotoxicology and Environmental Safety*, 76, 2012; [3] HAO, G. et al, *Mol. Inf*, 30, 2011.

**Área: __AMB__ Nº de Inscrição: _00210__**

# Life Cycle Assessment of the Synthesis of Mixed Nano Structured Matrix Membranes with Metal Organic Frameworks

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Palavras Chave: *Membranes, CO2, MOF, polymers,UMBERTO and permeability.*

## Highlights

- Life cycle analysis of mixed matrix membranes with two MOFs and compared with the commercial MATRIMID 5728@.
- Environmental assessment of the synthesis of two mixed matrix membranes.

## Abstract

Life cycle analysis (LCA) has been done as a method for assessing all direct and indirect environmental impacts of mixed matrix membranes (MMMs) with metal organic frameworks (MOFs). Mixed matrix membranes with MOFs and polymers (Figure 1) were previously synthesized and tested by our group. MMMs can be employed for different applications in the industry, such as: filters for water treatment, capture systems / permeability of gases such as $CO_2$ and tests in the petrochemical industry. In addition to versatility in applications, MMMs prove to be advantageous from economic and energetic points of view. After the synthesis of MMMs with two MOFs- MIL-101(Cr) and MIL-53(Al), CO2 permeability was analyzed and compared to the MATRIMID 5218® membrane. Table 1 shows the higher CO2 permeability of the synthesized MMMs: MMM-10% (MIL-101(Cr) and MMM-10% (MIL-52(Al) in comparison with MATRIMID. as for the permeability of CO2, as demonstrated in table 1. LCA of both MMMs-MMM10% (MIL-101(Cr) and MMM-10% (MIL-53(Al) as well as MATRIMID was done using UMBERTO NXT Software and the Ecoinvent v3® data platform. It was possible to model the processes of the three types of membranes studied and perform a comparison from the environmental point of view, that is, to assess the environmental impact that each of them generates from its productive process until the end of its "consumption". The 18 intermediate impact factors (or Midpoints) were determined with only 5 factors. The results showed that the most sustainable factors were Climate change (in kg CO2eq), Fossil depletion (in kg oil eq.), human toxicity (in kg 1,4-dcbeq.), metallic Depletion (in kg Fe eq.) and ionizing radiation (in kg U235 eq.).

| Membranes | CO2 permeability(Barrer) |
|---|---|
| Matrimid pure | 20.7 |
| MMM10%(MIL-101(Cr)) | 41.6 |
| MMM10%(MIL-53(Al)) | 95.1 |

***Table 1: It presents the relationship between membranes and their ability to permeate CO2 in Barrer (permeability unit).***

## Agradecimentos/Acknowledgments

**Área: AMB**

# Mercury determination (total and inorganic) in estuarine water samples from the Mundaú Lagoon (Maceió - AL, Brazil)

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Palavras-chave: *Monitoramento ambiental, espécies de mercúrio, contaminação aquática, CV AFS.*

## Highlights

- The organic Hg concentration was 90% higher than the inorganic Hg in the water samples.
- From 2017 to 2021 there was a systematic increase in the concentration of total Hg in the Mundaú lagoon.

## Resumo/Abstract

Considerado um dos mais importantes ecossistemas do Brasil, o Complexo Estuarino Lagunar Mundaú-Manguaba (CELMM) possui expressiva importância ambiental e um alto valor socioeconômico para o estado de Alagoas. O CELMM vem sofrendo um processo de degradação contínuo por meio de fontes antropogênicas (domiciliares e industriais), colocando em risco a biota e a polução que vive em seu entorno, a qual, por meio da pesca tem sua principal fonte de renda e alimentação[1,2]. Assim, estudos de monitoramento ambiental continuados na região são necessários. O presente trabalho teve como objetivo determinar a concentração de Hg total (Hg-T) e inorgânico (Hg-I) em amostras de água coletadas na laguna Mundaú (Maceió, AL). As amostragens foram realizadas em duas estações distintas, a primeira em período chuvoso (julho/2021) e a segunda em período seco (outubro/2021). Para a determinação de Hg inorgânico (Hg-I) as amostras foram coletas em frascos de vidro âmbar (sem acidificação), enquanto para a determinação de Hg total (Hg-T), coletou-se em frascos de vidro previamente acidificados com $HNO_3$ 10% (v/v). Para as análises microbiológicos, as amostras foram coletadas em tubos Falcon. Todas as medições de Hg foram realizadas empregando espectrometria de fluorescência atômica por vapor frio (CV AFS). Para a determinação de Hg-T adicionou-se o agente de bromação $KBr\text{-}KBrO_3$ (0,1/0,017 M) em meio ácido (HCl 0,6 M), e para a determinação de Hg-I as amostras foram apenas acidificadas (HCl 0,6 M). Os intervalos de concentração encontrados para Hg-T, Hg-I e Hg orgânico (Hg-O, estimado em função da diferença entre Hg-T e Hg-I), foram de 0,34 a 6,01, 0,00 a 1,64 e 0,2 a 5,45 $\mu g\ L^{-1}$, respectivamente, para os 11 pontos amostrais. Os resultados obtidos demonstraram uma situação preocupante, onde a concentração de Hg-T foi até 30 vezes superior ao valor de 0,2 $\mu g\ L^{-1}$ para águas salobras de classe 1 permitido pela legislação vigente (CONAMA 357/05)[3]. A concentração de Hg-O cerca de 90% superior ao Hg-I é fato preocupante, uma vez que, de forma geral, as espécies derivadas do Hg-O tendem a ter maior potencial toxicológico[4]. Essa situação foi constatada nas duas campanhas de amostragens realizadas, no entanto, a concentração de Hg-T foi maior para as amostras coletadas no período seco. Apesar do mercúrio possuir alta aplicabilidade na forma metálica, como compostos inorgânicos e como compostos orgânicos, o processo de metilação são os primeiros processos no meio aquático, o que pode promover maiores concentrações de Hg orgânico comparado a Hg inorgânico. Adicionalmente, as concentrações de Hg-T no presente trabalho, apresentaram um aumento de até 140 vezes em relação às obtidas por Silva et al. (2021)[1], que variaram de 0,02 a 1,31 $\mu g\ L^{-1}$, em monitoramento realizado na mesma região de 2017 a 2019. De modo geral, as análises microbiológicas, evidenciaram a presença de coliformes totais e termotolerantes com valor superior ao permitido pela legislação vigente (CONAMA 430/11)[4]. Assim, de acordo com os resultados obtidos, a laguna Mundaú pode ser considerada contaminada em relação os teores de Hg[3] e parâmetros microbiológicos[3], constituindo um problema que necessita de políticas públicas em caráter emergencial, uma vez que tal situação pode comprometer a qualidade dos alimentos extraídos deste ecossistema e sobretudo da saúde humana.

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## Agradecimentos/Acknowledgments

**[PPGQB-IQB-UFAL, CAPES, FAPEAL-FAPESP, CNPq, SBQ]**

**Área:** ***AMB***

# Multivariete triage of experimental variables using persulfate to degradation herbicides in tubular reactor

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Keywords: *Diuron, 2,4-D, Atrazine, Advanced Oxidative Processes, Factor Planning, Chemometrics*

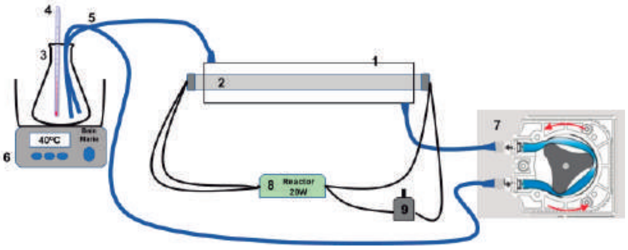
## Highlights

Factorial design is a tool that allows the triage of variables with a few numbers of tests. The temperature, pH, and persulfate concentration were significant variables for the studied systems.

## Abstract

Pesticides contribute to surface and groundwater contamination and cause long-term environmental and human health impacts. The demand for new remediation processes for these substances is growing up, and advanced oxidative techniques have shown promising results in the treatment of pesticides in water through the production of highly reactive species, such as hydroxyl (•OH) and sulfate (•$SO_4^-$) radicals. The persulfate anion generates these radicals when activated by temperature, UV radiation, pH and ultrasound. The objective of this work was to study the degradation of 2,4-D, Atrazine and Diuron in water in a tubular reactor and UVA radiation using persulfate (Figure 1). To select the best conditions was used an experiment factorial design with a central point with the variables of temperature, persulfate concentration and pH with the smallest possible number of tests (Table 1). In this work, the compound quantification was performed by HPLC-UV-Vis after being extracted by liquid-solid extraction. The results obtained with the factorial design showed that the variables persulfate concentration and temperature at the high level, and the interaction between the two, were the ones that most contributed to the degradation of 2,4-D (72%) and ATZ (80%). Throughout the experiment, the test with low temperature, high concentration, and UVA radiation made the Diuron degradation efficiency reach 95% in 45 minutes. The pH close to neutral was the best condition for the degradation of all herbicides. The results also show that the behavior of herbicides is not homogeneous in their degradation. In this case, it is essential having to be monitored or have optimized times for the total mineralization of all of them. Applying a factorial design with central composite (CCD), 2nd order model, is the next step to optimize the significant variables in these systems with tests at the start point.

**Figure 1. System for studying the degradation of herbicides in water**



**Note:** 1- Tubular glass with heating tape 2- Lamp; 3- Erlenmeyer; 4- Thermometer; 5- Connections; 6- Bain marine; 7- Pump; 8- Electric reactor; 9- Light switch

**Table 1. Levels used in factorial design with a central point**

| Variables | (-) | (0) | (+) |
|---|---|---|---|
| **Temperature (°C)** | 28 | 34 | 40 |
| **pH** | 6,8 | 7,8 | 8,8 |
| **Persulfate (mmol $L^{-1}$)** | 0,50 | 1,25 | 2,00 |

## Acknowledgments

The Universidade Estadual do Norte Fluminense Darcy Ribeiro, the funding agencies CAPES, CNPq and FAPERJ and the research groups GPQA and LAQUA.

**Área: AMB** **Nº de Inscrição: 00960**

# Occurrence of major ions in atmospheric particulate matter (PM10) sampled in the inspection area of the Customs-Federal Revenue Brazil / Paraguay

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Keywords: *Particulate matter, air pollution, ions, Ponte da Amizade.*

## Highlights

Determination of ionic species in particulate matter (PM10) at the Brazil / Paraguay frontier (Ponte da Amizade)
First study involving monitoring of contaminants in PM10 in this region
Relatively high values of $NO_3^-$ and $SO_4^{2-}$ ions in the sampled PM10

## Abstract

Particulate matter (PM) is among the main atmospheric pollutants, and consists of solid or liquid particles, which enter the atmosphere by natural or anthropic processes. The size distribution of the PM is a critical parameter, as it influences the transport dynamics of the particles and the chemical behavior. A parto f these particles (PM10) for example are inhalable, and are retained from the upper respiratory tract. The chemical composition is quite wide, consisting of organic, inorganic compounds, metals, matter of biological origin, ions, and elemental or organic carbon and are directly related to the emission sources of the particulate matter. The present work investigated the presence of major ionic species ($Cl^-$, $NO_3^-$, $SO_4^{2-}$, $K^+$, $Na^+$ and $Mg^{2+}$) in the PM10 (24 h) sampled in the inspection yard of the Customs of the Federal Revenue of Brazil, which is located next to the “Ponte da Amizade” in Foz do Iguaçu – PR, with 8,400 $m^2$ and average circulation of 40,000 vehicles per day. The PM10 was sampled using a large volume sampler (Hi-vol), (Energética, Brazil) and the collection of the PM10 was carried out on a Pall® quartz filter, with dimensions 20.3 $cm^2$ x 25.4 $cm^2$, at a flow rate of 1.3 $m^3$ $min^{-1}$, for 24 h by 7 days. Two campaigns were carried out in March and August 2018. The filter samples were subjected to a step of extraction of ionic species with ultrapure water using mechanical agitation for 5 min from circular aliquots of the filters with a diameter of 6 cm. Subsequently, anions ($Cl^-$, $NO_3^-$ and $SO_4^2$) were determined in aqueous extracts using an ion chromatograph model ICS 5000®, Dionex-Thermo Scientific. The metallic species ($K^+$, $Na^+$ and $Mg^{2+}$) were determined in the aqueous extracts using a flame atomic absorption spectrometer model AA 240 FS®, Varian. The values determined for the ionic species for the two campaigns are shown in Table 1.

**Table 1.** Average concentrations in ng $m^3$ of ionic species for the two campaigns.

| | Ionic species | | | | | |
|---|---|---|---|---|---|---|
| **Campaign** | **$Cl^-$** | **$NO_3^-$** | **$SO_4^{2-}$** | **$Na^+$** | **$K^+$** | **$Mg^{2+}$** |
| **March** | 190.4 ± 110.6 | 849.9 ± 61.2 | 1.226 ± 82.3 | 146.9 ± 6.7 | 254.1 ± 24.7 | 426.7 ± 25.4 |
| **August** | 61.8 ± 47.0 | 251.6 ± 22.1 | 450.4 ± 9.5 | 58.0 ± 1.5 | 116.3 ± 4.9 | 172.4 ± 40.2 |

The climatic condition proved to be a relevant factor in relation to the concentration of the ions under study, showing a significant reduction from the first to the second campaigns. The values determined for $SO_4^{2-}$ and $NO_3^-$ in PM10 showed significant representativeness, as they are correlated with the high flow of motor vehicles and their secondary reactions in the atmosphere. Finally, the concentrations for the ionic species studied had values similar to those determined in large urban centers, based on other previous studies. Thus, it can be inferred about the influence of anthropic activities on the concentration levels of ionic species in PM10 in the sampled region.

## Acknowledgments

**CNPq, CAPES, UTFPR and UFSM.**

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

# Occurrence of pesticides in soil and in mesocosm's waters during the management of pasture and sugarcane crop

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Palavras-Chave: *agrotóxico, cana-de-açúcar, manejo solo, 2,4-D, fipronil*

## Highlights

In the water samples, fipronil sulfone' concentration tripled after 20 days of application, while for 2,4-D, fipronil and fipronil sulfide, the concentration gradually decreased to < LOQ over 3 months.

The 2,4-D' concentration in soil decrease after application until < LOQ faster than fipronil.

## Resumo/Abstract

Brazil occupies a prominent place as one of the great food and energy producers in the world. Among the agribusiness' segments, the production of sugarcane stands out, with an evident increase in cultivable areas. However, there is a demand for economic and social development based on environmental sustainability principles through land use management practices with the purpose of: reducing deforestation, recovering degraded areas and preventing advance on food crops. Studies indicate that extensive areas of low-productivity pasture have been converted into sugarcane plantations in Brazil (Bento et al. 2018). This work proposed to study the occurrence of the herbicide 2,4-D and the insecticide fipronil, including its degradation products: fipronil sulfide, fipronil sulfone in the soil and in the artificial ponds (LA) and puddles (PA) (mesocosms) built in pasture and sugarcane cultivation areas during agricultural management. The sampling occurred monthly to PA and soil and weekly to LA, from Oct 2019 to Jan 2020 during the management of the second sugarcane cycle in degraded pasture (P, controlled area), intensive pasture (PI) and sugarcane crop (C) of an experimental farm located in Brotas (SP). The soil is Typic Ustipsamments. Fipronil was applied in Nov 2019 and 2,4-D in Dec 2019 following the national recommendation of EMBRAPA to the soil management. The target compounds were quantified using LC-MS/MS with electrospray ionization (Agilent Technologies) according to Goulart et al. (2020). The determination of fipronil and its degradation products in the waters was done using SPE-online system (Agilent model 1260 Infinity II Quaternary System), while for 2,4-D, direct injection into the LC-MS/MS system was used after previous sample filtration at 0.22 µm (PTFE hydrophilic syringe filter). The LOD and LOQ for soil analysis were 1.0 and 5.0 µg $L^{-1}$ (2,4-D), 0.1 and 0.5 µg $L^{-1}$ (fipronil, fipronil sulfide, fipronil sulfone), respectively; and to water analysis were 0.5 and 5.0 µg $L^{-1}$ (2,4-D), 0.1 and 0.5 ng $L^{-1}$ (fipronil), 1.0 and 5.0 ng $L^{-1}$ (fipronil sulfide, fipronil sulfone), respectively. The highest concentrations of pesticides in the soil were obtained just after the pesticide application, ranging from 2.2 to 13.4 µg $kg^{-1}$ for 2,4-D, 0.1 to 238 µg $kg^{-1}$ for fipronil, 0.1 to 5.2 µg $kg^{-1}$ for fipronil sulfide and 0.8 to 22.3 µg $kg^{-1}$ for fipronil sulfone. For the last one, the concentration tripled after 20 days, while for 2,4-D, fipronil and fipronil sulfide, the concentration gradually decreased to < LOQ over 3 months. In the water samples, the highest concentrations occurred for 2,4-D after one week of application, ranging from 2.5 to 216 µg $L^{-1}$ in C-LA and 8.3 to 542 µg $L^{-1}$ in C-PA. Fipronil concentrations ranged from < LOQ to 325 ng $L^{-1}$ in LA and < LOQ to 398 ng $L^{-1}$ in PA. The concentrations of fipronil sulfide were below the LOQ and fipronil sulfone showed a maximum value after 1 month of application (16.8 ng $L^{-1}$) in C-PA. The results showed greater persistence in the soil than in the waters of fipronil, fipronil sulfide and sulfone in all areas P and PI, but mainly in sugarcane crop. It was noted that the concentration values of the pesticide 2,4-D decrease until < LOQ faster than fipronil.

## Acknowledgments

FAPESP (Thematic Project Proc. 2015 /18790-3), CAPES and UFAM.

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**Área: AMB**

# Origin and secondary formation of DCA of an urban atmosphere in the Amazon

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Keywords: *$PM_{2.5}$, dicarboxylic acid, levoglucosan, BC, biomass burning, fossil fuel burning.*

## Highlights

The DCAs (C2-C9,Ph) were different between the two periods analyzed. $PM_{2.5}$ and the DCAs present in the particle were more influenced by biomass burning in 2018 and by fossil fuel burning in 2017.

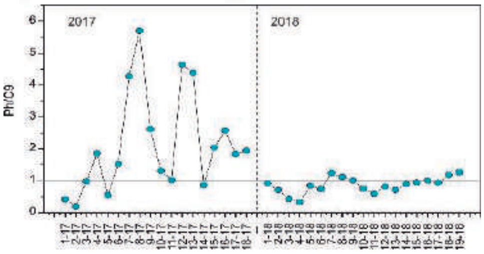
## Abstract

We investigated two different ways to understand the dicarboxylic acids (DCAs) in the atmosphere of Manaus (AM): the influence of burning sources on the primary origin and the secondary formation. Then, DCAs (C2-C9, Ph), black carbon (BC), and levoglucosan (LEV) were analyzed in the $PM_{2.5}$ collected during the dry season (August-September) of 2017 and 2018. The 2018 samples were collected during an intense biomass burning (BB) period with the presence of smoke covering the city. DCAs had higher concentrations in 2018 (2017), with an average value of a total sum of the DCAs analyzed (∑DCA) of 651.22 ± 289.65 ng $m^{-3}$ (578.65 ± 367.27 ng $m^{-3}$). The decreasing order of DCAs concentration, in both years, was C2>C3>C4 (Table 1). The mean value of ∑DCA (2018) was similar to values reported for the aerosol collected in the dry season Rondônia (Brazil) (644.9 ng $m^{-3}$) on a site under the influence of BB.[1] Therefore, Azelaic (C9) and Phthalic (Ph) acids were evaluated due to being indicators of primary aerosol sources and the ratio between them may indicate the preference of formation route: (i) Ph/C9<1 indicates the secondary formation preference of the DCAs by the pathway of the C9 (biogenic and BB sources) and (ii) Ph/C9>1 indicates the pathway of the Ph (fossil fuels burning).[2] C9 average concentration in 2018 was 1.7 times higher than in 2017. C9 presented Pearson correlation (R) with C2 (0.598, p-value = 0.007) only in 2018, pointing out a probable dependence between their sources. In the same year (2018), C9 had a strong R-value (0.72, p-value = 4.59 x $10^{-4}$) with the BB events log in the Metropolitan Region of Manaus.[3] Additionally, the lowest Ph/C9 ratio values (Figure 1), and the higher average value of LEV both data for 2018 also points out the probable influence of BB in this year. On the other hand, in 2017 was obtained the highest Ph/C9 ratio values (Figure 1) and the highest Pearson correlation values between: (i) Ph and C2 (R = 0.797, p-value = 7.37 x $10^{-5}$), and (ii) Ph/∑DCA and C2/∑DCA (R = - 0.802, p-value = 6.20 x $10^{-5}$). Then the data suggest different secondary formation mechanisms between the years that can be differentiated by the values of the Ph/C9 ratio. The dependence between ∑DCAs and LEV and BC was investigated through multiple linear regression. The equations obtained were: ∑DCA = 0.192BC + 0.073LEV (2017, $R^2$ = 0.845) e ∑DCA = 0.127BC + 0.499LEV (2018, $R^2$ = 0.899). Although ∑DCAs were influenced both by the BC and LEV sources, BC had a greater influence on ∑DCAs in 2017 (slope = 0.192) and LEV had a greater influence in 2018 (slope = 0.499). In this way, it is possible to observe a distinct primary source influence between the years for the origin of $PM_{2.5}$ and the DCAs present in the particle. In 2018 there was the favorability of the C9 pathway in the formation of DCAs and the higher influence of BB. On the other hand, the relationship between BC, C2, ∑DCA, and Ph, only in 2017, points out the preference in the formation of DCAs by the Ph pathway and a greater influence of fossil fuel burning. In this way, it is noted that the influence of BB on the origin of aerosol impacted not only visibility (due to the presence of smoke) and probably the health of the population in 2018, but also, possibly altered the composition, oxidative pathway, and secondary formation of the DCAs.

Table 1 – Average ± SD (ng $m^{-3}$) of the most abundant DCAs

| | C2 | C3 | C4 |
|---|---|---|---|
| 2017 | 506.59 ± 340.86 | 34.28 ± 20.78 | 14.81 ± 6.06 |
| 2018 | 533.01 ± 255.06 | 56.76 ± 27.98 | 23.63 ± 7.53 |

Figure 1 – Ph/C9 ratio in $PM_{2.5}$



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## Acknowledgments

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

**Área: AMB**

# Ozone impact on the emission of Biogenic Volatile Organic Compounds (BVOCs) in tropical tree species

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Key-words:*Chemical trait, Plant volatiles, Ozone, BVOC*

## Highlights

$O_3$-induced BVOCs in *C. floribundus*, *A. graveolens* and *P. gonoacantha* were determined.
*C. floribundus* was a SEQ-emitter and *A. graveolens* a MON-emitter.
*BVOCs of P. gonoachanta* did not affected by $O_3$.

## Abstract

Plants emit a broad number of Biogenic Volatile Organic Compounds (BVOCs) that can impact urban ozone ($O_3$) production. Conversely, the $O_3$ is a phytotoxic pollutant that causes unknown alterations in BVOC emissions from native plants. In this sense, here we characterized the constitutive and $O_3$-induced BVOCs for two ($2dO_3$) and four ($4dO_3$) days of exposure ($O_3$ dose 80 ppb) and evaluated the $O_3$ response by histochemical techniques to detect Programmed cell death (PCD) and hydrogen peroxide ($H_2O_2$) in three Brazilian native species. *Croton floribundus* Spreng, *Astronium graveolens* Jacq, and *Piptadenia gonoacantha* (Mart.) JF Macbr, from different groups of ecological succession (acquisitive and conservative), different carbon-saving defense strategies, and specific BVOC emissions. The three species emitted a very diverse BVOC composition: monoterpenes (MON), sesquiterpenes (SEQ), green leaf volatiles (GLV), and other compounds (OTC). *C. floribundus* is more acquisitive than *A. graveolens.* Their most representative BVOCs were Methyl Salicylate - MeSA (OTC), (Z) 3-Hexenal, and (E)-2-Hexenal (GLV), γ-Elemene and (-)-β-Bourbonene (SEQ) β-Phellandrene and D-Limonene (MON), while in *A. graveolens* were nonanal and decanal (OTC), and α-pinene (MON). *P. gonoachanta* is more conservative, and the BVOC blend was limited to MeSA (OTC), (E)-2-hexenal (GLV), and β-Phellandrene (MON). The $O_3$ affected BVOCs and histochemical traits of the three species in different ways. *C. floribundus* was the most $O_3$ tolerant species and considered an SEQ emitter. It efficiently reacted to $O_3$ stress after $2dO_3$, verified by a high alteration of BVOC emission, the emergence of the compounds such as α-Ionone and trans-ß-Ionone, and the absence of $H_2O_2$ detection. On the contrary, *A. graveolens*, a MON-emitter, was affected by $2dO_3$ and $4dO_3$, showing increasing emissions of α-Pinene and β-Myrcene, (MON), γ-Muurolene and β-Cadinene (SEQ) and $H_2O_2$ accumulation. *P. gonoachanta* was the most sensitive and did not respond to BVOCs emission*,* but PCD and $H_2O_2$ were highly evidenced. Our results indicate that the blend of BVOC emission in combination with histochemical and is a powerful tool to confirm the species tolerance to $O_3$. Furthermore, our findings suggest that BVOC emission is a trade-off associated with different resource strategies of species indicated by the changes in the quality and quantity of BVOC emission for each species.

## Acknowledgments

The authors would like to thank the Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP 2016/25109-3 and 2015/50128-9) and the Conselho Nacional de Desenvolvimento Cientifico e Tecnologico (CNPq,3055395/2019-0). The authors thank the financial and scholarship (Vanessa P. Bolsoni and Marcia Dias de Paulo) by Cnpq.

**Área: ___AMB______ Nº de Inscrição: __01030__**

# Pesticides behavior in the atmosphere of an urban area in Brazil. Risk assessment for human health.

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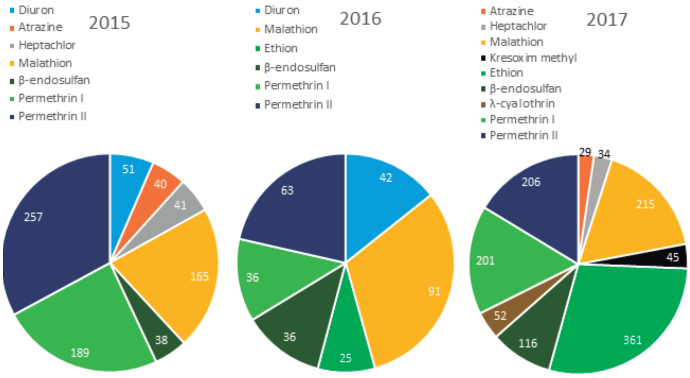
*Keywords: Air pollution, Particulate matter, Pesticides concentration, Risk assessment.*

## Highlights

-First determination of pesticides in the atmosphere of Capuava.
-Human inhalation risk assessment of outdoor airborne pesticides was performed.
-All measured reported Hazard Quotients < 1
-Cancer risk was found for heptachlor in adults, infants and children.

## Abstract



In the last few years, different types of pesticides have been detected in the atmosphere in rural and urban areas around the world. These, are chemical compounds used in agriculture to avoid plague, rodents, fungi and unwanted plants. Besides that, they are often used in public health to kill vectors of disease, such as mosquitoes. Some studies have showed the relations between pesticides exposure and some diseases, such as autoimmune and cardiovascular diseases, and respiratory problems. An attempt to investigate the composition of PM in the neighbor atmosphere of an industrial complex has been proposed in the last years due to the high rate of thyroid diseases in the population living near this region. In this work was determined the concentrations of pesticides in samples collected between 2015, 2016 and 2017 at an industrial and urban area. The assessment of the risk caused by inhalation of these compounds was calculated. Samples (n=42) were extracted and 11 pesticides were determined by gas chromatography coupled to a mass spectrometer. Samples collected in 2017 showed the higher concentrations. Pesticides such as malathion and permethrin, used in the control of domestic pests, presented the highest concentrations (537 pg $m^{-3}$ and 625 pg $m^{-3}$ respectively) due to the wide use in this area. The highest values of daily inhalation exposure were for heptachlor in infants, 2 x $10^{-4}$ mg $kg^{-1}$ $day^{-1}$. All values of the hazard quotients are lower than 1 indicating that there is no danger to human health by inhalation. Cancer risk was found for heptachlor in adults, infants and children in the three years.

## Acknowledgments

The authors thank FAPESP (Project 2017/20826-1). Vasconcellos thank CNPq for their research fellowships.

**Área: AMB**

# Photocatalytic removal of NO using cement-based mortars with incorporation of $TiO_2$ and mineral admixtures

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Keywords: hybrid photocatalysts, cementitious materials, $TiO_2$, NO, gas phase, heterogeneous photocatalysis.

## Highlights

- Effect of nano-$TiO_2$ incorporation in performance of cement mortars is studied.
- Porosity is investigated due to the relation with photocatalytic efficiency.
- Partial substitution of cement by metakaolin favors the photocatalytic efficiency of $TiO_2$ nanoparticles blended mortars.

## Abstract

Cementitious materials used in floors and buildings have received special attention in research on sustainability and climate change issues. Titanium dioxide has recently been applied in the construction industry to develop different products, since its photocatalytic properties can be used for pollutant degradation purposes. Thus, this study evaluated the performance of cementitious mortars with the incorporation of $TiO_2$ nanoparticles and mineral additives for NO degradation in the gas phase. In order to establish differences in porosity features among studied mortars, six compositions were defined considering two reference mixtures [with (REF) and without $TiO_2$ (REF-0)], two mineral additions [bentonite (B20) and metakaolin (MK20)] as a partial replacement of cement (20% in weight) and a residue from the processing of ornamental rocks in levels of 20% (SW20) and 40% (SW40) of partial replacement of natural sand. The photocatalytic experiments were carried out in an ISO 22197-1:2007 photoreactor with a flow of 3 L $min^{-1}$ and two Philips BL 8W lamps. The NO (1000 ppb) was monitored using Model 42i USA EPA $NO$-$NO_2$-$NO_x$ Thermal Analyzer referring to the RFNA-1289-074. The NO removal efficiency results for cement-based mortars are shown in Fig. 1 All mixes contains 2.5% $TiO_2$ in relation to cement weight, with exception of REF-0 that is photocatalyst free.

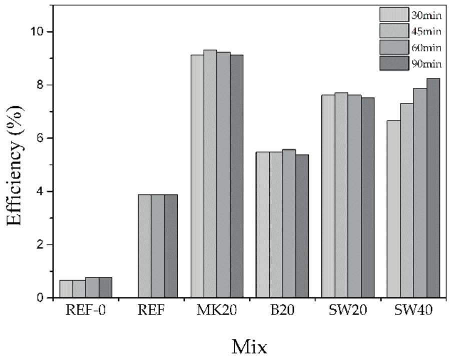

Fig. 1 Efficiency of photocatalytic NO removal using cement-based mortars at different time intervals.

As expected, the REF-0 sample did not show photocatalytic activity due to the absence of $TiO_2$ (0.6% of conversion). The samples containing $TiO_2$ showed photocatalytic activity to eliminate NO, obtaining an average efficiency of 9.3% for MK20, 5.5% for B20, and 3,8% for reference samples (REF). The MK20 samples showed the highest activity for NO conversion compared with the REF, B20 and SW20/40.

$NO_2$ selectivity can be performed taking into account the main reaction product. The results for selectivity are shown in the Fig. 2, and the order was REF > MK20 > SW20 > SW40 > B20. The complete removal of NOx is important because $NO_2$ is an important pollutant and precursor for photochemical smog. Then the best result considering the NO removal and low $NO_2$ production was MK20.

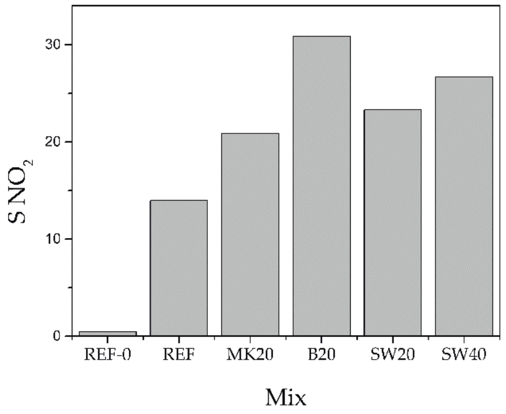

Fig. 2 $NO_2$ selectivity of samples during photocatalytic experiments

In the studies of photocatalytic conversion of NO with the different cementitious materials, it is observed that the photocatalytic efficiency was similar for MK20, SW20 and SW40 mortars, considering the NOx removal and $NO_2$ production. It was shown that higher porosity does not necessarily imply higher photoactivity, since large pores could lead to NO adsorption in the matrix towards deeper zones than those reached by light.

## Acknowledgments

UENF, INFES-UFF, ICP-CSIC e CIEMAT

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# Pollutants and biomarkers in *Piaractus mesopotamicus* (Pacu) and *Semaprochilodus* sp. (Jaraqui) marketed in Manaus, Amazonas, Brazil

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Keywords: Environmental quality, metals, oxidative stress, fish consumption, Amazon

## Highlights

Preliminary metal and oxidative stress biomarkers levels assessments in fish marketed in Manaus, Amazonas, Brazil indicate concerns, as both species are among the most consumed fish at Manaus markets.

## Resumo/Abstract

Samples from two fish species, *Piaractus mesopotamicus* (Pacú) and *Semaprochilodus* sp. (Jaraqui), sold at an open market in Manaus, Amazonas, Brazil were analyzed concerning metal and oxidative stress biomarkers in muscle tissue. Chromium (Cr), Copper (Cu), Cadmium (Cd), Zinc (Zn), were analyzed after soft extraction by Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Limit of quantification (LQ) 0.01 – 0.075 mg kg$^{-1}$), Total mercury (Hg) was analyzed by Direct Mercury Analysis System DMA-80 (LQ = 0.0005 mg kg$^{-1}$), while metallothionein (MT) and Reduced glutathione (GSH) were assessed by UV-Vis spectrophotometry. Preliminary results indicate public health concerns regarding the consumption of these fish, as both Jaraqui and Pacú muscle tissues presented Cr above the respective maximum permissible ingestion limit as stipulated by the Brazilian ANVISA (Figure 1). It seems that both species display the same level of MT induction, while 2.4-fold higher GSH levels were noted in Jaraqui. In addition, higher metal concentrations were observed in this species, except for Cd, and Hg was up to 3.9-fold higher compared to Pacú, probably due to the fact that this is a detritivorous species, while Pacú are omnivorous. Further assessments will be carried out with 40 individuals purchased in Manaus markets originating from the Purus River, according to fish sellers, and statistical correlations with the oxidative stress biomarkers shall be carried out.

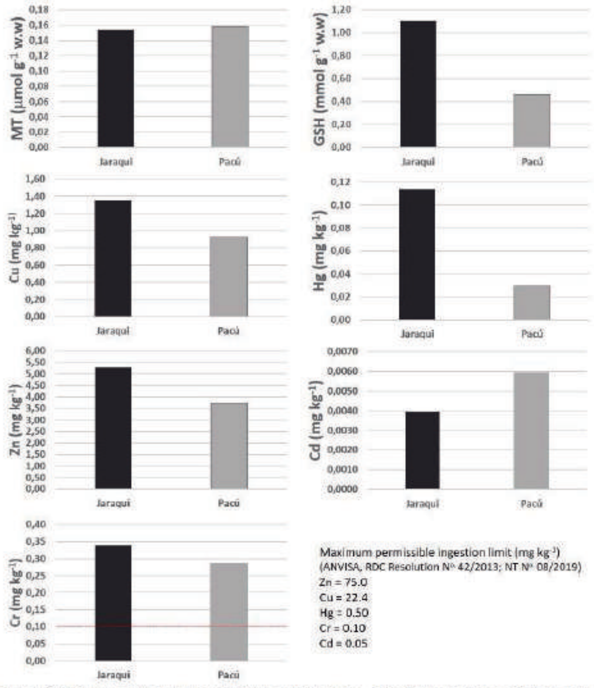

Figure 1. Preliminary results of analyzed concerning biomarkers (Metalotioneína - MT and Reduced glutathione - GSH) and metals (Zn, Cu, Hg, Cr, Cd) in muscle tissue of two species of fish *Semaprochilodus* sp. (Jaraqui) and *Piaractus mesopotamicus* (Pacú) of open market in Manaus, Amazonas, Brazil.

## Agradecimentos/Acknowledgments

Research Support Foundation of the State of Amazonas and Brazilian National Council for Scientific and Technological Development for student scholarships, and upport from the Graduate Program in Chemistry – UFAM.

**Área: AMB**

# Possible influence of ships in Guanabara Bay (Rio de Janeiro, Brazil) on metals associated with size-segregated particulate matter

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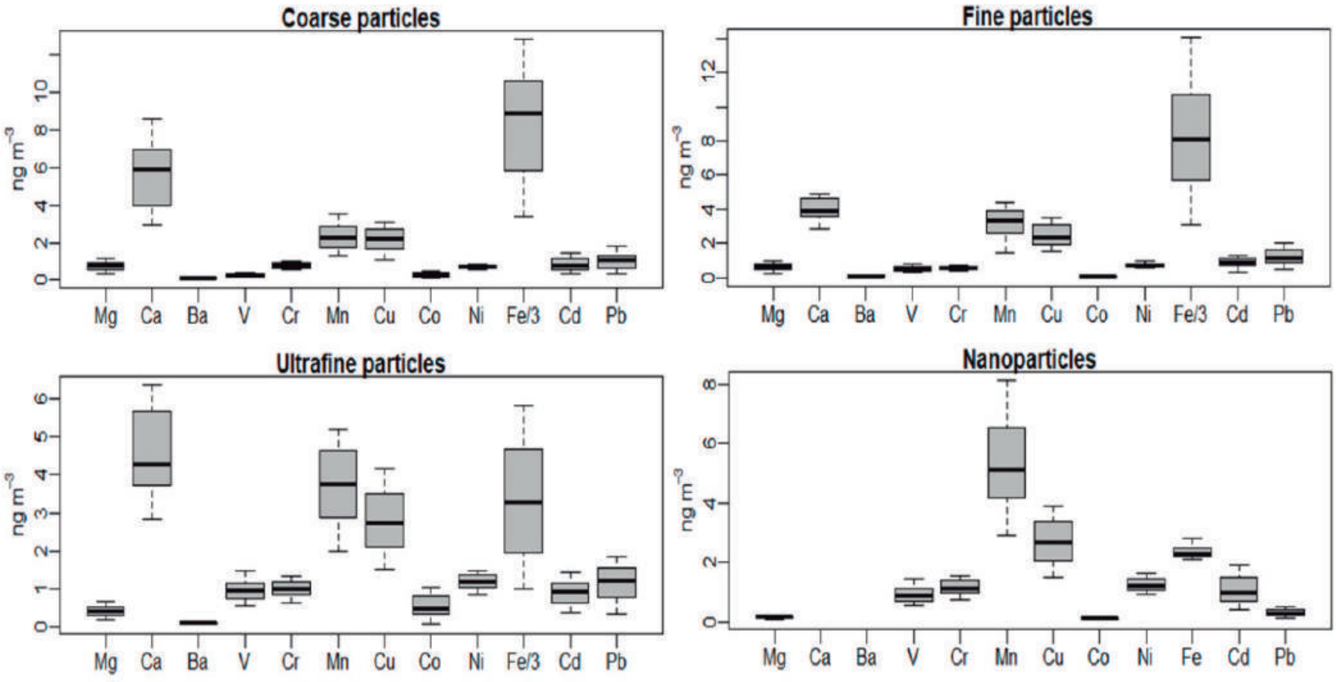
Keywords: *Air Pollution, Ships, Particulate Matter, Metals, Emission.*

## Highlights

- PM were sampled using a MOUDI and metals were determined by ICP/MS
- 57 samples were collected between 2019/2021
- Fe, Ca, Cu, Mn were the main components of Coarse, Fine, Ultrafine and Nano particles

## Abstract

A total of 57 samples lasting 24 h were collected between October 2019 and January 2021 with a 10-stage MSP MOUDI 120R cascade impactor at 30 L min-1 for 24 h. The stages were grouped into coarse (PMC), fine (PMF), ultrafine (PMU) and nano (PMN) particles. The opening of the samples followed the U.S.EPA IO 3.5 methodology and chemical analysis by ICP/MS (Perkin Elmer ELAN 6000). The results are presented in the form of boxplots below.



The data show that for PMC and PMF the predominant metals were Fe and Ca. For smaller particles, Mn and Cu are also representative. The correlation study indicates that for PMC and PMF the alkali metals present high correlation, indicating a similar source. Pb and Cd present high correlation for PMC, PMF and PMU, as well as the group formed by Cu, Cr and Mn. For all PM size ranges, they correlate with the vehicular flow of nearby roads. Other high correlations are also observed for the PMC between Zn+Fe, Pb+Cd and Ni+V, for the PMF between Mn+Fe, Pb+Cd and Ni+V, for the PMU between Fe+Mn+Ca and for the PMN between Pb+V+Fe.

## Acknowledgments

FAPERJ, CNPq e Marinha do Brasil.

**Área: AMB**

# Potential for phytoremediation of lead contaminated soils through the use *Capsicum annuum* cultivars.

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Key words: *pepper, potential toxic metals, ICP-OES*

## Highlights

Phytoremediation of soil contaminated by lead using *Capsicum annuum* cultivars.

This work aim to evaluate the potential use of the genus Capsicum to phytoremediation of soils contaminated by lead, with economic use of the capsicum fruits production.

## Resumo/Abstract

Peppers of the genus Capsicum originate from the Americas and are currently one of the most cultivated spices in the world. They are a source of several compounds of economic interest, such as capsaicinoids, flavonoids and vitamins, being used by food, pharmaceutical and cosmetics industry. One of the major problems in Agriculture today is the contamination of soils by potential toxic metals due to human action. These metals are absorbed by the plant due to their similarity to other metals with biological role and may cause several problems such as reduced cell growth and enzymatic inactivation, in addition to being toxic to humans if present in food. The objective of this work was to evaluate the potential for phytoremediation of lead contaminated soils using a pepper cultivar (Capsicum annuum UENF 1381). Sowing was done in a 128-cell polystyrene tray using commercial substrate, one seed per cell. Seedlings were watered daily and after reaching two pairs of definitive leaves they were transplanted to 5L pots prepared with soil and sand (1:1 ratio) and the addition of lead nitrate solutions to obtain four treatments containing about 0 $mg.kg^{-1}$, 90 $mg.kg^{-1}$, 180 $mg.kg^{-1}$ e 360 $mg.kg^{-1}$ of lead. The plants were watered daily and fruits harvested at 30 and 50 days after anthesis. The fruits were separated into pericarp and placenta + seeds, freeze-dried for five days, macerated with the aid of liquid nitrogen. Samples containing about 100 mg were digested in 10 mL of 65% nitric acid at 140°C for 2h and diluted in 25 mL volumetric flasks with deionized water and then submitted to lead content analysis by ICP-OAS. Samples of soil (beginning and end of experiment) , roots, stem and leaves (end of the experiment) were also collect and analyzed for lead content. All data were submitted to Tukey mean comparison test at 1% and 5% probability. It was observed the capacity of removal of lead from soil as well as the mobility of this metal in the plant. The low or absent lead levels of content in pepper fruits indicated the possibility of the use of *Capsicum annuum* cultivars in phytoremediation of contaminated soils with economic use of the fruits production.

## Agradecimentos/Acknowledgments

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Universidade Estadual do Norte Fluminense Darcy Ribeiro – UENF

**Área: AMB**

# Removal of emerging contaminant using activated carbons from licuri coconut shell

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keywords: *Salicylic acid, PPCP, adsorption, activated carbon, Syagrus coronata*

## Highlights

Both activation processes improved the salicylic acid adsorption capacity.
The KOH activation resulted in a material with a greater capacity than the commercial activated carbon.

## Abstract

The quality of water has been affected by the presence of emerging contaminants, which are compounds of anthropic origin, like pharmaceuticals, pesticides, and cosmetics. Their presence is hazardous because they are not eliminated by the traditional water and wastewater treatment and their presence can cause serious adverse effects on humans, animals, and plants. The process of adsorption on activated carbon is a promising strategy for the removal of these substances due to its low cost and efficiency (AHMED et al., 2021). This study aims to produce activated carbons from the licuri coconut shell and evaluate their use as an adsorbent of salicylic acid, a substance present in several cosmetics and the product of hydrolysis of aspirin, a high selling drug.

Two different activation processes were applied to the licuri biochar (**BC**) to increase its adsorption capacity. The activation process was done by mixing the biochar with KOH using a mortar and pestle, then the mixture was placed in a closed stainless-steel cup and remained at a muffle furnace at 500 °C for 2 h. After that, the mixture was washed with a 1 mol L$^{-1}$ HCl solution followed by ultrapure water until neutrality was reached – this material was denominated Base Activated Biochar (**BAC**). The second activation process was done by mixing biochar with $H_2SO_4$ (1:3 mass ratio) and heating to 200 °C for 1 h, the resulting biochar was washed continuously with ultrapure water using a Soxhlet apparatus until neutrality was reached, dried, and denominated Acid Activated Biochar (**AAB**). A Commercial Activated Carbon **(CAC)** was also evaluated as control. All materials were characterized by $N_2$ adsorption, Boehm titration, and point of zero charge (PZC).

The batch adsorption experiments were done in triplicate using samples with 10 mg of adsorbent and 20 mL of a salicylic acid solution that were placed at a Dubnoff bath with shaking at 20 °C and 150 RPM. Afterward, the samples were filtered and analyzed at a UV-Vis Spectrophotometer at 295 nm. In this experiment, the following parameters were evaluated: contact time between adsorbate and adsorbent, pH, and salicylic acid concentration. The fixed bed adsorption experiments were done eluting a salicylic acid solution through a column with 30 mg of biochar. The eluate was collected at fixed times for further analysis at the spectrophotometer. The adsorption experiments were not performed with BC due to the lack of adsorptive capacity

The results showed that BAC has the highest surface area (1006 $m^2 \cdot g^{-1}$), being even higher than that of the CAC (745 $m^2 \cdot g^{-1}$). The BC and the AAB have the lowest surface areas, of 13 $m^2 \cdot g^{-1}$ and 6 $m^2 \cdot g^{-1}$, respectively. The Boehm titration and the PZC showed that BAC is a stronger acid, followed by the AAB, CAC, and BC. The batch adsorption experiments showed that all materials have a quick equilibrium time, about one hour, and that the adsorption is higher at acidic solutions. The results of adsorption isotherms (Figure 1) showed that BAC has the highest adsorption capacity and the same behavior was observed at the fixed bed adsorption studies.

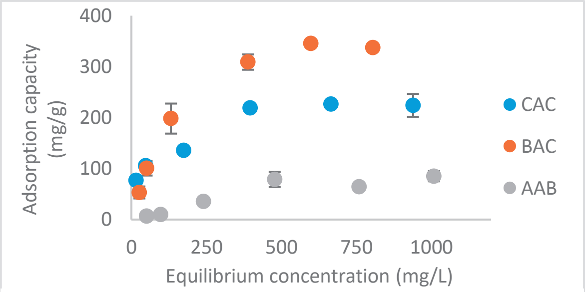

*Figure 1. Salicylic acid adsorption results*

These results represent a significant advance in the environmental area as they present an application for the licuri coconut shell, a residue of the agroindustry with potential use in the remediation of emerging contaminants.

## Acknowledgments

CAPES, CNPQ and FAPERJ

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**Área: AMB**

# Removal of micropollutants and toxicity reduction from MWWTP effluent by solar/photo-Fenton process using different iron complexes

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Palavras Chave: *Advanced Oxidation Process, Fipronil, Oxybenzone, Propylparaben, Acute toxicity, D. melanogaster.*

## Highlights

- Best operational conditions differed for each iron complex.
- Toxicity towards *D. melanogaster* fly was reduced in the presence of all iron complexes.

## Abstract

Solar/photo-Fenton process was evaluated as an alternative treatment to improve municipal wastewater treatment plant (MWWTP) effluent spiked with a mixture of three micropollutants: fipronil, propylparaben and oxybenzone (100 µg $L^{-1}$ each) at pH 6.9 (natural of this matrix). As iron ligands (L) are known to increase iron solubility at neutral pH, citrate (Cit), ethylenediamine-N,N´-disuccinic (EDDS), ethylene diaminetetraacetic acid (EDTA) and nitrilotriacetic acid (NTA) were evaluated as L. Best operational parameters (iron and $H_2O_2$ concentration, and iron/L molar ratio) were determined for each L. Iron concentrations (12.5, 25, 50 and 100 µmol $L^{-1}$) were assessed at a fixed iron:L molar ratio (1:1) for all iron complexes in the presence of 5.88 mmol $L^{-1}$ $H_2O_2$. Different iron/L molar ratios (1:2 for FeCit, FeEDDS, FeEDTA and FeNTA; 1:3 and 1:4 for FeCit and FeEDDS and, 1:5 and 1:6 for FeCit) were tested by using the best iron concentration (100 µmol $L^{-1}$) in the presence of 5.88 mmol $L^{-1}$ $H_2O_2$. Iron concentration and source strongly affected micropollutants degradation. For FeEDDS, FeEDTA and FeNTA, micropollutants degradation improved significantly by increasing the iron complex concentration from 12.5 to 100 µmol $L^{-1}$. This is justified by the higher concentration of dissolved iron, which contributes to Fenton reaction and formation of more hydroxyl radicals. On the other hand, only 30% of mixture degradation were obtained for FeCit at all iron concentrations assessed. This can be associated to the predominance of $FeOHCit^-$ (90%) and $Fe_2(OH)_2(Cit)_2^{2-}$ (10%) species which show lower photoreactivity compared to FeCit. These results can also be associated to lower stability of Fe(III)-Cit complex when compared to the other L. No improvement on micropollutants degradation rates were observed by increasing iron/L molar ratio from 1:1 to 1:2 for FeEDTA and FeNTA. This suggests that the 1:1 molar ratio was adequate to guarantee enough dissolved iron concentration to reach quantification limits (< 4.2 µg $L^{-1}$ for fipronil and oxybenzone and < 1.3 µg $L^{-1}$ for propylparaben) after a $t_{30W}$ of 64 min and 19 min for FeEDTA and FeNTA, respectively. For FeEDDS, increased iron/L molar ratio from 1:1 to 1:3 improved micropollutants degradation from 62% to 85%. The same behavior was also observed for FeCit, for which degradation improved from 37% to 84% by increasing the iron/L molar ratio from 1:1 to 1:5. However, no improvement was observed at higher iron/L molar ratios (1:4 for FeEDDS and 1:6 for FeCit). So, iron/L molar ratios of 1:1 (FeNTA and FeEDTA), 1:3 (FeEDDS) and 1:5 (FeCit) were chosen as the best conditions and used to evaluate the influence of $H_2O_2$ concentration (ranged from 0.74 up to 11.8 mmol $L^{-1}$ $H_2O_2$). For FeNTA and FeEDTA, best degradation rates were reached using 5.9 mmol $L^{-1}$ $H_2O_2$. In contrast, FeEDDS and FeCit required 1.5 and 2.9 mmol $L^{-1}$ $H_2O_2$, respectively. Acute toxicity to Canton S. strain flies *D. melanogaster* reduced significantly after the treatment conducted in the presence of all iron complexes evaluated. All flies died after 7 days of exposure to non-treated MWWTP effluent sample, whereas 50% of survival was observed after 15 days of exposure to treated samples, indicating the formation of low toxic by-products. Based on these results, it is possible to conclude that the degradation was strongly affected by iron complex source and operational parameters, thus emphasizing the importance of determining the ideal treatment condition for each L in order to enable MWWTP effluent at neutral pH, maximize degradation efficiency and reduce effluent toxicity.

## Acknowledgments

CAPES, CNPq and FAPEMIG

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

# SELEÇÃO DE UM AGENTE DESESTABILIZANTE DE EMULSÕES DO ÓLEO COMESTIVEL OBTIDO EM RESTAURANTES DO LITORAL DE PERNAMBUCO VISANDO SUA RECICLAGEM

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*Palavras Chave: Emulsão óleo–água, Tratamento de efluentes, Coagulação, Floculação.*

## Highlights

Selection of a destabilizing agent for emulsions of edible oil obtained in restaurants from Pernambuco coast for recycling. Wastewater treatment. Sodium chloride destabilized the emulsion. The system can be used in the treatment of wastewater containing oil.

## Resumo/Abstract

O grande problema em relação ao consumo de óleo comestível por estabelecimentos comerciais no litoral sul de Pernambuco está vinculado ao descarte inadequado dos óleos usados livres e emulsionados. O óleo em água emulsionado é de difícil separação e suas emulsões são estabilizadas por agentes tensoativos como sabões e detergentes comerciais que provocam a produção de uma emulsão estável caracterizando este como um importante poluente. Por isso trabalho teve como principal objetivo selecionar substâncias desestabilizantes de emulsões visando sua reciclagem. Primeiramente construiu-se um sistema simples e de baixo custo que é capaz de receber e separar mecanicamente o óleo da água proveniente do consumo do estabelecimento e destinados ao descarte não seletivo. Este sistema é baseado na separação e recolhimento do óleo devido à sua diferença de densidade com relação a água após a quebra da emulsão. Contudo a separação da emulsão necessita de um agente químico para ser efetiva e por isso foram testados alguns agentes selecionados a partir da sua ação conhecida como floculante/coagulante bem como pela viabilidade financeira para a aquisição pelos estabelecimentos comerciais. O peso selecionado das amostras para a cotação foi de 1 Kg (as formulações testadas foram sempre tablets ou pellets com 5 mm de tamanho). A Tabela 01 apresenta os agentes selecionados e o preço respectivo. Para avaliar a capacidade desestabilizante da emulsão os agentes foram inseridos em concentrações diversas (10, 20 e 40g/L) e foi mensurada a turbidez antes e após a adição deles nas diversas concentrações. Ademais, foi avaliada a curva de dissolução dos agentes com o tempo medido a partir dos sólidos solúveis totais (ppm) (Tabela 2) e o tempo total transcorrido para que o agente fosse completamente dissolvido (Tabela 1). A partir do exposto com relação ao preço de aquisição destacou-se o cloreto de sódio com o menor valor (R$ 1,00 por Kg) e ao mesmo tempo foi capaz de perdurar por 15 dias. Entre as diversas concentrações dos agentes testados para determinar sua dissolução na emulsão percebeu-se que a concentração de 20 g/L foi efetiva na quebra da emulsão logo após a sua introdução e comparando com a de 40g/L que também é efetiva se mostra menos onerosa e por isso se mostrou a escolha ideal para este sistema. Dentre os agentes empregados todos foram efetivos com exceção do sulfato de sódio.

**Tabela 1**: Custo e tempo do agente desestabilizante

| Agente empregado | Tempo durabilidade (dias) | Valor |
|---|---|---|
| NaCl | 15 | R$ 1,00 |
| KCl | 8 | R$ 21,90 |
| $Fecl_3$ | >30 | R$ 44,27 |
| $Na_2SO_4$ | 12 | R$ 13,90 |

KCl: Cloreto de potássio; $FeCl_3$: Cloreto férrico; $Na_2SO_4$: Sulfato de sódio, NaCl: Cloreto de sódio

**Tabela 2**. Sólidos Solúveis Totais (ppm) dissolvidos do NaCl em diversas concentrações ao longo do tempo

| Tempo de repouso | NaCl (g/L) | | |
|---|---|---|---|
| | 10 | 20 | 40 |
| 0 | 620 | 1910 | 2030 |
| 12 | 624 | 1640 | 2060 |
| 24 | 635 | 1460 | 1820 |
| 36 | 610 | 1640 | 1850 |

NaCl: Cloreto de sódio; g/L: gramas por litro; ppm: parte por milhão

**Área: AMB**

# Simultaneous degradation of pharmaceuticals by peroxidation, photolysis and photoperoxidation

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Palavras Chave: *Water Resources, Wastewater Treatment, Contaminants of Emerging Concern, Advanced Oxidation Processes.*

## Highlights

Atenolol, caffeine, carbamazepine, diclofenac, ibuprofen and propranolol in ultrapure water were subjected to oxidation by hydrogen peroxide, UV light source and UV-light/hydrogen peroxide combination. The treated solutions were used in phytotoxicity essays employing *Lactuca sativa* seeds to evaluate the effects originated from reaction products on plants.

## Resumo/Abstract

### INTRODUCTION

Nowadays, the maintenance of water supply conditions in the face of the densification of large population centers and the fall in the availability and quality of freshwater springs is a great challenge.[1] Therefore, the search for alternative water sources has been increasingly necessary to meet this growing demand. One of these alternatives is the use of wastewater for reuse water production aiming less noble purposes and, under certain conditions, for direct drinking purposes.[2] However, there is a great warning about the contaminants present in sewage, especially regarding contaminants of emerging concern, which are not regulated, have persistence and deleterious effect on human health, face long-term exposure. Thus, novel technologies for contaminants removal, such as advanced oxidation processes reactors, have been applied to promote the chemical oxidation of these compounds.

### EXPERIMENTAL

A mix solution of ATL, CAF, CBZ, DIC, IBU and PRP was added to a photochemical reactor (V = 1 L) and subjected to essays to direct photolysis (UV light, 16 W, 254 nm), peroxidation (4 mmol $H_2O_2$) and photoperoxidation (UV light, 16 W, 254 nm, 4 mmol $H_2O_2$) in times from 0 to 30 min. The compounds quantifications were carried out by UPLC-MS/MS isocratic method (60% NH4OH 0,05 v/v aqueous solution, 40% MeOH). For phytotoxicity essays, 5 mL from treated samples were added to Petri dishes containing a paper disc and 20 *L. Sativa* seeds. The seeds were incubated for 120 hours at 22 ± 1 ºC in the dark and afterward the radicles and hypocotyls lengths were measured.

### RESULTS

Obtained data point out that peroxidation has low efficiency in the removal of most compounds (-7.0±15.7% up to 17.7±13.6%, after 30 minutes and 4 mmol of hydrogen peroxide), photolysis has a moderate efficiency (1.4±3.1% up to 100.0±0.0%) and photoperoxidation has high efficiency (81.9±4.9% up to 100.0±0.0%, after 30 minutes). The phytotoxicity essays employing *Lactuca sativa* seeds, exposed to the to the treated samples, suggested the productions of potential phytotoxic products, generated during photoperoxidation reactions. The affected subjects showed growth inhibition, altered coloration and ramification for radicles, whereas hypocotyls did not seem to be harmed.

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## Agradecimentos/Acknowledgments

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**Área: AMB**

# Soil carbon sequestration in agricultural areas: Evaluation of C content and features of soil organic matter by laser photonic techniques

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Keywords: *Soil Organic Matter, Soil Carbon Stock, humin, LIBS, LIFS.*

## Highlights

Well-managed pastures were able to increase soil C stock
C determined by LIBS showed a good correlation with the reference method
LIFS was able to assess the aromaticity of soil organic matter in intact samples

## Abstract

Low-C-emission agriculture is essential for its sustainable growth, which aims at higher production with a low or zero C emission balance. Soil plays an important role in agricultural productivity, in which it has the potential to accumulate C.[1] The accumulated C can be transformed into C credits and is also profitable for the farmers. In addition to the C quantification, the evaluation of its chemical composition (quality) is essential to predict the resilience and lifetime in the soil. Laser-based photonic techniques are fast alternatives and less expensive than traditional ones; The technique principle is the excitation of elements or molecules, followed by the detection of the photons emitted using a spectrometer.[2,3] The study aimed to quantify soil C and evaluate its quality using Laser-induced breakdown spectroscopy (LIBS) and Laser-induced fluorescence spectroscopy (LIFS), respectively, in experimental agricultural areas, under well-managed pastures and integrated livestock-forest systems, compared to conventional pasture (DP) and an area of native vegetation (FO), located at Embrapa Pecuária Sudeste, São Carlos-SP, Brazil. Soil C was quantified using LIBS with a Q-switched ND:YAG laser, emitting at 1064 nm, with pulse energy of 40 mJ and 10 Hz, whose the emission line at 247.0 nm was used for C quantification. The soil C quantified by LIBS was correlated with a reference technique (Elemental analyzer, model 2400, PerkinElmer, USA). Soil organic matter (SOM) quality was evaluated by LIFS, whose the spectra were acquired directly on whole soil pellets with an excitation at 405 nm and emission 465−800 nm. The spectral area was normalized by C content, obtaining an aromaticity index ($H_{FIL}$). To evaluate a possible correlation between $H_{FIL}$ with the aromaticity of SOM by $^{13}$C NMR, SOM extractions were carried out from whole soil samples in the area with the highest C stock by solubility method, obtaining three humic fractions: fulvic acids (AF), humic acids (HA) and humin (HUM). All fractions were analyzed by $^{13}$C CP/MAS NMR. The rainfed pasture with a moderate stocking rate (RMS) increased the soil C stock (162.25 Mg C ha$^{-1}$) in relation to DP (102.54 Mg C ha$^{-1}$), reaching levels statistically equal to the native vegetation (148.32 Mg C ha$^{-1}$). LIBS showed a correlation of 0.80 with the reference technique, demonstrating feasibility to soil C quantification. The $H_{FIL}$ index of intact soil samples had a correlation of 0.83 with aromaticity degree of HUM fraction, detected by $^{13}$C NMR, suggesting that SOM aromaticity is mainly related to HUM content. Pasture management showed the ability to increase soil C stock, whose SOM from RMS comprised mainly aliphatic moieties. Well-managed pastures with fertilization, low animal stocking rate, and animal rotation seem to increase the introduction of fresh organic matter, leading to soil carbon sequestration, helping to achieve low-C-emission agriculture.

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FAPESP (grant 17/20084-5; grant 19/18267-0) and Sisfoton/CNPq (grant 440226/2021-0).

**Área: AMB**

# Study and characterization of agalmatolite and its use as metals adsorption

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Key words: *Water treatment, adsorption, agalmatolite, cations, metals*

## Highlights

Agalmatolite is used as mineral filler but few works could be found as metal removal. This work proposes the physicochemical characterization and the evaluation of metal removal from polluted water.

## Abstract

In 2016 and 2019 two environmental tragedy occurred due to the rupture of Vale's tailings dam at Mariana and Brumadinho at Minas Gerais State which were responsible to polluted rivers with toxic mud and metals. Thus, the present work has the main objective to evaluate the alternative use of the common agalmatolite mineral as strategy to remove metal from polluted waters, since conventional water and sewage treatments cannot remove the various toxic substances. The agalmatolite mineral used belongs to the class of phyllosilicates with a crystalline arrangement of $SiO_4$ tetrahedra in its structure (Fig. 1). The mineral has the ability to exchange cations with the cations that are inside the crystalline lamellae and, mainly, the interlamellar cations thus this material could remove by exchange toxic metal from superficial polluted water.

The mineral was characterized by X-Ray Fluorescence, Particle Size and Thermal Analysis techniques and the metal quantification atomic absorption was used. In addition, the Fe(III), Al(III) and Pb(II) adsorption experiments were made changing the time and amount of adsorbent. The results shown 80% of lead, iron and aluminum removal, in just 5 minutes of contact with this material (Fig.2). These metal adsorption promising results could be an alternative to low-cost, scale-up adsorbent material for metal remediation.

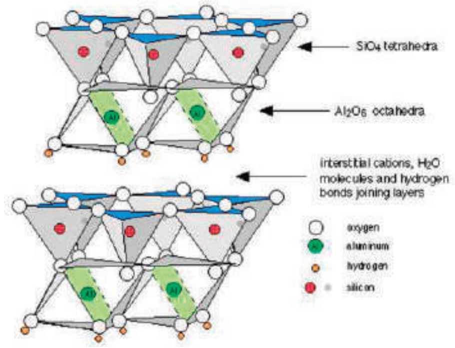

**Figure 1** – Structure of agalmatolite showing two layers of the stacked sheets.

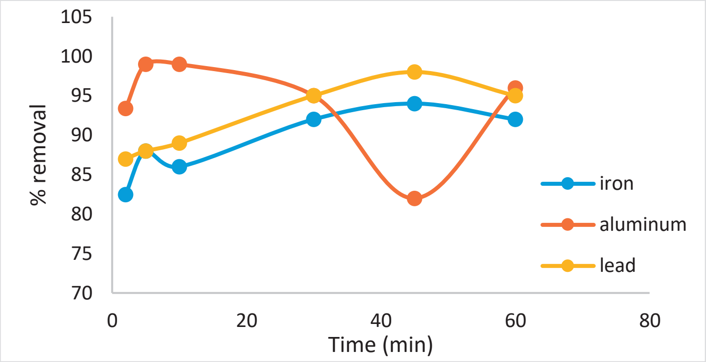

**Figure 2** – Removal rate as a function of time.

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**Área: AMB**

# Summer and Winter Variation of Alkanes and Polycyclic Aromatic Hydrocarbons Concentrations in $PM_{2.5}$ Samples Collected at an Urban Site of Rio de Janeiro, RJ, Brazil

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Key-words: Atmospheric Pollution, $PM_{2.5}$, Alkanes, PAH.

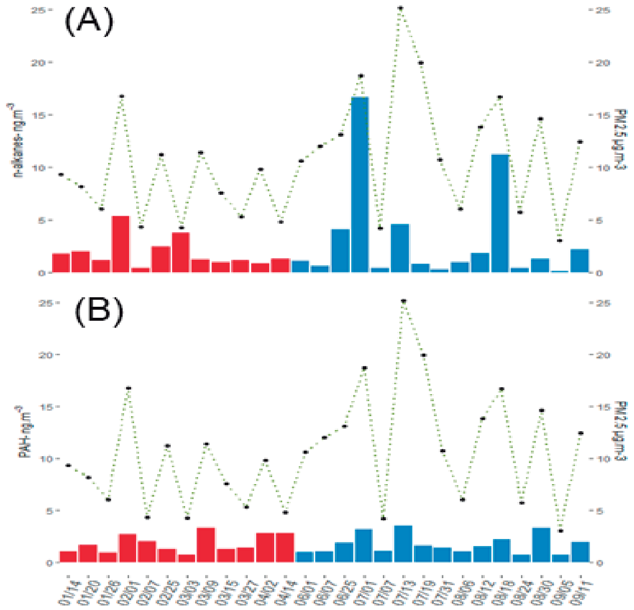
## Highlights

Predominance of the odd long chain *n*-alkanes and high molecular weight PAHs.
Traffic emissions, road dust and biomass burning were the major sources.
Petroleum residues were identified in both seasons.

## Resumo/Abstract

This study analyzed alkanes and polycyclic aromatic hydrocarbons (PAH) in $PM_{2.5}$ samples collected in the district of Bangu, metropolitan region of Rio de Janeiro during the wet (WS:January-April) and dry seasons (DS:June-September) of the year 2019. Bangu is an urban center located between two massifs characterized by high temperatures in summer and dry periods during winter. The methodology involved ultrasonic extraction, clean up by open column chromatography filled with silica gel and gas chromatography (GC-FID and GC-MS)[1,2].

**Figure 1.** $PM_{2.5}$ (lines), *n*-alkanes (A) and PAHs (B) during wet (red) and dry seasons (blue).



Regarding results for two seasons, there was a predominance of the odd long chain *n*-alkanes and the high molecular weight PAHs (5 and 6 rings).

**Table 1.** Medians diagnostic ratios of PAH in both seasons.

| Ratios | Values | Sources | WS[3] Median | DS[4] Median |
|---|---|---|---|---|
| Flt/ (Flt +Pyr) | 0.4-0.5 | Fossil fuels combustion | 0.46 | 0.45 |
| Flu/ (Flu+Pyr) | >0.5<br><0.5 | Diesel<br>Gasoline | 0.25 | 0.11 |
| Ind/ (Ind+Bpe) | 0.2-0.5<br>>0,5 | Petroleum combustion<br>Grass, wood and coal combustion | 0.45 | 0.89 |

Abbreviations: Flt (Fluoranthene);Flu (Fluorene);Pyr (Pyrene);Ind (Indeno[1,2,3-c,d]pyrene);Bpe( Benzo[g,h,i]perylene).

Furthermore, the values of Carbon Preferential Index (WS-1.45; DS-1.82), $C_{max}$ (WS-$C_{31}$; DS-$C_{31}$) and diagnostic ratios of PAH pointed out as polluting sources traffic emissions, biomass burning and road dust. Through the identification of pristane, phytane and unresolved complex mixtures (UCM), it was noticed the presence of petroleum residues[2].

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## Agradecimentos/Acknowledgments

The authors are thankful for the financial support of FAPERJ (E-26/010.101117/2018 and E-26/210.745/2021).

**Área: AMB**

# The use of agro-industrial waste from the Northeast in the production of a biodegradable and edible bioplastic

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Palavras Chave: *Bioplastic; Organic Waste, Biomass.*

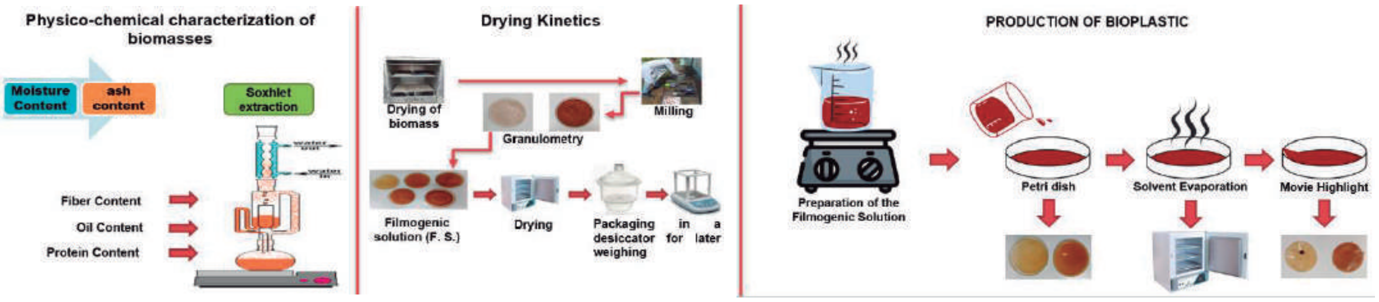
## Highlights

Use of agroindustry residues to production of bioplastics. Manufacture of a biodegradable and edible plastic using mangaba seed residues and sugarcane bagasse.

## Abstract

The lifecycle, petroleum-based plastics are associated with many environmental problems, including greenhouse gas emissions, persistence in marine and terrestrial environments, pollution, etc. Honwever, the bioplastic presents itself as a renewable source alternative to replace conventional plastic produced from synthetic polymers derived from petroleum. [1].

Initially, the selection of biomass, collection and cleaning was carried out. Biomass samples with 40 mesh granulometry were separated for the preparation of drying kinetics. The residues were submitted to physicochemical characterization to evaluate their behavior in obtaining the bioplastic.



The film-forming solutions were prepared in different proportions of plasticizer and biomass, then placed in an air circulation oven at 40 ºC and the time required for the formation of the film was observed. The drying time required was 24 hours at 40 °C in an air ventilation oven. The biofilms resulting from this research were homogeneous and easy to handle. The mixture of residues in the production of bioplastic proved to be a great opportunity for the development of by-products, in addition to aggregating the lost value and sustainable use of these residues.

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## Acknowledgments

**Área: AMB**

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

# UiO-66(Zr): characterization and gas adsorption

**Hiasmin Christine K. P. Sodré (IC),[1] João M. B. Neto (IC),[1] Suzane S. Oliveira (PG),[1] Luiza C. de Moura (PQ)[1], Jussara L. Miranda (PQ)[1].**

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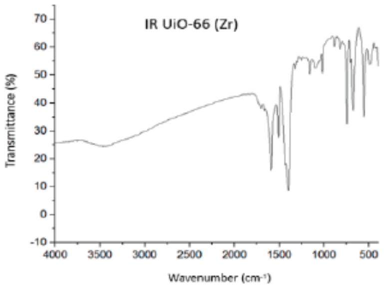
Keywords: *UiO-66(Zr), $CO_2$, $CH_4$, Adsorption, Synthesis.*

## Highlights

UiO-66(Zr) is a kind of MOF widely applicable in the capture of Greenhouse gas (GHE) due to its excellent properties as size and tunable porous, high superficial area, and others.

## Abstract

The industrial area, especially the oil industries, emit high rates of GHG. Therefore, considering issues related to sustainability, the development of CO2/CH4 adsorption and separation mechanisms can generate environmental and economic benefits, since they reduce the emission of pollutants and benefit the production of natural gas, which has a growing demand in this period. of the energy transition.[1] Some materials can be used to contribute to the capture of these gases, such as MOFs - Metal-Organic Frameworks - a new class of hybrid, organic-inorganic materials, in which an organic ligand, generally carboxylated, coordinates a metallic center originating structures with up to 3 dimensions.[2] Due to the range of organic structures that can be studied, as well as metallic centers, MOFs can be used in several areas, including the capture of greenhouse gases (GHG), such as the UiO-66(Zr) that has gained prominence in this field of study. That said, the objective of this work is to characterize the synthesis of UiO-66(Zr), carried out by the LACQUA/UFRJ Group, by means of x-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis, and volumetric analysis of adsorption. The results show that in the infrared region of the UiO-66 obtained (Figure 1) bands between 550 and 750cm$^{-1}$ were observed, attributed to symmetrical and asymmetrical stretching of the Zr-O bond and angular deformation of the O-Zr-O. The X-ray pattern shows the characteristic peaks of UiO-66 (Figure 2).



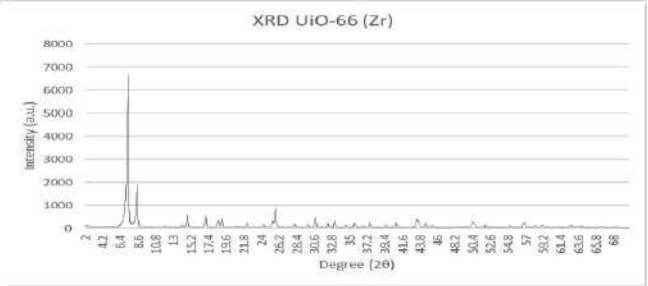


Figure 1 (left) – spectrum in the infrared region and Figure 2 (right) – diffraction pattern of synthesized and activated UiO-66.

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**Área: AMB**

# Use of coconut fiber as a stable support for $TiO_2$ in gas phase photocatalytic processes.

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Keywords: *heterogeneous photocatalysis; natural fibers; atmosphere; coconut fiber; titanium dioxide; air quality.*

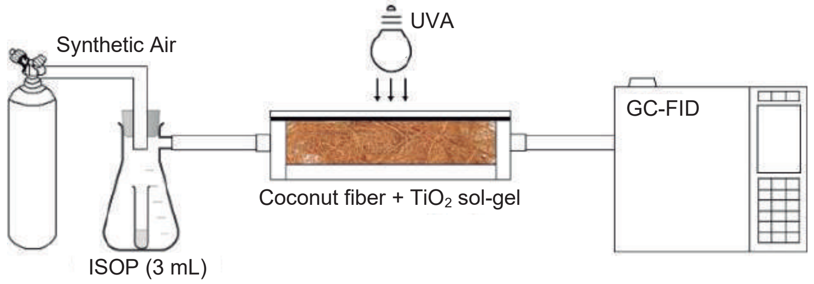
## Highlights

$TiO_2$ coated coconut fiber presented higher photocatalytic degradation of gaseous isopropyl alcohol than coated glass slides due to its more elevated contact surface and higher content of supported $TiO_2$.

## Resumo/Abstract

Heterogeneous photocatalysis (HP) is an advanced oxidative process widely used to degrade organic pollutants or inactivate microorganisms, with applications that include air, water, or surfaces.[1] The activation of a semiconductor by radiation is responsible for generating reactive oxygen species (ROS) in HP, promoting oxidation and reduction reactions. $TiO_2$ is a semiconductor widely used in HP due to several advantages: good adhesion to various supports. For application in the gas phase, the catalyst must be supported on a stable surface that keeps the photocatalyst immobilized without losing efficiency.[2] Most of the works fix $TiO_2$ in glass, polymers, metals, and ceramics. However, these materials still have some disadvantages such as specific area, fixation problems and even attack of the support by the reactive species generated by the photocatalyst. An alternative that has recently emerged is natural fibers, which, in addition to their sustainability benefits, present excellent resistance to photodegradation by light and ROS.[3] This work used coconut fiber as support for $TiO_2$ due to its high lignin content (40-45%), which gives the high fiber strength.[4] The fiber was cut (10 x 4 x 1 cm), washed with water, dried at room temperature, weighed (approx. 0.827 g) and impregnated by immersion three times with $TiO_2$ sol-gel (final mass of photocatalyst in the fiber: 0.182 g). The impregnated fiber was placed in a flat reactor that allowed air flow contaminated with gaseous isopropyl alcohol (ISOP). When illuminating the system with a UVA lamp, the radiation activates the $TiO_2$ generating ROS and degrading the ISOP adsorbed on the fiber. ISOP can undergo complete or partial photocatalytic degradation generating acetone (ACE).[5] ISOP and ACE concentrations were monitored in Gas Chromatograph coupled to a Flame Ionization Detector (GC-FID). The system set up for the experiments (**Figure 1**) consists of a flow of synthetic air (100 mL $min^{-1}$) evaporating 3 mL of liquid isopropyl alcohol, generating a flow of air contaminated with gaseous isopropyl alcohol and irradiated with UVA radiation. After 180 minutes, ISOP concentration was reduced by 98.3%, 75.5% was converted to acetone. The remaining 24.5% of ISOP may have undergone mineralization (complete degradation to $CO_2$ and $H_2O$). A photolysis test was also performed using fiber without catalyst, and there was no change in the ISOP concentration in 120 minutes of the experiment. In another experiment using a glass plate impregnated with $TiO_2$ sol-gel, only 22.1% of ISOP was reduced in 210 minutes under the same experimental conditions. A more significant amount of the semiconductor adsorbed on the fiber compared to the glass plate, higher turbulence in the system contributed to better results obtained in this work. Leaching and ageing tests also showed that this material has excellent applicability in photocatalytic systems for air purification. The photostability of natural fiber, surface area and sustainable use of waste are essential advantages in this work.

**Figure 1. System used for the photocatalytic tests for air decontamination.**



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## Agradecimentos/Acknowledgments

UENF, Fotoair – CIEMAT e CAPES.

# Use of iron ore tailing as raw material for two products: sodium silicate and geopolymers

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Keywords: *Iron Ore Tailing, Geopolymer, Sodium Silicate*

## Highlights

Mining tailings: high environmental impact; tailings are a good precursor for production of sodium silicate and geopolymers; production of sustainable geopolymers with several applications.

## Resumo/Abstract

Considering the large volume of mining tailings and the environmental impacts related to their storage, studies aiming at the reuse of these tailings are of great importance. In this work, an iron ore tailings (IOT) was used for the production of two different materials: sodium silicate and geopolymers. Geopolymers can be defined as inorganic polymers obtained by alkaline activation of aluminosilicates and, due to their characteristics, they have several applications, mainly in civil engineering, replacing Portland cement[1]. One of the main and most expensive raw materials for the production of geopolymers is sodium silicate, which can also be produced from tailings.

In this work, initially, reactions of IOT with NaOH were carried out by hydrothermal reaction in autoclave at 200 °C (1:1.5 and 1:2.5 molar ratio of $SiO_2$:NaOH) and reaction times of 4 and 8h. XRD, XRF, Mössbauer, SEM/EDS, and titrations, showed that IOT:NaOH ratios of 1:2.5 and reaction time 8 hours completely dissolved the quartz from the IOT, obtaining a solid fraction consisting mainly of hematite and an aqueous phase of sodium silicate, which showed contents of ca. 23% $SiO_2$ and 19% $Na_2O$.This sodium silicate obtained was then combined with IOT and metacaulim to produce geopolimeric material. Proof tests with 5 different formulations were produced: geopolymers with commercial sodium silicate solution: without IOT for comparison with the others (Matrix) and with the addition of 25% and 50% of IOT (IOT25 and IOT50); Geopolymers with produced sodium silicate solution: no IOT added (MSiIT) and 50% tailings added (IOT50SiIT). All materials produced (Figure 1) showed fast curing time, excellent physicochemical properties and excellent values of mechanical resistance to compression (41 to 58 MPa), better results than conventional concrete bodies, therefore they can be used for several applications. These results indicate that the use of the tailings was efficient for the production of sodium silicate and geopolymers.

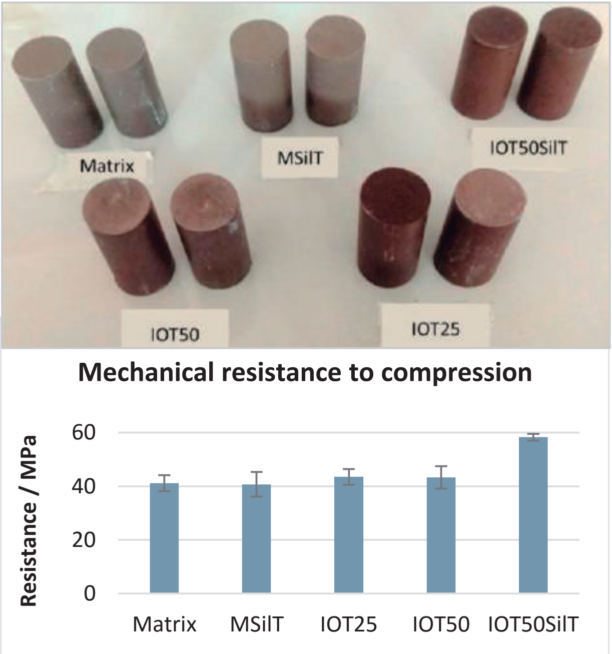

Figure 1. Photos of the produced geopolymers and graphic with values of mechanical resistance to compression of the materials.

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## Agradecimentos/Acknowledgments

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**Área: AMB**

# Volatile organic compounds in the museum and the effect on paintings

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Keywords: VOCs, museum, color, showcase, indoor air quality, pigment

## Highlights

- Volatile organic compounds are found inside of the museum and showcase.
- Organic acids and aldehydes change the color of pigments used in the paints.

## Abstract

Our research group has studied the presence of volatile organic compounds (VOCs) in museum environments since 2014 when a study was started at the Archaeological Museum of Madrid (MAN). A 4-year systematic survey was carried out from the renovation of this museum to its opening to the public (2014 to 2017).[1,2] VOCs are present inside the hermetic showcase and the museum itself, and they are from construction materials (adhesives, sealants and woods) and are also brought by visitors.[1] The effect of some VOCs, such as acetic acid and formaldehyde on metallic materials and carbonate-based pigments are studied more frequently. However, few studies have evaluated the influence of most of the other contaminants found in these studies.[3] Therefore, this work aims to present results obtained from VOCs inside the MAN and four showcases (Mumia Guanche, Sacerdote de Cádiz, Tebau and Plataria) in 2019. The non-polar VOC samples were analyzed by thermal desorption and gas chromatography equipped with a mass spectrometer (ATD-GC/MS), the aldehydes and ketones by high-performance liquid chromatography (HPLC/UV-Vis), and the organic acids by ion chromatography (IC). Sampling was done using Tenax TA tube for non-polar VOCs, SPE-DNPH (silica with 2,4-dinitrophenylhydrazine) for aldehydes and ketones and a filter impregnated with $Na_2CO_3$ for organic acids. The main compounds detected inside the showcases were aromatics (benzene, toluene and xylenes), siloxanes, aldehydes (hexanal, formaldehyde and acetaldehyde), formic and acetic acid. Compared to the non-polar VOC, a lower concentration was detected in 2019 compared with 2017 in the Tebau and Sacerdote de Cádiz. From the results obtained in the research in the museums, experiments were carried out with two pigments commonly used in paintings. The pigments used were malachite and white lead, basic carbonates. The pictorial models were made of the cotton canvas using a mixture of pigments and linseed oil. Some samples were painted with lead white or plaster as primers, usually by painters to prepare the canvases. The exposure took place inside airtight glass vats with a saturated atmosphere of acetic acid, hexanal and formaldehyde and a control system. Relative humidity and temperature conditions were also monitored. After 42 days of exposure, the following analyzes were performed on the surface of the paintings: color ($\Delta E= [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$) and Infrared Attenuated Total Reflectance -FTIR ATR- (for detection of metal carboxylates). There were significant color changes (minimum ΔE 2 times the control value) on exposure to acetic acid. For lead white, the ΔE variation occurred with an increase in Δb (towards yellow) (fig. 1), while for malachite, there was a decrease in Δb (towards blue). So we can say that the color change occurred because the samples turned yellow and blue, respectively.

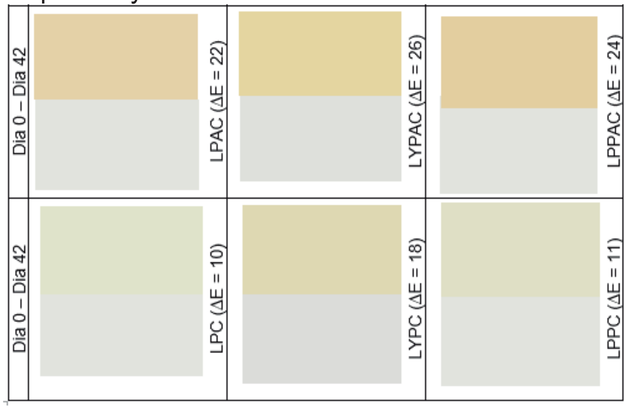

Fig. 1- Changing of color for lead white pictorial models. L – canva; P – lead; Y – gypsum; C-control, AC – acetic acid.

For both pigments, there was a decrease in luminosity. The color change may be related to the formation of lead and copper acetates verified in the FTIR-ATR analysis. In the exposure to hexanal and formaldehyde, there was also the formation of the metallic carboxylates (hexanoates and formates), although the color change was not significant. Although the exposure conditions occurred at high concentrations of VOCs, which is not common in natural museum environments, this work indicates the problem that can occur over years of exposure, thus reiterating the importance of studies involving indoor air quality of the museum and the effect on heritage.

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UENF, CNPq, e CIEMAT

**Area: AMB**

# Water quality and sustainability solutions for drinking water supply in the Taquari-Antas watershed, RS, Brazil

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*[3] Philip Morris Brasil*

Palavras Chave: Water quality, Watershed, Sustainability.

## Highlights

This work presents a diagnosis of the water supply quality of 101 residences located in the Taquari-Antas watershed, state of Rio Grande do Sul, Brazil, and the planning sustainability actions for water treatment.

## Resumo/Abstract

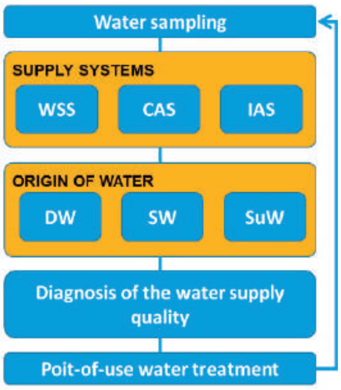

*Figure 1. Project flowchart.*

Sanitation has been increasingly a determining factor in human development, considering the sanitary, social and economic aspects, constituting one of the seventeen sustainable development goals of the United Nations 2030 Agenda. The construction of water supply systems for human consumption (WSS) has proven to be an important sanitation strategy. However, many smaller communities use alternative supply solutions, which can be classified into collective alternative solutions (CAS) and individual alternative solutions (IAS). Many of these alternative solutions present qualitative and quantitative supply problems, which must be identified and dealt with in a sustainable way. Thus, this research aimed to carry out a diagnosis of the water supply quality to 101 households located in the Taquari-Antas Hydrographic Basin, state of Rio Grande do Sul, and to develop sustainable strategies for water treatment (Figure 1). For this, 27 physical and chemical variables of water quality were determined between June and December 2021, according to the methodology described in APHA (2005)[1]. Principal component analysis was used to support the interpretation of results (ChemoStat, 2020)[2]. The results indicated that the biggest water quality problems are located in the population supplied by IAS, typically resulting from the excessive concentration of anions (fluorine, sulfate, chloride, carbonate and bicarbonate)[3] corresponding to 35.6% of the samples analyzed, especially when deep wells (DW) are used as a source of supply. When these systems are supplied from surface water (SuW) or shallow wells (SW), quality problems are associated with the presence of nitrate and turbidity, corresponding to 11.9% of the samples. Based on this diagnosis, point-of-use adsorption and filtration systems will be made and installed in homes with unsatisfactory water quality. Adsorption systems are indicated when excessive concentration of cations or anions is detected. For problems with water turbidity, membrane filtration systems are also tested. These systems will be dimensioned according to the problem variables and the consumption flow of each residence. References: [1]APHA, Standard methods for the examination of water and wastwater, 21st ed. Washington, 2005. [2]CHEMOSTAT V.2. Instituto Nacional da Propriedade Industrial, BR510017000736-5, 2016. [3] BRASIL, Portaria GM/MS nº 888, 2021.

## Agradecimentos/Acknowledgments

The authors thank Philip Morris Brasil, UNISC, CNPq, CAPES and FAPERGS for their support in the development of this project.

# ANA

# Química Analítica

**Área: ANA**

# Analytical approaches to characterizing shales from Ponta Grossa Formation (Paraná Basin) for depositional paleoenvironment evaluation

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*Keywords: Petroleum, Saturated biomarkers, Aromatic hydrocarbons, Marine regression-transgression*

## Highlights

Use of different analytical techniques for geochemical characterization. Petroleum hydrocarbons and biomarkers. Paleoenvironmental evaluation of shales.

## Resumo/Abstract

In this study, shale samples from the Ponta Grossa Formation, Paraná Basin were characterized by different analytical techniques for the geochemical evaluation of the depositional paleoenvironment. Seventy-one shale samples collected in the profiles of three outcrop points: two in Dom Aquino and one in Pedro Gomes formation were analyzed for analytical screening. Total organic carbon (TOC), hydrocarbon generating potential ($S_2$), maximum pyrolysis temperature ($T_{max}$), hydrogen (IH) and oxygen (IO) contents were determined by Rock-Eval pyrolysis. To identified of the total petroleum hydrocarbons (HTP) and biomarkers, samples were extracted by accelerated solvent extraction (ASE) and the soluble organic matter (MOS) were fractionated in saturated and aromatic. The fractions obtained were analyzed by gas chromatography with flame-ionization detection (GC/FID) and GC coupled to mass spectrometry (GC-MS). The results of the pyrolysis analysis for the shale samples from the Dom Aquino (Point I), low levels of TOC (0.01 to 0.66%) and IH (67 to 325 mg HC/g TOC) were obtained indicating samples as type III. The point II (also in Dom Aquino), TOC values between 0.24 and 4.46% and IH from 78 to 410 mg of HC/g of TOC, with a predominance of kerogens from types II and III, indicating a mixed/transitional material. The Pedro Gomes point presented the highest TOC contents among the three points evaluated, with a variation from 0.60 to 5.65% and IH between 100 to 350 mg of HC/g of TOC, indicating a predominance of kerogen types II and III. The possible occurrence of suboxic to oxic environment with contribution of continental material was obtainde by the pristane/phytane (P/F) and preferential carbon index (CPI) ratios. The proportions of regular steranes, the use of hopanes/steranes (HOP/EST), TPP/TPP+DIA and TR20/TR21 saturated hydrocarbon ratios and the graphical expressions of the saturated and aromatic hydrocarbon ratios versus the relative abundance of C29 sterane, DBT/FEN versus P/F and RET/9MF x P/F predict a paleoenvironment of transitional deposition with higher continental contribution and lower marine contribution to Dom Aquino point I. These results suggest the existence of a regressive marine event. In the point Dom Aquino II the transgressive event is indicated by the greater contribution of marine material compared to the continental, with algal/plankton input. The Pedro Gomes point presents both types of trends, regressive at the base and transgressive at the middle and top part, indicating a transitional environment, with contribution of continental material to the base of the outcrop, while for the middle and top a marine environment with plankton/algae contribution.

## Agradecimentos/Acknowledgments

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**Área: ANA Nº de Inscrição: 113**

# Análise simultânea de nicotina e umectantes em tabaco por cromatografia gasosa com detector de ionização em chamas (CG-DIC)

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Palavras Chave: *Análise simultânea, Nicotina, Umectantes, Validação de métodos analíticos.*

## Highlights

**Simultaneous analysis of nicotine and humectants in tobacco by GC-FID**. Development of analytical methods for tobacco and derivative products. Analytical methods validation.

## Resumo

O tabaco (*Nicotiana tabacum* L.) é uma planta cultivada no mundo todo, tendo grande importância econômica e social[1,2]. Atualmente cerca de 8 milhões de mortes são associadas ao tabagismo. Visando um maior controle, medidas de fiscalização foram adotadas por órgãos regulamentadores, uma vez que o tabaco dos cigarros é conhecido por conter diversas substâncias nocivas ao organismo humano[3,4,5]. O objetivo deste trabalho foi otimizar a análise simultânea de nicotina e umectantes (propilenoglicol, glicerol, e trietilenoglicol) por CG-DIC. O preparo de 2 amostras de cigarros comerciais e uma de fumo foi realizado como mostrado na Figura 1.

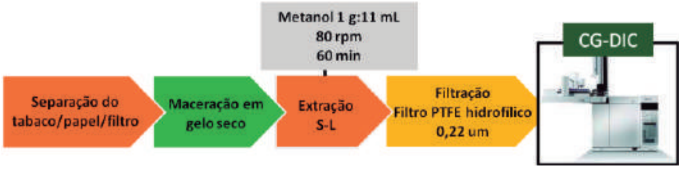

**Figura 1:** Preparo de amostras para extração simultânea de nicotina e umectantes.

Utilizou-se um CG-DIC 7890A (Agilent), coluna DB-WAX 15 m x 0,53 mm x 1,0 µm, hélio (1,8 mL min$^{-1}$), volume de injeção (1,0 µL), injetor e detector com temperaturas de 220 °C e 260 °C, respectivamente. Programação de temperatura do forno: 120 °C (1 min) > 60 °C min$^{-1}$ até 180 °C → 180 °C (3,5 min) → 40 °C min$^{-1}$ até 220 °C → 220 °C (1,5 min). Padrões internos 1-3, Butanodiol e Quinaldina. Os coeficientes de determinação ($R^2$) foram > 0,99 para as faixas de interesse, com exceção da curva analítica para determinação da nicotina ($R^2$ = 0,98). Desvios padrões relativos (DPR) menores que 5,0% foram observados (n=5). Os limites de detecção e de quantificação (LD/LQ) determinados a partir da curva analítica foram: glicerol (0,9/2,6 µg mL$^{-1}$); propilenoglicol (1,3/4,0 µg mL$^{-1}$); trietilenoglicol (0,2/0,7 µg mL$^{-1}$); nicotina (0,9/2,6 µg mL$^{-1}$). A Figura 2 mostra um cromatograma representativo do extrato de uma amostra de cigarro comercial.

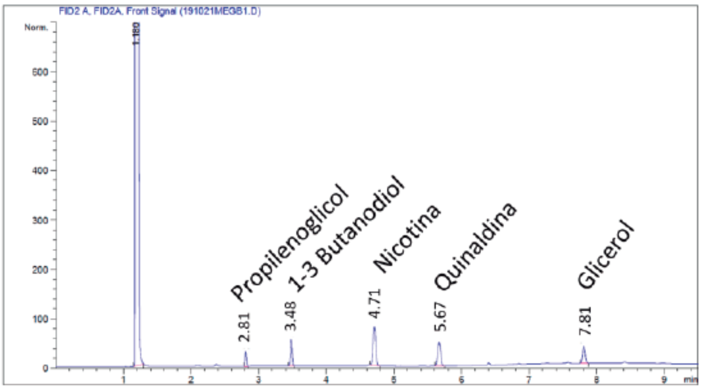

**Figura 2:** Cromatograma representativo do extrato de uma amostra de cigarro comercial.

Os resultados obtidos para a análise das amostras podem ser vistos na Tabela 1.

**Tabela 1:** Resultados (mg g$^{-1}$)da análise por CG-DIC.

| | Amostra A | Amostra B | Amostra C |
|---|---|---|---|
| Propilenoglicol | 3,20 ± 0,05 | < LD | < LD |
| Nicotina | 8,01 ± 0,16 | 7,60 ± 0,01 | 6,70 ± 0,01 |
| Glicerol | 9,04 ± 0,01 | 8,03 ± 0,05 | 1,32 ± 0,03 |
| Trietilenoglicol | < LD | < LD | < LD |

O método proposto permite a determinação simultânea de umectantes e de nicotina com um reduzido tempo de corrida (9 min), mostrando-se mais rápido e eficiente comparado, por exemplo, aos métodos individuais SOP06 (17 min) e CORESTA 62 (28 min) para análise dos respectivos analitos.

**Referências:** [1]Banožić M., et al. *Ind. Crop. Prod.* 144, 2020; [2]Drope J., et al. The Tobacco Atlas. American Cancer Society and Vital Strategies. Sixth ed. Atlanta - Georgia, 2018; [3]WHO. Third ed. Geneva: WHO, 2019; [4]WHO. Tobacco. Geneva: WHO; 2020; [5]Stepanov I.; Hatsukami D.K.; *Elsevier*, 121-150, 2020.

## Agradecimentos

Instituto Nacional de Tecnologia (INT) e Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq).

**Área: ANA**

# An efficient molecularly imprinted polymer for the determination of scopolamine in synthetic urine samples using disposable pipette extraction

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Keywords: *Sample preparation, Scopolamine, Solid phase extraction, Microextraction*

## Highlights

Synthesis of molecular imprinted polymer for selective scopolamine extraction. Application of the polymer as solid phase extraction in the miniaturization DPX device. Synthetic urine sample.

## Resumo/Abstract

Miniaturization in sample preparation has shown great advances related to the principles of Green Analytical Chemistry, such as the reduction of large volumes of sample and solvent, therefore generating less waste and lower energy consumption. An advance in sample preparation from the miniaturization point-of-view is the adaptation of the traditional solid-phase extraction (SPE) cartridge into a disposable pipette tip (DPX)[1]. In this device, much less solid-phase sorbent is employed as well as less sample and solvent volumes are used. Although conventional sorbents are conventionally used in the DPX approach, the sample preparation step may suffer from lack of selectivity of the adsorbent toward the analyte target. In this scenario, molecularly imprinted polymers (MIP's) represented an important advance to enhance selectivity of solid-phase sorbents, due to the capacity of producing polymers with specific recognition sites. Scopolamine (SCP) is a tropane alkaloid extracted from Solanaceae plant family with medicinal uses and hallucinogenic proprieties. However, the wide availability and psychoactive proprieties of SCP have been resulting in its usage in many criminal activities, such as the "good-night cinderella" scam, which has been increasing, especially among women, LGBTQIA+, and men susceptible to theft. In this study, we propose the synthesis and integration of a MIP with DPX as preconcentration step for the determination of scopolamine using Capillary Electrophoresis with $C^4D$ detection. For the synthesis of the MIP, scopolamine was used as template and the functional monomer was acrylamide with the ratio of 1:5 (template/monomer). Ethylenedimethacryl (EDGMA) was used as cross-linking reagent, 1,1′-Azobis (cyclohexanecarbonitrile) (ABCN) as radical initiator and methanol as porogenic solvent. After the synthesis procedure,the polymers were washed and centrifuged with methanol, then the template was removed using a Soxhlet system and the polymers were oven-dried for 24 hours. Non-imprinted polymers (NIP) were submitted to the same procedure, but without the addition of the template. The MIP showed higher affinity to SCP when compared to NIP as well to similar molecules, such as atropine and scopolamine butylbromide. For the preparation of the DPX devices, an amount of MIPs and NIPs were inserted into a 1000 µL pipette tip and sealed with glass wool. The electrophoretic separation was obtained in less than 2 minutes using a solution of 7 mmol sodium hydroxide and 20 mmol butyric acid as running buffer. The optimization of the extraction and elution conditions were conducted by evaluating the following parameters with 3 mL of standard solution of SCP with concentration of 50 µM: (i) preconditioning, (ii) polymer amount, (iii) extraction cycles, (iv) extraction time, (v) elution cycles, (vi) eluent volume and (vii) solvent concentration. The optimum preconcentration parameters were initial preconditioning with methanol, 10 mg of polymer, 10 extraction cycles, X minutes of contact, 2 elution cycles and 500 µL of methanol (100%) as eluting solvent. The MIP-DPX procedure was validated with standard solutions of SCP. Linearity over the concentration range from 0,5 to 6 µM was achieved with correlation coefficient ($R^2$) higher than 0.99.  Synthetic urine sample (pH 6) spiked with SCP were used to evaluated the method accuracy. Recoveries were calculated revealing results of 101,21% ± 3.8% and 83,8 ± 1.53%, for concentration 6 µM and 2 µM, respectively. The preconcentration factor, limits of detection (LOD) and quantification (LOQ) were 20, 0.04 µM and 0.12 µM, respectively. With a miniaturized and selective MIP-DPX device, it was possible to increase the selectivity towards scopolamine enabling its usage as preconcentration step for detectability enhancement using CE-$C^4D$.

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## Agradecimentos/Acknowledgments

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Área: ANA **Nº de Inscrição: 169**

# Arsenic speciation in red wines using zero-valent iron magnetic nanoparticles and hydride generation by atomic fluorescence spectrometry

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Palavras chave: Wines, speciation, arsenic, MSPE, AFS.

## Highlights

This work describes a direct arsenic speciation method applied in red wines samples using magnetic nanoparticles without functionalization exploring a rapid synthesis procedure, separations in a few steps and high sensitivity.

## Abstract

Arsenic is generally present in wine as a result of herbicides and insecticides used for grape production, soil, wine process production and storage conditions. Arsenic species are generally soluble compounds, this way, strategies as liquid separation techniques, high-performance liquid chromatography (HPLC), and capillary electrophoresis (CE) are most often used to separation of these species of the samples. The arsenic determination in wine is challenging due to the complexity of the sample, which has a relatively high content of phenolic compounds and ethanol, causing signal suppression and lack of sensitivity with atomic spectrometric detectors[1]. Non-chromatographic methods that employ magnetic nanoparticles for magnetic solid-phase extraction (MSPE) for chemical speciation have gained prominence in sample preparation have found application mainly in speciation analysis, taking advantage of their adsorptive, catalytic and optical properties and, mainly for the determination of analytes at trace levels because, as a pre-treatment of samples, MSPE avoids the main disadvantages of other conventional methods, such as the consumption of organic solvents. This work describes the determination of arsenic species (III and V) in red wine samples using zero-valent iron magnetic nanoparticles (ZVI MNP) associated with hydride generation atomic fluorescence spectrometry (HG-AFS). ZVI MNP excellent stability, surface area and not require functionalization on the surface for species adsorption. All parameters referring to MSPE such as magnetic nanoparticle mass that will be dispersed in the sample, sample volume, retention and elution time, as well as the experimental conditions for arsenic speciation are being optimized. The ZVI MNP was synthesized has by the co-precipitation method, which is low cost and operational safety[2]. The nanoparticles were characterized by FTIR, DRX and DLS techniques. The characterization confirmed the formation of the MNP ZVI. Initial results show more sensitive measures for As(III), thus, As(V) is pre-reduced to As(III) using KI / ascorbic acid before extractions. The extractions were performed in 25 mL of sample using 1.0 mL of 50 mg of ZVI MNP dispersed in 50 mL of ethanol with 30 s of agitation, before the application of the external magnetic field and elution with HCl 1M for 30 s before AFS determination. The results indicate that the ZVI MNPs have an average size of 6.43 nm, pH 8.0 was the best for extractions based on As(III) retention. The detection limit was 35 ng $L^{-1}$ based on the analytical curve from 1 to 10 µg $L^{-1}$. Besides, a signal gain of 204% with respect to the measurement performed in an extraction in relation to the signal of a reference standard, with deviations of around 1.59% was obtained.

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**Área: ANA** **Nº de Inscrição: 926**

# Automated and simultaneous analysis using electronic eye associated with machine learning for wide beer quality control

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Palavras Chave: *Beer, Optical analysis, Deep machine learning, Quality control*

## Highlights

The prototype analyzes the beer’s frontal and lateral image, scanning 6 parameters, in 12 seconds.
The obtained data is then used to determine which beer is more similar to the one analyzed and then can also be used to increase the database.

## Abstract

The current quality control of beers is performed by sommeliers, which have the human sensibility involved, and laboratories, that uses various tests to evaluate the beer quality**(1)**. A simple alternative is to make a device that automates this process, being faster and precise. Optical analysis is a good alternative and, in addition, is eco-friendly, preventing the use of chemicals. It gets the data by putting the aliquots in cuvettes inside the prototype, getting RGB (Red, Green, Blue) values of the beer images, then translating to HSV (Hue, Saturation, Value)**(2)**. These datas (performed in triplicates) are used to create a database in .XML file type, which is human and machine readable. Then, the database is used in the deep machine learning code, used for classifying new samples of beers with greater precision and accuracy**(3)**. The first stages of this research were the development of the optical analyzer and the machine learning program. Therefore, the goal of this work is to create an automated method of beer quality control of a vast range of beer styles using visual sensors. Afterwards, gradually contaminated beers will be analyzed.

The program was written in Python, in a Raspberry Pi 3 B+ board, using libraries like OpenCV, to get and treat the visual data, Numpy, to make the matrix calculations, Gpiozero, to use the Raspberry pinouts, and Lxml, to organize data in files easily. The device was designed and 3D-printed to prevent natural light to enter and vary the beer luminosity **(Figure 1)**. The exact brightness needed is regulated by a LED built-in the prototype. The two installed cameras capture the beer image. One is positioned in the front of the cuvette capturing the transmitted light and the other, positioned in the side of the cuvette, capturing the turbidity. Then, analyses were made with a wide range of styles and brands, creating the database with two hundred and forty samples. With this data, the machine learning code was able to correctly identify samples of these beers **(Chart 1)**. The next Step is to optimize the codes and analyze controled contaminated beer.

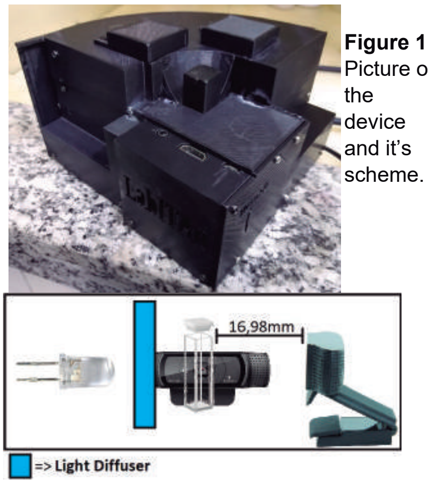
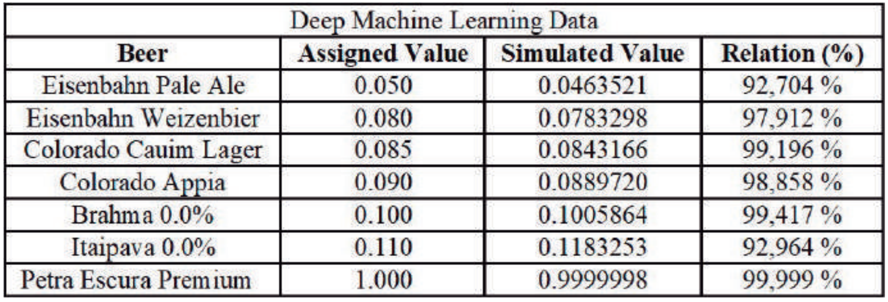


**Figure 1:** Picture of the device and it’s scheme.

**Table 1:** Results of the Machine Learning simulation.



| Deep Machine Learning Data | | | |
|---|---|---|---|
| **Beer** | **Assigned Value** | **Simulated Value** | **Relation (%)** |
| Eisenbahn Pale Ale | 0.050 | 0.0463521 | 92,704 % |
| Eisenbahn Weizenbier | 0.080 | 0.0783298 | 97,912 % |
| Colorado Cauim Lager | 0.085 | 0.0843166 | 99,196 % |
| Colorado Appia | 0.090 | 0.0889720 | 98,858 % |
| Brahma 0.0% | 0.100 | 0.1005864 | 99,417 % |
| Itaipava 0.0% | 0.110 | 0.1183253 | 92,964 % |
| Petra Escura Premium | 1.000 | 0.9999998 | 99,999 % |

## Acknowledgments

UFRJ.

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**Área:ANA**

# Avaliação de procedimentos analíticos usando reagentes alcalinos para a determinação de elementos inorgânicos em leite de búfala por ICP OES

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*Palavras-chave: Leite bubalino. Digestão ácida. CFA-C. TMAH. ICP OES.*

## Highlights

Evaluation of analytical procedures using alkaline reagents for the determination of inorganic elements in buffalo milk by ICP OES. CFA-C and TMAH were evaluated in sample preparation of buffalo milk. The procedures proposed using alkaline reagents proved to be applicable for the samples studied.

## Resumo/Abstract

Ácidos concentrados são comumente empregados em digestão de amostras de leite anterior as análises elementares. No entanto, esse procedimento requer elevado consumo de reagentes e pode oferecer riscos de contaminação para as análises. Por sua vez, procedimentos de diluição e solubilização alcalina são atrativos por possibilitar menor manipulação da amostra. Assim, neste estudo, dois procedimentos analíticos empregando reagentes alcalinos foram desenvolvidos para a análise de constituintes inorgânicos (Ca, Co, Cr, Cu, Fe, Mg, Mn, Na, P, Se, Sr e Zn) em amostras de leite bubalino por espectrometria de emissão óptica com plasma acoplado indutivamente (ICP OES). No primeiro procedimento, as amostras de leite de búfala foram diluídas com uma solução de aminas terciárias solúveis em água (CFA-C) 10% v $v^{-1}$ (pH = 8) na proporção (amostra: CFA-C) de 1: 9 mL ou 0,024: 11,976 mL. No segundo procedimento, um volume de 0,25 mL de hidróxido de tetrametilamônio (TMAH) foi adicionado a amostra (1 mL) e então o frasco foi aquecido em banho termostático por 30 min (80 ºC). Após esse tempo, ácido nítrico (14 mol/L) e peróxido de hidrogênio (30%; m/m) na proporção (mL) de 1:1 foram adicionados aos frascos e novamente foram submetidos à aquecimento por 30 min. Ao final do procedimento 2, as amostras solubilizadas foram diluídas com água ultrapura. Um procedimento de digestão em forno de micro-ondas usando ácido nítrico (2,5 mL; 14 mol/L), peróxido de hidrogênio (2,0 mL; 30% m/m) e 2,5 mL de água ultrapura foi realizado para comparar os teores dos elementos obtidos nos procedimentos propostos com os teores obtidos nos digeridos das amostras. A exatidão dos procedimentos propostos foi avaliada pela comparação das concentrações dos elementos obtidas nos procedimentos propostos com os resultados da digestão ácida das amostras. O test *t*-Student pareado com 95% de nível de confiança foi aplicado para avaliar a proximidade dos resultados analíticos obtidos nos procedimentos. Os resultados (mg/L) mostraram que as concentrações de Ca (2547,6-1672,9), Cr (<0,01- 0,03), Cu (<0,01- 5,0), Fe (0,3- 1,1), Mg (102,9- 240,1), Mn (0,01- 0,10), K (880,3-1336,3), Na (338,4- 720,5), P (949,6-1663,6) e Sr (0,41- 0,96) no procedimento 1 e os teores de Ca (2416,1-1661,0), Cr (<0,001- 0,04), Fe (0,27- 1,1), Mg (93,1- 237,7), Mn (0,01- 0,12), K (900,8-1143,7), Na (336,4-748,3), P (963,2-1650,3), Sr (0,46-0,77) e Zn (1,87-3,66) no procedimento 2 não apresentaram diferença significativa a um nível de confiança de 95% em relação aos valores encontrados pelo procedimento convencional de digestão ácida (Ca: 2426,9-1687,9; Cr: <0,01- 0,03; Cu: <0,02- 5,0; Fe: 0,28- 1,10; Mg: 98,6- 229,8; Mn: 0,01- 0,11; K: 850,8-1324,6; Na: 313,1- 708,8; P: 966,4-1813,2; Sr: 0,41- 0,96; Zn: 1,90- 4,04). Cobalto apresentou abaixo do limite de detecção em ambos procedimentos. Os valores de t calculado obtidos para selênio no procedimento 1 foram maiores que o t crítico (4,303), enquanto os níveis de selênio no procedimento 2 estavam abaixo do limite de detecção. Ambos os procedimentos propostos se mostraram atrativos, simples e rápidos, reduzindo tempo, consumo de reagentes e custos nas análises.

## Agradecimentos/Acknowledgments

Á Capes e a Embrapa Amazônia Oriental.

**Área: ANA**

# Chemometric evaluation of the thermal behavior of nicotinic, picolinic and isonicotinic acids and trivalent lanthanides coordination compounds

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Palavras Chave: *Chemometrics, Thermal Analysis, Lanthanides, Complexes, TG, DSC*

## Highlights

PCA and Cluster analysis were applied to 46 lanthanide coordination compounds with three isomers as ligands, and its thermal behavior is correlated with the lanthanide's atomic number in the complex.

## Resumo/Abstract

The application of Principal Component Analysis, associated with Cluster analysis through k-means clustering algorithm, is a useful way to reduce the dimensionality of datasets comprising multiple samples with multivariate data related to each one, and to classify the samples represented in this new coordinate system into groups with similar properties. In this work, thermal behavior data of 46 lanthanide coordination compounds samples [1-3] involving nicotinic (NIC) acid and its isomers (isonicotinic (IN) and picolinic (PIC)), and data related to the lanthanide ion present in each compound, were subjected to this chemometric treatment. The two first principal components explained 68.2% of data variance (Fig. 1A). The biplot shows that the initial decomposition temperature, ionic radius of the lanthanide, water content, and initial dehydration temperature are the variables that mainly contribute to the two first PC's. The cluster analysis (Fig. 1B) shows six groups formed by employing the K-means algorithm. The elbow method was used to decide the number of clusters to use in the algorithm's initialization (inset graph). All the compounds in group 6 are anhydrous, suggesting that this is its main feature. Groups 2, 3, and 4 comprise compounds with the highest hydration degree (2 $H_2O$), regardless of the ligand. The NIC compounds with light lanthanides are in group 3, while the heavier ones are in group 4. The PIC compounds with heavier lanthanides are in group 2, indicating that the initial decomposition temperature is the lowest for these compounds. This suggests that the lanthanide class and initial decomposition temperature may play a major role in separating these three groups. Also in group 4, we can see the IN compounds with heavier lanthanides (also with 2 $H_2O$), corroborating this last conclusion. Besides the importance of the hydration to the clustering, it is evident that the ligand also influences the observed grouping, as can be seen in groups 2 and 6 (PIC, except Lu compound in group 6), group 3 (NIC) and group 1 (IN, except 2 of them). Even though group 4 is formed by both NIC and IN compounds, we can see a subgrouping within it. In conclusion, for compounds formed between nicotinic acid and its isomers with lanthanide metals, it is suggested that the class of the lanthanide (light or heavy), the type of ligand, and the water content are the most important variables for the classification of these compounds regarding its thermal behavior in a thermogravimetric analysis.

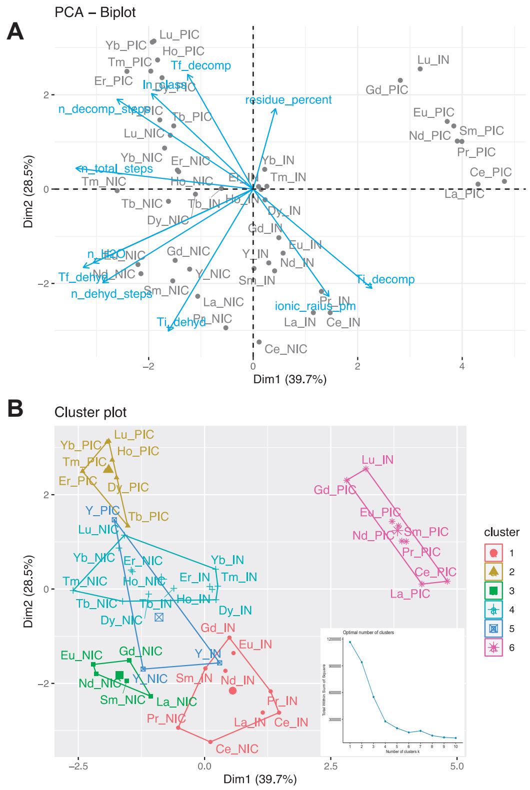

**Figure 1.** (**A**) PCA biplot showing the contribution of each variable and (**B**) Cluster plot highlighting the six groups formed by the k-means algorithm.

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## Agradecimentos/Acknowledgments

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**Área: ANA**

# COLORÍMETRO LAB-MADE DE BAIXO CUSTO PARA DETERMINAÇÃO DE DEMANDA QUÍMICA DE OXIGÊNIO EM ÁGUAS RESIDUÁRIAS

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Palavras Chave: *Colorímetro lab-made, Espectrofotômetro, DQO.*

## Highlights

Low cost lab-made colorimeter for determining chemical oxygen demand in water. A low cost and portable colorimeter was built, composed of one (LEDs - Blue) as a radiation source and an LDR as a detector to determine the chemical oxygen demand (COD) of waste.

## Resumo/Abstract

O emprego da absorção molecular de radiação eletromagnética na região visível do espectro tem se difundido cada vez mais em laboratórios de pesquisa e ensino, os equipamentos utilizados podem ser colorímetros que emprega um comprimento de onda especifico, ou espectrofotômetros que possuem sistemas de separação dos comprimentos de onda da luz. No mercado existe uma diversidade de fabricantes desses equipamentos, são comercializados com valores que podem variar de alguns milhares de reais até centenas de milhares. O elevado custo de aquisição muitas vezes é um fator impeditivo para que instituições de ensino e pequenas indústrias utilizem essa técnica. O desenvolvimento de dispositivos lab-mad apresentam resultados satisfatórios e custos reduzidos. O emprego de diodos emissores de luz (LED) proporciona uma fonte de radiação com elevada pureza espectral e estreita largura da banda de emissão, características desejáveis para utilização em fontes de colorímetros, a detecção da radiação pode ser realizada empregando fotoresistores do inglês (Light Dependent Resistor) (LDR), é um componente eletrônico cuja resistência varia conforme a intensidade da luz. Foi construído um colorímetro de baixo custo e portátil composto por um (LEDs - Azul) como fonte de radiação e um LDR como detector, o valor da resistência do LDR foi mensurada utilizando uma ponte de Wheatstone que apresenta relação linear potencial elétrico e a resistência do LDR. A medida da tensão de saída foi realizada utilizando um multímetro da marca minipa modelo ET-1400. O colorimetro foi avaliado frente a um espectrofotômetro UV/Vis comercial (Shimadzu® UV Mini 1240) na determinação da demanda química de oxigênio (DQO) de águas residuárias. As curvas analíticas obtidas da medida de dicromato de potássio ($K_2Cr_2O_7$) remanescente da digestão das amostras de água residuária obtidas com espectrofotômetro e com colorímetro home made apresentaram uma boa linearidade na faixa de concentração estudada, o tratamento das curvas por regressão linear pelo método de mínimos quadrados, forneceram coeficientes de correlação da ordem de 0,99. O colorímetro apresentou uma sensibilidade analítica de 2,0 vezes maior que o espectrofotômetro para determinação da Demanda Química de Oxigênio, isso deve-se ao colorímetro permitir o ajuste da intensidade luminosa do LED, proporcionando medidas mais sensíveis. Através da analise de variância (ANOVA) verificou-se com 95% de confiança que não há diferença significativa nos resultados obtidos nas analises com o colorímetro e espectrofotômetro demonstrando ser viável, com baixo custo de construção, menos de 100 reais. O equipamento desenvolvido no presente trabalho apresenta potencial para utilização em laboratórios de ensino e após devidas validações em laboratórios de análises que realizam determinações colorimétricas de DQO.

## Agradecimentos/Acknowledgments

Os autores agradecem à Universidade Tecnológica Federal do Paraná – Campus Londrina e à Universidade Estadual de Londrina.

**Área: ANA** **Nº de Inscrição: 00699**

# Colorimetric determination of Cl content in fuels using field-portable smartphone and USB camera: challenges and possibilities

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Keywords: *colorimetric analysis, mobile phone device, crude oil, chloride determination.*

## Highlights

Colorimetric chemical analysis in fuels using a portable device and a smartphone.
Free app for USB camera operation and image processing.
Partial least squares (PLS) regression models of digital images.

## Abstract

The presence of salts (expressed as chlorides) in crude oil depends on the origin and of the wells production. These chlorides, if not removed, can react to form a corrosive hydrochloric acid during the refining process, leading to operational problems as corrosion, incrustation and also in the deactivation of catalysts. Therefore, many analytical techniques or industry standard methods are routinely used to determine chloride in crude oil and fuels. Regardless of the analytical method selected, some aspects can be considered, such as: cost, time and analytical frequency. In this context, the colorimetric analysis using PhotoMetrix UVC app can be an approach easily performed with low-cost, portable instrumentation and high analytical frequency. The present work proposes the extraction of chloride from the fuel to an aqueous phase, followed by colorimetric quantification of silver chloride using digital images. For that, parameters for extraction (extraction solution, time and temperature) and for detection (light intensity, number of pixels and volume of solution) were evaluated. To obtain the digital images, an USB camera was placed in an open source 3D-printed chamber illuminated by a white light-emitting diode (LED) with light intensity controlled (Fig. 1). Sample and reagents (silver nitrate and the indicator) were added to an Eppendorf vessel, which was placed inside the chamber. Thus, the digital images were captured and converted into red, green, and blue (RGB) histograms, and partial least squares regression (PLS) models were used within the app. The PLS regression results (obtained directly from the app) were evaluated in terms of coefficient of determination ($R^2$), slope, offset, root mean squared error of calibration (RMSEC), root mean squared error of cross validation (RMSECV), and root mean squared error of prediction (RMSEP). The calibration curve (from 75 to 275 mg $L^{-1}$ of Cl) was obtained using a PLS model with a $R^2$ higher than 0.99. No significant differences ($p < 0.05$) between the measured and predicted values were identified. The RMSEC, RMSECV and RMSEP of PLS model were of 1.56, 20.2 and 20.9 mg $L^{-1}$, respectively.

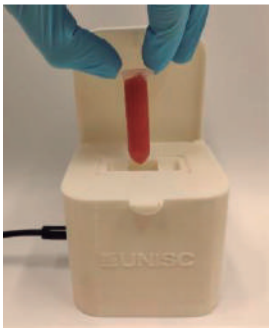

**Figure 1** - Source 3D-printed chamber equipped with USB camera and sample introduction.

## Acknowledgments

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**Área: QPN**

# Comparative Study Between Image Analysis and UV-VIS Spectrophotometry on the Quantification of Chromium VI Oxyanion Present in Water Solution

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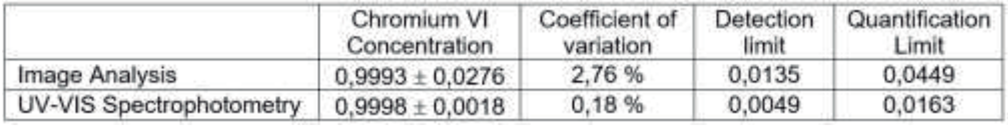
*Keywords*: *Image analysis. RGB matrix. Spectrophotometry UV-VIS. Cr (VI).*

## Highlights

UV-VIS spectrophotometry is an analysis method widely used for quantification of chromophores, organic or inorganic substances. However, it is also possible to perform the same analysis using digital images and data from the RGB matrix of the images, through calculations and based on the Beer-Lambert law. In this study, chromium VI oxyanion in aqueous solution was used for quantification by both methods and the efficiency was evaluated by statistical calculations.

## Abstract

Methods based on the interactions of radiation with matter, called spectroscopic methods, are widely used. In view of this reality, scientific research is increasingly common, in search of new analysis methodologies, new technologies, with the objective of developing alternative, cheaper techniques that do not compromise the quality of the results and that are as effective as the instrumental methods of traditional analysis. Digital photography for performing colorimetric assays is a potential alternative for quantitative analytical measurements, being favored by the rapid advancement of technology, both in terms of hardware and software, allowing the acquisition of high-performance images at low cost.[1] To construct the analytical curve in quadruplicate, Dynamics potassium dichromate was used to obtain aqueous solutions with chromium VI oxyanion concentrations between 0.00 and 2.00 mg $L^{-1}$. Ten 1.00 mg $L^{-1}$ aqueous solutions of this oxyanion were prepared to carry out comparative tests between UV-VIS spectrophotometry and digital image analysis. To perform the analysis, the Colorimetric Method with Diphenyl carbazide was chosen. The pH of the solutions adjusted to 1.0 with sulfuric acid P.A. by the brand Synth. The readings were carried out in a Spectrum SP 1105 spectrophotometer, using a quartz cuvette with an optical path of 1.0 cm and the readings carried out at a wavelength of 540 nm. The images were captured by the camera of a smartphone Samsung Galaxy J7 Prime 2. To analyze the images, the *ImageJ* program (v.1.47) developed by Wayne Rasband of the US National Institutes of Health (NIH) was used in the Java platform installed on a notebook Dell. The images obtained were loaded into the program, a measurement of 0.9 cm by 2.0 cm was selected in the middle of the height of each cuvette and then the average values of the RGB channels of the areas selected for analysis were obtained. The RGB channel used to build the curves for image analysis was Green, as it presented better results because it is the complementary color that is absorbed by the solution. The calibration curve obtained by UV-Vis spectrophotometry showed a correlation coefficient of 0.9976, while that of image analysis showed a value of 0.9985. The Table below presents the summary of the results obtained in the analysis of the ten test solutions with the two techniques.



| | Chromium VI Concentration | Coefficient of variation | Detection limit | Quantification Limit |
|---|---|---|---|---|
| Image Analysis | 0,9993 ± 0,0276 | 2,76 % | 0,0135 | 0,0449 |
| UV-VIS Spectrophotometry | 0,9998 ± 0,0018 | 0,18 % | 0,0049 | 0,0163 |

Despite the detection and quantification limits of image analysis being higher when compared to UV-VIS spectrophotometry, the method still becomes viable, even for analysis of industrial waste effluents, since CONAMA Resolution nº 397 establishes the limits maximum of 0.1 ppm of Cr (VI) for disposal in water bodies.[2] The *t-Student* for the difference in the means between the two analyzes was calculated, obtaining the value 0.0572. Considering the linearity in the analytical curves, good sensitivity, low detection and quantification limits and excellent reproducibility, the Image Analysis method presented similarity with UV-VIS spectrophotometry. Therefore, the use of digital images for quantitative analysis of chromium VI oxyanion seems feasible.

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## Acknowledgments

**Potentially Área: ANA**

# Comparison of decomposition methods of commercial soap samples and determination of Cd, Mg, Pb, and Zn by ICP OES

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Palavras-Chave: *Decomposition, Sample preparation, Soaps, Direct analysis.*

## Highlights

Dry decomposition of soaps by muffle furnace, wet decomposition by microwave and conventional heating, and direct analysis were compared. Levels of Cd, Mg, Pb and Zn were determined using ICP OES

## Resumo/Abstract

Soaps are composed of salts of carboxylic acids from vegetable or animal origin; these acids have a long apolar chain, ended with a polar head, they are known as fatty acids. Fatty acids of sodium or potassium as cations have detergent properties, they come from the saponification reaction between an alkaline base and a triglyceride. These features favor the interaction between the soap and a polar or an apolar environment, where micelles are formed, allowing cleaning. The soaps are products designed for a variety of uses, they act through contact with the human skin surface to clean it, perfume it, modify its appearance, prevent odors, and keep it in good condition.

Previous studies have shown the presence of potentially toxic elements in these matrices, in levels exceeding the limits established by regulations. In long-term use, contact with these elements can be harmful to health.

In this work, four different sample preparation methods were evaluated for further determination of Cd, Mg, Pb, and Zn in nine samples of commercial soaps (being one of them, a powder soap sample). The methods evaluated were, as follows: i) wet digestion assisted by microwave radiation; ii) wet digestion in an open system with conventional heating; iii) dry decomposition using a muffle furnace; iv) direct analysis. The elements were determined by Inductively Coupled Plasma Optical Emission Spectrometry (ICP OES). The definition of the best condition for digesting the samples was made through a set of tests performed; conventional heating, using 1 mol/L $HNO_3$ and $H_2O_2$ (30%), led to lower levels of dissolved organic carbon (<189 mg/L) and residual acidity (0.95 mol/L). The average hydrodynamic diameter of 525 nm was determined using dynamic light scattering (DLS) measures; no particle size distribution was greater than 5000 nm. After defining the ideal sample preparation method, the analyte recovery was evaluated through the addition of known concentrations of Cd, Mg, Pb, and Zn. Values between 83 and 118.9% were obtained, which are within the accepted range. The limits of detection (LD) and quantification (LQ) obtained for all analytes were smaller than 0.04 mg/L. The concentrations determined in soap and powder soap, in µg/g, were in the range, as follows: Cd (<LD), Mg (50.89 to 1119.04), Pb (<LD) and Zn (280.25 to 537.54), being within the limits established by legislation. Therefore, it can be concluded the determined elements do not present any hazards to consumers.

## Agradecimentos/Acknowledgments

The authors are grateful to FACEPE (PRONEX/NUQAAPE) and CAPES for financial support and Claudio Henrique Rodrigues da Silva for his collaboration.

**Área: ANA**

# Desenvolvimento de método para reutilização dos reagentes *4*-metilpiperidina e *N,N*-dimetilformamida para remoção do agrupamento Fmoc

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Palavras Chave: *Química ambiental, Meio ambiente, Recuperação, Analítica, 4-metilpiperidina, N,N-dimetilformamida*

## Highlights

Development of a new method for the reuse of *4*-methylpiperidine and *N,N*-dimethylformamide reagents in the Fmoc deprotection reaction; Characterization and quantification of 4-methylpiperidine in Fmoc deprotection solutions.

## Resumo/Abstract

O grupo fluorenilmetoxicarbonilo (Fmoc) é comumente empregado para a proteção de grupos amino livres e está presente nos derivados de aminoácidos empregado para a síntese de peptídeos em fase sólida (Cham and White, 2000). Nesta síntese, o grupo Fmoc é removido empregando-se solução de 4-metilpiperidina (4-PIPE) em *N,N*-dimetilformamida destilada (DMF) 20% (v/v) (MATOS, 2015), deixando o grupo amino livre para formação da ligação peptídica entre os resíduos de aminoácidos. Portanto, a etapa de remoção do grupo Fmoc é repetitivo sempre antes cada etapa de acoplamento (ligação peptídica) de um novo resíduo durante a síntese, resultando em um volume considerável de resíduo gerado, consideravelmente tóxico ao meio ambiente. Neste sentido, o presente trabalho teve como objetivo estabelecer uma metodologia de recuperação do resíduo da desproteção do Fmoc, atendendo assim aos princípios da Química Ambiental, além de promover a reutilização da solução de desproteção 4-PIPE/DMF, que apresenta elevado custo para a síntese de peptídeos.

Primeiramente, os principais reagentes constituintes da etapa de desproteção da síntese (álcool isopropílico; diclorometano; água; 4-metilpiperidina e *N,N*-dimetilformamida) foram analisados por espectroscopia na região do infravermelho (FTIR). Em seguida, foi realizada a destilação fracionada do rejeito da desproteção, separando as frações F40, F82, F100, F120, F153 nas respectivas temperaturas de destilação 40°C, 82°C, 100°C, 120°C, 153°C. As partes fracionadas retiradas foram analisadas por espectrometria de infravermelho, confirmando que as frações F40 e F82 correspondiam majoritariamente ao DCM e IPA, respectivamente. Os espetros das frações F120 e F153 mostraram grande similaridade, no entanto, a presença de bandas em 750cm$^{-1}$ e 700cm$^{-1}$ somente no espectro da fração F120 revelaram a presença do grupo Fmoc em mistura com DMF apenas nessa amostra. O resultado foi confirmado por espectrometria de $^{1}$H e $^{13}$C de RMN. Neste sentido, para determinação da concentração de 4-PIPE em DMF da amostra F120, foi estabelecida uma curva de calibração para soluções de 4-PIPE/DMF de diferentes concentrações em porcentagem v/v (15-55%), a partir da titulação com solução de HCl 1M. As soluções padrões de 4-PIPE/DMF foram previamente diluídas com 60% em volume de água. O ajuste linear da curva de calibração foi de R=0,99, atribuindo uma boa confiabilidade da curva. A titulação da fração F120 revelou uma concentração de 0,7% de 4-PIPE em DMF, que após o ajuste o foi reutilizada em reações teste em resina Rink-amide contendo Fmoc. A análise qualitativa por teste de ninidrina mostrou a eficiência da desproteção, enquanto que a quantificação de Fmoc após desproteção foi condizente com o valor esperado levando-se em conta o grau de substituição da resina Rink-amide-Fmoc de 0,79 mmol.g$^{-1.}$

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## Agradecimentos/Acknowledgments

Ao PET-Química, Departamento de Química e a Universidade Federal dos Vales do Jequitinhonha e Mucuri-UFVJM.

**Área: ANA** **Nº de Inscrição: 00277**

# Desenvolvimento de metodologia para determinação de $NH_4^+$ em cigarros, utilizando cromatografia de íons e cálculo de $NH_3$ e N por fator de conversão.

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Palavras Chave: *Amônio, Amônia, Nitrogênio Amoniacal, Cromatografia de íons.*

## Highlights

Determination of ammonium in cigarettes using ion chromatography and ammonia and ammoniacal nitrogen by conversion factor.

This work demonstrates that the developed method is efficient for the detection of ammonium in cigarettes, allowing the quantification of Ammonia and Ammoniacal Nitrogen by conversion factor.

## Resumo/Abstract

A OMS indica o tabaco com um fator de risco para seis das oito principais causas de morte no mundo, matando uma pessoa a cada seis segundos causando mais de cinco milhões de falecimentos, com previsão de mais de oito milhões em 2030 se nenhuma medida for tomada. Considerando a complexidade técnica exigida em análises desta natureza e que muitos dos produtos derivados do tabaco demandam de análises criteriosas, principalmente do ponto de vista fiscal, há uma necessidade premissa de desenvolvimento de métodos analíticos e suas validações, seguindo normas de qualidade que garantirão a confiabilidade dos resultados das análises, tornando-os compatíveis com os padrões internacionais, de forma que possam gerar o conhecimento do produto e corroborar com ações de vigilância sanitária. Foi realizada a quantificação de três maços de cigarro (marcas e fabricantes diferentes), de modo que o cátion amônio ($NH_4^+$) foi quantificado por cromatografia de íons com detecção por condutividade.e a partir disto foi possível quantificar a amônia ($NH_3$) e o nitrogênio (N) amoniacal através dos cálculos de fator de conversão. O preparo da amostra foi feito com 1g da mesma, adicionando 50 mL de água ultrapura, seguindo de 30 min de agitação (mesa agitadora). Logo após, filtrou-se 5 mL do sobrenadante em unidade filtrante 0,45 um e foi avolumado para 25 mL com a fase móvel. Os parâmetros utilizados foram: Coluna metrosep C4 (Sílica gel com grupos carboxílicos 150 x 4.0 mm); Fase móvel: Ácido tartárico 4 $mmol.L^{-1}$, Ácido 2,6 Piridinocarboxílico 0,75 $mmol.L^{-1}$ e Acetonitrila 1%; Volume de injeção 20 uL; Fluxo de 1,0 $mL.min^{-1}$; Temperatura da coluna: 35 ºC; Tempo de corrida: 18 min. Foi realizada uma curva analítica em seis níveis para determinação de amônio, nas seguintes concentrações: 1; 2; 4; 6; 8 e 10 $mg.L^{-1}$ com $R^2 = 0,9999$ (Figura 1). As amostras foram analisadas por triplicatas de injeção e os resultados estão representados na Tabela 1. A metodologia desenvolvida mostra-se promissora, uma vez que foi possível quantificar o analito de interesse com boa recuperação, sensibilidade e separação entre o analito e os outros compostos presentes na matriz.

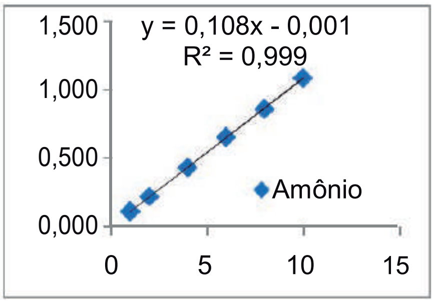

Fig 1: Curva analítica em seis níveis para determinação de amônio.

Tab. 1: Tabela de resultados – Concentração de amônio (IC), amônia e nitrogênio amoniacal (fator de conversão) nas 3 amostras.

| AMOSTRAS | Concentração de Amônio ($mg.L^{-1}$) | Concentração de Amônia ($ug.g^{-1}$) | Concentração de Nitrogênio Amoniacal (%) | Desvio padrão |
|---|---|---|---|---|
| **AMOSTRA 1** | 4,77 | 1070,20 | 0,08802 | 0,03 |
| **AMOSTRA 2** | 4,51 | 1023,35 | 0,084165 | 0,01 |
| **AMOSTRA 3** | 4,21 | 965,95 | 0,075005 | 0,00 |

## Agradecimentos/Acknowledgments

**INT, CNPQ.**

**Área:** ANA

# Desenvolvimento de um preparador amostral automático para análise cromatográfica.

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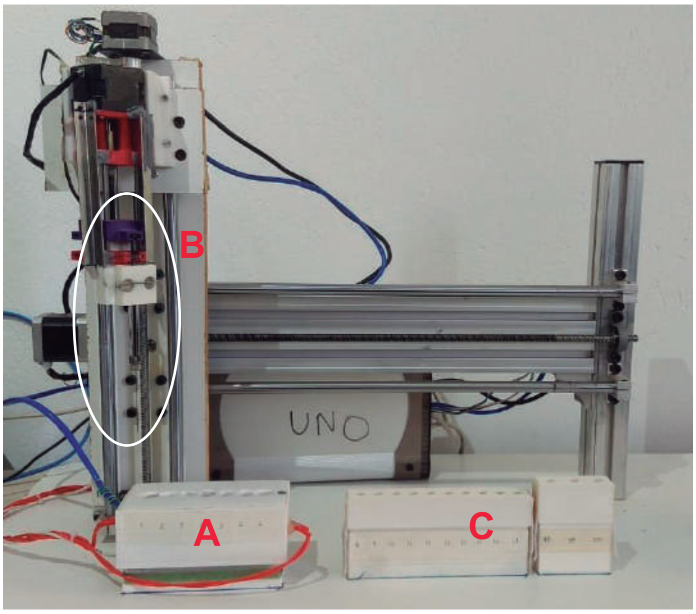
Palavras Chaves: *Automatização; Arduíno; Cromatografia; Derivatização; Aminoácidos.*

## Highlights

Development of an automatic equipment for sample preparation followed by chromatographic analysis. Automating sample preparation can reduce operating time and costs, and random errors in results.

## Resumo/Abstract

**Figura 1:** Preparador amostral automático.



O avanço tecnológico trouxe benefícios para o dia a dia das pessoas e das empresas através da automatização de atividades antes manuais. Essa inovação contínua, impacta a rotina dos laboratórios que demandam por análises cada vez mais rápidas, simples e sustentáveis. Isso induziu a mudança da etapa de preparo de amostras com a inclusão de equipamentos automatizados para miniaturização de sistemas, redução de riscos humanos, de erros aleatórios e, de tempo e custos dos tratamentos amostrais. Foi construído um robô cartesiano com propriedades capazes de preparar soluções e amostras líquidas. Todo o equipamento é controlado por um *software* escrito em Python 3 que roda em um computador e por dois microcontroladores Atmel 328P programados em linguagem C. O *software* é responsável pelo deslocamento da microseringa nos eixos cartesianos que são movidos por motores. O objetivo é fazer com que os motores de passos desloquem corretamente a microseringa até a posição desejada dos frascos e reatores, e realize as funções de pipetar ou verter o volume almejado. O *software* também é responsável pelo funcionamento do bloco reacional: sistemas de aquecimento e agitação. Um motor de eixo desbalanceado é responsável pela agitação do bloco (2965 rpm). O equipamento é composto por (**Figura 1**): **A)** um bloco reacional (contém 7 reatores) com controle de temperatura (isolados termicamente por placas de isopor) e agitação; **B)** por uma microseringa, e; **C)** por suportes para colocar frascos de reagentes e descarte. Utilizou-se metodologias de validação para a temperatura do bloco (temperatura ambiente até 84,9 ± 0,54 °C) e para o volume da microseringa (até 159,0 ± 0,34 µL), e os resultados dos coeficientes de determinação foram: $R^2_{TEMPERATURA} = 0{,}9994$ e $R^2_{VOLUME} = 0{,}9999$. O preparador amostral desenvolvido foi utilizado para o preparo de curvas de calibração de soluções e de reações de derivatização seguida de análise cromatográfica: **1)** Soluções com padrão de esteroides (30,0-180,0 mg $L^{-1}$): $0{,}9925 < R^2 < 0{,}9944$ – *GC;* **2)** Solução padrão de diclofenaco de sódio (25,0-125,0 mg $L^{-1}$): $R^2 = 0{,}9995$ – *HPLC*; **3)** Curvas com padrões de aminoácidos derivatizados (10,0-35,0 mg $L^{-1}$) com propil cloroformato: $0{,}9678 < R^2 < 0{,}9995$ – *GC*. Todos os resultados das curvas de linearidade das análises cromatográficas foram avaliados por testes estatísticos de normalidade e homoscedasticidade. A versatilidade desse preparador amostral automático vai além das aplicações desenvolvidas neste trabalho, pois ele executa funções que são responsáveis pelos principais parâmetros de estudos de otimização de processos. Podendo garantir maior repetibilidade/precisão de resultados.

## Agradecimentos/Acknowledgments

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**Área: ANA** **Nº de Inscrição: 00018**

# Determination of bisphenol A and phthalates in utensils and toys for infants using HPLC-UV and bioaccessibility study

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Palavras Chave: *Endocrine disruptors, Simultaneous determination, Factorial planning.*

## Highlights

Bisphenol A and phthalates are endocrine disruptors. The phthalate concentration is below the limits established by ANVISA. DBP migration values were detected above those allowed by ANVISA

## Abstract

Brazilian laws restrict the use of bisphenol A and some phthalates in plastic materials due to the risks they can cause to the endocrine system [1]. Bisphenol A and phthalates are chemical compounds used in the production of polymers. Studies show that these compounds are endocrine disruptors and when in contact with the body affect the hormonal system, generating various health problems to the individual [2]. In this research, a unified method was developed for the determination of bisphenol A and dibutyl phthalates (DBP), bis-2-ethylhexyl (DEHP), di-n-octyl (DNOP) and diisodecyl (DIDP) in utensils and toys intended for infants, as well as to evaluate the bioaccessibility of these compounds in artificial saliva. For this, ultrasound assisted liquid extraction and detection on HPLC-UV-VIS at 230 nm were performed. Gradient elution was performed with a binary mixture of methanol (solvent B) and deionized water (solvent A) ranging from 70% B to 93% B from 3 min to 5 min at a flow rate of 1.0 mL min$^{-1}$. The column used was Agilent C18 and had a total elution time of 20 min. After establishing the analysis parameters, the method was validated, finding detection limits of 0.003 to 0.051 mg L$^{-1}$ and quantitation limits of 0.011 to 0.155 mg L$^{-1}$ for bisphenol A and phthalates. Extraction in an ultrasonic system was performed with chloroform and optimized with a factorial design $2^4$, where optimal conditions were defined as 1.50 g of sample in 10 mL of chloroform, with ultrasound extraction time of 20 min at 65 °C. Matrix effect tests showed that the method does not suffer this type of interference and recovery studies showed values from 73.2 to 103 %. Ten commercially acquired samples from the city of Recife-PE were analyzed, and the results presented phthalate concentration values between 0.101 and 30.8 mg Kg$^{-1}$, being considered below the limits established by ANVISA, and bisphenol A concentration values between 0.060 and 21.1 mg Kg$^{-1}$. Migration tests with artificial saliva were performed and the results showed that all samples presented bisphenol A migrations in concentrations allowed by the current legislation. In nine samples, DBP migration values were detected above those allowed by ANVISA. One of the samples analyzed revealed inconsistencies in the packaging information as it claimed to have no phthalates. The proposed method has been shown to be suitable for analysis of endocrine disruptors in utensils and toys intended for infants within the parameters required by ANVISA.

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## Acknowledgments

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**Área: ANA**

# Determination of Ca, K, Mg and Na in sports supplements employing chemometrics tools and direct solid analysis by Laser-Induced Breakdown Spectroscopy (LIBS)

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**Keywords: Macronutrients, Whey protein, Calibration strategy, Factorial design, Principal Component Analysis**

## Highlights

New calibration strategies and chemometric tools were employed for fast and direct determination of macronutrients in sports supplements using LIBS.

## Abstract

Fonte Sports supplements as whey protein contain high protein content and are widely used by high-performance athletes and practitioners of physical activities for muscle regeneration. These supplements may also contain high concentrations of macronutrients such as Ca, K, Mg and Na, which play important physiological functions and therefore must be monitored to maintain a good functioning of the metabolism of users.[1] LIBS, is an analytical technique that enables qualitative and quantitative fast analysis (<1 s), direct analysis or with minimal sample preparation and low generation of residues.[2] Thus, new calibration strategies and chemometric tools were employed for the direct analysis of sports supplements using LIBS aiming at the determination of macronutrients Ca, K, Mg and Na. LIBS emission spectra of the analytes were obtained using an instrument model J200 (Applied Spectra, USA), with a Nd:YAG laser (1064 nm). Approximately 200 mg of each sample was used to obtain pellets using a press (70 kN for 2 min). A Doehlert factorial design with a central point was used to optimize the instrumental conditions for the analyte determinations, being evaluated delay time (0.8, 1.4 and 2 µs) and laser pulse fluence (368, 1422, 2476, 3530 and 4584 J cm$^{-2}$) variables. The following emission lines were monitored: Ca (393.36 and 396.84 nm), K (766.49 and 769.89 nm), Mg (383.83 and 518.36 nm) and Na (588.99 and 589.59 nm), then overall desirability (using signal-background ratio for all wavelengths) was calculated and used as design response. The final instrumental conditions were delay time of 1.4 µs and fluence of 2476 J cm$^{-2}$. Approximately 200 spectra (n = 3) were obtained for each sample, and twelve modes of spectral normalization were evaluated. All sports supplements were also analyzed by ICP OES to obtain reference values to assess the accuracy of direct determinations by LIBS. The concentrations determined by ICP OES were in the range of 3351 to 7069 mg kg$^{-1}$ Ca, 3870 to 13639 mg kg$^{-1}$ K, 626 to 2678 mg kg$^{-1}$ Mg and 1293 to 5170 mg kg$^{-1}$ Na. Three calibration strategies were evaluated for direct determination by LIBS: 1- matrix-matching calibration (MMC),[3] 2- one-point and multi-line calibration (OP MLC),[4] and 3- single sample calibration (SSC).[5] For the determination of Ca, MMC, OP MLC and SSC presented good values of trueness (68 to 119%) and RSD (2 to 30%). For K, OP MLC enabled the best trueness values (87 to 102%) and RSD (1 to 10%), except for some samples. For Mg, good trueness values (83 to 120%) and RSD (1 to 14%), with the exception of some samples, were obtained using MMC and OP MLC. For Na only using SSC presented reliable values for trueness (79 to 116%) and RSD (4 to 10%), for most samples. Unsatisfactory values of trueness were obtained for some elements in some samples due to the strong matrix effects in the LIBS determination. However, some calibration strategies evaluated were able to overcome or minimize the matrix effects for most determinations. The use of principal component analysis - PCA and LIBS spectra made it possible to observe two clusters of samples: high and low protein content in sports supplements. Fast, direct and green method is developed for the determination of macronutrients in sports supplements (whey protein) using LIBS.

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**Área: ANA**

# Determination of Cd and Pb in sediments from agricultural activities around the Anajé-BA reservoir

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Palavras Chave: espectrometria de absorção atômica, sedimentos, tóxicos

## Highlights

Sediments are considered environmental indicators. The GF AAS technique was used to determine Cd and Pb in sediments. The characteristic mass and detection limit for Cd were 1.1pg and 0.03 µg g$^{-1}$, while for Pb they were 17.4 pg and 0.2 µg g$^{-1}$.

## Abstract

The metals present in natural watercourses come from the leaching of chemical substances contained in the rocks, drainage of rainwater and urban, industrial and agricultural discharges. Sediments have a high capacity to retain and accumulate trace elements contained in the water column, which is why they are widely used as environmental indicators. Toxic metals are associated with organic matter in the fine fraction of the sediment, or adsorbed on hydroxides or oxides of iron and manganese, or precipitated as hydroxides, sulfides or carbonates. Under certain environmental conditions, sediments can become important sources of pollution. Thus, this work aimed to determine the concentration of Cd and Pb in sediments from the surroundings of Anagé-BA reservoirs, whose waters are used for consumption. The determinations were performed using a graphite furnace atomic absorption spectrometer (GF AAS) SIMAA-6000 model, with longitudinal Zeeman effect background correction, transverse heating of the graphite furnace and automatic sampler (AS-72). The spectrometer was programmed to detect Cd (228.8 nm) and Pb (283.3 nm). The chemical modifier used was 0.5% (m/v) $NH_4H_2PO_4$ + 0.03% (m/v) $Mg(NO_3)_2$. The volume of the reference standards or sample was 20 µL and the chemical modifier 10 µL. The collections were carried out at four points in the water reservoir of the municipality of Anajé-BA. Sediment samples were collected in plastic bags and frozen until analysis. The analytical procedure for the determination of the metals of interest in the sediment involved: drying at 60 °C, sieving in a plastic sieve (65 µm). A mass of 0.5000 ± 0.0001 g was digested using concentrated $HNO_3$ in a microwave oven. The results found are described in Table 1.

Table 1: Concentrations of Cd and Pb (µg g$^{-1}$) in sediment samples from Anajé-BA Reservoir.

| Concentration | Sediment | | | |
|---|---|---|---|---|
| | P1 | P2 | P3 | P4 |
| Cd | 0.96 ± 0.15 | 2.18 ± 0.14 | 1.20 ± 0.11 | 1.16 ± 0.20 |
| Pb | 7.45 ± 0.94 | 8.98 ± 0.20 | 7.98 ± 0.16 | 7.42 ± 0.16 |

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**Área: ANA**

# Determination of dexamethasone in water matrices using an anodically pretreated boron-doped diamond electrode

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Key Words: *Dexamethasone, Boron-Doped Diamond, Electrode material, Water matrix, Differential pulse voltammetry.*

## Highlights

This work presents a novel method for the determination of dexamethasone in water matrices and the monitoring of the degradation of this pharmaceutical by an advanced oxidation process.

## Abstract

Dexamethasone is a glucocorticoid first synthesized in 1957 and a member of the List of Essential Medicines described by the World Health Organization. In recent years, it has received attention due to its use in the treatment of COVID-19.[1] Furthermore, as a pharmaceutical, its contamination of the environment has also received attention in the last years. Hence, the development of fast, simple, and green methods to evaluate possible contamination of water bodies is necessary. This work presents an electrochemical method with the desirable characteristics to determine the concentration of dexamethasone in different water matrices using, as far as we could ascertain, a never reported anode material for this purpose, boron-doped diamond (BDD). Thus, a method for dexamethasone determination in an aqueous matrix using its oxidation process was developed using differential pulse voltammetry and tested in tap water. The determinations were performed after an anodic pretreatment of the BDD working electrode. Under optimized conditions, using 0.04 mol $L^{-1}$ $H_3PO_4$ as the supporting electrolyte, a linear working range ($R^2$ = 0,997) was attained between the oxidation peak current and the concentration of dexamethasone (from 3.0 to 60 μmol $L^{-1}$) – see the figure, with a detection limit (S/N = 3) of 0.16 μmol $L^{-1}$.

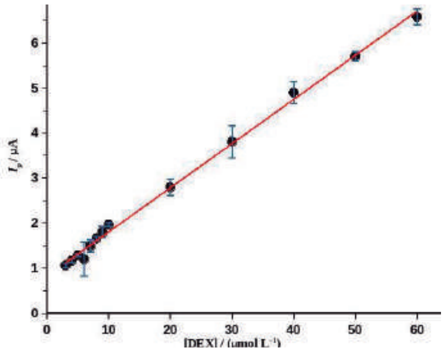

**Fig. 1.** Calibration curve for DEX obtained from the differential pulse voltammograms at the anodically pretreated boron-doped diamond electrode in 0.04 mol $L^{-1}$ $H_3PO_4$ with increasing concentrations of DEX under the optimized conditions.

The proposed method was tested for determining dexamethasone in a tap water sample using only acidification and dilution as sample preparation processes, when a recovery of 106% was attained. The proposed method will be tested with other water matrices samples and for monitoring the dexamethasone concentration during a degradation experiment by anodic oxidation also using a BDD electrode.

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**Área: ANA**

# Determination of Polycyclic Aromatic Sulfur Heterocycles in the Ascidians *(Phallusia nigra)*

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*Keywords: Ascidians, Solid-liquid microextraction Sulfur compounds, Gas chromatography.*

## Highlights

First report on the distribution of PASHs in Ascidians. A procedure for miniaturized solid-liquid extraction was proposed. The PASHs were quantified in different parts of the ascidian by GC-MS.

## Abstract

The ecological and applied importance of the ascidian as a bioindicator is well reported based on metal analysis, but little is known about organic compounds accumulation in these marine organisms. In this study, a miniaturized solid-liquid extraction method, combined with dispersive extraction cleanup (MSLE-DE) was optimized and validated for the determination of the PASHs in ascidia - *Phallusia nigra* samples. The main objective was to evaluate different parts of ascidia in order to determine the behavior towards the distribution of individual PASH compounds. The samples were collected in the Todos os Santos Bay, in the Bahia Marina region, near a gas station and in a control area situated in the Frades Island region. In laboratory, ascidians were dissected in three parts (tunic, hepatopancreas and branchial basket), lyophilized and weighed. The MSLE-DE procedure was optimized for extraction of fourteen PASH of the benzothiophene, dibenzothiophene and benzonaphthothiophene classes. Analytes were determined by gas chromatography coupled to mass spectrometry (GC-MS) operating in the selective ion monitoring (SIM). The methodology was evaluated using matrix-matched calibration. Under optimal conditions, average recoveries of the analytes were between 80.0% and 118.6% with intraday and interday precisions lower than 8.5% and 5.0%, respectively. Linearity ($R^2$) was ≥ 0.99 for all compounds. Method detection limits ranged from 0.10 $\mu g\ L^{-1}$ (4,6-dimethyldibenzothiophene) to 3.40 $\mu g\ L^{-1}$ (benzothiophene) and quantification limits, the values obtained ranged from 0.34 $\mu g\ L^{-1}$ to 11.34 $\mu g\ L^{-1}$ for the same compounds. The benzothiophene was the compound presented in the highest concentration in the hepatopancreas (937.5 ng $g^{-1}$) and tunic (1513.7 ng $g^{-1}$), and the 2,3-dimethydibenzothiophe in the branchial basket (439.3 ng $g^{-1}$). In general, the number of the compounds and concentrations of PASHs were highest in the hepatopancreas, followed by the branchial basket (not considering the benzothiophene). An increase in the concentration for all PASHs was observed when the results were compared with the control area. Thus, compounds such as dibenzothiophene, 4-methyldibenzothiophene, 2,4-dimethyldibenzothiophene and 4,6-dimethyldibenzothiophene presents in diesel were quantified in superior concentrations in samples from the gas station when compared to the control region, indicating a possible anthropogenic contribution of the petrochemical source.

## Acknowledgments

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**Área: ANA**

# Determination of toxic and potentially toxic metals in the phosphor material of fluorescent lamps by ICP-MS, ICP OES and CV AAS.

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Palavras Chave: *Fluorescent lamp, Metals, Mercury, Rare earth elements, Acid leaching.*

## Highlights

Fluorescent lamps are still a matter of environmental concern.

Lamps are inappropriately discard in many countries.

Toxic and potentially toxic metals are present in its composition and can be released into the environment.

Mercury is not the only metal of concern.

## Resumo/Abstract

Fluorescent lamps (FL) are known for the presence of toxic metals in their composition, which varies depending on the country of origin, year of manufacture and lamp brand. Despite a greater concern with Hg, other toxic and potentially toxic metals may be present in the lamp's composition.[1,2] Although FL are gradually being replacement by LED lamps, large amounts of FL are still consumed and discarded annually, often in inappropriate places or without adequate treatment, especially in developing and underdeveloped countries.[3,4] This raises concern about the release of these metals into the environment and consequent contamination of soils and water. In the present work, the content of toxic and potentially toxic metals present in FL phosphor material is determined. The phosphor material of 70 linear FL from at least 4 different brands, 6 countries and 2 wattages was collected and homogenized. About 0.2 g of the material was subjected to acid leaching with 1 mL of an aqua regia + $HClO_4$ solution (1:0.38) under heat for 2 h at 90 °C. The solutions were diluted and analyzed by ICP-MS, CV AAS and ICP OES. Analytical curves were prepared using multi and monoelemental standards with 2% $HNO_3$. Concentration of Al, Ba, Cd, Cr, Eu, Mn, Ni, Pb, Sr, W, Y and Zn were obtained by both ICP techniques, while Hg was determined by ICP-MS and CV AAS. Results are presented in Table 1, along with the corresponding Student t-test values ($t_{Tab}$= 2.776 for df=4 and $\alpha$ = 0.05). Higher concentrations are found for Al, Eu, Hg, Mn, Sr, W, and Y. Mercury concentration is affected by unavoidable losses during lamp breakage and sample preparation. Student t-test values indicates agreeable results. Considering the elevated number of discarded FL and evaluating the results for potentially toxic metals, it is possible to conclude that FL is a potential environmental hazard.

**Table 1.** Metal concentration found in phosphor material of FL by different techniques in mg kg$^{-1}$ or g kg$^{-1}$ (bold).

| | Al | Ba | Cd | Cr | Eu | Hg | Mn | Ni | Pb | Sr | W | Y | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **ICP-MS** | **11.7 ± 0.4** | 463.3 ± 13.4 | 67.9 ± 1.6 | 5.5 ± 0.5 | 926.6 ± 6.3 | 683.0 ± 17.2 | **8.7 ± 0.4** | 26.5 ± 3.8 | 7.3 ± 0.5 | **2.2 ± 0.2** | **1.8 ± 0.1** | **18.5 ± 0.4** | 204.0 ± 8.3 |
| **ICP OES/ CV AAS** | **12.1 ± 0.5** | 500.4 ± 28.7 | 65.6 ± 2.2 | 6.0 ± 0.1 | 931.9 ± 13.8 | 731.2 ± 33.5 | **8.3 ± 0.2** | 24.1 ± 0.7 | 6.6 ± 0.7 | **2.4 ± 0.1** | **2.0 ± 0.2** | **17.9 ± 0.2** | 189.0 ± 5.4 |
| **t-Test** | 1.1 | 2.0 | 1.4 | 1.7 | 0.6 | 2.2 | 1.9 | 1.0 | 1.4 | 1.3 | 1.6 | 2.4 | 2.6 |

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**Área: ANA**

# Development and optimization of a new LPME semi-automated device for the determination of 11 drugs of abuse in samples of wastewater and freshwater

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**Palavras Chave**: *Liquid-phase microextraction, GC-MS, Sewage water, Cocaine, Amphetamine.*

## Highlights

An innovative extraction device coupled to a peristaltic pump allowed for fast and effective liquid-phase microextractions. A liquid-phase microextraction procedure was successfully optimized. The concentrations of eleven drugs of abuse, including cocaine and metabolites, amphetamines and cathinones, were determined in freshwater, treated and untreated sewage water, using GC-MS without derivatization.

## Abstract

The present work reports the development of a customized device specially designed to perform liquid-phase microextractions and, after the optimization, was applied in the determination of residues of eleven drugs of abuse in environmental water samples. The device consisted of a borosilicate glass chamber attached to a glass narrow tube where the organic phase was collected after the extraction. The device was connected to a peristaltic pump, allowing for a simple automated transference of the organic phase to the top of the glass narrow tube. In order to achieve the optimal extraction conditions, the LPME procedure was optimized and the following variables affecting the extraction efficiency were investigated: type of extractor solvent and their mixtures, extractor volume (100 – 200 µL), time of vortex-assisted extraction (10 – 40 min), NaCl concentration (0 – 2.5%), and sample pH (9 – 12). The peak area of the analytes was considered as analytical response. According to the results, the best extraction conditions were obtained using 100 µL of a ternary solvent mixture composed of toluene:ethyl acetate:dichloromethane (60:20:20 %v/v/v), extraction time of 30 min at 500 rpm, and pH 11. The addition of NaCl resulted in a decrease in the peak area of the analytes, and therefore, the best conditions were achieved without salt addition. After the optimization, the proposed procedure was validated according to the following parameters: linear range; linearity; limit of detection (LOD); limit of quantification (LOQ); precision (as repetitivity and intermediate precision) and accuracy, at three concentration levels of recovery essays. In addition, the efficiency of the extraction procedure was calculated by means of the enrichment factor (EF), and extraction recovery (ER). The proposed procedure has shown good linearity ($R^2 > 0.9900$) without evidence of lack of fit in the investigated analytical curves (ANOVA, $p<0.05$). The LOD and LOQ ranged from 10.4 ng $L^{-1}$ (cocaethylene) to 27.8 ng $L^{-1}$ (MDEA), and from 34.5 ng $L^{-1}$ to 92.4 ng $L^{-1}$, respectively, for these same compounds. The precision, expressed as repetitivity (n=10), ranged from 3.80% (amphetamine) to 11.3% (cocaethylene) while the intermediate precision (n=30) ranged from 7.61% (amphetamine) to 13.67% (cocaine). Acceptable relative recoveries (72.8% - amphetamine to 114% - cocaethylene), enrichment factors (from 15.3 to 117), and extraction recoveries (12.7 % to 97.5%) were obtained for the proposed method. The method was applied in eight real samples of freshwater, treated, and untreated sewage waters, collected in Salvador-BA (Brazil). Cocaine (nd – 50.4 ng $L^{-1}$), was detected in untreated wastewater samples whereas cocaethylene (nd – 43.2 ng $L^{-1}$) was found below LOQ.

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**Área: ANA**

# Development of a focused ultrasound-assisted extraction method using ultrapure water for the speciation of Arsenic in plankton.

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*Extraction Method, Validation; Speciation*

## Highlights

Development of an extraction method using a focused ultrasound probe. Extraction of arsenic species with ultra-pure water in plankton samples. Speciation analysis was performed by HPLC-UV-HG-AFS.

## Abstract

Arsenic (As) occurs naturally in a variety of chemical forms in the environment, including organic and inorganic species. In the aquatic environment, the most frequent species are inorganic As(III) and As(V) and the organoarsenicals monomethylarsonic acid (MMA (V)) and dimethylarsinic acid (DMA (V)). Other less common organic species such as arsenosugars are present in aquatic organisms through the biotransformation process. Sample preparation for speciation analysis of As in aquatic organisms involves preserving diverse species in such complex matrices, avoiding interconversion between them. Thus, the objective of this work was to develop and validate a focused ultrasound-assisted extraction (FUAE) method for the analysis of arsenic speciation in plankton samples using water as an extractor in low extraction time, as well as to evaluate its applicability in real zooplankton and phytoplankton samples. The determination of total As concentration was performed with Hydride Generation Atomic Fluorescence Spectrometry (HG-AFS) after digestion of samples of BCR-414 certified material in a microwave oven. Optimization of different parameters was carried out, namely (a) extractor composition (b) ultrasound power (c) ultrasonication time. For the speciation analysis, High-performance liquid chromatography coupled to HG-AFS with online oxidation (HPLC-UV-HG-AFS) was used. After optimizing the parameters, it was verified if the extraction process did not result in species interconversion. This was performed by analyzing two standard solutions of each species, one submitted to FUAE and the other not. The analytical validation was carried out by determining the following parameters: Limit of Detection, Limit of Quantification, working range, recovery of species extracted in different extractors. Ultrapure water provided better recovery compared to other extractors (Table 1). After optimization, the parameters chosen were a time of 5 minutes and ultrasound probe power of 15%, which resulted in a global recovery of 86.2%. Species interconversion was not observed when comparing the composition of the solutions that were or were not submitted to ultrasound (Student *t*-Test). The validated extraction method was successfully used to quantify arsenic species in phyto and zooplankton samples collected in saline lakes from the Pantanal (MT). Species concentrations in these samples range from AsB (0.06 - 2.0 µg/g), AsIII (0.06 - 1.47 µg/g), DMA (0.10 - 4.04 µg/g), MMA (0.10-6.32 µg/g) and AsV (0.73 - 8.36 µg/g).

Table1- Different extractor solutions tested and recovery (%) of As species extracted.

| Extractor solutions | Recovery (%) |
|---|---|
| **Ultrapure water, pH 6.34 (18.2 MΩ cm)** | 93.70% |
| **Ethanol/ water (1/3)** | 83.14% |
| **$NaHCO_3$ 4mM, pH 8.6** | 84.82% |
| **$NaH_2PO_4 + Na_2HPO_4$, pH 6.2** | 63.59% |
| **Methanol/ water (1/2)** | 89.72% |

## Acknowledgments

The authors thank the FAPESP (Fundação de Amparo à Pesquisa do Estado de São Paulo) [grant numbers 2014/50867-3, 2016/14227-5, 2017/50085-3, 2018/25207-0, 2019/00018-3, 2019/24445-8, 2020/08543-7, and 2021/05927-1], and also the CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico, Brasília, Brazil) [grant number 303231/2020-3].

**Área: ANA** **Nº de Inscrição: 00991**

# Development of a green chromatographic method and dissolution test for determination of allopurinol in tablets

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Keywords: *Allopurinol, HPLC, Quality control, Dissolution, Green chemistry*.

## Highlights

Development of a method using green chemistry to determine allopurinol; factorial planning, applied in quality assessment methods of pharmaceutical specialties.

## Resumo/Abstract

Allopurinol is a drug used to treat gout and other conditions associated with increased serum uric acid levels[1,2]. In Brazil, it is manufactured by five laboratories in two presentations: 100 mg and 300 mg tablets (generic and reference), and the quality control of these products is relevant, based on the development of sensitive analytical methods, using the least amount of toxic solvents. **Objective**: To develop a quality control method for determination of allopurinol in tablets, using High performance liquid chromatography (HPLC). **Materials and methods:** Univariate factorial design was used to determine chromatographic conditions for drug detection and, multivariate for the selection of the dissolution medium. Six drug samples were acquired: 03 presentations of 100 mg (reference, generic 1 and generic 2) and 03 presentations of 300 mg (reference, generic 3 and generic 4). **Results**: The optimized conditions for the method were: Column C8 (150 mm x 4.6 mm x 5 µm), isocratic mobile phase: ethanol: 0.1 mol $L^{-1}$ HCl: ultrapure water (50:25:25 %), flow: 0.6 mL $min^{-1}$, DAD detector: 249 nm and running time of 5 minutes. The method was validated according to the parameters of Resolution – RDC nº 166/2017[3], exhibiting the following results: Accuracy (%) 99.01 – 99.76; Precision (DPR, %) <0,5; Limit of detection (µg $mL^{-1}$) 0.09; Limit of quantification (µg $mL^{-1}$) 0.14; Correlation coefficient (r) 0.9961; Working range (µg $mL^{-1}$) 0.14 to 0.80 and Robustness (DPR, %) <1.9 for accuracy. For dissolution method, the optimal conditions were: dissolution medium (0.001 mol $L^{-1}$ HCl), rotation (75 rpm) and apparatus 2 (paddle). The tablets dissolved until 15 minutes (Table 01) showing similar profiles after analysis of variance (ANOVA). **Conclusion**: the developed and validated method was able to quantify allopurinol in tablets, using the principles of green chemistry, by HPLC.

**Table 01-** Percentage of dissolution of allopurinol tablets using the developed method.

| Tablets | (%) after 3 minutes | (%) after 5 minutes | (%) after 10 minutes | (%) after 15 minutes |
|---|---|---|---|---|
| 100 mg reference | 34.62 | 62.20 | 83.42 | 92.89 |
| 100 mg generic 1 | 34.38 | 54.15 | 83.57 | 93.07 |
| 100 mg generic 2 | 16.94 | 52.14 | 76.87 | 86.99 |
| 300 mg reference | 33.27 | 52.70 | 85.81 | 94.65 |
| 300 mg generic 3 | 40.34 | 67.88 | 84.62 | 92.85 |
| 300 mg generic 4 | 36.74 | 59.41 | 83.27 | 94.04 |

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## Agradecimentos/Acknowledgments

We thank the Graduate Programs in Applied Chemistry (PGQA) and Pharmaceutical Sciences (PPGFARMA) at the State University of Bahia (UNEB).

**Área: ANA**

# Development of a microscale solid-liquid extraction method combined with gas chromatography-mass spectrometry for the determination of *n*-alkanes in marine sediments

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Keywords: *Microextraction, Gas chromatography-mass spectrometry, n-alkanes, Sediments.*

## Highlights

A novel microscale solid-liquid extraction was developed first time for extraction of n-alkanes. Factors affecting extraction efficiency were optimized by chemometric tools. The method was validated.

## Abstract

This study presents a simple, rapid and reliable microscale procedure for the extraction and purification of *n*-alkanes ($C_7$-$C_{40}$) in marine sediment by gas chromatography-mass spectrometry (GC-MS). To obtain satisfactory chromatographic performance and high extraction efficiency, several experimental variable parameters affecting the extraction efficiency of these compounds including the as sample mass, sorbent type, extraction time, vortexing time (cleanup), and sorbent mass, were optimized by means of experimental statistic approach using two-level full factorial design and response surface methodology. Analytes were determined by GC-MS in full scan mode (m/z 50 to 400). The methodology was validated in terms of matrix-matched calibration, detection and quantification limits and recovery. The factors extraction time and agitation time (cleanup) were significant and presented values of 25 min and 0.5 min, respectively. Under optimal conditions, the limit of detection (LOD) and limit of quantification (LOQ) of the *n*-alkanes ranged from 0.41 ($C_{13}$) to 0.64 μg $g^{-1}$ ($C_{36}$), and the LOQs ranged from 1.38 to 2.14 μg $g^{-1}$ for the same *n*-alkanes. Correlation coefficients ($R^2$) ≥ 0.9901 were obtained for all compounds within the linearity range of 0.025-0.800 μg m $L^{-1}$. The mean recoveries for *n*-alkanes ($C'_{15}$-$C_{40}$) varied in the range 64 -120%, with intra-day RSD less than 19.8% and inter-day RSD less than 19.9%. Finally, the proposed method was successfully applied to sediment samples collected in different point of Todos os Santos Bay and concentrations ranging from 1.44 ($C_{21}$) to 5.52 μg $g^{-1}$($C_{31}$). The results showed applicability and reliability of the novel solid-liquid microextraction for *n*-alkanes determination in sediments with advantages such as low use of solvent, sample mass and extraction time.

## Agradecimentos/Acknowledgments

The authors acknowledge financial support from the Brazilian Agencies Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Fundação de Apoio à Pesquisa do Estado da Bahia (FAPESB), Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) and Financiadora de Projetos e Estudos (FINEP).

**Área: ANA**

# Development of analytical methodology for sequential extraction of phenols compounds in bio-oil

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Key Words: bio-oil, silica, phenols, resins, Amberlisty

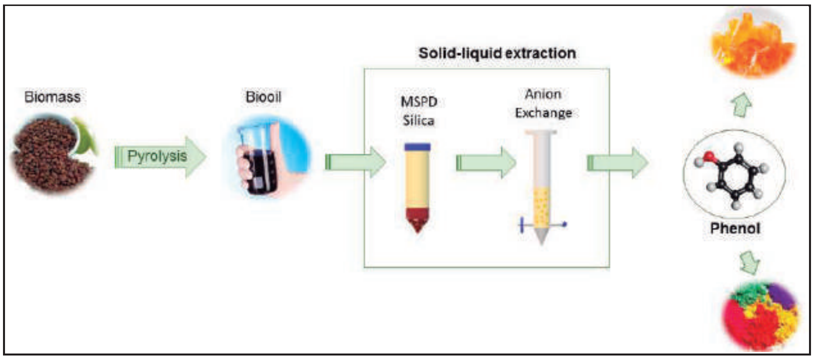
## Highlights

Sequential extraction of phenolic compounds using matrix solid phase dispersion (MSPD) and exchange resins. Evaluable phenols compositions in bio-oils fractions obtained by Amberlite resins.

## Abstract

The bio-oil components were identified as phenols, ketones, keto alcohols, N-heterocyclic compounds, aldehydes, alcohols, acids, esters, hydrocarbons and nitrogen-containing compounds. The phenols are possible alternative of renewable resources from resins and plastics production. The sequential extraction of phenol compounds by MSPD and Ion Exchange Extraction was used to evaluable phenols composition in bio-oil (Figure 1).

Figure 1: Sequential extraction of phenol in bio-oil.



Therefore, methods of extracting and purifying phenols compounds have been studied to evaluate the characteristics of the bio-oil. These compounds can be used in industries and cannot be disposed of in the environment due the toxicity. To the phenols quantification was developed a methodology using the sequential extraction of MSPD and SPE techniques. The silica as used as adsorbent for separation class compounds and the resins Amberlysts A-21 and A-27 to clean-up of the phenols compounds. The compounds were eluted with hexane and dichloromethane of the silica. The phenols fraction was eluted with DCM and the concentration approximately 145 mg L$^{-1}$s. The extraction with Amberlyst resin showed recoveries above 80% of the analyzed phenols. Both resins presented extractions with satisfactory yields to complex samples.

## Acknowledgments

**Área: ANA**

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

**Nº de Inscrição: 686**

*(Inserir o número de inscrição do autor que fez a submissão)*

# Development of an analytical method for crude oil digestion and metals determination by ICP-OES

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Keywords: Crude oil, ICP-OES, MAWD-PDC, Metals, Sample preparation.

## Highlights

It was possible to digest up to 1.2 g of crude oil.
The carbon concentration and the residual acidity of digests were lower than 3.5 g $L^{-1}$ and 10%, respectively.
Ultra-trace metals determination was possible (limits of quantification were from 0.10 to 0.52 µg $g^{-1}$).

## Abstract

Crude oil is commonly found in reservoirs associated with sedimentary rocks. It is a hydrocarbon-based matrix, containing some elements, such as sulfur, nitrogen, oxygen and metals (e.g, Ni, V, Na, Ca and others). Regarding to the metals presence in crude oil, it is well known that their concentration depends on the type of geological formation, location as well as age and depth of reservoir.[1] The presence of metals in crude oil may cause poisoning, corrosion, and affect equipment during crude oil refining process, even at low concentration.[1] However, taking into account the difficulties for crude oil digestion and the low levels of same contaminants typically found in crude oil, as well as the low carbon content and low acidity required in digests to use plasma-based techniques, the development of an accurate sample preparation is necessary. In this work, crude oil decomposition was performed using microwave-assisted wet digestion in a pressurized digestion cavity (MAWD-PDC)[2] for the determination of Ba, Ca, Fe, K, Li, Mg, Na, Ni, Sr and V by inductively coupled plasma optical emission spectrometry (ICP-OES). A high-pressure microwave-assisted digestion system (Multiwave 7000, Anton Paar, Austria) equipped with five quartz vessels (80 mL), with maximum temperature and pressure of 270 ºC and 160 bar, respectively, was used. The metals and carbon determination were performed by an ICP-OES equipment (Optima 4300DV, Perkin Elmer, USA). The determination of the residual acidity was performed by titration (836, Metrohm, Switzerland). Operational conditions, such as the sample mass (0.5 to 1.2 g), the volume of $HNO_3$ (6, 8, and 10 mL), the maximum temperature (220, 250, and 270 ºC), and microwave irradiation time (5, 10, 15, and 20 min) were investigated. Using the optimized conditions (8 mL of 14.4 mol $L^{-1}$ $HNO_3$, 270 °C and 20 min), the MAWD-PDC method allowed the digestion of 1.2 g of crude oil, resulting in a very low limit of quantification (from 0.10 to 0.52 µg $g^{-1}$). The proposed method was applied to four oil samples and the carbon content and residual acidity in digests were about 3.5 g $L^{-1}$ and 10%, respectively. No statistical difference was observed between the results obtained by ICP-OES after MAWD-PDC and the certified values of certified reference material (NIST 1634c, fuel oil). The proposed method was suitable for the determination of Ba, Ca, Fe, K, Li, Mg, Na, Ni, Sr and V at ultra-trace levels in crude oil and it can to be used for routine analysis in the petroleum industry.

## Acknowledgments

**CNPq, CAPES, FAPERGS and UFSM.**

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[2] Anton Paar, Instruction Manual and Safety information, Multiwave 7000, 43 pp.

**Área: ____________________**

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

# Development of a novel SERS-based serological test and validation using PLS-DA for Leishmaniasis detection

**Rodrigo S. N. Mancini (PQ)[1], Amanda E. Sabaine (PG)[1], Carlos E. Castro (PQ)[1], Juliana B. T. Carnielli (PQ)[2], Reynaldo Dietze (PQ)[2], Vivian L. de Oliveira (PQ)[6], Alexandre J. C. Lanfredi (PQ)[3], Lauro T. Kubota (PQ)[4], Mónica B. Mámian-López (PQ)[1], Wendel A. Alves (PQ)[1].**

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**Keywords:** *Leishmaniasis diagnosis, Sers, Immunogenic peptide,*

## Highlights

A time-efficient, robust, and reliable homogeneous SERS immunoassay was devised based on the aggregation of peptide-capped AuNPs. This immunoassay had 100% of sensitivity and 88.2% of specificity.

## Abstract

Leishmaniasis is a neglected disease in Brazil. The diagnoses are time-consuming and present a complex sample collection method in patients. A fast and reliable method for leishmaniasis antibody detection was developed by conjugating citrate-capped gold nanoparticles (AuNPs) with the immunogenic peptide from promastigote surface antigen ($PSAdP_{23-47}$). These conjugates recognize specific antibodies that promote the aggregation of AuNPs in solution, enabling a remarkable Surface-Enhanced Raman Scattering (SERS) activity which allowed the development of a novel indirect antibody detection test for humans Visceral Leishmaniasis (HVL). The dynamic and static light scattering methods, UV-Vis spectroscopy, and scanning electron microscopy (SEM) revealed the aggregate's internal structure. Experimental optimization of the new serological test based on SERS showed that increasing the peptide and citrate buffer concentration induces stronger Raman intensities. In addition, chemometric tools (MCR-ALS) allowed the identification of a fingerprint window in the range from 1043 to 1498 $cm^{-1}$, which enabled a refined approach to data analysis, differentiating robustly human sera (n=27) from HVL and non-HVL patients. Analysis of the data obtained using the Partial Least Squares Discriminant Analysis (PLS-DA) model determined the specificity and sensitivity of the method. It showed the potential of the SERS platform for building a point-of-need serological test for HVL detection.

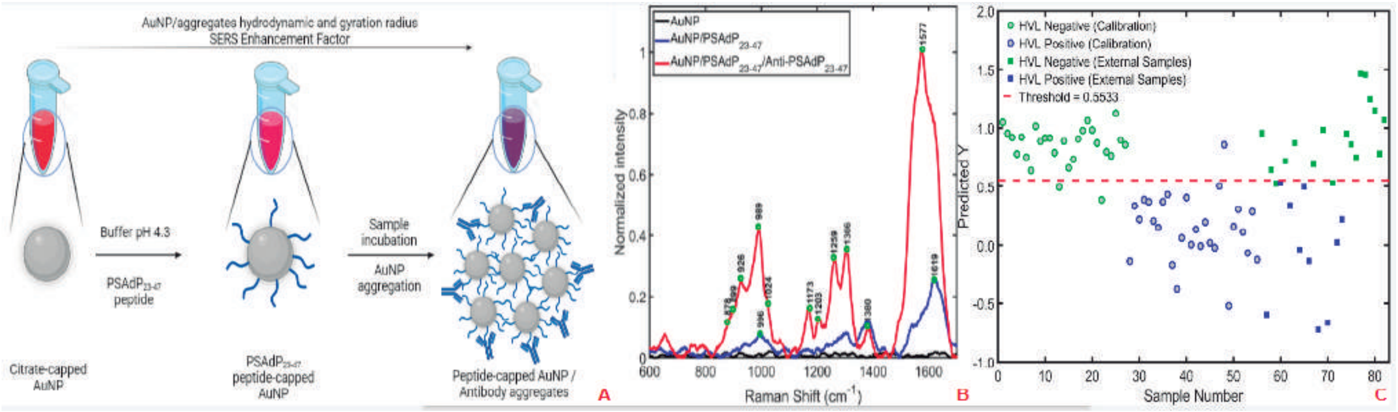

**Figure 1**. Scheme of sample preparation and formation of aggregates; Raman spectrum; Optimized classification of sera analyzed by SERS. (a) SERS immunoassay schematic and AuNP/PSA38S preparation. Images show the color change triggered by antibody recognition. b) SERS spectrum characterization for AuNP and its conjugates and prominent peaks. c) Estimated Y for each classified sera using the optimized SERS immunoassay. Samples placed above the threshold (dashed red line) are assigned as HVL negative, and samples placed below the threshold are given as HVL positive.

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**Área: ANA**

# Digital microfluidics: from sample preparation to colorimetric bioanalysis

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Keywords: *Digital microfluidics; Colorimetric detection; Automated protocol; Bioanalytical analysis.*

## Highlights

- Digital microfluidics coupled to colorimetric detection
- Novel do-it-yourself approach to luminosity control
- Successfully sample preparation and analyses of S-nitrosocysteine in biological fluids

## Resumo/Abstract

Digital microfluidics (DMF) is a lab-on-a-chip platform that allows integration with numerous detection methods. Among them, colorimetry. However, to promote a good homogeneity in lighting control can be challenging. Therefore, this study proposes a new simple and affordable strategy for colorimetric detection directly on the DMF chip. In this sense, a mini studio associated with an LED panel (ceiling lamp) for lighting control was manufactured using alternative materials. In addition, a webcam was used as a detector. As a proof of concept, nitrite and low molecular weight nitrosothiol, through the analysis of S-nitrosocysteine (CySNO), as a target molecules were explored. To promote the photolytic cleavage of CySNO for further conversion to $NO_2^-$ and analysis using Griess reagente, a UV LED degradation chamber was manufactured by low cost 3D printing technique and integrated into the DMF platform (Figure 1). The results showed that there was an excellent correlation between data obtained with the proposed system and that observed via scanner. The linear range obtained for CySNO and $NO_2^-$ and the detection limit of the proposed assay were between 12.5 to 400 μmol $L^{-1}$ ($R^2 = 0.997$) and 2.8 μmol $L^{-1}$, respectively A recovery assay was performed and compared with UV-Vis spectrophotometry, revealing that the obtained results did not differ statistically at a 95% confidence level via the paired t-test. Finally, synthetic blood serum and plasma samples were successfully analyzed, demonstrating the potential of the proposed detection system for bioanalytical application.

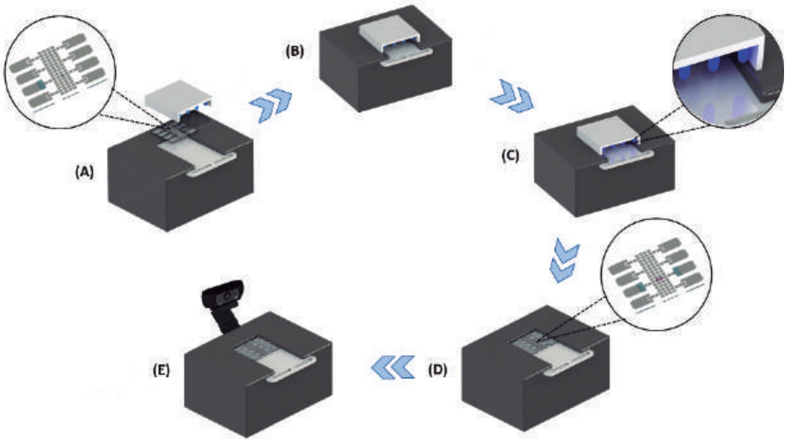

**Figure 1.** (A) DMF Components. (B) Integration between 3D printed UV chamber and DMF platform. (C) Decomposition of CySNO by UV radiation. (D) Mixture of the degradation product with the chromogen (Griess reagent). (E) Digital image capture of the drops using a webcam.

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**Área: ANA**

# Direct electrooxidation of melamine and its determination in different food samples using an anodically pretreated boron-doped diamond electrode

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Key words: *Melamine, Food Samples, Direct electrooxidation, Differential pulse voltammetry, Boron-doped diamond.*

## Highlights

For the first time, the direct oxidation of the allegedly non-electroactive melamine is reported. The oxidation process was used to determine melamine in infant food samples and soy milk.

## Abstract

In 2008, thousands of people in China, mostly infants, suffered from kidney stones and renal failure caused by the ingestion of milk and infant formula contaminated with melamine (MEL)[1]. Adulteration of lactic food products using MEL is perpetrated until today because of its high nitrogen content (66%, *m*/*m*), which elevates the nitrogen response in analysis methods that use this parameter for protein content determination. The U.S. Food and Drug Administration (FDA) established a safe limit of melamine of 2.5 mg kg$^{-1}$ (20 μmol L$^{-1}$) for food and 1 mg kg$^{-1}$ (8,0 μmol L$^{-1}$) for infant formula. Thus, dependable, accurate, and sensitive analytical methods are crucial for sensing MEL in food products and preventing exposure. This work demonstrates for the first time the direct oxidation of the allegedly non-electroactive MEL molecule using a boron-doped diamond electrode (BDD). The oxidation process was used to develop a method for determining MEL in infant food samples and soy milk. The determinations were performed by differential pulse voltammetry using an anodically pretreated BDD as the working electrode, with 0.05 mol L$^{-1}$ $H_2SO_4$ as the supporting electrolyte. Under optimized conditions, a linear working range from 1.0 to 300 μmol L$^{-1}$ (0.13 to 37.8 mg L$^{-1}$) was attained for MEL (see figure), with a limit of detection (S/N = 3) of 0.23 μmol L$^{-1}$ (0.03 mg L$^{-1}$).

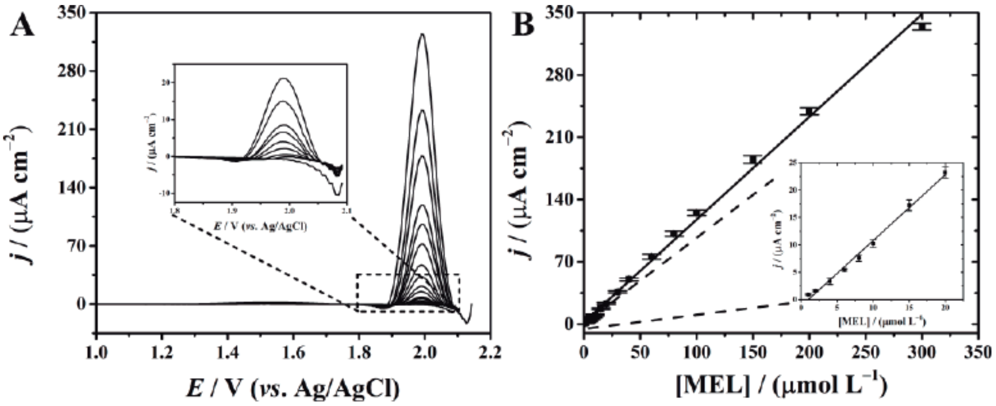

**Fig. 1. (A)** Baseline-corrected differential pulse voltammograms at the anodically pretreated boron-doped diamond electrode in 0.05 mol L$^{-1}$ $H_2SO_4$ with increasing concentrations of MEL; **(B)** Respective calibration curve for MEL obtained from the addition data under the optimized conditions.

As shown in the figure, the increase of the oxidation current peak with MEL concentration was observed, with a linear behavior ($R^2$ = 0.996). Thus, the method was applied to determine MEL in samples of infant foods and soy milk, with only dilution and acidification as sample preparation processes. As a result, excellent recovery values were attained, ranging from 93 to 112%.

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**Área: ANA**

# Dispositivo colorimétrico em papel: um arco-íris de possibilidades para determinação da urease

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**Keywords:** Indicadores ácido-base; colorimetria; modificação do papel; quitosana, TEOS, PVP.

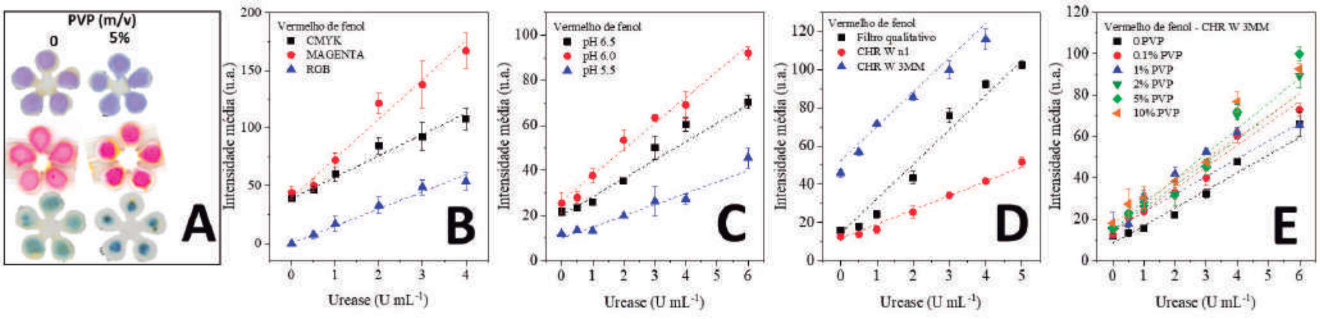
## Highlights

Colorimetric paper analytical: a rainbow possibilities for urease determination. Fabricação simples e de baixo custo de dispositivo de papel empregando indicadores ácido-base para quantificação de urease e avaliação da influência na modificação da superfície do papel com diferentes sistemas.

## Abstract

A urease é uma metaloenzima produzida por fungos e bactérias, associada à problemas na agricultura e na saúde humana, devido à hidrólise da ureia em $NH_3$ e $CO_2$, causando perdas de fertilizantes N-ureia e favorecendo à colonização da H. pylori no estômago humano. Nesse sentido, determinar a atividade dessa enzima de forma simples, rápida e econômica é uma demanda científica e de mercado para mitigar os efeitos da sua ação. Para isso, faz-se necessário a utilização de dispositivos analíticos em papel devido à facilidade de uso, baixo volume de amostra, portabilidade, e possibilidade de integração com uma variedade de métodos e técnicas de detecção. Neste contexto, a colorimetria merece destaque devido à simplicidade, capacidade de análise operacional usando *scanner* e/ou *smartphone* para obtenção de respostas quantitativas ou binárias (sim/não). A reação de hidrólise da ureia pela urease altera o meio reacional aumentando o pH, e essa mudança pode ser observada visualmente empregando indicadores ácido-base. Assim, esse trabalho tem como objetivo desenvolver um dispositivo colorimétrico em papel para determinação da urease explorando diferentes indicadores ácido-base. Os dispositivos em formato de flor foram produzidos usando um Furador Eva 16mm Flor Hélice Blister (Make+ Co., Ltda, China), três tipos de papel (filtro qualitativo, Whatman CHR n° 1 e CHR 3MM) sem e com modificação da superfície empregando quitosana (0,1 a 4 mg $mL^{-1}$), polivinilpirrolidona (PVP, 0,1 a 10%) e Tetraetoxissilano (TEOS, 4:1 TEOS:água). A determinação da urease (0 - 6 U $mL^{-1}$) foi feita empregando ureia (20 mM) e os indicadores 0,05% (m/v) (roxo de bromocresol, azul de bromotimol e vermelho de fenol) em tampão fosfato de sódio 0,5 mM (pH inicial avaliado). Um sistema modelo para cada indicador e os resultados de alguns parâmetros estão apresentados na Figura 1.

**Figura 1: A)** Avaliação dos indicadores sem e com PVP na superfície do papel; Otimização de **B)** canal de cor; **C)** pH inicial; **D)** tipo de papel; **E)** Concentração do PVP usando vermelho de fenol 0,05% (m/v), ureia 20 mM e urease.



Os resultados indicaram que para todos os indicadores o canal de cor CMYK e o papel Whatman CHR 3MM apresentaram melhor linearidade e sensibilidade. O pH inicial selecionado foi 6,0 ± 0,1, exceto para o roxo de bromocresol (5,5 ± 0,1), que pode estar relacionado com o pH inicial da transição de cor deste indicador ($pK_a = 6,43$). Os sistemas de modificação da superfície do papel resultaram em melhorias significativas na intensidade e uniformidade da cor para todos os indicadores com destaque para o PVP, demonstrando o potencial da aplicabilidade na melhoria desses parâmetros visando aplicação qualitativa (sim/não) do dispositivo em sistemas reais e para avaliação de possíveis inibidores da urease.

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LINQA, PPGQB, IQB, UFAL, IFAL, UFG, FAPEAL, CAPES, CNPq.

**Área: ANA**

# Elemental Impurity Determination in Oily Pharmaceutical Excipients by ICP-MS after Reversed-Phase Dispersive Liquid-Liquid Microextraction

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Keywords: *Oily pharmaceutical excipients, Sample preparation, RP-DLLME, Elemental impurity determination, ICP-MS, ICH Q3D.*

## Highlights

The RP-DLLME method allowed the use of a high sample mass (up to 5 g).
Detection limits were in agreement to the maximum levels recommended by ICH Q3D.

## Abstract

Pharmaceutical excipients are inactive ingredients widely used in the pharmaceutical industry. These constituents are used to ensure the stability of pharmaceutical products, enable formulations, as well as improve the bioavailability of active ingredients. Among the several types of excipients available, oily excipients have been used by the pharmaceutical industry in a variety of products, including injectable drugs.[1] The oily excipients used in injectable drugs include oils from castor, corn, soybean, and sesame, among others. Despite being of botanical origin, the oily pharmaceutical excipients are not completely free of elemental impurity and the quality control is mandatory.[2] In this way, the International Council for Harmonisation (ICH) classifies the elemental impurity according to their toxicities. Moreover, according to the ICH guideline Q3D, the quality control of class 1 (As, Cd, Hg, and Pb) is necessary in oily excipients used in the formulation of injectable drugs.[3] However, some difficulties are related to the sample preparation step mainly due to the matrix complexity and the low levels of the elements usually present in this kind of sample.[1,2] In order to overcome these drawbacks, a reversed-phase dispersive liquid-liquid microextraction (RP-DLLME) method was developed for further As, Cd, and Pb determination in oily excipients by inductively coupled plasma mass spectrometry (ICP-MS) and Hg by cold vapor generation coupled with ICP-MS. The RP-DLLME method is based on the analyte extraction from the organic phase to an aqueous phase using a dispersant and extractant solvents (alcohol/diluted acid solution). The microwave-assisted wet digestion in a single reaction chamber (MAWD-SRC) using concentrated $HNO_3$ and analytes determination by ICP-MS were applied in order to obtain the reference values. The determination was performed using ICP-MS (Elan DRC II model, Perkin Elmer-SCIEX, Canada) after RP-DLLME and MAWD-SRC methods. For the RP-DLLME procedure, a water-bath (Elmasonic P 120 H, Germany), with capacity of 9 L and temperature control (up to 85 °C) was used. A certified reference material of oil was used for recovery experiments. Soybean oil was used for the development of the proposed method. Operational parameters, such as total volume (1 to 2 mL) and proportion of dispersant and extractant (65:35 to 35:65% v/v) solvents, extractant solvent concentration and type (1 to 3 mol $L^{-1}$ $HNO_3$ and 2 to 10 mol $L^{-1}$ HCl), and sample mass (5 to 10 g) were evaluated. An Analytical GREEnness calculator was used to evaluate the proposed method and the reference method greenness. Suitable results were obtained by using 5 g of oily excipient, a mixture of dispersant (*n*-propanol) and extractant (3 mol $L^{-1}$ $HNO_3$ for As, Cd, and Pb and 6 mol $L^{-1}$ HCl for Hg) solvents with proportion of 50:50% (v/v) in 2 mL, 85 °C, and 10 min of centrifugation. No statistical difference (*t*-test, 95%) was observed between the results obtained by RP-DLLME method and the reference values. Due to the use of a high sample mass (5 g), diluted extraction solution, low volume of reagents, and low detection limits (ranged from 2 to 14 ng $g^{-1}$) were obtained.

## Acknowledgments

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**Área: ANA** **Nº de Inscrição: 00652**

# Enantioselective chromatographic separation of the fungicide penconazole

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Palavras Chave: *Enantioseparation, Fungicide, Pesticide, Penconazole.*

## Highlights

Enantioselective chromatographic method

Penconazole enantioselective analysis

## Resumo/Abstract

Penconazole is a systemic chiral fungicide applied mainly in grape, apple, tomato and cucumber to control powdery mildew. Its application is carried out by spraying the leaves with an emulsion of the racemic mixture of the pesticide. Recent studies have indicated an increase in the concentration of this pesticide in water and food[1-2], thus increasing the risk of contamination in non-target organisms, such as humans. It's also known that penconazole can exhibit enantioselective degradation and toxicity in some species[2-5]. Therefore, more efficient analysis methods that take into account the chiral character of this compound are necessary. This work aims to develop a new enantioselective chromatographic method to analyze the chiral fungicide penconazole. Seven different columns with different chiral selectors, different particle diameters as well as length were evaluated (Chirobiotic V®; Chirobiotic T®; Chiralpak AD-RH® and AD-3®; Chiralcel OD-H® and OD-3®; Chiralcel OJ®; Lux Cellulose 1® and Lux Cellulose 2®) in polar organic mode (100% acetonitrile, methanol or ethanol) and in reversed phase (70:30 v/v mixtures of acetonitrile, methanol or ethanol and water) modes of elution. The resolution values between the enantiomers were below 1.5 for all the chiral columns evaluated employing the polar organic modes. Good separation (resolution ≥ 1.5) was obtained using the Chiralpak AD-RH® column with methanol: water, and both Chiralcel OD-H® and OD-3® column by employing methanol: water and ethanol: water as mobile phases. Analysis time varied from 10 to 30 minutes. The best condition for the enantiomeric separation was obtained with Chiralcel OD-3® column by using ethanol: water (70:30 v/v) as mobile phase, in which the resolution was 1.9 and the total analysis time was 10 minutes.

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## Agradecimentos/Acknowledgments

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**Área: ANA**

# Estudo da potencialidade da radiação infravermelha na geração termoquímica de vapor de mercúrio

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Palavras Chave: *Geração Termoquímica de Vapor, Radiação infravermelha, Mercúrio, Especiação não-cromatográfica.*

## Highlights

Study of the potentiality of infrared radiation in the thermochemical vapor generation of Mercury

- Determination of chemical elements at ultratrace levels
- Spectrometric analysis with sample introduction as volatile species
- Non-chromatographic speciation of mercury

## Resumo/Abstract

A análise de elementos químicos a níveis traços e ultratraços em amostras complexas sempre se mostrou como um dos principais desafios da química analítica. Estudos envolvendo procedimentos para minimizar os efeitos de matriz e melhorar a sensibilidade das técnicas mais comumente empregadas têm sido explorados. Uma alternativa para melhorar a sensibilidade e separar o analito da matriz está no procedimento de introdução da amostra nos espectrômetros. A geração termoquímica de vapor (TVG) é uma técnica pouco explorada, não está estabelecida e seus mecanismos ainda não foram elucidados. Todavia, a termólise de ácidos orgânicos de baixo peso molecular, como os ácidos fórmico e acético, propicia o ambiente redutor que se mostrou adequado na formação de mercúrio elementar e detecção por espectrometria de absorção atómica com vapor frio (CV-AAS). Dessa forma, o objetivo deste trabalho foi desenvolver um sistema TVG, assistido por radiação infravermelha, de forma simples, eficiente, com menor consumo de reagentes, de baixo custo e com finalidade de aplicação em análises a nível ultratraço de mercúrio por CV-AAS. O reator termoquímico foi montado utilizando-se uma lâmpada de infravermelho de 500 W com regulador de tensão. Foram desenvolvidos dois sistemas de geração termoquímica de vapor (Figura 1). No sistema 1 foi empregado como percurso analítico da amostra um capilar de quartzo e no sistema 2 foi empregado um material de baixo custo, o perfluoroalcóxi (PFA). Foram avaliadas as condições experimentais para ambos os sistemas, incluindo tipo de separador gás-líquido (GLS), concentração de precursor orgânico (ácido fórmico), fluxo de amostra, temperatura do reator e vazão de gás carreador. O sistema 1 apresenta vantagens frente ao sistema 2, incluindo alta transparência do quartzo à radiação infravermelha e resistência a temperaturas elevadas, o que possibilitaram a especiação não-cromatográfica de mercúrio. Sob condições otimizadas, os limites de detecção no sistema 1 foram de 0,41 e 0,45 μg kg$^{-1}$ para o mercúrio total e mercúrio inorgânico, respectivamente, e 0,44 μg kg$^{-1}$ para mercúrio total no sistema 2. A exatidão foi verificada através da análise de materiais de referência certificados (1641d, DORM-1, DOLT-3 e PACS-2) com percentual de recuperação de 93% a 99%. O sistema 2 foi aplicado para a determinação do teor total de Hg em amostras de sedimento marinho das regiões atingidas pelo derramamento de óleo de 2019. As amostras analisadas apresentaram concentrações de Hg variando de 0,17 a 0,29 mg kg$^{-1}$. O sistema TVG desenvolvido tem potencial para ser usado como método simples e de baixo custo, eliminando o uso de reagentes instáveis e dispendiosos, para análise de Hg como alternativa viável ao método convencional.

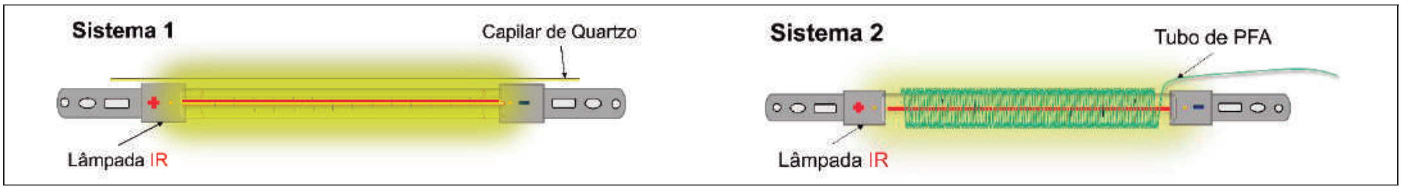

Figura 1. Configurações dos sistemas TVG.

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**Área: ANA**

# Evaluation of content hypochlorite and pH of commercial bleaches in Aracaju and Metropolitan Region

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Keywords: *Sodium hypochlorite, Bleach, Titration, pH.*

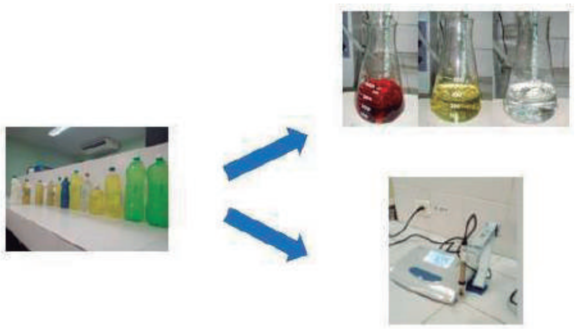
## Highlights

Check the quality of bleaches from the parameters of pH and sodium hypochlorite.

## Abstract

In this research, the instrumental method of determining pH with a digital pH meter and the classical volumetric titration technique were used, following the methodology of iodometric titration. The clandestine production of bleaches is on the rise, accompanied by low inspection and regulation of production that is not carried out by industries nor have their products verified in an analysis laboratory. Many do not have a technician responsible. The methodology applied is described below.

- Metodology



The maximum pH value allowed in the pure product is 13,5. According to the resolution, all samples comply with the regulated value. The active chlorine content must be 2.0% w/w and a maximum of 2.5% w/w during the product's shelf life. In this way, all samples are out of compliance with the established value. Among the numerous factors that can cause non-compliance, poor packaging sealing can cause chlorine to evaporate quickly, in addition to accelerating its release if exposed to light.

The form of bleach storage influences the quality of the product. The product packaging must be well sealed to prevent the escape and evaporation of chlorine present in the aqueous solution. In addition, the packaging must be matte to prevent the entry of light that accelerates the decomposition of the product.

Table 1: Free chlorine content in bleach samples

| Samples | 1 | 2 | 3 | 4 | 5 | 7 | 8 | 9 | 10 | 11 | 12 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| pH | 12,51 | 12,18 | 10,03 | 11,28 | 11,47 | 10,93 | 11,35 | 12,15 | 12,20 | 12,65 | 11,99 |
| %$ClO^-$ | 0,99 | 0,24 | 0,59 | 0,64 | 1,80 | 1,90 | 0,36 | 0,61 | 0,55 | 0,32 | 1,57 |

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## Acknowledgments

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

# Fast ultrasound-assisted acid digestion for the determination of potentially toxic elements in fluorescent lamp residues

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Palavras Chave: *Ultrasound-assisted acid digestion, Potentially toxic elements, Waste fluorescent lamp.*

## Highlights

Fluorescent lamps contain potentially toxic metals. Development of a fast digestion method for the determination of these elements. The method presented recoveries of 75-125% for Cu, Mn, Ni, Sr and Zn.

## Resumo/Abstract

Every year, millions of fluorescent lamps are produced worldwide, and at the end of their useful life these products are discarded. In Brazil, until the last decade the annual generation of fluorescent lamp (FL) waste was estimated at 206 million units[1]. Potentially toxic elements (PTE) such as copper, nickel, lead, chromium, cadmium, arsenic, and mercury may be present in these electronic wastes representing a growing global environmental concern [2,3,4]. PTE can be leached, contaminating soil, surface, and groundwater due to improper disposal[5]. Knowledge of the chemical composition of the fluorescent lamp matrix, especially regarding PTE, is essential for the elucidation of mechanisms that contribute to the minimization of environmental impact and risk to human health after disposal. The PTE studied in the present study were Al, Mn, Fe, Ni, Cu, Zn, Sr and Ba, because they have toxicological and physical-chemical profiles that led them to be included in a risk assessment spreadsheet developed by the Environmental Company of the State of São Paulo (CETESB)[6]. In the present study, a fast ultrasound-assisted acid digestion was used to determine PTE in FL residues, in order to evaluate its applicability as an alternative digestion method to conventional methods. The digestion procedure consisted of adding 4 mL of aqua regia ($HNO_3$ + HCl 1:3) to approximately 0.2 g of fluorescent lamp residues. Two variables (time and temperature) were studied from a full factorial design with two-level. The results obtained were compared with a reference method (digestion in heating plate) using statistical tools. The best results were obtained with the following conditions: digestion time of 10 min and temperature of 25°C. This digestion temperature decreases the possibility of loss of volatile elements, recurrent phenomenon in digestion procedures in heating plate and dry decomposition. An inductively coupled plasma optical emission spectrometer (ICP OES) was used for elements quantification. The proposed method provided concentrations equivalent to those obtained by the reference method for the elements Mn, Ni, Cu and Sr, according to student's t-test (95 %), and for Mn, Sr, Zn, Cu and Ni, by analyzing the confidence intervals. The proposed method showed satisfactory results (recoveries of 75-125%) for the elements Cu, Mn, Ni, Sr, and Zn. Therefore, the method can be considered promising, as faster alternative (39 times faster) and more economical (less spent on concentrated acids and energy) than the traditional method of acid digestion in heating plate, for these elements.

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## Agradecimentos/Acknowledgments

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**Área: ANA**

# Feasibility of single particle ICP-MS for detection and characterization of selenium nanoparticles synthesized by a green method

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Palavras Chave: *SeNPs, Green synthesis, Inductively coupled plasma mass spectrometry, spICP-MS, Collision/reaction cell, Hydrogen.*

## Highlights

- Monodisperse and spherical SeNPs were synthesized by a green method;
- A method for sizing SeNPs by SP-ICP-MS was developed;
- Hydrogen was used as a collision gas to overcome spectral interferences.

## Resumo/Abstract

Selenium nanoparticles (SeNPs) have recently attracted attention because of their antioxidant, antibacterial and anticancer properties. SeNPs can be synthesized using chemical, physical and biological methods, and present lower toxicity and higher bioavailability when compared to organic and inorganic bulk Se. Traditional techniques such as UV-Vis spectrophotometry, dynamic light scattering (DLS) and transmission electron microscopy (TEM) can be employed to characterize SeNPs. However, the detection and characterization of SeNPs in environmental relevant concentrations (in the order of parts per billion) is still a challenge. In this sense, single particle ICP-MS (spICP-MS) has emerged as an alternative technique to detect and size SeNPs even at very low concentrations. The aim of this study was to develop a method based on spICP-MS for characterization of SeNPs synthesized in aqueous solution. SeNPs were synthesized by a green method using polyvinyl alcohol as stabilizer and ascorbic acid as reducing agent (Boroumand *et al.*, 2019). Firstly, the nanoparticles were characterized by TEM. For spICP-MS, hydrogen ($H_2$) was used as a reaction gas to overcome spectral interferences. Different Se isotopes plus the $H_2$ flow rate and the electrical parameter of the collision/reaction cell (Energy Discrimination) were optimized. Commercial SeNPs and a reference material of gold nanoparticles (RM 8013) were used for instrument calibration and checking method accuracy. Results from TEM (Fig. 1A) showed that the synthesized SeNPs were spherical and monodispersed, with an average size of 50.1±5.6 nm. The ICP-MS method optimization showed that $^{78}$Se isotope with a $H_2$ flow of 3.5 mL min$^{-1}$ and an Energy Discrimination of 3.0 V were the best conditions, then, these conditions were applied to spICP-MS. The results showed a typical signal for synthesized SeNPs (Fig 1B). The mean diameter obtained for the synthesized SeNPs was 48 nm, in accordance with the results obtained by TEM. The size distribution (Fig 1.C) also revealed that SeNPs were between 40 and 65 nm. Therefore, the results showed that, using the developed method, it was possible to characterize SeNPs in terms of size and size distribution by spICP-MS.

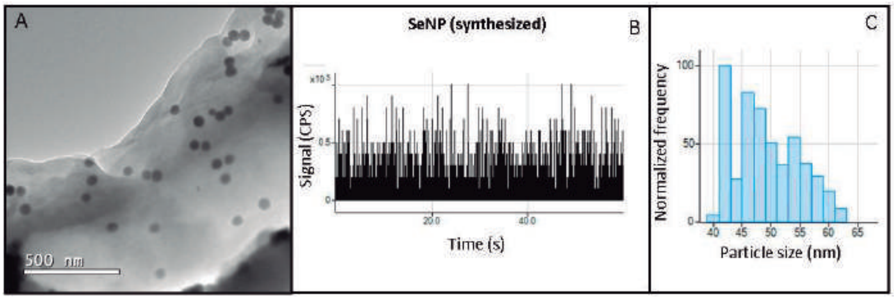

Fig 1. TEM image (A), time scan (B) and size distribution (C) of synthesized SeNPs obtained by spICP-MS using $H_2$ as reaction gas.

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## Agradecimentos/Acknowledgments

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**Área: ANA**

# Generalized algorithm for conversion of synchronous fluorescence matrices into excitation-emission matrices

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Palavras Chave: *Synchronous fluorescence, Excitation-emission matrices, Bilinearity, Trilinearity, PARAFAC.*

## Highlights

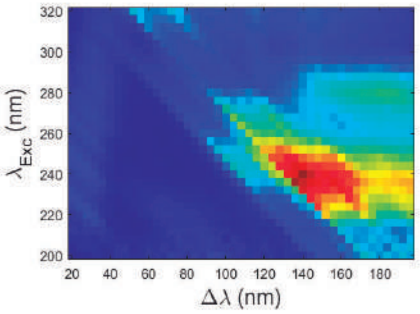
The shape of the converted matrices depends of the offset and excitation steps.

Converted matrices are bilinear and usable with compatible methods.

Method was tested with PARAFAC in different test sets.

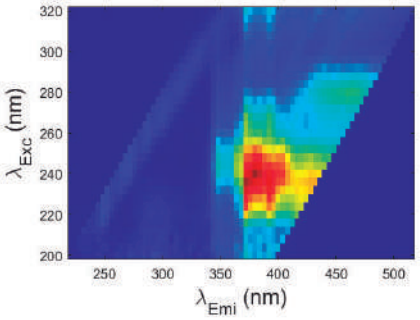
## Resumo/Abstract

Synchronous fluorescence is a spectroscopic technique in which the emission wavelength being measured always has the value of the excitation wavelength added to a constant offset. That is, if the incident light in a sample has the wavelength $\lambda_{Exc}$, the emission is measured at the $\lambda_{Exc} + \Delta\lambda$ wavelength.



By measuring these spectra in different Δλ values, a synchronic fluorescence matrix (SFM), with different excitation wavelengths row-wise and different offsets column-wise can be created. However, the generated SFM does not have bilinear characteristics due to the shearing of emission wavelengths row-wise, which makes it impossible to use it in algorithms such as PARAFAC and MCR-ALS.

In this work, a converter was developed focusing on converting a given SFM in a compact Excitation-Emission Matrix (EEM), with its shape depending solely on the ratio between the excitation and offset steps.



The following equation was then developed, being able to successfully convert SFMs in EEMs (as shown in the figure on the right), allowing its use with algorithms depending on data multilinearity and measuring a larger spectral region (compared with a classical EEM) while avoiding Rayleigh scattering regions.

$$\mathrm{X_{EE}}\big(\mathrm{i}, \mathrm{i} - \mathrm{m_{min}}(\mathrm{k}-1) + \mathrm{m_{min}}(\mathrm{j}-1) + \mathrm{m_{min}}\mathrm{n_{min}}(\mathrm{k}-1)\big) = \mathrm{X_{Sync}}(\mathrm{i}, \mathrm{j})$$

With $\mathrm{m_{min}}:\mathrm{n_{min}}$ being the simplest ratio between the offset and excitation wavelengths steps and $\mathrm{k}$ representing the position of a point in a row-wise subdivision of the matrix in $\mathrm{m_{min}}$ sized sections.

To test the method, 5 sets of SFMs were measured from mixtures of 4 PAHs in a Cary Eclipse spectrofluorometer (fluoranthene, anthracene, phenanthrene, and pyrene, using a partial factorial calibration design in 3 levels), each set using different $\mathrm{m_{min}}:\mathrm{n_{min}}$ ratios. The resulting tensors were then deconvoluted using PARAFAC, retaining quantitative and qualitative information, allowing its use for both calibration and characterization. SFMs with unitary values of $\mathrm{m_{min}}$ tended to have more consistent qualitative profiles.

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## Agradecimentos/Acknowledgments

CNPq, CAPES, and Finep.

**Área: ANA** **Nº de Inscrição:**

# Halogens and sulfur in nails: single analysis using ion chromatography with suppressed conductivity and mass spectrometry after combustion reaction

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Palavras Chave: *Ion chromatography; Mass spectrometry; Microwave-induced combustion; Biological matrices analysis.*

## Highlights

Halogens and sulfur were determined in human nails using a single analysis, and drawbacks of conventional analytical methods were overcome.

## Abstract

Human nail analysis is useful when investigating the mineral status of human organisms [1]. Nowadays, there is an increasing interest in the halogens and sulfur determination in biological samples, because they are associated with several important physiological functions and also with several adverse effects [1-3]. However, the challenge for the halogens and sulfur determination begins with the analytical tool, because only a few techniques provide accurate results for them [1-3]. Instrumental neutron activation analysis (INAA) is commonly used for this goal; however, its application in the routine analysis is hampered by nuclear reactor requirement, and its relatively low sample throughput [1-3]. X-ray fluorescence (XRF) and laser ablation-inductively coupled plasma mass spectrometry (LA-ICP-MS) have also been used [1-3]. Even avoiding exhaustive sample preparation steps, these techniques have some problems related to the matrix effects, calibration step and the lack of sample homogeneity, impairing their application in routine analysis. Our research group recently proposed the use of microwave-induced combustion (MIC) for digestion of human nail aiming Br and I determination by inductively coupled plasma mass spectrometry (ICP-MS) [3]. However, F, Cl and S determination by ICP-MS is impaired by high ionization potentials and by several polyatomic interferences. In this context, ion chromatography with suppressed conductivity and mass spectrometry detection (IC-CD-MS) emerges as a powerful technique for the multielemental determination of halogens and sulfur in biological samples. Thus, in the present study, the feasibility of the MIC method for further halogens and sulfur determination in human nails by IC-CD-MS was evaluated. Around 100 mg of the human nail were efficiently digested by MIC and 50 mmol $L^{-1}$ $NH_4OH$ was used as absorbing solution [3]. After sample preparation step, the final solution was analyzed by IC-CD-MS - Cl, F and S were separated as $Cl^-$, $F^-$ and $SO_4^{2-}$ by IC and determined by conductivity (IC-CD), while Br and I were separated as $Br^-$ and $I^-$ by IC and determined by MS (IC-MS), but in a single chromatographic run. Chromatographic conditions such as gradient elution mode using KOH (5 to 90 mmol $L^{-1}$ in 0 to 35 min) and spectrometric conditions such as cone voltage (135 V), needle voltage (4.2 kV), and probe temperature (600 ºC) were previously optimized [2] Inductively coupled plasma optical emission spectrometry (ICP-OES) and ICP-MS were used to compare the results. Trueness was evaluated, by recovery tests using the standard solution in two levels – 50 and 100% of the detected concentration (mean recoveries ranged from 94 to 106%) and using a mixture of the sample with certified reference material – 75 mg of sample mixed with 25 mg of CRM NIST 8435 whole milk powder (mean recoveries ranged from 93% to 106%) and by comparison of the results [results obtained by IC-CD-MS did not present significant differences ($p > 0.05$) from those obtained by ICP-OES (Cl and S) and by ICP-MS (Br and I)]. Relative standard deviations were always lower than 10%. Bromine (1.17 to 2.92 µg $g^{-1}$ by ICP-MS), Cl (589 to 793 µg $g^{-1}$ by IC-CD-MS), F (lower 30 µg $g^{-1}$ by IC-CD-MS), I (0.22 to 0.72 µg $g^{-1}$ by ICP-MS) and S (27.0 to 33.6 mg $g^{-1}$ by IC-CD-MS) concentration varied in a wide range. Low dissolved carbon (< 5 mg $L^{-1}$), particulate material absence and alkaline absorbing solution characteristic (pH ~ 8) made the final solution obtained by MIC fully compatible with IC-CD-MS. Limits of quantification were 3 µg $g^{-1}$ for Br, 40 µg $g^{-1}$ for Cl, 20 µg $g^{-1}$ for F, 1 µg $g^{-1}$ for I and 800 µg $g^{-1}$ for S. IC-CD-MS allowed analytes determination in 35 min in a single analysis.

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## Acknowledgments

The authors are grateful to CNPq – Brazil (grant numbers 409357/2016- 2 and 309424/2016-0), CAPES – Brazil (finance code 001), and FAPERGS – Brazil (grant number 16/2551-0000561-8) for supporting this study.

**Área: ANA**

# Identification of amino acids and sugars in basil leaves by Desorption Electrospray Ionization Mass Spectrometry Imaging after Cd Contamination

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Palavras Chave: *mass-spectrometry, imaging, metabolomics, toxic metals*

## Highlights

**Identification of amino acids and sugars in basil leaves by desorption electrospray ionization mass spectrometry imaging after Cd contamination**

- Imprinting on TLC plate was effective for analysis of amino acids and sugars in basil leaves;
- Some amino acids and sugars are potential biomarkers for Cd contamination.

## Abstract

Imprinting of basil leaves (Ocimum basilicum L.) contaminated with $Cd^{2+}$ under hydroponic cultivation were analyzed on different substrates (PTFE membrane and TLC plate) for amino acids and sugars determination by Desorption Electrospray Ionization Mass Spectrometry Imaging (DESI-MSI). The TLC plate was the best substrate since the images showed a superior definition, with lower extract scattering and mass deviations, providing excellent reliability in the analytes spatial distribution. DESI-MSI analysis identified eight images in contaminated and uncontaminated leaves of ions putatively identified as amino acids and sugars with high accuracy (mass errors varying from -0.860 to 0.985 ppm). The images showed that proline, histidine, glutamine, arginine, homoarginine, theanine, hexose sugars, and disaccharides accumulated in basil contaminated leaves as a defense mechanism to respond to cadmium stress (Figure 1). These images also revealed the spatial distribution of the amino acids and sugars throughout the basil leaves, showing that DESI-MSI is a valuable tool for metabolomic studies in plants exposed to toxic metals and potentially submitted to other stress conditions.

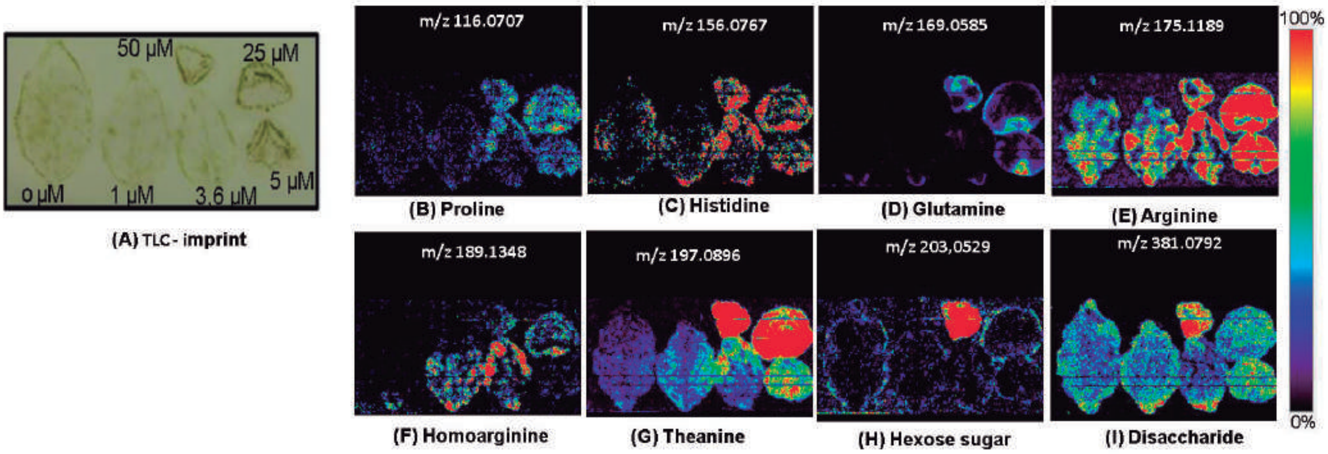

**Figure 1** (A) TLC-imprinting of basil leaves at Cd concentrations of 0, 1.0, 3.6, 5.0, 25.0 and 50 μM and their images, obtained by DESI-MSI, showing the spatial distribution of amino acids and sugars: (B) proline (*m/z* 116.0707), (C) histidine (*m/z* 156,0767), (D) glutamine ($Na^+$ adduct, m/z 169.0585), (E) arginine (*m/z* 175.1189), (F) homoarginine (*m/z* 189.1348), (G) theanine ($Na^+$ adduct of *m/z* 197.0896), (H) hexose sugar ($Na^+$ adduct of *m/z* 203.0529) and (I) disaccharide ($K^+$ adduct of *m/z* 381.0792).

## Acknowledgments

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**Área: ANA**

# Investigação Geoquímica do Material Petrolífero Proveniente do Derrame na Costa Litorânea de Pernambuco no Ano de 2019

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*Palavras Chave: Biomarcadores do petróleo, Derrame de petróleo, GC-MS/MS, Litoral de Pernambuco.*

## Highlights

**Geochemical Investigation of the Petroleum Material from the Oil Spill on the Coast of Pernambuco in 2019**

- Biomarkers of oil spill samples identified by GC-MS/MS
- Evidences of distinct chemical composition in one of the samples
- Oleanane isomers are a biomarker characteristic of the Venezuelan oils from the spill

## Resumo/Abstract

Diante do desastre ambiental causado pela chegada de grandes quantidades de material petrolífero trazido pelo oceano para as praias brasileiras no ano de 2019, o estado de Pernambuco se destacou como um dos mais afetados. Dados descritos na literatura por Oliveira et al. (2020) sugerem que há uma similaridade química desse material petrolífero com óleos provenientes de bacias petrolíferas venezuelanas. Diante das grandes proporções e do impacto negativo imensurável que o derrame provocou, buscamos inicialmente realizar uma caracterização química de diferentes amostras do material petrolífero coletado em diversas praias do estado de Pernambuco, e no decorrer do estudo, levantamos o questionamento quanto à possibilidade de contribuição ao derrame por possíveis eventos adicionais não reportados. Assim, com objetivo investigativo, foram realizadas análises de Cromatografia Gasosa/Espectrometria de Massas Sequencial (GC-MS/MS), utilizando o modo de aquisição por Monitoramento de Reações Múltiplas (MRM) para a caracterização de amostras de óleo coletadas no litoral pernambucano no ano de 2019, visando a identificação dos biomarcadores clássicos do petróleo pertencentes às classes dos terpanos e esteranos. A finalidade do estudo é a de buscar a constatação das similaridades ou eventuais dissimilaridades na composição química das amostras. Doze amostras do material (mistura de petróleo com areia) foram coletadas nos meses de setembro e outubro de 2019 em praias do litoral Sul ao Norte do estado. Os óleos foram extraídos com diclorometano na proporção 1:10 (*m/v*) e submetidos à análise por GC-MS/MS, num instrumento modelo TQ8040 (Shimadzu co., Japan), utilizando o modo de aquisição por MRM. O GC-MS/MS operou com ionização por impacto de elétrons (EI) com 70 eV e o sistema de MS monitorou as transições: *m/z* 370>191, 398>191, 412>191, 426>191, 372>217, 386>217 e 400>217, referentes as classes dos biomarcadores terpanos e esteranos. O estudo e comparação entre os perfis cromatográficos obtidos nos permitiu a identificação dos biomarcadores do petróleo presentes e a visualização da similaridade para todas as amostras, exceto para uma delas, que nomeamos de **amostra 10** (coletada na praia de Maria Farinha, litoral Norte de Pernambuco). Diferente das outras onze demais amostras, a **amostra 10** não apresentou os característicos biomarcadores *18α(H)-oleanano* (cuja presença em amostras provenientes do grande derrame do ano de 2019 foi relatada por Lourenço et al. (2020)) e seu isômero *18β(H)-oleanano*. A **amostra 10** também se diferiu das demais nos valores de algumas razões diagnósticas para diversos biomarcadores identificados, tais como: Esteranos/Hopanos; Ts/Tm; Ts/(Ts+Tm); Ts/$C_{30}$Hopano Gamacerano/(Gamacerano+$C_{30}$Hopano, e outras. Os valores das razões diagnósticas foram utilizados para realização dos estudos estatísticos por Análises de Componentes Principais (PCA) e Componentes Hierárquicos (HCA) com *heatmap*, cujos resultados reforçam que há uma dissimilaridade geoquímica da **amostra 10** em relação às outra onze amostras. Sendo assim, os resultados apontam que entre as diferentes amostras de material petrolífero proveniente do derrame no ano de 2019 e que foram coletadas em diferentes parais do estado de Pernambuco, uma delas se trata de um material petrolífero proveniente de uma fonte distinta das demais do supracitado derrame.

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## Agradecimentos/Acknowledgments

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**Área: ANA** **Nº de Inscrição: 01129**

# Isolation of mitraphylline from *U. tomentosa* barks and development of spectrophotometric method for alkaloids determination in cat's claw samples

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Palavras Chave: *Uncaria tomentosa (Willd. ex Schult.) DC., Total alkaloids, Mitraphylline, Control quality, Spectrophotometry*

## Highlights

Herbal medicines from *U. tomentosa* are used to treat deseases. A new way for mitraphylline isolation and its use as analytical standard to the development of a spectrophotometric method are presented.

## Resumo/Abstract

Herbal medicines obtained from *Uncaria tomentosa* (Willd. ex Schult.) DC.are indicated for the treatment of arthritis and osteoarthritis and are freely provided by the Brazilian State through the Public Health System [10]. The solid pharmaceutical forms of this medicinal plant contain dry extracts standardized in total alkaloids, expressed as mitraphylline, which is considered the marker substance [2]. Although *U. tomentosa* is native to the South America Amazon Region and is included as herbal medicine in the list of free essential medicines in Brazil, there are no monographs available in the national Pharmacopoeia and only expensive imported analytical standards are available for Brazilian researchers. The singularity of the reference analytical standards and the usual methods based on HPLC to quantify total alkaloids in *U. tomentosa* impact the cost of the quality control process and, consequently, the final products available for patients and the public health sector [3,4]. Therefore, this work proposes the isolation of mitraphylline from *U. tomentosa* barks to use the purified alkaloid as analytical standard in the development of a simple and low cost spectrophotometric method to determine total alkaloids in *U. tomentosa* samples. An alkaloid enriched extract was obtained by acid-base partition and mitraphylline was selectively precipitated using an 80:20% *v/v* toluene:hexane solution. The compound was characterized by HPLC-UV/DAD, mass spectrometry, UV/Vis, IR and $^1$H and $^{13}$C Nuclear Magnetic Resonance spectroscopy. Sample preparation for the spectrophotometric method consisted of an extraction with boiling methanol (3x 10 mL, 15 min), followed by a strong cation exchange solid phase extraction (SCX-SPE) clean-up. Mitraphylline with a purity of 98% was isolated in 0.05% *m/m* yield. All characterization results were in agreement with previous published data. The spectrophotometric method showed linear range between 0.40 and 20 µg/mL; limits of detection and quantification of 0.15 and 0.49 µg/mg, respectively; dispersion of results lower than 5% for repeatability and intermediate precision; and robustness in relation to sample mass extracted and extraction time. The accuracy of the method was evaluated by comparison of the data with reference values determined by Soxhlet (n = 3) and by an HPLC-UV/DAD method (n = 3). The samples of barks and capsules of *U. tomentosa* presented, respectively, 1.19 ± 0.0557 and 0.570 ± 0.00992 µg/mg of total alkaloids by the proposed extraction and spectrophotometric method (n = 3). The Soxhlet extraction led to 1.17 ± 0.0719 and 0.583 ± 0.0379 µg/mg for the same samples, while the HPLC-UV/DAD method led to 1.18 ± 0.118 µg/mg for the barks samples. A paired t-test showed that the results obtained were statistically identical when comparing with the spectrophotometric method. The developed method to obtain mitraphylline analytical standard from *U. tomentosa* barks and to determine total alkaloids by spectrophotometry, provided a cheaper and faster quality control alternative for *U. tomentosa* samples, and consequently, impacting in a lower cost of the final products. It is noteworthy that the Brazilian National Institute of Industrial Property (INPI) considered the isolation method presented in this work patentable (register number BR10201806821) [5]. It shows the appealing national market for this substance, which is currently imported, and suggests the relevance of the work as an alternative to the existing conventional methods.

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**Área: ANA**

# Isotopic Analysis of Mg, Sr and Pb in Crude Oil using Multi-Collector Inductively Coupled Plasma-Mass Spectrometry

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Palavras Chave: *Crude oil, Isotopic Analysis, MC-ICP-MS, Magnesium determination, Lead determination, Strontium determination.*

## Highlights

Efficient digestion and MC-ICP-MS provided a method for isotopic analysis of crude oil
Time-consuming methods and large amounts of reagents were avoided
Promising tool to decipher the formation history of oil reservoirs

## Resumo/Abstract

Information related to the geological formation processes, origin, type and migration of crude oil is imprinted in the isotopic composition of certain proxy elements in this substnce. Elements such as Mg, Sr and Pb have been used as isotopic tracers in geochemical, environmental and/or biomedical applications. The isotopic analysis of Mg, Sr and Pb has been performed in many matrices, including environmental, geological and archeological materials, as well as biological fluids and tissues. However, only a few studies were found in the literature on Pb isotopic composition in crude oil, and only a single study was found for Sr. Moreover, no papers have reported Mg isotopic analysis of crude oil so far. As a result, information on the isotopic composition of these elements in crude oil is still lacking. Thus, the goal of the present study was to develop methods for Mg, Sr and Pb isotopic analysis of medium crude oil using high-precision multi-collector inductively coupled plasma-mass spectrometry (MC-ICP-MS) to provide analytical tools for oil provenancing and tracing of the oil deposit formation. In this sense, two sample preparation methods were evaluated: (i) microwave-assisted wet digestion with a pressurized digestion cavity (MAWD-PDC); and (ii) solubilization of inorganic solids after the ASTM D4807 test method. Using MAWD-PDC, up to 0.5 g of crude oil was efficiently digested using just 6 mL of 14.4 mol $L^{-1}$ $HNO_3$ (75 min, temperature of up to 250 °C). MAWD-PDC was shown to be a suitable sample preparation method for subsequent Mg, Sr and Pb determination and their isotope ratios. On the other hand, the method based on ASTM D4807 does not require any sophisticated equipment nor the use of halogenated solvents. With this method, up to 10 g of oil could be dissolved in toluene and filtered through a nylon membrane. Elements present as inorganic solids, such as Mg and Sr, were retained on the nylon membrane and could easily be recovered in water. However, Pb was not recovered using this method, possibly because this analyte is present in crude oil in the form of organic complexes that are not retained on the membrane. Isolation protocols were fine-tuned to the composition of crude oil solutions obtained upon MAWD-PDC and solubilization. For Mg, isolation was successfully carried out using a cation exchange resin (AG 50W-X8). The isolation of Sr and Pb, on the other hand, was performed by applying a sequential isolation protocol using the Sr-spec resin. The Mg-Sr-Pb isotopic composition of the Brazilian crude oils evaluated in this study was within the range observed for seawater and the deposit bedrock. Finally, the methods developed in this study can be considered as promising tools to decipher the formation history of crude oil reservoirs.

## Agradecimentos/Acknowledgments

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**Área: ANA**

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

# MALDI (+) FT-ICR mass spectrometry (MS) combined with machine learning towards diagnostic screening for COVID-19

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KEYWORDS: MALDI FT-ICR MS; Machine learning; Saliva; COVID-19; SARS-CoV-2.

## Highlights

Rapid identification of respiratory viruses in biological samples.
Classifying SARS-CoV-2 positive samples in complex matrices and at low concentrations by MALDI FT-ICR MS combined with SVM.

## Resumo/Abstract

Rapid identification of existing and emerging respiratory viruses in biological samples, such as SARS-CoV-2, is of utmost importance in strategies to combat and control outbreaks and pandemics. The MALDI FT-ICR MS (matrix-assisted laser desorption ionization Fourier-Transform Ion Cyclotron Resonance Mass Spectrometry) technique has high sensitivity and specificity. Inputting its output into machine learning algorithms, MALDI FT-ICR MS could hold promise in classifying SARS-CoV-2 positive samples, even in complex matrices and at low concentrations. This study aims to develop a fast and effective methodology to perform screening of patients with suspected COVID-19 from saliva samples, using the MALDI FT-ICR MS technique with support-vector machines (SVM). Optimizing sample preparation and analysis parameters was necessary for efficiency in MALDI FT-ICR MS analyses. The highest efficiency in the shortest analysis time was obtained with the digestion of saliva in 10 µL of trypsin for 2 h. The optimization of the parameters of the MALDI analysis presented a satisfactory resolution for the analysis with 1 M, presenting an excellent number of signals in a short analysis time. SVM models were created with data from the analysis of 149 samples, 97 which were designated SARS-CoV-2 positive and 52 negative, confirmed by RT-PCR tests. Two models showed the best results, SVM1 and SVM2. The calibration group obtained 100% accuracy and the test group 95.6% (SVM1) and 86.7% (SVM2). SVM1 selected 780 variables and has a False Negative Rate (TFN) of 0%, while SVM2 selected only 2 variables (525.4 Da and 1410.8 Da) with a TFN of 3%. The proposed methodology suggests a promising tool to aid screening for Covid 19.

## Agradecimentos/Acknowledgments

The authors thank CAPES, FAPES, CNPq, FAPESB-PPSUS, UESC, NCQP, ICEPi, and SESA.

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

# Method development using chemometric tools and a customized device for determination of endocrine disruptors in mineral waters

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keywords: *Endocrine Disruptors, Liquid Cromatography, Chemometrics Tools.*

## Highlights

D-μSPE-LC/MS for analysis of EDCs in bottled water optimized using chemometrics tools.
The proposed D-μ-SPE-LC/MS method was simple, fast, and cost-effective.

## Resumo/Abstract

A method was developed to determine 14 endocrine-disrupting chemicals (EDCs) in bottled waters, based on dispersive micro-solid phase extraction (d-μ-SPE) and liquid chromatography-mass spectrometry (LC-MS). The custom glass device was proposed and evaluated. Extraction was optimized using 2 k$^{-1}$ factorial and Doehlert experimental designs. Optimized conditions were 80 mg C18, 25 min extraction at 1000 rpm, and 6 min desorption time. Repeatability was below 17 % for all EDCs. LOD and LOQ varied from 1.60 ng L$^{-1}$ (estradiol, E2) to 23.2 ng L$^{-1}$ (dimethylphthalate, DMP) and from 5.33 ng L$^{-1}$ (E2) to 77.3 ng L$^{-1}$ (DMP). We found DMP and bisphenol A (BPA) in samples after the heat treatment. DMP was up to 58.7 μg L$^{-1}$, while BPA was up to 1.34 μg L$^{-1}$. Tolerance of daily intake (TDI) for DMP were 2.50–2.94 μg kg$^{-1}$ day$^{-1}$ (children) and 1.43–1.68 μg kg$^{-1}$ day$^{-1}$ (adults). TDI for BPA were 0.03–0.07 μg kg$^{-1}$ day$^{-1}$ (children) and 0.01–0.04 μg kg$^{-1}$ day$^{-1}$(adults). However, the concentration levels found still considered safe up to date.

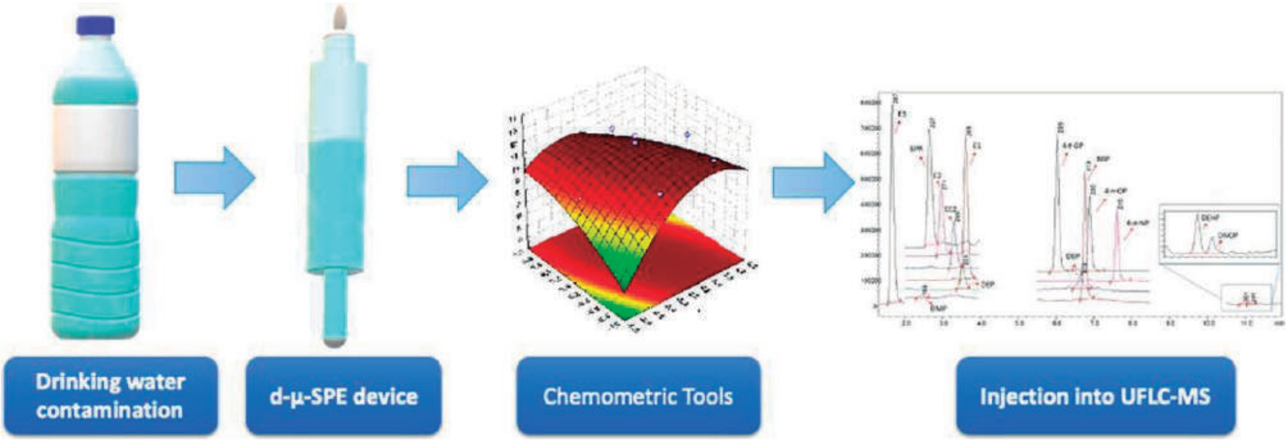

*Figure 1The method development steps*

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**Área: ANA** **Nº de Inscrição: 00669**

# Microwave-assisted ultraviolet digestion: an approach for the digestion of polymeric-based materials

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Keywords: *sample preparation, halogens determination, diluted acid solutions.*

## Highlights

Combination of microwave and ultraviolet radiation for improving sample preparation.
Decomposition of polymeric matrices using diluted acid solution.
Feasibility of halogens determination in acidic medium.

## Abstract

Spectrometric techniques have received permanent improvement allowing elemental determination at trace levels and in several matrices. Following this trend, sample preparation has received attention and many advances in instrumentation have been developed. Thus, automatized ovens, with conventional, microwave and combined microwave and ultraviolet heating are available. In this work, the feasibility of sample preparation by combining microwave and ultraviolet radiation is demonstrated and a hard-to-digest matrix was chosen as an example of application for further halogen determination. Polymeric-based materials are generally inert to acid attack, being difficult to perform a suitable sample digestion. In general, hard conditions (as concentrated acids, high pressure and temperature) are required to obtain a complete digestion. However, in these conditions, halogens can be lost by volatilization. Thus, if a method avoiding the use of acids could lead to high digestion efficiency it could be useful for halogens in hard-to-digest matrices. In this work, microwave-assisted ultraviolet digestion (MAWD-UV) was proposed for the digestion of polymers using a diluted acid solution for further halogen determination. A keyboard sample was used to optimize method parameters and after, the method was applied to other five polymer-based materials (mobile phone, food packaging film, nasogastric tube and two types of protection gloves). The irradiation power (500 to 1000 W) and the composition of the digestion solution (diluted $HNO_3$ plus $H_2O_2$) were evaluated. The digestion efficiency was evaluated by measuring carbon content in digests (the total acidity was also determined). The accuracy was evaluated using a certified reference material of low-density polyethylene (ERM EC680k) and by the comparison of the obtained results using MAWD-UV with the reference values obtained by neutron activation analysis (NAA) for Br and Cl and by inductively coupled plasma mass spectrometry (ICP-MS) or ion selective electrode (ISE) for F, Cl, Br, and I, after microwave-induced combustion (MIC), for all samples. Agreement was better than 90% with reference values for Cl, Br, and I (ANOVA, 95% confidence level) using 200 mg of sample and a diluted acid solution (15 mL of 0.5 mol $L^{-1}$ $HNO_3$ + 10.6 mol $L^{-1}$ $H_2O_2$), using 25 min of ramp to reach 700 W, maintaining for 15 min at this power and 60 min at 0 W for cooling. No losses were observed using the optimized conditions and digests were suitable for further halogen determination by ICP-MS and ISE.

## Acknowledgments

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**Área: _______ANA________**

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

# Molecular Forensic Geochemistry: Brazilian oil speciation in the oil sector and environmental crimes

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Palavras-Chave: *Biomarcadores, Geoquímica Forense, Petróleo, GC×GC-TOFMS, Orbitrap-HRMS*

## Highlights

Orbitrap-HRMS and GC×GC-TOFMS techniques applied in forensic geochemistry.
Analysis of Brazilian oils with a wide range of API gravity.
Evaluation of biomarkers in forensic studies aimed at environmental crimes.

## Resumo/Abstract

The increase in offshore oil production in Brazil has resulted in the need for a geochemical characterization of these new oils, as distinct aspects of molecular composition are essential for understanding the contribution of organic matter, thermal evolution, and biodegradation.[1,2] The aim of this study is to perform molecular analysis of five oil samples from different API gravity (18.4; 24.4; 28.4; 29.6; 45.6) using comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometry (GC×GC-TOFMS) and high-resolution mass spectrometry (Orbitrap-HRMS) for geochemistry biomarker investigation.[1] Oil samples were fractionated in liquid chromatography, separating them into saturated (average of 51.52% for light oils; 45.21% for intermediates; and 42.83% for heavy), aromatic (average of 10.12% for light oils; 14.51% for intermediates; and 20.74% for heavy oils), and polar (average of 2.03% for light oils; 31.17% for intermediates; and 27.90% for heavy oils) fractions. Cyclic and branched hydrocarbons were isolated in the saturated fraction using urea adduct, analyzed by GC×GC-TOFMS and the analytical data evaluated by ChromaTOF software. In the intermediate sample (°API= 28.4), it was possible to identify the chemical profile of 29 different biomarkers, while in the IBAMA sample 27 biomarkers were identified.[2] The main geochemical reasons studied so far, and which allow a greater differentiation of the samples, were the ratios: Pr/Fi>1; Pr/nC17= >1 and Fi/nC18<1, which are indicative of biodegradation. The ratios between the R and S isomers of hopanes H31, H32 and H33, as well as the ratio Ts/Tm< 1 that correspond to saline, marine, evaporitic or carbonate environments. Crude oils samples were also analyzed by ESI(±)Orbitrap-HRMS to identify the high boiling point polar substances (N, S and O). In the intermediate sample (API gravity= 28,4), for the cyclic and branched fraction were identified compounds as H30, Tr23 and GAM (*m/z*= 191); pristane, norpristane and farnesane (*m/z*= 183), and 25,28,30-TNH and 25NH (*m/z*= 177).[2] For Orbitrap-HRMS analysis the most abundant identified species corresponded mainly to the N[H], $N_2$[H], $O_3$[H], O[H], $O_2$[H], $NO_2$[H], NS[H], NOS[H], and OS[H] classes. Nitrogen class was 92.9% in light samples; 84.2% to 86.0% in intermediate samples; and 88.8% to 90.0% in heavy samples. The double bond equivalents (DBE) distribution in function of carbon number (CN) was obtained for the crude oils. In the N class the light oils showed a range of substances containing CN, ranging from $C_{12}$ to $C_{58}$ and a highest abundance of nitrogen compounds in DBE = 8 to 10. In intermediate samples, CN was $C_{12}$ to $C_{67}$ and DBE between 6 to 10. In heavy samples, CN was $C_{12}$ to $C_{59}$ and DBE between 6 to 9. These results are preliminary, and the next step will be to use statistical tools to better understand the behavior of biomarkers and apply them to real oil spill samples, assisting in forensic studies aimed at environmental accidents.

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**Área:ANA**

# Monitoring of emerging contaminants in real river water samples using biomimetic molecularly imprinted polymers

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Keywords: MIP, Emerging contaminant, Dye, Biomimetic sensors, Methotrexate.

## Highlights

Molecular imprinting technology has become a powerful tool in environmental research for the quantification of emerging pollutants due to the mimic recognition toward target analytes.

## Resumo/Abstract

This work aims to develop a highly sensitive and selective system of analysis for the quantification of emerging pollutants that are widely used in Peru in real river water. This research applied different methodologies as the development of an electrochemical sensor based on molecularly-imprinted polymers (MIPs) as selective adsorbent by subsequent modification. The materials obtained were characterized by imaging tools such as scanning electron microscopy (SEM), Porosity, and thermal techniques followed by studying affinity and selectivity($\alpha$=2.8). The analytical curve for the dye acid blue (AB29) was performed by HPLC in the range of 1 to 40 μmol $L^{-1}$ as well as by UV/Vis Spectrophotometer. The adsorption data followed the Langmuir model and showed a maximum time of 45 minutes and a $Q_m$ value of 7.90 mg $g^{-1}$ for MIP and 3.98 mg $g^{-1}$ for the corresponding non-imprinted polymer (NIP). For the emerging methotrexate, a linear range of 1 – 125 μmol$L^{-1}$ has been obtained with a detection limit of $5.5\times10^{-4}$ mol$L^{-1}$, using cyclic voltammetry and amperometric sensitivity of 0.021 μALmol$^{-1}$. In this way, there were obtained analytical devices with an excellent sensing performance, quick use, and low cost, with the additional advantage of higher durability and repeatability (RSD 2.5%) than the conventional traditional methods.

## Agradecimentos/Acknowledgments

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**Área: ANA**

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# New iron-based material as magnetic-solid phase extraction for ultratrace preconcentration and speciation of iAs in rice samples by ICP OES

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Keywords: *Rice, Arsenic speciation, Nanomaterials, Non-chromatographic methods, ICP OES, Magnetic-solid-phase extraction.*

## Highlights

A MSPE was developed for iAs preconcentration and speciation in rice samples for analysis by ICP OES using iron nanoparticles. The developed method showed lower sensitivity than HPLC-ICP-MS method.

## Abstract

Rice is an important food commodity being one of the most consumed grains in human diet. This product has the capability to bioaccumulate trace elements, especially arsenic due to the flooded conditions required for its farming. Brazil recommends total concentration of As in rice must not be higher than 200 µg $kg^{-1}$ except for products used in infant formula (100 µg $kg^{-1}$). Methods focused on arsenic speciation are required to guarantee the food security of this food product. The classical technique for this purpose is HPLC-ICP-MS, nevertheless, these methods are expensive, require expert analysts. In present work, a new iron-based nanomaterial was synthetized and functionalized with an organophosphorus compound (dimethyltriamine-pentamethylene phosphonic acid (DTPMP)) the material was characterized using DRX, FT-IR and TEM (Figure 1). This new nanomaterial was used as solid-phase for As preconcentration and speciation to be quantified by ICP OES. Around 0.250 g of *in natura* rice was grinded and decomposed using 65% w $w^{-1}$ $HNO_3$ in block digester for 3h (120°C). The water-soluble As species were extracted in 0.500 g of the same sample using 2% w $v^{-1}$ $HNO_3$ in block digester for 1h (90°C). The arsenic in digester and extracted solution was preconcentrated using 4 mL of buffer solution pH 4.0, 20 mg of nanomaterial with 15 min of extraction time, after this, 2 mL of 10% $HNO_3$ was used for desorbing As and the solution analyzed by ICP OES. The method proposed it is efficient for preconcentration of total As (tAs) in rice samples using ICP OES with recovery of 97% using CRM NIST 1568b – Rice Flour. Besides that, it is selective to inorganic As(iAs) being possible the speciation of this specie with good accuracy (101% recovery of iAs in CRM). The method proposed show good precision with RSD lower than 15% for all samples and LOD and LOQ (1.08 µg $kg^{-1}$ and 3.70 µg $kg^{-1}$) are compatible with current legislation in Brazil. The samples show tAs content between 0.090 and 0.295 µg $kg^{-1}$ and iAs mass fraction between 0.055 and 0.109 µg $kg^{-1}$. All these samples are in accordance with legislation but only one sample can be used in infant food. The present method is a good alternative for chromatographic speciation methods and could be used for tAs and iAs preconcentration for analysis using a low-cost technique as ICP OES.

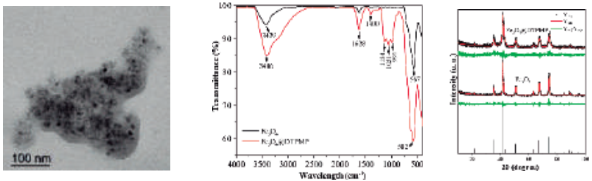

Figure 01: TEM image, FT-IR spetra and DRX pattern for nanomaterial synthetized

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**Área: ANA**
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# Occurrence, distribution, spatio-temporal variability and source identification of n-alkanes and isoprenoids in coastal sediments from beaches of the Brazilian semi-arid.

**Alessandro F. Barbosa (IC),[1*] Tayná F. Santos (IC),[1] Paloma G. Silva (IC),[1] Natália S. L. Silva (IC),[1] Kamylla M. M. Bezerra (PG),[1] André H. B. Oliveira (PQ).[1*]**

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Palavras Chave: *Marine Water and Sediments, Aliphatic hydrocarbons, Isoprenoids, Gas chromatography, Organic Pollutants.*

## Highlights

Determination of levels of aliphatic hydrocarbons and isoprenoids (pristane and phytane), estimating sources of release, using gas chromatography in sediments of beaches on the west coast of Ceará.

## Resumo/Abstract

Coastal regions are areas or environments that receive large amounts of organic pollutants. Thus, sediments in these areas have high concentrations of organic matter, which can compromise the health of the population and cause risks to the ecosystem. This work aims to determine the levels of aliphatic hydrocarbons and isoprenoids (pristane and phytane), estimating the sources of release on beaches on the west coast of Ceará. Surface sediment samples were collected at low tide and stored in metal containers, and kept under refrigeration until the Environmental Studies Laboratory (LEA-UFC). Sediment extracts were obtained through ultrasound-assisted extraction methodology followed by a clean-up step to remove interferents. The extracts (apolar fraction) were analyzed by gas chromatography coupled to a flame ionization detector (GC-FID). Analytes were quantified by the internal standard method. The characterization of the sediment matrix was performed according to the parameters: Granulometry, %CaCO3 and percentageOrganic Carbon (%OC), with values between 95.8% - 98.9% of sand, 1.61% - 7.49% and 0.1264 - 0.4573%, respectively. The sum of the concentration of the n-alkane series from n-C8 to n-C34 ranged to 2.74 - 4.69 ug.g-1 (mean = 3.82 ug.g-1). Diagnostic ratios such as Prist/nC17, Phit/nC18, Prist/Phit, TAR and CPI were used to evaluate the origin of sedimentary organic matter from the coastal zone of Icaraí, Tabuba and Cumbuco beaches. A predominance of short-chain n-alkanes (n-C12, n-C14 and n-C16) was observed, with the exception of point 2, where there is no significant concentration of n-C12. According to VOLKMAN 1988 indicating an input of marine organic matter (phytoplankton). The TAR ratios indicate a predominance of a marine hydrocarbon in the study area. In contrast, at points 2 and 3 the CPI points to a predominance of anthropogenic activities. These levels may be associated with urban runoff, as well as local shoreline containment works. Values obtained for Pris/Fit ratios (~1), Pris/n-C17 and Fit/n-C18 (<1) suggest an input of petrogenic sources (oil) in early stages of degradation in the environment.

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L A T Laboratório de Análises de Traços - UFC

**Área: ANA** **Nº de Inscrição: 00966**

# Otimização e aplicação de método analítico para a determinação de resíduos de fármacos em amostras de águas superficiais

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Palavras Chave: *Águas Superficiais, Fármacos, Extração em Fase Sólida, Cromatografia Líquida*

## Highlights

### Optimization and application of an analytical method for the determination of drug residues in surface water samples

Multivariate optimization of method (SPE/HPLC-DAD) for analyzing drug residues in real surface water samples. Identification and quantification of 3 drugs in seawater sample and 5 drugs in fresh water sample.

## Resumo/Abstract

Os meios hídricos são receptores de esgotos domésticos, industriais e agropecuários e, consequentemente, são um importante veículo de dispersão ambiental dos poluentes químicos.[1] Apesar de sua função vital, os fármacos, quando presentes como contaminantes no ambiente, podem ser prejudiciais aos animais e seres humanos.[2] Eles se enquadram em um grupo de substâncias conhecidas como micropoluentes emergentes, sendo encontrados em matrizes ambientais e biológicas em concentrações muito baixas (ng $L^{-1}$), mas potencialmente capazes de causar efeitos adversos em ecossistemas e/ou sobre a saúde humana.[3] O objetivo deste trabalho foi otimizar um método analítico, baseado em extração em fase sólida (SPE) e análise por HPLC-DAD, para a determinação de resíduos de sete fármacos em amostras reais de águas superficiais: cefalexina (CEF), cafeína (CAF), cloridrato de oxitetraciclina (OCT), tetraciclina (TC), sulfametoxazol (SMX), enrofloxacina (ENRO) e naproxeno (NPX). A separação dos fármacos foi realizada em coluna Poroshell 120 EC-C18 (100 x 2,1 mm, di = 2,7 μm) usando como fase móvel A: tampão 5 mM acetato de amônio/ácido acético B: acetonitrila/metanol (2:1, v/v), vazão de 0,2 mL $min^{-1}$, utilizando um gradiente de eluição, com tempo total de corrida de 42 min. A extração dos analitos foi realizada utilizando SPE e foi otimizada por meio de planejamento experimental multivariado. Foram otimizadas as variáveis: volume de solvente para acondicionar o cartucho, pH e volume da amostra, espécie e volume do solvente para eluição e efeito salting out. O método exibiu resposta linear para os sete fármacos ($R^2 \geq 0,9949$), em faixas de concentração variando entre 10 e 500 μg $L^{-1}$. Os limites de detecção e quantificação variaram de 7,4 a 18,1 μg $L^{-1}$ e 24,7 a 60,4 μg $L^{-1}$, respectivamente. A exatidão do método foi determinada a partir dos ensaios de recuperação, obtendo-se resultados que variaram entre 71,6% e 115% para os fármacos CEF, CAF, SMX, ENRO e NPX. No caso de OCT e TC, as recuperações variaram entre 28,8% e 70,3%, devido à possível degradação desses compostos. Estudos de estabilidade, executados durante um período de duas e vinte e quatro horas para os sete analitos, evidenciaram a rápida degradação para os fármacos OCT e TC. O método otimizado foi aplicado em amostra de água salgada (praia da Ribeira, em Salvador-BA, Brasil), de água doce (Rio Catu, município de Alagoinhas-BA, Brasil) e água de torneira (SENAI/CIMATEC, em Salvador-BA, Brasil). Na amostra de água salgada, foram encontrados os fármacos CEF, CAF e NPX, em concentrações de até 482 μg $L^{-1}$; 37,6 μg L-1 e 40,3 μg $L^{-1}$, respectivamente. Na amostra de água doce, foram encontrados os fármacos CEF, CAF, SMX, ENRO e NPX em concentrações de até 216 μg $L^{-1}$; 3026 μg $L^{-1}$; 290 μg $L^{-1}$; 113 μg $L^{-1}$ e 414 μg $L^{-1}$, respectivamente. Na amostra de água de torneira, não foram encontrados fármacos. Verificou-se que, dos 5 fármacos determinados nas amostras, a cafeína apresentou uma alta concentração em água doce, o que pode ser explicado pelo seu uso generalizado pela população da região estudada (ex., consumo de bebidas cafeinadas). Além disso, as maiores concentrações encontradas nas amostras de água doce podem ser justificadas pela presença de atividades antrópicas no local, uma vez que o rio fica próximo à área urbana e industrial. O método otimizado, baseado em extração em fase sólida (SPE) e análise por HPLC-DAD, mostrou ser eficiente para a extração simultânea dos compostos-alvo nas amostras reais de águas superficiais.

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**Área: ANA** **Nº de Inscrição: 01433**

# Proposal of an analytical method for Nd, Pr, Fe and B determination in super-magnet alloys by ICP OES

**Rodrigo Papai (PQ),[1] Gilmar A. Almeida (PQ/PG),[1,2] João R.F. Silveira (PQ),[1] André L.N. Silva (PQ),[1] Célia A.L. Santos (PQ),[1] Thiago P. Nagasima (PQ),[1] Eduardo G. Jabes (PQ/PG),[1,3] Fernando J. Landgraf (PQ),[3] and Maciel S. Luz (PQ),[1]***

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Palavras Chave: *Neodymium, Praseodymium, Iron, Boron, Super-magnet, ICP OES.*

## Highlights

Proposal of an analytical method for Nd, Pr, Fe and B determination in super-magnet alloys by ICP OES. Determination of rare earth elements in super-magnet alloys. Didimium Analysis.

## Resumo/Abstract

Present in motors, electric turbines and data storage devices (hard disk), magnets are indispensable in the manufacture of computers, televisions, cell phones, smart watches and several modern electronic devices. The chemical composition of the magnet directly influences its magnetic performance and consequently impacts the performance of the products with which it is associated. In this context, the knowledge of the majority chemical composition of these materials contributes to an efficient quality control in the act of production and helps the producers of the high-technology industry to select the magnets in order to maintain a uniformity of these materials. Although there are several types of magnets, those that use rare earth elements generally have strong magnetic activity, and are often called super-magnets. Among the rare earth elements, the mixture of neodymium and praseodymium (didymium) is widely used in metal alloys together with the elements iron and boron for its performance as a super-magnet. The (Nd,Pr)FeB alloy production consists, in summary, to obtain metallic didymium by electrolytic reduction of didymium oxide (mixture of neodymium and praseodymium oxides) followed by iron and boron elements incorporation. The chemical composition control is important to avoid undesirable phases, such alpha-iron, and to control the microstructure formation during the alloy manufacturing step. The chemical composition range must be optimized such that minimizes the use of rare earth elements (Nd and Pr). In this context, this work evaluated the best instrumental conditions for the determination of alloy elements by ICP OES. Interference studies were carried out and the developed method was validated through interlaboratory tests and addition and recovery tests.

## Agradecimentos/Acknowledgments

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# Prospects on pre-concentration methods for the determination at ultra-trace levels and application in a case study

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Keywords: *Roadmapping, Preconcentration, Trace elements.*

## Highlights

The determination at trace levels is achieved using preconcentration methods. Perspective for the highly sensitive analysis methods was studied. A technology roadmap for preconcentration methods was built. Miniaturized methods were applied for preconcentration. New materials were synthesized and applied for preconcentration methods.

## Abstract

The development and improvement of preconcentration methods prior determination of the analyte is crucial to improving the limit of detection (LOD) of a given method. Several pre-concentration methods have already been used, or are under development, however, the real demand for such methods and their applications is not yet elucidated. Therefore, firstly, the future trends in the preconcentration methods were investigated using the Road mapping technology, which is a decision-making tool used mainly in the industry for the development of planning strategies to align market, product, and technology interests, in a defined time horizon through the mapping of scientific and technological trends[1]. The roadmap revealed that efforts have been made (in the last decade) to improve "classical" techniques, such as liquid-liquid extraction and solid-phase extraction since environmental appeals have demanded its replacement by micro-techniques, which are less aggressive to the environment and make the analysis faster, more economical and efficient. Finally, we have developed and validated a method using magnetic nanoparticles of graphene oxide (GO)/$\gamma$-$Fe_2O_3$ for pre-concentration of estrogens in tap water samples followed by the determination using high-performance liquid chromatography with a fluorescence detector. The GO/$\gamma$-$Fe_2O_3$ nanoparticles were synthesized via co-precipitation[2] and characterized by X-ray diffraction, Fourier transforms infrared spectroscopy, $N_2$ adsorption-desorption, and scanning electron microscopy. The domain for the factors time, pH, and nanoparticle mass were optimized (for preconcentration) using a central composite design consisting of eight factorial points ($2^3$), six axial points, and five replicates of the central point. The optimal conditions were obtained at 40 min, pH 6, and 9 mg of magnetic nanoparticles. The analytes were eluted using 500 µL of a solution composed of ethanol/water/acetic acid (80:20:1, v/v/v), achieving an enrichment factor of 91 ± 6 for 17β-estradiol and 119 ± 7 for 17α-ethinylestradiol, whereas the limits of detection achieved for 17β-estradiol and 17α-ethinylestradiol were 2.7 and 0.8 ng $L^{-1}$, respectively. Recovery tests ranged from 83 to 98%, and the short-term precision was % RSD ≤ 7 (n = 10).

## Acknowledgments

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**Área: ANA**

# Quantification of sulfite in beverages *via* analyte volatilization and molecular gas-phase absorption using miniaturized gas cells coupled to deep-UV LED

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Keywords: *Sulfite, substrate-integrated hollow waveguides, deep-UV LEDs, molecular gas-phase absorption*

## Highlights

The method is based on the conversion of $SO_3^{2-}$ into gaseous $SO_2$ by sample acidification followed by direct absorbance measurement via molecular gas-phase absorption. The developed sensor may be a practical and fast alternative to the official method.

## Resumo/Abstract

Sulfites are classified as a series of chemical agents that are widely used by the food industry as preservatives. Due to their oxidative properties, they prevent the proliferation of fungi and bacteria in various types of food. However, excessive consumption of sulfites by humans can cause numerous health problems. Therefore, Brazil and many other countries follow the recommendations of the Joint FAO/WHO Expert Committee on Food Additives (JECFA), which guides that the Acceptable Daily Intake (ADI) is 0.7 mg/kg per body weight/day, expressed as $SO_2$[1]. Analytical methods based on the extraction of sulfite via sample acidification followed by collection and analysis of the generated gaseous $SO_2$ via a variety of analytical techniques (e.g. titration, colorimetry and voltammetry) are reported in the literature for the monitoring of sulfide concentration in foods. However, the laborious sample treatment – such as the distillation necessary in the classic Monier-Williams method – and the need for $SO_2$ collection prior to the analysis make this methodology time consuming, dependant of the collection efficiency and with low reproducibilty[2]. In this study, we propose an alternative approach for the sulfite determination *via* generation of $SO_2$ and its direct measurement by molecular absorption gas-phase at 280 nm. The absorbance measurement in the gas-phase were achieved by attaching a miniaturized aluminum coated gas cell (i.e. substrate-integrated hollow waveguides. iHWG) with an LED emitting @280 nm as a light source and a SIC photodetector. The iHWG gas cell allows light-analyte interaction while its highly reflective coating guides the light to the detector[3]. The analytical procedure consisted of the acidification of 10 mL of the sample with $H_3PO_4$ followed by the on-line injection of the generated $SO_2$ into the detection device using constant airflow at 100 mL $min^{-1}$. Absorbance measurements were enabled by using an appropriate log101-based electric circuit and the signal intensity was continuously recorded. The optimized conditions allowed limit of detection of 14.3 ppm, linear range from 50 to 1,000 ppm, analysis time of 40s, and accuracy between 80 and 120%. The compact, portable and low-cost device was employed for the determination of sulfite in coconut water, concentrated grape juice and beer. The coupling of a deep-UV LED at 280 nm to an Aluminum-iHWG is employed for the first time enabling a miniaturized, portable and compact optical sensor. The developed approach may be an alternative to official methods for the determination of sulfite in a variety foods and beverages.

## Agradecimentos/Acknowledgments

Federal University of Uberlândia, CAPES and CNPQ.

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**Área: ANA**

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

# Quantitative CG/MS analysis of sawdust bio-oil

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**Key words:** *pyrolysis; bio-oil; GC/qMS, quantitative analysis,*

## Highlights

Quantitative analysis of the composition of the bio-oil produced in the pyrolysis of wood sawdust. Use of some patterns for calculation of Response Factor by classes of compounds. Positive quantification of 9 compounds and identification using RRF of a further 48 compounds.

## Resumo/Abstract

The quantitative analysis of bio-oils is quite difficult as and requires a lot of standards. In this work we developed a methodology using only 17 standards for determining the concentration of 48 compounds, representatives of the main chemical classes commons in bio-oils, using the Relative Response Factors (RRF) and the analytical curves. Five different samples of sawdust bio-oils were analyzed, using a GC/MS (QP 2010 plus, Shimadzu) and a DB-5 column (60 m x 0.25 mm x 0.25 µm), in the follow conditions: carrier gas: (He, 99.999, 1 mL/min), electron impact of 70 eV, $T_{INJ}$ and $T_{DET}$ = 300 ºC – splitless injection of 1 µL of a 1000 ppm solution. Data treatment was performed using the GCMS solution software.

For ***qualitative analysis***, SCAN mode (from 45 to 450 Daltons) and the oven was heated from 40°C to 300 °C at 3 °C $min^{-1}$. Total time = 202 min. Retention Indices (LPTRI) were used.

For ***quantitative analysis***, SIM mode and heating rate from 40 ºC (0 min) – 2 ºC/min – 160 ºC (0 min) – 20 ºC/min – 300 ºC (5 min), total time = 72 min. Analytical curves: from an initial solution at 400 mg $g^{-1}$ of each of the 17 standards and the concentrations varied from 1 mg $g^{-1}$ to 150 1 mg $g^{-1}$ being added the IS (methyl hexanoate) at 70 mg $g^{-1}$. The samples were analyzed in a concentration of 10.000 ppm (mg $g^{-1}$).

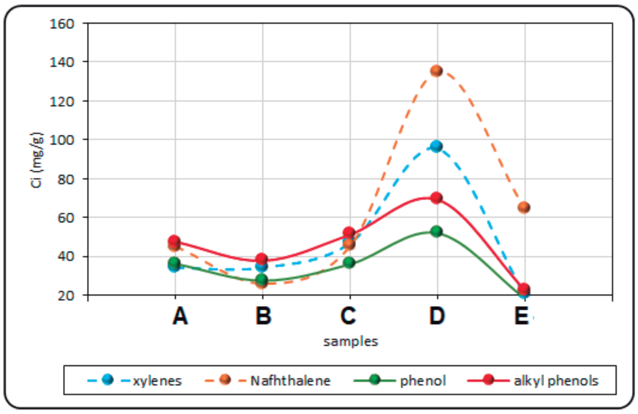
After the positive identification of **9** compounds (among the **17** standards used), the other compounds were quantified using the RRF obtained from a standard solution at 30 ppm. Ex. of application of RRF: all alkyl phenols in the samples were quantified using the RRF of m-cresol, benzenediols were quantified based on 4-methyl Catechol; benzaldehydes used 5-hydroxy-benzaldehyde curve, etc. RRF calculation: $RF_i = C_i/A_i$ and $RF_{is} = C_{is}/A_{is}$, *dividing* $RF_i/RF_{is}$it is obtained the $RRF_i$ *(Relative Response Factor for the compound i)* → $RRF_i = (C_i/A_i) \times (A_{is}/C_{is})$

**Results:**

Forty-eight compounds were quantified, highlighting the xylenes, naphthalene’s and alkyl phenols. The major compounds are described in Table 1:

| **TABLE 1:** | **Concentração (mg/g)** | | | | |
|---|---|---|---|---|---|
| **sample** | **A** | **B** | **C** | **D** | **E** |
| m-Xileno | 15.55 | 16.17 | 18.81 | 33.3 | 7.3 |
| p-Xileno | 17.92 | 17.68 | 27.41 | 60.49 | 12.73 |
| o-Xileno | 0.76 | 0.56 | 0.88 | 1.96 | 0.51 |
| Nafhthalene | 45.07 | 26.04 | 45.41 | 134.78 | 64.67 |
| phenol | 36.07 | 27.42 | 36.01 | 52.05 | 18.36 |
| m-cresol | 27.6 | 21.45 | 33.01 | 46.84 | 15.83 |
| 3,5 dimethyl phenol | 11.54 | 9.57 | 9.23 | 11.73 | 4.07 |
| 3,4 dimethyl phenol | 4.4 | 3.5 | 5.7 | 7.12 | 1.7 |
| 4-ethyl phenol | 4.04 | 3.33 | 3.46 | 3.68 | 1.31 |
| Vanilin | 0.34 | 0.33 | 0.65 | 1.03 | 0.34 |
| **total** | 163.29 | 126.05 | 180.57 | 352.98 | 126.82 |

Figure 1 shows the distribution of chemical classes, highlighting sample D with higher content.:



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**Área: ANA**

# Recovery of N-compounds from the pyrolysis of spent coffee grounds

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Palavras Chave: *spent coffee grounds; pyrolysis; bio-oil; acid/base/neutral extraction; N-compounds; GC/qMS*

## Highlights

Comparison of the pyrolysis of traditional and decaffeinated spent coffee grounds; Acid/base/neutral extraction of N-compounds from of bio-oils derived from the pyrolysis; N-compounds, characterized by GC/qMS.

## Resumo/Abstract

Coffee is an important agricultural product grown worldwide and one of the most consumed beverages in the world. However, its consumption produces a large amount of waste that can cause environmental problem mainly due to the presence N-compounds like quinolines and pyridines. However, if adequately treated, the compounds can be used in chemical are drug industry, benefiting the environment and adding value to this material. Thus, the objective of this work was to pyrolyze spent coffee ground generated in the preparation of coffee beverage using two types of coffee (traditional and the decaffeinated) for producing bio-oils and, subsequently, apply the acid-base-neutral (ABN) extraction technique to the bio-oils, aiming the isolation of N-compounds, due to their industrial and pharmacological importance. The ABN technique used is simple, of low cost and aims to pre-concentrate the nitrogenous compounds based on the basic character given by the nitrogen present in these molecules. The bio-oil was extracted 3 times with HCl (10%), the pH of the base fraction was adjusted to 10 with NaOH (10%) and extracted with dichloromethane. The analysis of bio-oils and fractions was performed by GC/qMS. Chromatographic conditions: column HP5 (60 m × 0.25 mm × 0.25 μm), equipment Shimadzu QP2110plus; heating oven from 40 ºC to 280 ºC at 3 ºC $min^{-1}$.

Considering the area% of the peaks, both bio-oils before fractionation, presented carboxylic acids as the majority class, followed by hydrocarbons. Phenols, ketones and esters were also identified in the two bio-oils, but at lower concentration. N-compounds were not identified neither at trace levels, except for hexadecanamide, that is normally associated to the presence of fatty acids. The absence of expressive amounts of N-compounds reinforces the need for pre-concentration of these compounds for their better characterization.

The ABN extraction allowed a kind of clean-up in the sample, allowing the pre-concentration of N-compounds and consequently their identification and semi-quantification. Quinolines appeared as the most important compounds and with the greatest biotechnological application. These compounds have several biological activities, including anticancer, antiviral, antibacterial activities, among others, constituting an important class of compounds in the pharmaceutical industry. Basic fraction of Traditional Spent Coffee Ground (TSCG) presented 19.38% of alkyl quinolines (sum of all the methyl- and C2- isomers) while basic fraction of Decaffeinated one (DSCG) shows 26.57% of these compounds. Other compounds such as caffeine, norharmane, N-methyl, indoles, pyridine derivatives and pyrazines were also identified.

The application of ABN to both bio-oils allowed the isolation and identification of N-compounds that could not be directly detected in the crude sample, thus proving their efficiency of the process. It was possible to pre-concentrate, identify and estimate the concentration of these compounds. Around 3% of the bio-oils are composed by N-compounds, which have wide application in the pharmaceutical industry, such as caffeine, quinoline and norharmane, with great biotechnological application.

## Agradecimentos/Acknowledgments

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**Área: ANA**

# Salting-Out Induced Liquid-Liquid Microextraction: a fast and green method for the extraction of pesticides in human urine samples

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Keywords: *Pesticides, Human urine samples, SILLME, GC-MS/MS, Validation.*

## Highlights

Multiclass pesticides were extracted from urine samples by SILLME and determined by GC-MS/MS.
The method was validated and applied to the determination of pesticides in several samples.

## Abstract

Different classes of pesticides are widely used worldwide to improve productivity and enhance quality of the products. In Brazil, this scenario is of great concern since it is the largest consumer with over 1500 products registered for use by Brazilian Ministry of Agriculture (CALDAS et al., 2019). Although pesticides are important to keep production, specially nowadays, due to the increased demand, these substances have been largely found as residues and contaminants, not only in foods and body waters but also in human matrix, such as blood, hair, serum and urine. Some matrices are considered more accessible to evaluate human exposure to pesticides, for example, the human urine. In this work, a method for the determination of pesticides in urine sample was developed and validated. The method combines an extraction step by Salting-Out Induced Liquid-Liquid Microextraction (SILLME) and determination by Gas Chromatography tandem Mass Spectrometry (GC-MS/MS). The extraction conditions were adapted from a previous method developed by our group (ARIAS et al., 2021). After optimized, the extraction was carried out as follows: 5 g urine sample was weighed in a 15 mL polypropylene tube, then, 1 mL acetonitrile was added to the mixture, which was vortexed for 1 min. After that, 2 g $MgSO_4$ were added to the mixture, which was agitated again, followed by centrifugation for 5 min at 7793 g. Finally, the upper acetonitrile layer was collected and transferred to a GC vial for further analysis, where 2 µL were injected into the chromatographic system. Experiments were performed in triplicate. The instrumental conditions used were obtained from the Smart Pesticides Database version 2, in a chromatographic run of 24.33 minutes. A total of 101 compounds were evaluated, among pesticides, their isomers and deuterated atrazine, which was used as surrogate standard. Analytical curves ranged from 1 to 100 µg $L^{-1}$, at least five points for each pesticide. The limits of quantification of the method were between 0.2 to 5 ng $g^{-1}$ for each pesticide. The proposed method was proven to be accurate and precise, with recoveries between 50 to 120% and relative standard deviation ≤ 20% for most of the pesticides under study. The proposed method was applied to the determination of pesticides in 296 urine samples from people of Rio Grande, RS, Brazil. Forty-four pesticides were determined at least in one urine sample. Finally, an efficient and simple method was developed that can be used for fast screening of pesticides in urine samples, with the advantages of being simpler and cheaper than the traditional ones.

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## Acknowledgments

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**Área: ANA**

# Soil Color: A simple and free App to measure soil color

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Keywords: *Soil Color, Soil Classification, Soil analysis, App.*

## Highlights

- Soil Color can be used to quantify various soil attributes;
- The objective of this study is to develop a free and simple app called "Soil Color";
- The app determines soil color index using digital images.

## Resumo/Abstract

Soil color is related to the physical, chemical, and biological composition of the soil[1]. By soil color using a portable chromameter, Konen et al. (2003)[2] have quantified organic carbon and texture. Using soil digital images, Morais et al. (2021)[3] have determined oxides contents in soil.

Moreover, soil color can also be used for classification[4], which it is of great value for soil use and management[5]. Generally, to classify the soil, several laboratories analysis are necessary, which are usually time-consuming, expensive, use toxic chemical reagents and generate large volumes of waste. On the other hand, other methods can be used, such as soil classification by determining its color. Han et al. (2016)[6] have proposed a method to classify soil by its color from digital images.

Given the importance of soil color, the objective of this study is to develop a free and simple app called "Soil Color" (available at: <https://play.google.com/store/apps/details?id=org.soilcolor.soilcolorapp>) to determine soil color index. Using this application, when taking a soil digital image, the index of the color channels: RGB, HSV and CMYK are determined. The app Soil Color was used to determine these color information from a soil sample, collected in Goiás. The Figure 1 shows the procedure for soil sample image acquiring using application developed.

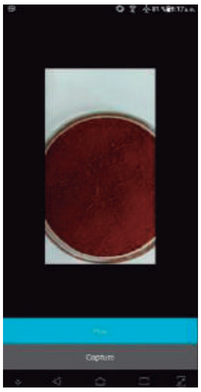

**Figure 1.** Image acquiring using Soil Color app.

After image acquisition, the average values of the RGB, HSV and CMYK color channels are determined automatically by the app, as shows in Figure 2.


Get your result!

Red:
220.2

Green
181.4

Blue
103.2

Hue:
31.6

Saturation:
220.2

Value:
96.3

Cyan
2.2

Magenta
35.1

Yellow
53.8

Black:
0.1

**Figure 2**. Color Index calculated by Soil Color from Soil Image

Using these color index, in addition to other parameters, the soil sample was classified as latosol. Although the measurement of color indices is fast and simple, their determination is influenced by external light and the distance from the soil sample. In view of this, the user still needs to standardize the acquisition of images.

## Agradecimentos/Acknowledgments

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**Área: ANA**

# Synthesis and application of a new hybrid monolith based on POSS-MA and dicationic imidazolium ionic liquid for PT-µSPE

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Palavras Chave: *pipette tip micro solid-phase extraction, ionic liquids, polyhedral oligomeric silsesquioxane.*

## Highlights

Preparation of a hybrid monolith with the combination of POSS-MA and ionic liquid for PT-µSPE.
The new monolith was applied for the extraction of different classes of analytes.
With anionic analytes, such as statins, strong ionic interactions occurred and the recovery of these analytes was low.
With non-ionic analytes, such as neonicotinoids, caffeine, carbamates and ureas, the monolith presented good retention and high recoveries.

## Resumo/Abstract

Nowadays, new miniaturized analytic platforms are increasingly being developed, as well as the sample preparation techniques. One of the latter is pipette tip micro solid-phase extraction (PT-µSPE), in which the sorbent is placed inside of a disposable pipette tip. In addition, the monolithic materials appear as new trends in sorbents because of their high permeability. This work performed the synthesis of hybrid monoliths employing innovative materials, such as polyhedral oligomeric silsesquioxane (POSS) and ionic liquids for use as a sorbent in PT-µSPE. The preparation of a hybrid monolith with the combination of methacryl substituted POSS and 1,12-di (3-vinylimidazolium) dodecane dibromide ionic liquid was performed for the first time.

The POSS is a hybrid molecule with silane and organic groups that forms an inorganic cage with organic groups on the vertices (in this case, methacrylate groups), and that acts as a crosslinker agent in thermal polymerization. Also, the ionic liquid employed in this work has a long carbon chain with 12 carbon atoms between 2 imidazolium cations. This can provide multiple interaction mechanisms for the monolithic sorbent.

The monolithic material developed in this work was characterized with different techniques, such as scanning electron microscopy, infrared spectroscopy, elemental analysis, thermogravimetric analysis, and surface area by nitrogen adsorption/desorption. With the information obtained by characterization, it was possible to propose a molecular structure for the monolith, since the structure is composed mostly by POSS-MA, with a low to intermediate surface area of 79.8 $m^2$/g.

The new monolith was applied for the extraction of different classes of analytes. With anionic analytes, such as statins, strong ionic interactions occurred due to the presence of the imidazolium cations in the monolith and, because of this, the recovery of these analytes was low (in the range from 0 to 28.3%). With non-ionic analytes with different levels of polarity, such as neonicotinoids, caffeine, carbamates and ureas, the monolith in PT-µSPE presented good retention and high recoveries (in the range from 81.9 to 131.2%). It was possible to obtain a theoretical concentration level of 200 times for the neonicotinoids.

This work showed some characteristics of a new hybrid monolith based on POSS and ionic liquid in PT-µSPE for different classes of analytes, and opened up new applications in future studies.

## Agradecimentos/Acknowledgments

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FAPESP 2019/04567-1; FAPESP/INCTBio 2014/50867-3
CNPq 465389/2014-7; CNPq 309363/2018-7

# Synthesis of superabsorbent polymers based on polyacrylate for the quantification of Brilliant blue dye by the technique of digital image analysis

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Keywords: *Hydrogel, Polymethacrylate, Digital image, Superabsorbing, Dye removal*

## Highlights

- Adsorption studies carried out on the hydrogel demonstrate the maximum adsorption capacity of 1993 mg.g$^{-1}$ in the Jovanovic model, with a correlation coefficient of 0.999. Moreover, thermodynamic studies assessed that the Jovanovic Model was the best fitting model.
- The linearity between the brilliant blue dye concentration and the amount of reflected color is satisfactory.
- The hydrogel produced is promising for the removal of azo dyes.

## Abstract

A hydrogel consists of a three-dimensional network of polymer chains, in which the hydrophilic structure makes them suitable for absorbing significant amounts of water. In this sense, the storage of fluids in its interior results in the ability to increase its dry mass up to a thousand times in relation to the original mass. This property, intrinsic to the composition of a hydrogel, implies a wide application in modern society, from tissue engineering to the treatment of effluents, given that they have great biocompatibility[1]. The objective of this work is to present the properties of hydrogels regarding the sorption of Brilliant blue an commonly used azo dye as well as the technical feasibility of their applications, such as quantification through digital image analysis. In image 1, the best adsorption model is presented in which curves that indicate how the adsorbent will adsorb the solute, for the Brilliant Blue dye under the hydrogel 75% Methacrylic acid (MAA) are represented. In image 2, with regard to obtaining the analytical signal, the concentration of the Brilliant Blue dye was evaluated by the hydrogel reflectance, which the value is calculated after the sorption of each dye under the polymer and the acquisition of the digital image by the microscope. To obtain the reflectance signal, the logarithm of the ratio between the blank of the hydrogel ($P_0$), and the sample (P), which represents the analytical signal of the hydrogel with the analyte, is calculated. Based on the results, it is possible to assess that the hydrogel produced is promising for the removal of pollutants, especially dyes.

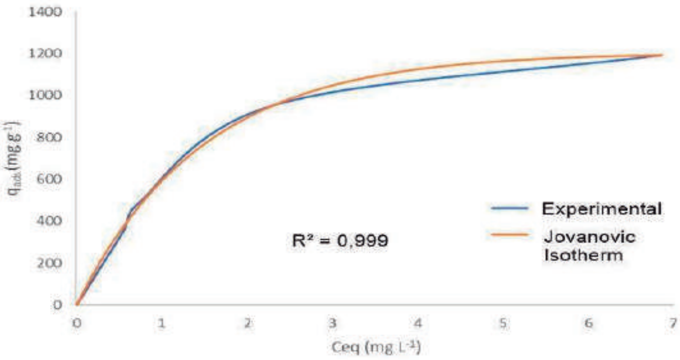

Image 1. Jovanovic isotherm for adsorption of the Brilliant Blue dye under the 75% MAA hydrogel (T 293K, 24h of agitation, concentration 0,1 - 4 mg L$^{-1}$).

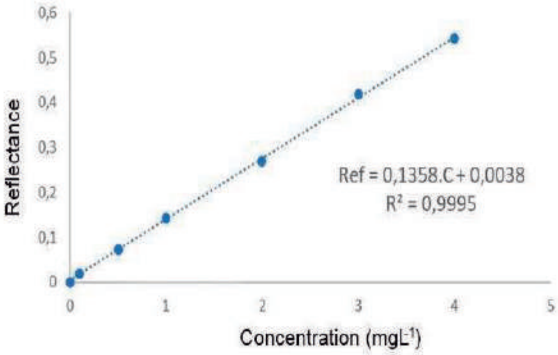

Image 2. Brilliant blue (BB) calibration curve at different concentrations obtained by the microscope image (pH = 7,0, 24h of adsorption, [BB] 0,10 - 4,00 mg L$^{-1}$).

## Acknowledgments

The authors would like to thank CAPES, UFF and Peter Sorensen Laboratory.

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**Área: ANA**

# The role of FT-ICR MS in the detection and characterization of tetrameric acids (ARN) in petroleum and naphthenates samples

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Palavras Chave: *ARN, naphthenate deposits, extraction, sample preparation, eltrospray ionization, FT-ICR MS*

## Highlights

The role of FT-ICR MS in the detection and characterization of tetrameric acids (ARN) in petroleum and naphthenates samples - High resolution and precision mass spectrometry, Extraction and characterization of naphthenic acids, Isolation of ARN, Waste treatment, Sample preparation, Unconventional analytical strategy, Analyze *in situ*.

## Resumo/Abstract

The high resolution and precision mass spectrometry (FT-ICR MS) is an analytical strategy applied to the characterization of naphthenic acids (NAs), including tetrameric acids (ARN), in petroleum and nathenates from production units.[a,b]

Among the challenges of identifying, extracting and characterizing those species from their complex matrix, we propose two new methodologies that comprise: (i) the transformation of residual naphthenates deposits into a high value-added standard sample, using an elution sequence with the aid of a silica-based sorbent material with aminopropyl functional groups, capable of providing the separation of the lower molecular weight NAs from the naphthenic deposit and the specific isolation of ARN, the high resolution and precision indicated mass spectrometry (FT-ICR MS), with 94.5% (%wt) purity of these species and (ii) the identification and characterization of ARN in oil samples and naphthenate deposits *in situ*, by an unconventional approach of negative mode electrospray ionization technique, ESI(-),combined with FT-ICR MS.

Both methodologies proved to be promising and unique, with the first giving an economic advantage to the concept of waste treatment, with differential against chemical synthesis processes for the production of standard ARN molecules and also of minor NAs, which may be present in the deposit. While the second methodology showed good application feasibility to identify the nature of the deposits, estimate fouling potential and treatment needs during oil production, with simple sample preparation and minimal consumption of reagents.

## Agradecimentos/Acknowledgments

IFES, UFES, LABPETRO e CENPES/PETROBRAS.

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[a] Barros *et al. Fuel*. 308, 122065, 2022.

[b] Barros *et al. Fuel*. 319, 123775, 2022.

**Área: ANA**

# Use of digital images and smartphone to determine soluble proteins in whey protein using the Bradford method

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Keywords: *PhotoMetrix, Colorimetry, Total soluble proteins, Sports supplements, Digital image*.

## Highlights

Simple, inexpensive and sensitive method for determination of total soluble proteins in 9 samples of sports supplements using digital images and mobile app.

## Abstract

Currently, there has been an increase in the consumption of sports supplements such as whey protein, consisting of proteins derived from milk, by practitioners of physical activity, with the aim of increasing the synthesis of muscle proteins[1]. One of the colorimetric methods used to determine total proteins is the Bradford method using UV-Vis spectrophotometer[2]. The use of digital devices such as cameras and smartphones and PhotoMetrix® software has been employed to perform colorimetric detection, aiming at the speed, practicality and low cost of analysis when compared to the spectrophotometer[3]. Thus, a study was developed in order to determine the total soluble proteins in 9 samples of sports supplements using digital images and PhotoMetrix. To prepare the sample, 100 mg of each sample was solubilized in 10 mL of ultra-pure water and centrifuged. The calibration curve was prepared with 0 to 0.8 mg mL$^{-1}$ of bovine serum albumin (BSA) protein. An aliquot of 20 µL of each sample was added to 1000 µL of Bradford's solution and homogenized. After 5 minutes of incubation (25 °C), the absorbance can be read at 595 nm using a spectrophotometer (reference method), as well as digital images were acquired with a 13 MP camera from a Samsung J500-M cell phone, then processed by the PhotoMetrix. Addition-recovery experiments were performed with 3 samples, adding 1 mg mL$^{-1}$ of BSA, to assess the accuracy of the method. To analyze the protein profile, supplement samples were submitted to gel electrophoresis. The analytical performance parameters obtained with the reference method were limits of detection (LOD) and quantification (LOQ) of 0.003 mg mL$^{-1}$ and 0.01 mg mL$^{-1}$, respectively of total soluble proteins, and RSD values in the range of 1-11%. When using PhotoMetrix for protein quantification, the LOD and LOQ obtained were 0.0002 mg mL$^{-1}$ and 0.0007 mg mL$^{-1}$, respectively. The method demonstrated good precision of the measurements with RSD in the range of 1-13%. The addition and recovery experiments demonstrated good accuracy for both methods, with recoveries of 82-112% using PhotoMetrix, and 84-106% using the reference method. It was observed that the LOD and LOQ values determined by PhotoMetrix were 15-fold lower than the values obtained by the reference method. The concentrations of total soluble proteins (n = 3), determined in the 9 samples of commercial sports supplements ranged from 17±1 to 253±12 g kg$^{-1}$ using the reference method, while PhotoMetrix presented results between 14±1 to 304±33 g kg$^{-1}$, demonstrating that the values determined by both strategies are in concordance. Besides that the formulations present great variability of concentration of total proteins solutions. Through the electrophoretic gel it was possible to observe that the sample #1 (S1) differs from the other samples qualitatively, and this result corroborates with the determined concentrations: this samples presented the lowest protein in its formulation. Thus the proposed procedure using PhotoMetrix proved to be an excellent analytical tool for the determination of low concentrations of soluble proteins using the Bradford method.

[1] F.K. Haraguchi et al., *Rev. Nutr.,* 19(4) (2006) 479-488.
[2] M.M. Bradford, *Anal. Biochem*., 72 (1976) 248.
[3] PhotoMetrix Database: http://www.photometrix.com.br.

## Acknowledgments

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**Área: ANA**

# Use of gold nanoparticles for signal intensification in Laser Induced Breakdown Spectroscopy (LIBS)

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Palavras Chave: *NELIBS, LIBS, Gold nanoparticles, Cu(II) ions, Cachaça*

## Highlights

Gold nanoparticles produce signal intensification in LIBS. Magnification factor of 3 is possible, providing detection limit of 30 µg $L^{-1}$ for Cu(II) ions. Nanoparticle density affects signal intensity.

## Abstract

The plasmonic properties of nanoparticles (NP), usually explored in Surface Enhanced Raman Spectroscopy, has been also employed in LIBS for signal intensification, providing detection limits in the µg $L^{-1}$ range for metal ions. This approach has been named Nanoparticle Enhanced Laser Induced Breakdown Spectroscopy (NELIBS). In the present work, gold nanoparticles were synthesized from chloroauric acid, using sodium citrate as a reducing agent. The Au NP were characterized by Scanning Electron Microscopy, Dynamic Light Scattering and UV-Vis spectroscopy, showing an average diameter of 20 nm and maximum absorption at 522 nm. A volume of 165 µL of a 3.0 µg $mL^{-1}$ Au NP aqueous suspension was deposited on to a Whatman 40 quantitative filter paper disk (diameter of 2.4 cm) and dried at 60 ºC for 1 h. Afterwards, 250 µL of 0.0 – 5.0 mg $L^{-1}$ Cu(II) standard solutions in borate buffer (20 mmol $L^{-1}$, pH 9.0) were deposited on the paper disk and dried in the same way. A set of paper disks was also prepared as described without the addition of Au NP. A Q-switched Nd:YAG laser, operating at 1064 nm, pulse of 4.8 ns, 90 mJ/pulse, 20 Hz, was employed for measurements. Emission radiation (324.76 nm) was collected with an optical fiber (50 µm diameter) and guided to an Echelle polychromator (200-975 nm, 52.13 grooves/mm, Mechelle 5000, Andor Technology) coupled to an ICCD detector (1024 × 1024, iStar DH 734, Andor Technology). Preliminary experiments demonstrated that particle density on the paper is an important variable to increase the signal intensity, as depicted in Figure 1. The analytical curve obtained with the Au NP (particle density of 1.1 x $10^{-4}$ mg $cm^{-2}$) produced a magnification factor around 3, when its sensitivity (slope) was compared with those obtained in the absence of NP, providing detection and quantification limits of 30 and 100 µg $L^{-1}$, respectively. Thus, analytical curves in the absence and presence of Au NP were constructed from hydroalcoholic Cu(II) solutions (40% ethanol) in the 0 - 3.0 mg $L^{-1}$ range for the determination of this ion in cachaça samples. The results obtained by LIBS and NELIBS were compared to those obtained by Graphite Furnace Atomic Absorption Spectrometry (GFAAS) and no significant difference were found at a confidence level of 95 %. However, low concentrations of Cu(II) in cachaça were possible to be determined only by NELIBS, demonstrating the effectiveness of signal intensification by gold nanoparticles.

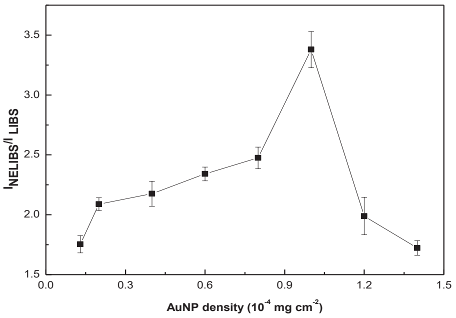

**Figure 1.** Effect of Au NP density on signal enhancement.

## Acknowledgments

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# BEA

# Alimentos e Bebidas

**Área: BEA** **Nº de Inscrição: 00399**

# Analysis of tabletop sweeteners by liquid chromatography coupled with mass spectrometry: identifying irregularities in commercial products

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Keywords: *High intensity sweetener*, *Food additives, Counterfeit products, Food analysis, LC-MS/MS, Quality control*

## Highlights

Chromatographic methods can successfully identify irregularities in commercial tabletop sweeteners.

## Resumo/Abstract

The use of high intensity sweeteners (HIS) has increased nowadays, due to worries about the consequences of high sugar consumption and weight gain. The active principles of sweeteners are molecules with higher sweetening power than sucrose and a small (or none) caloric contribution[1]. As so, this study aimed to determine some synthetic HIS [saccharin (SAC), cyclamate (CYC), aspartame (ASP), acesulfame-K (ACS) and sucralose (SUC)], and two of the main compounds extracted from *Stevia rebaudiana* [stevioside (STV) and rebaudioside A (RBD)], used as a natural sweetener, in commercial tabletop sweeteners (n=50).The obtained results were then compared with the information on the product label. Before analysis, solid samples were homogenized, 10,0 mg were weighted in polyethylene tubes and solubilized in 50,0 mL of ultrapure water. For liquid samples, an aliquot of 10,0 µL (approximately 10,0 mg) was transferred to polyethylene tubes and diluted to 50,0 mL. A second dilution was performed to match the concentration of the samples to the calibration curve. Finally, the samples were analyzed by liquid chromatography coupled with sequential mass spectrometry (LC-MS/MS), using a validated method. Among analyzed samples, 7 (14%) were labeled as natural product, but 3 (43%) of them presented synthetic HIS in their composition. In products which report that they're a mixture of synthetic and natural sweeteners (n=3, 6% of the samples), the amount of natural sweeteners is much lesser than the synthetic ones. In addition, 8 samples (16%) had informed on their label the content of each HIS in their composition, which has allowed a comparation between the obtained value and the informed one by t-test (Table 1).

**Table 1** Comparison between the informed content and the one found after analyzes. In blue, the values were statistically equal at a 95% confidence level. In yellow, the values were statistically equal at a 99% confidence level and in red they were statistically different. SAC = saccharin; CYC=Cyclamate; ASP=Aspartame; SUC=Sucralose. INF=informed content; EXP=experimental value.

| **Sample** | **SAC** | | **CIC** | | **Sample** | **ASP** | | **SUC** | |
|---|---|---|---|---|---|---|---|---|---|
| | INF | EXP | INF | EXP | | INF | EXP | INF | EXP |
| **7S** | 6,90% | 6,98% | 68,97% | 67,41% | **19S** | 3,6% | 0,56% | - | - |
| **8S** | 6,78% | 10,60% | 67,80% | 71,06% | **20S** | 27,69% | 3,32% | - | - |
| **10S** | 9,80% | 9,25% | - | - | **22S** | 3,60% | 1,78% | - | - |
| **23S** | 5,9% | 4,86% | - | - | **29S** | - | - | 1,3% | 1,01% |

As shown, some irregularities were found, indicating that improvements in quality control of these products are needed.

[1] Carocho, M., P. Morales and I. Ferreira (2017). "Sweeteners as food additives in the XXI century: A review of what is known, and what is to come." Food and Chemical Toxicology 107(Pt A): 302-317

## Agradecimentos/Acknowledgments

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**Área: BEA**

# Análise Físico-Química da polpa de *Euterpe Oleracea Martius,* oriunda do arquipélago do Bailique, estado do Amapá.

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Palavras Chave: *Açaí, Amazônia Ocidental*, Análise centesimal, *Bromatologia.*

## Highlights

Physical-Chemical Analysis of Euterpe Oleracea Martius pulp, from the Bailique archipelago, state of Amapá:

This work aims to disseminate the physiochemical analysis of açaí pulp (Euterpe Oleracea Martius) produced by the Agroextractive Cooperative of Bailique Producers, in Amapá.

## Resumo/Abstract

**Introdução:** O Brasil é o maior produtor de polpa de fruta *in natura,* e dentre as espécies comercializadas há o Açaí (*Euterpe Oleracea Martius*), no qual atualmente seu consumo vem sendo difundido para além da região Amazônica, tomando proporções não somente nacionais, mas também internacionais, assumindo assim as mais diversificadas formas de consumo, tais como: sorvetes; picolés; alimentos e bebidas energéticas; cosméticos. Desse modo, esta fruta estabelece oportunidades para agricultores de pequeno porte, fomentando a economia local e gerando renda para comunidades tradicionais da região amazônica. **Objetivos:** Nesse sentido se faz necessário analisar parâmetros físico-químicos a fim de avaliar a qualidade da polpa desta fruta. Portanto o presente trabalho busca analisar as variáveis físico-químicas (umidade, cinzas, lipídeos totais, e pH) da polpa de Açaí (*Euterpe Oleracea Martius*), adquiridos através de doação feita pela Cooperativa Agroextrativista dos Produtores do Bailique (AMAZONBAI), oriunda do Arquipélago de Bailique, Amapá, Amazônia, Brasil. **Metodologia:** Todas as análises seguiram as metodologias descritas no manual de Métodos Físico-químicos Para Análise de Alimentos do Instituto Adolfo Lutz (2008). Foram analisados três tipos de polpas de Açaí: A, B, C. **Resultados e discussão:** UMIDADE - na amostra A foi identificado o valor médio de 84,14g/100g ± 0,002, já na amostra B foi verificado o valor médio para umidade de 85,18 g/100g ± 0,007 e a amostra C apresentou em sua constituição o teor médio de 86,84 g/100g ± 0,005. Essa característica atribui a amostra analisada a configuração de alimento perecível. CINZAS – Referente ao parâmetro cinzas a amostra A apresentou em média de 0,4g/100g ± 0,002, para a amostra B 0,46 g/100g ± 0,007 e para a amostra C 0,36g/100g ± 0,005. LIPÍDEOS TOTAIS – Referente ao parâmetro lipídeos totais a amostra A apresentou em sua constituição o valor de 49,14 g/100g ± 0,62, na amostra B foi verificado o valor de 55,41g/100g ± 0,53 e na amostra C foi determinado o valor de 59,95g/100g ± 0,35, valores que se encontram dentro do intervalo (20-60g/100g) permitido pela legislação. PH - No que tange parâmetro de potencial hidrogeniônico a amostra A foi verificado o valor de 5,7, referente a amostra B foi determinado o valor 5,6 e na amostra C apresentou o valor de 5,7, valores que se encontram entre 4,00 e 6,20, intervalo estabelecido pela legislação, estes resultados encontram-se de acordo. **Conclusão:** Portanto, conclui-se que o alimento analisado se mostrou dentro dos parâmetros de qualidade estabelecidos pela legislação brasileira, vale destacar que essas variáveis podem sofrer alteração de acordo com a época de colheita, com manejo e cultivo, dessa maneira, a análise frequente dessas características se faz necessária.

## Agradecimentos/Acknowledgments

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**Área: BEA** **Nº de Inscrição: 00684**

# Arsenic Accumulation in Potato Plants in a Closed Soilless Cultivation System

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Palavras Chave: *Potato, Arsenic accumulation, Closed soilless cultivation system, MERCOSUL.*

## Highlights

Potato exposition to As. Arsenic accumulation in potato plants. Time of exposition and concentration of As are important factors for As absorption by potato plants.

## Resumo/Abstract

Potato (*Solanum tuberosum* L) is a good source of energy (starch), vitamins, minerals and fibers, as well as antioxidants in the human diet, being the most important staple food worldwide. On the other hand, some toxic elements such as arsenic can be assimilated by potato plants and might be harmful to the human health.[1] According to MERCOSUL legislation, As concentration in potato tubers cannot exceed 0.2 µg $g^{-1}$.[2] Considering the mentioned legislation and the possibility of As accumulation in potato, the aim of this work was to evaluate the As absorption by potato plants during cultivation. Thus, micropropagated potato plants were stablished in the closed soilless cultivation system with sand as substrate, following laboratory protocol. The potato plants (clone SMINIA 176) were planted in the experimental units and fertirrigated with a complete nutrient solution (pH 5.5) for two months. After this time, the nutrient solution of the treated plants received addition of As from a stock solution ($Na_2HAsO_4$) sufficient to achieve the concentrations of 10 and 20 mg $L^{-1}$. The control plants were kept receiving only the nutrient solution. The exposition to As was evaluated at 14 and 21 days. After the treatment, the plants were collected, dried (105 ºC for 3 days) and the aerial part fractioned in two parts (leaves + shoot and tuber). Both parts were milled separately and kept under refrigeration until use. The samples were digested in an open system, using a heated digestion block, with 6 mL of concentrated $HNO_3$ and 2 mL of $H_2O_2$ 30%. An inductively coupled plasma mass spectrometer (model ELAN® DRC II, PerkinElmer, EUA) was used for As determination ($^{75}As$). The results are shown in Table 1.

Table 1. As (µg $g^{-1}$) in potato plant aerial parts.

| Days of exposition | Treatments | | | | | |
|---|---|---|---|---|---|---|
| | Control (No As) | | 10 mg $L^{-1}$ As | | 20 mg $L^{-1}$ As | |
| | Leaves + shoot | Tuber | Leaves + shoot | Tuber | Leaves + shoot | Tuber |
| 14 | < LOD* | < LOD* | 1.5 ± 0.4 | 2.1 ± 0.3 | 4.4 ± 0.1 | 2.8 ± 0.1 |
| 21 | < LOD* | < LOD* | 2.3 ± 0.6 | 2.0 ± 0.3 | 15.9 ± 0.3 | 2.9 ± 0.1 |

* LOD = 0.05 µg $g^{-1}$

It was evidenced that the highest As concentration was in the aerial part "leaves with shoot" and that the higher As concentration in the nutrition solution leads to higher As concentration in the plants. The time of exposition was also an important factor since that As accumulation in the aerial part "leaves with shoot" was observed in the longest exposition time. All the exposed potato plants presented As concentrations higher than the limit stablished by MERCOSUL.[2]

[1] Tack, F. M. G. Potato Research (2014) 57:311–325.

[2] MERCOSUL, Regulamento técnico Mercosul sobre limites máximos de contaminantes inorgânicos em alimentos MERCOSUL Nº 12/11, 2013, pp. 1-18.

## Agradecimentos/Acknowledgments

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**Área: BEA**

# As, Cd, Cu e Pb em amêndoas de cacau do Brasil destinadas à produção de chocolates *Bean to Bar*

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Palavras Chave: *Cacau, Chocolate artesanal, Contaminantes inorgânicos, ICP OES*

## Highlights

As, Cd, Cu and Pb in cocoa beans from Brazil for production of Bean to Bar chocolate

- Inorganic contaminants in cocoa beans for production of Bean to Bar chocolate were studied.
- Cd levels above Brazilian and EU regulations in 100% of samples from Amazonas.

## Resumo/Abstract

O chocolate *Bean to bar* é um tipo de chocolate artesanal criado na década de 1990, onde apenas amêndoas de cacau selecionadas e com origem controlada são utilizadas. Na etapa de processamento são utilizados apenas dois ingredientes: a amêndoas de cacau e o açúcar orgânico[1]. No entanto, alguns estudos indicam a ocorrência de contaminantes inorgânicos em cacau e amêndoas de cacau devido a fatores ambientais, como solo e água de irrigação[2]. Considerando o exposto, os objetivos deste estudo foram validar e aplicar um método para determinar a presença de As, Cd, Cu e Pb em amostras de amêndoas de cacau destinadas à produção de chocolates *Bean to Bar* no Brasil, considerando as principais regiões: Amazonas, Bahia e Pará. As amostras foram adquiridas no comércio, identificadas e trituradas em moinho com hélice de tungstênio (Ika, Staufen, Alemanha). Uma porção de 0,6 g foi pesada em copos de digestão em PTFE e a digestão foi realizada em sistema fechado assistido com micro-ondas (Start D, Milestone, Sorisole, Itália) empregando 6 mL de ácido nítrico purificado por destilação *sub-boiling* (Berghof, Eningen, Alemanha) e 2 mL de peróxido de hidrogênio 30% (Merck, Darmstadt, Alemanha) e temperatura de até 170ºC, com tempo total de 37 minutos. A solução resultante foi transferida para tubo graduado com água desionizada (Gehaka, São Paulo, Brasil) até 25 mL. A determinação de As, Cd, Cu e Pb foi realizada em espectrômetro de emissão óptica com plasma indutivamente acoplado (ICP OES, Agilent Technology, Tóquio, Japão), em condições otimizadas[3]: potência RF = 1,3 kW, fluxo de Ar = 12,0 L min$^{-1}$, fluxo de Ar auxiliar = 1,0 L min$^{-1}$; vista axial; comprimentos de onda: As: 193,696 nm; Cd: 214,439 nm; Cu: 324,754 nm e Pb: 220,353 nm. Para a validação do método foi utilizado um material de referência certificado (MRC NRC Tort-2, *National Research Council Canada*), sendo observados valores entre 88 e 98% de recuperação e 4 e 13% de coeficiente de variação (precisão) para todos os analitos. Os resultados obtidos para as 19 amostras analisadas são apresentados na Tabela 1.

**Tabela 1.** Valores médios e intervalo de concentração observados nas amostras de amêndoas de cacau para chocolates *Bean to Bar* do Brasil.

| Região | As (mg/kg) | Cd (mg/kg) | Cu (mg/kg) | Pb (mg/kg) |
|---|---|---|---|---|
| Amazonas (n=8) | <0,17 | 0,68 (0,52 - 0,89) | 18,3 (15,2 - 24,8) | 0,012 (<0,06 - 0,094) |
| Bahia (n=9) | <0,17 | 0,048 (0,027 - 0,060) | 19,1 (10,3 - 26,9) | 0,052 (<0,06 - 0,31) |
| Pará (n=2) | <0,17 | 0,065 (0,042 - 0,087) | 22,4 (16,6 - 28,1) | <0,06 |

Os resultados mostraram que as amostras adquiridas em Amazonas apresentaram níveis de cádmio superiores ao limite máximo tolerado (LMT) estabelecidos pela legislação nacional[4] (Cd = 0,3 mg kg$^{-1}$ para pasta de cacau) e da União Europeia[5] (Cd = 0,6 mg kg$^{-1}$ para cacau em pó), 100% e 75%, respectivamente.

[1] Giller, M. Bean-to-bar chocolate: America's craft chocolate revolution: the origins, the makers, the mind-blowing flavors. North Adams, MA: Storey Publishing, 2017. [2] Abt, E., & Robin, LP. **J. Agric. Food Chem.**, 68(46), 13008-13015, 2020. [3] de Oliveira et al. **Food Control**, 119, 107455, 2021. [4] ANVISA, Resolução RDC nº 487, 2021. [5] Commission Regulation EC nº 1881, 2006.

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

# Avaliação *in vitro* da atividade biológica de hidrolisados de caseinato bubalino

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Palavras Chave: Atividade antioxidante, Caseína, Fitoprotease, Macambira.

## Highlights

*In vitro* evaluation of the biological activity of buffalo caseinate hydrolysates. Application of a phytoprotease from *Bromelia laciniosa* Mart. ex Shult. & Shult. f. Phytoprotease generated hydrolysates from buffalo caseinate source. Hydrolysates active in eliminating ABTS•+.

## Resumo/Abstract

A macambira (*Bromelia laciniosa* Mart. ex Shult. & Shult. f.) é uma espécie da família *Bromeliaceae*. Um complexo enzimático encontrado na macambira é a bromelina. A bromelina possui potencialidade para a utilização na indústria de alimentos, farmacêutica e de cosméticos. Em alimentos pode ser empregada na obtenção de hidrolisados protéicos. Neste sentido, o objetivo do trabalho foi investigar a atividade enzimática da bromelina obtida de *Bromelia laciniosa* sob o caseinato bubalino. Após a obtenção da enzima, a partir das folhas, foi realizada a purificação parcial por meio de precipitação com etanol. Após purificação parcial foi feita a aplicação na obtenção de hidrolisados proteicos por meio de planejamento Delineamento Composto Central Rotacional. Os mesmos foram avaliados quanto à sua atividade antioxidante. Foram obtidos 16 hidrolisados apresentando graus de hidrólise entre 14,47 e 19,43%. Verificaram-se os primeiros resultados da hidrólise da caseína bubalina utilizando bromelina da macambira. O estudo sugere que os produtos obtidos podem ser aplicados, pela indústria alimentícia, como antioxidantes naturais. A macambira pode vir a ser uma alternativa ao abacaxi.

**Tabela 4**. Atividade antioxidante dos hidrolisados de caseinato bubalino.

| Ensaios | Atividade antioxidante – ABTS•+ (%) | Atividade antioxidante – DPPH• (%) | Atividade antioxidante – Poder redutor (mg Ácido ascórbico/g amostra) |
|---|---|---|---|
| 1 | 78,69 ± 0,001 m | 0,00 ± 0,00 | 86,36 ± 0,02 e |
| 2 | 84,54 ± 0,002 g | 0,00 ± 0,00 | 75,45 ± 0,04 k |
| 3 | 83,16 ± 0,03 k | 0,00 ± 0,00 | 73,79 ± 0,006 l |
| 4 | 82,13 ± 0,001 l | 0,00 ± 0,00 | 80,30 ± 0,004 h |
| 5 | 78,69 ± 0,00 m | 0,00 ± 0,00 | 73,030 ± 0,001 m |
| 6 | 87,29 ± 0,003 d | 0,00 ± 0,00 | 77,12 ± 0,007 i |
| 7 | 73,88 ± 0,002 n | 0,00 ± 0,00 | 76,061 ± 0,006 j |
| 8 | 83,33 ± 0,00 j | 0,00 ± 0,00 | 88,64 ± 0,001 d |
| 9 | 87,97 ± 0,004 c | 0,00 ± 0,00 | 90,30 ± 0,004 c |
| 10 | 84,54 ± 0,002 g | 0,00 ± 0,00 | 92,73 ± 0,006 b |
| 11 | 88,32 ± 0,002 b | 0,00 ± 0,00 | 70,76 ± 0,02 n |
| 12 | 84,021 ± 0,004 h | 0,00 ± 0,00 | 83,79 ± 0,01 g |
| 13 | 86,60 ± 0,001 f | 0,00 ± 0,00 | 60,00 ± 0,006 o |
| 14 | 86,94 ± 0,001 e | 0,00 ± 0,00 | 43,33 ± 0,01 p |
| 15 (C) | 83,85 ± 0,001 i | 0,00 ± 0,00 | 84,55 ± 0,001 f |
| 16 (C) | 88,49 ± 0,002 a | 0,00 ± 0,00 | 98,79 ± 0,007 a |

Médias seguidas por letras distintas na vertical diferem entre si ao nível de 5 % de probabilidade pelo Teste de Tukey.

## Agradecimentos/Acknowledgments

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**Área: BEA** **Nº de Inscrição: 1272**

# Bioacessibility of Cd, Cu, Fe and Zn in basil samples (*Ocimum Basilicum L. grecco a palla*) after Cd intoxication

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Palavras Chave: *manjericão, intoxicação, cádmio, digestão in vitro gastrointestinal, cultivo hidropônico, bioacessibilidade*

## Highlights

Cd intoxication was supported by hydroponic cultivation for 15 days.
*In vitro* gastrointestinal digestion was realized in fresh and lyophilized leaves.
Bioacessability of Cu, Fe and Zn was affected by Cd.

## Abstract

The bioaccessibility, defined as the amount of metal that is converted to soluble forms in the gastrointestinal conditions can be evaluated by sequential analysis with artificial gastric and intestinal juices. The analysis of the soluble fractions is widely used to evaluate bioaccessibility of minerals and trace elements from different food products [1]. In this study, the bioaccessibility of Cd, Cu, Fe and Zn was accessed in basil samples after Cd intoxication. The seeds were germinated in Germitest® paper until the roots length ~ 0.5 cm. Afterwards, radicle were grown in hydroponic solution, using 5% v v$^{-1}$ Hoagland solution. The cuttings were exposed to Cd$^{2+}$ [as Cd(NO$_3$)$_2$.4H$_2$O] to varying concentrations (0, 1.5 and 3.0 $\mu$mol L$^{-1}$). Hoagland solution were replaced each 3 days and after 15 days the plants were transferred to vermiculite pots and kept for another 15 days, to increase the quantity of leaves. *In vitro* gastrointestinal [2] were applied in fresh and lyophilized samples. After, 1 mL of the digested sample were sonicated in a cup horn ultrasound, adding 100 µL HNO$_3$ and 500 µL H$_2$O$_2$. Final volume was completed to 2 mL. Total concentration was achieved after microwave (MW) acid digestion. Limits of detection and quantification after MW digestion for Cd, Cu, Fe and Zn were 0.07 and 0.23, 0.6 and 1.99, 10.7 and 35.3, 8.5 and 27.9 $\mu$g L$^{-1}$, respectively. Total concentrations and bioaccessibility values presented in Table 1 were obtained after quantification by ICP-MS.

Table 1. Results for Cd, Cu, Fe and Zn after microwave acid digestion and *in vitro* gastrointestinal digestion

| Cd intoxication concentration ($\mu$mol L$^{-1}$) | Elements | MW total concentration (mg kg$^{-1}$) | Lyophilized leaves | | Fresh leaves | |
|---|---|---|---|---|---|---|
| | | | Bioaccessible concentration (mg kg$^{-1}$) | Bioaccesibility (%) | Bioaccessible concentration (mg kg$^{-1}$) | Bioaccesibility (%) |
| 0 | Cd | <LQ | <LQ | - | - | - |
| | Cu | 13 ± 1 | 7.4 ± 0.5 | 59 ± 6 | 12 ± 2 | 94 ± 20 |
| | Fe | 759 ± 46 | 250 ± 7 | 33 ± 2 | 262 ± 10 | 35 ± 3 |
| | Zn | 74 ± 5 | 70 ± 2 | 95 ± 8 | 37 ± 16 | 50 ± 2 |
| 1.5 | Cd | 23 ± 1 | 11.9 ± 0.7 | 51± 4 | 5.7 ± 0.6 | 25 ± 3 |
| | Cu | 20 ± 2 | 16 ± 2 | 76 ± 12 | 20 ± 5 | 99 ± 26 |
| | Fe | 428 ± 27 | 240 ± 11 | 56 ± 4 | 276 ± 69 | 65 ± 17 |
| | Zn | 123 ± 16 | 98 ± 13 | 80 ± 15 | 42.5 ± 0.5 | 34 ± 5 |
| 3.0 | Cd | 46 ± 2 | 21 ± 1 | 45 ± 3 | 11 ± 1 | 25 ± 3 |
| | Cu | 49 ± 5 | 14 ± 1 | 28 ± 4 | 39 ± 8 | 79 ± 19 |
| | Fe | 405 ± 27 | 237 ± 29 | 58 ± 8 | 313 ± 64 | 77 ± 17 |
| | Zn | 234 ± 16 | 158 ± 38 | 68 ± 17 | 53 ± 5 | 15 ± 2 |

It can be observed that bioaccessibility of Cd does not differ statistically at 95% confidence level with the increasing of Cd intoxication concentration. For lyophilized and fresh leaves, there is a positive correlation between Cd and Fe. On the other hand, a negative correlation was observed to Cd with Cu and Zn ($p < 0.05$, Pearson test), except for Cd and Cu in lyophilized leaves. So, it is suggested that Cd interferes in the bioaccessibility of these elements.

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**Área: BEA** **Nº de Inscrição: 00789**

# Centesimal Composition of Nutritional Bar Prepared with Quercetin

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Palavras Chave: *Quercetin, Flavonoid, Functional Food, Nutritional bar, Centesimal*.

## Highlights

This work shows the centesimal composition and quercetin content of a nutritional bar. It's complies with the legislation, having potential for registration as a functional food.

## Abstract

Raw materials with high nutritional value and functional properties should be used in health products development. Cereal bars are complexly formulated food whose combination of ingredients should ensure that they complement each other in taste, texture and physical properties.(1) The association between cereal bars and bioactive substances is a trend in the food sector, resulting in a large profit for food market. Quercetin, for example, is a flavonoid with a high antioxidant capacity. Therefore, there is a growing body of literature that suggests the influence of daily consumption of quercetin in prevention of oxidative stress related diseases, such as cardiovascular disease, diabetes, cancer and inflammatory processes.(2) In this context, this work aimed to study the centesimal composition of a nutritional bar, that will be included in the military's diet, prepared with a combination of cereals, plant extracts and quercetin (500 mg/unit). Besides, quercetin content was also analyzed.

The cereal bars (50 g/unit) were evaluated for their physical-chemistry characteristics. The crude protein as was determined by the Kjedahl method, total lipids was analyzed by the Soxhlet method, ash was evaluated by burning the sample at 550 ºC, moisture was analyzed in an oven at 105 ºC until constant weight. Carbohydrate were calculated by the difference method (100-water-protein-lipid-ash) and energy values (cal) were evaluated applying the Atawater conversion factors of 4, 9 and 4 kcal/g for each gram of protein, lipid and carbohydrate, respectively.(3) The quercetin contend was analyzed by High Performance Liquid Chromatography (HPLC) with ultraviolet (UV) detection, as described in the American Pharmacopoeia, using USP quercetin standard. (4)

ANVISA determines(4) a 20% variation of label value to active substance content (80 - 120%; or 400 – 500 mg/unit) and a content of 101.4% was observed. The moisture, 8.9%, was also in accordance with the ANVISA specification(4), which recommends does not exceed 15%. Ashes were corresponded to 1.12%. The centesimal composition of cereal bar is presented in Table 1, as well the percent daily values (%DV) based on 2000 kcal diet.(5) The nutrients amounts were slightly higher than those found in commercial nutritional bars. However, this particular formulation was developed to compose the feeding of military troops, requiring high nutrients amounts for recovery after strenuous physical activities. In conclusion, the analyzed formulation complies with the legislation, having potential for registration as a functional food.

| Nutrients | Amount per unit (50 g) | %DV |
|---|---|---|
| Calories | 190.50 kcal | 9.5 |
| Carbohydrates | 39.00 g | 13 |
| Proteins | 2.55 g | 3.4 |
| Total Lipids | 2.70 g | 4.9 |

Table 1. Centesimal composition of the quercetin nutritional bar and percent daily values (%DV) based on 2000 kcal diet. (5)

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# CHEMICAL PROFILE OF PEQUI PRODUCED IN MATO GROSSO BY ENVIRONMENT IONIZATION IN PS-MS IN NEGATIVE MODE

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Palavras chave: *Caryocar brasiliense, Cerrado, PS-MS, Phenolic compounds.*

## Highlights

The PS-MS technique identified 36 compounds with antioxidant and bioactive characteristics in pequi pulp.

## Abstract

The pequi (*Caryocar brasiliense* Camb) is known as the gold of Cerrado, due to its nutritional and economic importance for families, who obtain their income from the sales of pequi. The fruits of the pequi tree, for being found in sunny regions, generate large amounts of free radicals, and in response produce compounds that have antioxidant capacity. Among these compounds there are phenolic compounds. A technique that has been increasing importance in the analysis of the chemical profile of foods is the Paper Spray Mass Spectrometry (PS-MS) due to its efficiency and capacity to analyze fixed compounds in a complex matrix, at low concentrations. The purpose of this work was to determine the chemical constituents of pequis pulp using PS-MS. The fruits were collected in the district of União do Sul-MT, sanitized under running water, and immersed in chlorine solution, after which they were pulped and stored (-18 °C). The extracts were obtained according to Rufino et al. (2010). The analysis of the chemical profile was performed using the PS-MS technique according to the methodology described by Silva et al. (2019). The ionization mode adopted was negative (-3kV), and the analysis was carried out, taking into account a range of mass charges (m/z) from 100 to 1000. The identification of the compounds consists of comparing the mass charge ratios of data in the literature with instrumental signals. It was possible to list in this attempt to identify 36 compounds from different classes such as organic acids, phenolic acids (Table 1), coumarins, tannins, flavanones, isoflavones, flavanols, flavones, flavonols and carbohydrates. Therefore, the present study shows great efficiency and potential of the technique in identifying the compounds and contributes to greater knowledge about the fruit and compounds with antioxidant and bioactive characteristics.

**Table 1. Chemical compounds of the pequi pulp by paper spray in negative mode.**

| Identification attempt | Formula | CAS | m/z $[M-H]^-$ | MS/MS |
|---|---|---|---|---|
| **Salicylic acid** | $C_7H_6O_3$ | 69-72-7 | 137 | 93 |
| **Vanillin** | $C_8H_8O_3$ | 121-33-5 | 151 | 123,136 |
| **protocatechuic acid** | $C_7H_6O_4$ | 99-50-3 | 153 | 109 |
| **Gallic acid** | $C_7H_6O_5$ | 149-91-7 | 169 | 97,125 |
| **Caffeic acid** | $C_9H_8O_4$ | 331-39-5 | 179 | 135 |
| **Ferulic acid** | $C_{10}H_{10}O_4$ | 537-98-4 | 193 | 149 |
| **Sinapic acid** | $C_{11}H_{12}O_5$ | 7362-37-0 | 223 | 179,208 |
| **Ellagic Acid** | $C_{14}H_6O_8$ | 476-66-4 | 300 | 284 |
| **Hezoside p-coumarinic acid** | $C_{15}H_{18}O_8$ | 14364-05-7 | 325 | 119 |
| **Caffeoylquinic Acid** | $C_{16}H_{18}O_9$ | 906-33-2 | 353 | 179,191 |

## Acknowledgments

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**Área: BEA** **Nº de Inscrição: 00663**

# Chemometric analysis of NIR fingerprints of *Coffea arabica* green bean extracts cultivated under different planting densities and harvests

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Palavras Chave: Statistical mixture design, coffee beans, NIRS, principal component analysis.

## Highlights

NIR was used to discriminate coffee bean extracts of *C. arabica*. Acetone, ethanol/dichloromethane and ethanol/dichloromethane/acetone resulted in better discrimination of different harvest periods.

## Abstract

Different technologies have been used to improve the production and quality of the coffee beverage and reduce its costs. Due to the increase in studies of metabolic fingerprints, faster and more economical analytical techniques, such as Near Infrared (NIR), are increasingly necessary. Therefore, the objective of this work was to compare different extracts of *Coffea arabica* beans prepared from a mixture design with three different solvents: ethanol (**e**), dichloromethane (**d**) and acetone (**a**). The beans were obtained from plants grown in a square arrangement (S) with two planting densities: 6,000 and 10,000 plants per hectare. In addition to the densities, three different harvest periods were investigated, following the stage of maturation (30 days between harvests). The extracts of coffee beans were analyzed by near infrared (NIR) spectroscopy and pre-processed using the first derivative (order 2 and 15-point window with "Savitzky-Golay" filter). After pre-processing, the dataset were submitted to principal component analysis (PCA). PCA results showed discrimination in both planting density and harvest period. PCA scores showed that extracts from the ternary mixture ethanol/dichloromethane/acetone (**eda**), binary mixture ethanol/dichloromethane (**ed**) and the pure acetone solvent (**a**) contain chemical fingerprint information that discriminates the beans. The **eda** fingerprint mainly discriminates the planting densities, while the **a** fingerprint distinguished the harvest periods. In order to confirm metabolic discrimination, replicates of each planting density and different harvest were prepared for these mixtures, i.e. **eda** and **a**. Thus, in relation to planting densities, all harvests could be discriminated, indicating that this factor may affect the chemical composition of the beans. This result can be justified by the solar luminosity, because the greater the density, the lower the amount of light incident on the coffee trees. When comparing harvests of the same density, the first harvest differs from the second and third. The similar chemical compositions of the second and third harvest may be related to the almost complete ripening process of the beans. Finally, the use of near infrared spectroscopy in association with chemometric methods is a fast and economical way to explore chemical composition of *Coffea arabica* beans grown with different planting densities and collected at different harvests, which can infer the maturation stage and in the future the quality of these beans.

## Acknowledgments

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**Área: BEA** **Nº de Inscrição: 00790**

# Desenvolvimento de métodos de decomposição em sistemas fechados para análise elementar de amostras de queijo branco

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Palavras Chave: *Queijo branco, Análise elementar, Preparo de amostras, Bloco digestor fechado, Micro-ondas de cavidade.*

## Highlights

**Title: Development of closed-vessel decomposition methods for elemental analysis of white cheese**

- Conductively heated and microwave-assisted decompositions using diluted nitric acid were investigated.
- Optimization step was performed using a full factorial design.
- The proposed methods have shown good accuracy and precision allowing to access mineral content in white cheese samples.

## Resumo/Abstract

O queijo é o produto lácteo mais consumido, sua popularidade é atribuída ao sabor, a versatilidade de uso, preço, variedade e valor nutricional [1]. Recentemente, os consumidores estão preferindo os queijos brancos aos queijos amarelos devido ao baixo teor calórico, entretanto, estudos sobre a determinação de elementos essenciais ou potencialmente tóxicos ainda são escassos [2]. Assim, o presente trabalho tem por objetivo a avaliação de procedimentos de decomposição em sistemas fechados com diferentes formas de aquecimento para análise elementar em amostras de queijo branco por ICP OES. A etapa de otimização foi realizada a partir de planejamento fatorial completo de dois níveis com domínio experimental para temperatura entre 140 e 180 ºC para ambos os métodos; e concentração de $HNO_3$ 2, 8 e 14 mol $L^{-1}$ a 40, 60 e 80 min e 2, 6 e 8 mol $L^{-1}$ por 20, 25 e 30 minutos, em bloco digestor fechado e micro-ondas de cavidade, respectivamente. A eficiência de decomposição foi avaliada pelo teor de carbono orgânico dissolvido (DOC). Para ambos os métodos, o parâmetro de concentração foi significativo ($p \leq 0,05$) com efeito negativo, bem como temperatura para o método por irradiação de micro-ondas. Adicionalmente, a interação entre ambos os fatores supracitados se mostrou significativa para decomposição em bloco digestor. Assim, as condições de decomposição estabelecidas por otimização multivariada foram de 180 ºC por 80 min e 140 ºC por 30 min, em bloco digestor e micro-ondas, respectivamente com emprego de 6 mL de $HNO_3$ 2 mol $L^{-1}$ e 2 mL of $H_2O_2$ 30% (v $v^{-1}$). A acidez residual determinada foram 0,76±0,0,04 mol $L^{-1}$ com aquecimento condutivo e 0,40±0,03 mol $L^{-1}$ por irradiação de micro-ondas. Os métodos propostos apresentaram boa precisão (RSD <10%) com ampla faixa de trabalho, boa linearidade ($R \geq 0,999$) e limite de detecção e quantificação abaixo de 0,18 e 0,61 mg $L^{-1}$, respectivamente. A exatidão de ambos os métodos foi comprovada por comparação com método de referência não havendo ocorrência de erros sistemáticos significativos ($p>0,05$). Os procedimentos de decomposição desenvolvidos foram aplicados para a análise de queijos brancos do tipo mozzarella de búfala, minas frescal e ricota, os valores encontrados foram comparados com os indicados em cada um dos rótulos e foi calculada a contribuição de cada nutriente no seu respectivo IDR.

## Agradecimentos/Acknowledgments

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# Determinação de elementos essenciais em queijo de búfala por ICP OES

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*Palavras Chave: Queijo de búfala, elementos essenciais, digestão ácida, ICP OES.*

## Highlights

Determination of essential elements in buffalo cheese by ICP OES. The samples were digested using nitric acid and peroxide hydrogen. Ca and Na were found in all samples. Cu, Fe, K and Se were below the detection limit. The buffalo cheese showed significant sources of nutrients for humans.

## Resumo/Abstract

Os produtos lácteos são componentes importantes na dieta humana. Entre esses produtos, o queijo de búfala se destaca, pois mesmo apresentando os mesmos nutrientes do queijo de vaca, se difere na quantidade. O queijo de búfala é mais rico em cálcio, vitamina A e proteína, mas também possui níveis maiores de gordura e é mais calórico. No entanto, esses valores podem variar, pois dependem do processo de fabricação e padrões de identidade. Por isso, o monitoramento e a definição da composição alimentar de queijos são de suma importância para o desenvolvimento de tabelas de composição nutricional. O objetivo deste estudo foi investigar os teores totais de cálcio, cobre, ferro, magnésio, manganês, potássio, selênio, sódio e zinco em queijo mussarela, ricota e creme de búfala do Norte do Brasil por espectrometria de emissão óptica com plasma acoplado indutivamente (ICP OES). Além disso, foi calculado o consumo diário para 100 g de queijo e comparado com a ingestão alimentar recomendada (RDA). As amostras de queijo de búfala do tipo ricota (QR), mussarela (QM) e creme (QC) foram digeridas em forno de micro-ondas com cavidade usando uma combinação de ácido nítrico 14 mol $L^{-1}$, água ultrapura e peróxido de hidrogênio 30% m/m. A eficiência do procedimento de preparo de amostra e a exatidão das medidas por ICP OES foram avaliadas pelo método de adição e recuperação do analito. As recuperações obtidas variaram de 82 a 112%. Os teores de Ca obtidos nas amostras foram 17101 (QM), 10800 (QR) e 1459 mg $kg^{-1}$ (QC). Os níveis maiores de magnésio foram encontrados em QM (563 mg $kg^{-1}$) e QC (354 mg $kg^{-1}$). O manganês foi encontrado apenas em QR (6,3 mg $kg^{-1}$). Sódio foi encontrado em todas as amostras (QM: 3020 mg $kg^{-1}$; QR: 3865 mg $kg^{-1}$; QC: 5554 mg $kg^{-1}$). As amostras QM (23,0 mg $kg^{-1}$) e QR (22,6 mg $kg^{-1}$) foram que apresentaram concentrações de zinco. Cobre, ferro, potássio e selênio em todas as amostras apresentaram abaixo do limite de detecção. As quantidades de Ca, Mg, Mn, Na e Zn calculadas para o consumo diário de 100 g de queijo por dia para indivíduos de 9 a 70 anos de vida foram de 146 (QC), 1080 mg (QR) e 1710,1 mg (QM); 8 mg (QC), 35 mg (QR) e 56 mg (QM); 0,63 mg (QR) de Mn; 302 (QM), 387 (QR) e 555 mg (QC); 2 mg (QR e QM), respectivamente. Para todos os tipos de queijo o valor de RDA excedeu para Na (1,2 a 1,5 mg/dia) e, a amostra QM excedeu o valor de RDA para Ca (1000 a 1300 mg/dia).

## Agradecimentos/Acknowledgments

CAPES

**Área: BEA**

# Determination of Polycyclic Aromatic Hydrocarbons in meliponinae honey samples employing QuEChERS and GC-MS/MS

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Keywords: *HPAs, honey, QuEChERS, GC-MS/MS, Validation, Extraction.*

## Highlights

Original, acetate and citrate QuEChERS were evaluated to extract PAHs from meliponinae honey samples.
The method was validated and applied to the determination of PAHs in samples from two regions.

## Abstract

Polycyclic Aromatic Hydrocarbons (PAHs) comprise a group of compounds with two or more condensed aromatic rings, being result of the incomplete combustion of organic material. The PAHs have been recognized as carcinogenic and mutagenic compounds, and, due to the risk they pose to the human health and environment, there are sixteen PAHs classified as priority organic pollutants by the United States Environmental Protection Agency (ESCARRONE et al., 2014). PAHs can occur in food categories by many pathways, such as grilling, cooking and also by deposition of air particulates. This last one is the main source of PAHs in honey samples, that can be used as a bioindicator. Honey, which is a natural food produced by bees, can be also produced by stingless bees (meliponinae), whose honey has different physicochemical properties (MARCOLIN et al., 2021). Thus, this work aimed at evaluating a method employing QuEChERS and Gas Chromatography tandem Mass Spectrometry (GC-MS/MS) to the determination of 16 priority PAHs in meliponinae honey samples. Firstly, the original, acetate and citrate QuEChERS were evaluated, in terms of accuracy (recovery) and precision, to extract PAHs from honey samples. The original QuEChERS showed recoveries from 78 to 96%, with relative standard deviation (RSD) ≤ 11.9%; the acetate QuEChERS presented recoveries from 71 to 96%, with RSD ≤ 16.9%, while to the citrate QuEChERS, recoveries ranged from 95 to 112%, with RSD ≤ 16.0%. Thus, the original QuEChERS was chosen, because it uses less amount of sample and reagents, being carried out as follows: 10 g honey sample and 10 mL ultrapure water were added to a 50 mL polypropylene tube, followed by vortex agitation for 1 min; then, 10 mL acetonitrile was added to the sample, which was agitated again. 4 g $MgSO_4$ and 1 g NaCl were added to the sample, which was agitated in a vortex, followed by centrifugation for 10 min at 15,904 g. 1 mL of the sample extract was transferred to 15 mL polypropylene tube containing 25 mg PSA and 150 mg $MgSO_4$, which was agitated and centrifuged for 5 min at 15,904 g. The supernatant was transferred to a vial, 50 µL of the internal standard was added and 2 µL was injected into the GC, whose conditions were adapted from Escarrone et al., 2014. The method was validated, where the limits of quantification (LOQ) ranged from 1 to 10 µg $kg^{-1}$. Linear ranges were from the LOQ for each PAH to 100 µg $kg^{-1}$, with $R^2$ higher than 0.99 for all the compounds. Recoveries were between 70 to 120%, with RSD ≤ 20%. After validated, the method was applied to the determination of PAHs in thirteen meliponinae honey samples, and 9 of the 16 PAHs were detected in concentrations from <LOQ to 9.33 µg $kg^{-1}$, which is according to other works in the literature. Finally, an efficient and reliable method was developed, with the advantages of being Quick, Easy, Cheap, Rugged and Safe - QuEChERS.

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## Acknowledgments

The authors acknowledge the financial support granted by the Brazilian agencies FAPERGS (21/2551-0000684-6), CNPq and FINEP and fellowships granted by CAPES. The authors are thankful to the Centro Integrado de Análises for the chromatographic determinations.

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

# Evaluation of ochratoxin A in specialty fermented coffees produced in Pedra Menina, Caparaó region (MG and ES), Brazil

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Palavras Chave: *coffee contamination; fermented coffees; OTA determination; mycotoxins in food, HPLC-Fluorescence*

## Highlights

- Evaluation of Ocratoxin A in fermented specialty coffees form Caparaó region, Brazil
- Immunoaffinity extraction and HPLC-Fluorescence were used
- The concentrations of OTA were below the MRL established by the legislation

## Resumo/Abstract

The qualified Denomination of Origin and coffee producer region of Caparaó, which is located on the border between Minas Gerais and Espírito Santo states, Brazil, has stood out over recent years for the production of specialty coffees, pioneering the use of fermentation as post-harvest processing to modify and improve the sensory profiles of the beans and of the beverage.[1] Although coffee fermentation can improve its flavour and quality, it can led to food security problems, since the presence of filamentous fungi of the genera *Aspergillus* and *Penicillium* can be associated with the production of mycotoxins, of which ochratoxin A (OTA) is the main and most studied one.[2] Several studies indicated that OTA has nephrotoxic, immunosuppressive, teratogenic and carcinogenic actions, and therefore the maximum residue limit (MRL) for OTA in roasted coffee (ground or beans) and soluble coffee established by the Brazilian legislation is 10 µg $Kg^{-1}$, whereas a MRL of 5 µg $Kg^{-1}$ in roasted coffee is adopted by the European Community (EC).[3] To evaluate OTA contamination, seven producers of the surroundings of Pedra Menina village, situated in the Denomination of Origin region of Caparaó, were selected because of their background in producing high-quality fermented specialty coffees in a controlled way. They gently provided the ripe coffee fruits studied that underwent the same postharvest processing, in the same fermentation facility at two different fermentation times (36 and 72 h), resulting in fourteen samples. The coffees obtained were evaluated and classified according to the Specialty Coffee Association (SCA) protocol and 11 of them were classified as specialty coffees. OTA was determined in all fourteen coffees using immunoaffinity for sample clean-up[4] and high-performance liquid chromatography with fluorescence detection for quantification. One sample showed a concentration of OTA of 0.75 µg $kg^{-1}$ and two samples showed OTA concentrations of 0.87 µg $kg^{-1}$. Concentrations of OTA below the limit of quantification (0.64 µg $kg^{-1}$) were found in the other samples. Thus, all samples showed OTA concentrations far below the MRL established for roasted coffees by EC.[5] Our results showed that OTA contamination due to fermentation should not be a concern for producers and consumers of these fermented coffees. Furthermore, the low levels of OTA in coffees found in the studied fermented were comparable to most of the previous data for Brazilian coffees.[5]

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## Agradecimentos/Acknowledgments

CNPq; CAPES; APRUPEM; Empresa Caparaó Jr

# Qualitative analysis of acetogenins presence in different parts of *Annona crassiflora* Mart. by paper spray mass spectrometry

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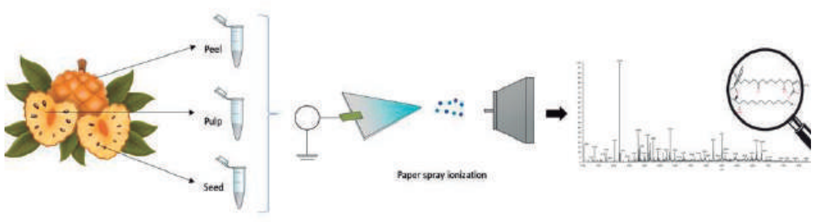
Key words: Cerrado; Acetogeninas; Araticum; *PS/MS*

## Highlights

The presence of acetogenins in all parts of the araticum fruit was confirmed. In this way, it is possible to suggest using its co-products and the pulp to investigate the action of the detected compounds.

## Abstract

Cerrado has a wide variety of native fruits, whose characterization has aroused the interest of science due to the presence of compounds with health-promoting properties. We can highlight the araticum (*Annona crassiflora* Mart.) as a fruit of social and economic importance for small farmers in Minas Gerais. Not all parts of these fruits are commonly used and are thus treated as waste. On the other hand, studies show the significant potential of using agro-food residues to promote greater income generation for small producers, habitat preservation, and health benefits. It is known that acetogenins stand out due to their diverse biological activities, especially the antitumor effect. Thus, this study sought to investigate the presence of acetogenins in different parts of the araticum. The fruits came from Cordisburgo - MG in the 2020 harvest. The fruits were sanitized, and the parts (pulp, peel, and seed) were manually separated. Subsequently, ethanolic extracts were prepared from the pulp and fruit by-products to analyze the compounds. With subsequent fragmentation, the mass spectrometry technique was used with ambient ionization by paper spray (positive ionization mode +4.5 kV). It was possible to observe that this chemical class is strongly present in all parts of the Annona fruits studied. Of the 12 compounds investigated, four were present in the skin, six in the pulp, and five in the seeds. We can highlight annonacinone and squamolinone, compounds present in the peel and pulp. On the other hand, 24-acetylguanacone(CO,10) and guanaconetin-4 were acetogenins present only in the pulp and seeds. In this way, it is concluded that acetogenins are naturally present in the whole araticum fruit, making its co-products and the pulp promising. Since this class of compounds is of great importance, studies related to the mechanism of action of the acetogenins found are necessary.



| *m/z* | Identification Attempt | Peel | Pulp | Seed | Reference |
|---|---|---|---|---|---|
| 595 | Annonacinone | X* | X* | - | Avula et al. (2018) |
| 552 | Montalicin-A | - | X* | - | Bermejo et al. (2005) |
| 574 | Dieporeticanin-2 | X* | - | - | Bermejo et al. (2005) |
| 590 | Bullatencin (D23) | X* | - | - | Bermejo et al. (2005) |
| 594 | Squamolinone | X* | X* | - | Bermejo et al. (2005) |
| 617 | Squamocin B | - | - | X | Avula et al. (2018) |
| 640 | Otivarinf | - | - | X* | Bermejo et al. (2005) |
| 646 | Squamocin | - | - | X* | Avula et al. (2018) |
| 648 | Annomontacin | - | X | - | Avula et al. (2018) |
| 662 | 24-acetylguanacone(CO,10) | - | X* | X* | Bermejo et al. (2005) |
| 664 | Guanaconetin-4 | - | X* | X* | Bermejo et al. (2005) |

## Acknowledgments

The authors would like to thank the Universidade Federal de Minas Gerais (UFMG); Pró-Reitoria de Pesquisa - PRPq – FMG; Universidade Federal de São João del-Rei (UFSJ); the Portuguese Foundation for Science and Technology (FCT) through the research unit UID/AGR/04129/2020 (Research Center LEAF- Linking Landscape, Environment, Agriculture, and Food); CAPES; CNPq, FAPEMIG and Instituto Brasileiro de Desenvolvimento e Sustentabilidade for the infrastructure to carry out the analyses and financial support.

**Área: BEA** **Nº de Inscrição: 01077**

# Reconhecimento do potencial hepatoprotetor baseado em PCA: correspondências em Solanum paniculatum L.

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Palavras Chave: *Jurubeba, Análise por Componentes Principais, Hepatoproteção, Klekota-Roth Fingerprint.*

## Highlights

PCA-based hepatoprotective potential recognition: Solanum paniculatum L matching: This work aimed to identify substances with hepatoprotective potential of the species Solanum paniculatum L. from the PCA analysis.

## Resumo/Abstract

Solanum paniculatum L., Solanaceae, conhecida como "jurubeba" se destaca por seus diversos usos medicinais além do seu consumo na alimentação, cujas raízes e caules são indicados no tratamento da anemia e distúrbios hepáticos e digestivos[1]. Um estudo in silico foi realizado para reconhecer o potencial hepatoprotetor de algumas substâncias encontradas na jurubeba verificando possíveis correspondências com compostos analisados encontrados na literatura e bancos de dados curados utilizando o método não supervisionado, análise de componentes principais (PCA, do inglês Principal Component Analysis). Os métodos não supervisionados são usados para identificar padrões nos conjuntos de dados com base apenas nos descritores moleculares[2] reconhecidos como variáveis independentes. Para a realização desse estudo foram selecionadas 56 substâncias do banco de dados ChEMBL, classificados como: hepatoprotetor (HP), pouco hepatoprotetor (PHP) e não hepatoprotetor (NHP) e 33 substâncias da S. paniculatum que foram pesquisadas e validadas com a base de dados SciFinder. A partir do banco de dados construído foi calculado os descritores moleculares para a obtenção das propriedades teóricas, do tipo fingerprint baseado na fragmentação proposta por Klekota-Roth com o auxílio do programa PaDEL. Os dados obtidos foram avaliados pela análise de PCA através do programa KNIME Analytics Platform. Os resultados mostraram que algumas substâncias presentes na jurubeba apresentaram correspondências com as substâncias classificadas como hepatoprotetoras (Figura 1) dentre essas substâncias estão: 6-O-β-D-Xylopyranosyl-(1''→3')-β-D-quinovopyranosyl-(22S,25S)-3β,4β,6α-trihydroxy-5α-spirostane, Diosgenin β-D-glucopyranoside, Diosgenin gentiobioside que correspondem com Daucosterin.

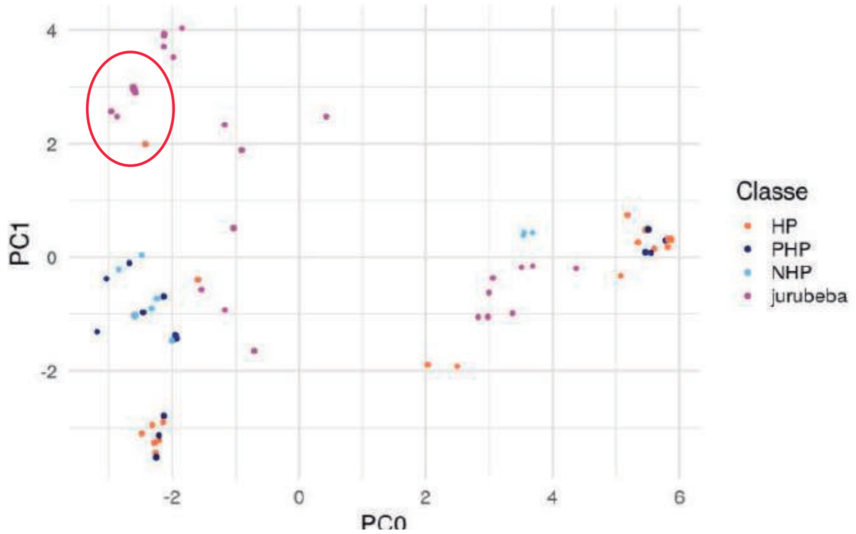

**Figura 1.** Gráfico dos padrões dos descritores moleculares, com PC0 vs PC1.

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## Agradecimentos/Acknowledgments

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**Área: BEA**

# Study of the extraction of non-volatile compounds in specialty and traditional coffees by infusion and decoction.

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*Key words: Coffees, Non-volatile compounds, Extraction, TDS, Quantification compounds.*

## Highlights

The proposed study evaluated different forms of extraction (infusion and decoction) for non-volatile compounds from specialty and traditional coffees. The study was exploratory, and the Dissolved Solids Content (TDS) value of the extractions and the identification of non-volatile compounds were used to choose the best extraction method.

## Resumo/Abstract

The coffee bean presents different volatile and non-volatile compounds in its formation, responsible for the flavor and aroma attributes of the beverage. The objective of this exploratory study was to evaluate the extraction of non-volatile compounds from specialty and traditional coffees by infusion and decoction to choose the best extraction method for the quantification of these compounds. One sample of each special and traditional classification, obtained from the local market, was evaluated. By the infusion method: 10 g of sample was added to traditional filter paper and 150 mL of water at 90 ºC was poured over, after filtering an aliquot was passed through the syringe filter and later injected into high performance liquid chromatography (HPLC). For the decoction method: 10 g of sample was added to 150 mL of water and heated for 2 min (90 ºC), then filtered through conventional filter paper and syringe filter and the sample was injected into HPLC. The extractions were performed in triplicate. The TDS measure was performed for all extractions. The TDS measurement was obtained using a ºBrix refractometer and through conversion calculations (% TDS = 0.85 × % ºBrix) from the %TDS, the percentage of extraction was calculated (Extraction = TDS x Drink/Dosage). The results found were evaluated together with the chemical composition data to designate the most satisfactory extraction method. The chemical composition of the non-volatile compounds was evaluated by high performance liquid chromatography with UV detection at 280 and 320 nm, C18 column (4.6 x 250 mm – 5 µm), mobile phase 95% (A) 5% acetic acid in water and 5% (B) acetonitrile, injection of 30 µL, flow rate of 0.8 mL/min, for 55 minutes. For both samples the compounds identified were 5-Hydroxymethylfurfural, 3,4-Hydroxybenzoic, Catechin, 4-Hydroxybenzoic, Caffeine, and Chlorogenic, Caffeic and Gallic Acids. The same non-volatile compounds were extracted, with no difference either by extraction method or type of coffee (special and traditional). The of TDS measure determines the percentage of coffee concentration extracted by a given extraction method and is commonly used by baristas to evaluate coffee brewing methods. In this way that decoction was the most satisfied extraction method, since the percentage of extraction (Special coffee = 45% and Traditional coffee = 39%) and the amount of compounds extracted by this method was higher in relation to the infusion (Special coffee = 25% and Traditional coffee = 26%).

## Agradecimentos/Acknowledgments

CNPq for the scholarship granted for the financial support.

# The bioaccessibility of bioactive compounds in *Annona crassiflora* Mart. using *in vitro* simulated digestion

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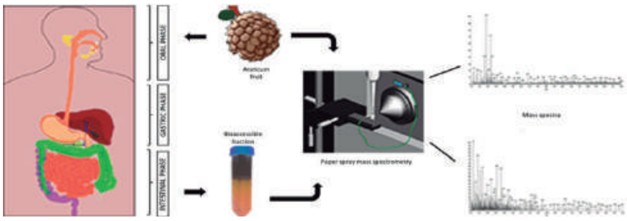
Key words: *Araticum; Cerrado; Flavonoids; Phenolic compounds; Polyphenolic; Mass spectrometry; Paper spray ionization.*

## Highlights

Araticum proved to be a promising fruit due to the fresh pulp's chemical characteristics and the bioaccessible fraction. The paper spray technique allowed the evaluation of the presence of bioactive compounds before and after the simulated digestion process.

## Abstract

*Annona crassiflora* Mart is a native fruit of the Brazilian Cerrado. Popularly known as araticum, this fruit has a sweet pulp and is widely consumed in the form of jellies, sweets, juices, and ice creams. This pulp has drawn attention due to bioactive compounds present in its composition and health benefits. However, it is known that one of the main limiting factors for these effects is the bioaccessibility of interest compounds after the digestion process. Thus, the present study aimed to evaluate the bioaccessibility of some bioactive compounds through the in vitro digestion process simulating the gastrointestinal tract. The pulps were obtained from fruits collected in Sete Lagoas - MG in the 2020 harvest. Three phases were simulated: the oral, gastric, and intestinal phases. The supernatant was collected and conditioned for further analysis at the end of the in vitro digestion process. Still, from the pulp, hydroalcoholic extracts were prepared. Mass spectrometry technique with paper spray ionization in negative ionization mode (-3.5 kV) was used to verify the presence of some bioactive compounds in the extract and the bioaccessible fraction. In the present identification attempt, eight compounds belonging to the class of polyphenols, phenols, and flavonoids were observed. When the presence of these compounds was verified after the simulated digestion process, only four of them remained (*p*-coumaric acid, *p*-coumaric acid methyl ester, citric acid, and feruloylglycoside). On the other hand, other new compounds emerged in this identification attempt (gallic acid, hydroxytyrosol hexoside, 3-(2-hydroxyphenyl)-propanoic acid hexose, and quercetin hexoside). This phenomenon may occur due to the interactions during the digestion process that can lead to the emergence of compounds from degradation processes. Therefore, although not all molecules remain after the digestive process, it can be inferred that most compounds are bioaccessible, which may provide beneficial effects. Thus, for future studies, it is suggested that these bioactives would be quantified.



## Acknowledgments

The authors would like to thank the Universidade Federal de Minas Gerais (UFMG), Pró-Reitoria de Pesquisa - PRPq - UFMG, Universidade Federal de São João del-Rei (UFSJ), Instituto Superior de Agronomia - Universidade de Lisboa (ISA-UL), CAPES, CNPq, FAPEMIG for the infrastructure to carry out the analyses and financial support. This research is developed within the framework of the Sustainable Rural Project - Cerrado, which emerged from the partnership between the Inter-American Development Bank (IDB), the Government of the United Kingdom, the Ministry of Agriculture, Livestock and Supply (MAPA), the Brazilian Institute for Development and Sustainability (IABS) and the ILPF Network and Embrapa, and also developed with the support of Portuguese Foundation for Science and Technology (FCT) through the research unit UID/AGR/04129/2020 (Research Center LEAF- Linking Landscape, Environment, Agriculture, and Food).

**Área: BEA**

# Total Arsenic Determination in Different Types of Canned Tuna Processing

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Palavras Chave: *Arsenic, ICP-MS; Canned Tuna.*

## Highlights

Total arsenic determination using ICP-MS. Analysis of canned tuna samples in different conserves and processing methods.

## Resumo/Abstract

Arsenic is a toxic element and high levels of this element in food and beverages poses a significant threat to human health.[1] The aim of this study was to evaluate the presence of arsenic in canned tuna samples, comparing solid and ground samples in different preservation media. Five different sample groups, consisting of five independent samples of canned tuna from one brand were studied. These sample groups were solid tuna in oil, in natural conserve, in oil with smoked flavor and ground tuna in oil and in natural conserve. The decomposition of the samples was done using a mixture of $HNO_3$ and $H_2O_2$ with heating assisted by microwave radiation. After, the total arsenic was determined by inductively coupled plasma mass spectrometry (ICP-MS). Good accuracy of the analytical method was verified analyzing two different reference materials, BCR-627 (tuna fish muscle) and DORM-4 (fish protein) (Table 1).

Table 1: Total arsenic concentration ($mg.kg^{-1}$) obtained for the reference materials BCR-627 and DORM-4 (n=3)

| Reference Material | Experimental Value ($mg.kg^{-1}$) | Certified Value ($mg.kg^{-1}$) |
|---|---|---|
| BCR-627 | 4.88 ± 0.05 | 4.8 ± 0.3 |
| DORM-4 | 7.04 ± 0.26 | 6.8 ± 0.64 |

Canned ground tuna samples showed values significative higher (t-test, $p<0.05$) for arsenic content than canned solid tuna (Table 2) indicating that processing is a factor more relevant than conservation media.

Table 2: Total arsenic concentration ($mg.kg^{-1}$) in the canned tuna samples.

| Samples | Concentration ($mg.kg^{-1}$) |
|---|---|
| Solid in oil | 4.55 ± 1.15 |
| Solid in water | 3.27 ± 048 |
| Solid and smoked in water | 3.48 ± 0.57 |
| Ground in oil | 5.87 ± 1.21 |
| Ground in water | 7.68 ± 1.13 |

Moreover, it is important to highlight that total arsenic content in all sample was upper to the limit (1.0 $mg.kg^{-1}$) established by ANVISA.[2] In order to evaluate the arsenic species present in these samples, speciation analysis is being executed.

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## Agradecimentos/Acknowledgments

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# BIO

# Química Biológica

**Área: BIO**

# Aerobic co-oxidation of hemoglobin and aminoacetone

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Palavras Chave: *Aminoacetone, Hemoglobin, α-Aminoketones, Electron Transfer, Superoxide Radical*

## Highlights

Aerobic hemoglobin and aminoacetone co-oxidation yield methylglyoxal and oxyradicals. Oxyhemoglobin (oxyHb) increases the aminoacetone oxidation rate. Superoxide and hydroxyl radicals plus $H_2O_2$ are reaction intermediates.. Oxyhemoglobin is oxidized to metHb and undergoes structural alterations.

## Resumo/Abstract

Aminoacetone (1-aminopropan-2-one), a putative minor biological source of methylglyoxal, reacts like other α-aminoketones such as 6-aminolevulinic acid (first heme precursor) yielding electrophilic α-oxoaldehydes, ammonium ion and reactive oxygen species by metal- and hemeprotein catalyzed aerobic oxidation [1,2]. A wealth of reports implicates methylglyoxal in protein crosslinking and DNA addition, leading to age-related disorders, including diabetes [3,4]. Importantly, methylglyoxal-treated hemoglobin adds four water-exposed arginine residues, which may compromise its physiological role and potentially serve as biomarkers for diabetes [5]. In this work, we investigate the co-oxidation of aminoacetone and oxyhemoglobin in normally aerated phosphate buffer, leading to structural changes in hemoglobin, which might reportedly be attributed to the addition of aminoacetone-generated methylglyoxal to the protein. Hydroxyl radical-promoted chemical damage to hemoglobin may also occur in parallel, which is suggested by EPR-spin trapping studies with 5,5-dimethyl-1-pyrroline-*N*-oxide and ethanol. Concomitantly, oxyhemoglobin is oxidized to methemoglobin, as indicated by characteristic CD spectral changes in the absorption Soret and visible regions. Overall, these findings may contribute to elucidate the molecular mechanisms underlying human diseases associated with hemoglobin dysfunctions (e.g., diabetes) and with aminoacetone in metabolic alterations related to excess of glycine and threonine (e.g., threoninemia, *cri-du-chat* syndrome).

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**Área: <u>QB</u>**

# Antimicrobial potential of the desCys$^{11}$/Lys$^{12}$/Lys$^{13}$-(p-BthTX-I)$_2$K peptide conjugated with Hy-a1 peptide or Cell Penetrating Peptides.

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Key Words: Antimicrobial resistance, p-BthTX-I, Hylin a1, Cell penetrating peptides.

## Highlights

Bioconjugation of antimicrobial peptides and cell penetrating peptides in order to potentiate antimicrobial activity.

## Abstract

Antimicrobial peptides (AMPs) have been evaluated as an alternative treatment for bacterial infections[1]. The peptides (desCys$^{11}$/Lys$^{12}$/Lys$^{13}$(p-BthTX-I)$_2$K) (p-Bt) and Hylin a1 (Hy-a1), are example found in the literature[2,3]. In this study, the Hy-a1 peptide or Cell Penetrating Peptides (CPPs)[4] were coupled to the p-Bt sequence, using solid phase peptide synthesis (SPPS), in order to increase its antimicrobial activity (Table 1). Circular dichroism spectroscopy was used to evaluated structure of conjugates. The biological activity was determined by broth microdilution tests and the minimum inhibitory concentration (MIC) and the minimum bactericidal concentration were obtained. The hemolytic activity was performed to measure the toxicity against erythrocytes. The peptides derived from Hy-a1 showed α-helix structure. The peptides derived from CPPs did not present a defined structure. All conjugates showed low MIC results. The Hy-a1 derivatives did not show improved activity in relation to the original peptide p-Bt in bacteria found in human infections, but two conjugates present better activity in *Aeromonas jandaei*. The peptides derived from CPPs, on the other hand, showed improved activity against *S. aureus*, with MIC decreasing from 128 to values between 16 μM and 8 μM. Peptides derived from Hy-a1 showed high toxicity to human and fish erythrocytes. In the CPPs conjugates, only the conjugated p-Bt-PPC$_2$ showed a low toxicity to human erythrocytes. The present study demonstrated that conjugates derived from the coupling of Hy-a1 did not increase the antimicrobial activity of p-Bt, while the addition of the fusion peptides to p-Bt peptide, improves the activity of the peptide against Gram-positive bacteria, without decrease its activity in Gram-negative bacteria.

Table 1: Sequences and codes of peptide bioconjugates.

| Codes | Sequence | Codes | Sequence |
|---|---|---|---|
| Cys-Bt-Hy-a1 | (KKYRYHLKPFCK)$_2$K-IFGAILPLALGALKNLIK | p-Bt-PPC$_1$ | (KKYRYHLKPF)$_2$K-KRLRWR |
| p-Bt-Hy-a1 | (KKYRYHLKPF)$_2$K-IFGAILPLALGALKNLIK | p-Bt-PPC$_2$ | (KKYRYHLKPF)$_2$K-PFVYLI |
| p-Bt[PEG]Hy-a1 | (KKYRYHLKPF)$_2$K-[PEG]-IFGAILPLALGALKNLIK | p-Bt-PPC$_3$ | (KKYRYHLKPF)$_2$K-YGRKKRRQRRR |

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## Acknowledgments

Capes, CNPq, Fapesp, LASEBio.

**Área: BIO**

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

# Antiviral evaluation of new synthetic bioconjugates based on GA-Hecate: A new class of antivirals targeting different steps of Zika Virus replication

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Palavras Chave: Zika Virus, Antiviral, Metabolites, Broad Spectrum, Peptides.

## Highlights

This study identifies a new synthetic antiviral compound targeting different steps of ZIKV replication *in vitro* and with the potential for broad reactivity against other flaviviruses. Our work highlights a promising strategy for the development of new antivirals based on peptide metabolism and bioconjugation.

## Resumo/Abstract

Re-emerging arboviruses represent a serious health problem due to their rapid vector-mediated spread mainly in urban tropical areas. The 2013-2015 Zika virus (ZIKV) outbreak in South and Central Americas have been associated with cases of microcephaly in new-borns and Guillain-Barret syndrome. We previously showed that the conjugate Gallic acid – Hecate (GA-FALALKALKKALKKLKKALKKAL-$CONH_2$) is an efficient inhibitor of the hepatitis C virus. Here, we have shown that the Hecate peptide is degraded in human blood serum into three major metabolites. These metabolites conjugated with gallic acid were synthesized and the inhibition of ZIKV replication in cultured cells was evaluated. The GA-metabolite 5 (GA-FALALKALKKALKKL-COOH) was the most efficient in inhibiting two ZIKV strains of African and Asian lineage at the stage of both virus entry and replication after 72 h post infection, especially as virucidal (>95% of inhibition) and protective (>80% of inhibition). We also demonstrate that GA-metabolite 5 does not affect cell growth after 7 days of continuous treatment, highlighting the specific target on virus replication and not in cell metabolism. Thus, this study identifies a new synthetic antiviral compound targeting different steps of ZIKV replication *in vitro* and with the potential for broad reactivity against other flaviviruses. Our work highlights a promising strategy for the development of new antivirals based on peptide metabolism and bioconjugation.

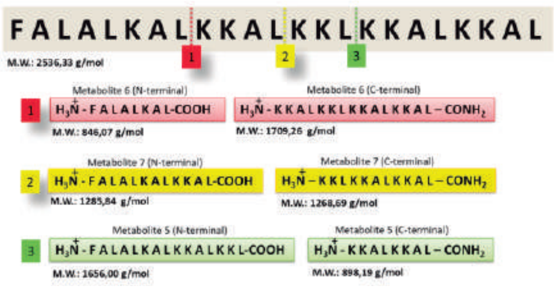

Figure 1 - Identification of Hecate peptide fragments after incubation with human blood serum.

## Agradecimentos/Acknowledgments

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**Área: BIO**

# Biophysical studies with DNA: evaluation of the biological target of aminoguanidine hydrazones and results for the treatment of leishimaniasis

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*Palavras chave: ctDNA, Leishmaniose, Hidrazonas de aminoguanidina, Fluorescência molecular, Docking molecular.*

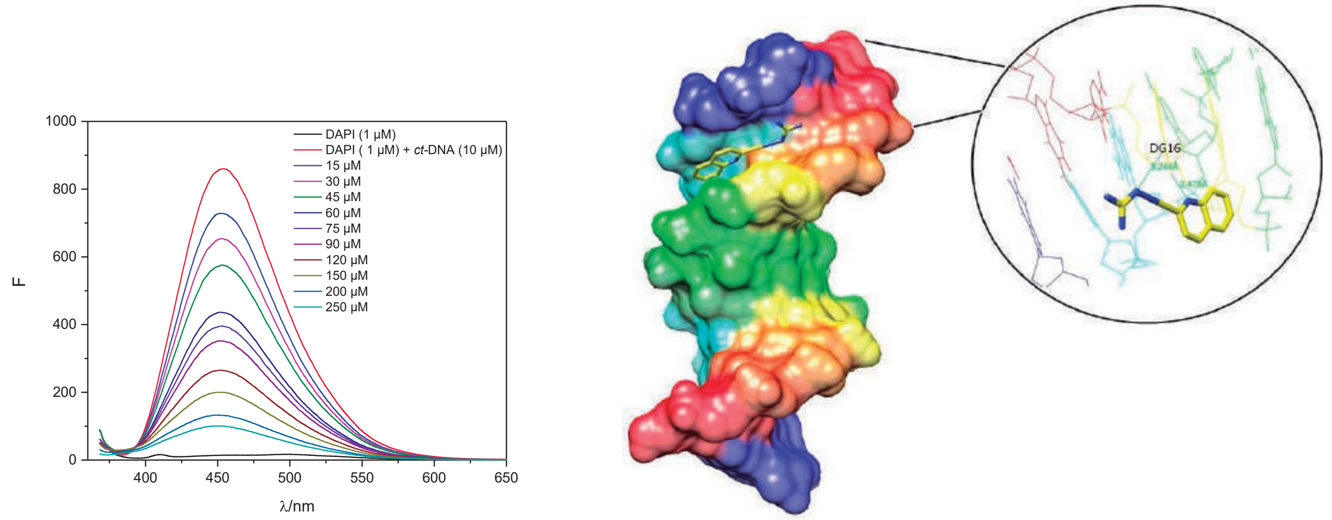
## Highlights

Fluorescence and molecular docking studies revealed that aminoguanidine hydrazone derivatives bind to ctDNA through the interaction of grooves by hydrogen bonds.

## Resumo

A leishmaniose, é uma doença negligenciada, causadas por parasitas e atingem principalmente a população de baixa renda, sendo algumas das principais causas de mortalidade em todo o mundo. Atualmente não existe vacina contra essa doença e os medicamentos à base de antimoniais pentavalentes são, no Brasil, utilizados como primeira escolha na terapêutica da leishmaniose. As hidrazonas de aminoguanidina (AGH's) constituem uma classe que se abre para uma grande variedade de estruturas e *design* de novos compostos estruturalmente relacionados com atividade antileishmanial. Estudos sobre interações de compostos com DNA são realizados também para investigar sua atividade leishmanicida, mostrando resultados promissores com o DNA como alvo principal. Dentro desse contexto, este trabalho teve como objetivo avaliar *in vitro* a interação entre o *ct*-DNA e oito compostos derivados das AGH's, empregando técnicas espectroscópicas, além de estudos de *docking* e dinâmica molecular. Nos estudos empregando fluorescência molecular foi observado que os compostos analisados apresentaram emissão em 450 nm quando excitados em 317 nm. Dessa forma, devido a variação na fluorescência intrínseca do composto, é possível calcular a constante de Stern-Volmer (Ksv) e a constante de ligação (Kb), apresentando Kb na ordem de $10^5$ L $mol^{-1}$. Além disso, o mecanismo preferencial de extinção da fluorescência dos compostos pelo *ct*DNA é o *quenchig* estático. Por meio de estudos de competição foi possível observar ainda que esses compostos interagem com DNA preferencialmente via *groove*. No que se refere aos resultados do *docking* molecular, os compostos apresentaram uma afinidade de ligação na faixa de -6.6 kcal $mol^{-1}$, interações via *groove*, formando ligações de hidrogênio com os resíduos DC15 e DG16 do DNA. Além disso, foram avaliadas as propriedades ADME desses compostos, que obedeceram às regras de Lipinski, Veber e Egan.

**Figura 1- a)** Perfil espectral do composto LQM195 com adição de incrementos crescentes, DAPI (1 µM) e *ct*DNA (10 µM). **b)** *Docking* molecular do composto LQM195 mostrando significativa ligação de hidrogênio (linha verde) com DNA.



**a)** **b)**

## Agradecimentos

CAPES, CNPq, FAPEAL.

**Área: BIO**

# Development of fluorescence method for HOCl scavenger capacity assessment under physiological conditions and in *ex vivo* system

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Keywords: *hypochlorous acid, scavenging capacity, selective probe, human neutrophils.*

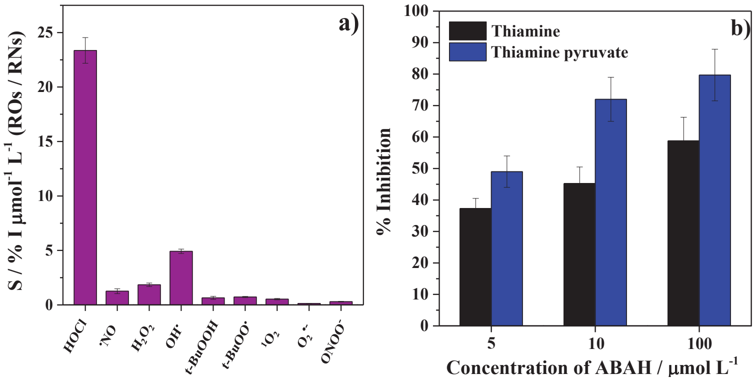
## Highlights

Hypochlorous acid scavenging capacity against antioxidant compounds and steroidal anti-inflammatory drugs in simulated inflammatory conditions and human neutrophils using thiamine as a fluorescence probe.

## Abstract

The methods developing to determine the antioxidant capacity and reactive oxygen and nitrogen species have been a challenge, considering mainly the sample complexity. Thus, methods to mimic physiological conditions using biologically active molecules as probes are required. High concentrations of HOCl can be associated with inflammatory processes; this way, this work aimed to develop a simple, fast, and sensitive method to determine the HOCl scavenging capacity ($C_{sc}$) of different compounds and anti-inflammatory drugs based on the inhibition of the thiamine to thiochrome oxidation under simulated physiological conditions mediated by HOCl. The method is based on reducing thiochrome formation ($\lambda_{ex}$ = 370 nm / $\lambda_{em}$ = 440 nm), a product of thiamine oxidation by HOCl. Species that can react with HOCl reduce the formation of thiochrome and, therefore, the intensity of the fluorescence signal. Gallic acid was used as standard, and the percentage of fluorescence inhibition was used as an analytical response. The probe's selectivity was analyzed against seven biologically active reactive species, using analytical sensitivity as the parameter (Fig 1a). According to the results, the probe used (thiamine) proved to be selective for HOCl, allowing its use under biological conditions in the presence of other reactive species. The selectivity was confirmed in human neutrophils isolated under inflammatory conditions (Fig. 1b). In the presence of the myeloperoxidase inhibitor ABAH (4-aminobenzoic hydrazide, 5 -100 μM), inhibition in the oxidation of 37-60% was observed for thiamine and 49-80% for thiamine pyrophosphate. The method allowed evaluating the $C_{sc}$ of 25 compounds *in vitro* from different classes: phenolics (*n* = 14); thiols (*n* = 5) and non-steroidal anti-inflammatory drugs (*n* = 6). The $EC_{50}$ (concentration of compound capable of inhibiting 50% of the reference signal) was calculated from the analytical parameters of the curves. The values ranged from 0.60 ± 0.01 to 33.8 ± 0.4 μM for the phenolic compounds (tannic acid and kaempferol, respectively), for the thiol compounds from 1.3 ± 0.2 to 15.5 ± 0.2 μM (penicillamine and captopril, respectively), while for the anti-inflammatory drugs from 0.010 ± 0.001 to 244 ± 20 μM (meloxicam and ibuprofen, respectively). Therefore, considering the $EC_{50}$ values, the antioxidant compounds showed higher efficiency, mainly to thiol and anti-inflammatory compounds analyzed. Eight compounds (tannic acid, Trolox®, gallic acid, quercetin, ascorbic acid, penicillamine, and meloxicam) analyzed *in vitro* assay were tested in human neutrophils under inflammatory conditions (*ex vivo* condition), and the $C_{SC}$ was determined by the proposed method. The results presented a similar profile to the *in vitro* conditions. The probe (thiamine) was applied to human neutrophils under inflammatory conditions, showing selective HOCl and determining the $C_{sc}$ of compounds in cell media. Finally, the proposed method proved to be selective and suitable for evaluating the scavenging ability of HOCl against natural and synthetic compounds in simulated and cell conditions.

**Fig. 1.** (a) Sensitivity of analytical curves ($C_{ROS}$ / a. u.$F_{440\ nm}$ μM$^{-1}$) and (b) ABAH inhibitor in PMA-stimulated human neutrophils (*n* = 3).



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**Área: ________BIO______**
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# Effect of dimerization on antibacterial and SARS-CoV-2 papain-like cysteine protease (PLpro) activity of the peptide (p-BthTX-I)

**Eduardo M. Cilli (PQ),[1*] Natália V. Bitencourt (IC),[1*] Norival A Santos-Filho (PQ),[1] Paulo R. S. Sanches (PQ),[1] Rafael V. C. Guido (PQ)[2], Mariana O. Godoy (PQ),[2] Gabriela D. Noske (PQ),[2] Glaucius Oliva (PQ),[2] Ilana L. B.C. Camargo (PQ)[2], Gabriela M. Righetto (PG)[2],**

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Palavras Chave:*(Antimicrobial peptides, Multidrug-resistant bacteria, p-BthTX-I, PLpro, SARS-CoV-2, Covid).*

## Highlights

Antimicrobial peptides against SARS-CoV-2. Antibacterial activity of the peptide $(p\text{-}Bt)_2$ against multidrug-resistant bacteria.

## Resumo/Abstract

The alarming data of resistance to first-choice antibiotics due to their excessive use and misuse in medicine, food industry, and agriculture worry scientists, making them search for new antimicrobial compounds. In recent years, peptide-based therapeutics have been studied to treat infectious diseases, including antibacterial and viral infections (including COVID-19). Our group has previously described the antibacterial peptide p-Bt [$(KKYRYHLKPF)_2K$], a peptide derived from the C-terminal region of the myotoxin bothropstoxin-I (BthTX-I), from *Bothrops jararacussu* snake[1]. The Bothropstoxin-I (BthTX-I) is a myotoxin isolated from the venom of the Bothrops jararacussu snake that is homologous to the Phospholipase $A_2$ ($PLA_2$) (Figure 1).

Figure 1: Schematic representation of the myotoxin bothropstoxin-I (BthTX-I), the peptide p-BthTX-I, and dimeric peptide.

This synthetic peptide also showed SARS-CoV-2 papain-like cysteine protease (PLpro) inhibition potencies[2]. In this study, we designed, synthesized by Solid Phase Peptide Synthesis (SPPS), purified using HPLC, and evaluated the antibacterial and PLpro inhibition for monomeric, dimeric, and tetrameric peptides synthesized with L- and D-amino acids. The antimicrobial activity against *K. pneumoniae* (ATCC 700603) increased with the dimerization. The monomeric peptides did not show activity (≥ 512 µg/mL). The dimeric peptides presented MIC values of 256 and 64 µg/mL for L- and D-isomer, respectively. The tetrameric compounds presented a MIC of 32 for both isomers. Other bacteria were evaluated and similar results were found. On the other hand, all peptides showed considerably decreasing in PLpro activity at 10 µM, with a minimum value of 85% for D-monomer and 98% for L-dimeric and L-tetrameric peptides. The synthetic peptides showed PLpro inhibition potencies (IC50) between 1.1 µM (L-monomer) to 3.0 (D-monomer) range and low inhibitory activity against Mpro. The activity of the peptide against bacterial strains and SARS-CoV-2 papain-like cysteine protease (PLpro) suggest that these lead peptides could be a promising alternative to treat SARS-CoV-2 and bacterial infections.

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## Agradecimentos/Acknowledgments

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- **Área:** Química Biológica - BIO

# Emission Color-Tuning *via* Anion Exchange in CdSe/ZnS Nanocrystals: Unraveling Local Atomic Structure by XAFS Analysis and *In Vitro* Study for Nanoprobe Development

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**Palavras Chave:** Color-tunable CdSe/ZnS QDs, Anion exchange, Biocompatibility, Bioimaging, Endocytosis.

## Highlights

This work presents the synthesis and characterization of sereis of color-tunable CdSe/ZnS core-shell QDs and their evaluation for biomedical purposes. Color-tuning was acheived *via* anion exchange (AE) of $Se^{2-}$ by $S^{2-}$ during overcoating of CdSe core by ZnS. Solvent system of 1-dodecanthaiol (DDT) and oleylamine (OLA) was used as a sensitive parameter to induce the AE. The QDs induced no cell activation and presented good biocompatibility in RAW macrophages. The cells endocytosed the QDs *via* energy-dependent pathways and displayed enhanced fluorescence in the intracellular regions.

## Resumo/Abstract

Herein, we report a new synthetic approach to prepare the core-shell (without alloying) and alloyed color-tunable CdSe/ZnS QDs induced *via* anion exchange (AE) of $Se^{2-}$ by $S^{2-}$, using 1-dodecanthaiol (DDT) and oleylamine (OLA) solvent system as a sensitive parameter. The rise in ratio of DDT to OLA tailored the composition and elemental distribution profile to produce a product of Cd(Se,S) while preserving the size in all QDs (average diameter of 4.47 to 4.8 nm), as determined by TEM. Interestingly, $CdS_{1-x}Se_x$ gradient alloy was produced while increasing the ratio of DDT to OLA or using only the DDT, resulting in color-tuning in the wide-visible range (467-584 nm). The internal structure, chemical composition, and nature of alloying (*via* anion exchange) in QDs was unraveled by EXAFS. The QDs were characterized by different techniques, including XRD, TGA, FTIR, EDS, DLS, UV-visible absorption, and photoluminescence spectroscopy. The QDs were studied in RAW macrophages by evaluating their biocompatibility, mechanism of internalization, intracellular localization, and their potentialities in bioimaging. The QDs presented high cell viability and induced no cell activation. Fluorescence images of live cells, acquired by CytoViva dual-mode fluorescence, manifested considerable amount of QDs in the vicinity of the cell membrane and intracellular regions. The cells internalized the QDs predominantly *via* macropinocytosis and other lipid raft-mediated endocytic pathways and accumulated in endosome/lysosmes. No significantly detectable signal was observed for QDs at lower temperature treatment, which is consistent with energy-dependent endocytosis. In summary, these unique features of QDs will open new possibilities in band edge engineering and developing nanoprobes *in vitro* bioimaging and biodetection.

## Agradecimentos/Acknowledgments

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# Fishermen chronic exposure to a polluted environment (Mundaú lagoon, Maceió-AL) can lead to oxidative stress and functional changes in blood cells

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**Keywords:** mercury; environmental contamination; Mundaú-Manguaba lagoon; oxidative stress; vulnerable population.

## Highlights

Oxidative stress found in blood cells from the population of polluted Lagoa Mundaú comes from the formation of cytosolic superoxide radical anion and hydrogen peroxide.

## Abstract

Previous studies from our group showed that in the Mundaú lagoon (Maceió-AL), high levels of mercury were determined in the water, sururu (bivalve), and in the blood/urine from the population that leaves around there [Silva et al. 2020; Santos et al. 2021]. However, some questions remain with no answer; in this case, what is the oxidative stress origin found in this vulnerable population? Therefore, this work aimed to analyze the effects and toxicological mechanisms of Hg against peripheral blood mononuclear cells (PBMCs) and erythrocytes, evaluating parameters related to functionality and oxidative stress. We have carried out experiments with 36 exposed volunteers (local fishermen) and 10 control volunteers. The fishermen's average age is 46 ± 10 years; 58% are women, and the main comorbidity in this group is hypertension; besides, the consumption of alcoholic beverages is prevalent. In addition, all fishermen volunteers have continuous environmental exposure contact with water and consume food (sururu and fish) from the lagoon. In a recent analysis of water samples from the region, we observed that in many places, the concentration of total Hg was higher than 10 times the limit value indicated by current legislation [CONAMA nº357 2005]. The results showed that the exposed fisherman group presented a decrease of 42% in $O_2$ binding capacity compared to the control group (**Fig. 1A-B**). In erythrocytes, it was possible to verify a high increase in the activity of superoxide dismutase and catalase (antioxidant enzymes) correspondent 63 and 27%, respectively, comparing exposed volunteers and controls. In PBMCs, the reactive oxygen species (ROS) generation was analyzed based on $O_2^{\bullet-}$ and $H_2O_2$. Overall, the cytosolic production of $O_2^{\bullet-}$ and $H_2O_2$ from the fisherman group presented an increase of 80% compared to control volunteers (**Fig. 2A-B and Fig. 2C-D, respectively**). Finally, considering the initial data, the source of oxidative stress is cytosolic, thus, constituting a possible factor that can lead to the functional changes observed in the blood cells of the fishermen caused by the environmental contamination of Mundaú lagoon (Maceió, AL).

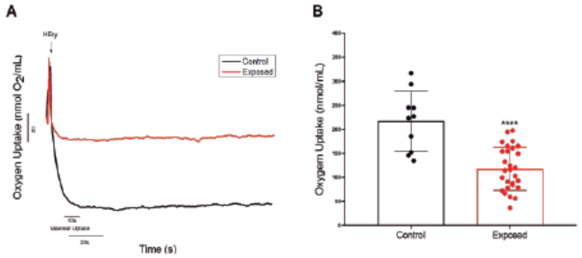

**Fig. 1.** Erythrocytes from fishermen exposed to Mundaú lagoon have low oxygen uptake capacity. (A) Representative experiment where the lines represent oxygen consumption by human erythrocytes (HEry) of the Control and Exposed groups. Arrow indicates addition of HEry. (B) Quantification of the maximum oxygen uptake capacity during 10 s. The experiments were performed in duplicate. Control: 217 ± 62.16 vs. Exposed: 124.7 ± 50.45 nmol $O_2$ $min^{-1}$ $mg^{-1}$ protein, adjusted $****p > 0.0001$ . With n = 32 (exposed) and n= 10 (control). $p<0.05$. mean is ± SD using Student's t test for unpaired samples.

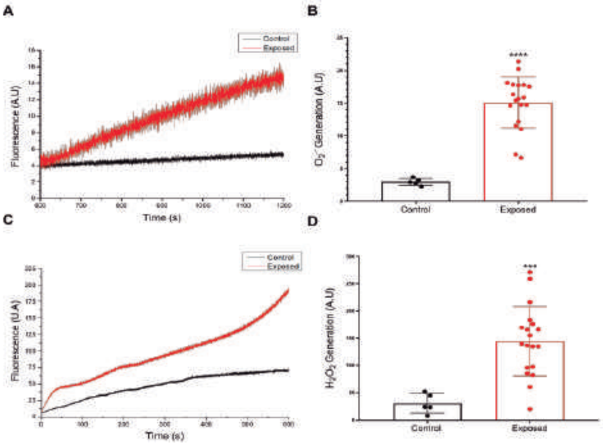

**Fig. 2.** Environmental exposure to Mundaú lagoon increases the production of reactive oxygen species in lymphomononuclear cells of exposed volunteers. (A) Representative experiment where lines show the production of cytosolic superoxide radical anion from PBMCs solated from Control and Exposed volunteers. (B) Quantification in arbitrary units (A.U.) of $O_2^{\bullet-}$ generation, with $***p<0.0001$ (C) Representative experiment where lines of the production of $H_2O_2$ of PBMCs isolated from Control and Exposed volunteers. (D) Quantification in arbitrary units (A.U.) of $H_2O_2$ generation, with $***p= 0.0008$. The experiments were perfomed in duplicate. With n = 31 (exposed) and n= 6 (control). $p<0.05$. mean is ± SD using Student's t test for unpaired samples.

## Acknowledgments

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**Área: BIO** **Nº de Inscrição: 00250**

# Identification and purification of a lectin from leaves of *Jatropha multifida* L. (Malpighiales: Euphorbiaceae)

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Palavras Chave: *(Merthiolate, Protein, Purification).*

## Highlights

Lectins are proteins that have many biotecnological applications. A glucose-binding lectin was isolated from leaves of *Jatropha multifida,* a plant known as merthiolate.

## Resumo/Abstract

*Jatropha multifida* is used in folk medicine as a healer for the treatment of oral thrush, gonorrhea, fever, arthritis, wounds and infections. Popularly known as merthiolate, it is a plant that belongs to the Euphorbiaceae family. Lectins are proteins capable of binding to carbohydrates and exerting various biological activities such as antimicrobial, insecticide, antitumor and immunomodulatory. The present study aimed to identify, isolate and characterize a lectin extracted from the leaves of *J. multifida*. Proteins were extracted from leaf by homogenization (16 h, 4 ° C) in three different solutions: 0.15 M NaCl, 50 mM Tris HCl pH 8.0 and 50 mM sodium phosphate buffer pH 7.2. Extraction with 50 mM Tris HCl pH 8.0 showed the highest hemagglutinating activity (AH: 512) as well as the highest protein content (3.15 mg / mL) and higher specific hemagglutinating activity (AHE: 162.44). Confirmation of the presence of lectin was made by the carbohydrate and glycoprotein inhibition of HA, which showed higher specificity to glucose. The obtained extract was treated with ammonium sulfate in different concentrations (0-20%, 20-40%, 40-60% and 60-80%) for protein fractionation and the 0-20% fraction was the only one that presented HA (2048). The 0-20% fraction was subjected to chitin column chromatography equilibrated with 0.15 M NaCl. 2 mL fractions were collected and evaluated for absorbance at 280 nm and HA. A single active protein peak obtained with the 0.5 M acetic acid eluent was pooled and dialyzed against Milli-Q water and 50 mM Tris HCl pH 8.0 for 6 h. To verify the purity of lectin, the sample was analyzed by electrophoretic method in 10% polyacrylamide gel under denaturing conditions, using sodium dodecyl sulfate, and in the presence and absence of reducing agent, where it was possible to visualize a single protein band in the absence of reducing agent. In conclusion, *J. multifida* leaves are source of glucose-binding lectin.

## Agradecimentos/Acknowledgments

Conselho Nacional de Desenvolvimento Científico e Tecnológico – CNPq

**Área: BIO**

# IDENTIFICATION OF NEW INHIBITORS OF NUCLEOSÍDE HYDROLASE ENZYME FROM *LEISHMANIA DONOVANI* USING A NEW SCREENING ASSAY

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Keywords: *Leishmania donovani, enzyme immobilization, liquid chromatography, screening assay, enzyme inhibitors.*

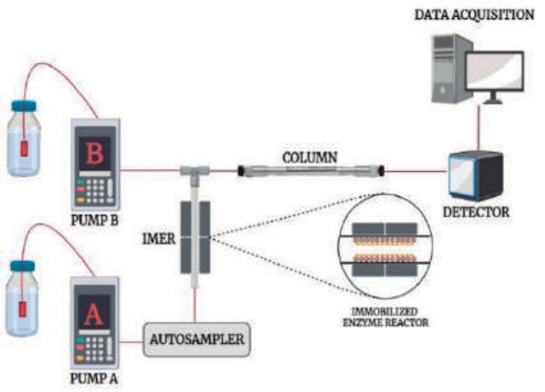
## Highlights

The activity of immobilized *Ld*NH enzyme was monitored on flow by liquid chromatography. 12 synthetic oxoquinoline ribonucleosides were screened and identified as *Ld*NH inhibitors.

## Abstract

Leishmaniasis are neglected diseases that affect some of the poorest people in the world. Visceral leishmaniasis is considered the most dangerous form of this disease and can be fatal. The high cost of drugs used for its treatment and the emergence of resistance from parasites evidences the need to develop new, effective, and less toxic treatments. Nucleoside hydrolase (NH) from *Leishmania donovani*, one of the protozoa that can cause visceral leishmaniasis, is a key enzyme in the purine salvage pathway, which is fundamental for biosynthesis of its DNA and RNA [1]. The *Ld*NH enzyme catalyzes the hydrolysis of the N-glycosidic bond of ribonucleosides, such as inosine, leading to the formation of a free ribose and corresponding nitrogenous bases, such as hypoxanthine.

In this work, the *Ld*NH enzyme was covalently immobilized on magnetic particles and trapped in a TFE Teflon tube (0.3 mm i.d. x 1.58 mm o.d.; 10 cm), furnishing an IMER (immobilized enzyme reactor) which was inserted in the first dimension of a chromatographic system. The chromatographic separation of the substrate (inosine) and the product (hypoxanthine) was conducted using an Eclipse XBD C18 Agilent column (150 x 4.6 mm) in the second dimension of the LC system and as mobile phase an aqueous solution of triethylamine (1% v/v, pH 6.0 acidified with AcOH)/Methanol (95:5), 0.8 mL.min$^{-1}$ and $\lambda = 249$ nm (Scheme 1). The proposed analytical method was validated and employed to monitor the *Ld*NH activity on flow by the direct quantification of hypoxanthine furnishing automation and reliability. *Ld*NH-IMER was characterized through kinetic assays yielding a $K_M$ 2079,25 ± 87,11 µmol.L$^{-1}$ for the inosine substrate. The developed activity assay was employed in the inhibitors screening in a library of 12 synthetic oxoquinoline ribonucleosides. First, the percentage inhibition at 200 µmol.L$^{-1}$ was assessed. In that step, all the compounds exhibited more than 70% of inhibition of the *Ld*NH-IMER activity. Then, the inhibitory capacities (IC$_{50}$) for the new inhibitors were determined varying the inhibitor concentration at a fixed substrate concentration. By plotting dose-response curves, IC$_{50}$ in the range of 72,7582 ± 8,5280 a 311,6576 ± 33,9593 µmol.L$^{-1}$ were obtained. In the next experiments, the inhibition mechanism and Ki will be assessed. Therefore, this work describes the identification of 12 new oxoquinoline ribonucleosides as *Ld*NH inhibitors using a new, reliable, and automated screening assay.



Scheme 1–Scheme referring to the on-flow chromatographic method.

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## Acknowledgments

FAPERJ, CNPq and CAPES.

**Área:** ____________________

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

# Inducing cytotoxic effects in murine skin cell line by photochemoterapy approach using ruthenium meso-substituted porphyrin complex

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Keywords: Photobiology of ruthenium complex, Photochemotherapy of ruthenium complex, nitrosyl ruthenium complex.

## Highlights

Ruthenium-based photosensitizers combined with photodynamic therapy have potential for cancer treatment.

The meso-substituted porphyrin ruthenium only presented cytotoxic for skin cells in the presence of irradiation.

## Resumo/Abstract

Cancer is one of the world's deadliest diseases despite currently advances in treatment. Skin cancer is the most prevalent form in the population. Traditional cancer therapies have limitations and undesirable side effects for patients. Therefore, in the last years photodynamic therapy (PDT) has gained popularity as a viable treatment option because it is more specific and has fewer adverse effects. This therapy requires the use of a photosensitizing agent, which is later activated by light at a specific wavelength. Currently, there are already approved photosensitizer agents for cancer treatment, such as Photofrin®, which is a porphyrin photosensitizer, but unfortunately it has some limitations. Therefore, to overcome these limitations and optimize the treatment of cancer, new molecules have been synthesized, many of which involve the combination of agents with already known antitumor potential, such as ruthenium complexes, together with photosensitizing agents and other molecules, such as nitric oxide (NO), which is well known to have different biological effects, such as antitumor potential when in high concentrations. The goal of this work was to analyze the cytotoxic effect of a new photosensitizer candidate, a meso-substituted porphyrin with ruthenium complexes, the TPyP-*meso*-$\{[Ru(bpy)_2(NO_2)](PF_6)_4\}_4$, abbreviated as $RuNO_2TPyP$, in the presence and absence of irradiation on tumor and non-tumor skin cells, of the L929 (murine fibroblast) and B16F10 (murine melanoma) cell lines, *in vitro* using the MTT method. This novel complex was designed to combine the production of singlet oxygen and the release of NO to evaluate the effects on cells between those two radicals. The results showed that the complex, after 4 h of treatment followed by PDT (415 nm, 4 $J.cm^{-2}$) in the absence of light, does not present toxicity in any of the cell lines studied with the concentrations tested (0-50 μM). However, high cytotoxicity when the cells are irradiated is observed in both cell lines, with $IC_{50}$ values less than 0.5 μM. We believe that the presence of cytotoxicity only after irradiation is due to the generation of singlet oxygen and the release of nitric oxide at the time of irradiation, so metal-based photosensitizers combined with PDT have a lot of potential in the treatment of cancer for ensuring a greater targeting of treatment, therefore enabling the reduction of traditional adverse effects. To continue the investigations, the group is currently conducting research on the complex's mechanism of action.

## Agradecimentos/Acknowledgments

This work was supported by FAPESP (grant 2020/03367-6; 2019/19448-8), CAPES (grant 88887.481871/2020-00), CNPq and FCFRP-USP

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

# Metabolomic evaluation of serum samples from newborns with neurological alterations caused by Zika virus

**Estéfane C. Nunes (PG),[1] Taiane E. S. Pereira (IC),[1] Ana Maria B. de Filipis (PQ),[2] Fernanda K. Barreto (PQ)[3], Isadora C. de Siqueira (PQ)[4], Gisele A. B. Canuto (PQ),[1*]**

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Palavras Chave: *Zika vírus, Metabolômica, Microcefalia, Alterações neurológicas,GC-MS.*

## Highlights

Metabolomics provides insights into the correlation between Zika infection and teratogenic effects.
Alterations in carbohydrate levels are correlated to abnormal fetal brain development.

## Resumo/Abstract

Zika is an arbovirus transmitted by the *Aedes aegypti* mosquito. The zika virus infection was associated with the development of neurological clinical complications, including fetal abnormalities and microcephaly[1,2]. Some studies showed that the infection could alter cellular metabolism, and the virus crosses the placental barrier, causing damage to fetal brain development[2]. Little is known regarding the metabolic profile during infection and its consequences, such as microcephaly. Thus, this work aimed was to evaluate the metabolic alterations in blood serum samples from newborns using an untargeted metabolomics approach. Three groups were evaluated: i) zika-positive with microcephaly (ZPMP), ii) zika-positive without microcephaly (ZPMN), and iii) zika-negative (ZNMN, control). Metabolomics analysis was performed using Gas Chromatography hyphenated to Mass Spectrometry. Sample treatment included protein precipitation with isopropanol, followed by derivatization (oximation and silylation reactions). The generated data were processed in XCMS software for peak picking and alignment. Discriminant entities were found using appropriate multivariate and univariate methods. The metabolite identification was carried out in the Automated Mass Spectral Deconvolution and Identification System after retention index and retention time analysis. Our results[4] showed some multifactorial implications in microcephaly development and viral replication. Sixteen metabolites and chemical classes showed significant statistical differences between comparisons. Alterations in amino acids and carbohydrates levels were correlated to Glycolysis and Gluconeogenesis metabolic pathways. Glycolysis has been associated with viral replication, and deficiencies in carbohydrates levels may be related to impaired brain development[4]. Here, we found lower levels of aldohexoses and sugar alcohols in ZPMP compared to ZPMN (microcephaly study) and ZPMP *vs.* ZMNM (infection and microcephaly evaluation). Amino acids are a source of energy and exert essential biological functions. We observed an expected increase in L-serine and L-threonine correlated to the microcephaly condition. This original work provides new insights and relevant metabolic alterations to the comprehension of Zika virus infection and consequent microcephaly.

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## Agradecimentos/Acknowledgments

The EU Horizon 2020 through ZikaPlan, CAPES and CNPq for fellowships, and LEPETRO-UFBA to provide the infrastructure for GC-MS analysis.

**Área: BIO** **Nº de Inscrição: 01382**

# Nitroso-BODIPY as a selective fluorescent probe to glutathione determination

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Palavras Chave: BODIPY, Fluorescent probe, Reduced glutathione, Thiols.

## Highlights

In this work, we describe an application of nitroso-BODIPY dye as a fluorescent probe for a selective determination of reduced glutathione in physiological conditions.

## Resumo/Abstract

BODIPYs play an important role in biological sciences and chemical biology as chemosensors and biological markers. Nitroso-BODIPYs were synthesized and characterized[1]. Considering that the nitroso group is reactive towards thiols, leading to a fluorescent reduced product, the application of the synthesized nitroso-BODIPY in the analysis of some biothiols was studied[1]. As such, the present work describes the use of 3-nitrosyl-8-(2,6-dichlorophenyl)-BODIPY. The emission spectrum of the probe at pH 7.4 (phosphate buffer), in the presence of reduced glutathione (50 µM) (Fig. 1A) was more intense, compared to N-acetyl cysteine (NAC) and cysteine (CYS), revealing a selectivity for this biothiol. The influences of pH, nature of buffers (Fig. 1B), were analyzed with the probe (5 µM), in the presence of reduced glutathione (10 µM). The best reaction conditions for the analysis were obtained: pH 6.5, Britton-Robinson buffer (50 mM). Three different concentrations of GSH (2.5, 5 and 10 µM) (Fig. 1C) were used and a linear relation between fluorescent intensity and GSH concentration up to 5 µM was obtained. The present results showed the potential application of nitroso-BODIPY dyes as fluorescent probes (off-on process) for analytical purposes. They encourage us to continue studying this class of compounds for further analytical applications. Additionally, other chemical and physical parameters are being optimized for the application of this probe in the quantification of GSH in real samples.

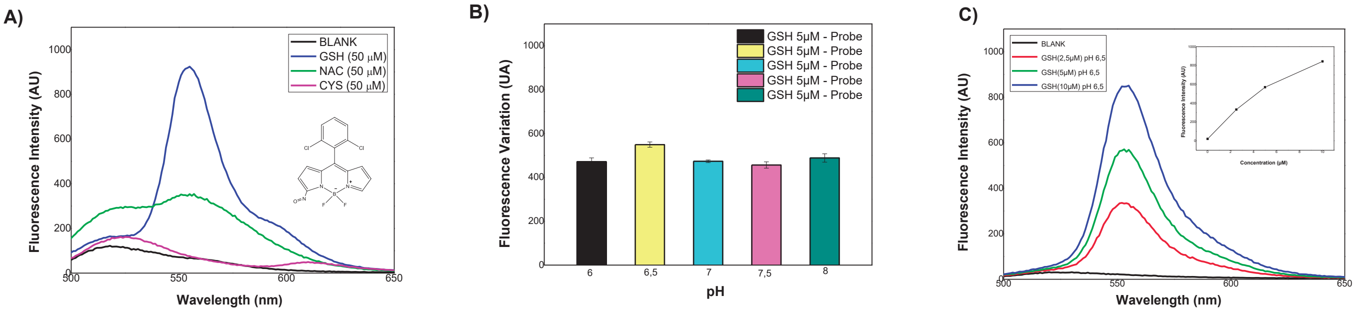

**Fig. 1**. (A) Nitroso-BODIPY (10 µM) in the presence of glutathione (GSH), N-acetylcysteine (NAC) and cysteine (CYS) (all at 50 µM), (B) Evaluation of pH influence with Britton-Robinson buffer using reduced glutathione and (C) Nitroso-BODIPY probe at pH 6.5 (Britton-Robinson buffer) in the presence of GSH at concentrations of 2.5, 5 and 10 µM.

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## Agradecimentos/Acknowledgments

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**Área: BIO**

# RAPID ISOLATION OF NUCLEOSIDE HYDROLASE LIGANDS THROUGH LIGAND FISHING ASSAY

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Palavras Chave: *Nucleoside Hydrolase, Ligand fishing, Moringa oleifera, Leishmania donovani*.

## Highlights

Ligand fishing assay was applied to screen potential Nucleoside Hydrolase from *Leishmania donovani* (*Ld*NH) inhibitors on *M. oleifera* flower extract. Seven out of ten identified ligands were elucidated by UHPLC-HRMS/MS.

## Resumo/Abstract

*Leishmania donovani* causes the most lethal form of leishmaniases, visceral leishmaniasis (VL). The enzyme Nucleoside Hydrolase (NH) acts on a vital pathway for this protozoan – purine salvage pathway. On top of that, the *Ld*NH is considered a potential target for the development of new leishmaniasis chemotherapy.[1,2] In previous work, it was performed a proof-of-concept experiment to validate the use of ligand fishing assay to recognize ligands from a compounds mixture.[3] In this work, the same affinity assay was applied to isolate potential LdNH inhibitors from a complex mixture – *Moringa oleifera* flower extract. The ligand fishing assay (Fig. 1) was performed using the following condition: 5 mg of magnetic beads-*Ld*NH were suspended in 1 mL of the extract (4 mg.mL$^{-1}$) with incubation of 10 min; for the washing step, it was used a 5 mM ammonium acetate buffer (pH 7.4); for the elution step was used a solution of acetate buffer and methanol (60:40). All supernatants were analyzed by UHPLC-HRMS/MS using a Supelco Ascentis C18 column (25 cm x 0.46 cm, 5 µm); and as mobile phase a mixture of formic acid 0.1% (A) and MeOH (B) at a flow rate of 0.8 mL.min$^{-1}$; injection volume of 20 µL. The gradient program was: 0-5 min, 3% B; 5-40 min, 3-97% B; 40-45 min, 97% B; 45-50 min, 97-3% B; 50-60 min, 3% B. The analyses of the crude extract and all the supernatants after the incubation with the active and inactive *Ld*NH (control assay) indicated missing peaks (Fig. 2) referring to compounds selectively retained in the active *Ld*NH incubation. Seven out of the ten identified missing peaks had their structures proposed by UHPLC-HRMS/MS through the similarity using virtual libraries as GNPS, Sirius, PubChem, and MassBank as palatinose, adenosine, 3-p-coumaroylquinic acid, 4-p-coumaroylquinic acid, hyperoside, quercetin-3-*O*-malonyl glycoside, and kaempferol-3-*O*-galactoside.

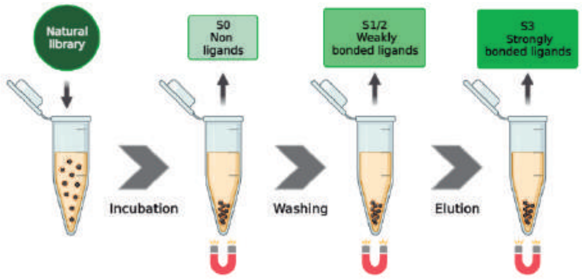

**Figure 1**: Scheme of the screening assay

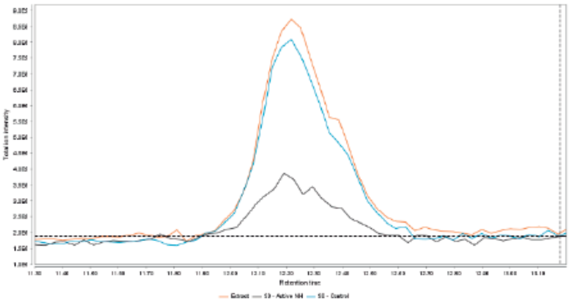

**Figure 2**: XIC of adenosine (m/z 268.1042) for the *M. oleifera* extract (orange), S0 of the active *Ld*NH (black), and S0 of control (blue)

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## Agradecimentos/Acknowledgments

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**Área: BIO**

# Recombinant insect chitinases: DNA cloning and the enzymes expression in *Pichia pastoris*

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*Keywords: Chitinases , Gene cloning, Protein expression, Insect group II chitinase*

## Highlights

Total RNA extracted from pupae of *Atta sexdens* ant; DNA cloning and enzymes expression in *Pichia pastoris* KM71H strain; three polypeptide chains containing different catalytic sites and chitin-binding domain presented chitinase activity.

## Resumo/Abstract

Chitin, a polymer formed by β-1,4-N-acetylglucosamine monomers, is degraded by enzymes called chitinases, which are found in a wide variety of organisms such as bacteria, fungi, insects, plants, and animals[1]. Chitinases are involved in many physiological processes and the defense against pathogens, thus showing potential fungicidal and insecticidal activities[2]. Insect chitinases which belong to group II have 4-5 catalytic domains (chit) and 4-7 carbohydrate biding modules (CBM)[1]. The purpose of the present work was to obtain three recombinant proteins from *Atta sexdens* ants for future studies of their fungicidal activities. The intended proteins are different combinations of catalytic domains and CBMs of group-II chitinase encoded by an *A. sexdens* cDNA: AsChtII-C2B3 (1 chit + 3 CBM), AsChtII-C3C4 (2 chit) and AsChtII-B1C5 (1 CBM + 1 chit). Since the genome of the *A. sexdens* is not available, the sequence of a homologous cDNA *Acromyrmex echinator* was used for primer design. The PCR products were cloned into the pJET vector and propagated in *E. coli* DH5α. The plasmids were digested with the appropriate restriction enzymes and the amplicons were sub-cloned into the pPICZαA vector for recombinant expression in *Pichia pastoris*. To induce protein expression, 1% methanol was added to the cultures every day for six days. The proteins were precipitated from the culture supernatants with 80% ammonium sulphate. The three proteins were successfully expressed in the extracellular medium and with molecular masses close to the expected, as determined by SDS-PAGE. The catalytic activity of the enzymes was investigated using colloidal chitin as the substrate and product formation was assessed using the DNS method. Our results showed that these enzymes were able to hydrolyzed colloidal chitin substrate. Since then chitin is material found in the fungal cell walls, these recombinants chitinases will be evaluated their possible fungicidal activity against different pathogenic fungi *Aspergilus fumigatus* and *Candida albicans*.

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## Agradecimentos/Acknowledgments

This work was supported by the FAPESP (2018/06297-9), CNPq (grant number 141424/2020-6) and CAPES – Finance Code 001.

**Área: <u>BIO</u>**
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**Nº de Inscrição: <u>00555</u>**
*(Inserir o número de inscrição do autor que fez a submissão)*

# Synergistic anticancer effect of singlet oxygen and nitric oxide in photodynamic therapy. Application using ruthenium-phthalocyanine compounds

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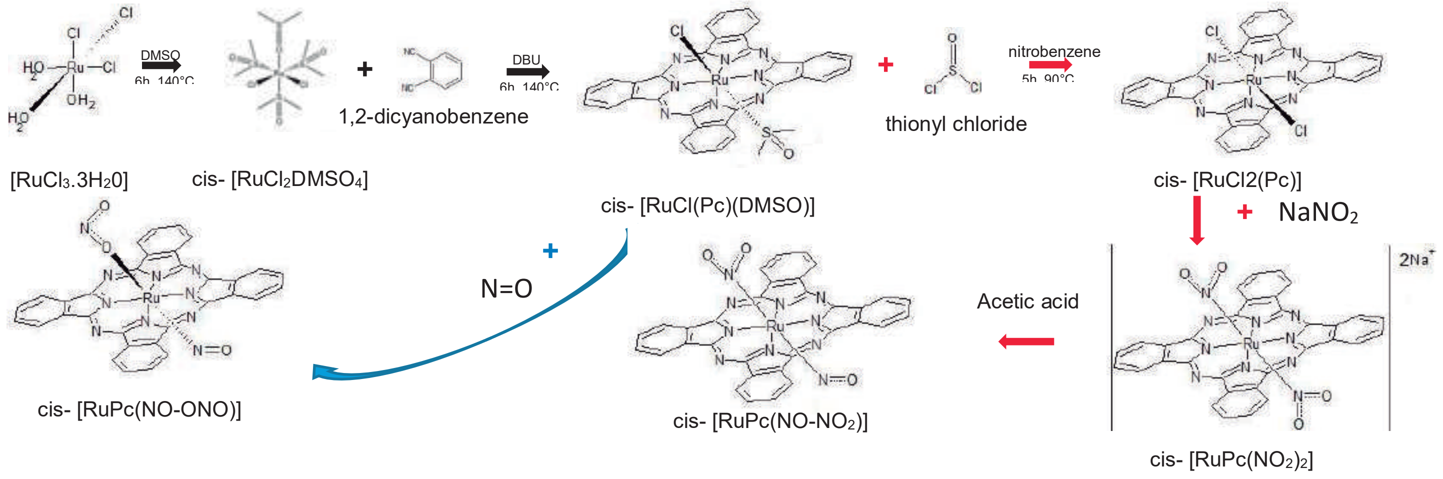
Palavras Chave: ruthenium; cytotoxicity; nitric oxide; photodynamic therapy.

## Highlights

Activity potentiated by the synergism between singlet oxygen and nitric oxide, It seems to be promising within photodynamic therapy applied to cancer

## Resumo/Abstract

Cutaneous melanoma, although less incident, is the major cause of mortality among skin tumors, this is partly due to the inefficiency of current systemic treatments. In the search for new compounds that can act in cancer chemotherapy, metal complexes have gained great attention, for the wide range of structure geometries, oxidation states, and mechanisms that these can Act. Among these metallic compounds, ruthenium complexes have stood out positively, especially after some complexes have entered clinical testing, an antitumor agent. Photodynamic therapy (PDT) is considered promising within the anti-tumor approach, mainly due to its intrinsic selectivity. Despite this, some factors commonly limit the success of this technique, such low availability of molecular oxygen. One direction that can help this limiting factor is the release of other chemical species in addition to the production of singlet oxygen, thus resulting in a synergistic action. Among these radicals, nitric oxide (NO) is considered promising, considering that it is involved in multiple molecular pathways and physiological responses. In view of the above, the present work aimed to synthesize and characterize two NO-donor ruthenium-Pc (phthalocyanine) complexes, cis-[RuPc(NO-ONO)] and cis- [RuPc(NO-$NO_2$)] (scheme 1), to perform the yield calculation quantum of singlet oxygen, as well as their cytotoxic evaluation in the melanoma line A375, using the MTT technique. The UV / Vis and FTIR spectroscopic techniques were used for characterization. The MTT test revealed greater toxicity of the cis-[RuPc(NO-ONO)] compound when incubated for 4 hours and irradiated at a dose of 4 J/$cm^2$, this is probably due to the higher production of singlet oxygen in this complex and possible difference in the release kinetics of NO.



Scheme 1: Synthesis route of cis- [RuPc (NO-$NO_2$)] and cis- [RuPc (NO-ONO)] complexes.

## Agradecimentos/Acknowledgments

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

**Nº de Inscrição:286**
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# Synthesis andpharmacologicalanti-inflammatoryevaluation of new 1,2,3-triazolic-sulfonylhydrazonic derivatives

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Palavras Chave: 1,2,3-triazole, oxidation, sulfonylhydrazone, diazotation, click reaction, inflammation

## Highlights

Synthesis of 1,2,3-triazoles with unique structure using a convergent five-step synthesis with good yields.
Molecules showed no toxicity in animal models and are being analyzed in *in vivo* inflammation models.

## Abstract

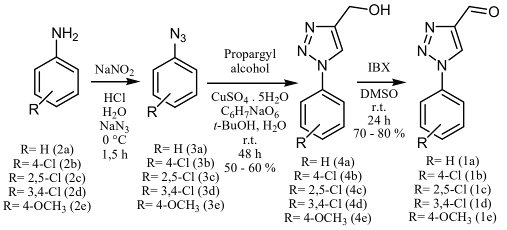
Despite benefit of inflammation to the body's homeostasis, chronic inflammation is an exacerbated and unregulated response. Thus, inflammation itself has deleterious effects to organism, being associated with a large number of diseases[1]. Thus, there is an urgent need for new and more effective anti-inflammatory drugs.

In this scenario, the objective of this work is synthesis and evaluation of anti-inflammatory action of new sulfonylhydrazones derivatives.

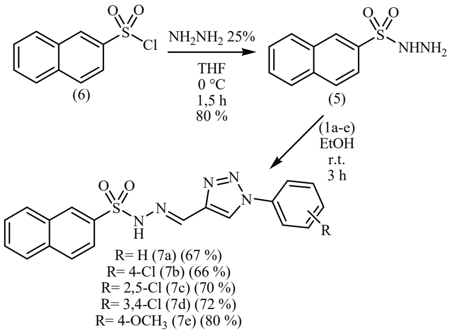
Sulfonylhydrazones were obtained in five-step convergent synthesis (Schemes 1 to 2). 1,2,3-triazole-aldehydes (**1a-e**) were obtained through a three-step linear synthesis (Scheme 1). Functionalized anilines (**2a-e**) underwent a diazotation reaction in the presence of sodium nitrite, hydrochloric acid, water and sodium azide at 0 °C to generate the corresponding azides (**3a-e**)[2]. Then, azides (**3a-e**) and propargyl alcohol reacted in a cycloaddition reaction to build functionalized 1,2,3-triazole ring with a primary alcohol (**4a-e**) in the presence of copper sulfate pentrahydrate, sodium ascorbate, tert-butanol and water at room temperature[3]. Finally, aldehydes (**1a-e**) were obtained through partial oxidation of primary alcohols (**4a-e**) by adding IBX in dimethylsulfoxide at room temperature[4].

In parallel, 2-naphthalenesulfonyl chloride (**6**) reacted with hydrazine hydrate 25% in tetrahydrofuran at 0 °C to generate 2-sulfonylnaphthoidrazide (**5**)[5] (Scheme 2). Finally, 2-sulfonylnaftoidrazide (**5**) was added, individually, to aldehydes (**1a-e**) in acid catalysis, ethanol and room temperature to generate the sulfonylhydrazones (**7a-e**)[5] in good yields (Scheme 2).

Next, molecules were evaluated for toxicity in mice at a concentration of 100 mmol / kg[6]. Fortunately, all molecules did not show acute toxicity.



**Scheme 1**. Synthesis of 1,2,3-triazole aldehydes (**1a-e**).



**Scheme 2**. Synthesis of sulfonylhydrazide (**5**) and sulfonylhydrazones (**7a-e**).

In conclusion, 5 molecules with new structure were synthesized using classic Organic Chemistry reactions. Regarding pharmacological evaluation, they did not present acute toxicity and are being evaluated in animal models of inflammation.

[1] Ward, S.G. *Brit. J. Pharmacol.*, **2008**, *153*, S5. [2] Richardson S.K. et al. *Tetrahedron Lett.*, **1987**, 43, 2925. [3] Rostovtsev V.V. et al. *Angew. Chem.*, **2002**, 114, 2708. [4] Frigerio, M. *Org. Chem.*, **1995**, *60*, 7272. [5] Lima, P.C. et al. *Eur. J. Med. Chem.*, **2000**, *35*, 187. [6] Cordeiro, N.M. et al. *Biomed Pharmacother.* **2020**, 23, 109739.

## Acknowledgments

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# Whole cells of *Geotrichum candidum* CCT-1205 applied to the Baeyer-Villiger reaction for the synthesis of ε-caprolactone: Dependence with pH and concentration

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Palavras Chave: *Geotrichum candidum*, Caprolactone, Baeyer-Villiger monooxygenase (BVMO), Alcohol dehydrogenase (ADH)

## Highlights

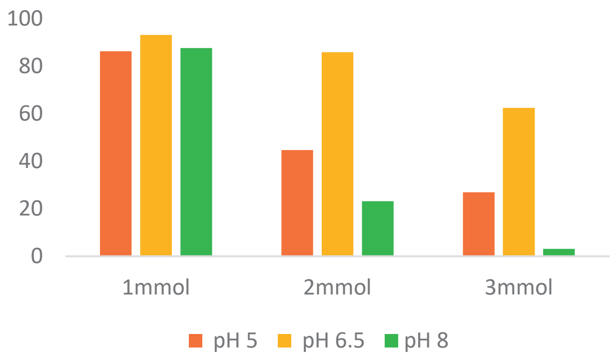
ε -Caprolactone was rapidly obtained from cyclohexanone using Geotrichum candidum. The Baeyer–Villiger monooxygenase (BVMO) enzyme was predominant and most active in pH=6,5 and low concentration.

## Abstract

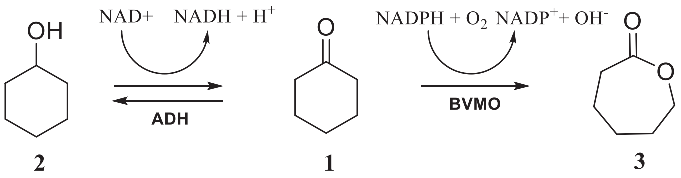
Baeyer-Villiger (BV) oxidation is one of the most important synthesis strategies in fine chemistry, especially in the production of building blocks of optically active lactones with relevant biological applications. In this work we studied the effect of variation of pH and concentration in the conversion of cyclohexanone (**1**) in caprolactone (**3**), were studied concentration of 1, 2 and 3mmol and of pH of 5, 6,5 and 8 (**Figure 1**).

The reaction was realized in 6 hours and analyzed by gas chromatography, as seen in Figure 1, the best result occurs when the reaction is performed in low concentration (1mmol) and the pH 6,5. The mechanism of reaction is well established in literature as shown in Scheme 1.

**Figure 1:** Effect of pH and concentration on the conversion of cyclohexanone to caprolactone



**Scheme 1:** Mechanism of caprolactone formation reaction



The oxidation of BV by the enzyme BVMO occurs simultaneously with the reduction/oxidation of the balance by the enzyme alcohol dehydrogenase (ADH) and the intermediate cyclohexanol (**2**) was observed as a by-product. The conversion values obtained for cyclohexanol were 5.27%, 12.5% and 4.31% at concentrations of 1, 2 and 3 mmol at the ideal pH (pH 6.5).

## Acknowledgments

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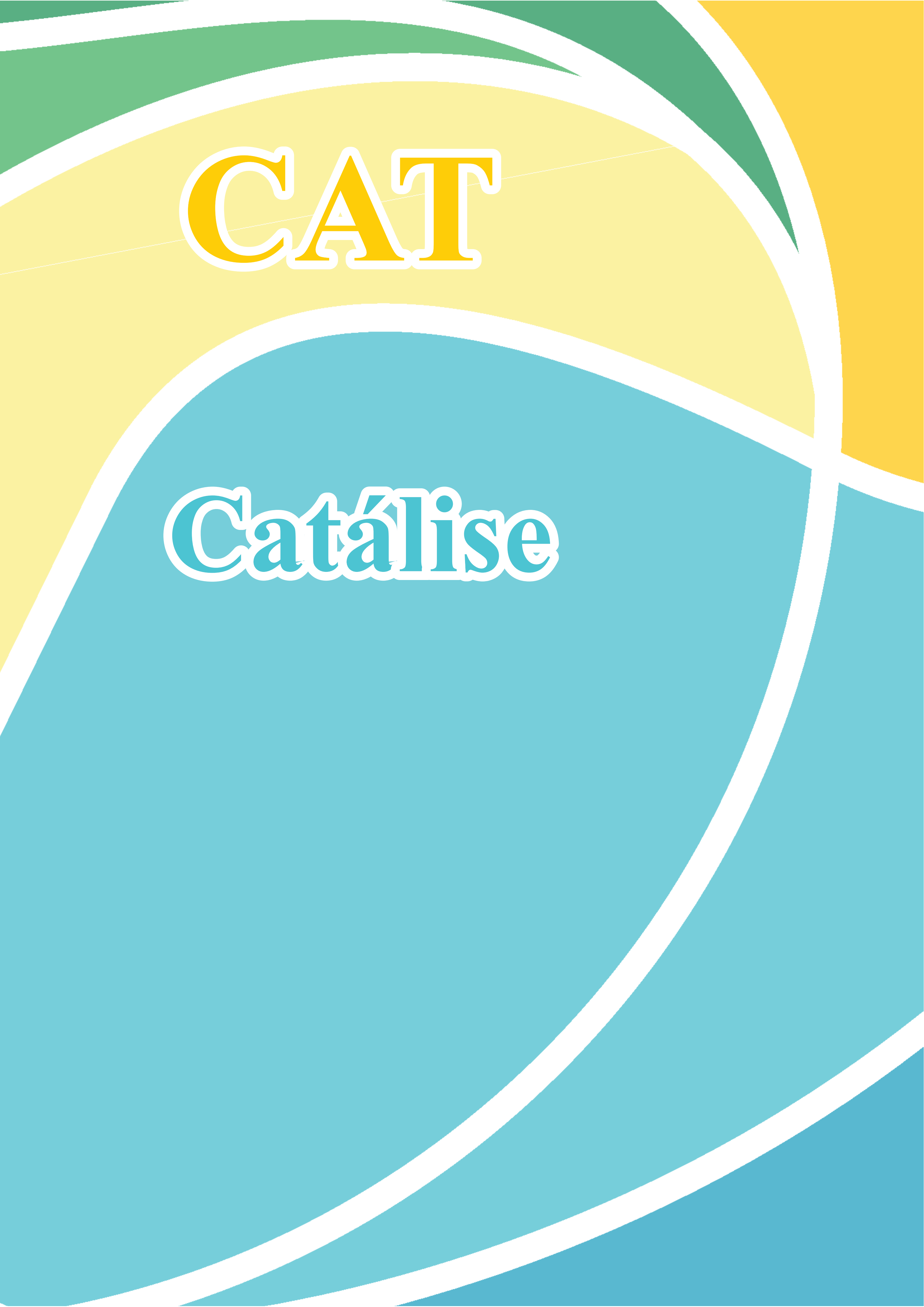
# CAT

## Catálise



**Área: CAT**

# Application of heterogeneous catalysts based on MOFs in the selective oxidation of cyclohexane under mild reaction conditions

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Keywords: *Metal-Organic Frameworks (MOFs); Heterogeneous Catalysis; Valorisation of Alkanes; Cyclohexane Oxidation.*

## Highlights

The MOF UiO-66(Zr) based catalyst was prepared by solvent-assisted cold impregnation using $FeCl_3$. The catalysed cyclohexane oxidation showed 47% conversion with 8% cyclohexanol selectivity after 2h.

## Abstract

Cyclohexane oxidation is an important process for the polymer industry such as nylon. Currently, the reaction takes place with homogeneous catalysts based on cobalt salts or metallic boric acid (Conditions: T = 140-180°C and P = 10-20 bar) with low yield (KA oil, ketone + alcohol = 7%) due to the inertia of the C-H bonds and the over-oxidation of the products [1]. Some types of heterogeneous catalysts have been studied, however, they have not been applied on an industrial scale. Therefore, finding a heterogeneous catalyst that makes cyclohexane oxidation more selective and with the high yield of KA oil is still a challenge. In this context, metal-organic structures (MOFs) have received attention for their structural versatility and properties such as crystallinity, high porosity, and large surface area, which allow the construction of catalysts according to the desired application [2]. In this work, MOF UiO-66(Zr) was synthesized by solvothermal methods, the catalyst - Fe(III)-UiO-66(Zr) - was obtained from solvent-assisted impregnation of Fe(III) agglomerates using $FeCl_3$ and it was applied in the oxidation of cyclohexane with hydrogen peroxide ($H_2O_2$, 70% v/v). The PXRD analysis showed a shift in the characteristic peaks of the diffractogram of the Fe(III)-UiO-66(Zr) compared to the diffractogram obtained for the MOF UiO-66(Zr), which indicates the incorporation of Fe(III) clusters. Catalytic tests on a reduced scale showed that increasing the amount of catalyst increases KA oil yield and selectivity for cyclohexanol. Doubling the scale of the test with 30 mg of Fe(III)-UiO-66(Zr), it was observed that the conversion of cyclohexane was 47%, with a yield of 4% (quantified by GC-FID) KA oil and 8% selectivity for cyclohexanol in only 2 h reaction at 40 °C and atmospheric pressure. The low yield can be justified by the over-oxidation of the products, therefore, the reaction parameters will be optimized to avoid this phenomenon.

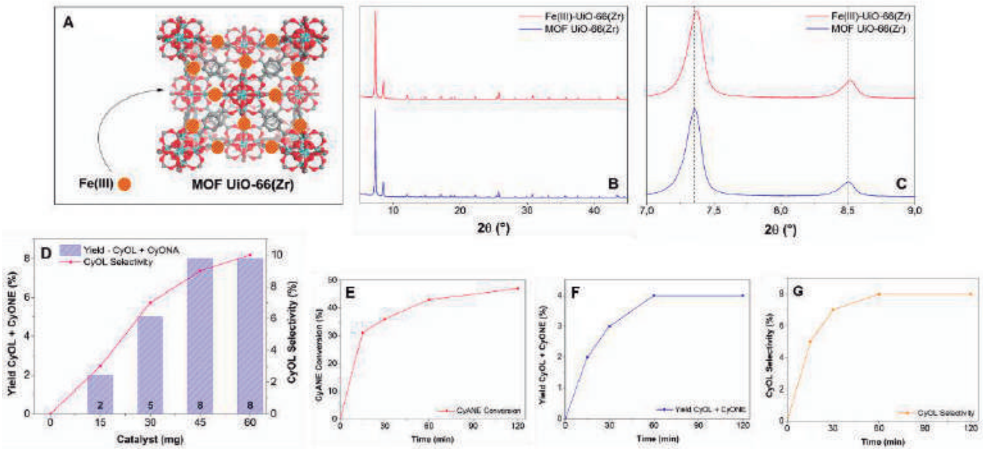

**Figure 1. A.** Synthesis of Fe(III)-UiO-66(Zr); **B.** PXRD of MOF-UiO-66(Zr) and Fe(III)-UiO-66(Zr); **C.** PXRD of MOF-UiO-66(Zr) and Fe(III)-UiO-66(Zr) amplified (2θ = 7,0-9,0°); **D.** Catalyst tests on a reduced scale with variation of the catalyst mass (**Conditions D:** 15, 30, 45, and 60 mg of Fe(III)-UiO-66(Zr), 2.75 mmol of CyANE, 5.27 mmol of $H_2O_2$ (70%, v/v), 2.0 mL of MeCN, T = 40 °C, magnetic stirring = 1000 RPM and t = 120 min); **E.** Conversion of CyANE; **F.** Yield of KA oil; **G.** Selectivity for CyOL. (**Conditions E, F, G):** 60 mg of Fe(III)-UiO-66(Zr), 5.50 mmol of CyANE, 10.54 of mmol $H_2O_2$ (70%, v/v), 4.0 mL of MeCN, T = 40 °C, magnetic stirring = 1000 RPM and t = 120 min).

[1] REISI, Bahareh et al. Synthesis and characterization of Pd-Ni catalysts supported on KIT-6 and their application in cyclohexane oxidation using molecular oxygen. **Journal of Industrial and Engineering Chemistry**, v. 102, p. 103-111, 2021;
[2] ZHANG, Yingmu; YANG, Xinyu; ZHOU, Hong-Cai. Synthesis of MOFs for heterogeneous catalysis via linker design. **Polyhedron**, v. 154, p. 189-201, 2018.

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**Área: ____CAT_____**

# Carbon nanotube-supported iron oxides catalysts for degradation of rhodamine B in wastewaters

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Palavras Chave: Rhodamine B , Carbon Nanotube, Catalysis, Fenton, Wastewater Treatment

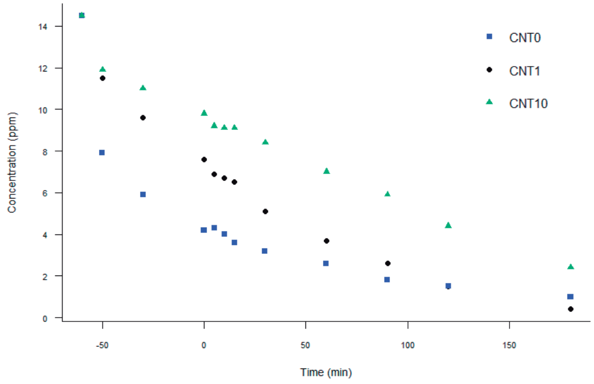
## Highlights

Carbon nanotube-supported iron oxide prepared by wet impregnation was investigated as a promising catalyst for Fenton degradation of rhodamine B wastewaters.

## Resumo/Abstract

Carbon nanotubes (CNT) are sp² carbon hexagonal lattice tubular structures that were first described in 1991 by S. Iijima. Since then, they have been gaining increasing attention for catalysis applications due to their chemical and thermal stability and electrical conductivity, besides their high specific surface areas. These properties increase the catalyst efficiency and durableness. Hence, this work aims to investigate CNT-supported iron oxide prepared by wet impregnation for Fenton degradation of rhodamine B (RhB), a persistent dye. This pollutant is often present in industrial wastewaters, giving an undesirable color, demanding its removal before being disposed of in natural waters. In pursuance of this goal, commercial carbon nanotubes (280-350 m$^2$/g) were impregnated with iron at different concentrations (1 and 10% w/w). UV-vis spectroscopy ($\lambda$=554 nm) was used to follow RhB removal using Fenton reaction over the catalysts. Sampling before hydrogen peroxide addition (t= 0 min) has shown high RhB adsorption capability for all catalysts, as shown in Fig. 1. The addition of iron increased this ability, depending on the amount. Pure CNT was able to remove up to 93% of RhB, a fact that can be related to the catalytic activity of oxygenated groups on the surface. Although iron oxide has been recognized as a classical Fenton catalyst[1], its addition did not improve the catalyst activity in the beginning of reaction. This suggests that iron oxide is covering the active sites (oxygenated groups) decreasing their activity. However, after 180 min of reaction, the CNT with 1% w/w of iron removed 97% of RhB, showing that iron oxide plays a role in the reaction. These results indicate that the oxygenated groups on CNT surface are catalytic sites more efficient than those of iron oxide at high concentration. However, at the end of reaction, when the RhB concentration is low, iron oxides are able to oxidize the pollutant even more. It can be concluded that efficient catalysts for RhB can be designed by combining the activity of surface groups of CNT and the amount of iron in the solids. The results showed that 1% is the most suitable concentration for the catalysts.

Fig 1. Rhodamine removal by Fe supported on carbon nanotubes



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**Área: CAT**

# Carbon Nitride-Based Materials: A Sustainable Catalyst for Biodiesel Production

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Keywords: *Biodiesel, Carbon Nitrides, Basic Catalysis, Transesterification Reactions, Solvent Free.*

## Highlights

- Carbon Nitride-Based Materials as a promising alternative heterogeneous catalyst in transesterification reactions.
- Syntheses and complete characterization of seven different carbon nitride-based materials.
- Basic sites are the main responsible for catalyzing the biodiesel production.

## Abstract

Biodiesel fuel production remains one of the most promising sustainable alternatives to non-renewable fossil fuels derived energy, such as conventional oil and diesel.[1] In this regard, heterogeneous catalysts have been extensively investigated as a suitable alternative catalyst for these reactions, since heterogeneous catalysts have the advantage of being recoverable and reusable.[1,2] In this work, it was used canola oil and methanol to produce biodiesel and glycerol with carbon nitride-based materials as catalysts. The synthesized materials were completely characterized by elemental analysis (CHN), ICP-OES, TGA, XRD, UV-Vis, FTIR, TEM and XPS. It was observed these materials presented different amounts of metals in their structures and the increases of metals quantity improve the yield of transesterification reactions (**Fig.1a**). In addition, as the transesterification of vegetable oil for biodiesel production can be catalyzed by acidic and basic sites, the titration of the catalysts was performed and it was proved that these reactions are catalyzed by basic sites, since the yield of these reactions increases with the number of basic sites (**Fig.1b**).

**Table 1.** Contents of C, H, N and metal obtained by elemental analysis and ICP-OES for the synthesized materials

| Materials | N (%) | C (%) | H (%) | $M_{total}$ (%) | C/N (molar) |
|---|---|---|---|---|---|
| H-PHI | 37.2 | 23.8 | 2.8 | 0.5 | 0.64 |
| mpg-$C_3N_4$ | 50.5 | 33.3 | 2.3 | 0.1 | 0.66 |
| PCN | 63.4 | 35.3 | 1.72 | 0.0 | 0.56 |
| Na-PHI | 40.1 | 26.0 | 2.11 | 7.3 | 0.75 |
| Mg-PHI | 40.5 | 26.6 | 2.6 | 5.4 | 0.66 |
| CN-OA-m | 45.4 | 29.7 | 1.88 | 8.3 | 0.76 |
| K-PHI | 40.7 | 26.5 | 1.96 | 10.0 | 0.76 |

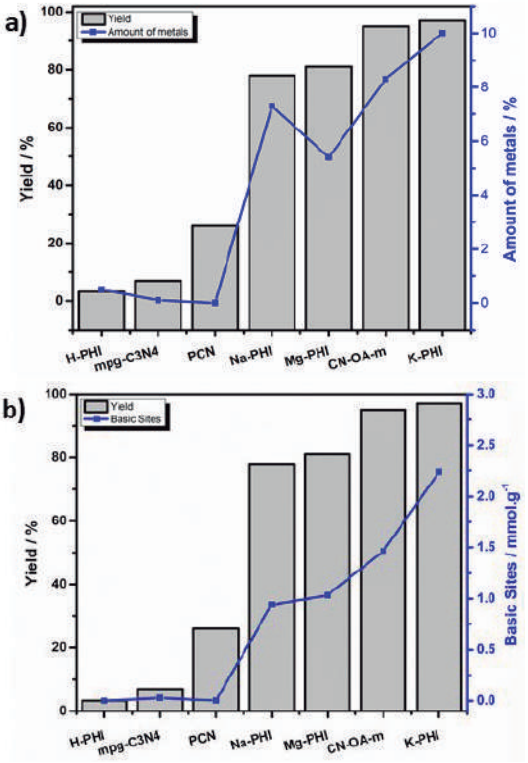

**Figure 1.** Biodiesel production vs **a)** amount of metals (%) and **b)** basic sites (mmol $g^{-1}$) present in the synthesized carbon nitride-based materials catalysts. Reaction conditions: 25 mg of catalyst, 1:30 of canola oil to methanol, 150 °C, 6h of reaction.

[1] Macina, A., *et al. J. Mater. Chem. A*, **7**, 23794 (2019); [2] de Medeiros, T. V., *et al. Nano Energy*, **78**,105306 (2020).

## Acknowledgments

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**Área: CAT**

# Catalytic Investigation of Antimony Species in the Esterification of Glycerol

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Keywords: *glycerol, acetines, esterification, antimony.*

## Highlights

- $SbCl_5$ and $SbCl_3$ were investigated in comparison to $Sb_2O_3$ and $Sb_2O_5$ in the acetylation of glycerol (GLY);
- $SbCl_3$ and $SbCl_5$ provided the best results;
- Use of $SbCl_5$ leads to a decrease of around 40 % of the activation energy.

## Resumo/Abstract

Biodiesel production generates huge amounts of glycerol (GLY) as co-product and esterification of GLY is considered a promising alternative [1]. In the study reported herein, $SbO_3$, $SbO_5$, $SbCl_3$ and $SbCl_5$. were evaluated in GLY acetylation, varying the catalyst concentration, molar ratio of the reagents, temperature and reaction time, with the aim of broadening the discussion around the behavior of antimony species as catalysts for this type of reaction. It is important to highlight that, to the best of our knowledge, this is the first time that this class of catalysts is evaluated in GLY acetylation to produce MA, DA and TA [2-3].

Figure 1 presents the experimental setup and Figure 2 shows the results obtained. In addition, comparison was made in the condition without catalyst. Noteworthy, for $SbCl_5$, total conversion in 15 min was observed with selectivity of 31, 47 and 22% for MA, DA and TA in 180 min, respectively.

The results obtained with $SbCl_5$ were satisfactory when compared to the other catalytic species tested as well as to data available in the literature. The result obtained with $SbCl_5$ at 0.0166 mmol (80 °C) showed the highest $k_{ap}$ value, as well as the highest yields for the main esters substituted (33%). However, it was possible to achieve 100% conversion even at 40 °C, using a concentration of 0.083 mmol of $SbCl_5$ (4.2% in relation to the GLY mass), and 91% with a concentration of 0.042 mmol of the catalyst, in 180 min of reaction. The $E_a$ for the GLY conversion in the absence of catalyst was estimated at 23.9 KJ mol$^{-1}$ and using $SbCl_5$ there was a reduction of approximately 50% (14.6 KJ mol$^{-1}$).

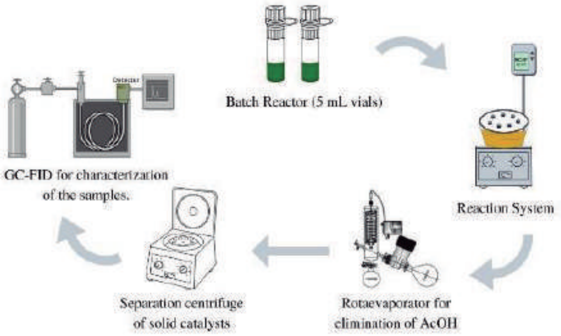
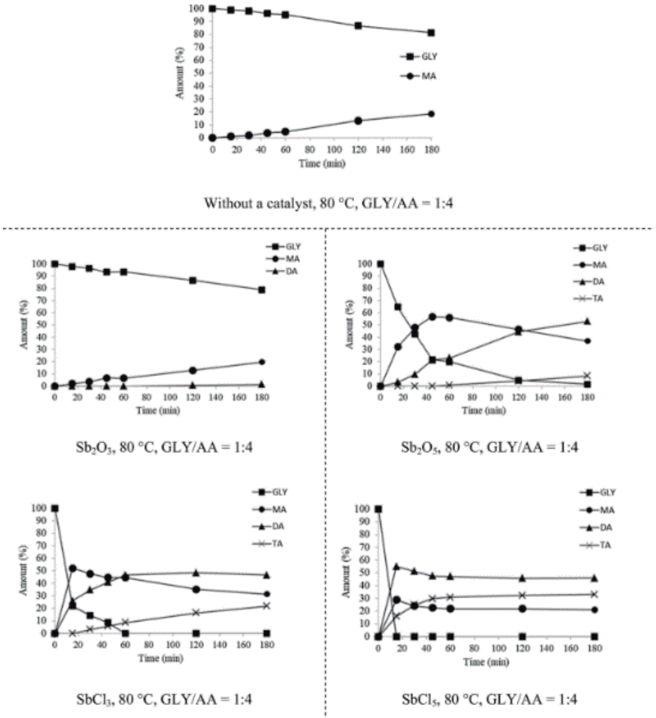


Fig 1. Experimental setup



Without a catalyst, 80 °C, GLY/AA = 1:4

$Sb_2O_3$, 80 °C, GLY/AA = 1:4

$Sb_2O_5$, 80 °C, GLY/AA = 1:4

$SbCl_3$, 80 °C, GLY/AA = 1:4

$SbCl_5$, 80 °C, GLY/AA = 1:4

Fig. 2 Esterification of GLY at 80 °C, as a function of reaction time (min), using a GLY/AcOH molar ratio of 1:4 in the absence of a catalyst and in the presence of 0.166 mmol of catalyst (errors were 0.8. 0.5, 0.7, and 0.4% for GLY, MA, DA, and TA, respectively).

[1] Hu W, Zhang Y, Huang Y, Wang J, Gao J, Xu J (2015) .J Energy Chem 24(5):632–636.
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INCT catálise
CAPES
PPGQB Programa de Pós-Graduação em Química e Biotecnologia
FAPEAL Fundação de Amparo à Pesquisa do Estado de Alagoas
CNPq

**Área: CAT** **Nº de Inscrição: 947**

# Cyanosilylation Reaction Catalyzed by Lanthanide Frameworks (Ln-MOFs).

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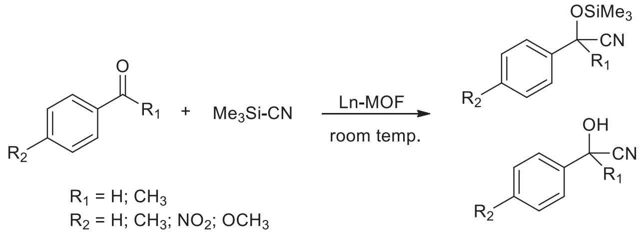
Key words: Cyanosilylation reaction, Catalysis, Lanthanides, Ketones, Aldehydes.

## Highlights

Solvent-free cyanosilylation reaction presented aldehyde selectivity for the catalyst [La(2-MeSBz)$_3$]. The reaction with ketones afforded low to moderated yields only with [Eu$_2$(Fum)$_3$(H$_2$O)$_4$]$_n$·3H$_2$O.

## Resumo/Abstract

The application of lanthanide based MOFs (Ln-MOFs) as heterogeneous catalysts has grown due to its stability, easy recovery and reuse, and in many cases its selectivity. The catalytic activity of [Eu$_2$(Fum)$_3$(H$_2$O)$_4$]$_n$·3H$_2$O (**1**) and [La(2-MeSBz)$_3$] (**2**) in the cyanosilylation reaction of aldehydes and ketones with trimethylsilyl cyanide (TMSCN) was studied (Scheme 1). Ln-MOF **1** was chosen due to the excellent results obtained in the reaction of aldehydes with potassium allyltrifluoroborate and framework **2** due to the presence of unsaturated La$^{3+}$ sites.



Scheme 1: Cyanosilylation reaction

The best results of reaction of 4-NO$_2$-benzaldehyde and TMSCN was in DCM and MeOH with a reduction in reaction time from 72 h (reaction without catalyst) to 4 and 3h with catalysts **1** and **2**. When benzaldehyde and 4MeO-benzaldehyde were tested in the presence of **2**, only traces of product were observed after 24h. A reduction in reaction time was observed in the solvent-free reactions for both catalysts, table 1, and the non-catalyzed reaction still showed 4-NO$_2$-benzaldehyde after 5h. Again, catalyst **2** presented shorter reaction times when compared to **1** and complete reaction conversion, due to the presence of unsaturated La$^{3+}$ sites. The scope of aromatic and aliphatic aldehydes is being investigated with catalyst **1**.

**Table 1**: Solvent-free cyanosilylation reaction catalyzed by Ln-MOF.

| **Substrate** | **Catalyst 1** Yield[a]; Time | **Catalyst 2** Yield[a]; Time |
|---|---|---|
| 4NO$_2$-benzaldehyde | 100%; 1.5h | 100%; 0.5h |
| benzaldehyde | 77%; 3h | 100%; 1.5h |
| 4MeO-benzaldehyde | 88%; 1h | 100%; 0,5h |
| 4NO$_2$-acetophenone | 41%; 24h | Traces; 72h |
| 4Me-acetophenone | Traces; 24h | - |
| 4F-acetophenone | 29%; 24h | - |
| Cyclohexanone | 74%; 24h | - |

a) Conversion yields by GC

Expanding the reaction scope to ketones, only 41% conversion of 4NO$_2$-acetophenone with catalyst **1** and only traces of product with catalyst **2** after 72 hours were obtained (Table 1). The ketones 4Me-acetophenone, 4F-acetophenone and cyclohexanone were also tested with catalyst **1**, leading to the best result with cyclohexanone (74% conversion). These results suggest that MOF **1**, despite requiring a longer reaction time for aldehydes than catalyst **2**, is more versatile because it can be used for ketones. On the other hand, catalyst **2** is more efficient and selective for aldehydes.

## Agradecimentos/Acknowledgments

FACEPE, CNPq, CAPES and UFPE.

**Area:** CAT
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# Dehydration of glucose to levoglucosan over polymeric catalysts

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Keywords: *Glucose, levoglucosan, resin polymeric*

## Highlights

Glucose dehydration over acid catalysts can lead to 1,6-Anhydro-β-D-glucose (levoglucosan) under controlled conditions. Polymeric catalysts were shown to be promising systems for glucose valorisation.

## Resumo/Abstract

Glucose has been attracting much attention as it is an abundant source of renewable carbon available from waste biomass. It can be obtained from the starch present in a vast amount of residues from the food and agricultural industries and from cellulose, which constitutes about 40-50% of the lignocellulosic biomass composition.[1] Dehydration of glucose can lead to 1,6-Anhydro-β-D-glucose, also known as levoglucosan (LGA) or 5-hydroxymethylfurfural (HMF). Levoglucosan, in particular, may be used as an intermediate in the production of pharmaceutical products, biodegradable surfactants and polymers. In this work, glucose dehydration was performed using three commercials polymeric resins as heterogeneous catalysts, Amberlyst 15, 35 and 36 (A-15, A-35 and A-36, respectively) holding only Brönsted acid sites. Glucose dehydration was evaluated in a batch reactor (PARR) at 130 °C, under an $N_2$ atmosphere (10 bar), for 3 h, using glucose/DMF solution at 50 mmol $L^{-1}$. Conversion and LGA yield were estimated using HPLC on a Waters Alliance 2695 chromatograph with an Aminex HPX-87H column. The results displayed in Figure 1 show that all polymeric catalysts were active for glucose dehydration, reaching 78% conversion over A-15, and a LGA yield of 59%. This result agrees well with Ohara *et al.* (2010), who reported glucose dehydration of ~80% and 60% yield of LGA using a similar catalyst.[2] Poorer performances were observed over A-35 and A-36 samples, which led to lower glucose conversions. It is worth mentioning that control tests carried out in the absence of catalyst showed no glucose conversion.

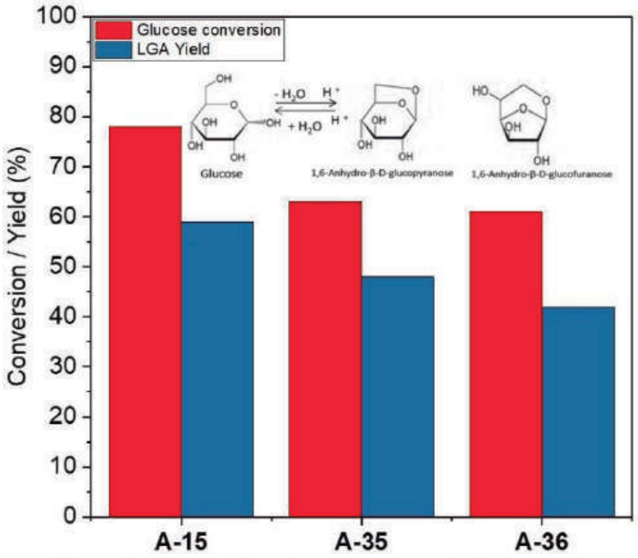

Figure 1. Conversion of glucose and yield levoglucosan.

As reactions were performed in a polar aprotic solvent (DMF), the impact of water in the reaction dynamics was also investigated using A-15 under the same reaction conditions. It was found that glucose conversion decreased significantly with an increase in water amount. Conversion and LGA yield dropped to 58% and 7%, respectively, when only 2.5 %vol of water was added and no conversion was accomplished at all when water was used as the sole solvent. These findings can be rationalized by the establishment of intermolecular interaction (hydrogen bond) between glucose and water molecules, hindering the interaction of glucose with the surface protonic acid sites, reducing sugar conversion. Chemical stability of the polymeric catalysts was also assessed by successive runs unveiling their promising role for liquid-phase glucose upgrading to valued products under controlled conditions.

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## Agradecimentos/Acknowledgments

The authors are grateful for the financial support of CNPq and FAPERJ.

**Área: CAT** **Nº de Inscrição: 234**

# Efeito do tempo na síntese de decanoato de dodecanoila catalisada pela lipase de *Candida rugosa* imobilizada em Accurel MP 1000.

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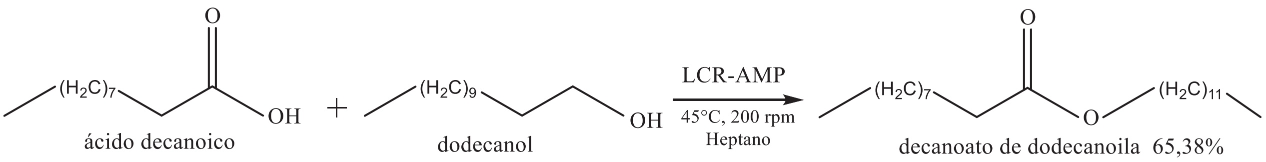
Palavras Chave: *Biocatálise, esterificação, lipase.*

## Highlights

Synthesis of dodecanoyl decanoate by lipase of *Candida rugosa* immobilized on Accurel MP 1000. The global lubricants market size was valued at USD 125.81 billion in 2020 and is expected to grow at a compound annual growth rate (CAGR) of 3.7% from 2021 to 2028[1]. Immobilized lipases reduce the loss of activity due to the influence of solvents or polar molecules present in the medium, in addition to allowing the reuse of the biocatalyst for other reactions[2].

## Resumo/Abstract

Ésteres são compostos orgânicos amplamente utilizados nas indústrias farmacêuticas e de cosméticos, podem ser obtidos de fontes naturais, como animais e vegetais[2]. As lipases catalisam reações de esterificação e o uso dessas enzimas imobilizadas em suportes hidrofóbicos apresenta vantagens econômicas, pois permite a sua recuperação e posterior reutilização, além de aumentar sua estabilidade[3]. No presente trabalho foi realizada a esterificação do ácido decanóico (0,5 M) com o dodecanol (0,5 M) (Esquema 1) em um período de 2 horas retirando alíquotas a cada 6 min. A reação foi repetida sucessivas vezes, recuperando o biocatalisador e reutilizando-o para avaliar a sua estabilidade. A maior conversão observada foi em 120 min (2 h) (Figura 1A). Na reutilização do biocatalisador, após 4 ciclos, houve uma perda de menos de 20% da atividade catalítica, e manteve-se a atividade catalítica próximo a 50% até 11 ciclos (Figura 1B). A imobilização da lipase de *Candida rugosa* em Accurel MP 1000 (LCR-AMP1000) demonstrou alta eficiência catalítica na esterificação, além de boa estabilidade após 10 ciclos.



**Esquema 1.** Síntese do decanoato de dodecanoila pela LCR-AMP. Os reagentes foram adicionados em proporções iguais (1:1).

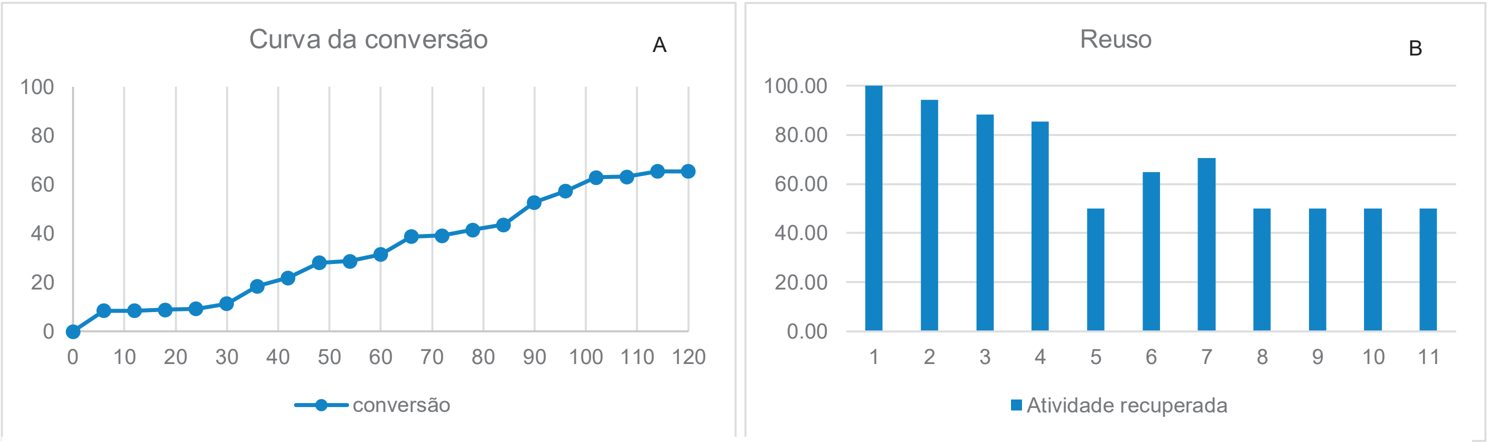


**Figura 1. A)** Síntese do éster pela LCR-AMP em função do tempo. **B)** Reuso da LCR-AMP.

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## Agradecimentos/Acknowledgments

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Área: CAT

# ESTUDO DA HIDROGENAÇÃO DE $CO_2$ UTILIZANDO CATALISADORES A BASE DE FERRO OBTIDOS DE REJEITOS DA INDÚSTRIA DE ACIARIA

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*Palavras Chave: CONVERSÃO DE $CO_2$, REJEITOS DE ACIARIA, HIDROGENAÇÃO, CATÁLISE AMBIENTAL.*

## Highlights

Study of $CO_2$ hydrogenation using iron-based catalysts obtained from tailings from the steel industry.
Hydrogenation of $CO_2$ combined with the use of iron based catalysts is one of the most promising alternatives for using this gas in the chemical industry.

## Resumo/Abstract

Uma vez que o $CO_2$ possui um dos maiores índices de emissão, ele acaba sendo um dos maiores Gases do Efeito Estufa (GEE). Com isso a hidrogenação de $CO_2$ é uma técnica que vem sendo estudada. A conversão do dióxido de carbono a partir da hidrogenação a hidrocarbonetos é de grande importância visto que os hidrocarbonetos de cadeia curta e as chamadas olefinas apresentam alto valor agregado[1,2,3]. O diferencial deste trabalho é a utilização de rejeitos da indústria de aciaria como catalisadores a base de ferro. A utilização destes causa uma diminuição no impacto ambiental no descarte dos mesmos, bem como a diminuição dos gastos com catalisadores por se tratar de um rejeito. Metodologia: A reação foi realizada utilizando 1g do catalisador em uma unidade catalítica microactivity effi da PID Eng&amp;Tech, com reator de leito fixo, acoplada a um cromatógrafo a gás, modelo Shimadzu, com TCD e FID. Inicialmente, procedeu-se a redução em atmosfera de $H_2$ a uma temperatura de 400 °C. Após o processo de redução, o reator foi resfriado a 320 °C e pressurizado a 20 bar, logo após foi conduzida a reação com uma mistura de $H_2$ e $CO_2$ em uma vazão de 30 $mL.min^{-1}$, nas seguintes proporções: 1:1; 1:2 e 1:3 ($CO_2/H_2$), com diferentes catalisadores. Depois também foi testada uma vazão de 15 $mL.min^{-1}$. Através da técnica de cromatografia em fase gasosa com os detectores de ionização por chama (FID) e de condutividade térmica (TCD), foi possível quantificar a conversão de $CO_2$ em hidrocarbonetos, dentre eles: metano, etano, propano, butano, pentano e hexano. Além das olefinas leves, eteno, propeno, buteno e penteno. Os resultados iniciais evidenciaram conversões de 4 (1/1) até 24(1/3) % de $CO_2/H_2$ com uma alta seletividade para hidrocarbonetos mais leves. Ainda foram observada seletividade para olefinas, sendo estas importantes para diversas aplicações industriais. Experimentos com vazão de 15 ml/min estão em execução em nosso laboratório.

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**Nº de Inscrição: 00518**
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# Fatty acid esterification over mesoporous [Al]-SBA-15 catalysts

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Keywords: biodiesel, aluminosilicate, fatty acids

## Highlights

[Al]-SBA-15 is an efficient and stable catalyst for fatty acid esterification.

## Resumo/Abstract

Biodiesel is normally obtained by the transesterification of vegetable oils on basic catalysts. However, its yield is strongly affected by the presence of free fatty acids (FFA) in the feedstock since it poisons the basic catalyst. An alternative approach to overcome this issue, relies on a multi-step process configuration at which acid-catalyzed esterification of FFA precedes the triglyceride transesterification step. There is still a need to develop a catalyst that present a good activity and stability for this first reaction stage. In this contribution, the use of [Al]-SBA-15 as an acid catalyst for esterification of oleic acid is investigated. [Al]-SBA-15 with different Si/Al ratios were synthesized following the method described elsewhere.[1] High surface area solids (600 and 711 $m^2\ g^{-1}$) were obtained. $^{27}$Al NMR-HPDec spectra exhibited the presence of tetrahedral Al sites (Td) and a small presence of octahedral sites (Oh). Catalytic tests were performed in a semi batch PARR reactor at 20 bar $N_2$, using a desired methanol:oleic acid molar ratio (MeOH:OAc) and 10%wt catalyst. Different reaction times and temperatures were evaluated. Oleic acid conversion was assessed through titration with KOH 0.1 mol $L^{-1}$ solution. Table 1 shows that there was almost no conversion at 60 °C after 6 h (Entry 1) but it increased considerably at 120 °C (Entry 2), reaching full conversion at 150 °C (Entry 3). It was also noticed that changing the reaction time from 6 to 4 h (Entry 4) did not influence oleic acid conversion significantly. However, despite the conversion be 20% lower after 2 h of reaction (Entry 5), it is still high and clearly shows the efficient role of the catalyst. Indeed, a control experiment performed without catalyst (Entry 6) presented only 56% of conversion after 6 h. The same control experiment was carried out for 2 h and the conversion obtained was of 35% (Entry 7).

**Table 1.** Conversion of oleic acid over [Al]-SBA-15 (Si/Al=20).

| Entry | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|
| Catalyst (%wt) | 10 | 10 | 10 | 10 | 10 | - | - | 5 |
| MeOH:OAc | 30:1 | 30:1 | 30:1 | 30:1 | 30:1 | 30:1 | 30:1 | 30:1 |
| Temperature (°C) | 60 | 120 | 150 | 150 | 150 | 150 | 150 | 150 |
| Reaction time (h) | 6 | 6 | 6 | 4 | 2 | 6 | 2 | 2 |
| Conversion (%) | 3 | 64 | 98 | 95 | 86 | 56 | 35 | 52 |

The results obtained in this study are outstanding since the performance of a mesoporous catalyst with a similar design was studied before[2] and only 33% of oleic acid conversion was achieved at 140 °C after 2 h with a MeOH:OAc 15:1 and 5%wt catalyst. It must be considered that in that study 30% conversion level was achieved even when no catalyst was used. As a benchmark, the catalysts presented herein was also tested under conditions similar to ref 2, i.e. 5%wt of catalyst (Entry 8) and the result confirmed that [Al]-SBA-15 is an active and efficient catalyst for fatty acid esterification.

## Agradecimentos/Acknowledgments

The authors acknowledge Petrobras (5850.0108150.18.9) for the financial support and NMR analyses. CNPq is also acknowledged.

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**Área: ___CAT_____________**
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# FUNCTIONALIZATION ON DEMAND FOR CATALYSIS: EFFECTS OF SUPPORT, COVERAGE, GROUP IDENTITY AND NEIGHBORING

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Palavras Chave: *Neutralization of organophosphates, Nanocatalysis, Polymeric catalysis, Covalent functionalization, Sustainable catalysts.*

## Highlights

Catalysts-by-design. Functionalized nano-, bio- and waste-derived materials as catalysts for neutralization reactions.
A higher degree of functionalization not always leads to the best catalyst.

## Resumo/Abstract

Catalysts-by-design is a promising approach for neutralizing toxic organophosphates (*e.g.* agrochemicals and chemical warfare), since these reactions are extremely slow. Our group has been interested in the covalent functionalization of various materials derived from carbon nanomaterials, biopolymers (carboxymethylcellulose, gum arabic) and waste (rice husk and shrimp shell) with specific functionalities (imidazole, thiol, hydroxamate) that can be strategically anchored. Briefly, these materials are functionalized on its oxygenated groups (carboxylic acid and epoxy) either by mono or bifunctionalization using methods such as carboxyl activation in aqueous medium or basic epoxy ring opening. Over 30 homogeneous and heterogenous catalysts have been evaluated. We also varied the degree of functionalization and combined different groups on the same support and evaluated how all this affects the neutralization reaction of typical organophosphates. Rice husk functionalized with hydroxamate is highly effective, despite its low degree of functionalization and constitutes a sustainable catalyst derived from waste. For the graphene oxide derived catalysts, the ones monofunctionalized via the epoxide opening show pronounced the activity, accounted to neighboring cooperative effects such as general basic catalysis with hydroxyl groups. Among the bifunctionalized materials (with both thiol and imidazole moieties), the one with the lower degree of functionalization showed the best performance (Figure 1). An elegant bioinspired bifunctional catalysis with both thiol and imidazole is proposed.

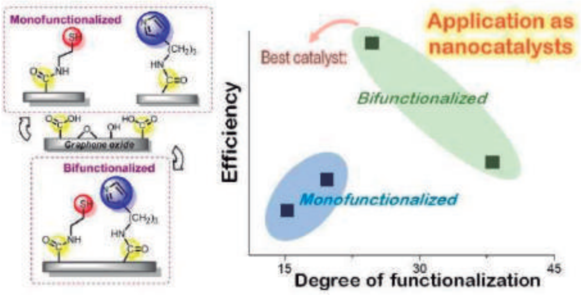

**Figure 1.** Catalytic efficiency of the mono- and bifunctionalized nanocatalysts in the organophosphate neutralization

In conclusion, the strategy for functionalization depends on the application since not always a higher degree of functionalization should be pursued. Furthermore, we show how the support, coverage, group identity and neighboring are decisive for developing an optimized catalyst: it should be by-design and on demand.

## Agradecimentos/Acknowledgments

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**Área: <u>CAT</u>**

# Heterobimetallic complexes based on Ru$^{II}$/Ni$^{II}$ as potential multifunctional catalysts

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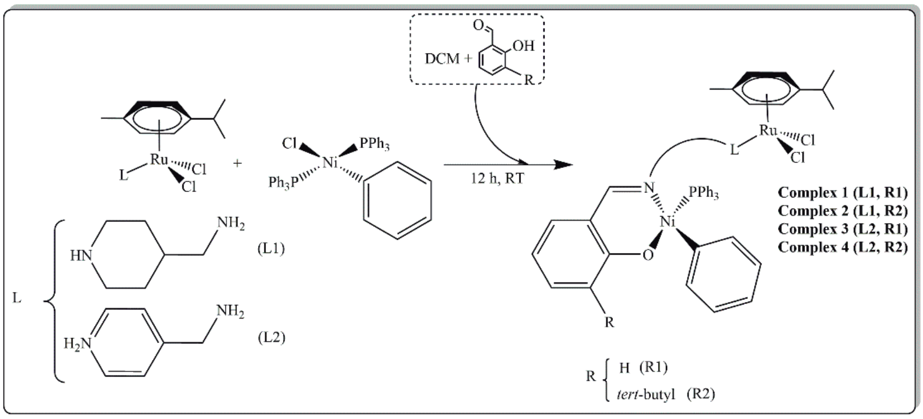
Keywords: polymerization; multifunctional catalyst, synergistic effect.

## Highlights

Heterobimetallic complexes based on Ru-Ni metallic centers linked by iminic bridge.
Bimetallic complexes as potential multifunctional catalysts.

## Abstract

Monometallic complexes based on nickel and ruthenium have demonstred to be effective in a wide range of catalytic reactions. The use of heterobimetallic complexes as homogeneous catalysts aims to expand the catalytic scope, besides increase their reactivity via an electronic or mechanistical synergism. In this work, was reported the synthesis and characterization of four new heterobimetallic complexes based on Ru$^{II}$ and Ni$^{II}$ as a potential multifunctional catalyst. The new heterobimetallic complexes [Ph(PPh$_3$)Ni(N,O)-Ru(*p*-cymene)pip] (**1**), [Ph(PPh$_3$)Ni(N,O-tert-butyl)-Ru(*p*-cymene)pipCl$_2$] (**2**), [Ph(PPh$_3$)Ni(N,O)-Ru(*p*-cymene)piridineCl$_2$] (**3**), and [Ph(PPh$_3$)Ni(N,O-tert-butyl)-Ru(*p*-cymene)piridineCl$_2$] (**4**) were obtained by the reaction of the appropriated ruthenium precursor, [(Ph)Ni(PPh$_3$)$_2$Cl], and the desired aldehyde (salicilaldehyde or 4-tert-butylbenzaldehyde) in an 1:1:1 eqv. This reaction generates an *in-situ* Schiff-base (N,O), which links the metallic fragments (Ru$^{II}$ and Ni$^{II}$) by an iminic bridge (**Scheme 1**). All complexes were fully characterized by spectroscopy techniques as FTIR, UV-Vis, and $^1$H and $^{31}$P{$^1$H}. The heterobimetallic complexes (**1** to **4**) FTIR spectra showed the presence of $\nu$(C=N) stretch, which indicates the formation of the Schiff-Base (NO type) by the reaction between the aldehyde and primary amine. The presence of both metal centers (Ru and Ni) were confirmed by the $\nu$(Ni-Cl) and $\nu$(Ru-Cl) stretch at 355 and 300-250 cm$^{-1}$, respectively. UV-Vis spectra were obtained in CH$_2$Cl$_2$ at 25 °C and demonstrated new absorption bands when compared to precursor species. $^{31}$P{$^1$H} NMR spectra of bimetallic complexes showed a singlet around 24 ppm, confirming the presence of one PPh$_3$ in the coordination sphere of the Ni center. Cyclic voltammetry of heterobimetallic complexes were performed using CH$_2$Cl$_2$ as solvente, tetrabutylammonium hexafluorophosphate as supporting electrolyte, a platinum disco (2 mm) as working electrode, a platinum wire as auxiliary electrode, and Ag/AgCl as reference electrode. All bimetallic species showed two anodic processes assigned to the Ni$^{II/III}$ redox pair, and to the Ru$^{II/III}$ pair. The molecular ion of complexes **3** to **6** were observed from MALDI-TOF spectra, which confirming the achievement of heterobimetallic species.



**Scheme 1**. Overview of the reaction to obtain the heterobimetallic

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**Área: ________CAT________**

# Heterobimetallic ruthenium(II) and palladium(II) complexes as bifunctional catalysts to obtain functionalized polymers via coupling of Heck and ROMP reactions

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Palavras Chave: *Reductive Heck, ROMP, functionalized norbornene.*

## Highlights

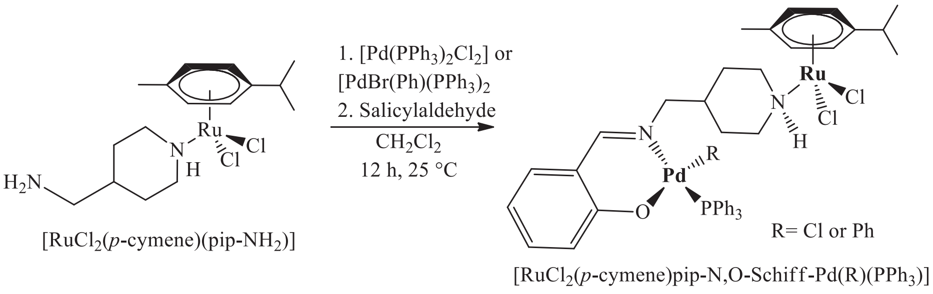
Synthesis and characterization of new ruthenium/palladium heterobimetallic complexes.

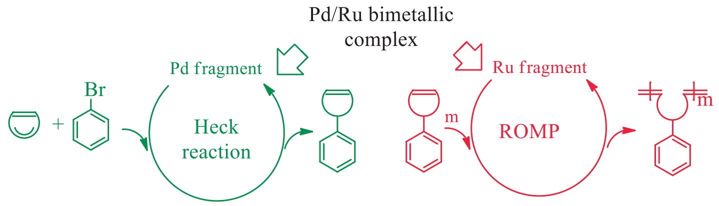
Investigation of bimetallic complexes as catalysts to act as catalysts in Heck reaction and ROMP.

Synthesis of functionalized norbornene by Reductive Heck reaction.

## Resumo/Abstract

Bimetallic complexes of palladium(II) and ruthenium(II) were synthesized to mediate two different catalysis reactions: Heck reaction and ring opening metathesis polymerization (ROMP). The proposal is to systematically evaluate different reaction conditions for the bimetallic complexes in the Heck and ROMP reaction and, consequently, achieve a fine adjustment of the parameters of each reaction separately, functionalizing the olefin (norbornadiene) via the Heck reaction and then using this functionalized olefin as substrate in polymerization via ROMP, considering that a thorough understanding of individual reactions will be a key step in the development of multifunctional catalysts for the simultaneous catalysis of these reactions.





The functionalized norbornene syntheses via reductive Heck using the complexes as catalysts were evaluated under reaction conditions of [PhBr]/[Norbornadiene] = 3/1,using $Et_3N$ or $CsCO_3$ as a reductive agent and, 5% of heterobimetallic complex for 4 hours at 60 or 120 °C.

The Heck reactions were monitored by GC and the functionalized norbornene was purified by flash chromatography in ether to isolate the pure product.

## Agradecimentos/Acknowledgments

**Área: CAT**

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# Improving Hydrogen Production for Carbon-Nitride-Based Materials: Crystallinity, Cyanimide Groups and Alkali Metals in Solution Working Synergistically

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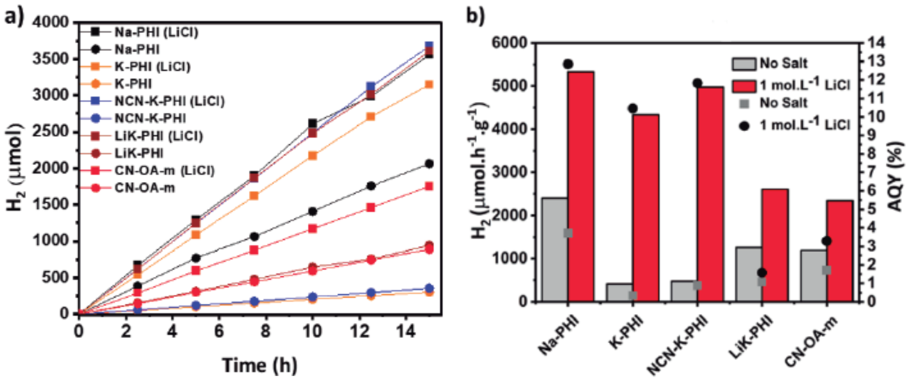
Palavras Chave: *HER, carbon nitrides, poly(heptazine imide), photocatalysis, hydrogen.*

## Highlights

Demonstration of strategies to further drive activity and AQY for a variety of carbon nitride based-materials for hydrogen evolution reaction.

## Resumo/Abstract

The recent findings on the fundamental understanding of the activity of carbon nitride-based materials in the hydrogen evolution reaction (HER) allow designing rationally the photocatalytic systems with improved activities. Herein, combining highly ordered materials with cyanimide defects and alkali metal cations in the solution, we demonstrated an important synergistic effect which for cyanimide modified K-PHI is revealed in 12 times higher apparent quantum yield (AQY) compared to K-PHI free of surface cyanimide groups.



## Agradecimentos/Acknowledgments

### Área: CAT

# Investigação de catalisadores de Sn(IV) na conversão de glicerol em insumos químicos de valor agregado

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Palavras Chave: *Biocombustíveis, Coproduto, Acetilação, Catalisador de Sn(IV), Ésteres de glicerol*

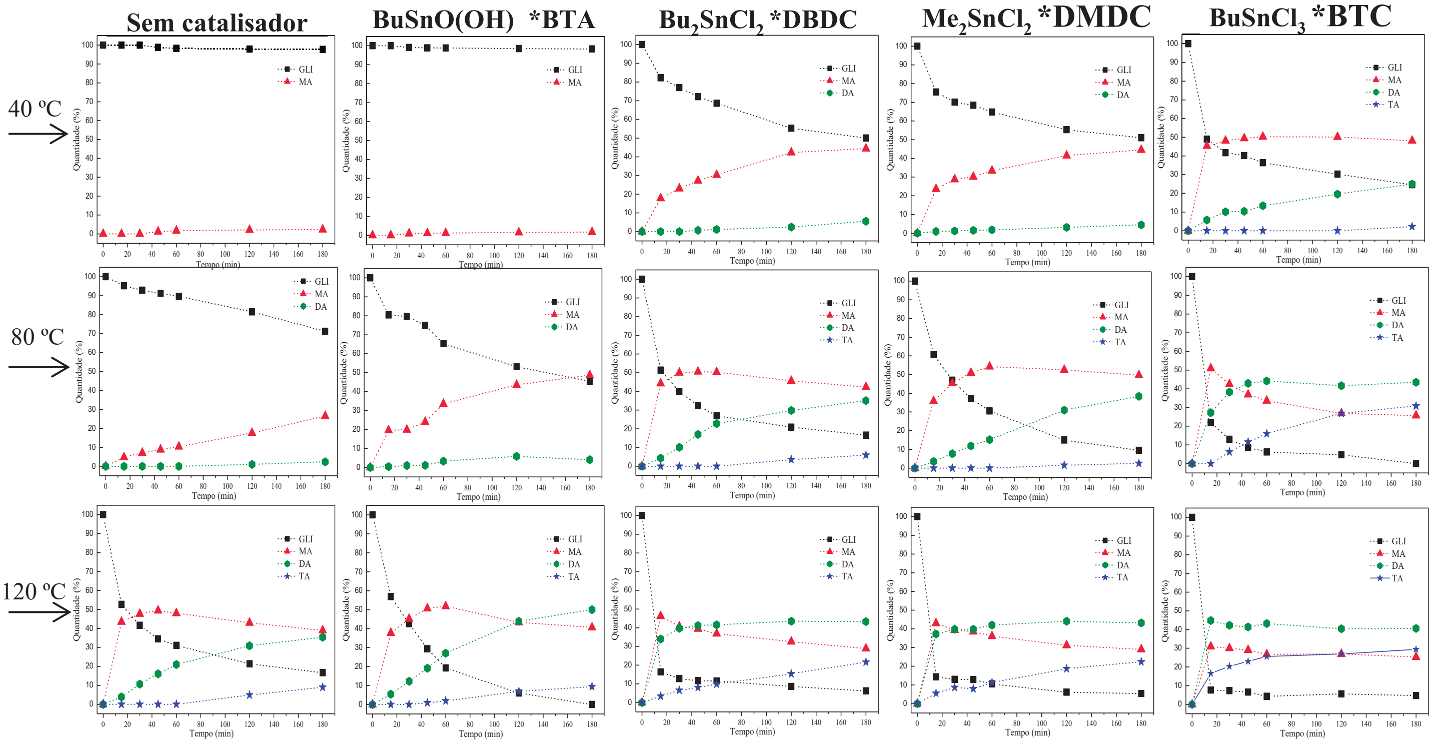
## Highlights

The present work proposes to obtain acetines from the conversion of glycerol with acetic acid in the presence of Sn(IV) catalysts.

## Resumo/Abstract

A esterificação do glicerol (GLI) com ácido acético (AA) é uma alternativa promissora para a valorização do excesso de glicerol oriundo das biorrefinarias. Assim, nesse trabalho, essa reação foi investigada empregando catalisadores de Sn(IV) e sem catalisador sob os diferentes parâmetros (quantidade de catalisador de 0,166 mmol de Sn; razão molar AA:GLI = 4:1; temperaturas de 40, 80 e 120 °C; e tempos reacionais = 15-180 minutos). Os produtos obtidos foram analisados por cromatografia gasosa com detector de ionização em chamas (GC-FID). A partir da Figura 1, os resultados demonstraram o efeito positivo do uso dos catalisadores de Sn(IV) e do aumento da temperatura na reação, pois em apenas 15 min de reação na temperatura de 40 ºC foram obtidas conversões de até 51,0%, ao utilizar o catalisador $BuSnCl_3$, com a formação de MA (45,3%) e DA (5,7%), diferentemente da reação não catalisada.

**Figura 1.** Estudo da temperatura reacional representando a quantidade de GLI (glicerol) e dos produtos formados MA (monoacetina), DA (diacetina) e TA (triacetina), nas condições de: T = 40, 80 e 120 °C; razão molar AA:GLI = 4:1; quantidade de catalisador = 0,166 mmol de Sn; e tempos reacionais = 15 – 180 min; empregando BTA - ácido butilestânico, DBDC - dicloreto de dibutilestanho; DMDC - diclorodimetilestanho e BTC – butiltricloroestanho.



A reatividade dos catalisadores foi estabelecida como BTC > DMDC ~ DBDC >> BTA, a qual está relacionada diretamente com a natureza dos ácidos de Lewis. Em suma, os catalisadores de Sn(IV) mostraram-se eficientes na conversão do glicerol em acetinas.

## Agradecimentos/Acknowledgments

CNPq, CAPES, FAPEAL, FINEP e INCT Catálise.

**Área: CAT**

# Investigation of a new ternary catalyst for sour low-temperature water–gas shift reaction.

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Palavras Chave: *Water-gas shift, sulfur tolerance, Cu-based catalysts, support effect.*

## Highlights

$CuO/ZnO/Nb_2O_5$ was more active, even in sour conditions, than a commercial LTS catalyst formulation.

Presence of residual hydroxycarbonates and niobia support possible contributed to improve activity.

## Resumo/Abstract

Hydrogen production via water-gas shift reaction (WGSR) using heavy oil residues as syngas source is an attractive way to improve refinery margin. However, this low cost syngas may present significant concentration of sulfur, leading to poisoning of usual WGS catalysts, especially at low-temperature conditions (LTS).

A combination of co-precipitation and deposition-precipitation methods was employed to preparation of $CuO/ZnO/Nb_2O_5$. During the synthesis, changes in ph and solution color implied that the product formed underwent similar alterations to those reported to the commercial LTS catalyst, $CuO/ZnO/Al_2O_3$.

Catalytic activity measurements of in-situ reduced catalyst consisted of three sequential tests at 230°C for evaluated different properties for the catalyst: 1) The stability during clean WGS reaction, 2) the sulfur tolerance of catalysts and 3) the capacity of recovering the catalytic activity after $H_2S$ was removed from the feed. Table 1 presents the results of isothermals tests compared to the measurements over $CuO/ZnO/Al_2O_3$ catalyst.

Table 1 - Comparison between averages forward TOF obtained in the three stages of isothermal WGSR tests. Feed gas composition: 5%$H_2$, 15%CO, 5%$CO_2$ and 20%$H_2O$ plus 50 ppm of $H_2S$ to sour condition and balance with $N_2$.

| Catalyst | Average forward TOF ($10^{-3}$ $s^{-1}$) | | | |
|---|---|---|---|---|
| | Stability test (16 h) | Sulfur tolerance test | | Recovery test (16 h) |
| | | 3,5 h | 7 h | |
| **$Cu/ZnO/Nb_2O_5$** | 58.7 → 54.1 | 32.8 | 29.4 | 24.4 →21.5 |
| **$Cu/ZnO/Al_2O_3$** | 5.1 → 5.7 | 4.0 | --- | 5.0 |

$CuO/ZnO/Nb_2O_5$ catalyst reached the highest activity with initial TOF values more than ten times higher than those presented for $CuO/ZnO/Al_2O_3$ catalyst. The results suggest that the substitution of alumina, considered an inert support for the WGSR, by a reducible oxide such as niobia improved the catalyst activity. XPS analysis of reduced and passivated catalyst revealed the existence of $Nb^{4+}$ in addition to $Nb^{5+}$. Another possibility for higher activity of $CuO/ZnO/Nb_2O_5$ catalyst is the presence of residual Cu/Zn hydroxycarbonates in the calcined sample.

A slight trend of deactivation after 10 h of reaction was observed for $CuO/ZnO/Nb_2O_5$ catalyst under clean condition. The average crystallite size of CuO, estimated by XRD analysis of spent catalyst, suggests that there was agglomeration of copper particles for CuO/ZnO/Nb2O5. This made it difficult to assign the drop in activity in the contaminated condition only to exposure to sulfur. However, the catalyst activity remained the highest along all the steps of catalytic test, even with twice the exposure time to $H_2S$. No methanation parallel reaction was observed during WGSR tests.

## Agradecimentos/Acknowledgments

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**Área: CAT**

# Investigation of esterification of levulinic acid in the presence of Sn catalysts

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*Keywords: Biomass, Catalysis, Organotin (IV), Levulinate esters, Solvent-free.*

## Highlights

Organostannic complex BTC stands out as catalyst in the esterification reaction of levulinic acid with ethanol. The formation of ethyl levulinate is evaluated by GCMS and by the release of green apple smell. Using only 0.01 mol of catalyst it was possible to increase the apparent velocity rate by 79.5% when compared to the reactions without catalyst.

## Resumo/Abstract

The present work evaluated tin (IV) based catalytic systems (CAT), including butylstannoic acid (BTA), butyltin trichloride (BTC), dibutyltin dichloride (DBDC) and dimethyltin dichloride (DMDC) compared to reactions without the use of catalyst, in the esterification of levulinic acid (LA) with ethanol (EtOH) to produce ethyl levulinate. The reactions were conducted at 70, 80, 90 and 110°C for reaction times ranging from 0.25 to 6h with AL/EtOH/CAT molar ratios of x/y/z, where x = 1, y = 4, 5 and 6 and z = 0.01 and stirring speed of 1000 rpm. The experiments were carried out in closed glass vial-type reactors. The quantification of the remaining levulinic acid in the reaction mixtures was performed by HPLC and the results were expressed in terms of conversion (%) of LA. The catalysts were characterized by FTIR and it was possible to verify the characteristic vibrations of each one. The results point out that the catalyst BTC showed better catalytic activity with LA conversion of 92.2 % in 6 hours of reaction using 1/6 AL/EtOH conducted at 110°C and 0.01 mol of catalyst. Such efficiency may be associated with increased Lewis acidity at the metal center due to the presence of electronegative and less bulky substituents, temperature tested and alcohol proportion[1,2]. The apparent rate constant (kap x $10^{-3}$) for the reaction without catalyst in the molar ratio 1/6/0.01 = Al/EtOH/CAT conducted at 110ºC was estimated to be 1,6 $\text{min}^{-1}$ while in the presence of BTC at the same parameters was 22,1 $\text{min}^{-1}$, an increase of 79.5% in the process.

**Figure 1**. Conversion (%) of AL at 70°C using BTA, DMDC, DBDC, BTC and reaction without catalyst with 1/5/0.01 molar ratio (AL/EtOH/CAT).

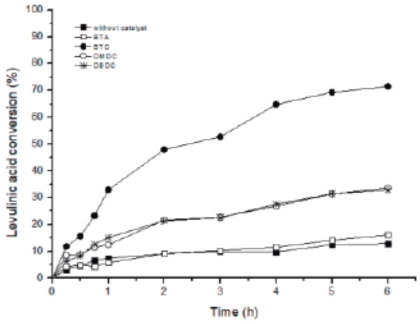


**Figure 2.** Influence of reaction temperature on conversion (%) of AL in reactions conducted at 50, 70, 90 and 110° C using 5:1 molar ratio of EtOH/AL with 0.01 BTC catalyst by weight of AL.

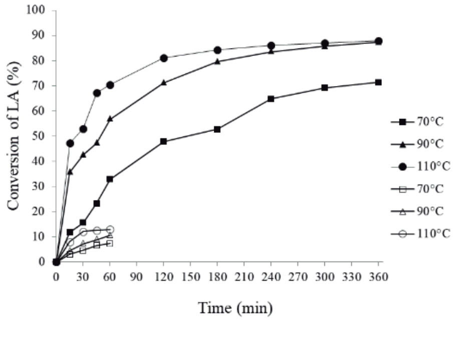
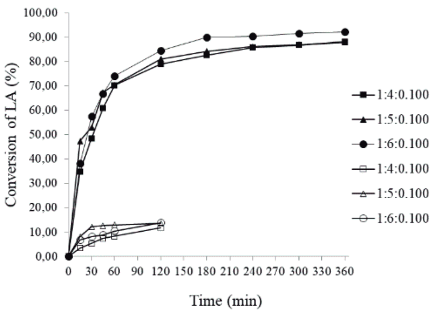


**Figure 3.** Conversion of AL (%) using different molar ratios of AL/EtOH of 1/4, 1/5 and 1/6 conducted at 110°C using 0.01 BTC and without catalyst.



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## Agradecimentos/Acknowledgments

**Área: CAT**

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# Investigation of Reactive Radicals Production by Metal-Crystalline Carbon Nitride Photocatalysts

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Key words: *Carbon Nitride, Poly(heptazine imide), Photocatalyst, Hydroxyl Radicals, Superoxide Radicals.*

## Highlights

The generation of reactive radicals was evaluated by EPR experiments, whereby was observed that the interaction of hydrogen peroxide is distinct between Fe-PHI (holes) and Cu-PHI (electrons).

## Resumo/Abstract

Highly crystalline carbon nitrides can be synthesized using a thermal treatment of melamine and NaCl, yielding a solid called Na-PHI, whereby PHI stands for poly(heptazine imide). Sodium cations are stabilized between the layers and can be exchanged by other metals (Fe, Co and Cu). The production of radicals was evaluated by EPR (**Fig. 1a-c**), it is observed that Co and Fe-PHI does not produce ·OH radicals. Cu-PHI, instead, can generate high amounts of hydroxyl in aprotic systems ($CH_3CN$). This result indicates that $H_2O_2$ reacts with photogenerated electrons of Cu-PHI. While Co-PHI does not produce any other radical in aprotic conditions, Fe-PHI yields superoxide radicals ($O_2^{-}$) (**Fig. 1d**), indicating that hydrogen peroxide is oxidized by holes. Thus, Cu and Fe-PHI show distinct mechanisms (**Fig 1e**) with $H_2O_2$ in acetonitrile.

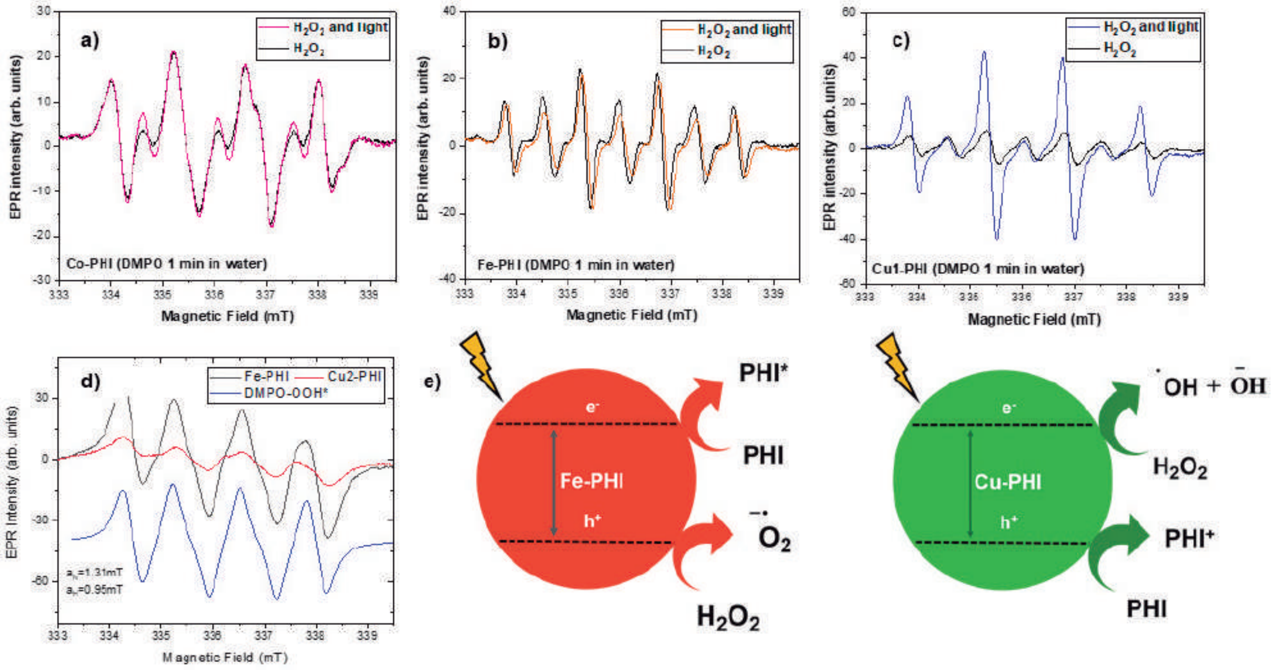

**Figure 1:** EPR spectra of DMPO adducts in water with $H_2O_2$ in the presence and absence of visible light radiation for hydroxyl radicals (**(a)** Co-PHI, **(b)** Fe-PHI and **(c)** Cu-PHI) and superoxide radicals (**(d)** Cu and Fe-PHI); **(e)** interaction of $H_2O_2$ with Fe and Cu-PHI.

## Agradecimentos/Acknowledgments

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**Área: CAT**

# Isomerization of limonene over sulfonated carbon

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*Palavras Chave:(Sulfonated carbon, heterogeneous catalysis, limonene)*

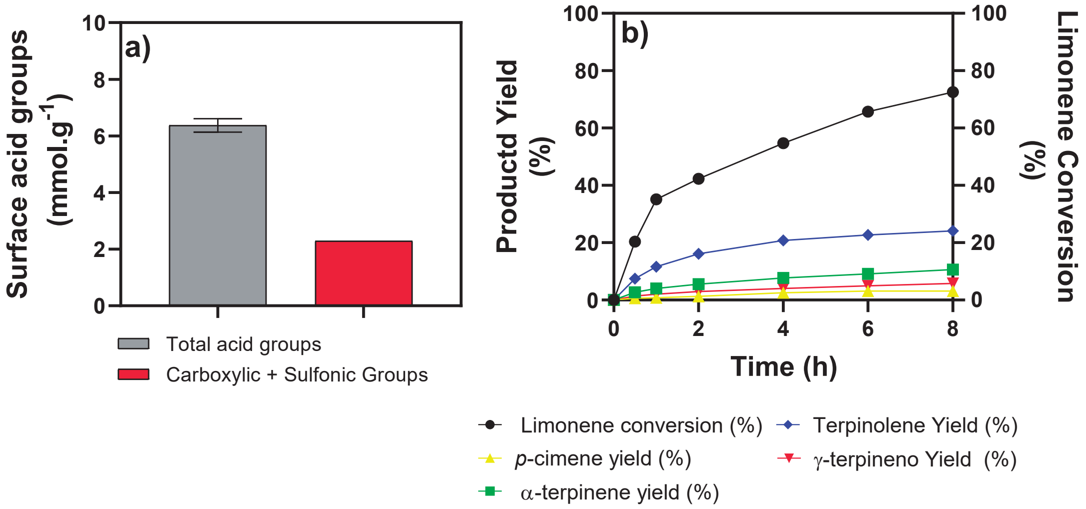
## Highlights

Sulfonated carbon was used as a catalyst for limonene isomerization, in solvent-free conditions. A conversion of 72% was reached after 8 h, giving terpinolene as the main product (yield of 24%).

## Resumo/Abstract

Sulfonated carbon was prepared by hydrothermal carbonization with concentrated sulfuric acid (CHT-$H_2SO_4$). This method is promising when developing sulfonated carbon. The values of total acid groups and carboxylic + sulfonic groups were, respectively: 6.4 and 2.3 mmol $g^{-1}$(Figure 1a). The FTIR technique and the acidity confirmed the presence of functional groups in sulfonated carbons. The bands at 1600, 1700, and 3400 $cm^{-1}$ confirm, respectively, the presence of C = C groups, C = O groups, which are related to carboxylic and lactonic groups, and O-H groups, which are related to phenolic and carboxylic groups. The bands centered at 1043, 1173 and 1396 $cm^{-1}$ indicate the presence of $-SO_3H$ groups (O = S = O symmetric and asymmetric) [1,2]. Due to the presence of acidic surface groups, sulfonated carbon proved to be active in the isomerization of limonene, thus obtaining the main products: α-terpinene, *p*-cymene, γ-terpinene, and terpinolene (Figure 1b).

Figure 1: a) Surface acid groups; b) Catalytic results of limonene isomerization (reaction were carried out in a two-necked round bottom flask heated in an oil bath and fitted with a reflux condenser. 19mmol limonene, catalyst 15% wt, T=150ºC).



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# Lamellar MWW type zeolite: different ways to arranging the layers and its applicability

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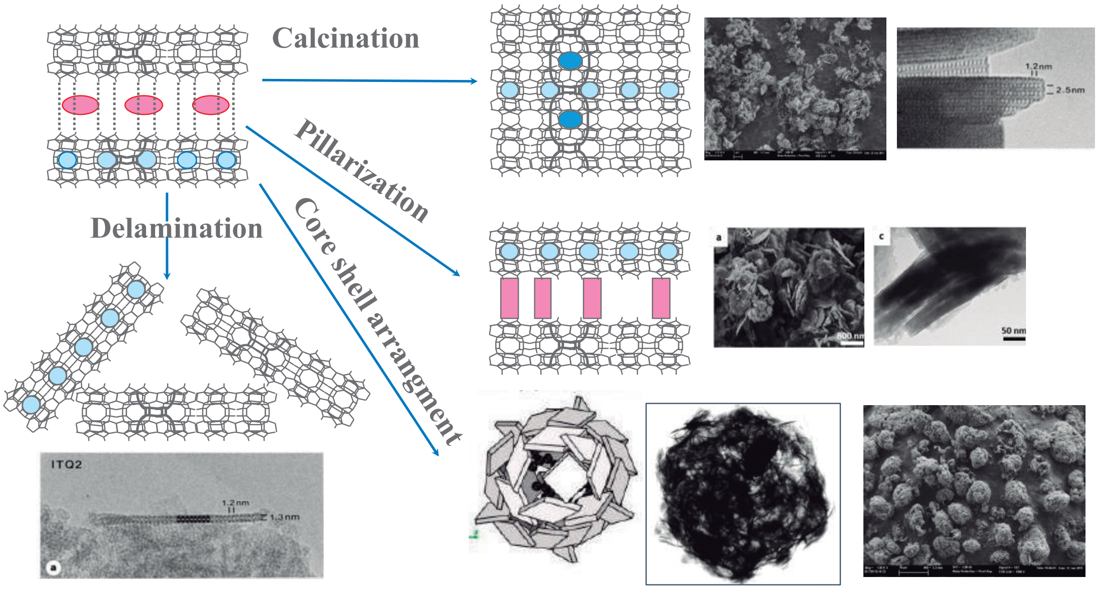
Palavras Chave: MWW, Zeolites, Lamellar, Molecular Sieves, MCM-22.

## Highlights

Lamellar MWW type Zeolite can give different materials.
Layers in different ways of arranging and composition lead to a wide range of applications

## Resumo/Abstract

The MWW type zeolite (MCM-22) has a lamellar precursor [1] that can be swelled [2,3], desordenated [4] and pillared [2,5]. The properties of these materials are very different and depends of chemical composition and the way that the layers are arranged [5]. In this study we present different ways to arrange this layers by swelling with different surfactants and in different conditions, also using silicon and niobium oxides pillars. Desordenated layers were also synthetized (ITQ2) and a core shell arrangement of the layers. The materials were very well characterized and it be shown some applications in fructose dehydration to 5-HMF, oxidation of VOCs and gasoil cracking. These materials are very versatile to design materials with different accessibilities and activity.



## Agradecimentos/Acknowledgments

To CNPq and CAPES for financial support.

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**Área: CAT**

# Manganese-cobalt oxides nanowires as non-precious catalysts for fuel cells

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Keywords: *fuel cell, catalyst, non-precious metals.*

## Highlights

- A catalyst has been successfully prepared based on simple microemulsion and heat treatment methods;
- The composite presented remarkable catalytic activity and potential use for fuel cell applications;
- The measurement results prove that this carbon-modified support with $MnCo_2O_4$ nanowires has broad prospects for energy storage and energy conversion as an effective ORR catalyst.

## Resumo/Abstract

Recently, studies on the manufacture of low-cost nanocatalysts with higher electrocatalytic activity focused on improving the properties of non-noble transition metals, such as Mn and Co, aiming to reduce the final cost of fuel cells [1, 2]. Herein, we proposed the development of catalysts using non-precious metals that are efficient in the oxygen reduction reaction (ORR) and resistant to the negative effects caused by metals commonly used in the market. Bimetallic oxides of $MnCo_2O_4$@C were synthesized by a simplified microemulsion method. The success of the synthesis to obtain these materials was confirmed through physical characterizations of scanning electron microscopy (SEM) and X-ray diffraction (XRD). Electrochemical studies were carried out in an alkaline aqueous solution using a rotating disk approach. Studies for ORR showed that $MnCo_2O_4$@C presented good electrocatalytic performance since it has the most positive initial potential at -0.10 V and maximum diffusion limit current of -1.0995 mA, which is close to that of commercial Pt/C, more precisely -1.11 mA. The reaction proceeds according to first-order kinetics concerning dissolved oxygen and a mechanism involving 4 electrons per reagent molecule.

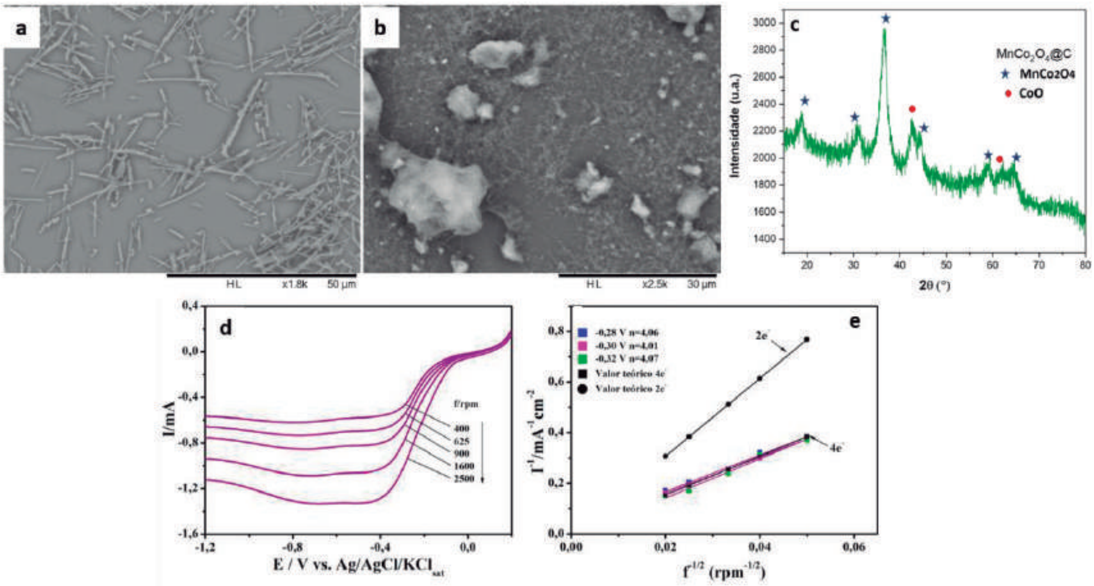

**Figure 1:** SEM images of the MnCo-based oxalate (a) and $MnCo_2O_4$@C composite (b). XRD pattern of the $MnCo_2O_4$@C composite (c). Rotating disk electrode polarization curves in 0.1 M KOH, v = $10 mVs^{-1}$ (d). Corresponding Koutechy-Levich plots at different potentials vs. Ag/AgCl (e).

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## Agradecimentos/Acknowledgments

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**Área: CAT**

# Metal/Support Interface Modulation Through the Heterogenization of Complexes Aiming $CO_2$ Conversion

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Palavras Chave: *Heterogeneous Catalysis, Complexes, $CO_2$, Platinum.*

## Highlights

The work presents the heterogenization of different platinum complexes that were designed to elucidate how modifications of the metallic precursor impact on the final catalyst, aiming $CO_2$ conversion.

## Abstract

Single-atom catalysis has become one of the main areas of research, not only to optimize the use of scarce metals but also to take advantage of a myriad of possibilities to modulate the properties of the catalytic sites by the local coordination and interaction with the support. Among the efforts to develop reproducible and practical methods for the synthesis of single-atom catalysts, the heterogenization of coordination complexes on high area supports is promising. To elucidate the role of the ligand design on the properties of the final heterogeneous catalyst based on oxide supports, this work proposes modifications on the salen ligand and complexation with $Pt^{2+}$ to produce the heterogeneous catalysts after impregnation on supports and controlled decomposition methods. As the final goal, we hope to identify universal parameters/descriptors that will help to guide the design of metal supported catalysts, from single-atom to nanoparticles on oxides supports. These catalysts have been used in strategic reactions and below we show the results obtained in the $CO_2$ conversion to syngas through the reverse water gas shift reaction (RWGS, $CO_{2\,(g)} + H_{2\,(g)} \leftrightharpoons CO_{(g)} + H_2O_{(g)}$).

Figure 1 (a) shows selected complexes' synthesis and their respective yields. These compounds differ in their carbon content and electronic structure, in which C2 and C3 have more carbon atoms than C1, and C3 is an example of $\pi$ extended system. All the complexes were impregnated on $TiO_2$ and carbon black (CB) through wet impregnation, followed by pyrolysis. This last step was crucial to the metallic phase stabilization, in which the organic phase is decomposed under inert atmosphere, leaving a residual content on the support surface capable of fixating the Pt, hindering agglomeration, also modulating its electronic density through the presence of nitrogen and oxygen atoms. Figure 1 (b) depicts the specific rate of reaction for $CO_2$ conversion of a sub-set of catalysts (1% Pt w/w in $TiO_2$, pyrolyzed at 500 ºC). It is possible to verify the activity trend $C3/TiO_2 < K_2PtCl_4/TiO_2 < C1/TiO_2 < C2/TiO_2$. No methanation was detected (100 % selective to CO). Characterization by electron microscopy and infrared spectroscopy are underway revealing the dependence on the precursor structure, namely the characterization of the metallic and organic residual phase to the catalytic results. Overall, the use of complexes has shown to be a promising strategy for modulating catalyst's properties according to the reaction.

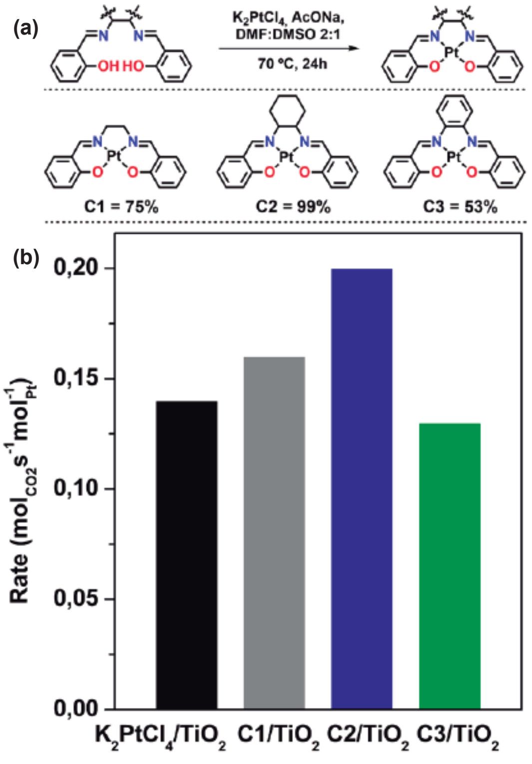

**Figure 1. (a)** Complexes' synthesis and their respective yield; **(b)** RWGS reaction rate for four catalysts (Reaction conditions: 400 ºC, 2% $CO_2$, 8% $H_2$, 90% He, 100 ml.min$^{-1}$).

## Acknowledgments

(20/08575-6; 20/00691-7; 18/01258-5 ) (309412/2018-8)

**Área: CAT**

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

# Niobium oxophosphate catalysis activity on sugarcane straw hydrothermal pretreatments

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Palavras Chave: *Sugarcane straw, Niobium oxophospate, Hydrothermal pretreatment, Pentoses, Furfural, Hemicellulose.*

## Highlights

Niobium oxophosphate showed a high activity in hemicellulose (Hc) deconstruction to pentoses and also to convert pentoses to furfural.
For a liquor rich in pentoses and poor in inhibitor of microbial fermentation (i.e., furfural), the reaction without NbP is better.
Applying NbP as catalyst was possible to reach the maximum Hc solubilization at lower times than classical hydrothermal pretreatment and it could be beneficial to cellulignin production.

## Abstract

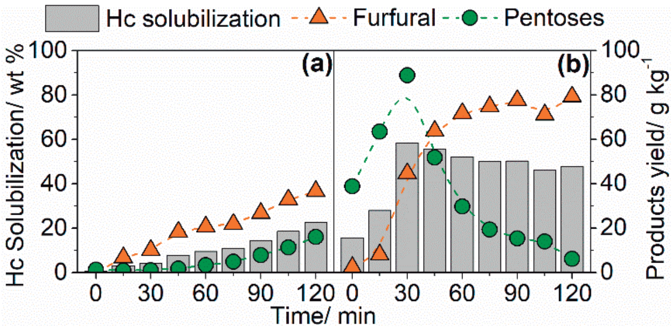

Figure 1: Effect of time and temperature on sugarcane straw pretreatment in the presence (a) and absence of NbP (b). Experimental conditions: Sugarcane biomasses (15 g), water (150 mL), NbP (50 % wt), 170 °C, 120 min, agitation (900 rpm).

Agricultural residues from large crops such as sugarcane have great potential to be explored within the concept of biorefineries. Lignocellulosic biomass has a high carbohydrate content in the polymeric form of cellulose and hemicellulose (Hc)[1]. After processing the sugarcane to produce sugar or ethanol, the excess straw is left in the field[2]. The use of these residues as low-cost raw materials is possible by pretreatments to increase the efficiency of biochemical processes[3]; however, they demand a high energy expenditure. An alternative for cost reduction is undoubtedly the use of heterogeneous catalysts. They stand out due to their easy of handing and are non-corrosive. Among these, niobium-based catalysts have high acidity and high availability in Brazil. In this work, the use of niobium oxophosphate (NbP) was explored for sugarcane straw, aiming a cellulignin production rich in cellulose and a liquor rich in pentoses. Carbohydrates, furanic compounds (i.e.; furfural and HMF) and degradation products (i.e.; glucuronic, formic, acetic and levulinic acids) were quantified by Shimadzu Prominence HPLC in a Bio-Rad Aminex® HPX-87H column. After NbP addition (Fig. 1b), the maximum Hc solubilization was reached faster than reactions in its absence (Fig. 1a). The same was observed to the maximum amount of pentoses in the liquor. In the same way, furfural got faster its maximum concentration at equilibrium in the presence of the catalyst. NbP has both, Bronsted and Lewis acid sites[4] to catalyze all the steps: Hc deconstruction releasing pentoses and pentoses dehydration to furfural.

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## Acknowledgments

This study is supported by Biovalue Project (Petrobras, Suzano Papel e Celulose, Klabin, Embraer), FAPEMIG, FAPESP, FACEPE and FAPERGS. To CNPq and CAPES for the financial incentive and Brazilian Metallurgy and Mining Company (CBMM) for the niobium phosphate catalyst.

**Área: CAT**

# Pd-catalyzed Suzuki-Miyaura(SM) Cross-Coupling Reaction in Glycerol; A Green and Non-Innocent Solvent

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Palavras Chave: *Suzuki-Miyaura; Cross-Coupling; Palladium; Glycerol; Green solvent; Recycle.*

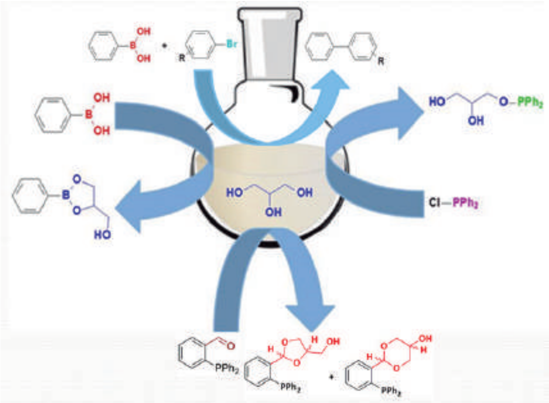
## Highlights

Glycerol as solvent for the SM coupling reaction.

Products were easily isolated by hexane extraction and catalytic medium was recycled.

Glycerol reacts with ArB(OH)$_2$, PPh$_2$Cl and PPh$_2$(*o*C$_6$H$_4$CHO).

## Resumo/Abstract



The current study describes use of glycerol as an efficient reaction medium for the Pd-catalyzed Suzuki-Miyaura cross-coupling of aryl bromides with arylboronic acids. A simple catalytic system based on PdCl$_2$(PPh$_3$)$_2$ in glycerol offers an environmentally benign, cheap, and practical protocol for the synthesis of substituted biaryls. The reaction proceeded smoothly with low catalyst loadings (up to 0.5 mol%) providing excellent yields (up to 99%) of the cross-coupling products by simply extracting the reaction mixture with a glycerol-immiscible solvent. Since, the use of glycerol provides the advantage of using the catalytic system to recycle, therefore, the glycerol recycling experiments by using 2 mol% of Pd loadings revealed that the catalytic medium is recyclable up to 8 cycles with a slight loss of catalytic activity after 8th cycle.

A very good yield of the cross-coupling product was obtained using PPh$_2$Cl, whereas only a moderate yield of the cross-coupling product was obtained using diphenylphosphine-2-benzaldehyde as phosphine source. In the presence of diphenylphosphine-2-benzaldehyde as ligand, 5- and 6-member cyclic acetals were formed from the reaction with glycerol. On the other hand, we expected *the in situ* formation of phosphinite ligand from the reaction with PPh$_2$Cl with glycerol. The isolation and characterization of the glycerol-based phosphinite ligand are currently under investigation in our group.

## Agradecimentos/Acknowledgments

We would like to acknowledge the TWAS-CNPq for providing the PhD fellowship to Z.H. (190090/2014-9). We also would like to acknowledge the following Brazilian agencies for the partial financial support: CAPES (001), INCT-Catálise, CNPq (304132/2017-9) and PRONEX-FAPERGS (16/2551-0000481-1).

**Área: CAT** **Nº de Inscrição:** **00028**

# Reduction of transition metal exchanged ZSM-5 zeolites by ethane

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Palavras Chave: *Zeolites, ZSM-5, Ethane, Bifunctional Catalysis.*

## Highlights

Ethane can reduce transition metals in zeolite pores at low temperatures. The temperature for reduction with hydrogen is higher than with ethane. Different transition metals are studied.

## Resumo/Abstract

Zeolites are one of the most important and utilized catalysts on refining industries throughout the world. The properties of a zeolite can be modified by cation exchange with transition metals. This metal exchanged zeolites can serve as catalysts for a variety of reactions such as dehydrogenation and cracking of organic feedstocks.[1] However, the metal usually needs to be present in a zero-valence state and, to obtain the reduced metal, the catalyst can be reduced by hydrogen, which requires high temperatures.[2] Then the use of a cheaper and more efficient type of reducing agent is of concern.

As reported in 2018, light paraffins, such as isobutane and n-butane, performed the reduction of nickel exchanged ZSM-5 in temperatures as low as 120°C.[3] The effect of confining a transition metal cation in a zeolite pore gave different properties compared to the impregnated zeolite, elevating conversion rates and olefin selectivity in cracking of molecules, such as n-hexane.[4] These facts highlights the importance of studying these types of bifunctional catalysts.

In this study we proposed the use of ethane as a reducing agent for ZSM-5 zeolite exchanged with Ni, Co, Cu and Fe. The effect was studied by Dispersive X-ray Absorption Spectroscopy (DXAS) for the NiZSM-5 sample and the results are presented in Figure 1. The oxidation state was changed from $Ni^{+2}$ to $Ni^0$ in a lower temperature with ethane than with hydrogen. The effect was also studied from 50°C to 500°C by a Micro Gas Chromatography (MicroGC) during a heating ramp for all samples. The NiZSM-5 reduction was detected at the same temperature range as the DXAS experiment and it was compared to the Co, Cu, Fe and pure ZSM-5. All samples were characterized by Powder X-ray Diffraction (XRD), Wavelength Dispersive X-ray Fluorescence (WDXRF) and $N_2$ physisorption.

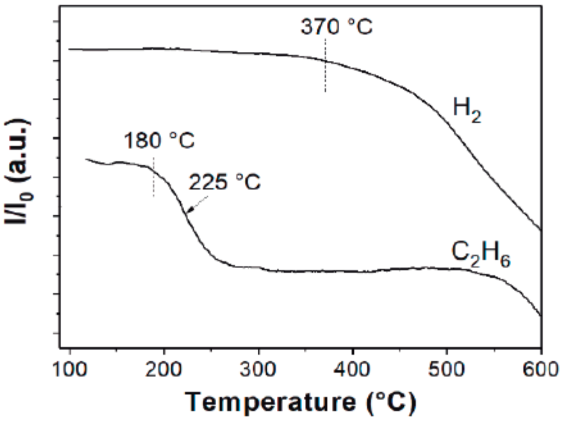

***Figure 1.** DXAS monitoring of ethane and hydrogen reduction in NiZSM-5. Where $I/I_0$ represents the difference between $Ni^{+2}$ and $Ni^0$ white lines.*

**References:** [1] Armor J. *Micro. and Meso. Materials.* 22 (1998) 451–456
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[4] Maia A. *Journal of Catalysis 269 (2010) 103–109*

## Agradecimentos/Acknowledgments

**Área: CAT**

# Studies on base-catalyzed inter- and transesterification of different triacylglycerol mixtures having the same fatty acid composition

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Palavras Chave: Biodiesel, Castor oil, Soybean oil, Coconut oil, Intramolecular esterification, Estolides.

## Highlights

FA redistribution in TAGs does not kinetically affect transesterification of soybean oil:coconut oil mixtures. High viscosity castor oil estolides are formed under interesterification conditions.

## Resumo/Abstract

In this work, the results and discussions of studies on the transesterification of binary mixtures between castor (CO), soybean (SO) and coconut (CNO) oils in the presence of methanol and NaOH, before and after interesterification, in the latter case in the presence of $CH_3OK$ as a catalyst, are reported. For cases in which CO is not present, redistribution of fatty fragments in triacylglycerols (TAGs) does not significantly affect the kinetic behavior of the transesterification reaction (Fig. 1A). On the other hand, binary mixtures containing CO, before and after interesterification, showed different kinetic profiles (Fig. 1B). In other words, the kinetics of the transesterification reaction does not depend only on the fatty acid (FA) composition when utilizing CO. From the results obtained, it was found that during interesterification of the mixtures containing this oil, a parallel transesterification reaction occurs. It was confirmed that the hydroxyl group present on the 12th carbon of the ricinoleic portion of the CO acts as a transesterification agent in the interesterification conditions adopted in this work. In these cases, increases in viscosity in relation to physical mixtures containing CO (from 14 to 93%) and peaks of high retention times in high performance liquid chromatography (HPLC) determinations were observed. Carbon-13 nuclear magnetic resonance ($^{13}C$ NMR) analyzes confirmed that during the interesterification reaction in the presence of CO, acylglycerol estolides are formed, which explains the lower transesterification rates for interesterified mixtures. This is the first time that the production of estolides, FA ester oligomers, has been reported under TAG interesterification conditions. Quantitative $^{13}C$ NMR studies indicated high degrees of esterification (72-97%) for the samples produced.

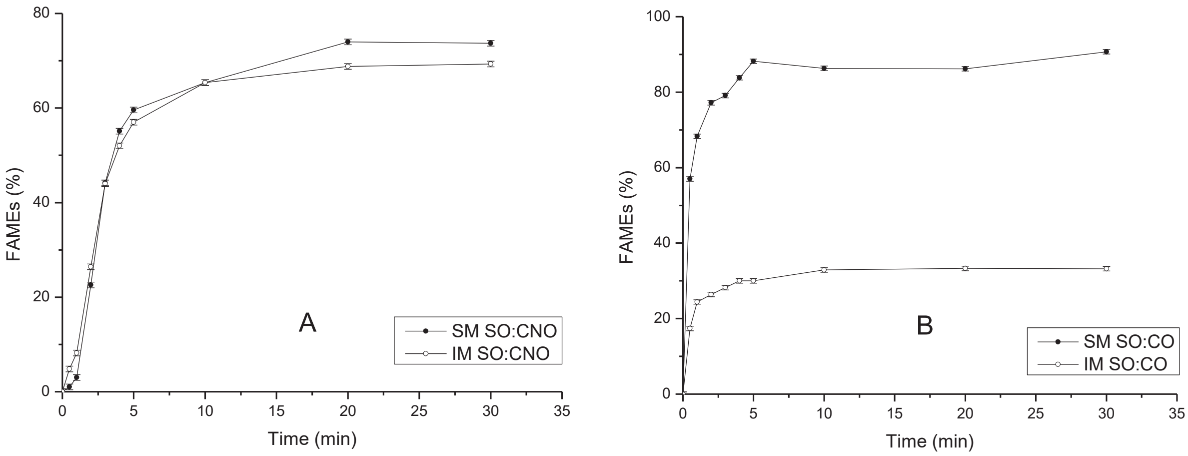

Fig. 1. FAME production from (A) SO/CNO and (B) SO/CO before and after interesterification. Transesterification conditions: oil/MeOH/NaOH of 1.00:5.00:0.14 and 70 °C (SM, simple mixture; IM, interesterified mixture).

## Agradecimentos/Acknowledgments

CNPq, CAPES, FINEP, FAPEAL and INCT Catálise.

**Área: CAT**

# Synthesis and characterization of $CaO\text{-}FeO_3$, $CaO\text{-}ZrO_2$ e $CaO\text{-}Al_2O_3$ bifunctional mixed oxide catalysts.

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Palavras Chave: Heterogeneous catalysts, Mixed oxides, Bifunctional catalysts

## Highlights

CaO based mixed oxides were synthesized as potential bifunctional industrial catalysts. Characterization showed the formation of pure and mixed oxides with different physical and chemical properties.

## Resumo/Abstract

Several industrial reactions use catalysts with specific functionalities. Alkaline earth metal oxides are suitable basic catalysts; however, they present disadvantages such as low specific area, low stability, and deactivation. This work aims to synthesize and characterize a series of mixed oxide catalysts based on CaO ($CaO\text{-}FeO_3$, $CaO\text{-}ZrO_2$ e $CaO\text{-}Al_2O_3$) to obtain stable catalysts with differentiated acid-base properties for potential use in industrial catalytic reactions. CaO was obtained from the calcination of eggshells. Mixed oxides were obtained by precipitation of zirconium, iron, and aluminum hydroxides from aqueous solutions of the respective salts and CaO, with a molar concentration of 50%. The precursors were calcinated at 500 °C (10 °C/min) for 4 h, obtaining the solids CZ_50, CF_50 and CA_50. Characterization was performed by TGA-DSC, XRD, $N_2$ physisorption, and $CO_2$-TPD. In all solids, $N_2$ physisorption showed the presence of mesopores with type IV isotherms; additionally, the surface areas were 15.6 $m^2/g$, 17.5 $m^2/g$, and 76.4 $m^2/g$ for CZ_50, CF_50, and CA_50, respectively, Fig. 1. XRD diffractograms showed the obtention of mixed and pure oxides for all solids, with the formation of $Ca_2Fe_2O_5$, $\gamma\text{-}Fe_2O_3$, and $Fe_2O_3$-hematite for CF_50 catalyst, $Ca(ZrO_2)$ and $ZrO_2$ for CZ_50 and non-identified semicrystalline phases for CA_50, Fig. 2. Basic sites were characterized by $CO_2$-TPD. In all cases, a mixture of weak, medium, and strong basic sites was observed. Particularly, CA_50 showed four desorption peaks between 150 and 900 °C. Further characterization is being performed to elucidate the nature of the acid-basic sites and their influence on the catalytic activity.

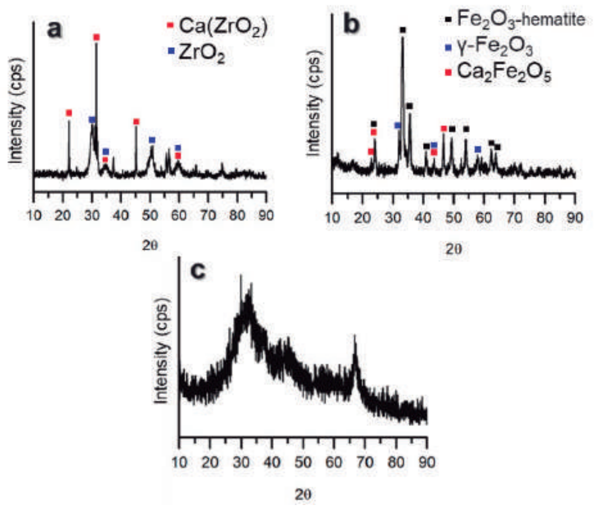

**Fig. 1**. X-ray Diffratograms: (a)CZ_50, (b)CF_50, (c)CA_50

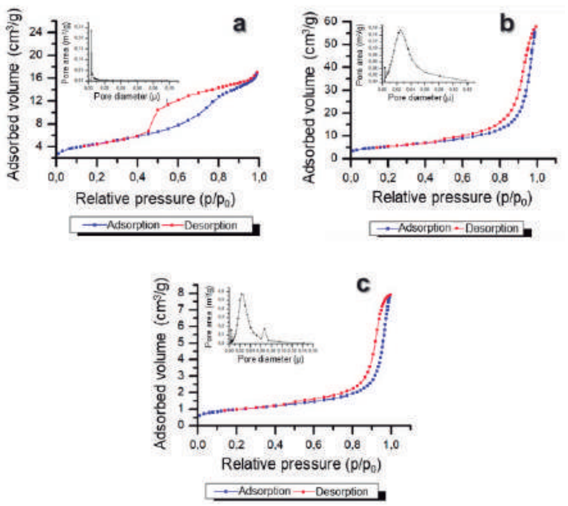

**Fig. 2**. $N_2$ physisorption isotherms: (a)CZ_50, (b)CF_50, (c)CA_50

## Agradecimentos/Acknowledgments

The authors gratefully acknowledge UFAL, FAPEAL (scholarship for Daniell D. C. da Silva), Laboratório RECAT-UFF, Laboratório LSCat-UFAL, PETROBRAS and ANP (laboratory infrastructure).

**Área: CAT**

# Synthesis and characterization of Ru(II) complexes coordinated to sulfoxides and bisphosphines as potential multifunctional catalysts for ROMP and ATRP.

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Palavras Chave: *Multifunctional Catalysts, Copolymerization, tandem catalysis.*

## Highlights

New complexes based on Ru(dppp)-DMSO were synthesized as potential catalysts for ROMP and ATRP reactions.

## Abstract

New Ru(II) complexes were synthesized from the reaction between the fac-[$RuCl_2$(S-DMSO)$_3$(O-DMSO)] and an appropriated bisphospine for 4 h under reflux in a methanolic solution (figure 1).

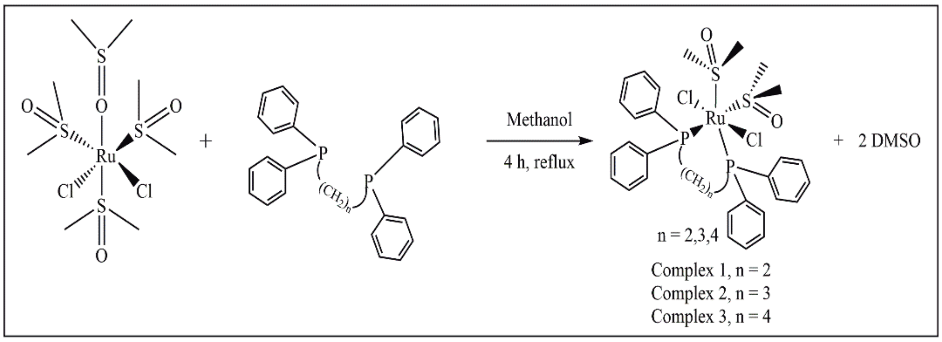

Figure 1 - Illustration of the synthesis procedure of complexes 1, 2 and 3.

The complexes [$RuCl_2$(S-DMSO)$_2$(dppe)] (**1**), [$RuCl_2$(S-DMSO)$_2$(dppp)] (**2**), and [$RuCl_2$(S-DMSO)$_2$(dppb)] (**3**), were characterized by spectroscopic techniques such as FTIR, $^1H$, $^{13}C$ and $^{31}P\{^1H\}$ NMR and UV-Vis. The electrochemical characterization of complexes 1, 2, and 3 was also performed by cyclic voltammetry. The FTIR spectra of complexes 1, 2, and 3 indicate the presence of vibrational stretches attributed to $\upsilon$(P-C). The absence of $\upsilon$(Ru-O) at 475 cm$^{-1}$ on complexes spectra obtained indicates the coordination of bisphosphine to the metal center. The UV-Vis spectra demonstrated new absorption bands when compared to precursor species, which indicates the formation of new compounds. All UV-Vis spectra of complexes showed a transition shoulder around 340, which can be attributed to the intraligand transition (IL) $\pi \rightarrow \pi^*$ from the aromatic groups of the phosphinic ligands. Intense bands between 400 and 550 nm were observed and are attributed to metal-to-ligand charge transfer (MLCT), resulting from the charge transition from the metal's d$\pi$ orbitals to the phosphines $\pi^*$ orbitals.

The $^{31}P\{^1H\}$ NMR spectra of complexes 1 and 3 showed a singlet at 44.95 and 38.36 ppm, respectively, demonstrating that both phosphorus atoms on complexes are equivalents. To evaluate the electrochemical behavior of complexes 1, 2, and 3, the redox potentials were evaluated by cyclic voltammetry, under an argon atmosphere, using a platinum disk as working electrode, a platinum wire as the auxiliary electrode, and Ag/AgCl as reference electrode, using 0.1 mol.L$^{-1}$ of *n*-$Bu_4NPF_6$ as support electrolyte. The cyclic voltammograms obtained for complexes 1, 2, and 3 showed reversible processes related to the $Ru^{II}/Ru^{III}$ redox pair, with anodic peak at 0.56, 0.51, and 0.60 V, respectively.

## Acknowledgments

**Área: CAT**

# Synthesis and characterization of Ru-NHC complex as a potential catalyst for ROMP

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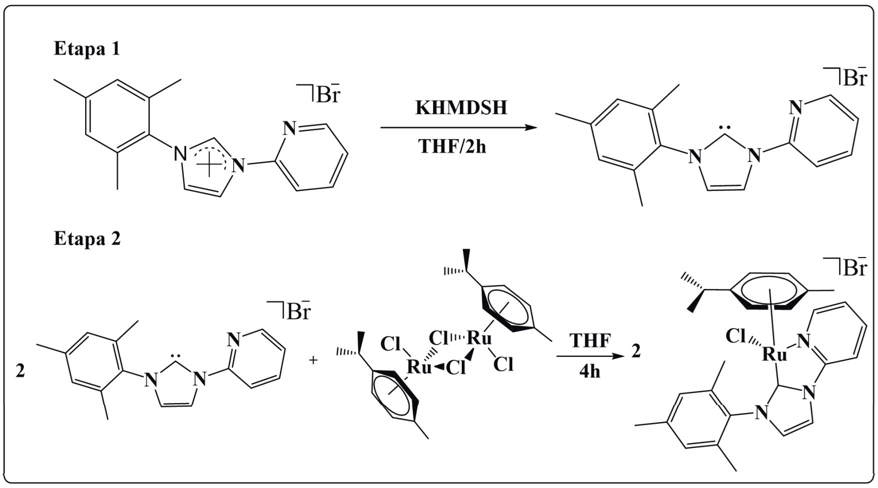
Palavras Chave: *Ruthenium, N-Heterocyclic carbene, Polymerization.*

## Highlights

Asymmetric bidentate NHC coordinated to $\text{Ru}^{II}$(*p*-cymene) to mediate ROMP.

## Abstract

Complexe containing $\text{Ru}^{II}$ metal center have attracted the research community due its large possibilities of catalytic reactions. In particular, these complexes have been employed as a good alternative for Ring Openning Methathisis Poymerization (ROMP) to obtain polymers with high molecular weights and low polydispersity indexes. Thus, In this work, we reported the synthesis and characterization of the complex Br as a potencial catalyst for ROMP reactions. The 2,4,6-trimethlaniline-imidazole was synthesized according to the literature procedure, in which 2,4,6-trimethlaniline, glyoxal, and paraformaldehyde reacted in a 1:1:1 eqv. The 2,4,6-trimethlaniline-imidazole was reacted with Bromo pyridine to obtain N-Mesityl-N-2-pyridylimidazolium bromide (L), which was characterized by spectroscopic techniques as FTIR, UV-Vis, and $^1$H NMR. A band around $\nu$(1200 cm$^{-1}$) was identified on L spectrum, which was signed to the $\nu$(C-N) streatch. The $\nu$(C=N) streatch appeared at $\nu$(1630 cm$^{-1}$), indicating that the species was obtained as expected. The [$\text{Ru}^{II}$L(*p*-cymene)Cl]Br was synthesized by the reaction between L previously deprotonated with Potassium bis(trimethylsilyl)amide (KHMDS) and {[Ru(*p*-cymene)$Cl_2$]}$_2$ at RT for 4 h. The complex obtained was characterized by FTIR, in which was observed the absence of $\nu$(C=N) from carbene, indicating that the NHC was deprotonated and coordinated sucessfully to the Ru center. [$\text{Ru}^{II}$L(*p*-cymene)Cl]Br was also characterized by $^1$H NMR spectrum and all H expected were identified.



**Scheme 1**. Overview of the reaction to obtein the asymmetric Ru-NHC complex

## Acknowledgments

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**Área: CAT**

# Tin and niobium oxides applied in fructose conversion: influence of the presence of Lewis and Brønsted acids on catalytic performance

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Keywords: Biomass, fructose, biorefinery, mixed oxides.

## Highlights

Fructose conversion was investigated using heterogeneous tin and niobium oxide catalysts in order to obtain chemicals of industrial interest.

## Resumo/Abstract

Currently, there is a growing demand for chemicals resulting from the transformation of biomass[1]. As a result, the search for catalysts that meet the demand for conversion and selectivity is growing. Among heterogeneous systems, oxides are still slight used in the conversion of biomass[2]. Initially, the oxides were synthesized by the Pechini method, using two distinct precursors, glycerol (G) and ethylene glycol (EG), and these systems were named $SnO_2$, $Nb_2O_5$ and SnNb ((EG) or (G)) and characterized by FTIR, DRX, Raman and textural analysis. Then, the catalytic tests were carried out at 150 °C, from 0.5 to 6 h. The mixed oxide spectra revealed the presence of bands attributed to the bonding of the metal to oxygen. The XRD diffractograms of the SnNb (EG) and (G) systems show the predominant presence of the tetragonal phase, and the signals are broader and less intense compared to pure oxides. Raman scattering suggests that the methodology used was effective to obtain the mixed material. For the SnNb (EG) and (G) samples, characteristics of the mesoporous materials were observed [3,4]. Figure 1 shows the conversion of fructose as a function of the reaction time. For the reaction carried out without a catalyst, low conversions are observed. For mixed oxides, an increase in terms of converted fructose is observed, when compared to pure systems.

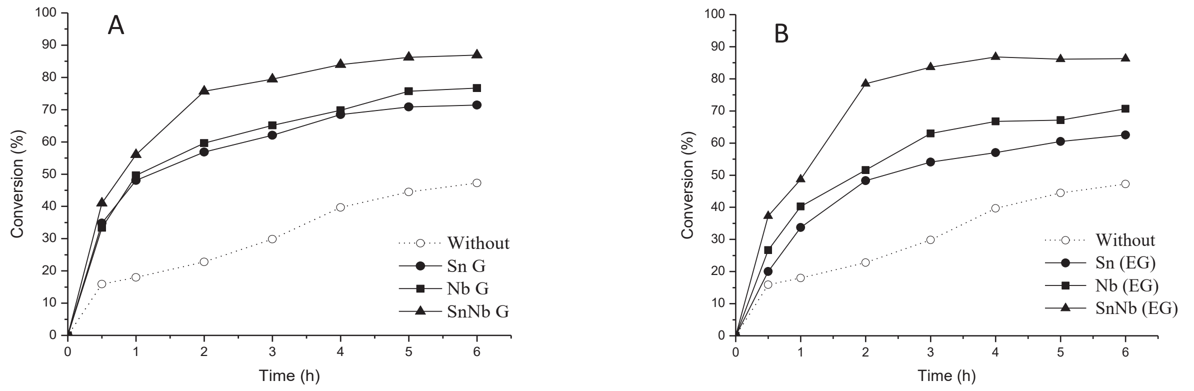

**Figure 1.** Fructose conversion at 150 °C using $SnO_2$ (G), $Nb_2O_5$ (G) and SnNb (G) (**A**) and $SnO_2$ (EG), $Nb_2O_5$ (EG) and SnNb (EG) (**B**).

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## Agradecimentos/Acknowledgments

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# EDU

# Ensino de Química

**Área: EDU**

# A CONSTRUÇÃO DE SABERES DOCENTES NO ESTÁGIO SUPERVISIONADO DE LICENCIANDOS EM QUÍMICA

**Thayna M. Matos (IC)*, [1]Rafaela O. de Lima (IC), [1]Mariana S. Rocha (IC), [1]João Paulo S. Carvalho (IC), [2]Danielle R. M. da Costa (PQ)**

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Palavras Chave: Estágio supervisionado, Formação docente, Licenciatura em Química, Saberes docentes.

## Highlights

**THE CONSTRUCTION OF TEACHING KNOWLEDGE IN THE SUPERVISED INTERNSHIP OF LICENSEES IN CHEMISTRY.** The work highlights the construction of teaching knowledge during the supervised internship and its importance for the teaching training of undergraduates in chemistry.

## Resumo/Abstract

A prática e os saberes docentes exercem influência na constituição dos saberes desde a formação inicial por meio dos estágios1. O estágio supervisionado é compreendido como um processo que cria, investiga, interpreta e intervém na realidade escolar, educacional e social, favorecendo ao estagiário, conhecimentos necessários à formação e atuação docente2. Compreendemos ser uma das etapas mais significativas durante a formação do licenciando, no estágio "aprende-se" ser professor diante da complexidade do contexto escolar. O objetivo deste trabalho é evidenciar a mobilização de saberes docentes durante o estágio supervisionado de licenciandos em química, e a importância desses saberes para a prática profissional. A pesquisa foi realizada com 16 discentes de um curso de licenciatura em química de uma IES pública na cidade de Marabá-PA, após a disciplina de estágio supervisionado do curso. A abordagem foi qualitativa, descritiva, através de um questionário online compondo perguntas semiestruturadas.

Foi possível observar nas respostas que a realização do estágio supervisionado oportunizou a observação e a regência, os discentes puderam ter um olhar mais atento ao que acontece dentro da sala de aula, destacaram a importância da teoria, mas consideram não ser suficiente para o exercício profissional. Na prática vivenciada pelo estágio aprende-se a compreender os próprios alunos, a gestão escolar e toda a diversidade do ambiente escolar, e nessa oportunidade são mobilizados diversos saberes docentes3. Além de possibilitar a construção de saberes a respeito da docência (experenciais), e a construção dos currículos escolares (saberes curriculares). Em suma, é durante o estágio que se tem a oportunidade de aprender e ensinar junto com os profissionais experientes (saberes profissionais) no âmbito institucional do trabalho. Através do estágio se pode observar a proximidade do futuro professor com a realidade, onde temos a certeza que nem tudo é como se imagina e que é preciso lançar mão de metodologias diversas para que o aluno aprenda determinado conteúdo.

Diante disso, podemos concluir que o estágio possibilita uma outra visão sobre a prática docente e que somente a formação teórica não é o suficiente para as atividades de docência, que é necessário que haja uma interação com os professores regentes, direção e alunos para que o futuro professor adquira habilidades e competências necessárias a sua futura profissão.

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[3] TARDIF, Maurice. Saberes docentes e formação profissional. 17ª ed. Petrópolis: Vozes, 2014

## Agradecimentos/Acknowledgments

Á Universidade do Estado do Pará – Campus VIII-Marabá e aos Licenciandos em Química que participaram da pesquisa.

**Área: EDU**

# ACS Student Chapter UFC: an academic nucleus to enhance the experience of undergraduate students and prepare them for successful career

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Keyword: *Student Chapter, ACS, Scientific Divulgation, Experience report*

## Highlights

ACS Student Chapter UFC is the first chapter from the Northeast region of Brazil.

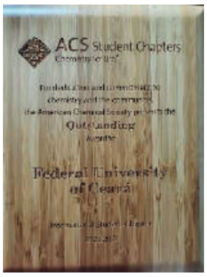
Online activities are developed for scientific dissemination to the society.

Scientific activities are also developed to students from public high school.

## Abstract

ACS student chapters are academic organizations composed by undergraduate students with interest in the chemical science. Members of the chapters participate in a wide range of activities to enhance their experience in the academia and prepare them for successful careers. The ACS Student Chapter UFC (Fig. 1) was created in February 2020, and it was officially recognized by ACS in March 2020. Being the first student chapter established in the Northeast region of Brazil, it started its activities with six members from undergraduate and graduate courses in Chemistry at the Federal University of Ceará (UFC). Currently, the chapter is officially registered as an extension activity in UFC, and it contains ten members. Because the chapter was created during the Covid-19 pandemic, all activities involved virtual meetings through Google Meets, Zoom, YouTube and Instagram platforms. The activities included (i) scientific dissemination through Instagram; "Recaptulando", a monthly podcast interviewing a scientist; (ii) Webinar Series promoted by ACS Brazil and CAS Brazil; (iii) "ACS Student Chapter at School", a partnership with a public high school; (iv) "Coffee with Scientist" as part of the "2022 Global Women Breakfast" promoted by IUPAC; "Introducing the UFC Chemistry Courses", a live on YouTube to introduce the Chemistry courses to new academic students. Although with only 2 years of existence, the chapter and its members have achieved international recognition. One member was awarded the Leadership Development Award from the ACS Younger Chemistry Committee. The chapter was awarded Commendable (2019-2020) and Outstanding (2020-2021), Fig. 2, the latter being the highest honor given for a student chapter by the American Chemical Society (ACS).

Fig. 1. ACS Student Chapter UFC Logo



ACS Student Chapters

Outstanding

Federal University of Ceará

Fig. 2. Outstanding Award 2020-2021

## Acknowledgments

UNIVERSIDADE FEDERAL DO CEARÁ

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AMERICAN CHEMICAL SOCIETY

**Área: EDU**

# “When will this class be over?”: using drawings to explore students (dis)-identification with Chemistry classes

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Keywords: *Chemistry Identity, Drawing, Disidentification.*

## Highlights

- Dissimilarities between who students want to be and how they are positioned as learners produce disidentification.
- Disidentification is expressed by boredom and frustration with Chemistry.

## Resumo/Abstract

This study analyzes how students represent themselves in Chemistry classes. The concept of identity is especially useful for this research purpose. Identity in educational research has been broadly defined as what “kind of person” one is in a given context [1]. By using drawing as its main data-collection strategy, this work intends to answer the following question: what drawings can reveal about the patterns of students identification with Chemistry classes? High-school students in 10 focus groups were asked to draw a self-portrait of them in Chemistry classes. We categorized 36 drawings and their interpretations by students as an expression of their identification with Chemistry. Results indicate that students express their affiliation with Chemistry classes in a continuum of frustration-neutral-enjoyment (Fig. 1). However, most students (n = 27) do not express identification with Chemistry, but actually show signs of *disidentification*, while fewer express neutral views (n = 6) or some form of interest (n = 3).

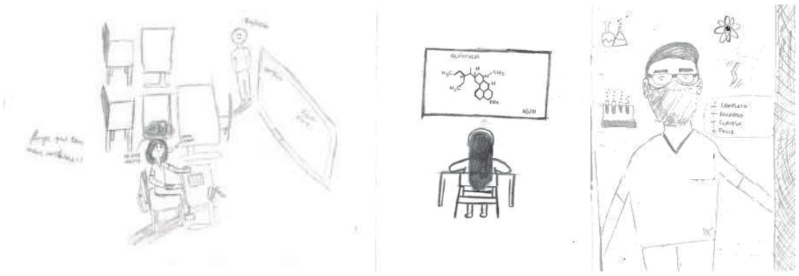

**Figure 1:** from left to right, the first self-portrait (frustration) represents a student with signs of “confusion” on her head; the second one (neutral) is a student sitting in her desk looking to the blackboard; the third one (enjoyment) represents a student surrounded by chemistry symbols and words like “curious” and “excited”.

The typical drawing is of an individual sitting in a desk with symbolic representations of being “sleepy”, “bored”, “confused”, and “frustrated” during lessons. We argue that these aversive emotional states in Chemistry classes might denote expressions of students’ disidentification and distancing from Chemistry. These negative signs might not only be the result of a perception of Chemistry concepts as meaningless, but also an effect of students forced positioning of behavioural compliance, passivity and individuality. Although these seem to be the implicit principles in the organizational culture of high-school Chemistry of what it means to be a good learner, students’ representations of disaffection with Chemistry indicate they might not want to fulfil that role. Thereby, the disconnection between how Chemistry classes are organized and who students want to be might contribute to produce these negative emotional states. By using drawings to reveal how students’ experience Chemistry in the classroom, this research suggests the need for Chemistry education researchers to go beyond the usual interventionist focus on gaining students attention by also trying to disentangle the nature of students negative reactions to Chemistry learning.

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## Agradecimentos/Acknowledgments

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**Área: EDU**

# Análise dos erros em atividades avaliativas do conteúdo de termodinâmica de soluções no ensino superior

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Palavras Chave: *Erros, Avaliação, Termodinâmica de Soluções.*

## Highlights

Analysis of errors in evaluative activities of the content of thermodynamics of solutions in higher education. The errors were categorized and classified as: entry, organization of information and execution. The result showed that the execution error appeared more frequently in all investigated classes.

## Resumo/Abstract

No processo de ensino e aprendizagem é inevitável que o aluno desvie da meta prevista pelo professor, assim o erro é o resultado mais provável. Segundo Luckesi[1], a ideia de erro só emerge quando se tem um padrão considerado correto. No contexto da aprendizagem, esses padrões conceituais são estabelecidos pela ciência e/ou tecnologia[1]. Ou seja, se não alcançar o objetivo desejado, mediante os padrões exigidos e pré-estabelecidos, o aluno “erra”. Porém é preciso admitir esse “erro” não como um obstáculo que impeça o avanço no conhecimento, mas como um obstáculo motivador e provocativo para a busca do mesmo[2]. Assim, tratar os erros de forma construtiva nas avaliações é importante para o processo de ensino e aprendizagem.

O objetivo deste trabalho foi categorizar os erros cometidos pelos discentes nas atividades avaliativas referente ao conteúdo de Termodinâmica de Soluções, ministrado no componente curricular Físico-Química II do curso de Química do CA/UFPE.

A análise das avaliações foi realizada para seis turmas de diferentes semestres, e a escolha dessas turmas foi feita com base nas médias das notas da avaliação referente ao conteúdo de termodinâmica de soluções. Durante o processo de análise das avaliações, foi realizada a categorização e classificação dos erros cometidos referentes às questões que envolviam apenas a parte de cálculo do referido conteúdo. A análise, categorização e classificação dos erros foram realizadas utilizando o Modelo de Análise Didática dos Erros (MADE), apresentado por Torre[2]. Além dos erros terem sido identificados e categorizados nas dimensões de entrada, organização e execução, também foram classificados em cada subcategoria, de acordo com o campo específico.

O resultado da análise documental das avaliações mostrou que o tipo de erro que aparecia com maior frequência eram os “erros de execução”, sendo maioria em todas as turmas investigas, em seguida os “erros de entrada”, enquanto os “erros de organização da informação” eram mais raros, chegando até não existir em algumas turmas. De forma geral, os erros marcados pela omissão de letra, alteração ou substituição de sinal por outro e aqueles potencializado pelo nervosismo causando o esquecimento foram os mais comuns na categoria de “erros de execução”. Os equívocos de organização referentes a isolar elementos (análise) e combiná-los de maneira diferente (síntese) apareceram de forma rara na análise. Foi observado o aparecimento quase unânime de um erro de entrada em uma determinada questão que aponta a distorção no enunciado, despertando assim outras metas no aluno sem serem aquelas predefinidas pelo professor. Os resultados também mostraram que as duas turmas de Físico-Química II que apresentavam o desempenho mais baixo na avaliação analisada, foram as que tiverem um maior número de erros categorizados, evidenciando a relação direta entre os erros e o desempenho da turma.

Por fim, podemos dizer que categorizar os erros foi bastante significativo, pois com essa análise e categorização é possível perceber não só o desempenho dos discentes, mas “onde” e “como” estão se equivocando na realização de uma atividade avaliativa. No entanto, vale salientar que muitas vezes é inviável para o docente fazer tal categorização periodicamente, pois a análise requer um determinado tempo que nem sempre o docente dispõe.

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## Agradecimentos/Acknowledgments

Campus do Agreste - UFPE

**Área: EDU**

# ANALOR platform: a portal for systematic analysis of organic compounds and an organic chemistry teaching-learning tool.

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PalavrasChave: *Organic analysis, Teaching-learning organic chemistry assisted by TICs, ANALOR software, Organic compound database.*

## Highlights

The ANALOR platform is an online tool for systematic search of organic compounds and an interactive means of assisting in the teaching-learning process of organic chemistry.

## Resumo/Abstract

The ANALOR software was created in 1992by Professor Claudio Costa Neto with the aim of managing the possible analysis steps and with the aid of a database. It carry out searches on the systematic identification of organic compounds through chemical functional groups and carbon skeletons of the analyte. This is possible due to the ECGF linear notation to describe the molecules (Esqueletos de Carbono, GruposFuncionais Químicos (in Portuguese), Carbon Chains Skeleton, Chemical Functional Groups), described in detail in the Organic Analysis book.[1] This type of search is not possible to be performed by others search tools currently available. This program was designed to be used by microcomputers and was developed using the Visual dBase platform (dBase Inc., USA). The computer evolution changing the operational system from 32-bit to 64-bit, turned the ANALOR program dead. This program has being used as an important organic chemistry teaching tool to analysis organic and in chemistry courses at both technical and graduate levels. Being so, and based in the original ANALOR concepts an online platform was developed.The original database was expanded from 2200 molecules to 4500. The construction of the online platform, used the languages PHP, HTML and CSS, HTML and CSS for the visual part of the page (front - end) and PHP for the connection to the ANALOR database. When the page is loaded the table is dynamically assembled according to the filters used. The searches can be done using the following parameters: presence of the chemical elements most present in organic molecules, values of melting and boiling points, molar weight and Chemical Functional Group/Carbon Skeleton (ECGF). To teach organic chemistry, this new tool allows student to build their own questions on structure-property relationship inserting appropriate filters such as, for example, a boiling point and a chemical functional group to verify the relationship between chain type and boiling point or just a molecular weight range to look at the relationship between a physico-chemical property and different types of intermolecular interactions. In organic analysis, this tool has become universal and can be used by anyone connected to internet through the www.analor.com.br site. In the future, this platform will also have sections for interaction and feedback among users and links to educational videos on various topics in the discipline of chemistry and organic analysis, such as derivatives of the main chemical functional.

## Agradecimentos/Acknowledgments

Ao Instituto Federal de Educação Ciência e Tecnologia pelo auxílio concedido.

1- Costa Neto, Claudio. Análise Orgânica: métodos e procedimentos para caracterização de organoquímios. Rio de Janeiro: Editora UFRJ, 2004.

**Área: EDU**

# ANÁLISE DA PRESENÇA DA QUÍMICA VERDE E DOS OBJETIVOS DO DESENVOLVIMENTO SUSTENTÁVEL EM UM LIVRO DE CIÊNCIAS DO 6º ANO

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Palavras Chave: *Sustentabilidade, PNLD, Ensino de Ciências, Química Verde, Objetivos do Desenvolvimento Sustentável*

## Highlights

ANALYZING THE PRESENCE OF GREEN CHEMISTRY AND SUSTAINABLE DEVELOPMENT GOALS IN A 6TH GRADE SCIENCE BOOK

The science book analyzed presents themes related to sustaintability and ambiental educacion. However, there is no mention to Sustainable Development Goals neither Green Chemistry.

## Resumo/Abstract

Diversos movimentos em escala mundial têm ocorrido para buscar soluções para garantir a sobrevivência na Terra. Há mais de 20 anos a Química Verde (QV) foi proposta para tornar os processos químicos menos perigosos e poluentes, mais energeticamente eficientes e com mais utilização de matérias primas de fontes renováveis. Os 17 Objetivos do Desenvolvimento Sustentável (ODS), incluídos na Agenda 2030, foram aprovados em 2015 na assembleia geral da ONU e reconhece que a erradicação da pobreza é um grande desafio global, mas que é imprescindível para o desenvolvimento sustentável. A UNESCO lançou em 2021 resultados de um estudo nos currículos e programas de educação de 50 países. Os resultados, muito preocupantes, mostraram, por exemplo, que em mais da metade dos documentos analisados não há menção às mudanças climáticas. Diante da importância do livro como recurso didático e de fonte de informação para os docentes, nosso grupo de pesquisa vem se dedicado a estudar aspectos relacionados à Sustentabilidade e QV nas obras aprovadas pelo PNLD utilizados no Ensino de Ciências e Química. Neste trabalho, descrevemos a análise do livro do professor aprovado para o 6º ano da Editora Moderna (2018, 1ª edição). A metodologia utilizada pode ser classificada como qualitativa, com objetivos exploratórios e com a utilização de procedimentos técnicos de análise do discurso. Essa coleção foi selecionada pois, segundo dados no FNDE, foi a mais adquirida para distribuição entre as escolas públicas brasileiras. No volume do 6º ano, são trabalhados temas relacionados ao planeta Terra, à água e materiais, entre outros. Nesses temas, a introdução de aspectos relacionados à sustentabilidade, ainda que haja um foco maior no aspecto ambiental pode ocorrer de maneira mais simples. Essa análise não tem a pretensão de criticar essa obra, que passou por análise rigorosa de especialistas antes de ser aprovada, mas sim de apontar caminhos para que aspectos tão importantes possam ser considerados para inclusão em próximas edições. Observamos que questões importantes como consciência socioambiental, decisões éticas e sustentáveis, preservação do meio ambiente, formas de mitigar as ações do homem nos ecossistemas, desigualdade no acesso à água potável, reciclagem, entre vários outros estão presentes. Esses resultados podem apontar para uma possível, e muito positiva, inclusão desses debates nas escolas nacionais diferenciando-se assim do apresentado no relatório da UNESCO. A educação ambiental deve buscar formar cidadãos que se preocupem não apenas com a atual geração, mas também com as gerações futuras apoiando-se no tripé da sustentabilidade: ambiental, social e econômico. No entanto, apesar da relação intrínseca entre os temas descritos e os 17 ODS e a Química Verde, não é feita menção a eles ao longo do livro. Como sugestões, poderiam ser citados os objetivos que tratam de agricultura sustentável, água potável e saneamento, consumo e produção responsáveis e ação contra a mudança global do clima. Com relação ao capítulo de materiais, poderia ser discutida a importância de modificar os processos de obtenção de produtos para que poluam menos ou sejam provenientes de fontes renováveis. Outras unidades dessa coleção continuam em análise pelo nosso grupo, assim como outras coleções aprovadas. Esperamos em breve ter um panorama mais holístico a respeito da abordagem dessas questões nos livros aprovados pelo PNLD para o Ensino de Ciências.

## Agradecimentos/Acknowledgments

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**Área: EDU**

# Aplicação de sequência didática no estudo das propriedades do metano a partir do biodigestor.

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Palavras Chave: *Ensino de Química, Perspectiva CTS, Biogás.*

## Highlights

Application of a didactic sequence in the study of the properties of methane from the biodigester. Construction of a biodigester as a proposal to adapt to the study on methane. Build scientific knowledge and relate it to other areas in order to build a broader view of environmental issues.

## Resumo/Abstract

A perspectiva Ciência, Tecnologia e Sociedade (CTS)[1] vem sendo objeto de grande interesse como proposta educacional, nos mais diferentes níveis de ensino, porém são grandes os desafios e aparecem algumas dificuldades encontradas pelos professores de química do ensino médio, muitas vezes, delicadas e desafiadoras que levam à busca por estratégias didáticas e propostas através de trabalhos e projetos investigativos.[2] Para o estudo e ensino da química devem, necessariamente, buscar a articulação permanente dos aspectos fenomenológicos, teórico e representacionais, que surgem de modo cooperativo na abordagem dos diversos temas químicos. Metodologicamente, o estudo baseou-se numa abordagem Ciência, Tecnologia e Sociedade, com o desenvolvimento de algumas atividades, objetivando proporcionar a uma turma de 31 alunos do 3º ano do ensino médio do turno matutino condições de aprendizagem sobre as propriedades do metano, avaliar como os estudantes de química tentam representar uma reação química em nível atômico/molecular, além de criar condições e possibilidades de reprodução posterior de um material de fácil produção de biogás a partir de materiais alternativos e de fácil aquisição, sobretudo, trazendo possibilidades para refletir problemas locais e criar soluções possíveis para aprender e transmitir o mesmo aprendizado. Para uma análise inicial, foi aplicado um primeiro questionário para avaliar a opinião dos estudantes quanto à afinidade com a disciplina, percepção dos processos químicos no cotidiano, além da qualificação (adjetivos) pelos estudantes sobre a presença da CTS na disciplina de química. Posteriormente, foi exibido um vídeo sobre lixo/resíduo e a geração de energia. Diante de muitos questionamentos aos alunos foi possível verificar que eles se interessavam mais pelos conhecimentos químicos quando eram relacionados com os seus cotidianos e, principalmente, se explorados através de atividades experimentais. Alguns pesquisadores expressam que a pesquisa é a base da construção do conhecimento e, no contexto escolar, tal exercício é imprescindível.[3,4] Por meio dela, o sujeito desenvolve a criticidade e assim é capaz de transformar o contexto em que está inserido. Portanto, nesta proposta de ensino para o tópico sobre propriedades do metano a partir da produção de biogás, apresentada neste trabalho, foram contempladas as novas tendências pedagógicas em CTS e interdisciplinaridade, além de se apresentar eficiente no que se refere ao grau de aprendizagem dos alunos sobre o tema trabalhado.

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**Área: EDU** **Nº de Inscrição: 0831**

# A representação socialmente compartilhada sobre Ciência entre ingressantes do curso de Química da USP

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Palavras Chave: *Representação Social. Abordagem Estrutural. Ciência. Curso de Química. Universidade de São Paulo.*

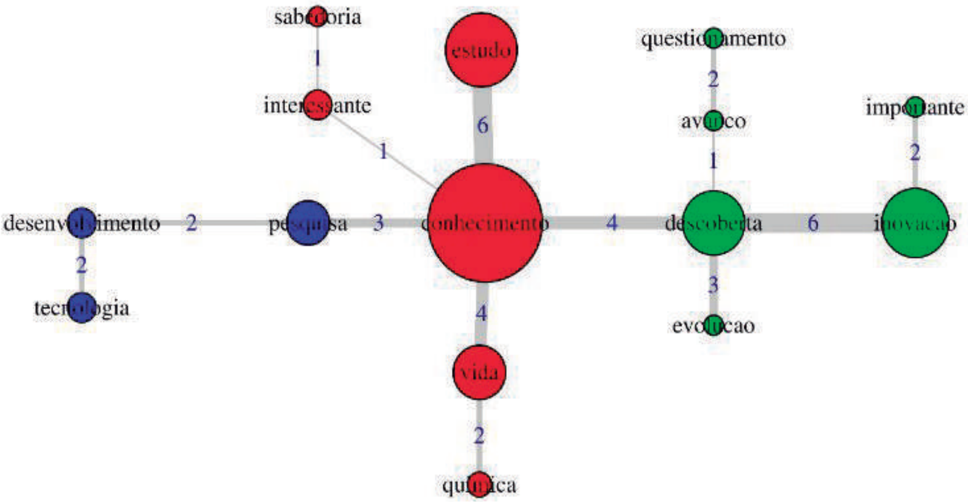
## Highlights

**USP Chemistry Undergraduate Students' Social Representations on "Science".** The Social Representation concerning an object are shared by a social group. The terms *knowledge* and *discovery* characterize the USP Chemistry Undergraduate students social representation concerning Science.

## Resumo/Abstract

Esse trabalho apresenta os resultados de uma investigação sobre a Representação Social (**RS**) de ingressantes do curso de Química da Universidade de São Paulo sobre o objeto *Ciência*. A **RS** é uma reconstrução da realidade por um grupo social que emerge da necessidade prática de compreender e explicar o mundo[1]. Para acessar o universo semântico que compõe a **RS** utilizou-se como instrumento um questionário respondido, em 2019, por 84 estudantes. Solicitou-se aos participantes que associassem espontaneamente as palavras que lhes eram evocadas ao lerem a expressão indutora "*Ciência é*"; posteriormente, as evocações foram analisadas com auxílio de *softwares* de análise textual, em especial o IRaMuTeQ,[2] para a obtenção do grafo denominado árvore de similitude máxima. Através do grafo obtido (figura 1), identificou-se que a **RS** sobre *Ciência* é organizada em torno do termo *conhecimento* fortemente correlacionado ao termo *descoberta.* Depreende-se, da Análise de Conteúdo,[3] que, *conhecimento* é significado como conjunto de saberes referentes à natureza, enquanto *descoberta* faz alusão à obtenção de tecnologias, direcionadas às necessidades da sociedade. Conclui-se que a **RS** de Ciência é marcada como sendo uma fonte de saberes sobre o mundo que, quando aplicados, podem vir a beneficiar a sociedade.

**Figura 1** – Árvore de similitude máxima para os ingressantes do curso de Química da USP em 2019.



## Agradecimentos/Acknowledgments

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**Área: EDU** **Nº de Inscrição: 00869**

# As Funções do Jogo Pedagógico no Ensino de Química

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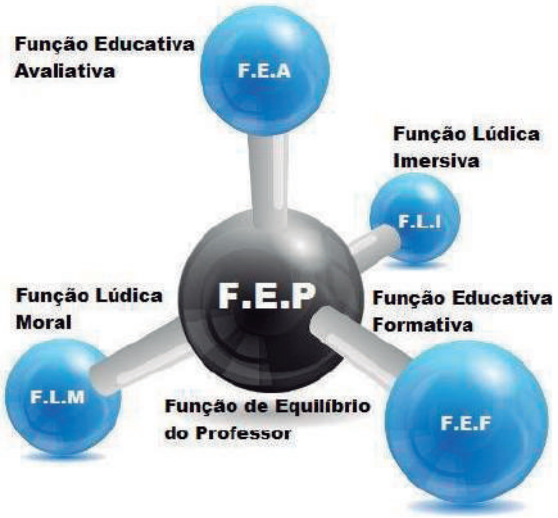
Palavras Chave:*(Jogo, Educação, ARG).*

## Highlights

The Functions of the Pedagogical Game in the Teaching of Chemistry. In the pedagogical game there are five functions that balance pleasure and learning: Educational Formative Function, Educational Evaluative Function, Immersive Play Function, Moral Play Function and Balance Function.

## Resumo/Abstract

A utilização de jogos pedagógicos no ensino de química deve levar em conta aspectos que permitam o aparecimento de características como a liberdade, voluntariedade, autonomia, curiosidade, discussão entre os pares e com o professor, diagnóstico, imersão do jogador e o jogo social, com regras explicitas e implícitas. O jogo Pedagógico, ou seja, aquele utilizado em um ambiente formal de aprendizagem, deve apresentar um equilíbrio entre a função lúdica do jogo, ligada ao divertimento e a função educativa, ligada ao aprendizado. Assim, jogar em sala de aula se torna prazeroso, uma atividade livre e voluntária, que avalia e ensina o aluno. Pensar o jogo pedagógico requer atenção a cinco funções do jogo que, quando equilibradas, permitem uma maior imersão dos jogadores, a avaliação dos conhecimentos existentes, a estruturação da personalidade e da capacidade de convívio social e o aprendizado. Neste sentido, apresentamos cinco funções do jogo pedagógico presentes em todos os tipos de jogos e que, quando equilibradas, podem potencializar a diversão (função lúdica) e o aprendizado (função educativa) dos alunos. A Função Educativa Formativa se caracteriza pela discussão conceitual que o jogo pedagógico proporciona. A discussão conceitual permite a aprendizagem colaborativa e cooperativa. A Função Educativa Avaliativa se caracteriza pela capacidade do jogo em avaliar o conhecimento dos alunos acerca dos conceitos e procedimentos de laboratório. Um diagnóstico importante para prática pedagógica. A Função Lúdica Imersiva se caracteriza pela capacidade do jogo em promover a imersão do jogador. Quanto mais imerso no jogo, mais livremente o jogador discutirá os conceitos objetivados. A Função Lúdica Moral se caracteriza pela capacidade do jogo em fazer com que os jogadores entendam as regras do jogo e as utilizem para o bem-estar coletivo. Entender, seguir e modificar as regras do jogo caracteriza os jogadores como iguais e cria laços sociais afetivos. A Função de Equilíbrio do Professor se caracteriza pela capacidade do professor em, ao propor eu utilizar um jogo pedagógico, observar a presença das outras funções e realizar adequações sempre que houver disparidade entre elas. Neste sentido, apresentamos o tetraedro do jogo educativo:



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**Área: EDU** **Nº de Inscrição: 0255**

# A TEACHING SEQUENCE FOR THE STUDY OF SOLUTIONS IN HIGH SCHOOL

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Palavras Chave:*(Study, Chemical, Solutions, High school).*

## Highlights

A study of the viability of a didactic sequence focusing on the on the science, technology and society approach and with the objective of studying concepts involved with the topic of chemical solutions.

## Resumo/Abstract

A Sequência Didática foi elaborada numa abordagem em Ciência, Tecnologia e Sociedade (CTS)[1] para o estudo de soluções, baseou-se na experiência dos pesquisadores que observam excesso de conteúdo na segunda série do ensino médio, além do obstáculo que o professor geralmente encontra durante a contextualização de soluções.

A sequência didática foi construída a partir de um levantamento de conhecimentos anteriores, abordando os temas "tratamento de água e soluções químicas", apresentação de vídeos sobre o tema. A aplicação de um questionário contendo questões dissertativas serviu como indicação do conhecimento dos alunos sobre o assunto[2], visita a uma estação de tratamento de água, atividade no laboratório envolvendo análise de amostras de água, e, posteriormente, um questionário após as atividades que continha questões dissertativas sobre o assunto abordado[3]. Participaram desta pesquisa 25 alunos de uma escola pública na cidade de Barra do Garças, estado de Mato Grosso, Brasil.

O Questionário final continha as seguintes indagações: 1- Quais as etapas para o tratamento da água e as substâncias químicas utilizadas em cada etapa?; 2- Diferencie: água natural e tratada; 3- Como podemos definir soluções?; 4- Você acha que é possível calcular a quantidade (concentração) de substâncias químicas presentes na água?, Se sua resposta for SIM, teria uma ideia de como calcular essa concentração?; 5 - O que é uma água dura?; 6- Diferencie: titulante e titulado.; 7- O que é uma titulação química? Os resultados das questões foram organizados no Gráfico 1, a seguir.

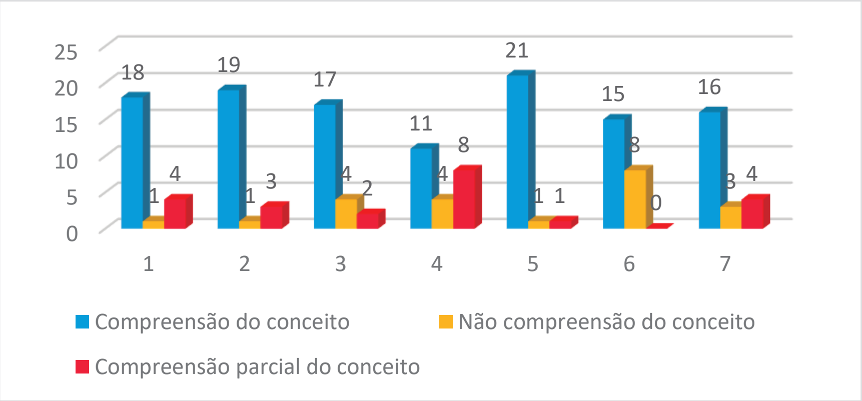

**Gráfico 1: Análise do questionário pós-sequência didática. Fonte: Arquivo pessoal dos pesquisadores (2019)**

A sequência didática desenvolvida para o ensino de soluções químicas, proporcionou aos educandos melhorar seus conhecimentos e contribuiu para contornar as dificuldades encontradas nos temas abordados no processo de obtenção, classificação e tratamento de água para consumo humano, além da análise de parâmetros físico-químicos.

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**Área: EDU**

# A utilização dos três momentos pedagógicos como forma de elaboração de uma oficina sobre chuva ácida

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Palavras Chave: *Oficina, Chuva ácida, Três Momentos pedagógicos, Estratégia de ensino, Ensino de química.*

## Highlights

The use of the three pedagogical moments as a way of elaborating a workshop on acid rain. It exposes the elaboration of a workshop as a chemistry teaching strategy. This methodology is based on the following order: initial problematization, knowledge organization and knowledge application.

## Resumo/Abstract

A proposta didática dos três momentos pedagógicos é atualmente incorporada em diversas propostas de ensino e, em especial, no ensino de química, esta metodologia dialógico-problematizadora é organizada em três momentos com funções específicas: 1) Problematização inicial: momento em que o professor age como mediador, fomentando uma discussão de modo a explorar explicações, levantando as limitações do conhecimento; 2) Organização do conhecimento: momento em que são apresentados e organizados os conhecimentos para responder aos possíveis questionamentos que surgiram no momento anterior; 3) Aplicação do conhecimento: momento em que a situação inicial é analisada e interpretada com base nos conhecimentos expostos no segundo momento para que os estudantes possam responder a situação-problema. Sendo assim, este trabalho teve por objetivo analisar possíveis contribuições da didática dos Três Momentos Pedagógicos na formação de seis Licenciandos em Química da Universidade Tecnológica Federal do Paraná – Campus Londrina. Os referidos licenciandos são participantes do Programa Institucional de Bolsa de Iniciação à Docência (PIBID) e tinham como uma das atividades o planejamento e desenvolvimento de uma proposta pedagógica sobre a temática da chuva ácida, desenvolvida com alunos do terceiro ano do ensino médio do período matutino do Colégio Estadual Professor Carlos Augusto Mungo Genez de Londrina – PR, durante o período pandêmico, portanto, no contexto de ensino remoto, com o intuito de desenvolver o conhecimento científico e estimulando o processo de ensino e de aprendizagem. Em termos metodológicos, a pesquisa de abordagem qualitativa, foi desenvolvida a partir da análise de diários da prática pedagógica dos licenciandos e análise documental do planejamento da aula. A análise deste material foi baseada na análise de conteúdo, considerando as contribuições da didática dos três momentos pedagógicos na formação destes Licenciandos em Química, especificamente, no que se refere a três categorias: problematização inicial, organização do conhecimento e aplicação do conhecimento. Um dos grandes desafios foi planejar e desenvolver a temática mencionada a partir de uma problematização inicial que apontasse as situações do cotidiano relacionadas à realidade educacional dos estudantes da escola. Nessa etapa, os licenciandos definiram que levariam os estudantes a pensar sobre as causas e consequências da chuva ácida. Nessa etapa, os pibidianos perceberam que a etapa da problematização inicial precisaria contemplar situações reais que os alunos conheçam, não restringindo ao uso de exercícios que exijam dos estudantes a memorização e reprodução do conhecimento, é uma etapa que deve instigar os estudantes a levantar hipóteses. No momento da organização do conhecimento, esclarece o que é a chuva ácida, sua formação, pH, reações químicas, a partir da seleção e utilização de recursos didáticos distintos como imagens, slides, formulários e sites. Nesse sentido, os acadêmicos puderam notar que uma diversidade de estratégias metodológicas e recursos podem auxiliar na construção dos conhecimentos. Essas atividades foram pensadas para promover a interação entre o aluno-aluno e professor-aluno, estimulando a autonomia na construção do conhecimento. Na etapa da aplicação do conhecimento, a situação problema foi retomada utilizando os conhecimentos científicos desenvolvidos na fase anterior. Além disso, foram escolhidas atividades propostas pelo Exame Nacional do Ensino Médio (ENEM), relacionadas à temática proposta. Por fim, outras possíveis contribuições dos três momentos pedagógicos no processo formativo destes futuros professores foi a percepção de que esta abordagem metodológica foi um campo interessante de investigação e motivação para pensar e fazer o ensino de química mais interessante.

## Agradecimentos/Acknowledgments

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

**Nº de Inscrição: 00698**
*(Inserir o número de inscrição do autor que fez a submissão)*

# Can women be scientists? Engaging girls in STEM in Southern Brazil

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Palavras Chave: *Girls in Science, Black women, Chemistry, Biology, Stereotypes, Scientific education*

## Highlights

Gender stereotypes affect the ratio of women in science. Obstacles are related to women's ability to research in science. Science has proven to be particularly difficult for black women to access.

## Resumo/Abstract

Nowdays, 50% of the available vacancies in Brazilian Public Universities are reserved - quotas law- for students from public high school students, low-income families, colored (black and brown) and native people. According to government statistics, the enrollment of colored students has had a significant increment. Today, black students represent more than 50% of the undergraduate enrollments. However, only 12% of black and brown women are in STEM courses, such as Engineers and Mathematics. About 35% are enrolled in social science, administration and law, followed by 24% in education. This scenario is similar in the US, despite the country's long-term programs to increase women's participation in these fields.The percentage of African American women is only 13.02% in STEM in the USA. It shows asymmetries between men and women in the sciences are a transcultural phenomenon. Studies on intersectionality draw attention to the importance of multiple stereotypes related to student's cross-identities and their impact on the professional achievements of black women in general. Other studies showed that Elementary School is the better place/time to stimulated girls to study Science and Math. The goal of this paper is to present the results of the project called "Girls in Science" that was developed in 2019 at Santa Cruz do Sul, at the Southern state of Rio Grande do Sul, Brazil with the purpose to address these asymmetries. The Project developed school practices and didactic experiments on Natural Science with girls students (12 to 15 years) and also includes discussion about gender bias and race. The activities were coordinated by Professors and graduate students from the Bioprocess e Biotechnology Engineer course of Universidade Estadual do Rio Grande do Sul for nine months. We used different strategies to teach experimental activities in the Biology and Chemistry fields: movies, experiments in the laboratory and lectures.


Figure 1: Chemistry activities


Figure 2: Biology activities

At the end of the project, participants shown significant interest in sciences and a better self-trust in running experiments. We evaluate their perception about the nature of the professional work on Natural Sciences have not only improved but also becomes a personal alternative for their own future.

## Agradecimentos/Acknowledgments

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Escola Estadual de Ensino Médio Alfredo José Kliemann, Santa Cruz do Sul/RS.

**Área: EDU** **Nº de Inscrição: 235**

# Case Studies as active teaching methodology in Biochemistry

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Palavras Chave*: Inquiry based learning; Teaching of Biochemistry; Teaching-as-research; Active methodology*

## Highlights

In this work the case studies were used to develop an active teaching methodology as a tool to teach biochemistry with the aim to connect scientific knowledge to day-by-day experiences.

## Resumo/Abstract

According to QUADROS and MORTIMER (2014), teaching methodologies proposed in the 1970s require students to be more active during teaching and learning processes. Therefore, teachers should organize classes to train critical thinking, using teaching strategies that approach scientific concepts to day-by-day life. When talking about inquiry as teaching method, ZÔMPERO e LABURÚ (2018) confirm that this approach, also known as learning by discovering, needs the student to assume a more investigative, proactive position to assure improvement of the student's capability to understand and memorize new facts, to create better cooperation skills and responsibility in scientific work. In this sense, the authors understand the need for pedagogic strategies that meet current demands of science teaching. In the present work a methodology was developed having in mind teaching by answering problems in biochemistry class, 9 students divided in three groups, in chemistry course at Universidade Federal do Pampa (Unipampa) during semester 2021/1.

The teaching strategy was divided in three stages. First, students received a research topic to be examined within 30 days from the following areas: fatty acids, carbohydrates, and biological oxidations. They should search the answer using books, articles, and other reliable sources. Second, students formulated hypotheses and discussed them in the group and with the biochemistry class teaching assistant. Third, abstracts resuming the results of their research were compiled and presented at 1st Investigative Biochemistry Program of UNIPAMPA, which was held during the Integrated Academic Week of the chemistry graduation course during the first semester of 2021. After construction of hypotheses and conclusion of the research, each group elaborated a summary, which was presented to the academic community in the "1st Symposium of Investigative Biochemistry: Case studies".

The teaching assistant observed that understanding the literature and other sources was one of the major problems. This directly impacts on their sovereignty and initially caused a surprisingly low number of ideas and hypotheses to be worked on. At this moment, the interference of the teaching assistant was vital to resume and organize ideas, to voice the knowledge, to analyze everyday phenomena and to discuss biochemistry on atom or molecular level. Writing an abstract about a certain problem needs acquisition and organization of new information to assure that students not only are able to reproduce the content but also to discuss and to opine about their results, showing plain dominance as well as being capable to contextualize the problem and its solution. The most important result of those activities is that the students improved their research skills by observing and analyzing all relevant points to construct and develop new hypotheses and ideas until they finally came to new conclusions.

It can be concluded that the inquiry methodology provides new perspectives for teaching and learning biochemistry, contributing to the development of the students' investigative autonomy, as well as to the ability to link theoretic knowledge to *in vivo* processes. In addition to improve investigative skills, this approach can be considered an incentive to practice active methodologies since it was applied in a class of future chemistry and natural sciences teachers.

## Agradecimentos/Acknowledgments

The authors would like to thank Universidade Federal do Pampa (UNIPAMPA) for the possibility to develop the presented ideas.

**Área: EDU**

# Chemistry Beyond Beauty: A Proposal for an Approach to Organic Functions Based on Cosmetics from Research Teaching

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Palavras Chave: *Ensino por Investigação, Cosméticos, Ensino de Química.*

## Highlights

The teaching of organic functions is considered difficult, due to the students' difficulties in associating the functional group that characterizes them to each function, leaving them to memorize each of these groups. Therefore, the investigative approaches seem promising to approach this concept, being understood as a pedagogical posture adopted by the teacher in the way of thinking and teaching science and characterized, mainly, by a problem, contextualization, elaboration and debate of hypotheses and communication, as well as students are motivated to assume a new attitude in the face of a problem situation so that they can socialize hypotheses, debate them among themselves and restructure them to promote their arguments and reach a solution, in this way expanding their scientific knowledge or understanding of phenomena natural. In this work, we trace a didactic sequence for the study of organic functions in a teaching proposal by investigation based on the chemistry of cosmetics, which was applied in a third year high school class.

## Resumo/Abstract

Este trabalho consiste em uma sequência didática sobre o ensino das funções orgânicas com base no conceito dos cosméticos, aplicada em dez etapas em uma turma do terceiro ano do ensino médio regular do Colégio Interativo de Maracás situado na cidade de Maracás – BA. A sequência didática (SD) aplicada fundamentou–se na Sequência de Ensino por Investigação (SEI), descrita por CARVALHO (2013). A SEI estruturou-se em três atividades: primeiramente o problema que, orienta os alunos a pensarem e trabalharem com as variáveis importantes do fenômeno científico envolvido no conteúdo, posteriormente a contextualização e por fim, possível solução para problema. Assim, A SD estruturou-se em três categorias: nas duas primeiras etapas reuniu os conhecimentos prévios dos estudantes, ao longo da terceira e quarta etapa houve a contextualização do problema e, nas etapas finais, analisou-se a alfabetização cientifica e a percepção da aprendizagem dos alunos sobre as funções orgânicas. O problema a ser investigado foi *"Você conhece as substâncias presentes nos cosméticos que utiliza e quais são as relações entre os benefícios e malefícios à saúde e as funções orgânicas que pertencem?" as respostas dos alunos foram obtidas através de questionário e aulas gravadas, a* contextualização foram por meio de duas reportagens intituladas "Mulher morre ao ter reação alérgica a tintura de cabelo" e "Cosméticos podem causar problemas à saúde" e abordagem do conteúdo. Posteriormente, os alunos foram orientados a escolher um cosmético de uso próprio e investigar quais os componentes haviam presentes, quais as funções orgânicas pertencia cada um e bem como, identificar os possíveis benefícios/riscos à saúde que esses componentes podem oferecer. E por fim, participaram de uma oficina de preparação do xampu e perfume e responderam o questionário final. A SD foi avaliada de forma qualitativa através de dados coletados dos questionários, relatórios e roda de conversa. Os resultados da SD, demonstraram que os estudantes precisavam saber interpretar os rótulos dos cosméticos e a importância de discuti-los nas aulas de química, e que este é um recurso interessante para a abordagem dos conceitos químicos e capaz de aprimorar o conhecimento cientifico aos estudantes. Obtivemos resultados satisfatórios sobre a identificação das funções orgânicas, no entanto, vale salientar que a SEI aqui proposta, não foi suficiente para que, os alunos estabelecessem a relação entre as estruturas moleculares e suas respectivas funções orgânicas. As atividades experimentais sobre a produção de xampu e do perfume enriqueceu a aprendizagem dos estudantes por oportunizar a compreensão de alguns compostos presentes nestes cosméticos e de como atuam, quais os aspectos do produto com sua ausência e a quantidade presente e necessária. Além, de possibilitar aos estudantes a produção dos seus cosméticos de maneira segura, assim, podem se posicionar as "receitinhas caseiras" divulgadas na internet. Por fim, a elaboração e aplicação desta SD contemplaram os objetivos desta pesquisa. Pois, a proposta de abordagem das funções orgânicas com base nos cosméticos e estrutura no ensino por investigação permitiu uma aprendizagem contextualizada, sendo uma estratégia e recurso didático diferente capazes de inserir os estudantes no processo de desenvolvimento da alfabetização científica.

**Area:** **EDU**

# Chemistry Deck: An active methodology for resuming classes and resocializing students at IFCE Campus Caucaia post pandemic period

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Keywords: *Pandemic, Adaptation, Reconstitute, Game, Periodic Table.*

## Highlights

Reinforcement of the learning deficit due to the COVID-19 pandemic

Use of active methodologies: games

Students producing his knowledge

Work under construction (will be applied in the classroom)

## Resumo/Abstract

During the first two years of the COVID-19 pandemic, an adaptation to remote teaching was necessary, leaving a general perception of a difficulty for students in learning. After this adaptive period, the students returned to the classroom with a lag in teaching, emerging even more the need to innovate didatic techniques, wich is decades-old problem, inside and outside the classroom, seeking to facilitate learning and resocialization at school, that will recover the previous years.

With that in mind, two PIBID-Chemistry fellows from IFCE, Caucaia *campus* (Ceará, Brazil), created a way to reconstitute teaching with the return of face-to-face teaching. A didactic game was designed and produced to recover part of the outdated learning of the remote period, in a fun and playful way, and in order to increase student's empathy with the Periodic Table and explain how elements with similar properties can form triads and show themselves in everyday life. This game is on the Periodic Table, and consists of 62 cards, divided into groups (1-8A's, 1B, and 8B), having the name, symbol, family and atomic mass of each element. It can be played by up to 4 participants. Hydrogen is the famous joker card, where it, by having "similar" properties with alkaline metals and halogens, can replace both in a trio of cards in the game. The game starts by shuffling the cards and randomly delivering 9 cards to each player. The first player takes a card from the deck, and chooses to keep it or not, as long as he discards another, thus creating a block of disposable cards. The next player will have the option of taking the card from the block, or the one from the deck, choosing which one to abandon. In this way, the game continues until a player forms 3 sets of cards, each set from the same family on the Periodic Table - this will be the winner. It's worth mentioning that the project is stil in progress.

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## Agradecimentos/Acknowledgments

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**Área: Ensino de Química - EDU**

# CHEMISTRY TEACHING CHALLEGENS DURING PANDEMIC COVID-19: a case study at IFMA Campus Santa Inês – MA

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Palavras Chave: Remote teaching, Chemistry, Pandemic, Google classroom, Learning.

## Resumo/Abstract

The COVID 19 pandemic generated a series of impacts on the school context, bringing with it new challenges for students and teachers who needed to learn a new teaching modality using technologies, ICT's. The main objective of this work is to discuss the main challenges to the teaching-learning of the discipline of chemistry in the context of remote teaching established during the pandemic of the new coronavirus in the institution studied. In this way, we sought to describe how this type of teaching took place and point out the main challenges to the teaching of the discipline of chemistry, through an interview with the students of the IFMA Campus Santa Inês (IFMA-SIN). Students from the 1st and 2nd years of IFMA-SIN from the technical courses in buildings, electronics, electromechanics, logistics and computing were interviewed, as well as a sample of 33 students. Data from the questionnaires were collected by Google forms. In times of a pandemic, even experienced teachers or teachers did not have difficulties using ICTs, so the institution provided a "Training Trail for the use of digital tools (MENDONÇA, 2020). For the development of remote teaching, Google Classroom was used with access by academic email and it was observed that students had difficulties to enter the digital platform. In the results some points of the interview were observed. In the first question, the student's ability to use academic email accounts to access Google Classroom was evaluated, 84.9% did not agree because the use of email made it difficult to enter the application, and only 15.1% agreed. Regarding the availability of internet, more than 50% of the students do not have it, and most of them use mobile data, and in other locations the signal does not arrive with quality. Regarding the electronic device, 48.5% had an adequate device to access classes, 24.2% had old devices and did not allow monitoring of activities, 15.2% did not have cell phones to follow classes and deliver activities. In addition, 10% of the interviewees stated that they had obtained paid work to help their families, and this worsened the students' learning, as they had to work and did not follow the activities. Respondents were also asked if the home environment was suitable for studying, 36.2% said they had to share their studies with homework and this conflicted with the student routine, bringing low performance, 42.4% said that the space was conducive to study. Another issue to be pointed out is whether the students had family support in this new modality of remote teaching, 48.5% did not have this support and organization in their studies and only 27.3% had family support. Another factor that discouraged the students was the excess of activities they had to perform, so the teachers rethought in other strategies, using different activities that took into account reasoning, chemical language, writing, the execution of experimentation/research activities, the use of simulators were strategies used to circumvent this situation and improve student learning. And in the last question, it was asked if the time/interaction between students and teachers was satisfactory in the teaching of chemistry, 88.9% responded that they were satisfied with this interaction with the discipline and only 11.1% were not satisfied due to difficulties in accessing the virtual environment. Therefore, remote teaching has advantages in terms of savings in school educational expenses, however the poor infrastructure, the lack of experience of students with this type of teaching, especially in terms of autonomy, teacher training, the existence of experimental subjects weigh against this teaching modality, yet it changed the perspectives of teaching and learning in a profound way.

## Agradecimentos/Acknowledgments

IFMA – Campus Santa Inês, Fapema

**Área: EDU**

# CluQui (Clube da Química): A University-School Partnership for the Dissemination and Popularization of Chemistry.

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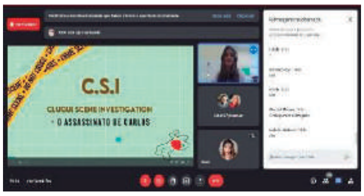
Palavras Chave: *Desmistificação da Química, Escolas Públicas, Mídias Digitais.*

## Highlights

Dissemination, popularization and demystification of chemistry in public schools and in the community; Development of extension activities through the use of digital media (Google Meet and Instagram); Conducting playful workshops at events.

## Resumo/Abstract

The CluQui project (Clube da Química): A University-School Partnership for the Dissemination and Popularization of Chemistry is an extension project of the Federal University of Ceara, created in the International Year of Chemistry (2011). The main objective of the project is the dissemination, popularization and demystification of Chemistry, targeting public high school students. In addition, CluQui works with a social initiative by collecting bottle caps for the Peter Pan Association. The project currently has 1 paid scholarship holder and 30 volunteers. During the pandemic period, the group adapted to this new reality, starting to develop remote activities through the Instagram platform. Among these, we highlight the “CluQui na UECE and CluQui na UFC”, “Desmistificando a Química”, “Tem Química Nisso”, “CluQui em casa” and the creation of interactive and informative videos in the “REELS” tool. Partnerships with some schools were also established, one of them being the EEEP José Maria Falcão school. In this, weekly classes were implemented for 3rd year students focused on ENEM. In the presentations in the schools, playful activities were carried out involving interactive experiments and games with chemistry content. On Chemist's Day (June 18), CluQui promoted a virtual event on the Instagram platform where it performed a "Super Live of experimentation" involving the following experiments: "The hydrogen balloon", "Fire that doesn't burn", "Test of flames”, “Chemical rocket” and “pH test”. After each experiment, all explanations were provided and doubts and curiosities were removed from both students and Live viewers. This same event was held for EEEP José Maria Falcão students. CluQui also participated in a virtual way in the event “Semana da Química” at the Federal University of Ceara (UFC), where the workshops “The chemistry of gel alcohol” (2020) were held, addressing the manufacture of gel alcohol and fakes news involved in its use and “CSI: CluQui Scene Investigation” (2021), addressing issues related to the techniques used by criminal expertise to solve crimes. With this, it is evident the effective performance of CluQui in the demystification and popularization of Chemistry in schools and the strengthening of UFC extension actions with the community.



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**Área: EDU** **Nº de Inscrição: 728**

# Concepções prévias de alunos do 6º ano do ensino fundamental sobre plásticos e microplásticos

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Palavras Chave: *Conhecimentos Prévios; Ensino de Química; Microplásticos; Polímeros; Poluição.*

## Highlights

**Previous conceptions of 6th grade elementary school students about plastics and microplastics.**
Survey of previous conceptions about plastics and microplastics.
Data evaluation by content analysis method
Need for actions to meaningful learning the pollution, plastic and microplastic concepts.

## Resumo

Os microplásticos, assim como objetos de plástico, de maior tamanho, não são incorporados ao ambiente, visto que são constituídos por polímeros sintéticos, dificilmente degradados nas condições ambientais. A problemática ambiental faz parte do dia a dia dos estudantes, contudo, para que uma atitude crítica perante esses problemas seja desenvolvida faz-se necessária uma educação científica e tecnológica que promova reflexão a respeito do uso e descarte dos plásticos no cotidiano. É consenso na literatura que as concepções que os estudantes possuem são ponto de partida para a construção de novos conhecimentos. Nesse sentido, com o intuito de fornecer subsídios para o desenvolvimento de metodologias de ensino capazes de possibilitar a evolução conceitual a respeito de plásticos e microplásticos dos indivíduos envolvidos no processo de ensino-aprendizagem, foi realizado um levantamento de concepções prévias (LCP) em relação aos plásticos e microplásticos, junto a 73 estudantes do 6º ano do Ensino Fundamental de uma escola estadual do município de Jaboticabal (SP) aplicando-se questionário com 6 perguntas dissertativas. No presente trabalho, é apresentada apenas a análise das respostas dadas pelos alunos para as questões 5 ("O que você sabe sobre microplásticos?") e 6 ("O que acontece com os lixos de materiais plásticos, como os canudinhos de refrigerante, quando são jogados no mar?"). Os dados foram avaliados por análise de conteúdo. A maioria dos respondentes (58 alunos) não sabe o que são microplásticos (Fig. 1A). Os demais estabelecem relação entre a palavra "microplástico" e "plásticos pequenos" ou "menores" (Fig. 1A), contudo inferimos que estes sujeitos não possuem dimensão microscópica disso que referem como "pequeno". Para a questão 6 os estudantes se referem ao plástico ainda em sua forma observável (macroplástico) (Fig. 1B). Nenhum aluno se referiu ao microplástico resultante da degradação de resíduos como canudinhos e sacolas plásticas (Fig. 1B). A palavra poluição é citada pela quase totalidade de alunos, contudo não é possível, pelo teor das respostas, inferirmos que os estudantes não possuem o conceito de poluição, apenas reconhecem os efeitos de agentes poluentes.

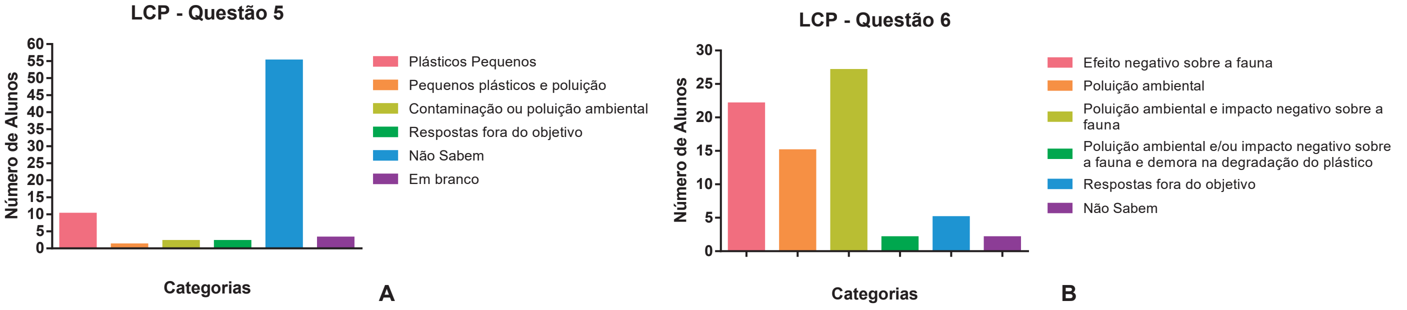

**Fig. 1.** Resultados e análise das questões 5 (A) e 6 (B) do levantamento de concepções prévias.

Os resultados evidenciam as lacunas conceituais existentes no aprendizado dos alunos, principalmente o que se refere à dificuldade dos estudantes em conceituarem poluição e de estabelecerem relação entre o potencial do plástico para a poluição e seu tempo de degradação. Sugerem ainda a necessidade de ações em espaços de ensino que promovam uma aprendizagem significativa dos conceitos de poluição, plástico e microplástico. Para tanto, advogamos por metodologias de ensino numa perspectiva CTSA (Ciência, Tecnologia, Sociedade e Ambiente) utilizando estratégias em educação ambiental, visando discussão a respeito de alternativas, como a substituição dos plásticos convencionais pelos biodegradáveis e adoção de medidas de sustentabilidade (redução, reutilização, reciclagem e substituição de objetos de plástico por outros menos nocivos ao ambiente). Com a compreensão desses conceitos e a incorporação dessas atitudes, há a possibilidade da diminuição da poluição e da interferência do homem em ambientes naturais.

**Área: EDU**

# Contribuições das Histórias em Quadrinhos (HQs) para o processo de ensino e aprendizagem em química.

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Palavras Chave: *Ensino de química, Histórias em Quadrinhos, Ludicidade, Eletrólise.*

## Highlights

Contributions of Comics to the teaching and learning process in chemistry. The production of comics by the students was used as a strategy for the appropriation of chemical knowledge worked during the classes, with good participation and acceptance by the students.

## Resumo/Abstract

Histórias em Quadrinhos (HQs) costumam ser utilizadas em livros didáticos para ilustração de conceitos e também como meio para avaliação do ensino, sobretudo em conteúdos curriculares vinculados às ciências da linguagem, humanas e também da natureza. Especificamente para o ensino de química [1], existem algumas estratégias que podem ser empregadas, como, por exemplo, utilizar quadrinhos já publicados para discussão de conceitos químicos, ou o professor pode desenvolver o roteiro e produzir uma HQ para iniciar a discussão do conceito alvo do estudo, ou ainda pode-se trabalhar os temas fazendo com que os alunos possam produzir suas próprias HQs. No presente resumo a produção de HQs pelos alunos foi utilizada como uma estratégia para verificar a apropriação dos conteúdos de química trabalhados com os estudantes de um colégio localizado na região do litoral do Paraná, sendo uma turma do nono ano do Ensino Fundamental II e duas turmas do Ensino Médio (primeiro e segundo anos). Os temas estudados junto às turmas foram: no Ensino Fundamental II reações endotérmicas e exotérmicas; Primeiro ano do Ensino Médio Coloides e o Efeito Tyndall; e para o Segundo Ano eletrólise (recorte com um exemplo de HQ produzida por um estudante do Segundo Ano na imagem ao lado). De forma geral em todas as HQs (total de 17 HQs entregues) os estudantes conseguiram abordar os conceitos químicos dos temas estudados, buscando combinar tanto os desenhos com a parte textual das HQs, sendo esta uma grande potencialidade da exploração da verbo-visualidade que as HQs proporcionam [2]. A produção das HQs é uma atividade desafiadora aos estudantes, mas que pode contribuir de forma significativa para uma abordagem não convencional dos conteúdos de química ou mesmo de ciências em geral [3], inclusive para a avaliação dos conteúdos apropriados pelos estudantes. Os resultados encontrados demonstram a importância de se buscarem sempre novas estratégias para o ensino de Química, sendo as HQs uma forma lúdica e interessante para aplicação junto às turmas do Ensino Fundamental e Médio, pois pode motivar os estudantes e contribuir positivamente para o processo de ensino e aprendizagem em química.

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**Área: EDU** **Nº de Inscrição: 00767**

# Contributions of the Braille script and audio description for the inclusion of visually impaired students in an experiment on polymers

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Palavras Chave: *Ensino de Química, Inclusão, Experimentação, Áudiodescrição, Deficiência visual.*

## Highlights

O estudo mostra como o roteiro em Braille e a audiodescrição da atividade pode auxiliar na participação de alunos com deficiência visual em experimento possibilitando a inclusão no ensino de Química.

## Resumo/Abstract

Baseados em Vygotsky, a aprendizagem se constitui por meio de interações interpessoais numa relação mediada pelo professor com o uso de signos e instrumentos. Na Química, os signos são representações (modelos, equações, etc.) que auxiliam na manifestação e na produção do conhecimento que permitirão o desenvolvimento da imaginação conforme as evidências observadas de dados analisados e do potencial de cada sujeito em criar modelos explicativos.[1] Já os instrumentos são ferramentas (vidrarias, equipamentos, etc.) próprias para agirem sobre os materiais e substâncias promovendo dados empíricos específicos para análise. Contudo, como alunos com deficiência visual (DV) vão relacionar as informações dos roteiros experimentais mediados pelo professor com o procedimento e manipulação de materiais e substâncias em aulas de laboratório?

Pautamo-nos em elementos da pesquisa participante para o uso de recursos que atuem como tecnologia assistiva para a inclusão de DV em aulas experimentais. Sendo assim, este trabalho versa sobre as contribuições do uso de roteiro em Braille e áudiodescrição de materiais em aulas experimentais para a inclusão de DV no ensino de Química. Participaram deste estudo 2 professores em formação inicial (PFI) e 12 DV (A), realizado em instituição de apoio destinada aos DV de escola pública regular. No extrato 1, PFI1 acompanha a leitura do roteiro em Braille por A6 para audiodescrever os materiais do experimento: produção de geleca para discussão sobre polímeros.

Extrato 1

**PFI1:** *Vamos usar dois béqueres de vidro que estão do lado direito de vocês: um de 100 mL, o maior, e um de 50 mL, o menor; um bastão de silicone à frente e; uma balança semi-analítica vocalizada, à esquerda. A6 continue a leitura do procedimento experimental.*

**A6:** *No béquer 1, coloque 25 mL de água boricada Adicionar aos poucos os 20g de bicarbonato de sódio até perceber que não há mais liberação de bolhas. No béquer 2, colocar 45g de cola. Em seguida, adicionar aos poucos no béquer 2, contendo cola, a mistura do béquer 1, agitando com o bastão até atingir a consistência gelatinosa.*

Figura 1: A6 fazendo leitura em Braille (acima); Mistura dos conteúdos dos béqueres por A8 (abaixo).

Na realização do experimento, PFI1 usa a audiodescrição (AD) para trata a posição e características dos materiais usados. A AD é uma atividade de mediação linguística, uma tradução audiovisual do tipo intersemiótica (também chamada de transmutação) que permitiu PFI1 traduzir um sistema de signos visual para um sistema de signos sonoro.[1] Contudo, ressaltamos que a AD do experimento não trata somente em descrever o que se vê, mas exige perícia do audiodescritor em descrever o que é fundamental para a compreensão da organização semiótica do material, pois é um elemento indispensável para que os DV entendam o procedimento, lido por A6, colaborando para sua significação.[2] Portanto, não se deve explicitar, interpretar ou adiantar informações, mas sim, ser sensível à composição do cenário e sua importância para o contexto prático.

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**Área: EDU**

# Development of an elective discipline: a contribution of scientific divulgation to the demands of public schools.

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*Keywords: scientific divulgation, teacher training, university, public school, action research.*

## Highlights

This study has important implications for discusses the use of science dissemination.
Continuing teacher education as a tool to bridge the gap between public schools and universities.
The potential of activities developed in a professional development group for reflection and improvement in the teaching practice of public school teachers.

## Abstract

In order to contribute to the dissemination of the university, the Laboratory of Investigations in Teaching Natural Sciences (LINECIN) of the São Carlos Institute of Chemistry of the University of São Paulo (IQSC/USP) promotes interactive lectures in partnership with IQSC researchers to discuss the importance of scientific research and bring the community and public university closer together. One of the lectures was based on research by the Electrochemical and Environmental Processes Group (GPEA), which addresses aquatic and terrestrial contamination by dyes, drugs, and pesticides, presenting electrochemical processes as possible treatments for these contaminated matrices. Another way to contribute to scientific dissemination is through partnerships between the university and schools. These partnerships usually occur between university professors and elementary school teachers, who seek to reflect on teaching and learning practices in the classroom. Partnerships take place through continuing teacher education groups, specifically in professional development groups[1]. The objective of this paper is to present how an elective course developed through a partnership between a Chemistry professor, undergraduate students, graduate students, and university professors contributes to bringing the university closer to the public school. For the execution of the present work, action research was used, in which it seeks to unite research with practice[2]. In other words, action research applies to projects in which professionals seek transformations in their own practices[3]. Collectively, it was decided that one of the activities developed by the group in the year 2021 was the planning of an elective subject as it is a challenge posed to basic education teachers. Within the scope of Inova Educação, this subject is one of the curricular components that make up the Curriculum of the State of São Paulo. The discipline was called "I, the scientist", with the main purpose of introducing students to the scientific method and the role of the scientist in society. The discipline was applied to the eighth year of elementary school II of a public school in the interior of the state of São Paulo. The professor worked on concepts of chemical transformations, substances, and mixtures, relating them to the theme "Water". In addition, activities were carried out with the students based on the interactive lecture on scientific research by the GPEA. The students carried out a practical investigative activity that illustrates a technique used by the research group for the degradation of dyes in water samples. The students also watched a scientific dissemination video and participated in a conversation circle with a graduate student. The activities carried out in the discipline were designed to strengthen the partnership between the public school teacher and the university, in addition to bringing public education students closer to what is developed within universities by research groups, presenting possible solutions to the real environmental problems faced by the population.

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**Área: EDU**

# Didatic sequence using podcast on Chemical Kinetics with an investigative and experimental approach

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Palavras Chave: *Chemical Kinetics, Didactic Sequence, P. O. E Technique, Podcast, High School.*

## Highlights

We evaluated if the use of a podcast in a didactic sequence is a useful tool for teaching Chemical Kinetics to high school students, allowing the subjects to investigate phenomena through the technique of Predict, Observe and Explain (P. O. E.) and using easy-to-perform experiments within the classroom, aiming to facilitate the understanding and providing easy access to the educational material.

## Resumo/Abstract

Meaningful learning is mainly related to the students' prior knowledge and the connections and reconnections of their previous concepts. We aim to facilitate the development of knowledge inducing students to place these concepts hierarchically and connect and organize them.

The use of podcasts in education is in line with public policies that encourage the use of Information and Communication Technologies (ICTs) in classroom. An example of this is the Brazilian *Domínio Público* portal, which offers free access to artistic and scientific works in different forms already in public domain or with authorized disclosure. The use of podcasts by itself does not change the learning process, it should be planned as a tool that combines other educational resources in order to attract interest and make the construction of the knowledge more flexible[1].

Chemical Kinetics is taught on in the second year of high school and is often associated with calculations and distant reality from the students. With the construction of our pilot experiment and didactic sequence, it was possible to conclude it has the potential to build significant knowledge. The integration with research using the *Predict, Observe and Explain* (P. O. E.) technique and having as guidance a podcast induced conflict of predicted with observed knowledge. It was then possible to re-signify the concepts already solidified by the students. Lately, by integrating videos, experimental classes and conceptual maps, students had a new possibility of perceiving the content and a new path for construction of their learning.

Podcast is one of the most used tools for education, and it is of crucial importance to guidance compared to other classical techniques of teaching, such as the use of the blackboard or PowerPoint presentations. To the best of our knowledge, this is the first quantitative study using a podcast as a teaching tool, and students reacted favorably. These findings can facilitate didactic counseling regarding teaching.

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## Agradecimentos/Acknowledgments

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**Área: EDU** **Nº de Inscrição: 00196**

# Do aluno ao consumidor: a necessária reflexão da implementação de metodologias ativas no ensino de química

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Palavras Chave: *Ensino de Química, metodologias ativas, ensino-aprendizagem*

## Highlights

From pupil to consumer: a necessary reflection about active methodologies' implementation on chemistry teaching

There is an increasing proliferation of methodologies which "promise" to make pupils more active in the process of building knowledge. However, most of them disregard the sciences' epistemology.

## Resumo/Abstract

Esse trabalho apresenta reflexões de professores de química, também doutorandos na área de ensino de Ciências, sobre o uso das metodologias ativas no processo de construção de conhecimento em Química de alunos da educação básica. A área de Ensino de Química e a Pedagogia, de um modo geral, vêm lançando novas propostas de ensino há pelo menos três ou quatro décadas com a intenção de redefinir não só os papéis do docente e do discente na escola básica, como também os mecanismos relacionados à transmissão de conteúdos entre esses dois atores do ambiente escolar. Essa redefinição pode ser vista nas mudanças da posição das carteiras, a arquitetura da sala de aula e especialmente nos últimos tempos, no uso de um novo vocabulário relativo às situações de aprendizagem, as chamadas metodologias ativas. Sem desmerecer as boas intenções e nem ignorar os acertos desses métodos de ensino, podemos perceber que há uma crescente proliferação de siglas (*slogans*) que "prometem" tornar o aluno mais ativo no processo de construção de conhecimento. No entanto, todos esses esforços e as tentativas de reformular os dispositivos pedagógicos presentes na escola não parecem ter ido suficientemente longe em sua contundência. Uma das grandes dificuldades que aparentam ter as metodologias ativas, é a falta de profundidade na epistemologia de cada área do conhecimento em que está sendo aplicada. No mundo contemporâneo, os alunos estão cada vez mais imersos em um universo midiático, em que o pensar com critérios é, quase sempre, suprimido por uma opinião ou um ponto de vista. Assim, cada vez mais podemos perceber a disseminação das metodologias ativas, como recurso salvacionista da aprendizagem, que se preocupam basicamente com a transmissão de um conhecimento que é instantâneo em vez de estar atenta ao ensino de maneira profunda e eficaz, propagando, então, uma visão reducionista, individualista e excludente de determinados conceitos. Diante do exposto, é essencial ressaltar que as metodologias ativas no ensino de química são muito bem-vindas, quando se preocupam com a construção do conhecimento a ser propagado mediante a coletividade, e como um recurso para que essa área da ciência seja cada vez mais conhecida na sociedade. O ensino de química precisa ser repensado para a escola básica não a partir das "metodologias ativas", que se preocupam somente em apresentar um novo nome e/ou sigla com o objetivo de impactar e impressionar os "consumidores" da educação. A área precisa implementar ações nas instituições de ensino, como também na sociedade, que se preocupem em promover a emancipação e a reflexão a partir do diálogo com os aprendizes, a fim de que se possa compreender as demandas sociais que envolvem a Química em seus mais variados contextos

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## Agradecimentos/Acknowledgments

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**Área: EDU**

# Educação Patrimonial na Formação Docente em Química

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Palavras-Chave: *Museu*, *Acervo Histórico*, *Patrimônio, Formação Inicial, Formação Continuada*

## Highlights

Patrimonial Education in the teacher training in Chemistry: analyze the process of the Patrimonial Education beside to teachers of Chemistry and students of the Licenciatura from the experience of study and visitation to a historical museum.

## Resumo/Abstract

Os museus se constituem como espaços com potencialidades formativas para docentes em Química por oportunizarem práticas educativas orientadas pela Educação Patrimonial (EP)[1], que se relaciona com a educação escolar e com a cultura científica. Ademais, proporcionar o acesso de docentes a exposições e instituições museológicas colabora com a ampliação de seus repertórios pedagógico, científico e cultural, para a formação humana e para a consciência crítica sobre patrimônio. Neste sentido, este trabalho se situa em uma experiência formativa ocorrida no âmbito de uma disciplina de 60 horas que tinha a centralidade na Educação em Museus e contou com a participação de estudantes de Graduação e Pós-Graduação, com estudos e visitas a museus de diferentes tipologias ao longo do período letivo. No recorte exposto, trazemos dados e análises da visita realizada ao Museu da História da Medicina do Paraná (MHMP), a partir de um Grupo Focal (GF)[2] realizado com um licenciando, uma licencianda e três docentes de Química do Ensino Médio. Tomando como pressuposto metodológico a pesquisa qualitativa do tipo estudo de caso, o roteiro do GF foi articulado com o Método da Lembrança Estimulada[3], fazendo uso de fotografias tiradas durante a visita e projetadas durante a constituição de dados. Das falas das e do participante, emergiu a *apreensão sobre os objetos expostos*, com grande ênfase nos produtos químicos localizados na exposição da "Pharmacia", sendo o momento em que se perceberam fazendo mais registros, observando com maior curiosidade, explorando e se apropriando do espaço, o que vai ao encontro da EP[1]. Este local ganhou centralidade nos relatos por "ter relação com nossa área de formação" (P1), como ilustra uma das professoras e que teve concordância das(do) demais participantes. O interesse maior pelo acervo deste espaço expositivo do museu e as articulações com o campo da Química suscitaram memórias da mediação protagonizada pelo educador do museu e das potencialidades didáticas dos materiais. Cumpre ressaltar que o Museu funciona dentro do prédio do Hospital da Santa Casa, e a "Pharmacia" mantêm o mobiliário preservado, os objetos e produtos químicos na mesma disposição de quando cumpria a função de farmácia hospitalar. O processo da EP considera a relevância das experiências com as fontes de conhecimento que são os objetos materiais e imateriais e com a mediação sobre esses nos processos educativos, o que ficou marcado para as professoras e estudantes de Licenciatura em Química, que valorizaram o bem cultural com aprofundamento da análise crítica e envolvimento com o patrimônio e suas contribuições para a prática pedagógica.

## Agradecimentos/Acknowledgments

Ao Museu da História da Medicina do Paraná e aos participantes da pesquisa.

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**Área:*EDU*** **Nº de Inscrição: *207***

# Educação para todos: construção de materiais adaptados para alunos com paralisia cerebral

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Palavras Chave: *Paralisia cerebral, Material adaptado, Laboratório, Química Geral.*

## Highlights

Education for all: building materials adapted for students with cerebral palsy. The materials are intended for use in the General Chemistry I laboratory.

## Resumo

O objetivo do trabalho foi construir e/ou adaptar materiais de laboratório, para serem utilizados nas aulas experimentais de Química Geral I, para um aluno que apresentava paralisia cerebral, com comprometimento nas mãos, no curso de graduação de Biologia, do Instituto Federal do Rio de Janeiro, campus Maracanã, com o intuito de inclusão real do aluno com necessidades específicas. O pensamento neste trabalho foi de uma educação inclusiva, que é concebida pela difusão de valores de justiça, igualdade social, solidariedade, e inserção democrática no meio, como descrito na Declaração de Salamanca (UNESCO, 1994). Strφmstad (2003) aborda em seu trabalho que caminhos alternativos para alunos diferenciados, é algo inevitável, sendo necessário aprender com eles e a escola é o melhor local para se fazer este aprendizado. O desdobramento de uma educação inclusiva exige mudanças dos diferentes agentes educativos (docentes, monitores e técnicos de laboratório), ocorrendo modificação, no caso, o laboratório, do currículo e também do processo de ensino-aprendizagem, isto provoca resistência e até um certo medo por parte dos docentes (FULLAN, 2001), mas aprender a lidar com as diferenças e aceitar as modificações, é um ato fundamental do docente, para promover de fato, a inclusão. A metodologia foi desenvolvida por meio da observação, reflexão e desenvolvimento de construção ou de adaptação de matérias para que o aluno pudesse realizar as aulas de laboratório. O resultado do trabalho foi que o aluno participou ativamente de todas as aulas experimentais de Química Geral I (o que não ocorreu nas outras disciplinas). Para medir volumes, foram utilizados pipetas, béqueres, provetas e bastões, de plástico, substituindo assim, todas as vidrarias. Para as pesagens, foi feito um adaptador de espátula, para que o aluno pudesse manuseá-la (o aluno não apresentava o movimento de pinça). Para o aquecimento, foram feitas várias adaptações: um suporte de ferro para o bico de Bunsen; para acender o mesmo, foi adquirido um adaptador de isqueiro; foi construído uma alavanca para ser adaptada a torneira de saída de gás, numa pinça de aço, foram feitas duas adaptações: uma trava de ferro, para que o aluno não quebrasse o béquer de vidro aquecido e com um tubo de plástico, foi feito uma alça para que o aluno pudesse segurar a pinça sem a necessidade de usar o movimento dos dedos; numa pinça de madeira foi colocado um prolongamento, também de madeira, para ser encaixado no adaptador de espátula. Conclui-se que mesmo com todo o comprometimento que o aluno com paralisia cerebral apresentava, foi possível fazer a inclusão deste aluno à turma, à disciplina, ao curso, ao conhecimento, e consequentemente, ao mundo, com o professor refletindo, analisando e construindo materiais que melhor se adaptasse ao aluno.

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

# Efeitos da Mineração no Meio Ambiente como Quadro Temático para Promoção de Conhecimentos Químicos

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Palavras-Chave: *Mineração, Estudos de Caso, Ensino de Química.*

## Highlights

Effects of Mining on the Environment as a Thematic Framework for the Promotion of Chemical Knowledge

The mining industry in Brazil, despite contributing to economic growth of the country, is one of the human activities that has caused and still causes the most negative socioeconomic and environmental impacts in the country.

Three interrupted case studies on the topic were implemented in two classes of first-year undergraduate Chemistry students at the University of São Paulo, Brazil.

Results obtained from a quiz provide evidence of the effectiveness of the case studies in promoting students' understanding of several chemical concepts, mainly associated with the topics of heavy metals, sediments, and principles of instrumental chemical analysis.

## Resumo/Abstract

Apesar de gerar crescimento econômico, a indústria extrativa mineral está entre as atividades antrópicas que mais causaram e causam impactos socioeconômicos e ambientais negativos no país, devastando quilômetros de recursos naturais e inserindo no ambiente altas concentrações de metais pesados. A temática dos impactos da mineração se relaciona diretamente com a química, já que esta é a chave nas buscas por transformações sustentáveis, ao mesmo tempo em que impulsiona muitos dos problemas ambientais, de maneira que a mesma pode promover a contextualização e discussão de diversos conteúdos químicos que escapam dos estudantes quando seus estudos tradicionalmente se limitam a capítulos isolados de livros. Desse modo, foram aplicados três estudos de caso interrompidos sobre a referida temática em um curso de bacharelado em química de uma universidade pública. Os resultados encontrados, derivados da análise da aplicação de um questionário com 11 afirmativas a serem classificadas como verdadeiras ou falsas, apontam as contribuições da metodologia para a compreensão pelos estudantes de diversos conteúdos químicos: origem dos metais pesados no meio-ambiente; bioacumulação de metais; composição e importância dos sedimentos em investigações ambientais; teores de metais pseudototais e biodisponíveis; princípios de análise química instrumental relacionados à etapa de preparo de amostras e à espectrometria de absorção atômica. Ademais, durante todas as etapas de aplicação foi observada a participação ativa dos grupos nas atividades e debates. As respostas fornecidas para a resolução dos estudos de caso estavam adequadas do ponto de vista científico, o que demonstra a pertinência da atividade ao nível de conhecimento de estudantes do primeiro ano do curso de química e corroboram novamente as contribuições das atividades para a compreensão dos conceitos químicos.

## Agradecimentos/Acknowledgments

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**Área: EDU** **Nº de Inscrição: 00071**

# Elaboração de sistema de gerenciamento de resíduos químicos oriundos dos laboratórios de ensino do Instituto de Química e Biotecnologia da UFAL

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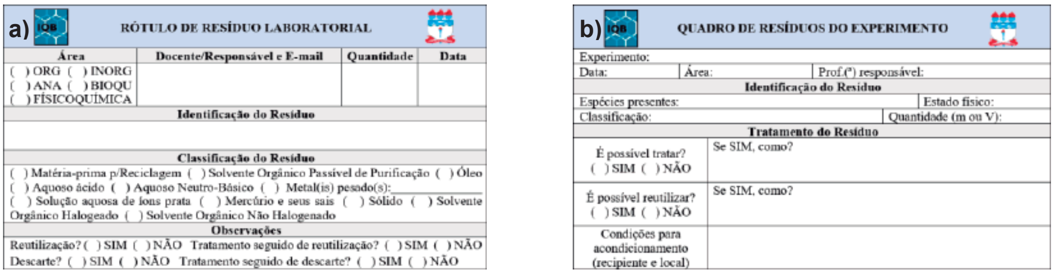
Palavras-chave: *Gerenciamento, Resíduos químicos, Química verde, Laboratórios de ensino.*

## Highlights

– Importance of chemical waste management system at the university for environmental education
– Actual proposal for experimental classes in the IQB/UFAL including the adjustment of scripts in order to minimize the volume of residues.

## Resumo

O tratamento e manipulação adequados de resíduos gerados em aulas experimentais dos cursos de Química é uma demanda de diversas instituições de ensino superior (IES), a exemplo da Universidade Federal de Alagoas (UFAL). O presente trabalho visa a implantação de um sistema de gerenciamento de resíduos ativos e passivos oriundos das aulas práticas que têm lugar nos laboratórios de ensino do Instituto de Química e Biotecnologia (IQB) da UFAL. Para tanto, foi feito um levantamento de resíduos ativos e passivos dentre os quais haviam frascos acumulados desde 1994. De posse dessas informações, foi feita a segregação dos resíduos identificados de acordo com a compatibilidade química e requisitos necessários para armazenamento e/ou destinação. Estes foram classificados, embalados, rotulados e enviados ao destino final. Além dos rótulos (Fig.1a) foi elaborado um modelo de roteiro experimental (Fig. 1b) de forma a incluir informações relevantes quanto à geração e gerenciamento dos resíduos líquidos provenientes das aulas experimentais do IQB/UFAL, a fim de minimizar o volume de resíduos gerados semestralmente. Para melhor compreensão dos discentes e docentes no que tange aos resíduos, desde a etapa de sua geração até sua disposição final, também foi elaborado um fluxograma (Fig. 2) o qual se encontra disposto nos laboratórios de ensino ao lado dos mapas de risco elaborados em etapa anterior deste projeto, em 2019. Assim, este trabalho não apenas viabilizou melhor compreensão acerca da problemática de resíduos químicos de aulas experimentais como também proporcionou a divulgação e implantação de uma proposta de educação ambiental nas dependências do IQB tendendo a se expandir nos demais cursos da UFAL onde há aulas experimentais de Química.



**RÓTULO DE RESÍDUO LABORATORIAL**

| Área | Docente/Responsável e E-mail | Quantidade | Data |
|---|---|---|---|
| ( ) ORG ( ) INORG<br>( ) ANA ( ) BIOQU<br>( ) FÍSICOQUÍMICA | | | |

**Identificação do Resíduo**

**Classificação do Resíduo**

( ) Matéria-prima p/Reciclagem ( ) Solvente Orgânico Passível de Purificação ( ) Óleo ( ) Aquoso ácido ( ) Aquoso Neutro-Básico ( ) Metal(is) pesado(s):________ ( ) Solução aquosa de íons prata ( ) Mercúrio e seus sais ( ) Sólido ( ) Solvente Orgânico Halogeado ( ) Solvente Orgânico Não Halogenado

**Observações**

Reutilização? ( ) SIM ( ) NÃO Tratamento seguido de reutilização? ( ) SIM ( ) NÃO
Descarte? ( ) SIM ( ) NÃO Tratamento seguido de descarte? ( ) SIM ( ) NÃO

**QUADRO DE RESÍDUOS DO EXPERIMENTO**

Experimento:
Data: Área: Prof.(ª) responsável:

**Identificação do Resíduo**

Espécies presentes: Estado físico:
Classificação: Quantidade (m ou V):

**Tratamento do Resíduo**

| | |
|---|---|
| É possível tratar?<br>( ) SIM ( ) NÃO | Se SIM, como? |
| É possível reutilizar?<br>( ) SIM ( ) NÃO | Se SIM, como? |
| Condições para acondicionamento (recipiente e local) | |

**Fig. 1:** Rótulos aplicáveis tanto nos frascos de armazenamento temporário quanto nas bombonas (a) e roteiro (b).

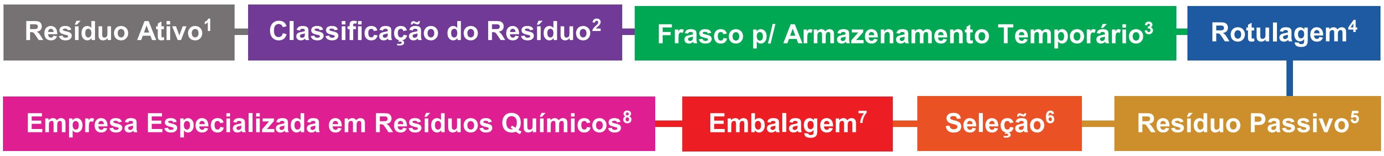


**Fig. 2:** Fluxograma do protocolo para o gerenciamento dos resíduos gerados em aulas experimentais. 1) Resíduo gerado continuamente; 2) Classificação estabelecida pela instituição; 3) Frascos de 1,0 – 2,0 L; 4) Embasado no modelo desenvolvido; 5) Resíduo acondicionado (frasco com 80% do seu volume preenchido); 6) Abrange três categorias: reutilização, tratamento e descarte; 7) Bombonas de 10,0 L – 20,0 L; 8) Responsável pelo tratamento e/ou descarte adequado do resíduo.

## Agradecimentos

**[IQB-UFAL, CAPES, FAPEAL, CNPq, SBQ]**

**Área: EDU**

# Elaboration of summary sheets in Organic Chemistry I classes.

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*Writing-to-learn; Meaningful learning; Undergraduate*

## Highlights

The act of writing is closely linked to the act of learning. Thus, writing about important concepts for organic chemistry leads to the construction of knowledge in a significant way.

## Resumo/Abstract

It is common for students who take introductory courses in organic chemistry to seek to memorize the content to achieve approval. However, what is observed is an increase in the knowledge base, but a poor cognitive understanding. Several metacognitive strategies can be used by the student to help the knowledge construction process. The present work focused on the use of writing. Several authors argue that the act of writing is closely linked to the act of learning. This is because the act of writing about a topic forces the author to reflect on what is being written and with that the author creates links between his previous knowledge and the content he is writing about. Thus, this work aimed to propose writing activities, in such a way that the students were encouraged to reflect on important topics in organic chemistry. Before each assessment, the students (36 in total), divided into pairs, were instructed to prepare a summary sheet on topics that were covered during the course. Each pair received a theme and specific instructions for the theme. The summaries sheets were reviewed and then made available to all students in the class so that they could be used prior to assessments, as review material, and during assessments, as reference material. At the end of the semester, students answered a questionnaire about the proposed writing activities. **Figure 1** shows the responses obtained. The students stated that the writing activity stimulated reflection on the content and contributed to their studies. They also stated that reading the abstracts, before and during the assessments, were helpful. In addition to the questions presented in **Figure 1**, in the questionnaire most students stated that the activity aroused greater interest in the discipline.

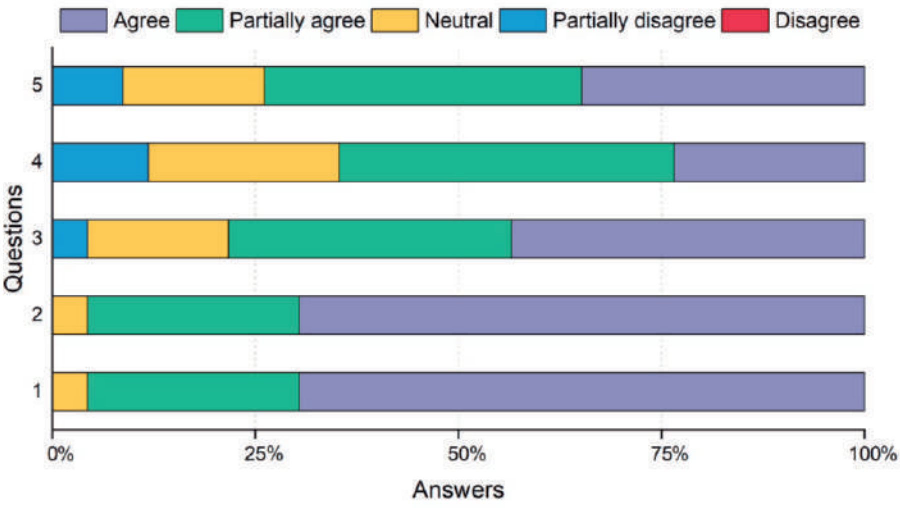

**Figure 1**: Student responses to the questionnaire regarding the activity of writing summaries. Questions: 1: The elaboration of the summaries encouraged their reflection on the content; 2: The elaboration of the summaries contributed to their studies in organic chemistry; 3: Reading the summaries was an efficient way of studying for the tests; 4: The use of summaries during the tests helped in solving exercises; 5: Contact with the summaries prepared by colleagues was useful for your study.

## Agradecimentos/Acknowledgments

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**Área: EDU**

# Elaboration of term signs in Libras as a facilitating resource in teaching Organic Functions for deaf students

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Keywords: *Inclusion, Deaf, Term signs, Chemistry Teaching, Organic Chemistry, Organic Functions.*

## Highlights

The creation of term signs is essential to promote the inclusion and participation of deaf students in Chemistry teaching-learning process.

## Resumo/Abstract

The inclusion of Brazilian Sign Language (Libras) as a mandatory curricular subject in undergraduate courses, by decree n° 5.626, of December 22, 2005[1], resulted in an increase in research for effective methodologies that guarantee the learning of deaf students. It is also known that the part of the deaf community has difficulty learning science-related subjects, such as Chemistry, due to the complexity and absence of specific signs for the contents, increasing the use of dactylology and students' lack of interest during Libras' classes. In some cases, however, there are several term signs that represent the same concept, as a result of an insufficiency of signs and the regionalism present in Libras. Furthermore, the need of more sign language teachers and, as a result, the lack of teaching materials for these students are factors that interfere with learning of Chemistry. Thus, the present study aims to develop didactic tools adapted for deaf students, using term signs in Libras, which were created by the students themselves to facilitate the teaching-learning process of Organic Functions content. The research was carried out with third year high school students of the Libras Instruction course, which included deaf and hearing students, from Joaquim Nogueira State School of Professional Education (EEEP), located in Fortaleza, Ceará. A bibliographic research to choose the theme was the first stage of the work followed by an analysis of the main Organic Functions covered in the National High School Exam (ENEM). The application of the activity took place through a study group, and the students elaborated term signs for this Organic Chemistry content. In addition to the signs created, the work led to the creation of a chemistry game called "QuíFunção?", which was later presented to the students. Finally, a research was carried out in order to verify the existing term-signs for Organic Functions in the literature. The analysis showed the presence of several signs for the same Organic Function, and it was possible to identify similarities between some signs created by the students in the city of Fortaleza and in the city of Linhares, in Espírito Santo[2]. According to the results achieved, most of deaf students had difficulty in studying Organic Functions, since they consider Chemistry as a subject that is difficult to understand. However, the students agreed that the use of images and signs facilitated the learning of the content, since the deaf students created term signs according to the chemical functional groups and the applications of molecules in their everyday life. The activity also allowed the production of digitalized didactic material to facilitate the teaching of Organic Functions, initially, for future classes of the Libras Instruction course and, later, for use in other schools with bilingual education for deaf students. It is worth mentioning the interaction between the students, since the hearing students are future interpreters of Libras. They helped with the translation and with some concepts about Organic Chemistry for the elaboration of new signs.

## Agradecimentos/Acknowledgments

UFC e E.E.E.P Joaquim Nogueira.

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**Área: EDU** **Nº de Inscrição: 01327**

# Ensino de Química Orgânica: Uma Analise dos Aplicativos Disponíveis no "*App Store*".

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Palavras Chave*: Aplicativos, Ensino de Química, Dispositivos Móveis, Química Orgânica*.

## Highlights

Organic Chemistry Education: an analysis of applications available in "*App Store*".
Analysis and investigation of applications that address Organic Chemistry content, technical and educational aspects.

## Resumo

A ampliação do acesso aos dispositivos móveis, como tablets e smartphones, em todo o mundo têm promovido mudanças no modo de comunicação, produção e compartilhamento do conhecimento. Sendo a utilização destes dispositivos cada vez mais frequentes em salas de aula como instrumento de ensino.

Tendo em vista as mudanças ocorridas e os avanços tecnológicos que permitem a relação e implementação de novas metodologias de ensino no ambiente escolar, nesta pesquisa estabelecemos critérios de seleção e analise, reportando resultados de análise de aplicativos para dispositivos móveis voltados ao ensino de Química Orgânica. Os critérios empregados para a seleção e análise dos aplicativos foram resumidos no Quadro 1, como mostrado a seguir:

**Quadro 1** – Critérios empregados como instrumento de seleção e análise dos aplicativos disponíveis na loja virtual "*App Store*".

| **Critérios considerados** | **Modo de aplicação do critério** |
|---|---|
| Facilidade de busca e relevância | Foram considerados os 15 primeiros aplicativos listados após busca empregando os 3 termos de pesquisa. |
| Idioma | Descarte dos aplicativos em língua estrangeira. |
| Caráter geral ou específico | Descarte dos aplicativos de caráter geral. |
| Utilização adequada dos conceitos | Descarte dos aplicativos com grande número de erros ou erros conceituais graves. |
| Adequação dos conteúdos ao Ensino Médio | Determinação da adequação total ou parcial dos conceitos abordados em comparativo aos conteúdos abordados no Ensino Médio |

Existe um número expressivo de aplicativos gratuitos disponíveis para *download* que abordam conteúdos de Química. No entanto, quando se considera apenas aplicativos em língua portuguesa e que tratam exclusivamente da Química Orgânica, o número de opções é bem restrito. Dos aplicativos encontrados na loja "App Store", apenas três atenderam concomitantemente a estes critérios, sendo eles os Apps: "Hidrocarbonetos", "Estereoquímica The Game" e "Funções Orgânicas". Os mesmos apresentam ótimo rigor conceitual, não tendo sido observados erros que inviabilizem a sua utilização. Com relação à adequação dos conteúdos ao Ensino Médio, os Apps "*Hidrocarbonetos"* e *"Funções Orgânicas"* podem ser considerados parcialmente adequados, sendo necessária uma efetiva intervenção do professor para limitar a utilização às fazes iniciais dos jogos. No caso do aplicativo *"Estereoquímica The Game"* os conteúdos estão adequados e os estudantes deverão ser capazes de alcançar os níveis mais avançados, sendo possível a utilização deste aplicativo como ferramenta de ensino no ambiente escolar de maneira a proporcionar benefícios no processo de ensino e aprendizagem.

## Agradecimentos

Os autores gostariam de agradecer a Universidade Federal de Viçosa pelo apoio.

**Área: EDU**

# Estratégias didáticas para o ensino de Química a partir do modelo da aprendizagem tecnológica ativa

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Palavras Chave: *Aprendizagem Tecnológica Ativa, Estratégias Didáticas, Ensino de Química, Tecnologias Digitais.*

## Highlights

**Didactic strategies for chemistry teaching from the active technological learning model**. We propose three didactic strategies in the use of Digital Didactic Resources for Teaching Chemistry based on Active Technological Learning.

## Resumo/Abstract

Nos últimos anos, vem crescendo uma demanda de pesquisas relacionadas às tecnologias digitais (TD) na educação como recurso nos processos de ensino e aprendizagem, sendo as tecnologias consideradas como uma estratégia didática atrativa e importante para que os estudantes construam seus conhecimentos. As TD, em especial os Recursos Didáticos Digitais (RDD), exercem um papel importante no processo de ensino e aprendizagem. Elas contribuem para a formação dos professores e para a construção do conhecimento dos estudantes. Neste trabalho, apresentamos uma pesquisa que teve como objetivo propor estratégias didáticas para o ensino de Química com base na Aprendizagem Tecnológica Ativa (ATA). A ATA é composta de cinco pilares bases (papel do docente; protagonismo do estudante; suporte de tecnologias; aprendizagem; avaliação) para que o processo de ensino e aprendizagem ocorra de forma ativa e significativa. Cada pilar tem uma importância fundamental na estrutura da aprendizagem tecnológica ativa, pois estão alicerçados nas abordagens construtivistas, construcionistas e conectivistas. De modo a alcançar o objetivo proposto, a pesquisa foi realizada em duas etapas: 1) Realizou-se um levantamento de artigos científicos sobre aplicativos e *softwares* educacionais aportados pela ATA no ensino de Química publicados nos últimos 10 anos em periódicos Qualis A e B; 2) Proposição de estratégias didáticas baseadas na ATA para utilização de RDD no ensino de Química. Em relação a primeira etapa da pesquisa, nosso levantamento resultou em 22 trabalhos que abarcavam os pressupostos da ATA. Além disso, os resultados indicavam que as propostas nesses trabalhos buscavam que os RDD fossem utilizados de modo que os estudantes se sentissem engajados para aprenderem ao utilizaram as TD. No que diz respeito as propostas de estratégias didáticas baseadas na ATA, elaboramos três estratégias fundamentadas na ATA: uma utilizando a Sala de Aula Invertida, outra considerando a Instrução por Pares e a terceira usando o *Design Thinking* (DT). Essas estratégias indicam a possibilidade de atividades com maior participação e autonomia dos estudantes, pois enfatizam seu protagonismo e cooperação. A estratégia da sala de aula invertida possibilita maior envolvimento dos estudantes considerando a interação e participação dos envolvidos. Já a Instrução por pares tem sido utilizado como estratégia em contextos em que na sala de aula não se tem a presença maciça das TD pelos estudantes. O DT é uma estratégia que o docente pode promover em suas etapas maior autonomia e cooperação entre os estudantes, o que facilita no processo de construção do conhecimento. Ao refletirmos sobre a ATA no ensino de Química, consideramos importante que os professores promovam atividades que valorizem o aprendizado centrado nos estudantes, além de proporem estratégias didáticas baseadas neste modelo para sua aplicação no ensino de Química. Por fim, acreditamos que esta pesquisa poderá contribuir para outras investigações no que tangencia as contribuições de estratégias didáticas baseadas no modelo da Aprendizagem Tecnológica Ativa.

## Agradecimentos/Acknowledgments

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**Área: EDU - Ensino de Química**

# IMPACTO DA UTILIZAÇÃO DE RECURSOS PEDAGÓGICOS NO PROCESSO ENSINO APRENDIZAGEM NA DISCIPLINA DE CIÊNCIAS

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Palavras Chave: *Aprendizagem significativa, Contextualização, Ensino público, Objetos educacionais.*

## Highlights

Impact of the use of pedagogic resources in the teaching-learning process in the science discipline. Didactic games are configured as an important learning tool. Technologies help the teacher in the teaching-learning process. Continuing training of the teacher should be carried out periodically, aiming at a greater use of the available technological resources.

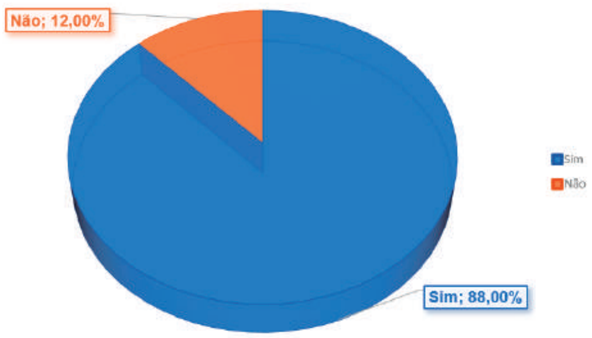
## Resumo/Abstract

Na educação, diversos recursos podem ser utilizados para que as aulas saiam do modelo tradicional de ensino, como a tecnologia, jogos didáticos, novas metodologias de ensino, entre outros. A partir do exposto esse trabalho teve como objetivo analisar o impacto da utilização de recursos pedagógicos no processo ensino aprendizagem dos discentes da disciplina ciências (Química e Física) do 9° ano (ensino fundamental II) das escolas municipais da cidade de Barreiros - PE. A pesquisa ocorreu no ano de 2021, por meio de questionários on-line, utilizando a plataforma *Google forms,* onde os mesmos continham perguntas subjetivas e objetivas, que falavam sobre os recursos pedagógicos utilizados nas escolas e os seus impactos no processo ensino aprendizagem. Participaram da pesquisa os discentes do 9° ano de cinco instituições de ensino fundamental da rede municipal . Os resultados obtidos foram analisados e dispostos em gráficos (questões objetivas) e nuvens de palavras (questões subjetivas). Segundo os discentes, os docentes tentam deixar as aulas dinâmicas, utilizando recursos didáticos de baixo custo, como é visto na Figura 1, onde é mostrado na nuvem de palavras, em tamanho maior os recursos didáticos: livros, vídeos, jogos, músicas e revistas, pois esses foram os recursos mais citados por eles. Os discentes (88%) relataram que os docentes contextualizam as aulas (Figura 2), prática que ajuda bastante no aprendizado dos escolares. Nas escolas existem recursos tecnológicos, porém, os docentes não utilizam, por não possuírem afinidade com a tecnologia. As escolas municipais da cidade de Barreiros, mesmo com a evolução da educação e da tecnologia, ainda possuem diversos problemas que afetam a qualidade de ensino que é ofertado e, consequentemente, faz com que a aprendizagem dos discentes seja prejudicada. Concluiu-se que mesmo sendo pouco os recursos pedagógicos nessas escolas, a utilização deles tem um relevante impacto no processo ensino aprendizagem dos discentes. A qualidade do ensino ainda pode melhorar bastante, já que existem diversos recursos didáticos que os professores podem utilizar em suas aulas, e, melhorar ainda mais o processo ensino aprendizagem dos educandos.

**Figura 1**: Nuvem de palavras com as respostas dos discentes sobre quais os recursos que os docentes utilizam.

**Fonte**: O autor, 2021.

**Figura 2**: Porcentagem de discentes que afirmaram que os docentes contextualizam as aulas.



**Fonte**: O autor, 2021.

**Área: EDU** **Nº de Inscrição: 665**

# INTERACTIVE PERIODIC TABLE FOR USE IN SCIENCES LABORATORY

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Keywords: Periodic Table; interactivity; QRCode;

## Highlights

Manufacture of a Periodic Table using MDF plates and a laser cutter;

Interactivity in the study of the Periodic Table;

Obtaining vídeos on elements of the Periodic Table through QRCodes;

## Resumo/Abstract

2019 foi o ano internacional da Tabela Periódica em homenagem aos 150 anos da publicação do trabalho de Dmitri Mendeleev. Como homenagem, no IFSP, Câmpus Campinas, dois alunos do primeiro ano do ensino médio fizeram um trabalho de divulgação, aos colegas de classe, desta data tão importante para a ciência como um todo. Neste trabalho, utilizando placas de MDF e uma cortadora a laser, uma Tabela Periódica foi confeccionada, com as principais informações acerca de cada elemento (símbolo, nome, massa atômica, número atômico e distribuição eletrônica nas camadas). Na parte posterior de cada um dos elementos foi gerado um QRCode, que pode ser lido através de um smartphone, remetendo a um vídeo ilustrativo sobre algumas informações/curiosidades a respeito do elemento químico em questão.

A Figura ao lado ilustra o resultado de uma dos elementos químicos. O conteúdo de cada um dos vídeos faz parte de um trabalho de divulgação muito bem elaborado e pode ser obtido no youtube através do endereço: https://www.youtube.com/watch?v=LfS10ArXTBA (no caso do lítio). Para cada um dos elementos presentes na Tabela Periódica existe um vídeo ilustrativo do mesmo. A interatividade dos estudantes com a Tabela Periódica foi muito estimulante no estudo da mesma como ficou evidenciado nos depoimentos dos estudantes.

Através de materiais de baixo custo, foi possível desenvolver um trabalho interessante e proveitoso para que os estudantes se interessem mais para os conceitos relacionados à Tabela Periódica. A Tabela Periódica com todos os elementos ficará a disposição dos estudantes no laboratório de Ciências da escola para que todos possam utilizá-la, além de fazer parte de um projeto de extensão junto às escolas no entorno do IFSP.

## Agradecimentos/Acknowledgments

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**Área: EDU**

# Investigation of Meaningful Learning in organic chemistry I: A case study

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*Organic chemistry; Previous knowledge; Case study; Higher education*

## Highlights

The importance of prior knowledge in higher education, become increasingly important for the training of qualified professionals.

## Resumo/Abstract

Organic Chemistry is considered a challenging discipline. It has a lot of information with cumulative and hierarchical knowledge that is presented in a short time. It requires learning pattern recognition and visualization, and representation of various structures, in addition its concepts are hierarchical and cannot be divided into different topics, which means that initial topics that underlie the discipline will be used throughout the learning process. Converging with the described, significant learning states that previous knowledge is the most important variable to affect learning. Thus, it was considered important to investigate this knowledge in a discipline of Organic Chemistry I through a case study. In total, 15 evaluations were analysed, totalling 119 different questions, resulted in 622 resolutions of these evaluations that were performed by 215 students of the Bachelor's degree in Chemistry from IQSC-USP between the years 2015 to 2019.When we analysed only the first evaluations of each year, we concluded that 88% of the students who failed the course, obtained a score below the average, while only 27% of the students who were approved achieved the same result. In other words, 88% of the non-approved students already showed signs of difficulty in the first evaluation. Two reasons could be considered to explain this result: the first is that the group of non-approved students already had difficulties about previous fundamental concepts to the learning of Organic Chemistry. The second is that this group failed to assimilate the demand for new concepts required for the learning of the discipline or did not want to correlate the new knowledge consciously and deliberately to the existing ones (one of the requirements for meaningful learning in **Figure 1**). Regardless of origin, the possibilities are associated with previous knowledge and demonstrate the need for their investigation. As one can see the data reported are guiding, but require more detailed investigations, and therefore, they are part of a broader research that aims to investigate the difficulties of students in Organic Chemistry.

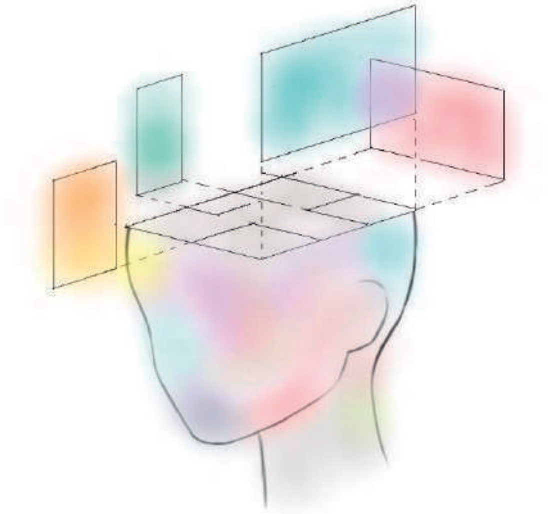

**Figure 1:** A solid foundation is needed to built a good home. Similarly, relevant, and well-founded prior knowledge is needed for meaningful learning to occur. Three main characteristics are necessary for meaningful learning:
1- Previous knowledge relevant to new learning (Ausubel 1968)
2- The material containing the new knowledge must be potentially significant (Novak 1998)
3- The student must choose to relate the new knowledge to the previous one, that is, he/she must decide to learn significantly (Novak 1998).

## Agradecimentos/Acknowledgments

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**Área: EDU** **Nº de Inscrição: 199**

# Jogo análogo ao ‘cara a cara’ na revisão de conteúdos de Química Orgânica

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Palavras-chave: *Jogo de tabuleiro, Cara a cara, Revisão de conteúdos, Química Orgânica*.

## Highlights

**Analogous game to ‘face to face’ in review of the contents of Organic Chemistry**

Elaboration and application of a board game similar to 'face to face', to evaluation and review of the content of Organic Chemistry of the 3rd year of the technical course integrated to the High School at IFSP.

## Resumo/Abstract

Kishimoto [1] sugere que os jogos auxiliam desde a fixação de conteúdos até as relações interpessoais e o pensamento crítico. O jogo cara a cara, a citar, mostrou-se um recurso interessante na Fonoaudiologia, investigando habilidades comunicativas de alunos com paralisia cerebral sem oralidade [2] e em investigações psicológicas foi aplicado na análise heurística de idosas [3].

Buscando-se uma estratégia lúdica para melhor envolver os estudantes em retomadas de conteúdos de Química Orgânica, envolvendo funções orgânicas, nomenclatura, classificação, identificação e construção estrutural, objetivou-se, através da empregabilidade de um jogo análogo ao cara a cara, avaliar o aprendizado da turma em função deste recurso. Questionaram-se, também, os discentes acerca da ferramenta didática utilizada.

Estiveram envolvidos alunos do último ano do Ensino Médio (n= 40) de curso técnico integrado do IFSP, da cidade de Catanduva/SP. Como um dos critérios avaliativos (20% da menção bimestral), estipulou-se, para eles, a participação em uma atividade lúdica que envolvia jogar, no arranjo de duplas ou trios, a adaptação do jogo cara a cara. A aplicação se deu em duas aulas sequenciais (100 min). O jogo de tabuleiro foi elaborado com materiais acessíveis ou de reaproveitamento (papelão, papel-cartão, cola e marcador de texto).

Coube avaliar os envolvidos observando a dinâmica entre eles *in loco*, aplicando-se um breve questionário ao término do jogo e, em encontro posterior, estabelecendo um debate, extraindo assim maiores informações a respeito das dúvidas pré e pós-aplicação sobre o conteúdo, ou aquelas não sanadas durante a atividade. Aconselhou-se o não uso de materiais de consulta, mas era livre o diálogo entre os “competidores”.

Da percepção docente, durante o jogo, o envolvimento do alunado foi muito satisfatório. Tratando-se do conteúdo, dificuldades na linguagem foram observadas. As confusões mais recorrentes eram os termos ciclo e insaturação. Esqueceram também, ocasionalmente, o nome correspondente das funções orgânicas, ao questionarem os “adversários”. Entretanto, nestes episódios, o colega da dupla ou trio intervia e isso “destravava” o jogo, oferecendo ao mesmo tempo a condição de revisão do assunto. Uma situação inusitada foi o esquecimento do nome da função éster, por um dos grupos. O fato o impedia de responder (mesmo que no chute) e isso implicava também no estratagema do “adversário” – que, por sua vez, interviu, cooperando com a dica sobre o fragmento estrutural característico dos ésteres.

Percebeu-se, com isto, um paralelismo com os princípios teóricos de Vigotski, que considera as interações fundamentais para a aprendizagem; cuja transição entre o plano social e individual pode proporcionar, através do lúdico, a mediação dos conhecimentos (dos mais aos menos sapientes) [4].

Acerca do questionário 90% responderam ter o hábito de jogar e, destes, 87% acusaram já ter experiências com tabuleiros. Entre todos, 92% responderam que o jogo se assemelhava ao típico cara a cara. Portanto, além do jogo ser assertivo sobre uma turma com hábitos de jogar a adaptação foi muito exitosa. Sobre o quanto representou aos estudantes a possibilidade de recordar ou relacionar os conteúdos, com o jogo, teve-se 76% deles indicando relação muito boa ou total. De todos, 80% da turma atribuiu notas 8 (10%), 9 (30%) e 10 (40%), para a atividade.

**Agradecimentos/Acknowledgements**: Aos estudantes envolvidos na aplicação.

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**Área: DE** **Nº de Inscrição: 233**

# Multi Jogos Tabela Periódica - ferramenta para ensino lúdico tornando a aula divertida e atrativa

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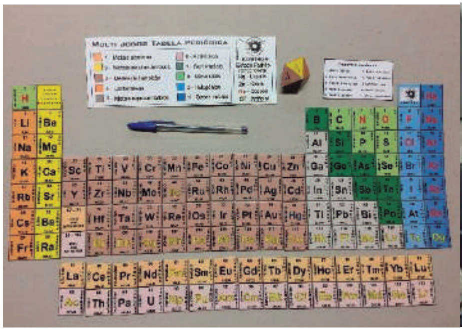
Palavras Chave: *ensino, jogos, tabela periódica, aula lúdica.*

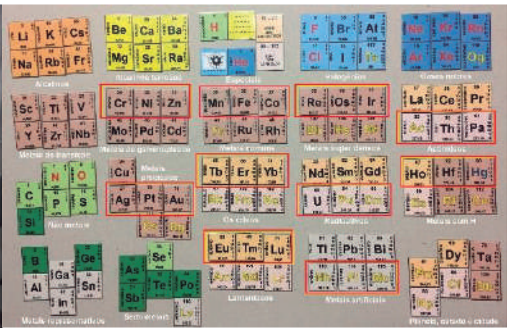
## Highlights

Multi Games Periodic Table - tool for ludic teaching making the class fun and attractive. How to use in chemistry classes, domino and “set of three” card game. The real learn by playing.

## Abstract

Launched during the Periodic Table International Year, at 42nd RASBQ Joinville 2019[1], this game is now in all regions of the country, being used by more than 100 chemistry teachers. Among the 23 Periodic Table Multiple Games, here we are going to address the use of two of them in the classroom, domino and “set of three”, this last an adapted game of cards, and disclose some of the observed results. The domino game facilitates the memorization of the chemical elements in the periodic table and their families, favoring the understanding of their properties. Due to the necessary concentration to find the position of the piece on the table, after a few times playing domino the student learns the location of the element. With the set of three game, the student learns some of the properties, uses or characteristics of the elements (in 3 by 3 sets) that can be discussed right after the match. In the below images, respectively, there are domino at the end of the game, students playing domino, and the chemical elements arranged in 3 by 3 pieces, forming 20 sets.





Therefore, using the games breaks the barrier that students eventually have with Chemistry, considered a difficult subject. Early contact with the names, atomic numbers and characteristics of the elements will make feasible the learning. Within the other 21 games that are part of the total set there are some with didactic application and their use in the classroom should be evaluated during this year.

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## Acknowledgments

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**Área: EDU**

# Online scientific dissemination video: impact on the perception of basic school students in relation to scientific research in electrochemistry.

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Keywords: Scientific dissemination, science dissemination vídeo, elementary school students.

## Highlights

Youtube videos used as a tool for disseminating scientific research.

Perception of elementary school students.

Disseminate the value and importance of scientific research in public universities.

## Abstract

The role of communicating scientific findings is extremely important, as its main objective is to bridge the gap between the scientific community and the general population [1]. Youtube videos are used as a teaching tool and have effectively contributed to student learning [2-4]. However, with regard to the dissemination of research carried out by universities, there are no reports of this type of disclosure. In the present work carried out the dissemination and analysis of the impact of a scientific dissemination video of an electrochemical research on the perception of elementary school students in relation to scientific research and the public university. The video was developed to promote the project entitled "Study and application of electrochemical technology for the analysis and degradation of endocrine disruptors: materials, sensors, processes and scientific dissemination, and shows the importance of dyes for everyday life and how much they have been research targets. The video was used as an activity for eighth grade students of an elective subject called "I scientist" at a public school in the city of Ibaté. The analyzes were based on two questionnaires, the first being answered before the students watching the video and the second being answered after the students watching the video. The data were analyzed by the simple categorization process [5] according to the categories: A Perception of the Public University and the Importance of Research at the Public University. It was found that it is possible to disseminate scientific research through videos used as an activity in classes for elementary school students, and that the video was able to propagate the value and importance of scientific research in public universities.

## Acknowledgments

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**Área: EDU**

# Organic Battle – Remote: a game about carbonyl compounds

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Keywords: *Didactic game, Remote teaching, Organic chemistry, Carbonyl compounds*.

## Highlights

Didactic game adapted for the remote teaching of the board game Battle Organic. The game is expected to promote discussion about reactions and mechanisms involving carbonyl compounds.

## Abstract

Students on learning of organic chemistry in college use reactions to plan pathways to do organic synthesis, and then they must be able to remember the large number of functional groups, including their characteristics, reactions and mechanisms discussed in the disciplines.[1]

Therefore, the traditional teaching of chemistry is still focused on the process of transmission and reception of knowledge. A more effective learning must be according to the expectations of the student, by dedicating time and effort, and the teacher, by delivering content using a wide variety of teaching strategies. In teaching organic chemistry, rote memorization can be a great problem that can lead to a superficial understanding of the concepts.[2] Educational games - pedagogical or didactic[3] - emerge as a motivating tool for learning, balancing the playful and educational functions.

The objective in this paper is to discuss the content of carbonyl compounds – aldehydes, ketones, carboxylic acids and their derivatives – using an adaptation of a board game that was already used in our research group, applied to remote teaching. The adaptation to the virtual environment was carried out using the Microsoft PowerPoint® program and its hyperlinks resources. Organic Battle - Remote uses the same principles as the original game: theoretical approaches, reactions and mechanisms. It involves moving teams' pieces on a board through spaces labeled "Battle", "Did You Know?" and "Luck/Setback". For example, when a certain team is on a battle house, must roll a second die that will indicate the opposing team, and both must answer the question presented on the screen. The game ends when the first team reaches the end of the board, but only the one with the most points is the winner.

The game was applied to a class of the Chemistry course at UFPE, during the discipline of Organic Chemistry II, in the city of Caruaru - PE, utilizing Google Meet®. At the application, the teacher led the main screen, being responsible for moving the pieces on the board screen, controlling the roll of the dice (using a mobile application), selecting the cards chosen by the students during the battles, etc. The teacher's intervention took place precisely when one of the teams was mistaken in the moments of battle. The explanation, especially in the most difficult questions that often were about reactional mechanisms, helped to solve the participants' doubts.

In addition to the observations during the game, the validation was carried out later using an evaluation questionnaire following criteria such as motivation, user experience and learning.[4] In it, the participants enjoyed the visual aspects of adaptation, the proposed challenges, the interaction with other participants and with the interface itself, even if remotely. Finally, the game provided students a better understanding of how reactions and their mechanisms work, among other aspects, with fun and intuitiveness. Thus, aspects associated with games, such as entertainment, were associated with content assimilation.

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## Acknowledgments

To the research group NIDEJE/CA/UFPE. To the Students of Organic Chemistry II class 2020.2.

**Área: EDU**

# O uso de jogos digitais como estratégia motivadora em ensino de Química no Ensino Fundamental

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Palavras-Chave: *Química, Jogo, História da Química, Ensino Fundamental*

## Highlights

The use of digital games as a motivating strategy in teaching Chemistry in Elementary School
This work aims to show that knowledge about the history of Chemistry and the evolution of atomic models can be understood in a playful and attractive way.

## Resumo/Abstract

Apesar de oficialmente a disciplina Química só ser ministrada no Ensino Médio, alguns conteúdos, com seus conceitos e teorias, já são vistos no Ensino Fundamental na disciplina de Ciências, como a história da Química, a descoberta do átomo e suas principais características e modelos. Sendo conceitos relativamente novos e de grande abstração para os alunos, é comum a falta de compreensão e o consequente desinteresse pelo estudo da disciplina. Visando estimular e motivar esse aluno desta etapa da educação básica, é pensado o uso de jogos didáticos. Este trabalho teve como objetivo desenvolver um jogo didático virtual sobre a História da Química e Modelos Atômicos, que pudesse ser aplicado tanto em ambiente virtual como em aulas online, quanto de forma presencial em sala de aula mediante o uso de alguns recursos tecnológicos. O jogo desenvolvido se tratou de um jogo de Tabuleiro, criado na plataforma digital Flippity[1] para criação de jogos e atividades lúdicas, cuja interface do jogo é mostrada na figura 1.

*Figura 1 - Interface do Jogo de Tabuleiro*

O jogo foi aplicado em turmas de 9° ano do ensino fundamental, em duas escolas municipais do estado do Rio de Janeiro, sendo em uma escola de forma online, que estava com o ensino remoto, e em outra de forma presencial. Após a aplicação do jogo, os alunos responderam um questionário de feedback cujo objetivo era avaliar qualitativamente a opinião deles em relação à aula com o jogo. O resultado com as respostas a uma das perguntas está resumido na figura 2.

*Figura 2-Gráfico da pergunta 2 do Questionário de feedback*

Fonte: Própria do autor

As respostas dadas ao questionário mostraram que a maioria dos alunos prefere e se interessa mais por aulas com jogos, que são em sua maioria mais dinâmicas, interessantes, divertidas e cativantes. A conclusão foi que os jogos didáticos podem ser importantes aliados como estratégia motivadora no processo de ensino e aprendizagem na área da Química.

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## Agradecimentos/Acknowledgments

**Área: EDU**

# O uso de redes sociais como ferramenta de divulgação científica, contextualização do ensino de Química e atuação no combate às *fake news*

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Palavras Chave: *Química, Ciência, Ensino, TDICs, Instagram.*

## Highlights

The use of social networks as tools for scientific dissemination, contextualization of chemistry teaching and action in the fight against fake news.

Use of Information and Communication Technologies (ICT). Important link between learning in Chemistry, the dissemination of scientific knowledge and the fight against fake news.

## Resumo/Abstract

No contexto da pandemia da Covid-19, causada pelo Sars-CoV-2, foi observado um aumento significativo de disseminação de notícias falsas sem qualquer embasamento técnico-científico, comumente chamadas *fake news*. Durante esse período a utilização de Tecnologias Digitais de Informação e Comunicação (TDICs) tornou-se crucial para a manutenção dos processos de ensino e aprendizagem, desta forma, o uso de mídias sociais tornou-se um grande aliado dos processos educativos, ampliando as possibilidades de sala de aula, fomentando novas oportunidades de aprendizagem. Ademais, de acordo com a Lei de Diretrizes e Bases da Educação – LDB, o ensino deve ser ministrado com base na liberdade de aprender, ensinar, pesquisar e divulgar a cultura, o pensamento, a arte e o saber [1]. Diante desse cenário, esse trabalho teve como objetivo o desenvolvimento de materiais de divulgação científica nas redes sociais com potencial para contribuir na aprendizagem em Química, desse modo, fomentando a democratização do acesso a informações e auxiliando no combate às *fake news*. Neste trabalho foram utilizadas diversas ferramentas da rede social Instagram para publicação dos materiais de divulgação elaborados nos formatos de *feed, reels, story* e *lives*. Os conteúdos digitais foram planejados possuindo como alicerce um processo de investigação de notícias falsas que estavam circulando nas redes sociais relacionadas à Química e/ou diferentes áreas que dialogam com essa Ciência. A partir da análise dos dados coletados foram realizadas pesquisas e revisões bibliográficas seguidas da elaboração de textos que possuíam em sua estrutura discussões técnico-científicas dos temas abordados nas notícias encontradas, desmistificando as *fake news* investigadas. Posteriormente, os textos foram transformados em materiais para publicação em formato de vídeo e imagem. O perfil do Instagram do trabalho, *@quimiconifba*, apresentou grandes indícios de aceitação e engajamento, resultando em um aumento considerável no número de seguidores e no crescimento percentual de contas que interagem (curtem, comentam e compartilham) com os materiais publicados. Ressalta-se que o maior alcance de público foi detectado nas publicações dos conteúdos que estavam associados aos *reels*, as atividades experimentais, a execução de *lives* e os debates de temas de grande repercussão midiática. Diante dos resultados encontrados, foi possível notar que a utilização devidamente planejada e apropriada das TDICs promoveu um elo importante entre aprendizagem em Química, divulgação de conhecimento científico e combate às fake *news*, além disso, suscitou reflexões sobre a importância das bases científicas e tecnológicas do país.

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## Agradecimentos/Acknowledgments

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**Área: Ensino de Química**
*(EDU)*

# Soap production and sustainability in Chemistry Teaching

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*Key Words:* Sustainability, Teaching Chemistry, Environmental Chemistry , Green Chemistry, Ecology

## Highlights

The production of soap in the teaching of chemistry is an activity widely experienced in schools in order to strengthen the knowledge of sustainability in the teaching of chemistry. This work highlights the teaching of environmental chemistry, interpolating entrepreneurship between young people and the school community.

## Resumo/Abstract

Work carried out with students of the first year of high school. The work was developed with a single class the 1st year C, where this class was the pioneer to carry out the experiment, where they served as monitors, for other classes.
The students had some meetings and classes involving the teaching of environmental chemistry. At the beginning of the work, they collected the PET bottles to "reuse" as a support for the synthesized substances. We carried out a saponification reaction with the students, where we synthesized the saponifying substances using used oil, water, caustic soda (NaOH) in scales and ethanol ($C_2H_6O$).
Alcohol was measured in different amounts in different attempts to find the equivalent amount to optimize the chemical reaction between oil and caustic soda. At the end, the students placed the sustainable product in the "recycled" containers and presented it at the school's sustainability fair, for the entire community. Showing a sustainable and entrepreneurial proposal. The experiment was of great importance for the development and learning in the discipline of chemistry, where we noticed a great evolution and interest on the part of the students in the disciplines of natural science.

Figure 1 (Lecture on the environment)

Figure 2 (Soap production)

Figure 3 (Final product)

## Agradecimentos/Acknowledgments

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# Proposition of Games for Chemistry Teaching according to the Playful Culture: experience with undergraduates in chemistry from Alagoas

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Palavras Chave: *Cultura lúdica, Educação química, Ensino de química, Formação docente, Jogos no ensino).*

## Highlights

Games can be importante resources to teach chemistry. They are little discussed and used in teacher training. Using games in teaching always requires considering the student's playful culture.

## Resumo/Abstract

A escola contemporânea não gera interesse nos jovens e aparenta desconsiderar seu convívio social.[1] O uso de jogos no ensino de química está muitas vezes distante do gosto dos estudantes por negligenciar a Cultura Lúdica Discente (CLD), bem como, os licenciandos precisam aprender como propor jogos desde sua formação inicial, para usá-los quando forem docentes.[2] Este trabalho é um recorte de uma pesquisa em Ensino e Formação de Professores na perspectiva da criação de jogos por licenciandos em sua formação. O público-alvo da pesquisa consistiu em 13 (treze) licenciandos do 7° período do curso de Licenciatura em Química da UFAL, Campus Arapiraca-AL, divididos em 4 grupos (G1 a G4). A aplicação foi feita de forma remota no ano de 2022, com quatro encontros via Google Meet: 1) apresentação da pesquisa; 2) aula sobre jogos em química; 3) proposição de jogos pelos licenciandos e 4) validação dos dados obtidos. Essa pesquisa caracteriza-se como qualitativa do tipo estudo de caso, com triangulação de seus dados (questionário, observação, gravação), dos pesquisadores (pesquisado e orientador) e das hipóteses, para tentar evidenciar uma relação que contribua no processo de ensino, aprendizagem e formação do professor. Para essa proposição, os licenciandos se colocaram como docentes, considerando: um conteúdo químico a ser proposto em um jogo; uma CLD dos proponentes. Importante salientar que eles tomaram sua própria cultura lúdica como exemplo. No G1, 2/3 não jogam e 1/3 joga jogos colaborativos. Assim consideraram uma CLD de jogos multiplayer; e propuseram o jogo “Senhas periódicas”, de perguntas e respostas. No G2, 3/5 jogam raramente ou não jogam, já 1/5 joga jogos colaborativos que exercitem o corpo e 1/5 joga jogos virtuais de tiro, apresentando uma CLD de jogos de mesa, propondo um “Banco imobiliário químico”. Como a maioria desses graduandos não jogam ou fazem-no raramente, propuseram com base em artigos encontrados na literatura, mas tiveram dúvida sobre a função do jogo elaborado, se didático ou pedagógico. Já o G3, 2/4 jogam jogos de cartas, 1/4 jogos de tiro e 1/4 não joga, considerando CLD como jogos virtuais de tiro; sugeriram então, dois jogos: um de batalha e outro de cartas, ambos de perguntas e respostas. No G4, apenas um licenciando participou, ele joga jogos de cartas e de banco imobiliário; considerou uma CLD de mundo aberto; e propôs um jogo de “mundo aberto em busca de plantas que deem cura”. Os grupos com licenciandos “jogadores ativos” ressignificaram jogos autorais de acordo com sua própria cultura lúdica, apesar de indicarem erroneamente a função do jogo, dizendo ser pedagógico, mas sendo didático, de acordo do a explicação dada. É evidente que a proposição de jogos é mais eficiente quando se considera a CLD, pois assim, a familiaridade facilitará a aplicação do jogo e o aprendizado. Os grupos em que os discentes buscaram sobre jogos na literatura, tiveram dúvida sobre a função do jogo, já os outro erraram seu uso, sendo esse um sinal de que o conhecimento teórico melhora o uso dos jogos e que eles sabiam superficialmente o tema. Por outro lado, os dois grupos que seus membros jogam frequentemente, propuseram jogos conforme a sua CLD, o que demonstra a importância de uma cultura lúdica docente em sintonia com a dos discentes.

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**Área: EDU**

# PROPOSTA DIDÁTICA COM ABORDAGEM LÚDICA NO ENSINO DE MODELOS ATÔMICOS

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Palavras Chave: *Lúdico, Modelos atômicos, Jogo da memória.*

## Highlights

TEACHING PROPOSAL WITH A PLAYFUL APPROACH IN THE TEACHING OF ATOMIC MODELS

Elaboration and application of a playful game for students of the 9th Year of Elementary School II, as a tool to aid in the learning of atomic models in a school in the city of Marabá-Pará-Brasil.

## Resumo/Abstract

Em particular no ensino de química percebe-se que os alunos, muitas vezes, não conseguem aprender, e portanto não são capazes de associar o conteúdo estudado com seu cotidiano, o que causa desinteresse pelo tema estudado[1].O jogo desenvolvido foi intitulado “QUÍmi-Testando”, trata-se de um jogo da memória elaborado pelos próprios autores. O presente trabalho apresenta uma proposta didática para o ensino dos modelos atômicos através do lúdico. A pesquisa foi realizada em uma escola de Ensino Infantil da Cidade de Marabá-PA, no 9º ano do Ensino Fundamental II. As cartas foram impressas em folha A4 e confeccionadas com papel cartão, cola e tessoura. O jogo contém 10 pares de cartas, com a finalidade de facilitar a aplicação a turma que contém 9 alunos dividiu-se em 3 duplas e 1 trio e cada grupo recebeu um jogo de cartas completo. As regras do jogo permaneceram similares às regras do jogo da memória, exceto que, ao acertarem as cartas os alunos ganhavam metade dos pontos, e para que conseguissem a pontuação total iam ao quadro e escreviam a qual modelo atômico ou cientista aquelas figuras pertenciam.

Antes da aplicação do jogo houve a realização de uma aula sobre da Evolução dos Modelos Atômicos, e após a aplicação do jogo um questionário quantitativo com 5 perguntas foi aplicado, os alunos mostraram-se participativos e muito empolgados com a aula e a didática aplicada.

Os resultados obtidos acerca da 1° pergunta “Você já jogou algum outro tipo de jogo didático na escola?”, indicaram que 90% dos alunos da turma já utilizaram o lúdico como ferramenta de aprendizagem, mostrando que os discentes já estavam familiarizados com o lúdico como ferramenta de aprendizagem. A 2° pergunta “A respeito do jogo ´´Quími- Testando``, você considera que foi: (A) Animado, mas não consegui assimilar o conteúdo explorado no jogo com o conteúdo das aulas, (B) Animado, e ainda consegui assimilar o conteúdo explorado no jogo com o conteúdo das aulas ou (C) Nenhuma das respostas anteriores”, onde 100% dos participantes assinalaram o comando de letra “A”, demostrando que o Lúdico proporciona um ambiente de aprendizado prazeroso. Na 3° pergunta do questionário foi “Você acredita que o jogo ´´Quími- Testando`` ajudou de alguma forma na compreensão do conteúdo?”, 100% da turma respondeu que sim. Na 4° pergunta “O jogo aplicado despertou o interesse em aprender um pouco mais sobre modelos atômicos?”, com as respostas obtidas, observou-se que cerca de 100% dos alunos responderam que sim, mostrando novamente que jogo impulsionou o interesse de aprendizado sobre o conteúdo aplicado. E na 5° questão “Você gostaria que os professores utilizassem mais jogos didáticos como complemento às aulas tradicionais?” 100% dos alunos responderam que sim.

Ademais, foi evidenciado um grande aproveitamento da turma acerca da aprendizagem do tema proposto, com isso ressaltamos o uso dessa ferramenta para o ensino de química, o lúdico proporciona um ambiente prazeroso de aprendizagem além de proporcionar uma interação maior entre aluno-aluno e professor-aluno.

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## Agradecimentos/Acknowledoments

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**Área:** *EDU* **Nº de Inscrição: 00653**

# Quer que eu desenhe? Fazendo arte com a química

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Palavras Chave: *Animação, Aprendizagem, Química, Vídeo,.*

## Highlights

Do you want me to draw? Making art with chemistry. The goal of the project was to elaborate animated video explaining topics to Chemistry subject.

## Resumo

O objetivo do trabalho foi o de facilitar a aprendizagem e aguçar a capacidade criativa dos alunos, por meio da elaboração de vídeos de animação, com conteúdos relacionados à disciplina de Química. Os resultados do trabalho, realizado com os alunos do Ensino Médio regular do Colégio Técnico da Universidade Federal Rural do Rio de Janeiro (CTUR), foram bastante expressivos, com vídeos muito criativos, o que conduz à conclusão de que a utilização da referida ferramenta pode colaborar na aprendizagem.

A metodologia empregada foi, de início, a seleção de tópicos referentes a personagens históricos importantes, conteúdos pertinentes à disciplina de Química e, por último, a construção de vídeos de animações. Para a elaboração das animações, além da pesquisa bibliográfica sobre o tema, os alunos também deveriam seguir alguns critérios como a duração do vídeo e o conteúdo do mesmo. As turmas foram divididas em grupos com temas distintos, tendo cada grupo a missão de pesquisar sobre o tema designado e, ao final, elaborar uma animação audiovisual para expor o conteúdo para a turma.

Os resultados obtidos com a produção dos vídeos de animações foram muito relevantes, promovendo o interesse e o aprendizado do aluno de forma criativa e divertida, demonstrando, desta maneira, ser um facilitador da aprendizagem. Algumas das animações que os alunos construíram foram sobre radioatividade (figura1), superácidos, carboidratos, proteína, pectina e sobre personalidades históricas significativas para a disciplina de Química: Carl Wilhelm Sheele, Nicolas Flamel, Dimitri Mendeleev, Ida Eva Tacke, John Dalton e Ernest Rutherford. Uma coletânea das animações foi apresentada na Semana Acadêmica do CTUR, que é um evento envolvendo toda a comunidade escolar, o que gerou muito orgulho e o aumento da autoestima dos alunos como autores das criações.

Figura 1 – Animação sobre Marie Curie

Conclui-se que trabalhar com ferramentas diferenciadas em sala de aula pode ser um trabalho árduo para o professor mas muito significativo para os alunos, porque, além de despertar muito o interesse dos mesmos pelo conteúdo, auxilia-os, também, na aprendizagem.

**Área: EDU** **Nº de Inscrição: 00769**

# Science and teaching for all: development of a vocal scale for the inclusion of visually impaired students in an experimental class

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Palavras Chave: *Ensino de Química, Inclusão, Experimentação, Tecnologia assistiva, Deficiência visual.*

## Highlights

Este estudo mostra como a tecnologia assistiva pode contribuir com a participação de alunos com deficiência visual em experimento possibilitando a inclusão e o desenvolvimento de habilidades técnicas.

## Resumo/Abstract

Na Química os experimentos geram informações que normalmente são coletadas pela visão, como a mensura da massa de um soluto no display de uma balança semi-analítica, atividade que exclui o aluno com deficiência visual (DV) colocando-o em posição de desvantagem frente aos demais alunos. Sendo assim, quais os recursos necessários para incluir os DV em atividade de pesagem permitindo-os uma atuação autônoma nos experimentos?

Partindo deste pressuposto, criamos um Núcleo para o desenvolvimento de tecnologia assistiva (TA) de laboratório, pois acreditamos que experimentos mediados com o auxílio de TA (mediação instrumental) podem contribuir para a atribuição de sentidos aos fenômenos observados por outros canais sensitivos que não o visual.[1]

Contendo elementos da pesquisa participante, enfocando a participação autônoma dos DV nas aulas experimentais de Química, discutiremos neste trabalho as contribuições do uso de uma balança semi-analítica vocalizada (Figura 1) como TA para o desenvolvimento de habilidades técnicas de pesagem em experimentos. Participaram deste estudo 2 professores em formação inicial (PFI) e 12 DV (A), realizado em instituição de apoio à escola pública regular, especificamente para DV. No extrato 1, PFI2 apresenta e explica como usar o equipamento.

Extrato 1

PFI2: Vou passar a balança vocalizada pra vocês sentirem. A11: É tipo aquelas balanças de restaurante? PFI2: Essa aqui é pequena e o prato também é bem pequeno. Na parte esquerda tem um botão bem grande que será a primeira coisa que vocês vão sentir. É só apertar por um segundo e soltar. A balança vai falar o peso do béquer. No botão da direita ainda vamos incluir a tara que irá zerar a balança quando necessário. A10 pese este béquer para aprender a usar a balança. Depois vamos aprender a pesar solutos sólidos. (A10 tateia a balança e coloca o béquer no prato para pesagem). Balança vocalizada: Quarenta e sete gramas. PFI2: Então, esse béquer pesa 47 gramas, se a gente colocar 45 gramas de soluto, no total...
A10: Vai pesar 92 gramas.

**Figura 1: Balança vocalizada**

O processamento auditivo diz respeito às operações mentais realizadas por uma pessoa a partir das informações ouvidas do ambiente, tornando-as funcionalmente útil.[2] Numa perspectiva inclusiva, nossos resultados sinalizam que a compreensão do conceito não está atrelada apenas a visão, mas a um processo consistente de interatividade com o outro (geralmente com videntes), como a mediação feita por PFI2, envolvendo a linguagem cultural (conjunto de signos) e o uso de instrumentos que também atendam a especificidade (tecnologia assistiva), como a balança vocalizada, ferramenta cultural da Química que permite o acesso à informação pela audição podendo contribuir com a elaboração conceitual, o desenvolvimento de habilidade técnica e o controle daquilo que a falta da visão impossibilita de acessar: os dados empíricos dos experimentos.

## Agradecimentos/Acknowledgments

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**Área: EDU** **Nº de Inscrição: 00061**

# Scientific Literacy Indicators in Nanotechnology in the Collection Química Ser Protagonista PNLD 2012 to 2020

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Palavras Chave: Livros Didáticos, Nanotecnologia, Alfabetização Científica

## Highlights

Identification of the potential of scientific literacy indicators in the didactic books of the collection Química Ser Protagonista. Topic covered: nanotechnology.

## Resumo/Abstract

A Nanotecnologia é uma área da ciência que foi reconhecida a menos de um século atrás, e gerou uma grande revolução científica e tecnológica, representando hoje um dos temas de maior interesse no mundo. Desta forma, torna-se imprescindível a abordagem deste tema nas escolas de nível básico e da presença de eixos temáticos deste porte em livros didáticos. Para desenvolver este tema em sala de aula é importante um processo de alfabetização científica - AC que para Pizzarro (2014) são alternativas para a compreensão das ações dos alunos como reflexos das aprendizagens adquiridas em sintonia com a prática docente. Pizarro (2014), define alfabetização científica em oito indicadores: articular ideias, investigar, argumentar, ler em ciências, problematizar, criar e atuar, que norteia o caminho de observação de quais habilidades são potencialmente estimuladas pelos livros didáticos, considerando sua importância para o processo de aprendizagem. Dentro desse contexto, o lócus da pesquisa deste trabalho foi a coleção *Química Ser Protagonista (QSP)*, dos triênios 2012 a 2020, totalizando 9 livros (três para cada coleção) que foi a segunda coleção mais selecionada pelos professores no presente triênio. Para os resultados expostos abaixo, o trabalho seguiu três etapas: 1º identificação dos textos/questões de Nanotecnologia nas coleções; 2º identificação dos indicadores de AC; 3º reconhecimento dos eixos temáticos a partir de um instrumento de análise, criado pelos autores. Nas análises, observamos primeiramente que os livros didáticos desta coleção, em termos de número de páginas, abordam em menos de 2,5 % a temática Nanotecnologia, seja de forma direta ou indireta. Quanto ao potencial de AC encontrado sob a luz dos indicadores de AC, considerando textos e questões, observou-se que o indicador mais contemplado foi o "ler em ciências", estimulando o aluno a realizar leitura de imagens, gráficos, tabelas e informações com características científicos textuais. Em contrapartida, os indicadores "criar" e "atuar" não estão presentes em nenhum dos livros da coleção, ou seja, pode-se considerar que neste tópico os livros não estimulam o desenvolvimento da autonomia dos alunos em ações que envolvam esta temática. Como consequência, esta análise possibilita o desenvolvimento de um produto educacional que busque preencher as lacunas de potencial de AC encontradas nos livros SP adotados, para auxiliar desta forma a atividade docente em sala de aula e o desenvolvimento de novas habilidades nos alunos no Novo Ensino Médio.

| INDICADOR | 2012 | 2015 | 2018 | TOTAL |
|---|---|---|---|---|
| LER EM CIÊNCIAS | 9 | 7 | 17 | 33 |
| ARTICULAR IDEIA | 6 | 13 | 11 | 30 |
| ARGUMENTAR | 2 | 2 | 1 | 5 |
| PROBLEMATIZAR | 2 | 1 | 0 | 3 |
| INVESTIGAR | 0 | 0 | 1 | 1 |
| ESREVER EM CIÊNCIAS | 1 | 0 | 0 | 1 |
| CRIAR | 0 | 0 | 0 | 0 |
| ATUAR | 0 | 0 | 0 | 0 |
| | | | | 73 |

**Tabela 1.** Quantidade de indicadores por triênio

| EIXO | 2012-2014 | 2015-2017 | 2018-2020 | TOTAL |
|---|---|---|---|---|
| Hist. e Conc. da Nanotecnologia | 18 | 22 | 25 | 65 |
| Saúde | 1 | 0 | 0 | 7 |
| Tecnologia | 1 | 1 | 5 | 1 |
| Fontes Energéticas | | 0 | 0 | 0 |
| Meio Ambiente | 0 | 0 | 0 | 0 |
| | | | | 73 |

**Tabela 2.** Quantidade de eixos temáticos por triênio

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**Área: EDU**

# Scientific research as a source of scientific dissemination in school visits to the university

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Keywords: Lectures, Chemistry, Scientific Dissemination, Public Schools, High School, Researchers.

## Highlights

Scientific research as the subject of lectures of scientific dissemination for school visits to the university;

The project so far has involved 1,400 students from public schools who did not know the university;

The research themes of the lectures became a book to support the school teacher.

## Resumo/Abstract

Science, technology, and innovation are fundamental factors for the progress of several nations, being present in numerous sectors and contexts of society (VALENTE; CAZELLI; ALVES, 2005). However, studies show that people's images of science and scientists are distorted and often controversial (FINSON, 2002). In relation to students, there may be a lack of interest in carrying out activities related to science and a weakening of the preference for a scientific career (VAN GRIETHUIJSEN et al., 2015).

As Chemistry is not very prestigious, scientific dissemination activities that promote interaction, that arouse curiosity and favor the cognitive involvement are important and can serve as a way of stimulating students' interest in science and scientific careers (ILLINGWORTH; LEWIS; PERCIVAL, 2015). To collaborate with the dissemination of Chemistry at the University of São Paulo (USP), interactive lectures were prepared on research developed at the Institute of Chemistry of São Carlos (IQSC), such as Analytical Chemistry and Electrochemistry. The lectures were produced in a way that involved the participation of students, addressing topics correlated with their reality, so they could find meaning in the research published and in the chemical concepts discussed, through experimental, audiovisual resources and moments of interaction, where the opinion and the knowledge brought by the student were crucial. These lectures are presented at USP where students go to visit the campus facilities, a research laboratory related to the theme of the lecture, receive information about scholarships, grants and other matters related to student permanence, participate in the lecture, and have lunch at the University restaurant. Following is the report of a student after participating in the lecture: - *"It was easier to understand because you worked a lot with young text, but without leaving what you needed to go through. Ah, I felt happy to be learning, because it was the first lecture I had that I was not sleepy, that I could understand, that I had the pleasure of being there and watching you explain something you like to us".*

Since the beginning of the project, the Physical-Chemistry lectures were presented to more than 1,400 students from public schools in the city of São Carlos and the region, totaling about 56 lectures, whose themes were: medicinal chemistry, and electrochemical degradation of organic compounds and corrosion of metals.The lectures produced so far were organized in the book *What Scientists Do: Scientific Dissemination Texts for Science Teaching and Learning* and made available to teachers participating in school visits. In a new phase of the project, it is expected to use the themes of scientific research as a source of contextualization of Chemistry classes in basic education.

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**Área: EDU** **Nº de Inscrição: 00454**

# Studies of the application of Virtual Learning Object in focus: analysis of formaldehyde present in hair straighteners

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Palavras Chave: *Ensino de Química, Tecnologia educacional, Objeto virtual de aprendizagem, Alisantes capilares.*

## Highlights

The study shows how Virtual Learning Object can help in Chemistry teaching and in the critical formation of students regarding the indiscriminate use of hair straighteners.

## Resumo/Abstract

O Brasil é o quarto maior consumidor mundial de produtos para cabelos.[1] Em paralelo à essa grande procura 'ainda' persistem as denúncias em função de irregularidades do uso indiscriminado do formaldeído em alisamentos capilares, prática de embelezamento muito comum em nossa região. Visando a necessidade de um ensino que possibilite a compreensão dos riscos causados pelo consumo constante desses produtos defendemos a temática 'alisamento capilar' como uma rica possibilidade de contextualização no ensino de Química.

Constituída por elementos da pesquisa participante[2], este trabalho versa sobre o uso de um objeto virtual de aprendizagem (OVA) como ferramenta da ação mediada para discutir a estrutura química do cabelo e as ações do formaldeído pela prática constante de alisamento capilar. Gravadas em áudio e vídeo, a aula foi realizadas pelo professor em formação inicial (PFI) com alunos (A) do 1º ano do ensino médio de uma escola pública de Goiânia. Composto por diversos recursos de imagem, vídeos, animações, textos, dentre outros, o OVA busca contribuir para que os estudantes compreendam os conhecimentos envolvidos na análise química de produtos cosméticos, os riscos inerentes ao processo de alisamento capilar e os efeitos causados no fio de cabelo, como apresentado no extrato 1.

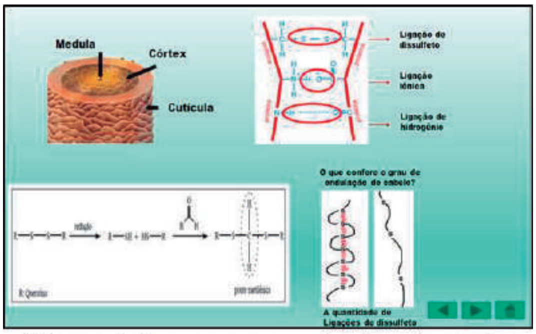

**Figura 1: Frame representando principais estruturas e ligações químicas do cabelo.**

**Extrato 1**

**PFI**: Quantas de vocês já fizeram alisamento capilar com produto químico? Qual o motivo? **TODAS AS MENINAS**: Sim! (nenhum menino levantou a mão). **A1**: Facilidade para manter no dia-a-dia. **P1**: Facilidade do dia-a-dia, o cabelo fica com uma aparência mais hidratada. **PFI**: O processo (de alisamento), caso use produto inadequado, pode provocar desbotamento e rigidez na fibra provocando perda da cutícula e quebra do fio. **A1**: Então, quando alisa é por que acaba com a ligação "$S_2$", né (A1 se refere à ligação de dissulfeto). **PFI**: Essa ligação "$S_2$" é chamada de ligação de enxofre. Durante o relaxamento essa ligação é quebrada e sua reestruturação com a participação do formaldeído possibilita o alisamento.

O diálogo conduzido por PFI1 no extrato 1 trata da identificação, entre os sujeitos da investigação, daqueles que fazem alisamento capilar e o motivo do uso e as respostas de A1 demonstram a forte influência das diversas transformações que a sociedade vem sofrendo em suas estruturas sociais e econômicas. Já na segunda parte da fala de P1 podemos observar informação a respeito dos efeitos causados pelo alisamento capilar no cabelo, evidenciando a importância da abordagem do tema para além da visão simplista ou do viés meramente exemplificativo sobre as implicações desse tipo de procedimento na saúde das pessoas. Sendo assim, ressaltamos que o OVA foi construído para atuar como ferramenta da ação mediada objetivando a aprendizagem de conteúdos químicos de maneia contextualizada com vistas à formação crítica cidadã. Contudo, para que os alunos pudessem compreender como essas ligações estão organizadas no fio de cabelo, PFI1 utilizou o aspecto representacional da estrutura molecular do cabelo, representação simbólica da linguagem química[3] (figura 1). Nesse sentido, O OVA desenvolvido pode contribuir, enquanto instrumento de mediação do professor – ator de primeira ordem no processo de ensino, para a aprendizagem dos alunos viabilizando as informações de origem atômico–molecular baseadas em modelos abstratos, como as explicações feitas por PFI1 sobre as ligações de enxofre presentes no fio de cabelo que são quebradas com o uso do produto para alisamento capilar.

## Agradecimentos/Acknowledgments

Ao CNPq.

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**Área: EDU**

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

# Study on the insertion of radioactivity content in the training of chemistry teachers in Goiás

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Palavras Chave: *Licenciatura em Química, acidente radiológico, Projetos Pedagógicos de Curso.*

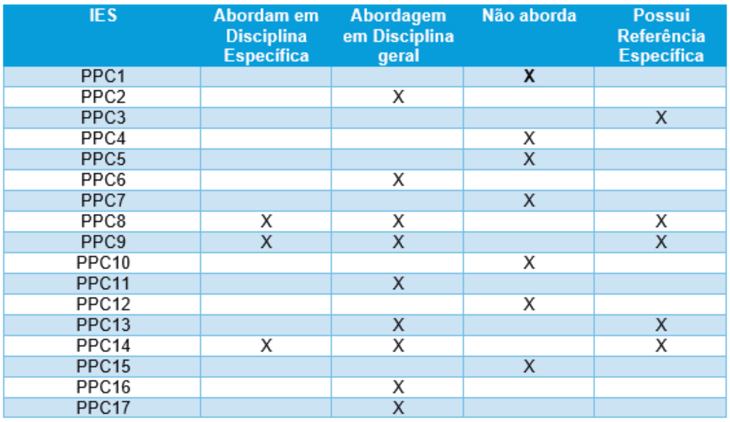
## Highlights

A serious radiological accident occurred in Goiânia. However, the training courses for chemistry teachers in the state do not include this theme in their pedagogical proposals.

## Resumo/Abstract

No ano de 1987, na cidade de Goiânia, capital do estado de Goiás-Brasil, ocorreu o maior acidente radiológico do planeta ocasionado pela violação de um equipamento de radioterapia que se encontrava abandonado em local que, anteriormente, abrigava uma clínica médica. Tal equipamento continha uma cápsula com aproximadamente 20 g de cloreto de Césio 137, um sal radioativo, azul brilhante e solúvel em água. A partir da violação da máquina, uma série de eventos resultou em contaminação radioativa, mortes e consequências que perduram até hoje, como pessoas em tratamento e acompanhamento médico, além do monitoramento dos rejeitos gerados pelo acidente. Entende-se que uma das causas do acidente se refere ao desconhecimento da população sobre o que é a radioatividade, suas características e consequências. Nesse sentido, a educação básica tem papel fundamental na alfabetização científica da população ao promover, a partir do trabalho pedagógico, a significação de conhecimentos científicos. Tendo a formação de professores de química como foco investigativo, buscamos, nos Projetos Pedagógicos de Curso (PPC) do estado de Goiás, os aspectos que relacionassem a futura atuação docente na educação básica a partir do tema radioatividade. Foram analisados, por meio da Análise Textual Discursiva (ATD), os 17 PPC de Licenciatura em Química do estado de Goiás. Na Figura 1, podemos identificar as formas de inserção do tema radioatividade nos cursos em tela.

Apenas 3 cursos ofertam disciplinas específicas sobre o tema, 7 cursos não abordam o tema radioatividade, o que é preocupante, pois para se trabalhar com esse objeto de conhecimento no ensino médio, é importante que professores de química tenham acesso aos conhecimentos em suas formações iniciais. Dos 9 cursos que apresentam o conteúdo em disciplinas de caráter geral (Química Fundamental, Química Descritiva, Química Geral, dentre outras), as discussões não são específicas sobre acidente radiológico.



| IES | Abordam em Disciplina Específica | Abordagem em Disciplina geral | Não aborda | Possui Referência Específica |
|---|---|---|---|---|
| PPC1 | | | X | |
| PPC2 | | X | | |
| PPC3 | | | | X |
| PPC4 | | | X | |
| PPC5 | | | X | |
| PPC6 | | X | | |
| PPC7 | | | X | |
| PPC8 | X | X | | X |
| PPC9 | X | X | | X |
| PPC10 | | | X | |
| PPC11 | | X | | |
| PPC12 | | | X | |
| PPC13 | | X | | X |
| PPC14 | X | X | | X |
| PPC15 | | | X | |
| PPC16 | | X | | |
| PPC17 | | X | | |

A partir da análise realizada, inferimos que, no caso específico do estado de Goiás, a temática radioatividade não é contemplada de forma satisfatória na maioria das propostas de formação de professores. Isso compromete a futura atuação pedagógica no ensino básico considerando-se a alfabetização científica como importante elemento formativo por meio das aulas de química.

**Área: ______________ Nº de Inscrição: ________**

# Sustentabilidade e protagonismo na aprendizagem mediada pela educação ambiental em experimentos de química geral

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Palavras Chave: *Educação ambiental, Química verde, Tratamento de rejeito, Toxicidade.*

## Highlights

Students´ protagonism in the managment of experiments in Chemistry. Proposal for replacement of highly toxic chemical experiments with less toxics ones.

## Resumo/Abstract

Buscando inserir a ideia de associação da sustentabilidade com o protagonismo dos próprios alunos de graduação de Química e de Engenharia, foi elaborado um projeto compartilhado para a gestão ambiental das aulas experimentais de Química, assim como o tratamento de efluentes químicos gerados. Foi proposta também a substituição dos experimentos existentes por outros de menor grau de toxicidade visando promover a educação ambiental[1] mediante a discussão dos temas associados, assim como contribuir para o processo formativo de profissionais mais conscientes das suas responsabilidades socioambientais. O tratamento de efluentes de rejeitos químicos de aulas experimentais de Química Geral foi realizado pelos próprios alunos da disciplina, com a prévia contextualização ambiental, mediada pelos docentes, com discussão da importância e conteúdo da Resolução do CONAMA 430/2011, que dispõe sobre as condições e padrões de lançamento de efluentes[2]. O tratamento do rejeito dessa aula, além de trazer economia, contribuiu para que os alunos elaborassem uma nova perspectiva de responsabilidade ambiental. Ademais, os alunos puderam experienciar uma situação em que tiveram que resolver um problema, trabalhando em equipe para buscar uma solução. A análise e substituição de experimentos existentes por outros de menor grau de toxicidade está em fase de desenvolvimento e tem como objetivo principal a substituição de reagentes e reações envolvidas nas aulas de Química Geral por outros menos tóxicos, sem que haja perda qualitativa de aprendizado. Para atingir este objetivo, acompanharam-se as aulas laboratoriais da disciplina Química Geral experimental durante um semestre a fim de analisar e selecionar os procedimentos de maior grau de toxicidade que poderiam ser substituídos. Os critérios para esta seleção foram os seguintes: a) grau de exposição a reagentes de alto grau de toxicidade, b) manutenção dos objetivos didáticos do aprendizado, c) disponibilização de reagentes e procedimentos nos laboratórios da Universidade. Dessa forma, foram selecionados dois experimentos, onde se utilizam compostos de 1) arsênio e 2) cianeto. A tabela abaixo esquematiza as propostas de substituição, bem como aponta características de cada experimento.

| | | |
|---|---|---|
| **Atual** | **1. Síntese $As_2S_3$**<br>• Carga superficial (-)<br>• Alta toxicidade<br>• Borbulhamento $H_2S$ | **2. Síntese azul da Prússia**<br>• Pigmento<br>• Risco de produção de HCN |
| **Proposta** | **Síntese sol de Raffo**<br>• Carga superficial (-)<br>• Menor toxicidade | **Síntese clorofila modificada**<br>• Pigmento<br>• Troca do íon metálico |

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## Agradecimentos/Acknowledgments

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**Área: EDU**

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

# The concept of Electronegativity: being a support in most part of Chemistry bringing a Meaningful Learning.

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Palavras Chave: *Resignification, Concepts, Electronegativity, Chemistry,*

## Highlights

Conceptual resignification, providing meaningful learning, with real experimentation, so that electronegativity is the conceptual basis for understanding Chemistry, an Educational Product created, through didactic sequences.

## Resumo/Abstract

This research started from the counterpoint, due to the existing difficulties in how to consider the conceptual correlation of Chemistry, with the existing difficulties both in the understanding of chemistry and its conceptual correlations.

A process of conceptual resignification of most of the concepts of chemistry was carried out, through the theme electronegativity, precursor that allows a greater integrative conciliation of these relationships. An applied, participatory and open action research was then carried out, targeting 25 students from the IFRS mechanics technical course – Campus Ibirubá. Then, it aims to present a methodological proposal in which it seeks to re-signify most of the concepts of chemistry from a base theme, such as electronegativity, which can provide significant learning using differentiated teaching strategies combined with problem solving proposals for students. . students.

It is possible to observe with this new methodological proposal an improvement in the students' performance, as well as a better global understanding of chemical science, this being demonstrated from the reflections and development of the content.

With the application of an Educational Product directed to this proposal. Which originated through a conceptual rereading, among the most diverse qualitative research on the subject, in addition to qualitative assessments in textbooks in high school and higher education, it is possible to create the possibility for students to interact directly with a practical situation in the classroom. class, build theoretical knowledge through this proposed resignification.

Associated with this, the theories of meaningful learning proposed by Ausubel and Marco Antonio Moreira were also considerable references in the elaboration of this research, creating the necessary predisposition for students to act together with the educator. With this re-signification, the students sought to construct a consistent chemical conceptual alignment, without fragmentation, providing a better cognitive development. This proposal can be seen in Figure 1.

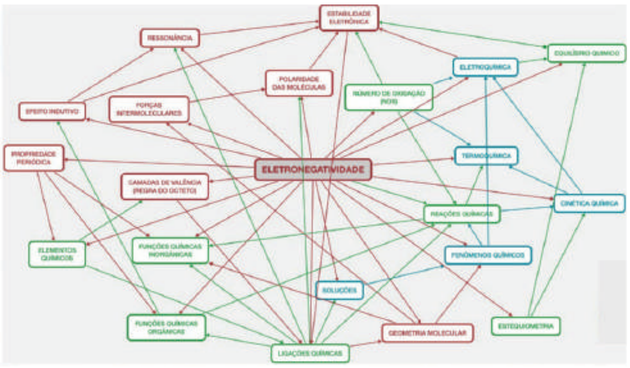

Figure 1: Mental Map of the conceptual base correlation applied, starting from Electronegativity. By: OLIVEIRA, M.A.M; MIGLIORINI, M.V.,2021.

## Agradecimentos/Acknowledgments

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**Área: EDU**

# The development of Live Pharmacies: sharing knowledge in an intercultural perspective

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Palavras Chave: *Povos e Comunidades Tradicionais; Matriz Africana; Interculturalidade; Plantas Medicinais.*

## Highlights

Dialogue between scientific knowledge and traditional knowledge. Horizontal dialogue between the academy and two traditional communities of African origin religions.

## Resumo/Abstract

O conhecimento científico e o tradicional dizem respeito a duas possibilidades distintas de compreender, organizar informações e, sobretudo, atuar sobre o mundo. O conhecimento científico é produto do contexto sócio-histórico, sendo possível continuidades e descontinuidades em seu desenvolvimento, à medida que ciência é socialmente construída.[1] Já o conhecimento tradicional refere-se a algo que está presente na história humana desde o surgimento das relações, surge com o intuito de satisfazer, e de auxiliar na formação de identidade de um povo.[2] Uma forma desses conhecimentos caminharem juntos seria pela interculturalidade, a qual propõe o diálogo e uma relação horizontalizada entre ciência e tradição,[3] não renunciando a temas como eurocentrismo e o universalismo que marcaram o processo histórico do colonialismo e do racismo antinegro que articula processos de aniquilação de culturas subalternizadas e estigmatizadas como selvagens, inferiores chegando ao ápice do epistemicídio.[4] O exercício dessa pedagogia do diálogo intercultural não se restringe às escolas e às universidades. É preciso reabilitar e capacitar espaços educativos informais "para se protagonizarem no campo da educação para a interculturalidade, nomeadamente as famílias, as associações religiosas, desportivas e culturais".[5] Dito isso, defendemos que uma iniciativa que poderia estreitar laços entre o conhecimento científico e o conhecimento tradicional, em uma perspectiva de intervalorização, seria a construção das farmácias vivas[6] nas comunidades tradicionais de matriz africana. Construída por elementos de uma pesquisa participante.[7] Assim, este trabalho buscou estabelecer um diálogo horizontal entre a academia e duas lideranças de duas comunidades tradicionais de religiões de matriz africana: candomblé e umbanda localizados em Goiânia. Essas comunidades têm em seus rituais o uso de plantas consideradas sagradas com propriedades fitoterápicas. O cultivo e o uso dessas plantas são passados dos mais velhos para os mais novos dentro dos terreiros religiosos garantindo que o conhecimento tradicional seja mantido.[8] Trazemos como resultado, um extrato de uma visita. Os participantes da pesquisa, nesse extrato, são denominados **P1**: um(a) líder religioso; **PFI**: professor/a em formação inicial. Cada fala corresponde a um turno representado no texto por **T** que são enumerados de acordo com a sequência das falas na pesquisa. **Extrato 1:** ***T.18-P1:*** *Dessa aqui ó, ela também cresce sozinha como mastruz, vermífugo fazer o que a gente conhece de emplastro, já ouviu falar nisso?* ***T.19- PFI1:*** *Não!* ***T.20- P1:*** *Emplastro que o povo antigo fala é coisa que você põe em cima da pele para que ela absorva. [...]. Então tipo, você tem uma artrite que não é um machucado exposto; aí você põe em cima passa a faixa e segura.* ***T. 55-PFI2:*** *Então, a gente veio aqui com os nossos conhecimentos de químicos, biomédicos e biólogos, para poder contribuir com vocês.[...] O que vocês acham?* ***T. 91- P1:*** *Mas o conhecimento de fazer a pomada vocês vão me ensinar a fazer?* ***T. 92-PFI2:*** *Sim, a gente vai ensinar.* O participante (P1) traz consigo conhecimentos adquiridos ao longo das gerações, por exemplo em **T.20**, na definição de emplastro. Esse termo se refere a uma base adesiva que contém um princípio ativo, e essa base deve ser colocada em contato com a pele para atuar como protetor ou agente queratolítico.[8] Em **T.55** e **T.92** IC2 faz alusões aos propósitos da universidade para com as comunidades, nesse caso os conhecimentos científicos na produção de pomada, gel e tintura, por exemplo toxidade, armazenamento e validade.[8,9] Nossos resultados indicam que essa pode ser uma alternativa de estabelecimento de diálogo entre a universidade e uma determinada comunidade.

## Agradecimentos/ Acknowledgments

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**Área: EDU Nº de Inscrição: 00194**

# The Importance of Interdisciplinarity in the Teaching of Environmental Chemistry: A Look Through Chemistry Students at the State University of Para.

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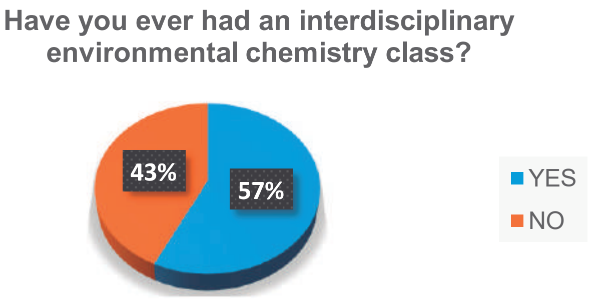
*Keywords: Environmental chemistry, Interdisciplinarity, Teaching of environmental chemistry*

## Highlights

1. The importance of interdisciplinarity in the teaching of environmental chemistry.
2. Chemistry students' point of view from the State University of Para.

## Abstract

The teaching of Chemistry, as the Exact Sciences, still generates discomfort in many students, who say they do not like or do not understand the contents, making the learning difficult. Often, this teaching follows the traditional line, impairing the student's way of learning and relating the content[1]. Thus, it is necessary to insert resources to assist teaching: one of them is interdisciplinarity. Studying Chemistry is not just about decorating formulas. This knowledge helps to understand the complex society in which we live[2]. Furthermore, it is worth noting that knowledge from other scientific areas is necessary to understand natural phenomena and, therefore, it is essential to optimize such teaching and use interdisciplinarity for environmental learning, obeying the National Curriculum Parameters, which says that transversal themes are not only they seek to modify the traditional order of knowledge, but they also place on the teacher the initiative to incorporate themes responsible for increasing the student's critical sense[3]. Thus, the work aims to identify the students' opinions about the multidisciplinary use in the teaching of Environmental Chemistry in their future classes. The methodology consisted of using an ICD (Data Collection Instrument) to interview them, through an online questionnaire called "Google Questionnaires". This ICD consisted of the questions: "What is your point of view about the use of interdisciplinarity in the teaching of Environmental Chemistry?"; "Have you ever had an interdisciplinary class in Environmental Chemistry?"; "Would you use interdisciplinarity to teach Environmental Chemistry?" From the ICD, 21 students participated in the research. In the first question about interdisciplinarity linked to EC, it was mentioned: "interdisciplinarity with other Natural Sciences subjects, as the Humanities, mainly Geography". In addition, the students stated that, in the teaching of EC, it is essential to associate it with other subjects to facilitate students' understanding. In the second question, the answers were based on "Yes or no" and the following graph was generated:



At the end, students were asked if they would use interdisciplinarity to teach EC. Regarding the answers, stands out a student who answered yes, being able to unify close knowledge and he also cited an unusual proposal involving art classes. From the research, it is concluded that most of the interviewed graduates did not participate in any interdisciplinary class, a worrying fact, because they are in College. Therefore, it is necessary to reverse this situation, better preparing these students for the future, wherefore their students know how to relate the contents to reality.

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**Area: EDU**

# The use of the controlled controversy to study pesticides in the STS perspective

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Keywords: Green Chemistry; STS approach; sustainable teaching; chemistry teaching.

## Highlights

The spread of Green Chemistry can be of help to sustainable teaching development. The controlled controversy technique is an alternative for studying the green concepts in the CTS approach.

## Abstract

Environmental issues have been the subject of discussion and constant worldwide concern motivated mainly by the consequences of the lack of the human/environmental relationship balance. In the 1990s, the concept of Green Chemistry (GC) emerged, which is concerned with developing processes that generate minimal or no waste, focused on prevention instead of remediation. In this way, it is believed that this issue should be widely spread beyond the industry to promote sustainable education. Many studies point to this theme discussion in universities; however, this study should be discussed since school. By working with problematizing themes of students' daily lives, the Science, Technology and Society (STS) approach emerges as a possibility for studying this area's concepts because it seeks to increase the content understanding beyond propaedeutic teaching. Nevertheless, these things are still little known or even unknown to many High School teachers.

Thus, this work presents the results of using the controlled controversy technique for the GC concepts study. A workshop that discussed pesticides from the STS perspective has been given to 22 undergraduates in Chemistry Teaching and high and Middle School teachers. The controlled controversy promotes the discussion of a controversial topic, in which participants debate from different perspectives (social actors) to reach a consensus.

The workshop has had three meetings and a six-hour workload. During the first meeting, participants were invited to answer an online survey in *Poll Everywhere*, a digital tool, to investigate their previous knowledge about the subject, followed by a video about pesticides to raise theme awareness. In the second meeting, the participants were divided into groups that represented four social actors involved in the theme: population, regional farmers, rural workers, and industry. The activity goals were to promote a discussion and have the groups present the social actors' points of view in a debate. At the end of the workshop, the participants answered another online survey to investigate their opinions about the meetings.

The first investigation showed that most participants think pesticides control diseases and pests and cause environmental imbalance. Next, the attendees have watched different specialists in the area talking about the subject, and these thoughts help them prepare their speeches. After that, there was a debate in which each social actor exposed their point of view about pesticide use explaining the arguments that made them decide. It is important to emphasize that the opinion of the social actor does not necessarily represent the position of the participant who is defending it but promotes his reflection to present relevant arguments that contribute to the social actor's view, even if they think differently. Finally, the final survey showed that 100% of the participants considered the STS approach a viable alternative for the implementation of GC concepts and considered the controversy a valuable tool to foster research and curiosity, thus contributing to the construction of more critical opinions.

Thus, it is believed that the workshop contributed to the teaching practice, uniting concepts of Green Chemistry with the STS approach through the controlled controversy.

## Acknowledgements

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**Área: EDU**

# Tic’s em química: Desenvolvimento de programas e suas aplicações

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Palavras Chave:*(Tic´s, programas, aplicações).*

## Highlights

Chemistry ICT: Program development and its applications

Labreal is an augmented reality game.

VRLabe is a virtual reality game.

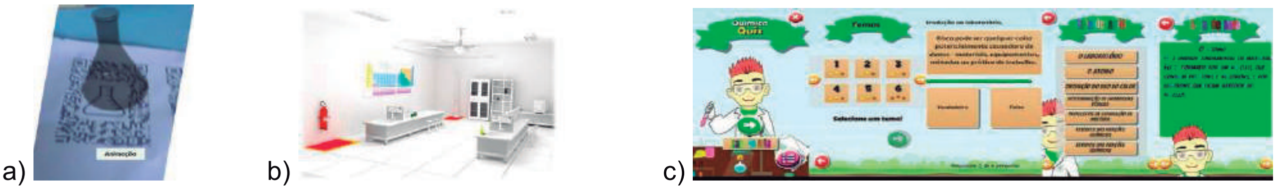
QuizQuimica is a trivia-style game (questions and answers).

All three programs were registered as computer programs at the INPI.

## Resumo/Abstract

Society has become increasingly computerized, as observed in the recent years mostly by the easiest access to information and communication technologies (ICT), which has increased considerably and brought as an advantage for its users the practicality in terms of information and communication. Each time more computers, smartphones and other technologies play important roles in several areas, one of which is the educational area due to the increasingly frequent contact of young people and children with electronic devices thus showing the importance of ICT in education. The use of ICT therefore has the role of increasing students' interest and performance in disciplines considered hard to understand such as Chemistry specifically in the city of Penedo / Alagoas where the use of ICT is almost not found, mainly in state, municipal and federal schools. The work aimed to develop apps and chemical games for students from state, municipal and federal schools in the city of Penedo-AL. The methodology applied to develop the games was divided into five groups: 1) Field analysis – To understand the students' situation, the procedures and skills that needed to be developed; 2) Game Designer – The games were shaped according to the behavior and characteristics of the students; 3) Development – After gathering all the necessary data, the games started to be developed; 4) Application – the games were distributed through online servers; 5) Training process – a short demo was held on each new game that was released so that students could adapt easily. As a result, subsequent Chemistry students at IFAL-Campus Penedo develop three programs: Labreal, VRlabe and QuizQuimica. In the augmented reality game Labreal, user can point with the camera of his smartphone to few already selected images and view three-dimensional objects and specific information about each one of them. Access to this data occurs through a two-dimensional bar code (QR Code). VRLabe however is a virtual reality game through which the user can get to know a laboratory, interact with it, see equipment and types of glassware. It makes it possible to visit the environment without having to leave the place by using only one accessory as an intermediary (in this case, the virtual reality glasses). QuizQuimica is a Trivia style game (questions and answers), which allows evaluate the student according to their knowledge. It consists of seven levels adapted for each series in order to follow the current subject of Chemistry classes. The user's level changing in the game is conditioned on achieving a good score. VRlabe and Labreal have great potential to be implemented in schools that do not have the conditions for a Chemistry laboratory. The limitation of VRlabe is only the purchase of virtual glasses, as many public schools do not have. Labreal and QuizQuimica have no limitations.

Picture 1. Image of the programs: a) Labreal, b) VRlab and c) QuizQuimica



All three programs were applied in high school classes at the Dr. Alcides Andrade State School and during the IFAL-Penedo Chemistry Week, which took place in June 2019. The use of games as teaching resources showed how much it is possible to target new technologies that are so present in the lives of young people and children as well as the

learning of subjects considered difficult to understand and in doing so to increase school performance. These programs were registered with the INPI in the form of a computer program registration.

## Agradecimentos/Acknowledgments

IFAL-Campus Penedo e ao programa PIBITI do IFAL.

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

**Nº de Inscrição: 00900**
*(Inserir o número de inscrição do autor que fez a submissão)*

# Tic’s em química: Desenvolvimento de programas e suas aplicações

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Palavras Chave:*(Tic´s, programas, aplicações).*

## Highlights

Chemistry ICTs: Program development and its applications

Labreal is an augmented reality game.

VRLabe is a virtual reality game.

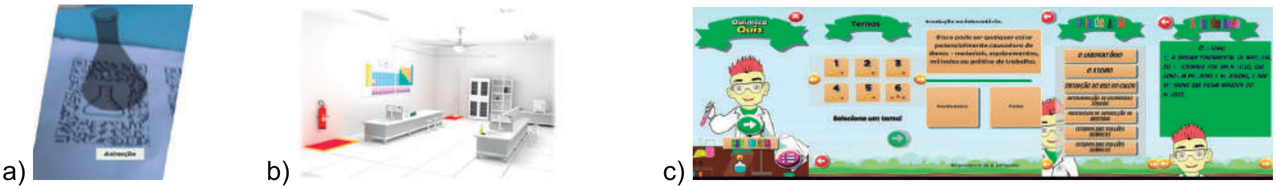
QuizQuimica is a trivia-style game (questions and answers).

All three programs were registered as computer programs at the INPI.

## Resumo/Abstract

Society has become increasingly computerized, as observed in the recent years mostly by the easiest access to information and communication technologies (ICT), which has increased considerably and brought as an advantage for its users the practicality in terms of information and communication. Each time more computers, smartphones and other technologies play important roles in several areas, one of which is the educational area due to the increasingly frequent contact of young people and children with electronic devices thus showing the importance of ICTs in education. The use of ICTs therefore has the role of increasing students' interest and performance in disciplines considered hard to understand such as Chemistry specifically in the city of Penedo / Alagoas where the use of ICTs is almost not found, mainly in state, municipal and federal schools. The work aimed to develop apps and chemical games for students from state, municipal and federal schools in the city of Penedo-AL. As a result, subsequent Chemistry students at IFAL-Campus Penedo develop three programs: Labreal, VRlabe and QuizQuimica. In the augmented reality game Labreal, user can point with the camera of his smartphone to few already selected images and view three-dimensional objects and specific information about each one of them. Access to this data occurs through a two-dimensional bar code (QR Code). VRLabe however is a virtual reality game through which the user can get to know a laboratory, interact with it, see equipment and types of glassware. It makes it possible to visit the environment without having to leave the place by using only one accessory as an intermediary (in this case, the virtual reality glasses). QuizQuimica is a Trivia style game (questions and answers), which allows evaluate the student according to their knowledge. It consists of seven levels adapted for each series in order to follow the current subject of Chemistry classes. The user's level changing in the game is conditioned on achieving a good score.

Picture 1. Image of the programs: a) Labreal, b) VRlabe and c) QuizQuimica


a) b) c)

All three programs were applied in high school classes at the Dr. Alcides Andrade State School and during the IFAL-Penedo Chemistry Week, which took place in June 2019. The use of games as teaching resources showed how much it is possible to target new technologies that are so present in the lives of young people and children as well as the learning of subjects considered difficult to understand and in doing so to increase school performance. These programs were registered with the INPI in the form of a computer program registration.

## Agradecimentos/Acknowledgments

IFAL-Campus Penedo e ao programa PIBITI do IFAL.

**Área: EDU**

# Training of chemistry teachers: dialogues between experimentation and the analytical elements of the relationship with knowledge

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Key words: *Relationship with knowledge, Experimentation, Training Teacher, Degree in Chemistry.*

## Highlights

Theoretical profile construction on the role of experimentation can contribute to work of training of chemistry teacher.
The analytical elements - intellectual activity and mobilization - are the most evidenced by the students of Degree in Chemistry.
Training aspects of undergraduates is more operational with an approximation between the effectiveness of experimentation and a personal sense of their role in teaching and learning.

## Abstract

This work seeks to identity the vision of students of Degree in Chemistry of the state Tocantins about the role of the experimentation in teaching and learning process. Since the theorical profile construction those comprehensions of students can contribute to work of training of chemistry teacher on experimental activities in science teaching[1], we led a case study research to analyze and characterize by Content Analysis[2] the 43 future chemical teachers' answers. We supported our analysis in the seven analytical elements from relationship with knowledge (intellectual activity, meaning network and normativity – relationship with the world; questioner teacher and relation of knowledge – relationship with another; mobilization and subject – relationship with itself)[3] to establish dialogues between the role of the experimentation and the training teacher. The results are presented in the Frame 1:

**Frame 1.** Categorization of the answers about three affirmations directed by undergraduates.

| Affirmations about experimentation | Identification of the categories | Elements from the relationship with knowledge |
|---|---|---|
| Experimental activities are often in the course and provide learnings of Chemical and technical knowledges | Absentee experimental activities (5) | Mobilization and subject; intellectual activity |
| | Theorical-practice association of the content (25) | Meaning network and intellectual activity; questioner teacher; mobilization |
| Experimental activities are important in the chemistry teaching and learning process | Pleasant teaching activity (11) | Intellectual activity; mobilization and subject |
| | Theorical-practice association of the content (19) | Meaning network |
| Experimental activities are contributing to increase your curiosity and questions in the scientific teaching | Absentee experimental activities (6) | Mobilization and subject |
| | Desperta o senso crítico do estudante (23) | Intellectual activity; mobilization |
| | Difficulty from relationship with content (1) | Questioner teacher |

Training teacher profile on the role of the experimentation in teaching and learning process is more restricted among experimentation as an intellectual activity and the its benefits can provide to the students themselves (mobilization and subject). We understand that the historical process of training teacher followed by the students of Degree in Chemistry so far is more operational, seeking approximations between the effectiveness of experimentation and the personal sense of their role in teaching and learning.

## Acknowledgments

To the research participants for contributing to the study and mapping of training in the state of Tocantins.

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**Área: EDU**

# Um olhar sob o viés do enfoque contextual dos artigos publicados na seção “Química e Sociedade” da revista Química Nova na Escola (QNEsc)

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Palavras-Chave: *Ensino de Química*; *Contextualização; Química nova na escola*

## Highlights

A look at the bias of the contextual approach of the papers published in the “Química e Sociedade” section of the journal Química Nova na Escola (QNEsc). The use of contextualization may contribute to the formation of conscientious citizens in the chemistry teaching and learning process.

## Resumo

De acordo com a Base Nacional Comum Curricular, na educação básica, a área de Ciências da Natureza é responsável pela construção do conhecimento de forma contextualizada, a fim de que os estudantes possam intervir em suas realidades locais, sociais, culturais e ambientais propondo soluções para problemas e desafios locais e/ou globais[1]. Nesse sentido, as pesquisas focadas na temática contextualização são fundamentais no ensino de química. O objetivo do trabalho foi analisar as publicações da seção “Química e Sociedade” de 2018 a 2020 da revista (QNEsc) com enfoque na contextualização. A pesquisa pautou-se nos parâmetros estabelecidos por RAUPP; REPPOLD, 2020 e dessa forma identificou-se se a abordagem das publicações em cotidiana, metodológica ou socioambiental. A Abordagem Cotidiana faz uso de situações do cotidiano apenas exemplificando ou fazendo associações superficiais envolvendo o conteúdo químico, sem proporcionar para o estudante uma reflexão econômica, social e/ou cultural mais ampla. A abordagem metodológica tende, por meio dos acontecimentos cotidianos, a contribuir para o entendimento e aprendizado dos conteúdos de Química, de uma forma que um tema seja o ponto de partida para as atividades pedagógicas de maneira que os conhecimentos químicos que serão abordados façam sentido para os alunos. A abordagem socioambiental requer um conteúdo mais amplo, que envolva a sociedade, um fato histórico, ou seja, o desenvolvimento de um ser crítico, facilitando assim, a sua compreensão sobre a utilidade da ciência no nosso cotidiano, melhorando sua capacidade de atuação frente à sociedade, assim, destacando-se o ensino com enfoque Ciência, Sociedade e Tecnologia (CTS)[2]. Para seleção dos artigos, levou-se em conta a presença de pelo menos um desses termos: ensino de química; ensino de ciências; contextualização e abordagem CTS no resumo, título ou palavras-chave. Pelos resultados obtidos, foram encontrados 43 artigos. A abordagem socioambiental é a preponderante, correspondendo a (22; 51%) das publicações, na qual proporciona um desdobramento mais completo dos mais diversos temas em discussão na sociedade, tendo como objetivo estimular o desenvolvimento do pensamento crítico-reflexivo ao tratar sobre o ambiente, o aspecto social, cultural e educacional, considerando os temas que relacionam o meio a qual professores e alunos estão incluídos[3]. A abordagem metodológica corresponde (20; 46,5%) dos artigos, que utilizaram as situações do cotidiano do estudante como métodos para tentar facilitar a compreensão e aprendizagem dos conceitos químicos[4]. E por último, a abordagem cotidiana foi evidenciada somente em (1; 2,3%) das publicações, apresentando uma participação pouco significativa. Segundo Moraes e Bedim (2017), essa abordagem permite que os alunos relacionem os conteúdos trabalhados em sala de aula com as suas vivências sendo de fundamental importância para o bom êxito do processo de ensino e aprendizagem[5]. Os resultados da pesquisa preconizam que a abordagem socioambiental foi a que liderou as publicações (22; 51%) nesse período selecionado, sendo uma ferramenta que pode contribuir na formação de cidadãos conscientes no processo de ensino e aprendizagem de Química.

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## Agradecimentos

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

# Uso das TIC no ensino remoto e o impacto da pandemia em uma turma de terceira série do ensino médio

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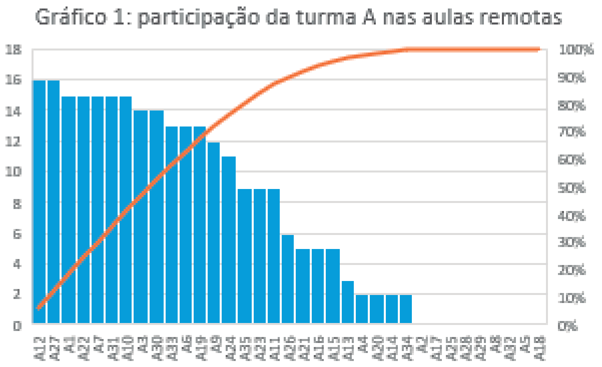
Palavras Chave: *aulas remotas, pandemia, da covid19.*

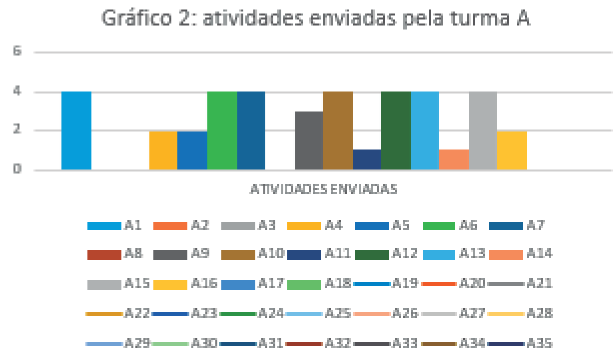
## Highlights

Use of ICT in remote teaching and the impact of the pandemic on a third grade high school class. The objective of this work was to evaluate the number of students who participated (frequency/attendance, completion and submission of activities) of remote classes in 2021. The observation took place in a class of a public school in the metropolitan region of Goiânia, Goiás, during a cycle/two months.

## Resumo/Abstract

A pandemia da Covid-19, em 2020, paralisou as atividades presenciais de ensino em todo Brasil (BRASIL, 2020). Em Goiás, o decreto nº 9.637 de 17 de março, suspendeu as aulas e quaisquer atividades presenciais nas instituições de ensino, que aconteceram de forma remota, usando as tecnologias digitais de informação e comunicação (TIC). O problema que se coloca é: qual o impacto da pandemia na alfabetização científica dos/as estudantes do ensino médio de uma escola pública? Os gráficos 1 e 2 demonstram a quantidade de estudantes que enviaram atividades avaliativas e quantos deles participaram das aulas de químicas, remotas, no segundo bimestre de 2021.





O gráfico 1 aponta que apenas dois estudantes, A12 e A27, participaram das dezesseis aulas remotas e quinze estudantes (A1, A22, A7, A31, A10, A3, A30, A33, A6, A19, A9, A24, A35, A23 e A11) apresentaram uma assiduidade superior a 50% nas aulas que aconteceram por videoconferência – Zoom, empresa que fornece serviço de conferência remota, entre os meses de abril e junho de 2021. Esses dados revelam que as aulas remotas, utilizando as TIC, amenizaram o impacto da pandemia na formação desses estudantes. No entanto, pode-se observar que nove estudantes não participaram de nenhuma das aulas remotas e outros nove estudantes tiveram uma frequência abaixo de 50%, ou seja, dezoito estudantes, mais 50% da turma, tiveram uma assiduidade inferior 50%. Um dos fatores que, possivelmente, comprometeu a frequência e assiduidade nas aulas remotas foi o fato de que alguns estudantes estavam sem aceso à internet, uma quantidade substancial de estudantes dessa escola, justificavam suas ausências nas atividades remotas afirmando que não tinha acesso à internet. Dados de 2020 revelaram que uma parte considerável da população estudantil, nível médio, não tem acesso à internet em banda larga ou 3G/4G em seu domicílio (BRASIL, 2020). O número de estudantes que participaram das avalições também foi baixo (gráfico 2), uma vez que somente quatorze estudantes dessa turma participaram ativamente dos mecanismos de avalição, adotado durante o bimestre. Enfim, a participação dos estudantes nas aulas e atividades remotas não foi uniforme, mesmo assim as TIC foram fundamentais para manter as atividades de ensino-aprendizagem de forma remota, na pandemia.

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**Área: EDU**

# Utilização de Fake News como recurso para a construção de conhecimento em Química

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Palavras Chave: *Ensino de química, Fake News, Conhecimento.*

## Highlights

Use of Fake News as a resource for knowledge construction in Chemistry.

Chemical knowledge has been the victim of fake news, which requires educators to work to combat the "disservice" presented, transforming it into knowledge with their students.

## Resumo/Abstract

Fake news, termo utilizado para representar notícias falsas, tem colaborado para muitos problemas na sociedade mundial, através das desinformações propagadas. Nesse contexto, a política não tem sido o único alvo desse desserviço. Notícias como: “vacinas matam” e que “medicamento A ou B” é indicado para tal doença, mesmo sem comprovação científica, reforçam a ideia de que as ciências têm sido, frequentemente, alvejadas. Entre as notícias, uma que envolvia o sumo do limão em jejum, um alimento de pH 22 muito indicado para infecções. Além de desrespeitar a comunidade científica, essa falsa informação propaga um valor inexistente para a escala de acidez e basicidade desenvolvida pelo bioquímico dinamarquês Sörensen. Diante desse cenário, indaga-se: como nossos alunos têm recebido essas informações? Pensando nessa problemática, surgiu a ideia de trazer essas fake news para dentro da sala de aula e mostrar, de fato, o que é verdade e científico no que se divulga. Primeiramente, foi necessário debater com os alunos o conceito de fake news; o que ocorreu por meio da apresentação de argumentos com base na vivência dos alunos. Em seguida foram apresentados alguns exemplos que estiveram presentes nesses últimos dias. Para essa etapa, foi necessário um tempo de 1h40min (duas aulas). Logo depois, foi solicitado que os alunos pesquisassem em casa, no prazo de uma semana, algumas fake news relacionadas, diretamente, ao conhecimento químico, as quais foram trazidas para um debate em sala de aula. Não foi determinado um conteúdo específico, apenas que fosse relacionado a conhecimentos químicos. Daí o desenvolvimento dessa atividade com uma turma de terceiro ano do ensino médio, devido a quantidade de conteúdos de Química que já tinham visto. Finalizando a atividade, o que precisou de mais duas aulas, a turma de 42 alunos foi dividida em grupos e realizou-se a produção de informes para serem divulgados em murais na escola. Apesar de ter sido acordado que as informações seriam transmitidas por meios de memes, produção de histórias em quadrinhos ou, ainda, produção de pequenos textos, a primeira opção foi a que mais se sobressaiu e parte desse trabalho pode ser conferido nas imagens abaixo.

Com essa atividade, foi possível discutir sobre a presença da Química nos produtos do dia a dia, escalas de pH, impactos do álcool na nossa imunidade, entre outros temas, envolvendo Química, trazidos pelos alunos. Além de confrontar informações falsas sobre o conhecimento químico, a criatividade dos alunos transbordou de diversas formas, o que, certamente, colaborou para o sucesso da atividade proposta.

## Agradecimentos/Acknowledgments

EEEPJF – Escola Estadual de Educação Profissional Júlio França

**Área: EDU**

# Utilizando plataformas digitais para apresentar temas relacionados ao papel do cientista na preservação ambiental para estudantes da Educação Básica

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Palavras Chave: *Ciência, Ferramentas tecnológicas, Tratamento de resíduos, Redes sociais.*

## Highlights

Using digital platforms to present, to high school students, the discussion of themes guided by the conservation of the environment and the role of the scientist. Use of YouTube and Instagram as tools for the discussion and dissemination of works guided by environmental preservation and the role of Science, seeking to inspire high school students.

## Resumo/Abstract

O cenário pandêmico paralisou as atividades da universidade, ao mesmo tempo, que foi visto o crescimento do negacionismo científico e pautas anticiência. Diante da importância de se discutir temas, como aqueles norteados pela preservação do meio ambiente e buscando retomar e estreitar o diálogo entre a universidade e a comunidade, o projeto de extensão, desenvolvido pelo Grupo de Pesquisa em Materiais e Catálise (GPMC-UNEB), "Experimentos sobre síntese de materiais e fotocatálise para a aplicação a estudantes no Ensino Médio", tem promovido entrevistas através da plataforma *Instagram*, convidando profissionais que trabalham com ciência na Educação Básica e no ensino superior de diversas instituições de ensino. Outra atividade é a apresentação de palestras por integrantes do GPMC, no *Youtube,* sendo transmitida a estudantes do Programa Universidade para Todos e do Ensino Médio, por uma professora da rede estadual de ensino da Bahia. No momento da transmissão a professora utiliza um formulário para verificar o impacto nos estudantes. Entendendo as redes sociais como ferramentas tecnológicas e ambientes de grande alcance entre os jovens, discutir ciência nesses espaços mostra ser cada vez mais viável e efetivo. Nessa vertente, os integrantes do projeto acreditam que é importante conhecer e divulgar os trabalhos realizados por professores e discentes pesquisadores sobre temas diversos como: catálise ambiental e a sua relação com a sustentabilidade, desenvolvimento de novas tecnologias e produtos a partir de distintos resíduos. Os temas discutidos incentivam a participação de um público diverso, principalmente dos estudantes da Educação Básica, contribuindo na promoção e disseminação das discussões propostas. Analisando as atividades realizadas entre agosto e dezembro de 2021, por meio da interação no *chat*, ao vivo, bem como de visualizações posteriores e outros indicadores, no *Instagram* e no *Youtube* e das respostas enviadas pelos estudantes, no formulário aplicado, pode-se inferir que o objetivo das atividades foi alcançado. Ao estender a discussão sobre as questões ambientais para fora dos muros da universidade foi possibilitado acesso à informação, que contribua para a qualidade de vida de todos, a mais pessoas tendo também o reconhecimento do profissional da ciência.

## Agradecimentos/Acknowledgments

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# ELE

# Eletroquímica e Eletroanalítica

**Área: ELE**

# 3D-printed electrochemical cell and working electrode for detection and quantification of indole-3-acetic acid by batch injection analysis

**Gabriel C. da Fonseca (IC),[1*] João Vitor F. dos S. Silva (IC),[1] Marilene S. Oliveira (PQ),[1] Luciana C. Vitorino (PQ),[1] Polyana F. Pereira (PQ),[1] João Carlos P. de Souza (PQ).[1]**

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Key Words: Batch Injection Analysis, Indole-3-Acetic Acid, Amperometric Detection, Printed Electrode, 3D Print.

## Highlights

Electroanalytical performance of 3D-printed working electrode with black-polylactic acid (CB-PLA) conductive filament. Rapid and low-cost detection and quantification of indole-3-acetic acid (IAA) by batch injection analysis.

## Abstract

Phytohormones are important molecules produced by plants for growth and development; IAA, for example, a hormone also produced by bacteria, regulates cell division and controls plant growth under stress conditions[1]. The detection and quantification of IAA have been focus in several studies mainly to understand the influence of some stress conditions onto IAA production in plants and microorganisms. Modern analytical techniques used for the quantification of IAA, such as liquid chromatography and gas chromatography-mass spectrometry show good sensitivity and selectivity[2]; however, they require expensive apparatus. Herein, we used a three-dimensional printer to fabricate an electrochemical cell with non-conductive filament, and a working electrode (WE) with CB-PLA conductive filament; reference (RE) and auxiliary electrodes (AE) were Ag/AgCl (3 M KCl) and Pt, respectively (Fig. 1A). The 3D-printed WE activation treatments were: mechanical (polishing) and electrochemical (0.5 M NaOH, -0.8 and +1.4 V, 200s). The IAA standard solution was prepared in NaOH as a supporting electrolyte (pH 13.5); the measurements were performed from -0.8 to 1.3 V, with a scan rate of 50 mV s$^{-1}$. The electrochemical behavior showed a reduction peak centered at -0.4 V, which linearly increased with concentration until 250 mg L$^{-1}$ (Fig. 1B). The potential of -0.4 V was chosen for amperometric analysis. For the calibration curve, IAA concentration varied between 0.5 and 100 mg L$^{-1}$; however, the linearity was only observed up to 50 mg L$^{-1}$ (Fig. 1C). Then, the calibration curve was done between 0.5 and 50 mg L$^{-1}$ ($R^2$ = 0.998). The limit of detection and limit of quantification were 1.31 and 4.37 mg L$^{-1}$, respectively. The results show that is possible to detect and quantificate IAA with 3D-printed electrode. Thereby, this system can be applied as a low-cost and rapid method for IAA detection and quantification.

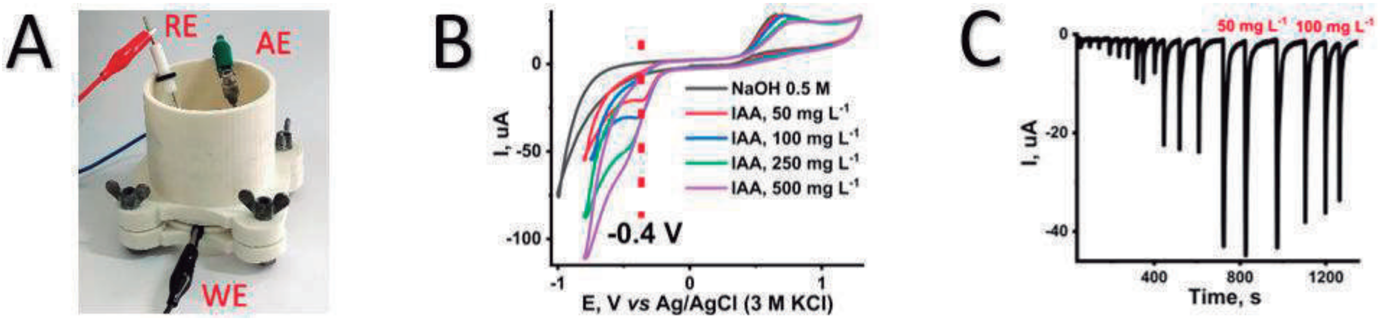

Fig. 1. (A) 3D-printed electrochemical cell and three-electrode system, (B) Cyclic voltammogram for different IAA concentrations, and (C) chronoamperometry with addition of IAA aliquots for linearity study.

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2. Hu, Y. *et al.* A multifunctional ratiometric electrochemical sensor for combined determination of indole-3-acetic acid and salicylic acid. *RSC Adv.* **10**, 3115–3121 (2020).

## Acknowledgments

Goiano Federal Institute, CNPq, and CAPES for financial support.

**Área: ELE**

# A calibration-free method using microelectrodes and chronoamperometry

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**Keywords:** *Calibration-free, Microelectrode, Chronoamperometry.*

## Highlights

This work addresses the issue of calibration-free determinations using a disc microelectrode. Such a goal was accomplished by chronoamperometric measurements from which the diffusion coefficient value can be determined. Armed with this value, the concentration of a target analyte can be determined from the steady-state current if the radius of the microelectrode is known.

## Abstract

There is a crescent demand in the chemical sensor research to move the measurement out of the traditional laboratory and close to the site of interest. A key issue is to develop calibration-free sensors primarily understood as being maintenance-free, and such features are particularly important for in-vivo implantable miniaturized electrochemical sensors. Here we show our efforts to develop an electrochemical calibration-free method that allows estimating the diffusion coefficient and the concentration of a target analyte simultaneously. The idea relies on the measurement of the steady-state current ($I_L$) at a disc microelectrode, which is established as $I_L$ = 4nFDCr, where F is the Faraday constant, D is the diffusion coefficient, n is the number of electrons involved in the electron-transfer step, C is the bulk concentration of the electroactive species, and r is the radius of the microelectrode. However, information on the diffusion coefficient is not always available, particularly in biological medium or complex matrices. Hence, if the diffusion coefficient is measured using an independent method, information on the concentration can be extracted, given that the microelectrode radius is known. This can be accomplished by using a chronoamperometric approach devised by Denuault and coauthors [1], according to which there is no need for the bulk concentration and the number of electrons participating in the electrode reaction. The only required information is the microelectrode radius, and the value can be obtained experimentally or by observation with an optical microscope. A proof of concept experiment was designed to examine the usefulness of the proposed approach. Accordingly, a chronoamperometric experiment was performed with a 6 µm radius carbon fiber disc microelectrode in a 4.00 mmol $L^{-1}$ $[Fe(CN)_6]^{3-}$ + 1.0 mol $L^{-1}$ KCl solution. Figure 1 shows the chronoamperogram obtained and by using the approach described in the literature [1], the diffusion coefficient was found to be (6.6±0.3)x$10^{-6}$ $cm^2$ $s^{-1}$, which is in close agreement with the literature value (6.32x$10^{-6}$ $cm^2$ $s^{-1}$) [2]. From the steady state current and by taking into account the microelectrode radius electrochemically determined (5.52±0.05) µm, the concentration of the electroactive species was determined as 3.79±0.04 mmol $L^{-1}$, i.e., a 5.25% deviation from the expected value. Further experiments are in progress by changing the solution viscosity with glycerol. The final goal is to monitor the concentration of NO in the cerebral cortex of a rat brain.

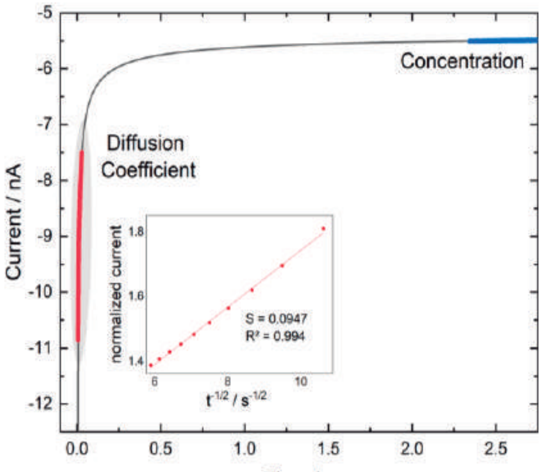

*Figure 1. – Chronoamperometry of the carbon fiber disc microelectrode in 4.0 mmol $L^{-1}$ $[Fe(CN)_6]^{3-}$ + 1.0 mol $L^{-1}$ KCl. Inset: Linearization of the transient response.*

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## Acknowledgments

The authors would like to thank the São Paulo State Research Foundation (FAPESP 2018/08782-1 and 2019/14418-3) and the National Council for Scientific and Technological Development (CNPq) for the generous funding.

**Área: CAT/ELE**

# AgPt Hollow Nanostructures supported on $SiO_2$ as Efficient Components for Methanol Crossover Effect Tolerance in Fuel Cells

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Keywords: Hollow structures, Oxygen reduction, Methanol crossover, Fuel cell.

## Highlights

- Low-metal loading heterogeneous catalysts for direct methanol fuel cells (DMFC);
- Optimization of Pt usage by alloying it with Ag and highly selective electrocatalyst.

## Abstract

Fuel cells have been considered an excellent alternative for generating clean and efficient power, converting chemical energy into electrical one. The DMFC, in which methanol is fed directly into the cell, has excellent potential to replace the conventional batteries used in portable devices due to quick refueling and higher energy density. However, a severe problem in these devices is the methanol crossover effect [1], which reduces the cathode potential, prompting studies of more selective electrodes. In this work, we aimed to synthesize AgPt hollow nanomaterials (shells and tubes) supported on $SiO_2$ to study their efficiency and selectivity to promote the oxygen reduction reaction (ORR) in alkaline solutions containing methanol. The results showed that the electrode modified with nanotubes was more selective than the nanoshells-based one to promote the ORR in 0.1 M KOH solutions containing up to 8,0 M $CH_3OH$ (Figure 1). Such results still needs to be unraveled; however, we can notice that the random composition of both catalysts, i.e., the synergy of Pt and Ag, is essential for the selectivity when compared to the Pt/C commercial catalyst, which counts on 20 times more Pt than our prepared catalysts.

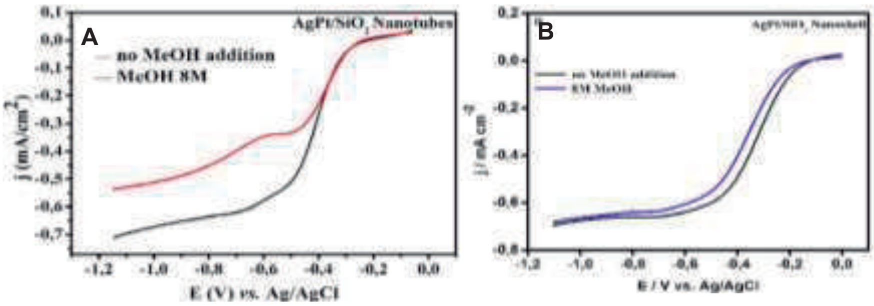

Figure 1. Oxygen reduction polarization curves on AgPt/$SiO_2$ nanotubes (A) and on AgPt/$SiO_2$ nanoshell (B) in 0.1 M KOH solutions before and after addition of 8,0 M $CH_3OH$, *f*= 1600 rpm, v= 10 mV $s^{-1}$.

[1] Carlos C. Lima, Weliton S. Fonseca, Flávio Colmati, Lara K. Ribeiro, Mesaque C. França, Elson Longo, Marco A. S. Garcia, Auro A. Tanaka, Electrochim. Acta 363 (2020) 137256.

## Acknowledgments

The authors acknowledge the financial support from the Brazilian science funding agencies CAPES (Finance Code 001), FAPEMA, FAPERJ, and CNPq.

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

# An e-tongue with flexible nanostructured sensors for impedimetric detection of ibuprofen in water

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Palavras Chave: *e-tongue, emmergent pollutant, nanomaterials, ibuprofen, impedimetric sensors*

## Highlights

E-tongue with flexible nanostructured
Impedimetric detection of ibuprofen in water
Sensors comprised silver interdigitated electrodes stamped on polyester substrates coated with ultra-thin films

## Resumo/Abstract

A multisensorial system electronic tongue (e-tongue) with flexible nanostructured sensors was developed for impedimetric detection of ibuprofen in water. Its individual, cross-sensitive sensor comprised silver interdigitated electrodes stamped on polyester substrates further coated with ultra-thin layer-by-layer films of polyelectrolytes, doped polyaniline, nickel phthalocyanine, iron oxide and gold nanoparticles, and reduced graphene oxide (figure 1A). The electrical fingerprint for different ibuprofen concentration was built with the electrical resistance of each individual sensor (figure 1B). The data matrix in which columns represented by each sensor and rows represented by different ibuprofen concentrations or fixed concentration (200 µmol $L^{-1}$) of different substances was processed by principal component analysis (PCA). It is observed that all sensors respond in the same way, although with different sensitives, in which the electrical resistance decreases as the ibuprofen concentration increases. On the range from 100 to 300 µmol $L^{-1}$ the system has a linear response, score(PC1) = -5.7 +$2.97.10^4$[ibuprofen] ($R^2$ = 0.989), for ibuprofen concentration, with limit of quantification and detection of 145 µmol $L^{-1}$ and 48 µmol $L^{-1}$, respectively (figure 1C). Finally, the system was evaluated in the presence of other important emergent pollutants, including caffeine, atenolol and acetaminophen. As the chemical sensors are not specific, they should respond to any change in composition, then with proper training, the e-tongue discriminated the atenolol mix from caffeine and acetaminophen.

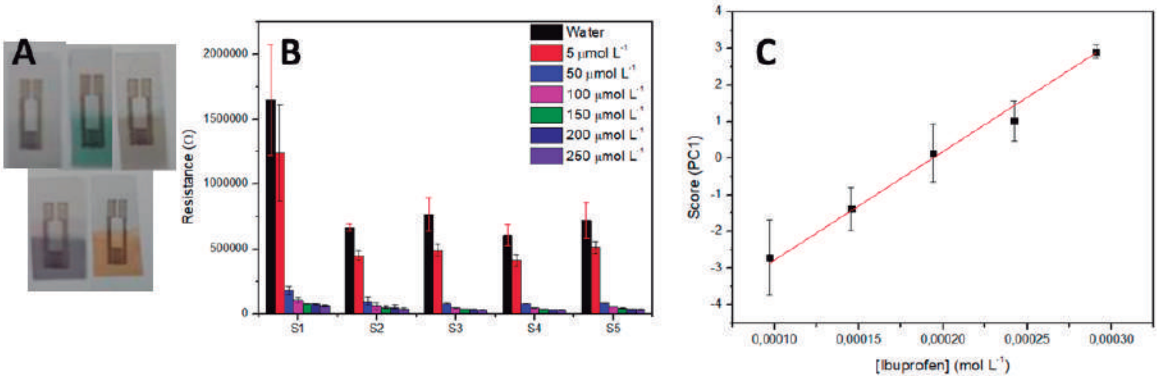

Figure 1 – A) Picture of flexible nanostructured sensors. B) Electrical fingerprint for ibuprofen at different concentration. C) Plot of [ibuprofen] x score of PC1, black dot and linearization of the curve, red line.

## Agradecimentos/Acknowledgments

To Capes, CNPQ and FAPDF for the financial support

**Área: ELE**

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

# Anodic oxidation of nitrite at a pre-treated carbon fiber microelectrode

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**Keywords:** *Nitrite, Electrochemical sensors, Microelectrodes.*

## Highlights

Herein we describe a procedure to enhance the response of a carbon fiber microelectrode towards the nitrite oxidation

## Abstract

Nitrite is an important pollutant in modern society, with several implications on human health and the environment. It poses a serious health problem due to its use as a preservative in food and beverages. Inside the human body, it can interact with hemoglobin forming methemoglobin by oxidizing the iron core from, $Fe^{2+}$ into $Fe^{3+}$, which inhibits the ability of blood to transport oxygen. Therefore, according to the World Health Organization (WHO), the permitted level of nitrite in drinking water should not exceed 0.9 ppm. Many methods to detect this anion, including chemiluminescence, capillary electrophoresis, chromatography, spectrophotometry, and electrochemical techniques were described. Among these, the electrochemical procedures have been of great interest, due to the low cost, fast response, and high sensitivity. The electrochemical detection of nitrite can be achieved by oxidation or reduction, but the latter tends to be largely affected by the oxygen reduction reaction. Moreover, the electrochemical detection of nitrite tends to be hampered by the degradation of the electrode by products generated during the anodic oxidation process. In this work, we bring a new approach to achieve more reproducible responses and enhanced sensitivity for nitrite detection. The proposed method uses a potential program to clean and regenerate the electrode surface during the measurements. Briefly, the potential is scanned in the negative region before the voltammetry sweep. Figure 1 shows results regarding the comparative voltammetric response of a carbon fiber microelectrode before and after employing the proposed protocol, and two main advantages can be noticed. Firstly, the nitrite voltammetric profile is more well-defined using the pre-treated electrode and a steady state situation is observed. Moreover, the bare microelectrode leads to a continuous current loss, whereas a more stable response is achieved using the modified electrode. Further studies are in progress to optimize the experimental conditions and maximize the sensor response.

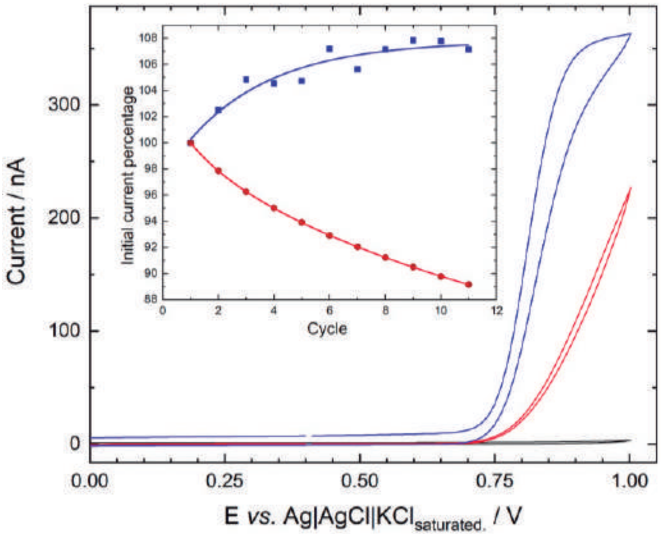

*Figure 1 – Voltammograms recorded in phosphate buffer saline (in black) and in 5 mmol $L^{-1}$ nitrite using a bare (red) and a pre-treated carbon fiber microelectrode (blue). Scan rate: 0.1 V $s^{-1}$. Inset: Current at 0.9 V during continuous voltammetric cycles.*

## Acknowledgments

The authors would like to thank the São Paulo State Research Foundation (FAPESP 2018/08782-1) and the National Council for Scientific and Technological Development (CNPq) for the generous funding.

**Área: ELE**

# Application of manganese and sulfur nanohybrids for the development of high capacitance supercapacitors

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Keywords: Asymmetric Supercapacitors, Nanowires, $MnO_2$-based supercapacitors, High-performance.

## Highlights

- High-performance supercapacitors based on manganese oxide-sulfur nanohybrids;
- A rapid and straightforward synthetic approach to prepare nanohybrids;
- 1 D morphology correlation with energy-storage performance.

## Abstract

Energy production through renewable feedstocks is one of the most critical challenges to developing a sustainable world. Therefore, the design of new energy storage systems is paramount for efficiency. Manganese oxide-sulfur nanohybrids were prepared by the solvothermal method, in which pure sulfur and $MnO_2$ nanowires were physically mixed and added in a Teflon-lined autoclave [1]. Electrochemistry measurements were performed on a three-electrode system with 2.0 M KOH as the electrolyte. For the working electrode, manganese oxide-sulfur nanohybrids were mixed with polyvinylidene fluoride and Super-P Carbon black in a solution of N-Methyl-2-pyrrolidone. The slurry obtained was deposited on nickel foam and pressed with a nickel wire as a current conductor. A platinum wire and an Ag-AgCl electrode (in 3 M KCl aq) were used as the counter electrode and reference electrode, respectively. For comparison, a $MnO_2$-nanowires electrode was prepared. Figure 1a shows the SEM image of the obtained material; the process maintained the 1 D (nanowires) shape, which is still visible at such low magnification. Better SEM/TEM images will be obtained. Figure 1b shows the galvanostatic charge-discharge plot for material, in which the electrode shows plateaus of charge-discharge potentials in the voltage profile, confirming the redox reaction of sulfur with manganese oxide. Figure 1c displays cyclic voltammetry for the material (agrees with the charge-discharge plot). Figure 1d shows the comparison between $MnO_2$ nanowires and manganese-sulfur discharge curves; the specific capacitance of the manganese-sulfur supercapacitor electrode during discharge was significantly increased compared to that of a $MnO_2$ electrode, showing results of 1622,44 F/g at the first discharge curve.

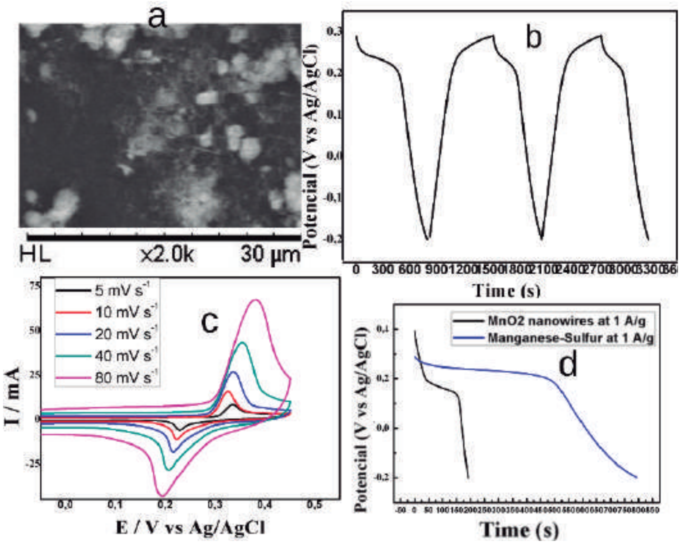

Figure 1: a) SEM image, b) charge-discharge plot, and c) cyclic voltammetry of the manganese oxide-sulfur nanohybrids. d) comparison among the hybrid prepared and $MnO_2$.

References: [1] Susana Chauque, Anderson G.M. da Silva et al. Electrochimica Acta, 382, 6, 2021

## Acknowledgments

The authors acknowledge the financial support of Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – Brasil (CAPES), FAPEMA and CNPq.

**Área: ELE**

# Biocompatible Wearable Electrodes on Leaf Toward On-Site Monitoring of the Water Loss from Plants

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Keywords: *flexible electrode, impedance, machine learning, wireless, precision agriculture, soy.*

## Highlights

- Monitoring of the water loss from leaves is reproducibility and sensitivity using two different devices.
- 2D nano-XRF maps are able to determine the long-term biocompatibility.

## Resumo/Abstract

Impedimetric wearable sensors are a promising strategy for determining the loss of water contents (LWC) from leaves as they can afford on-site and nondestructive quantification of cellular water from a single measurement. Since the water content is a key marker of leaf health, the monitoring of LWC can lend key insights into the daily practice in precision agriculture, toxicity studies, and development of agricultural inputs. Ongoing challenges with this monitoring are the on-leaf adhesion, compatibility, scalability, and reproducibility of the electrodes, especially when subjected to long-term measurements. This paper introduces a set of sensing material, technological, and data processing solutions that overwhelm such obstacles. Mass production-suitable electrodes consisting of stand-alone Ni films obtained by well-established microfabrication methods and eco-friendly pyrolyzed paper enabled the reproducible determination of LWC from soy leaves with optimized sensibilities of 27.0 (Ni) and 17.5 k$\Omega$ $\%^{-1}$ (paper). Moreover, the freestanding design of the Ni electrodes was key to deliver high on-leaf adhesion and long-term compatibility. Their impedances remained unchanged under the action of wind at velocities of up to 2.00 m $s^{-1}$, whereas X-ray nanoprobe fluorescence assays allowed us to confirm the Ni sensor compatibility by closely monitoring the soy leaf health in an electrode-exposed area. Both electrodes operated through direct transfer of the conductive materials on hairy soy leaves using an ordinary adhesive tape. We used a handheld and lowpower potentiostat with wireless connection to a smartphone to determine LWC over 24 h. Impressively, a machine learning model was able to convert the sensing responses into a simple mathematical equation that gauged the impairments on water contents at two temperatures (30 and 20 °C) with reduced root mean square errors (0.1% up to 0.3%). This data suggests a broad applicability of the platform by enabling the direct determination of LWC from leaves even at variable temperatures. Overall, our findings may help to pave the way for translating 'sense–act' technologies into the practice toward on-site and remote investigation of plant drought stress. These platforms can provide key information for aiding efficient data-driven management and guiding decision-making steps.

## Agradecimentos/Acknowledgments

For the financial support from São Paulo Research Foundation (FAPESP, grant 2020/09102-4) and for the proposal 20210015/Carnaúba beamline of the Brazilian Synchrotron Light Laboratory.

**Área: ELE**

# Chitosan bio-based electrode for ultrasensitive interleukin-6 monitoring in COVID-19 samples

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*Electrochemical sensor; fluorine-tin-oxide; green cross-linker; sepsis; COVID-19 prognosis biomarker;*

## Highlights

- Novel bio-based electrode for antibody immobilization.
- Voltammetric determination of interleukin-6.
- Simple method to estimate a biomarker of severity in COVID-19 samples.

## Abstract

Ultrasensitive and fast monitoring of interleukin (IL)-6 levels in serum samples has recently emerged as a valuable tool for the early diagnosis of inflammatory diseases such as sepsis and COVID-19. Voltammetric electrochemical techniques are promising strategies for immunoassays towards the point-of-care diagnoses, due to their low-cost equipment, fast response and high sensitivity. Despite its advantages, there is a lack of strategies for the label-free voltammetric determination of cytokines in biological fluids such as sera. Here, a fluorine tin oxide electrode was modified with a chitosan biofilm and applied for the ultrasensitive detection of interleukin (IL)-6, a major proinflammatory cytokine. Transmission electron microscopy, cyclic voltammetry and electrochemical impedance spectroscopy indicated the successful immobilization of antibody by using a green cross-linker. By square wave voltammetry, this sensor achieved a detection limit of 0.05 pg $mL^{-1}$ with a wide linear range of 0.05-1000 pg $mL^{-1}$. Additionally, it displayed a high selectivity index when tested in the presence of IL-12, IL-1β and TNF-a, three inflammatory cytokines. The produced bio-based electrode was applied for the quantification of IL-6 using 5 µL serum samples of septic mice and COVID-19 patients. The resultant values were comparable to those found by the conventional ELISA testing. The proposed platform can be applied as a green low-cost immunosensor that displays ultra-sensitivity and suitability for one-drop analysis, which are promising features for clinical diagnoses.

## Acknowledgments

Ampere, CNPq, Capes and UFSC

**Área: ELE**

# Comparative study between Fenton and electrochemical oxidation in decontamination of real urban effluent

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Palavras Chave: *Tratamento de Efluente Real, Eletro-oxidação, Fenton, Esgoto Urbano, Toxicidade.*

## Highlights

Raw sewage was effectively treated combined AOPs. The electrochemical followed by Fenton processes reduced energy consumption, toxicity, Nitrite, COD, Chloride, Turbidity and Suspended solids.

## Resumo/Abstract

Advanced oxidation processes have been used for wastewater treatment due to their capacity to reduce the organic loading and for their fast reactions. In this paper, we explore the viability of isolated and sequential use of electrochemical oxidation and Fenton processes into treatment of urban sewage. The electrochemical process was carried out using DSA®-$Cl_2$ electrodes and factorial planning in order to investigate the pH influence, current density, and electrolyte. Fenton reaction was also used and $H_2O_2$ and $Fe^{2+}$ concentration effects were investigated. The efficiency was estimated by chemical oxygen demand (COD) reduction and in the optimized conditions the effluent was characterized by turbidity, suspended/dissolved/total solids, ammonia, chloride ions, free chlorine, nitrite, and potassium analysis and bioassays with *Artemia ssp*. and *Lactuca sativa*. The study demonstrated that the use of electrochemical technique followed by Fenton allowed an improvement in the degradation of organic matter and reduction of turbidity and solid content (Fig. 1), reaching reductions of 86.8, 96.4, 99.4, 56.1, and 66.7% for COD (Fig. 2), turbidity, SS, DS, and TS, respectively. The associated treatment also contributed to the reduction of energy consumption by 74.9%, from the 23.9 kWh $m^{-3}$ observed during the electrochemical treatment isolated to the 6 kWh $m^{-3}$ during the associated process. All the treatments presented toxicity reduction, with the electrochemical process achieving the best results.

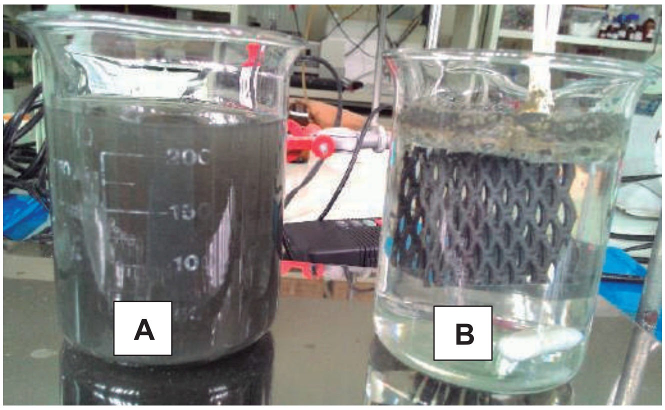

**Figure 1.** Effluent (A) before and (B) after electrochemical treatment during the use of sequenced processes.

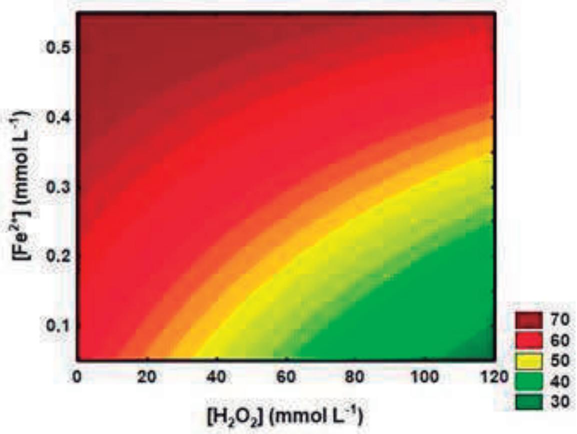

**Figure 2.** Response surface for COD reduction during electrochemical treatment followed by Fenton.

## Agradecimentos/Acknowledgments

FAPEAL, CAPES e CNPq.

**Área: ELE**

# Complete 3D printing of carbon black/polylactic acid electrodes and fast pre-treatment for development of highly stable electrochemical devices

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Keywords: *Fused deposition modeling*, Multi-material structures, Carbon-based electrodes, Advanced oxidation processes, Low-cost analytical instrumentation

## Highlights

Fully 3D-printed electrochemical cell was proposed based on additively manufacturing.

A combination of Fenton reaction and electrochemical oxidation processes were realized to expose carbon particles.

Detailed material characterizations revealed better electron-transfer upon treated surface.

Electrochemical experiments using treated sensors indicated excellent response stability.

Electroanalytical applications including environmental, forensic and biological areas were successfully demonstrated.

## Resumo/Abstract

Three-dimensional (3D) printing is an emerging manufacturing technology that has revolutionized the rapid prototyping process in several fields of scientific research. 3D printing technologies associate to conductive materials have emerged as powerful tools for the development of electrochemical sensors. However, pre-treatment methods are often required to improve electrochemical properties of 3D printed sensing surface to enable higher electroanalytical performance. In this sense, this study describes the fabrication of a compact 3D printed electrochemical cell via multi-material FDM technology using ABS and PLA/CB filaments and their activation through a novel pre-treatment process based on electrochemical/Fenton method within 8 min. The proposed pre-treatment involves a combination of photochemical and electrochemical oxidation processes to degrade the excess of binder material impregnated on the cell surface. This strategy is simple, toxic-free, fast and exposes the carbon black nanoparticles to facilitate the faradaic reactions. The reported method ensured long-term stability (~ 2 months) and high heterogeneous rate constants (1.2 ± 0.3 x 10-3 cm $s^{-1}$). In addition, peak currents were remarkably increased up to 353 ± 13%, clearly highlighting the potential use these 3D electrodes for electroanalytical applications. The treated electrode offered low detection limits (at µmol $L^{-1}$ levels) for different analytes including metals like Cd(II) (0.009) and Pb(II) (0.006), midazolam maleate (0.54) and uric acid (0.71). In this way, we believe that the carbon black/PLA sensor activated through the proposed protocol may be extensively used in many electrochemical applications due to its highlighted performance in terms of stability, sensitivity, and reproducibility.

## Agradecimentos/Acknowledgments

The authors would like to thank Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES, Brazil), Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq, Brazil) (Grants 426496/2018-3, 308140/2016-8, 307554/2020-1 and 142412/2020-1) and Instituto Nacional de Ciência e Tecnologia de Bioanalítica (INCTBio, Brazil) (Grant 465389/2014-7) for the financial support and granted scholarships. The authors acknowledge the Multi-user Laboratory of high-resolution microscopy (LabMic/UFG) for using their facilities during SEM and Raman analysis. The authors acknowledge Sensors and Actuators B: Chemical for the divulgation (https://doi.org/10.1016/j.snb.2021.130721).

**PÁrea: ELE** **Nº de Inscrição: 01003**

# Comportamento eletroquímico da espécie *Maytenus Rígida* Mart. em fração acetato de etila, na presença de Betaciclodextrina.

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Palavras Chave:*(Maytenus, eletroquímica, betaciclodextrina, antioxidantes).*

## Highlights

Electrochemical behavior of the species Maytenus Rígida Mart. in ethyl acetate fraction before Betacyclodextrin. *Maytenus rígida* Mart. antioxidant species. Cyclic voltammetry proves the presence of antioxidants in the ethyl acetate fraction. Increased current with the addition the addition- cyclodextrin.

## Resumo/Abstract

A espécie *Maytenus rígida* Mart. vêm se mostrando uma excelente fonte de produtos terapêuticos, estudos da espécie evidenciaram que essa característica se dá pela presença de substâncias químicas com propriedades antioxidantes. Diante disso o objetivo do trabalho é avaliar a entrecasca do gênero Maytenus rígida em fração acetato de etila, por meio da técnica eletroquímica de voltametria cíclica (VC), que permite, detectar o comportamento eletroquímico da espécie presente no extrato em maior quantidade correlacionar potenciais de oxidação, intensidade de corrente, com o intuito de aumentar e avaliar a solubilidade e a biodisponibilidade do extrato na solução eletrolítica utilizamos a molécula betaciclodextrina ( β-CD), que tem um papel importante em diversas áreas tecnológicas. O estudo eletroquímico foi realizado em célula eletroquímica de 10 ml composta por três eletrodos imersos em solução tampão 6,9,o extrato foi adicionado estabelecendo uma concentração de 0,4g/L da fração acetato de etila e variando a concentração de betaciclodextrina em 0,4g/L, 4g/L e 40g/L.

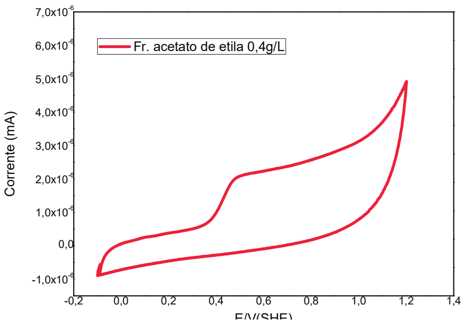

Figura1: Voltamograma cíclico da fração acetato de etila 0,4g/L

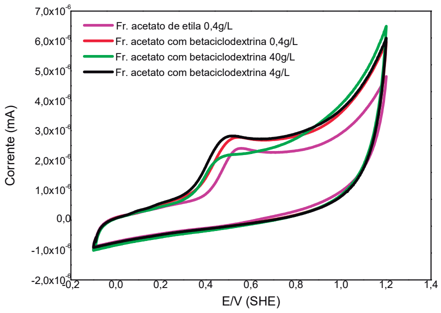

Figura2: Voltamogramas cíclicos da fração acetato de etila 0,4g/L e β-CD em diferentes concentrações.

O extrato apresenta única onda anódica em +0,5V, de natureza irreversível. Observa-se que com a adição da β-CD em proporção 1:1 e 1:2 ouve um aumento na densidade de corrente referente à oxidação da substância sem deslocamento significativo no potencial. Esse comportamento se dá inicialmente pelo aumento da solubilidade do extrato no meio eletrolítico favorecendo assim a oxidação. Quando há um aumento na proporção 1:10 de β-CD, observou-se um diminuição na corrente, isso se dá pelo encapsulamento da substância ativa no extrato na molécula de β-CD, desfavorecendo assim a oxidação. Diante do resultado podemos verificar que a molécula de β-CD se mostrou bastante eficiente no processo de diluição do extrato, para testes eletroquímicos, não modificando o perfil eletroquímico da espécie.

## Agradecimentos/Acknowledgments

# Determination of carbendazim in natural waters using a sensor based on magnetite nanoparticles modified with ascorbic acid/β-cyclodextrin

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Keywords: *Carbendazim, Environmental chemistry, Magnetite nanoparticles, β-cyclodextrin, Sensor*

## Highlights

Synthesis of a novel nanomaterial-based on magnetite nanoparticles, ascorbic acid, and β-cyclodextrin;
Construction of a sensor for carbendazim determination in lagoon water samples.

## Abstract

Growing concerns about the overuse of pesticides and their impact on human health and the environment requires a constant search for new technologies and methods designed to examine and monitor environmental samples. In that regard, this work presents the development of a novel nanomaterial through the synthesis of magnetite nanoparticles ($Fe_3O_4$NPs) stabilized with ascorbic acid (AA) and modified with β-cyclodextrin (β-CD). The nanomaterial was utilized for modifying the surface of a glassy carbon electrode (GCE) to quantify the fungicide carbendazim (CBZ). The $Fe_3O_4$NPs nanoparticles were characterized by transmission electron microscopy, and the sensor performance was evaluated by electrochemical impedance spectroscopy and cyclic voltammetry. Figure 1 shows a schematic diagram of the CBZ redox reaction on the surface of the proposed sensor ($Fe_3O_4$NPs-AA-βCD/GCE). The CBZ electrochemical process is based on the oxidation reaction of the nitrogen atoms on the carbamate group and benzimidazole ring (+0.88 V *vs.* Ag/AgCl, KCl (3 M)), involving the transfer of 2 protons and 2 electrons. The calibration plot of CBZ was constructed using the $Fe_3O_4$NPs-AA-βCD/GCE sensor under optimized conditions (square wave voltammetry, 0.1 mol $L^{-1}$ acetate buffer, pH 5.0) obtaining linear ranges of 3.33 – 13.29 and 16.61 – 29.8 μmol $L^{-1}$ with detection and quantification limits of 0.43 and 2.34 μmol $L^{-1}$, respectively (Fig. 2). Adequate precision results were obtained with relative standard deviations of 5.37% (repeatability intra-day) and 5.58% (repeatability inter-day). Quantification of CBZ in spiked lagoon water samples was realized with accuracy obtaining recoveries ranging from 96.3% to 100.7%. Thus, the proposed sensor represents a fast, efficient, and low-cost analytical tool for monitoring the fungicide carbendazim in natural waters.

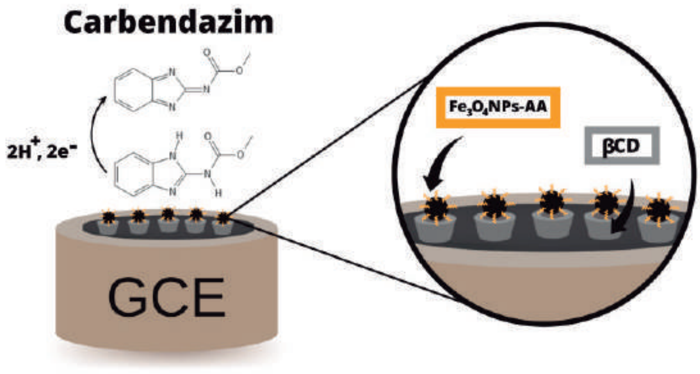

**Fig. 1.** Schematic representation of CBZ redox reaction on the surface of the $Fe_3O_4$NPs-AA-βCD/GCE sensor.

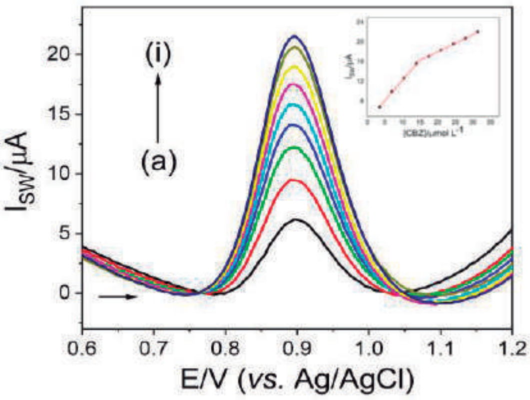

**Fig. 2.** Square wave voltammograms obtained with $Fe_3O_4$NPs-AA-βCD/GCE in acetate buffer solution (0.1 mol $L^{-1}$, pH 5.0) containing different concentrations of CBZ. Inset: Calibration plot for the CBZ (S/N =3).

## Acknowledgments

The authors are grateful for the financial support received from CNPq. This research was also supported by the Central Laboratory of Electron Microscopy at the Federal University of Santa Catarina (Florianópolis, SC, Brazil).

**Área: ELE**

# Determination of the stimulant modafinil in authentic saliva using screen-printed electrodes with stripping voltammetry for application in doping control

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Keywords: Adsorptive stripping voltammetry, Anti-doping analysis, Banned drugs; Carbon nanotubes, Non-invasive samples.

## Highlights

- Simple method to detect modafinil using stripping voltammetry with screen-printed electrodes.
- The method is applied to the sensitive and selective detection of modafinil in authentic human saliva.

## Abstract

Modafinil is used as a stimulant for treatment of excessive daytime sleepiness, which is related to several sleep disturbances such as restless leg syndrome and narcolepsy. Due to its stimulant effects some doping cases have been reported from modafinil intake before or during competitions. Anti-doping analysis has been performed in urine samples and is regulated by World Anti-Doping Agency (WADA), which publishes an annual list of prohibited drugs. In addition, the concomitant use of saliva and urine samples offers an improvement to anti-doping analysis, allowing the correlation between the unchanged drug in saliva with its metabolites in urine, as reported for the stimulant modafinil and for others [1]. Furthermore, due to the simple and non-invasive collection, the saliva sample is a more viable approach to application of screening methods for doping control. Several analytical methods have been widely used for drug detection and disease diagnosis using saliva samples, but most notably chromatographic methods with mass spectrometry detection. Nevertheless, electroanalytical methods offer easy on-site analysis or screening of saliva samples. Moreover, portable and disposable electrochemical sensors such as Screen-printed electrodes (SPE) provide a simple and attractive prospective method to anti-doping analysis in authentic saliva. In this context, this work presents the electrochemical detection of modafinil, for the first time, using carbon nanotubes screen-printed electrodes (SPE-CNT) with adsorptive stripping wave voltammetry (AdSWV) [2]. The stimulant modafinil exhibited an irreversible oxidation process in acidic medium at glass carbon electrode and at carbon SPEs. Studies showed that the modafinil oxidation process is adsorption-controlled at carbon electrodes and the AdSV technique can be usually used to detect this analyte in undiluted human saliva. The modafinil adsorption on SPE-CNT was well-described by the Langmuir isotherm. Using this isotherm and a rectangular box model [2], the approximate area of possible molecular orientations of the modafinil adsorption on SPE-CNT was estimated. Thereby, assuming one monolayer and a close packing, the real surface area available for adsorption of the porous layer of carbon nanotubes on SPE-CNT was estimated to be 42-62 cm$^2$. The proposed electrochemical method was applied to authentic human saliva for modafinil determination (LOD of 2.0 μM) without interference from uric acid or ascorbic acid. The analytical performance of the SPE-CNT with AdSWV for detection of modafinil in authentic saliva samples suggests its possible application as a simple and fast method for doping control.

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## Acknowledgments

**UFVJM, CNPq and FAPEMIG.**

**Área: ELE**

# Development of a gold nanostructured microsensor for determination of carbendazim in water samples.

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**Keywords:** *carbendazim, nanoporous gold, environmental analysis, electrochemical sensors.*

## Highlights

A nanoporous gold film with reduced graphene oxide was electrodeposited on a gold microelectrode and then used for the electrochemical detection of carbendazim. The promising results indicate the possibility of using this sensor for CBZ monitoring in water samples.

## Abstract

Carbendazim (CBZ) is a well-known fungicide from the group of carbamate compounds with wide application in agriculture, mainly in beans, soybean, wheat, and citrus crops. CBZ has been classified as a potential carcinogen to humans if exposed for the long term. Based on the health hazards and environmental risks, environmental protection and health care agencies have set the compound maximum acceptable level in drinking water as 120 µg $L^{-1}$ and 120 µg $L^{-1}$ in Brazil and Australia, respectively [1]. Despite being a legal product in Brazil, its misuse leads to environmental problems as it is persistent in water and soil. In addition, CBZ is associated with an increased risk of liver tumors, and for this reason, the substance is not allowed in the USA and Europe [2]. Hence, developing a CBZ monitoring device becomes desirable as a helpful tool for water quality control. In this sense, a nanoporous gold (NPG) film was electrodeposited on a gold microelectrode, and the generated platform was investigated for electrochemical CBZ sensing. The µNPG sensor was fabricated by the Dynamic Hydrogen Bubble Template method, i.e., a potential of – 4.0 V was applied for 250 s in a 0.5 M $H_2SO_4$ solution containing 1 mM $HAuCl_4$. Subsequently, the same procedure was repeated, placing 1 mg of graphene oxide (GO) in the precursor solution to obtain the µNPG-rGO sensor. Voltammetric studies showed no well-defined peak in a CBZ solution using the bare Au microelectrode (µAu). In contrast, an electrochemical process at E = + 1.2 V was clearly noticed with the µNPG sensor. A 100-fold current enhancement was obtained with the µNPG compared with the µAu electrode at such potential. An even more significant increase in the peak oxidation current was noticed by using the µNPG-rGO sensor, evidencing a gain in sensitivity. Scanning electrochemical microscopy (SEM) images confirm the formation of highly porous surfaces and that electrodeposition parameters, mainly applied potential ($E_d$) and time ($T_d$), have a notable influence on the structure of the films. The crystallographic orientation of gold atoms in the NPG films has a strong influence on the electron transfer process, hence further studies are in progress to optimize the electrodeposition parameters in an attempt to develop a suitable sensor for CBZ detection.

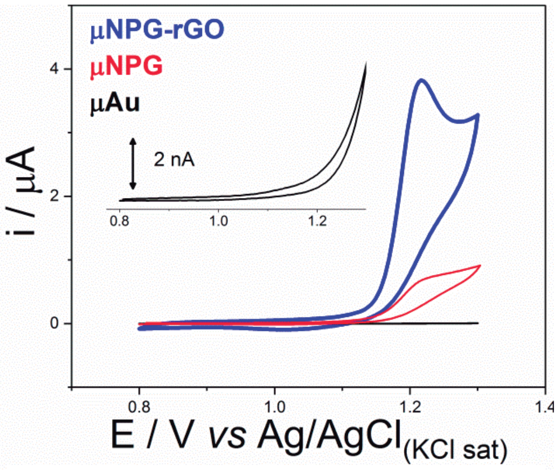

**Fig. 1 -** Voltammograms recorded with different electrodes in a 5 mM CBZ solution. Scan Rate: 10 mV/s.

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## Acknowledgments

The authors would like to thank the São Paulo State Research Foundation (FAPESP 2018/08782-1, 2019/14418-3, 2022/00064-8 and 2019/06293-6) for the generous funding.

**Área: ELE**

# Development of a *Graphene Quantum Dots* based-electrochemical sensor for estrone determination in water and synthetic urine

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*Keywords: Seawater, Wastewater, Nanomaterial, Endocrine disruptors, Emerging pollutants.*

## Highlights

- *Graphene Quantum Dots* are easy to prepare;
- The developed sensor is capable of monitoring estrone at trace levels.

## Abstract

Hormones such as estrone (E1) and estradiol (E2) interact with the body's metabolism by activating or blocking hormone receptors, hindering production and causing hormone degradation. high levels of E1 and E2 are associated with an increased possibility of breast cancer and prostate cancer [1]. Thus, it is necessary to monitor these species. Nanomaterials such as Graphene Quantum Dots (GQD) may have some characteristics such as high surface area and good electrical conductivity, which makes them excellent electrode modifiers [2]. In this work, a carbon paste electrode modified with GQD (GQD/E) was developed for the voltammetric determination of E1. The analysis parameters were optimized and the results obtained for the GQD/E show an increase in the sensitivity of the proposed sensor, highlighting the importance of optimizing the parameters of the analytical method developed for the determination of E1 in complex samples. Figure 1 shows that the variation of current intensities in relation to concentrations resulted in two linear regions within the concentration range studied, the first of 0.05 – 1.30 μmol L$^{-1}$ and the second of 0.89 – 10.00 μmol L$^{-1}$, ($R^2$ = 0.997). The calculated limit of detection (LOD) and quantification (LOQ) were 28.00 nmol L$^{-1}$ and 96.00 nmol L$^{-1}$, respectively. The determination of E1 using GQD/E in seawater, tap water, wastewater and synthetic urine matrices resulted in excellent recovery values between 95.9% – 108.1%. Concomitant species analyzes showed no significant interference (≤ 10%) on the estrone electrochemical signal.

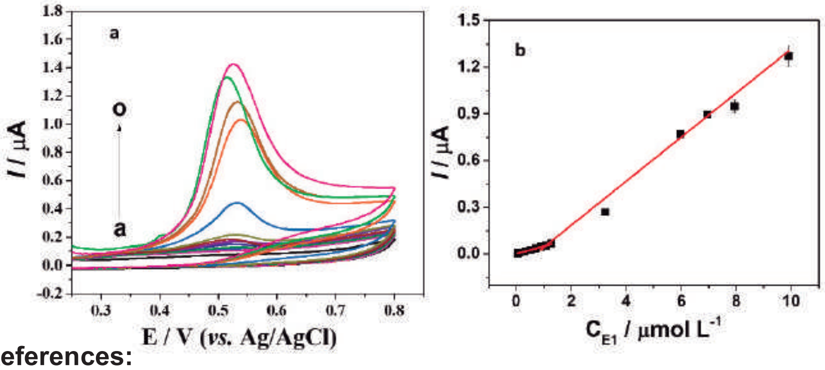

**Figure 1: a)** Representative cyclic voltammograms obtained using GQD/E under optimized analysis conditions in the presence of different concentrations of E1. **b)** Relation between the anodic peak current and the concentration of E1.

**References:**

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## Acknowledgments

**Área: ELE**

# Effect of Electrogenerated Random Defects on Pt(111) Surfaces onto Methanol Electrooxidation: A Study of Oscillatory Dynamic.

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*Keywords: Methanol Electrooxidation, Pt(111), Disordering surfaces, Potential Oscillations, Cyclic Voltammetry.*

## Highlights

This work aims to determine the influence of disordering surfaces generated from Pt(111) over MEOR using electrochemical techniques.

## Abstract

In the present work was possible to determine the influence of disordered surfaces obtained from Pt(111) over methanol electro-oxidation reaction (MEOR), using electrochemical techniques under potential and current regimes. The random defects electrogenerated on Pt(111) can be achieved upon cycling the electrode up to 1.3 V (RHE).[1] In this work, three disordered Pt(111) surfaces were prepared with different defect densities, by fixing the number of excursions to a high potential region where surface roughening may take place. Electrodes are denoted here as "Pt(111)-X", where "X" indicates the number of cycles performed between 0.05 V - 1.30 V.[1] Thereafter the characterization in acid media, the CVs for MEOR was obtained (Fig. 1). Herein is possible to observe the displacement of onset potential and an increase of current for disordered surfaces, at 0.53 V the current densities on Pt(111)-X become more significant and the performance is higher than Pt(111) as the {110}-defects increase. After this potential, the current increases and reach a maximal value at 0.73 V for Pt(111), while for disordered surfaces the current peak increases reaching the highest value for Pt(111)-16, indicating that the defects influence the mechanism reaction and the performance of the electrode. Considering the negative-going scan, the hysteresis effect is observed for most surfaces because of CO formation at low potentials until being oxidized at high potentials (*ca.* 0.70 V). Under the galvanodynamic regime (Fig. 2 a), the presence of small amounts of defects causes the emergence of potential instability, between 0.6 - 0.8 V, as can be seen in Fig. 2 b-d. Results in the literature show that this potential region is associated with the formation and oxidation of $CO_{ads}$, which leads us to conclude that the presence of defects on the Pt(111) surface favors the increase in the formation of this species and, thus acting as a poison on the surface.[2]

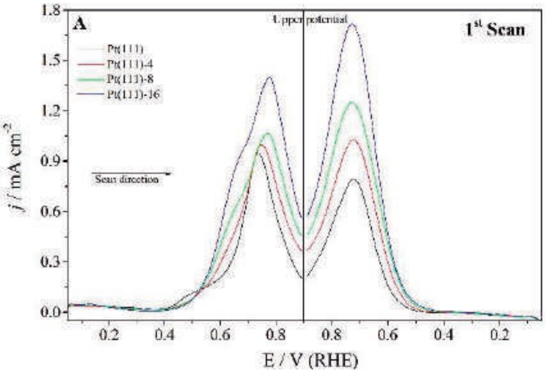

**Fig. 1.** 1st Scan of MEOR for: Pt(111), Pt(111)-4, Pt(111)-8 and Pt(111)-16. 0.1 M $HClO_4$ + 0.2 M MetOH. 0.050 V $s^{-1}$.

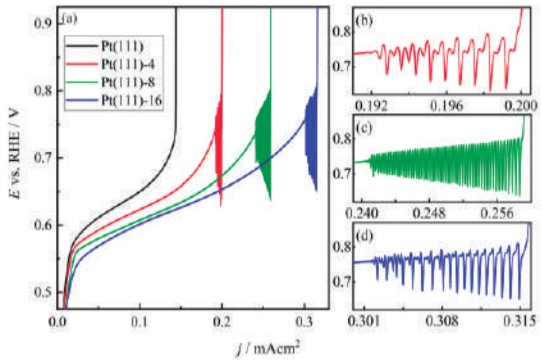

**Fig. 2.** (a) Galvanodynamic curves of MEOR on: Pt(111), Pt(111)-4, Pt(111)-8 and Pt(111)-16; (b-d) The inset highlights the potential instabilities. 0.1 M $HClO_4$ + 0.2 M MetOH; dj/dt = 5 $10^{-9}$ A $s^{-1}$.

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## Acknowledgments

Authors gratefully acknowledge financial support from FAPESP, FAPEAL, CNPq and CAPES.

**Área:ELE**

# Electrochemical adsorption of 4-(phenylazo)benzoic acid on Pt and Au polycrystalline electrodes

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Palavras-Chave: Photoswitch, Azobenene, Electroreduction

## Highlights

Electrochemical reduction of 4-(phenylazo)benzoic acid leads to the rupture of the molecule forming aniline and 4-aminobenzoic acid and presents irreversible at Pt and reversible process at Au electrode.

## Resumo/Abstract

Azobenzene molecules and derivatives are widely studied due to their molecular photoswitch property[1]. This class of molecules exhibits cis/trans isomerization under UV/visible light radiation. Its use allows ON/OFF modulation, being of great value for the photocontrol of different systems[2]. Knowing this, in this work we studied the influence of the isomerization cis/trans in the adsorption of the molecule 4-(phenylazo)benzoic acid (azo) on Pt and Au polycrystalline electrodes. The experiments were carried out with a Pt or Au working electrode, Pt counter electrode and saturated calomel electrode (SCE) reference, and the solution consisted of 15 mmol L$^{-1}$ 4-(phenylazo)benzoic acid and 0.1 mol L$^{-1}$ NaOH. The solution is deaerated with N$_2$ before starting the experiments. Trans → cis isomerization is performed with 340 nm LED and cis → trans with ambient illumination (SR). The cis/trans isomerization of azo did not show noticeable changes in the cyclic voltammetry (CV) performed in Pt and Au (Figure 1). However, it has been observed by FTIR experiments that the azo reduction process is reversible in Au, while in Pt the process is irreversible. It was also observed that the electrochemical reduction of azobenzene occurs not only with the formation of hydrazobenzene[3], but also with the rupture of the molecule, forming aniline and 4-aminobenzoic acid.

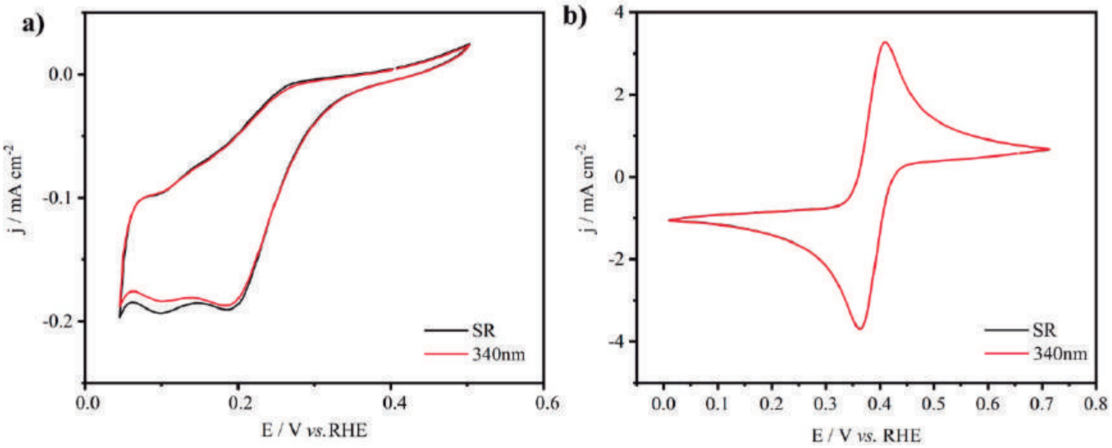

**Figure 1.** CV of the 4- (phenylazo)benzoic acid in: a) Pt and b) Au. In black with ambient illumination (SR) and in red with 340 nm LED.

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## Agradecimentos/Acknowledgments

Processo: 2020/09601-0

**Área: ELE**

# Electrochemical and *in situ* UV-Vis spectroelectrochemical investigation of novel nitrones

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Palavras-Chave: *Nitrones, Organic electrochemistry, Cyclic voltammetry, Spectroelectrochemistry, Redox mechanism.*

## Highlights

The electrochemical and spectroelectrochemical behavior of nitrones was investigated and correlated with leishmanicidal activities.

## Abstract

The nitrones, known as radical traps, are synthetic antioxidants with considerable potential as drug candidates to treat oxidative stress related diseases[1,2,3]. For example, LQB-303, a novel hybrid molecule containing nitrone and nitroaromatic functions, has been reported with potent trypanocidal effect, exhibiting high selectivity and low toxicity, is, therefore, an interesting alternative therapy for Chagas disease[4]. In the present work, were investigated the electrochemical and spectroelectrochemical behavior of nitrones and derivatives to obtain data on their redox mechanism and electrogenerated intermediates in order to corroborate, explain or predict the molecular mechanisms of biological action. Cyclic (CVs) and differential pulse (DPVs) voltammograms on a glassy carbon electrode (GCE) were recorded in an aprotic medium (acetonitrile + 0.1 M TBAPF$_6$) in order to mimic the lipophilic biological environments. The ***p*-nitrobenzaldehyde** and **5-nitro-2-furaldehyde** standards were studied electrochemically under the same conditions. All compounds studied showed to be electrochemically active in the cathodic region of the voltammograms. The **LQB-109** and **LQB-123** nitrones showed similar behavior, with irreversible reduction waves and a potential more negative than -2.0 V, relative to the nitrone reduction (Figure 1). As for the compounds **LQB-569**, **LQB-303**, **LQB-484**, **LQB-304** and **LQB-534** that have double redox function, that is, nitrone and nitro groups, reduction peaks characteristic of both were observed (Figure 1). When compared to the standards (compounds that have only the nitrone group or only the nitro group), it is noted that the nitroaromatic group is reduced first in a quase-reversible monoelectronic transfer. The spectroelectrochemical investigation for the nitronitrone **LQB-303** revealed a decrease in the absorbance of some absorption bands and the appearance of new ones, during the application of cathodic potentials, which suggest the reduction of the nitronitrone and formation of its reduction products (Figure 2). Electro- and spectrochemical methods proved to be adequate in the redox study of nitrones, derivatives and precursors and were correlated with leishmanicidal activities, mainly for the more electrophilic nitronitrones **LQB-303** and **LQB-484**, which were significantly leishmanicidal, with low toxicity.

Figure 1. CVs for **LQB-303** (green line), **5-nitro-2-furaldehyde** (orange line) and **LQB-109** (blue line), ***p*-nitrobenzaldehyde** (black line) and **LQB-569** (red line) in CH$_3$CN + TBAPF$_6$, GCE, ν = 100 mV s$^{-1}$.

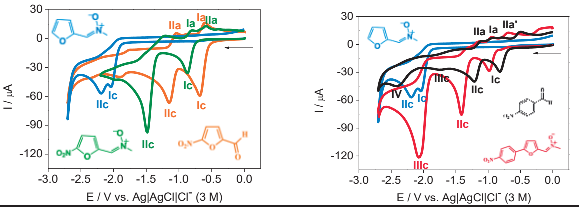
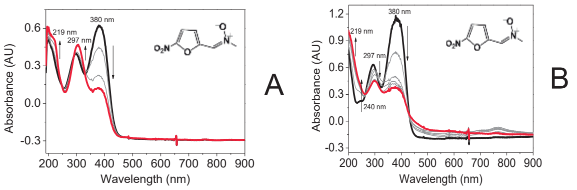


Figure 2. (—) Initial UV/Vis spectrum of **LQB-303**, (––) (—) UV/Vis spectra during the spectroelectrochemical reduction of **LQB-303** at an applied potential of -0.9V (A), -1.5V (B).



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## Acknowledgments

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**Área: ELE**

# Electrochemical and theoretical studies of fluometuron oxidation at glassy carbon electrodes

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*Glassy Carbon Electrode; Differential Pulse Voltammetry; Unmodified Electrode; Phenylurea Herbicide; Density Functional Theory.*

## Highlights

- New insights on the electrochemical behavior of FTN were proposed.
- DFT was used to examine the electrooxidation mechanism of fluometuron on bare GCE.
- Simple method for FTN detection in ppb levels.

## Abstract

Phenylurea herbicides such as fluometuron (FTN) are persistent contaminants that present a long-term residual effect in soil, often leaching to surface and groundwater [1]. This work investigates the mechanisms of fluometuron (FTN) oxidation by density functional theory (DFT) calculation and voltammetric measurements. Complementary data from experimental and computational studies provided new insights into the reaction mechanisms of the FTN. It allows the understanding of factors that influence the direct electrooxidation of FTN on the glassy carbon electrode (GCE) surface. The CV results showed a well-defined irreversible FTN oxidation peak at +1.2 V in the investigated pH range of 2-7. By using the Nernst equation, it was possible to evaluate the linear dependence of pH versus peak potential in CV analysis. The slope of 46 mV $s^{-1}$ suggested an oxidation mechanism involving an equal number of protons and electrons [2]. Chemical calculations showed that the presence of defects on the GCE surface induces strong interaction leading to FTN dissociation and/or its adsorption with orientation parallel to the substrate, which compromises the electroanalysis. Raman spectroscopy confirmed the surface fouling. The electroanalytical determinations of FTN were performed using differential pulse voltammetry (DPV) under optimized conditions. It was possible to observe a linear increase of the anodic peak current with increasing concentrations of FTN in the range from 207 to 3846 µg $L^{-1}$; the theoretical detection limit was statistically estimated as 63 µg $L^{-1}$. According to the possible surface interactions provided by theoretical studies, the analyte can remain adsorbed onto the glassy carbon electrode after oxidation. From this point of view, comparative calibration plots were investigated by using the standard addition method and calibration curve for FTN determination. Also, the bare electrode offered proper selectivity in the presence of other pesticides and potential interfering species. Intra and inter-day presented a standard relative deviation of 3.72 and 5.20 %, confirming an adequate precision of the proposed method. The electrode was applied for FTN determination in real samples, presenting a recovery range of 81.8–98.9% (n=3), which suggests the absence of matrix effects. The results showed that the GCE can be used as an efficient strategy for environmental monitoring of persistent organic compounds, such as FTN.

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**Área: ELE** **Nº de Inscrição: 00879**

# Electrochemically reduced graphene oxide films on interdigitated electrodes as field-effect transistors

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Palavras Chave: *graphene, transistor, electrochemical reduction, sensor, conductivity.*

## Highlights

Graphene oxide sheets were deposited onto interdigitated gold electrodes and reduced via cyclic voltammetry (CV)

Electrochemical reduction avoids the use of dangerous chemicals and high temperatures usually required in graphene oxide reduction

Solution-gated field-effect transistors (SG-FETs) were successful fabricated

SG-FETs as chemical sensors and can discriminate solutions with different pH values and saline concentrations

## Resumo/Abstract

Graphene oxide (GO) is a graphene derivative with oxygen-containing functional groups in its basal plane and its borders. These functional groups facilitate GO dispersion in various solvents, including water, allowing the deposition of this material on numerous kinds of substrates and surfaces. GO contains a mixture of carbon atoms with sp2 and sp3 hybridization, which gives an insulating character to this material [1]. However, the partial reduction of oxygen-containing functional groups produces another derivative of graphene. Reduced graphene oxide (rGO) presents a certain π conjugated structure and consequent electrical conductivity [2]. rGO has been proving to be an excellent alternative to pristine graphene in electronic devices, especially in terms of cost and processability. In this study, GO sheets were deposited onto interdigitated gold electrodes and reduced via cyclic voltammetry (CV) to realize solution-gated field-effect transistors (SG-FETs) [3]. GO reduction was carried out in a conventional electrochemical cell containing the electrolyte and three electrodes: interdigitated electrode containing GO films as a working electrode, Ag/AgCl reference electrode, and a platinum plate as the auxiliary electrode. Electrochemical reduction avoids the use of dangerous reductants agents, high temperatures, and also eliminates byproducts. SG-FETs with high transconductance (over 100 μS) can be achieved in optimized conditions. SG-FETs were also applied as chemical sensors. It is shown that these sensors can discriminate solutions with different pH values and saline concentrations. In the future, the devices will be applied as sensors for the detection of cyanotoxins. Experiments in this direction are in progress.

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## Agradecimentos/Acknowledgments

The authors are grateful for the financial support provided by CNPq and FAPESP (Process: 2018/07508-3) funding agencies.

**Área: ELE**

# Electrochemical sensor based on copper nanoporous and molecularly imprinted polymer for determination of xylobiose in banana peel and pulp

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Palavras Chave: *Molecularly imprinted polymer, copper nanoporous, L-arginine, xylobiose, banana, electrochemical sensor.*

## Highlights

Xylobiose is a xylooligosaccharide that presents prebiotic potential. A simple and low-cost electrochemical sensor was developed for determination of xylobiose. Copper nanoporous amplified the surface area for the imprinted cavities in the MIP using L-arginine as functional monomers. The sensor showed low limit of detection and quantification and high sensitivity for the determination of xylobiose.

## Abstract

The banana is among the 20 most important commodities in the world and in 2018, it reached a production of 115.7 million tons, and Brazil accounted for over 5.8 % of this production. The pulp represents approximately 70 % of the banana, while the peel represents 30 %, which becomes the main residue. Associated with this, during the processing of the fruit, waste can reach up to 40 % of total production. In this sense, based on the circular economy, it is necessary to optimize the processing of this fruit in the context of a biorefinery and recovery compounds that can add value to lignocellulosic waste, such as xylan, which is a hemicellulose that, after it being hydrolyzed, generates xylooligosaccharides (XOS). Xylobiose is the main XOS that presents high prebiotic potential with applications in the areas of health and food. Thus, the objective of this work was to develop an electrochemical sensor based on molecularly imprinted polymer (MIP) modified with copper nanoporous (3DnpCu). The sensor was developed in a conventional electrochemical system with three electrodes: Ag/AgCl reference electrode, auxiliary electrode of Pt and a glass carbon electrode (GCE) as a work electrode. The eletrodeposition of copper nanoporous was performed on the GCE during 45 s, applying - 1 mA of constant current from a solution containing 0.5 mol $L^{-1}$ $H_2SO_4$ and 5 mmol $L^{-1}$ of $CuSO_4$. Then the activation of the copper oxide nanoporous was performed by Cyclic Voltametry (CV) in 0.1 mol $L^{-1}$ NaOH for 50 cycles at 100 mV $s^{-1}$ in the potential range of - 0.5 V to + 0.4 V. The nanoporous showed rough structures that considerably increase the electroactive surface available for MIP formation. The copper oxides, in alkaline medium, was able to electrocatalyst the oxidation of carbohydrates by reducing highly oxidizing species such as $Cu^{3+}$. After that, to form the MIP on the modified surface, a PBS buffer solution (pH 7) containing $1.0\times10^{-4}$ mol $L^{-1}$ of arginine and $8.0\times10^{-5}$ mol $L^{-1}$ of xylobiose was electropolymerized using CV for 10 cycles at 100 mV $s^{-1}$ and in the potential range of -1.5 V to + 2.0 V. Poly-L-arginine showed conductive behavior on the modified electrode surface due to the guanidyl group on the side chain remains protonated, which facilitates the electron transfer reaction of the $Fe(CN)_6^{3-/4-}$ probe. After the electropolymerization process, the xylobiose was electrochemically removed from the MIP using a solution containing 0.25 mol $L^{-1}$ NaOH for 2 cycles at 50 mV $s^{-1}$, in the potential range of 0 V to + 1.2 V, obtaining the MIP/3DnpCu/GCE. The optimized conditions for the formation of this sensor were studied from the indirect determination of the xylobiose. For this, $5.0\times10^{-3}$ mol $L^{-1}$ $Fe(CN)_6^{3-/4-}$ in 0.1 mol $L^{-1}$ of KCl was used as a probe solution and the technique applied was Differential Pulse Voltammetry (DPV). This electrode was characterized by CV, Energy Dispersive X-ray Spectroscopy (EDS), Scanning Electron Microscopy (SEM) and Electrochemical Impedance spectroscopy (EIS). Under optimized conditions, the MIP/3DnpCu/GCE showed two linear working ranges: $1.0 \times 10^{-12}$ mol $L^{-1}$ to $1.0 \times 10^{-11}$ mol $L^{-1}$ and $1.0 \times 10^{-11}$ mol $L^{-1}$ to $2.0\times10^{-10}$ mol $L^{-1}$. The first linear range was used to obtain the figures of merit. The values found for limit of detection (LOD), limit of quantification (LOQ), and amperometric sensitivity (As) were $7.7\times10^{-13}$ mol $L^{-1}$, $2.6\times10^{-12}$ mol $L^{-1}$, and $1.4\times10^{12}$ µA L $mol^{-1}$ respectively. In order to study the selectivity of the sensor, the interferents that may be present in the real sample were tested: xylose, glucose, maltose, fructose, sucrose and arabinose. The MIP/3DnpCu/GCE was successfully applied towards the selective determination of xylobiose in biotransformed wastes from the banana industry, thus making it, in essence, a valuable tool for the accurate and reliable determination of this molecule.

## Acknowledgments

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**Área: ELE**

# Electrochemical sensor based on protic ionic liquid used in the determination of carbendazim in grape samples

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Keywords: *2-hydroxyethylammonium Acetate, Fungicide, Contaminate, Selective monitoring, Differential Pulse Voltammetry.*

## Highlights

Electrochemical sensor modified with protic ionic liquid showed greater sensitivity. The sensor developed was successfully applied for monitoring carbendazim in grape juice.

## Resumo/Abstract

The protic ionic liquids (PIL) is a class of ionic compounds with a melting point below 100 °C. The set of adjustable properties make some of the PIL interesting for application as an electrode modifier. The detection of electroactive species by means of modified electrodes is a highly viable and low-cost strategy, which can be used to monitor contaminants in the environment. In this work, a electrode modified with 2-hydroxyethylammonium acetate (2-HEAA), denominated of MCPE/2-HEAA, was developed for the detection of carbendazim (CBZ). The protic ionic liquid 2-HEAA was synthesized and characterized by spectroscopy FTIR, by Raman spectroscopy and NMR. CBZ detection was performed using the differential pulse voltammetry technique in Britton-Robinson (BR) buffer solution. The optimizations of the electrochemical parameters, using MCPE/2-HEAA, resulted in the following conditions of analysis: buffer BR pH 6.0, pre-concentration time of 450 seconds, scanning speed of 20 mV $s^{-1}$, time of 2.5 ms pulse and 60 mV pulse amplitude.

In these conditions, the analytical method was validated and the MCPE/2-HEAA electrode showed a dynamic linear range from 9.98 to 476.20 nmol $L^{-1}$ ($R^2$ = 0.9964) and limits of detection and quantification of 1.69 nmol $L^{-1}$ and 5.63 nmol $L^{-1}$, respectively. The proposed sensor was applied for the determination of CBZ in three grape samples (Figure 1). Recovery levels from 89.0 to 100.6% were found, Due to its ease of operation,si mple pretreatment, and good cost–benefit, the 2-hydroxyethylammonium acetate-based carbon paste electrode offers a new alternative to determining pesticide residues in food samples.

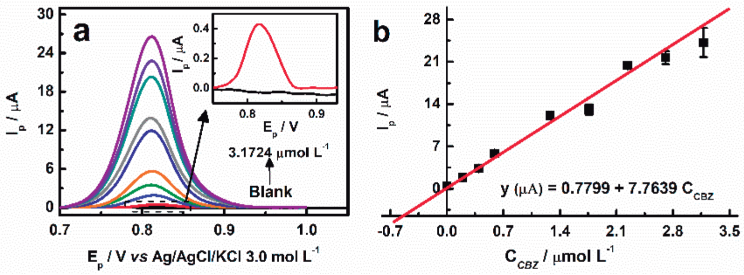

**Figure 1 -** VPD voltammograms for the determination of CBZ in a grape juice sample at concentrations of 0.198; 0.396; 0.593; 1.28; 1.76; 2.24; 2.71; 3.18 μmol L-1 under optimized conditions (A). CBZ standard addition curve (B).

## Agradecimentos/Acknowledgments

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**Área: ELE**

# Electrochemical sensor modified with reduced graphene oxide and ionic liquid for detection of ciprofloxacin in different samples

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Keywords: *Modified electrode, Graphene-derived, Ionic liquid, Emerging contaminant, Quinolone.*

## Highlights

- The novel sensor modified with reduced graphene oxide and ionic liquid showed high sensitivity for detection of ciprofloxacin;
- The method presented LOD = 4.21 nmol $L^{-1}$ and LOQ = 12.80 nmol $L^{-1}$.

## Resumo/Abstract

The intense use of ciprofloxacin (CPX) for the treatment of human and animal infections has been responsible for produce residues of this drug in aquatic environments and effluents, which classifies this substance as an emerging contaminant. In this work, a modified electrode (E/rGO-BIA) with reduced graphene oxide (rGO) and ionic liquid 1-butyl-3-methylimidazolium acetate (BIA) was developed and used for determination of ciprofloxacin (CPX). rGO and BIA were characterized by Transmission electron microscopy (TEM), infrared spectroscopy (FTIR) and Raman spectroscopy. E/rGO-BIA electrode exhibited greater sensitivity than the unmodified electrode in the detection of CPX. Under the optimized electrochemical conditions (Figure 1), the modified electrode showed a linear dynamic response (LDR) in the range from 6.99 nmol $l^{-1}$ to 6.95 $\mu$mol $l^{-1}$ ($R^2$ = 0.998), limit of detection of 4.21 nmol $l^{-1}$ and limit of quantification of 12.80 nmol $l^{-1}$. The proposed method also showed excellent repeatability (1.12%) and reproducibility (5.96%). In addition, E/rGO-BIA was successfully applied in detecting CPX in pharmaceutical, wastewater and synthetic urine samples presenting a good linearity and a recovery range from 96.1 to 112.1%. Thus, the proposed method proved to be efficient and suitable for detection of ciprofloxacin.

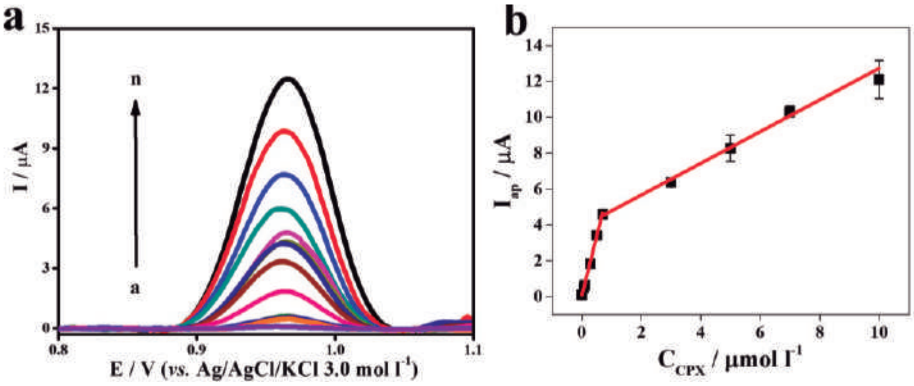

**Figure 1 a)** AdDPSV voltammograms (baseline corrected) obtained using E/rGO-BIA in the presence of different concentrations of CPX under optimized conditions. **b)** Variation of $I_{ap}$ as a function of CPX concentration.

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**Área: ELE**

# Electrodeposited bifunctional $MoS_x$/Ni-P electrocatalyst for overall water splitting

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*Keywords: Nickel phosphide, Molybdenum sulfide, Electrodeposition, Water splitting*

## Highlights

Deposition of a layer of $MoS_x$ enhances the $NiP_x$ electrode performance for overall water splitting. The best performance for HER and OER was obtained by loading a thinner layer of $MoS_x$.

## Abstract

Electrochemical water splitting is an efficient and environmental-friendly technique to produce highly pure hydrogen. The electrocatalysts performance is a critical issue for efficient electrochemical water splitting into industrial scale. Developing robust, low-cost, and active catalysts for both hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) is crucial to achieving cost-effectiveness. Recently, nickel-based phosphide (Ni-P) has been regarded as a potential alternative for replacing noble metal-based electrocatalysts for water splitting, owing to their excellent electronic properties and corrosion resistance [1]. Meanwhile, the deposition of molybdenum sulfide ($MoS_x$) has shown to be an interesting strategy for tailoring transition metal-based bifunctional catalysts properties [2]. The present work reports the development of $MoS_x$/Ni-P electrodes for overall water splitting in alkaline media. The $MoS_x$/Ni-P electrodes were prepared by electrodeposition of the Ni-P film on the substrate followed by the deposition of $MoS_x$. The $NiP_x$ films were prepared by galvanostatic deposition using Ni foam as substrate with a deposition bath containing $NaH_2PO_2$, $NH_4Cl$, and $NiCl_2$ with molar ratios of (3:1.5;1). The $MoS_x$ deposition was based on the methodology reported by Medina et al [3]. The effect of the $MoS_x$ deposition time on the HER and OER performance was tested in KOH 1.0 M electrolyte in a typical three-electrode system. Figure 1 shows the polarization curves of the bare and $MoS_x$-modified Ni-P electrodes for HER and OER. The electrode prepared with the lowest deposition time presented the best performance for overall water splitting. For the HER performance, the bare Ni-P and $MoS_x$/Ni-P-6 electrodes exhibited similar overpotential at -100 mA $cm^{-2}$ (204 mV and 195 mV, respectively). However, from the polarization curves in Figure 1 is observed that the $MoS_x$ presence is most relevant for overpotentials obtained at higher current densities (> -100 mA $cm^{-2}$). In contrast to OER performance, the $MoS_x$ deposition significantly lowered the overpotential even at 50 mA $cm^{-2}$. In addition, the $MoS_x$ modification facilitated the bubble detachment on the electrode surface indicating improvement of the hydrophilicity of the Ni-P film. In summary, the deposition of $MoS_x$ improved the performance of Ni-P films for both reactions. The $MoS_x$/Ni-P overpotentials are better than other reported nickel phosphides catalysts in the literature, showing promising performance for application in overall water splitting.

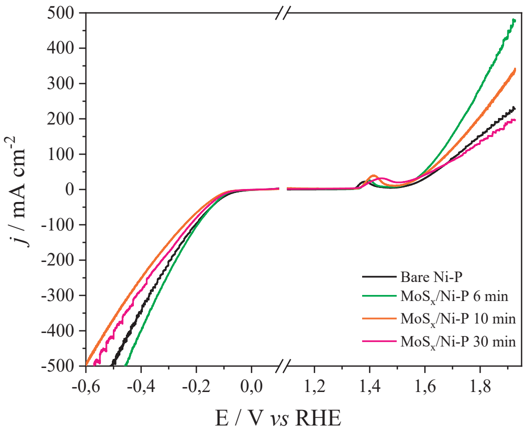

**Figure 1***:* Polarization curves registered in 1.0 M KOH at 1 mVs-1 for the Bare and $MoS_x$-modified Ni-P films for HER and OER.

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**Área: ELE**

# Enhanced electrochemical oxidation of ethanol using a hybrid catalyst cascade architecture containing pyrene-TEMPO, oxalate decarboxylase and carboxylated multi-walled carbon nanotube

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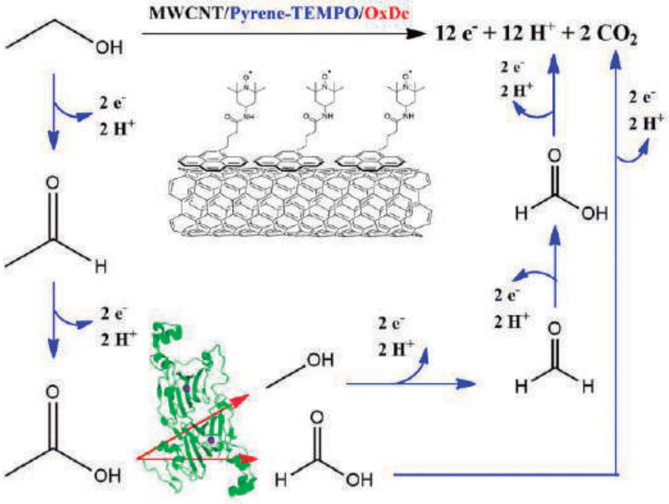
Palavras Chave: *Ethanol, Organic Catalyst, Oxalate Decarboxylase, Enzymatic Biofuel Cell.*

## Highlights

The bi-catalytic electrode showed excellent electrocatalytic performance
The multi-catalytic electrode achieved the complete ethanol oxidation
The new biofuel cell can be applied as a promising energy management system

## Resumo/Abstract

In this work, we report a new design of a biofuel cell (BFC) in order to improve the stability and catalytic activity of the hybrid system by combining the advantages of the enzyme, oxalate decarboxylase (OxDc), with a recently developed organic catalyst, Pyrene-TEMPO (TEMPO = 2,2,6,6-tetramethylpiperidinyl-N-oxyl) immobilized on the surface of carboxylated multi-walled carbon nanotubes (MWCNT-COOH) via hybrid system for the complete electrochemical oxidation of ethanol. Long-term bulk electrolysis was performed in order to achieve the complete electrochemical oxidation of ethanol. The products of ethanol oxidation were characterized and confirmed by nuclear magnetic resonance (NMR) and gas chromatography with a thermal conductivity detector (GC-TCD). Electrolysis revealed a stable amperometric curve and an excellent current density value over a duration of 10 hours. In addition, the hybrid system immobilized on carbon electrode exhibits outstanding stability after electrolysis. Nuclear magnetic resonance (NMR) and gas chromatography (GC) demonstrate that the hybrid electrode system is able to oxidize ethanol to $CO_2$ after 10 h of electrolysis. Our previous findings for ethanol oxidation using a bi-catalytic system corroborate with the proposed scheme (Scheme 1). By comparing the data obtained by NMR and GC-TCD for all the systems, we confirm the identity of each substrate in the reaction cascade demonstrating the need for the bifunctional organic/enzyme the hybrid bioelectrode to harvest all $12e^-$ electrons from the fuel. Overall, this study illustrates the enhancement of an enzymatic biofuel cell through the hybrid multi-catalytic systems, which exhibit high oxidation rates for all substrates involved in complete ethanol oxidation, enabling the collection of up to 12 electrons per molecule of ethanol.



**Scheme 1.** Electrocatalytic cascade for ethanol oxidation at the MWCNT-COOH/Pyrene-TEMPO/OxDc catalytic system. The blue line represents the oxidation mediated by Pyrene-TEMPO, while red line representd the action of OxDc enzyme, which catalyze the decarboxylation of acetic acid by cleavage the carbon- carbon bond.

## Agradecimentos/Acknowledgments

The authors are grateful for the financial support from Brazilian research funding agencies FAPESP (2017/20431-7) and (2018/24180-1). Coordenação de Aperfeiçoamento de Pessoal de Nível Superior Brasil (CAPES) Finance Code 001, as well as the Army Research Office MURI (W911NF-14-1-0263).

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

# Enhancement of performance for iron oxide-modified carbon cathode for norfloxacin degradation in heterogeneous electro-Fenton systems

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Palavras Chave: *heterogeneous electro-Fenton; wastewater treatment; advanced electrochemical oxidation process, hydrogen peroxide*

## Highlights

Heterogeneous electro-Fenton with a novel modified carbon felt with carbon printex L6 and iron oxides shows superior performance for norfloxacin degradation and mineralization in neutral environment

## Resumo/Abstract

Antibiotics pollution in the aqueous environment constitutes a serious threat to human health and aquatic ecosystems. Besides toxicity, the presence of antibiotics is also related to the development of antibiotic-resistant bacteria [1]. Thus, advanced electrochemical oxidation processes (EAOP) appears as technologies of great interest for removal of recalcitrant organics, including antibiotics [2]. Among EAOP, those based on Fenton reaction stands out by its high effectiveness due to the great production of hydroxyl radicals (·OH), a strong oxidant, generated by catalytic reaction of dissolved $Fe^{2+}$ and $H_2O_2$ at acid environment. However, need of acid pH and production of iron sludge is still a great challenge of classical electro-Fenton. Thus, the development of environmental-friendly iron-based materials for application as cathodes in heterogeneous electro-Fenton (HEF) systems is a promising strategy to overcome main drawbacks of homogeneous EF process due to its efficiency in a wide pH range, catalyst reusability and no sludge formation. In this work, two iron-based cathode materials were prepared by using two different approaches: 1) deposition of iron oxides over a previously modified carbon felt with Printex L6 Carbon (PL6C)-PTFE and 2) incorporation of iron oxides with PL6C-PTFE on an unmodified carbon felt. All materials prepared were thermally treated at 360 °C. Then, the electrodes were employed as cathodes in HEF system to evaluate the electrocatalyic activity for norfloxacin (NOR) antibiotic removal during 90 min in 0.05 mol $L^{-1}$ $K_2O_4$. Moreover, the catalytic mechanism involved in HEF with produced electrodes was investigated by means of quenching experiments. Among iron-based cathodes, higher removals efficiencies for NOR degradation were observed for the iron-incorporated electrodes in HEF process, leading to a complete removal of NOR in 30 min and attaining 40 % mineralization in 90 min, at neutral pH. These findings demonstrate that iron supported with CPL6 and PTFE in carbon felt led to a faster removal and mineralization of NOR. Finally, the developed iron oxide-based cathodes of low cost and simple to prepare constitutes good alternative electrodes, and shows the promising prospect of HEF process as a water treatment technology for the degradation of pharmaceuticals, including antibiotics.

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## Agradecimentos/Acknowledgments

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**Área: ELE** **Nº de Inscrição: 01258**

# Estudo comparativo do processo de eletrodeposição de Fe-Co a partir de banhos de eletrodeposição à base de citrato e EDTA

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*Palavras Chave: Liga de Fe-Co, Eletrodeposição, Voltametria.*

## Highlights

Comparative study of the Fe-Co electrodeposition process from citrate and EDTA electrodeposition baths.
Voltammetric study of Fe-Co electrodeposition revealed a cathodic process (-0,95 a -1,10 V) and the use of citrate as a complexant was beneficial.

## Resumo/Abstract

O interesse pela eletrodeposição de ligas de ferro e cobalto têm aumentado consideravelmente nos últimos anos, principalmente devido às diversas propriedades físicas e químicas relacionadas a essas ligas. Ligas de Fe-Co exibem boa resistência à corrosão, boas propriedades mecânicas e magnéticas. O objetivo do presente trabalho foi realizar um estudo comparativo do processo voltamétrico de deposição de Fe-Co a partir de banhos contendo citrato e ácido etilenodiamino tetra-acético (EDTA) como agentes complexantes para os íons metálicos em solução. Para os estudos voltamétricos foram utilizados uma célula eletroquímica do tipo metrohm para três eletrodos, eletrodo de carbono vítreo como eletrodo de trabalho (ET), Ag/AgCl 3,0 mol/L como eletrodo de referência e uma espiral de platina como eletrodo auxiliar. Para o voltamograma cíclico do substrato de carbono vítreo para o sistema Fe-Co/citrato (pH 4,0) observou-se um processo catódico c (-0,95 a -1,10 V) e processos anódicos ax (-0,70 a + 0,05 V). O processo catódico c está relacionado com a codeposição de Fe-Co, visto que o voltamograma da solução “branco” não apresentou processos catódicos e os voltamogramas dos metais individuais Fe-citrato e Co-citrato apresentaram um processo catódico entre 1,00 a 1,10V e 1,10 a 1,25V respectivamente. Para o sistema Fe-Co/EDTA, o voltamograma do ET na solução de trabalho não apresentou picos de deposição, mostrando um significativo aumento na densidade de corrente a partir de -1,10 V siando de 0,5 mA cm-2 para 16 mA cm-2. Comportamento semelhante é observado para os metais individuais, sistemas Fe-EDTA e Co-EDTA, entretanto, por inspeção visual, foi verificado eletrodepósito na superfície do eletrodo (a partir de -1,00 V) para ambos os sistemas e para Fe-Co/EDTA. Os resultados mostram que há uma diferença significativa no processo de eletrodeposição de Fe-Co quando comparados os complexantes utilizados, com variações nos voltamogramas cíclicos. Ademais é possível verificar que para o sistema Fe-Co/citrato a utilização do complexante foi benéfica deslocando o potencial de deposição da liga para valores mais positivos quando comparado aos metais individuais.

## Agradecimentos/Acknowledgments

Universidade Estadual Vale do Acaraú (UVA)

**Área: ELE** **Nº de Inscrição: 00817**

# Estudo voltamétrico do processo de eletrodeposição de Ni-Mo a partir de um banho não cianetado

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*Palavras Chave: Liga de Ni-Mo, Eletrodeposição, Voltametria.*

## Highlights

Voltammetric study of the Ni-Mo electrodeposition process from a non-cyanide bath
Voltammetric study of Ni-Mo electrodeposition revealed a cathodic process (-0,80 a -0,92 V) and the use of EDTA as a complexant was beneficial.

## Resumo/Abstract

Electrodeposition is a very used method for obtaining metallic coatings resistant to corrosion. It promotes the ion reduction reaction, present in solutions, in its metallic species, which is deposited in an electrode. Metallic alloys are materials with metallic properties that contain two or more chemical elements, at least one of them is metal. Ni-Mo alloys are widely studied and used due to the properties that are conferred to them, mainly owing to molybdenum: high resistance to corrosion, low thermal expansion coefficient and high resistance against mechanical shocks. The objective of this work was to study voltammetrically the Ni-Mo electrodeposition process using 1,2-diaminoethane (EDTA) as a complexing agent. For voltammetric studies, a meter-type electrochemical cell was used for three electrodes, glassy carbon electrode as working electrode (ET), Ag / AgCl 3.0 mol /L as electrode reference and a platinum spiral as an auxiliary electrode. In the cyclic voltamogram of the carbon substrate glassy bath containing deposition salts, a cathodic process *c* (-0.80 to -0.92 V) and anodic $a_x$ (0.60 to + 1.00 V) (Figure 1). The cathodic process c is related to the Ni-Mo codeposition, since the voltammogram of the "white" solution did not present cathodic processes. The voltammogram of ET in the Ni-EDTA presented a cathodic process in the region *c* (1.00 to 1.20V) (Figure 1) and for the Mo-EDTA solution, no reduction processes, since the deposition of Mo occurs by induction from other metals. Can be checked that the use of EDTA as a complexant was beneficial since the deposition potential for Ni-Mo was more positive when compared to Ni-EDTA deposition. The disposition bath used in the electrodeposition of Ni-Mo is proved adequate, allowing the objectives of the present work to be achieved.

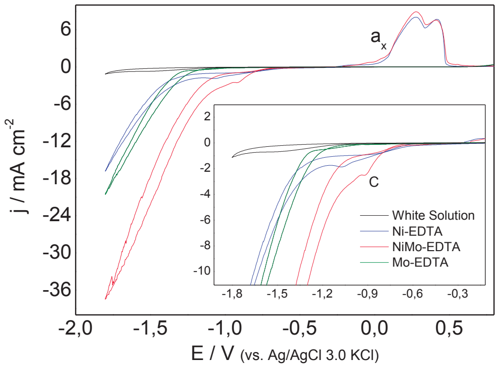

*Figure 1: voltammetric studies of the carbon substrate. 10 mV s$^{-1}$, pH 4,0.*

## Agradecimentos/Acknowledgments

Universidade Estadual Vale do Acaraú (UEVA),
Instituto Federal de Educação, Ciência e Tecnologia do Ceará- Campos Sobral

**Área: ELE** **Nº de Inscrição: 590**

# Evaluation of complex formation between 5-nitrothiophene-thiosemibazonic derivatives with β-cyclodextrin free and chemically linked to the glassy carbon electrode.

**Renata Costa dos Santos (PG),[1*] Fabricia da Rocha Ferreira (PQ)[1], Thiago Mendonça de Aquino (PQ)[1], Fabiane Caxico de Abreu (PQ).[1]**

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Key word: *Nitrocompounds*, *Cyclodextrin*, Electrochemical.

## Highlights

Construction of glassy carbon-amino-β-cyclodextrin platform via electrochemistry.
Interaction of 5-nitrothiophene-thiosemibazonic derivatives with β-cyclodextrin free and chemically linked to glassy carbon (GC).

## Resumo/Abstract

In the planning and development of new therapeutic agents, the nitroheterocyclic compounds are of great importance, enabling the introduction of various substituent radicals, which gives the compounds different activities and properties, both chemical and biological. Its bioreduction mechanism can be reproduced in electroanalytical system and identified via electrochemical methods. A characteristic common to many nitrocompounds (such as those under study) is the low solubility in water, which justifies its association with versatile substances such as cyclodextrin, which can form inclusion complexes with a variety of molecules[1]. In the present study, an amino β-cyclodextrin graft was performed on glassy carbon electrodes, through the amine electrooxidation, without the need for additional ligands or intermediates[2]; then, the formation of inclusion complexes between 5-nitrothiophene-thiosemibazonic derivatives (LNN) and β-cyclodextrin was evaluated using Differential Pulse Voltammetry (DPV). The electrochemical system was composed of 3 electrodes, Ag / AgCl / $Cl^-$ saturated (reference), platinum (auxiliary), glassy carbon (GC) with immobilized β-cyclodextrin amino (work), in buffered medium pH 7.00 with ethanol as co-solvent. UV-Vis studies were also carried out in an aqueous medium containing 5% –ethanol, varying the concentration of β-Cyclodextrin. The GC-amino-β-cyclodextrin platform made it possible to analyze the interaction of 5-nitrothiophene-thiosemibazonic derivatives with β-CD, which was identified by linearly increasing the peak current of the analyte as a function of the increase in the concentration of the same until the saturation point between the substances and the β-CD immobilized on the electrode surface and it was possible to calculate the formation constant between the studied derivatives and the cyclodextrin with values of the $5.87x10^4$ for LNN01, $2.199x10^5$ for LNN03 and $7.61x10^5$ for LNN05. By spectrophotometric methods, the calculated average constants were $2.107x10^5$ for LNN01, $2.174x10^6$ for LNN03 and $2.223x10^5$. Both constants demonstrate good formation of the complexes among the LNN: β-CD.

Cyclodextrin is already considered a pharmaceutical excipient, used in drugs, so its good results via electrochemistry with the studied derivatives are quite hopeful in a future association and development of a drug.

## Agradecimentos/Acknowledgments

CNPq, UFAL e LEMAN

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**Área: ELE**

# Evaluation of voltammetric and degradation behavior of Reactive Black 5 (RB-5) azo-dye in synthetic effluent using different electrodes

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*Keywords: Wastewater, Dye, RB-5, Electro-oxidation, DSA, Voltammetry.*

## Highlights

Reactive Black 5 is a hazardous azo-dye. Two electrochemical proceedings were performed using a Dimensionally Stable Anode and a Glassy Carbon Electrode. The experimental results were satisfactory.

## Resumo/Abstract

The environmental degradation promoted by industrial activities has become a great problem for modern societies. The highly persistent dyes and pigments, such as the reactive black dye 5 (RB5), are species largely used in industries that are difficultly degraded or removed by traditional treatments. For these reasons, technologies based on electrochemical methods have been developed with the aim of promoting the treatment of effluents contaminated by toxic substances[1]. In order to understand the behavior of these species in the aqueous medium, studies were carried out by cyclic voltammetry measurements (applying glassy carbon electrode (GCE)) and by indirect electro-oxidation (applying dimensionally stable anode (DSA)) to evaluate the electrochemical behavior of the RB-5 dye[2]. In this context, we carried out the indirect electro-oxidation with active mediators (*e.g.,* HClO, $ClO^-$ or $Cl_2$), electro-generated *in situ* by a DSA ($Ti/Ir_{0.3}Sn_{0.7}O_2$ in chloride-containing medium) towards the degradation of the RB-5 azo-dye. UV-Vis spectra scans were performed to follow the complete degradation of the chromosphere portion of the dye, up to 900 s. The decolorization index (ID) was 99.02%. The reaction kinetics were controlled by a pseudo-first-order process, and its rate constant was 0.0078 $s^{-1}$. On the other hand, electrochemical investigations using GCE indicated three irreversible oxidation processes, evidenced by the voltammetric peaks located at +0.485 V, +0.731 V, and +0.899 V *vs*. Ag/AgCl, associated with an irreversible reduction process at -0.075 V. Moreover, the studies of the variation of the scan rate showed that the anodic peak current increases as the scan rate increases, while the potential undergoes a positive displacement due to the referred increase. These characteristics suggest an irreversible behavior governed by diffusion-controlled processes[3]. From these results, it was possible to verify that the method of indirect electro-oxidation was feasible, kinetically fast, and highly efficient for the degradation of azo-dye molecules, and the cyclic voltammetric studies were essential to improve the understanding of the electrochemical nature of the evaluated dye.

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## Agradecimentos/Acknowledgments

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**Área: ELE**

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# Experimental and theoretical evaluation of green-synthetized benzylidene derivatives as corrosion inhibitor for mild steel in acid media

**Caio Machado Fernandes (PG),[1*] Lucas G. Pereira (IC),[1] Leonardo X. Álvarez (PQ),[2] Adriana M. Barrios (PQ),[1] Hassane Lgaz (PQ),[3] Han-Seung Lee (PQ),[3] Eduardo A. Ponzio (PQ).[3]**

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Palavras Chave: Green chemistry; Corrosion inhibitor; Electrochemistry; Surface analyses; DFTB; Molecular dynamics.

## Highlights

Green synthesis of two benzylidenes derivatives.

Maximum anticorrosive efficiency of 92 and 82% at 2.20 mmol $L^{-1}$.

Experimental studies, surface analyses and theoretical calculations.

## Resumo/Abstract

Corrosion is a serious problem that directly affects metal structures and the industrial sector, causing billions of dollars in losses. The use of organic corrosion inhibitors directly in the aggressive media has been a useful way of mitigating this problem. They have structural elements (n and π-electrons) that allow the interaction with the alloy, forming a protective film. With that in mind, two benzylidene derivatives (CMBG and DBHP) were prepared according to the principles of Green Chemistry. They were evaluated as corrosion inhibitors for mild steel in acid media (HCl 1 mol $L^{-1}$) via gravimetric and electrochemical measurements (electrochemical frequency modulation, electrochemical impedance spectroscopy, linear polarization resistance and Potentiodynamic polarization). The average maximum anticorrosive efficiency reached was 82.5 and 90.6%, respectively, at 2.20 mmol $L^{-1}$. Physicochemical calculations showed that the adsorption process has a greater physical character and obeyed the theories of Halsey (CMBG) and Freundlich (DBHP), both multilayers. Atomic Force Microscopy and Scanning Electron Microscopy with Energy Dispersive X-Ray Analysis suggested the formation of a protective layer. Theoretical calculations (Density-Functional Based Tight Binding and Molecular Dynamics) corroborated and helped to understand the experimental results.

(*E*)-2-cyano-1-((*E*)-4-methoxybenzylidene)guanidine

CMBG

(*E*)-2-((4-(dimethylamino)benzylidene)amino)-2-(hydroxymethyl)propane-1,3-diol

DBHP

Figure 1: Chemical structure of the proposed substances.

## Agradecimentos/Acknowledgments

The authors thank Conselho Nacional de Pesquisa e Desenvolvimento (CNPq) for the scholarship received and Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) and Fundação de Amparo à Pesquisa do Estado do Rio de Janeiro for all the financial support.

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

# Fast and efficient electrochemical thinning of ultra-large supported and free-standing $MoS_2$ layers on gold surfaces

**Nicolli de Freitas (IC)[1], Bianca R. Florindo (IC) [1], Vitória M. S. Freitas (IC) [1], Maria H. O. Piazzetta (TC) [1], Carlos A. O. Ramirez (PQ) [1], Jefferson Bettini (PQ) [1], Mathias Strauss (PQ) [1], Edson R. Leite (PQ) [1], Angelo L. Gobbi (PQ) [1], Renato S. Lima (PQ)[1,2], Murilo Santhiago (PQ)[1,2 *]**

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Palavras Chave: *2D materials, $MoS_2$, microfabrication, monolayer, electrochemical thinning.*

## Highlights

Ultra-large $MoS_2$ layers were obtained by electrochemical thinning.

Electrochemical thinning starts at the edge of bulk crystals.

Suspended monolayers were formed on Au micromeshes.

## Resumo/Abstract

Molybdenum disulfide ($MoS_2$) is a very promising layered material for electrical, optical, and electrochemical applications because of its unique and outstanding properties. To unlock its full potential, among different preparation routes, electrochemistry has gain interest due to their simple, fast, scalable and simple instrumentation. However, obtaining large-area monolayer $MoS_2$ that will enable the fabrication of novel electronic and electrochemical devices is still challenging. In this work, we reported a simple and fast electrochemical thinning process that results in ultra-large $MoS_2$ down to monolayer on Au surfaces. The high affinity of $MoS_2$ by Au surfaces enables the removal of bulk layers while preserving the first layer attached to the electrode. With a proper choice of the applied potential, more than 90% of the bulk regions can be removed from large-area $MoS_2$ crystals, as confirmed by atomic force microscopy, photoluminescence, and Raman spectroscopy. We further address a set of contributions that are helpful to elucidate the features of $MoS_2$, namely, the hyphenation of electrochemistry and optical microscopy for real-time observation of the thinning process that was revealed to occur from the edges to the center of the flake, an image treatment to estimate the thinning area and thinning rate, and the preparation of free-standing $MoS_2$ layers by electrochemically thinning bulk flakes on microhole-structured Ni/Au.

## Agradecimentos/Acknowledgments

This work was supported by the Serrapilheira Institute (grant number: Serra-1912-31228). We thank Mariane P. Pereira, Davi H. Camargo, Fabiano Montoro, Carolina. P. Torres, Carlos A. R. Costa, and Cleyton A. Biffe for their help in this work with instrumentation and laboratory facilities. We also thank SisNano for the support.

**Área: ELE**

# FREE RADICAL FORMATION EVIDENCE FROM NIMORAZOLE ELECTROCHEMICAL REDUCTION IN AQUEOUS MEDIA

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Palavras Chave: *nimorazole, eletrochemical reduction, cyclic voltammetry, nitro-anion radical.*

## Highlights

A simple, fast and 100% aqueous media method to study behavior of nimorazole (NMZ) was evaluted by cyclic voltammetry. This study aims to generate the nitro radical anions and detection by cyclic voltammetry in alkaline medium and is compared by digital simulations.

## Resumo/Abstract

Nimorazole (NMZ) belongs to the group of nitroimidazoles and as a chemotherapeutic agent, has a broad spectrum of biological activities, such as antiprotozoal[1] and anticancer[2]. The proposed mechanism of action predicts the formation and stabilization of nitro-anion radical (R-$NO_2^{\bullet -}$). Cyclic voltammetry was applied in aqueous media to study NMZ reduction, a pH-dependent process[3]. All voltammograms were recorded by using an electrochemical cell with three electrodes: Ag/AgCl, Pt, and glassy carbon electrode as the working electrode. In alkaline media (pH > 8), the NMZ reduction occurred in two steps, the first one being associated with the nitro-anion radical formation in a one-electron reversible process. The reversibility of the NMZ voltammetric response was evaluated by comparing it with the model proposed by voltammetric simulation using the Digisim software. Voltammograms in Figure 1A correspond to the electron-transfer process involving the R-$NO_2$/R-$NO_2^{\bullet -}$ couple at pH 10.02, and the experimental results are in close agreement with the simulated ones over the 80 to 500 mV $s^{-1}$ scan rate range. Under aerobic conditions, the nitro-anion radical can react with molecular oxygen and produce the superoxide $O_2^{\bullet -}$, which is biologically active. From voltammograms in Figure 1B (black and red lines), one can clearly see the cathodic peak associated with the R-$NO_2^{\bullet -}$ in which oxidation is absent. These results confirmed that the nitro-anion radical was only stable in anaerobic conditions and also underwent a chemical decomposition in the presence of dissolved oxygen. The current ratio (Ipa/Ipc) was used to evaluate the radical kinetic stability, as the electrogenerated nitro-anion radical underwent a second-order disproportionation chemical reaction. The rate constant of this reaction, $k_2$, was determined in 0.1 mM and 0.5 mM NMZ solutions, and the values were found to be 29987 and 7621 L/mol s, respectively, and the half-life times, $t_{1/2}$, 0.33 and 0.26 seconds, respectively.

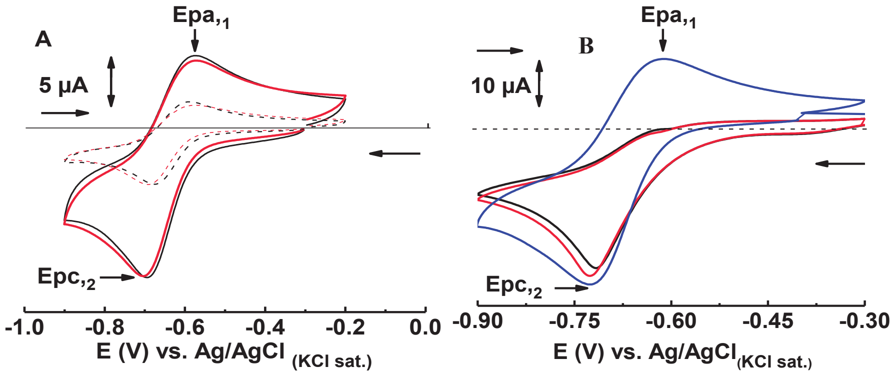

**Figure 1. (A)** Simulated and experimental cyclic voltammograms recorded at 80 (dashed lines) and 500 mV $s^{-1}$ (continuous lines), **(B)** Cyclic voltammograms recorded in NMZ solution in the absence (**blue**) and presence of molecular oxygen after gas bubbling (1 mL/min) for 5 min (**black**) and 10 min (**red**). pH = 10.02, [NMZ]= 0.5 mM, $\nu = 0.1$ V $s^{-1}$.

[1]Dunn, L.A.et al.; Int. J. Antimicrob. Agents 36, 37-42, 2010; [2]Knon, Y.P.et al.; Bioorg. Med. Chem. 133, 2021; [3] Brito, C.L. et al., Electrochim. Acta, 403, 2022.

**Área: ELE**

# Glycerol photo-electrooxidation on a CdS photoanode: efficiency enhancement and photocorrosion inhibition

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Palavras Chave:*CdS Photoanode, CdS Photocorrosion, Glycerol Photo-electrooxidation.*

## Highlights

Fresh new CdS synthesis using a microwave;

CdS thin film photoanode for glycerol photo-electrooxidation;

The role of glycerol as a photocorrosion inhibitor in a neutral pH.

## Resumo/Abstract

The rapid growth in energy demand leads us as a society to pursue new ways to obtain energy in a greener and more sustainable way. Cadmium Sulfide is the most known chalcogenide used for the water splitting, with a bandgap of 2,4 eV which suits very well with the solar spectrum.[1] However, there are two main questions concerning the water oxidation reaction (WOR) on CdS photoanodes. Firstly, the use of water as an electron donor on the anodic compartment is not something that must be encouraged, once oxygen evolution reaction (OER) has high overpotentials and sluggish kinetics. Secondly, depending on the pH and potential range of the system, photocorrosion could play an important role as it may destroy the thin CdS film deposited compromising the oxidation reaction onto the photoanode.[2] Fortunately, organic molecules oxidation reaction could be an alternative anodic reaction once it has higher power density, renewability and lower costs, which could be used to solve the first main issue approached.[3] As for the second question, glycerol could also play an outstanding role, since it could also hinder the photocorrosion effect. In this work we focused in the glycerol oxidation reaction (GOR) using a CdS photoanode under visible light irradiation. The CdS synthesis was carried out adopting a fast fresh new microwave synthesis which consists of using cadmium sulfate and thiourea as precursors to deposit CdS in a FTO substrate. The as prepared thin films were characterized by DRX, Raman Spectroscopy, Uv-Vis Spectroscopy and SEM cross-section. For the photoelectrochemical measurements a 3 electrode cell containing a quartz window were employed with a FTO/CdS photoanode, a Ag/AgCl/KCl$_{(sat)}$ and Platinum plate as WE, RE and CE, measurements were carried in a 6,5 pH $Na_2SO_4$ 0.5 mol $L^{-1}$ solution with addition of 1.0 mol $L^{-1}$ glycerol under 100 mW $cm^{-2}$ solar simulator irradiation. Cyclic and linear sweep voltammetrys were performed and when glycerol is added to the solution under irradiation the results show an increment in the photocurrents obtained of up to 8 times the value observed without glycerol addition at 0,6 V vs ERH. Also, chronoamperometric measurements show that at 0,6 V vs ERH the photocurrents in the first 30 minutes for GOR decrease to 15% of its max initial value while for WOR the photocurrents density decreases to 3,3 %, showing that GOR are more stable and reach higher values than that observed for WOR, indicating that glycerol could act as an inhibitor of photocorrosion at 6,5 pH and 0,6 V vs ERH. SEM cross-sections of the CdS thin films were taken before and after the chronoamperometric measurements, the results show that for WOR the films are almost completely photocorroded, while for GOR the films suffer much less from photocorrosion. In short, the findings corroborate to the fact that GOR is a great alternative to WOR and that glycerol may play an interesting role to diminish CdS thin films photocorrosion.

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## Agradecimentos/Acknowledgments

The authors thank to FAPESP (2013/07296-2) and CNPq (430426/2018) for financial support. C.H. thanks to CAPES for scholarships.

**Área: ELE**

# How plasmonic materials could boost the production of fuels through $CO_2$ reduction?

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Key-words: *$CO_2$, Electrocatalysis, Electroreduction, Ethanol, Ethylene, Plasmonics*

## Highlights

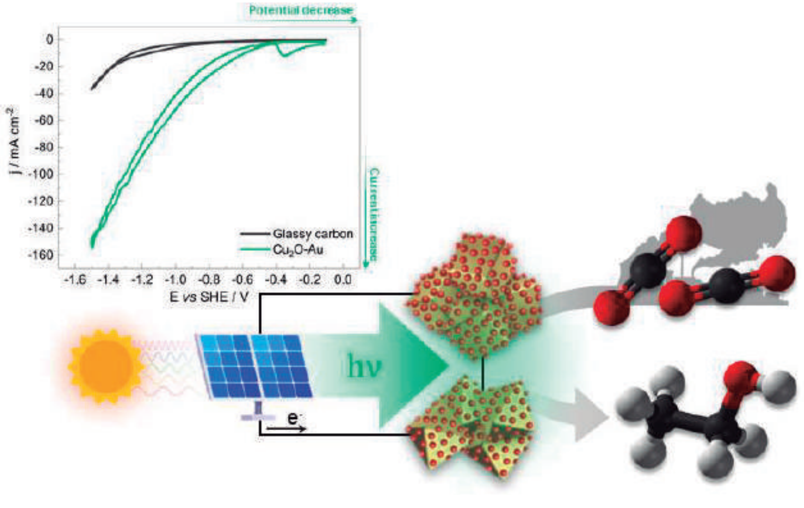
- The $CO_2$ reduction to higher value-added chemicals is a way to simultaneously reduce $CO_2$'s impact in the environment while producing fuels and industrial inputs.

- The employment of a plasmon-assisted $Cu_2O$-Au electrocatalyst could enable C-C coupling at lower overpotentials and minimize competing reactions.

## Abstract

Allied to the growing global energy demand, the increase in the global average temperature, mainly attributed to the high $CO_2$ emissions from the burning of fossil fuels, brought impacting consequences to the planet. In order to alleviate both issues simultaneously and boost the use of sustainable means of obtaining energy, it is proposed the electrochemical reduction of $CO_2$ to higher value-added chemicals, such as ethylene and ethanol. This reaction still present knowledge gaps that prevent its application on a large scale, mainly its low yield and selectivity for the synthesis of $C_2$ compounds, with the hydrogen evolution reaction being the major competing reaction.

In recent decades, the plasmonics branch has emerged as a possible solution to macroscopic barriers. The possibility of manipulating the light stimulus in matter on a nanometric scale allowed the discovery of new reaction pathways that are not possible in purely electrochemical conditions or in non-nanostructured electrocatalysts, in addition to enabling more precise control of selectivity. The various possible enhancements for plasmon-assisted $CO_2$ reduction, and the lack of detailed studies in the literature, make this study very promising. This project aims to unite the well-known localized surface plasmonic resonance of Au nanospheres with the selectivity towards $C_2$ compounds of Cu-derived materials, synthesizing $Cu_2O$-Au nanoparticles of different facets. The application of this electrocatalyst is herein targeted at a detailed study in favoring the C-C coupling over competing reactions, and therefore enhancing $C_2$ faradaic efficiencies. Preliminary experiments utilizing visible radiation (532 nm) exhibit greater current and lower overpotentials when compared to bulk glassy carbon electrodes (see graphical abstract below).



## Acknowledgments

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2021/08007-0

**Área: ELE**

# Hydrogen peroxide production from light-assisted oxygen reduction reaction using a photoactive Gas-Diffusion Electrode under air flow

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Keywords: *Water Remediation, Heterogeneous Photocatalysis, Gas Diffusion Electrode, Oxygen Reduction Reaction, Antibiotics Removal.*

## Highlights

A photoactive gas diffusion electrode *in situ* produced $H_2O_2$ from $O_2$ reduction reaction. Associated with a photoanode and a solar cell, this water remediation system removed antibiotics from aqueous solutions.

## Resumo/Abstract

Technologies for wastewater treatment based in semiconductor photocatalysis have been widely studied from several years.[1] In this work we are investigating the in-situ production of $H_2O_2$ from photo-assisted oxygen reduction reaction (ORR) using gas diffusion electrodes (GDE) prepared with graphite and the multiphasic Ag/$AgBiW_2O_8$/$Bi_2WO_6$ (Ag/ABW/BW) as photocatalyst. The Ag/ABW/BW particles were synthesized by hydrothermal method and present very interesting properties due to the association of Ag nanoparticles with the ABW/BW p-n junction.[2] Also, as shown in Fig. 1a, electrodes of Ag/ABW/BW behave as p-type semiconductor and exhibit electrochemical activity for ORR that was intensified by irradiation, as demonstrated considering the voltammogram (20 mV $s^{-1}$) obtained using rotating disc electrodes at 100 rad $s^{-1}$ with RDE-graphite and RDE-graphite|Ag/ABW/BW in ambient illumination (dark) and under 1 sun irradiation provided by a solar simulator. Since the studies also revealed that the irradiated GDE|Ag/ABW/BW under air flow produced $H_2O_2$ from ORR this electrode was used in a photoreactor for remediation of aqueous solutions containing amoxicillin and ciprofloxacin antibiotics. The GDE|Ag/ABW/BW photocathode was associated with an FTO|$TiO_2$ photoanode, and these electrodes were externally connected to a solar cell. Powered by sunlight, this solar-driven photoreactor exhibited excellent performance for water remediation and can be considered an environmentally sustainable technology for *in loco* remediation of effluents containing organic contaminants.

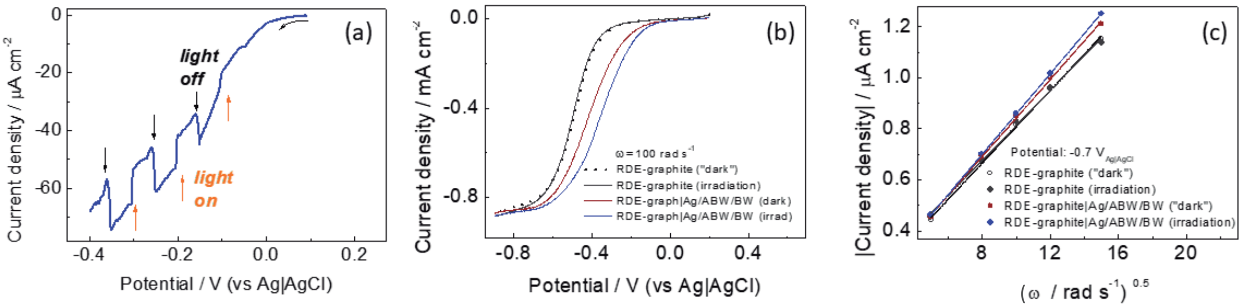

**Figure 1.** Electrochemical measurements in in $Na_2SO_4$ aqueous solution saturated with air (21 % $O_2$).: Voltammogram under intermittent irradiation for FTO|Ag/ABW/BW (a); voltammograms at 100 rad $s^{-1}$ (b) and limiting current densities at -0.7 V for all rotation rates (c) for RDE-graphite and RDE-graphite|Ag/ABW/BW in ambient illumination ("dark") and under irradiation

1 – Loeb, S. K.; et al. *Environ. Sci. Technol.* **2019**, 53 (6), 2937–2947.
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## Agradecimentos/Acknowledgments

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**Área: ELE**

# Impedimetric biosensor based on ZnO nanorods for detection of antibodies against SARS-CoV-2

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*Keywords: COVID-19, SARS-CoV-2, Electrochemical biosensor, Zinc oxide.*

## Highlights

Electrochemical biosensors; Serological diagnosis; Biosensors to be used in immunosurveillance; Inorganic oxide based bioelectrodes.

## Abstract

Diagnostic methods based on electrochemical biosensors are promising alternatives to conventional laboratory tests to detect antibodies against SARS-CoV-2. In this work, we developed a label-free impedimetric biosensor based on zinc oxide nanorods (ZnONRs) coated onto the FTO electrode. The recombinant Spike protein SARS-CoV-2 (S) was immobilized by physical adsorption (Granted by LECC/COPPE/UFRJ). Finally, the system was validated using clinical samples (1:500 v/v dilution) from healthy (pre-pandemic), convalescent, and vaccinated (Sinovac-Coronavac) individuals (CAAE:43139921.2.0000.5594). The presence of the ZnONRs matrix provides a suitable biocompatible environment for the immobilization of biomolecules. All modification steps were followed by scanning electron microscopy (SEM) and electrochemical techniques. The morphology of the positive and negative samples was different (**Fig. 1A**). In **Fig. 1B**, the strategy used allowed the retention of S, which was observed by the increase in charge transfer resistance ($R_{ct}$) due to barriers created by the presence of the protein that delays electron transfer. As these are complex samples, glycine was used to avoid unspecific reactions with the medium, helping the system distinguish positive and negative samples, with a detection limit (DL) of 0.057 mg $mL^{-1}$ of total protein (**Fig. 1C**). In the test with clinical samples (**Fig. 1D**), we studied four groups of individuals **(1)** Pre-pandemic; **(2)** Convalescents; **(3)** Vaccinated, and **(4)** Vaccinated and diagnosed with COVID-19. From (1) we define the cut-off point (5.2 KΩ) and separate the three groups with good statistics. In group (3), we have some red points representing patients with negative responses in the ELISA and positive responses in the electrochemical system. The ROC curve for the electrochemical system showed AUC ~ 0.91, indicating the high accuracy of this assay. Thus, the results suggest the surface of ZnONRs was able to keep S in its trimeric form, allowing the differentiation of blood serum from pre-pandemic, convalescent, and vaccinated individuals, proving to be a versatile platform for the development of electrochemical biosensors for COVID-19 immune surveillance[1].

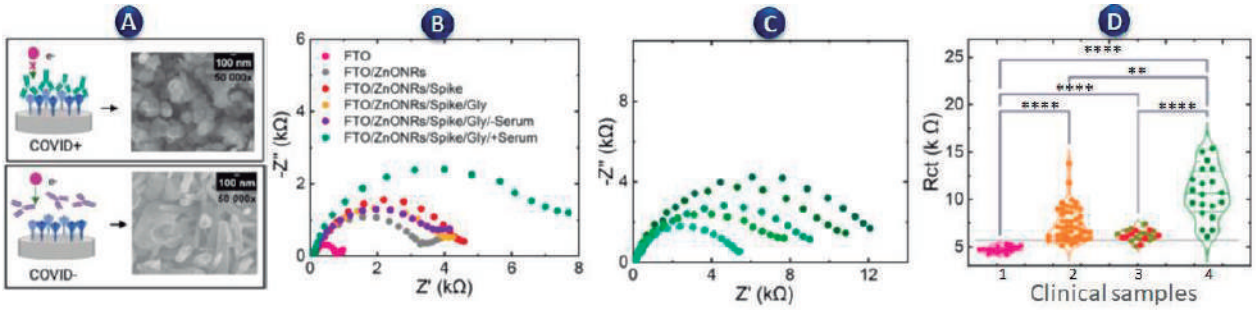

**Figure 1.** Electrochemical biosensor for monitoring COVID-19 **(A)** Representative bioelectrode scheme with SEM images showing surface morphology in the presence of positive serum (COVID+) and negative serum (COVID-). **(B)** Nyquist diagrams of each stage of the biosensor construction. **(C)** The Nyquist diagram of increasing concentration responses of the total amount of proteins present in serum samples from convalescent individuals (Positive for COVID-19) was used to determine the calibration curve and calculate the LD. (D) Violin graphs of the clinical samples studied: (1) pre-pandemic; (2) Convalescents; (3) vaccinated and (4) vaccinated and diagnosed with COVID-19, ****p<0.0001, **p<0.0021. Electrolyte: 0.1 mol $L^{-1}$ of KCl containing 5 mM $L^{-1}$ $[Fe(CN)_6]^{3-/4-}$

[1] *Nunez, FANE. et al. Electrochemical biosensor based on Zinc Oxide nanorods for detection of antibodies against SARS-CoV-2 Spike protein in COVID-19 natural infected and inactivated SARS-Cov-2 (Sinovac-Coronavac) vaccinated individuals, ACS Applied Nano Materials,* ***2022*** *-* ***submitted***

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**Área: ELE**

# Improved electrochemical performance of 3D-printed sensors by sequential $CO_2$ laser-scribing and electrochemical treatment

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Keywords: *3D printing, $CO_2$-laser scribing, Electrochemical treatment, Tyrosine determination, Urine analysis.*

## Highlights

Combining $CO_2$ laser-scribing and electrochemical treatment provides high electron performance in 3D-printed electrodes; The 3D-printed sensor was applied for the non-enzymatic determination of tyrosine in real urine samples.

## Abstract

The advent of 3D printing technology has generated a revolution acquiring multifaceted objects. This technology employing conductive filaments has proved to be an attractive alternative for the development of new electrochemical sensors, thanks to the freedom of design, low cost and disposable characteristics. However, one of the great challenges in this field is the development of activation methods aiming to improve the electrical properties of these materials, since the conductive filaments used have a high amount of insulating thermoplastic [1]. In this regard, this work presents a new method of activation of carbon black and polylactic acid-based 3D-printed electrodes (CB/PLA) (Figure 1). Such activation employs a sequential $CO_2$ laser-scribing treatment [2] and electrochemical treatment in alkaline media (NaOH 0,5 mol $L^{-1}$) [3]. A significant improvement in the electrochemical behavior of the electrodes was verified by the decrease in the peak-to-peak separation and increase in current peaks of the voltammetric response for the $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$. Also, the electrochemical impedance spectroscopy confirmed low charge transfer resistance after performing the proposed treatment protocol. As a proof-of-concept, a non-enzymatic, sensitive, fast, and simple method for tyrosine sensing in real urine samples was developed. Acceptable limit of detection (0.25 µmol $L^{-1}$), wide linear range (1.0 µmol $L^{-1}$ to 250.0 µmol $L^{-1}$), good repeatability (RSD = 2.7%; *n* = 10) and reproducibility (RSD = 3.0%; *n* = 10) and adequate recovery values (between 106% and 109%) for the analysis of spiked urine samples were obtained. Additionally, the 3D sensors presented advantageous characteristics, such as low cost and disposability. In addition, the developed treatment proved to be very fast (~7 min), effective, and environmentally friendly because it does not use toxic organic solvents.

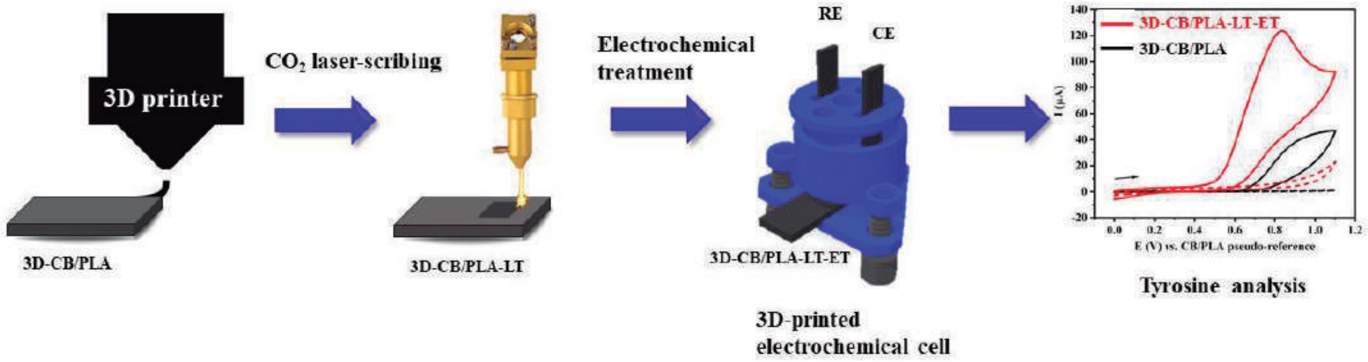

**Figure 1 -** Schematic of the printing process and activation of 3D sensors.

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## Acknowledgments

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

# Improving photoelectrochemical activity with g-$C_3N_4$/$BiVO_4$ heterojunction synthesis for degradation of organic compounds

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Keywords: Heterojunctions; Photoanodes, g-$C_3N_4$/$BiVO_4$, Degradation.

## Highlights

Photoanodes with heterojunctions present better performance when compared to pure photoanode;The g-$C_3N_4$/$BiVO_4$ heterojunction has better characteristics and is more efficient in removing 4-nitrophenol.

## Resumo/Abstract

Semiconductor photoanodes are alternative materials that attracts great attention for water depollution using solar energy. The composition of the semiconductor is extremely important, so we can avoid undesirable characteristics. The carbon nitride (g-$C_3N_4$) and bismuth vanadate ($BiVO_4$) heterojunction is very promising, as it shows an efficient separation of the electron-hole pair that can lead to increased photocatalytic activity [1]. Photoanodes were synthesized by deposition of the solution using spin coating. Five different compositions were synthesized, which was BiVO4 over g-C3N4, g-C3N4 over BiVO4, BiVO4 and g-C3N4 deposited togheter (i.e. dispersed in bulk solution), and the BiVO4 e g-C3N4 solely, for comparison. Finally, calcination in a muffle at 500°C at 10°C/min heating rate. Subsequently, the electrochemical measurements were performed in a single compartment cell containing the working electrode (photoanodes prepared), the platinum counter electrode and the Ag/AgCl reference electrode. For the degradation tests, 5 mg/L of 4-Nitrophenol (4-NP) was added to a 60 mM NaCl solution and a potential of 1.1 V was applied using a 100 mV solar simulator as light source. The absorption spectra the 4-NP were obtained by using a UV–V in spectrophotometer for analysis of compound concentration during treatment. In figure 1a it is possible to observe the photocurrents of the synthesized anodes. The heterojunction g-$C_3N_4$/$BiVO_4$ was the photoanode with the highest photocatalytic activity, about 1.5 mA/cm² and the g-$C_3N_4$ had the lowest photocurrent, almost null. In addition, the photoelectrocatalytic performance was evaluated on the degradation of 4-nitrophenol. As can be seen in Figure 1b, the photoanode of the g-$C_3N_4$/$BiVO_4$ heterojunction was able to remove more than 70% of the compound. This can be attributed to the optimal photocurrent obtained by this heterojunction.

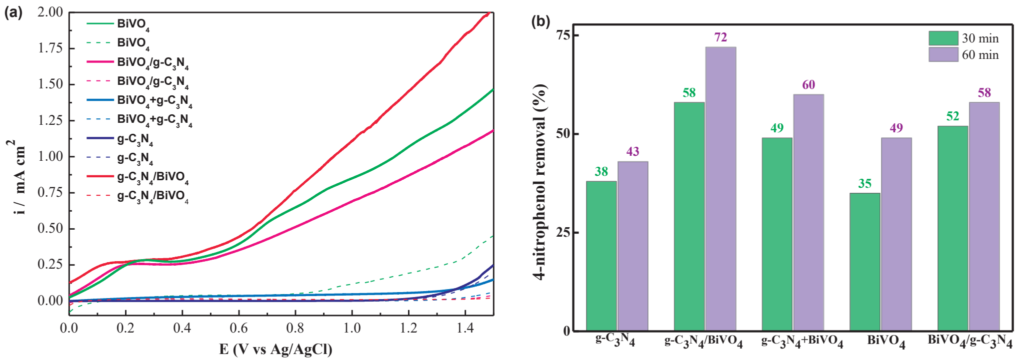

Figure 1: (a) Photocurrent of the materials in dark (dotted line) and in ligth (solid line) obtained at 5 mV s$^{-1}$ (b) removal of 4-NP in 60 mM NaCl solution applying 1.1 V using the different photoanodes under illumination with a solar simulator.

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## Agradecimentos/Acknowledgments

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**Área: ELE**

# Investigation of the pH anolyte influence in the electrochemical $CO_2$ reduction in non-aqueous catholyte using lead electrode

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Keywords: $CO_2$ reduction, Pb-plate electrode, anolyte influence, electroreduction, non-aqueous system.

## Highlights

Study of the pH anolytes effects on the surface of Pb plates. High pH value demonstrated better catalytic performance for $CO_2$RR. Pb electrode showed erosion and high current density over time.

## Abstract

Electrochemical $CO_2$ reduction to fuels or commodity chemicals, using renewable energy, has attracted considerable attention for closing the anthropogenic carbon cycle.[1] Although the research mainly focuses on the aqueous media for the $CO_2$ electrochemical reduction reaction ($CO_2$RR), the use of non-aqueous electrolytes has the advantage of suppressing Hydrogen Evolution Reaction (HER) and controlling the proton-assisted reduction reactions.[2,3] Among the metallic electrodes, Pb has shown the higher faradaic efficiency and selectivity to $C_2$ products in an aprotic electrolyte,[3] but few publications have investigated the behavior of the electrode in aprotic media and the effect of the anolyte pH during the reaction. This work reports the investigation of the anolyte pH effect on the $Pb^0$ cathodes surface during the $CO_2$RR. The experiments were carried out in an H-type cell configuration with a cation exchange membrane (Nafion 117) using a Pb plate and Pt mesh as working and counter electrodes, and an $Ag/Ag^+$ reference electrode. The catholyte used was 0,1 M $TBAPF_6$ in acetonitrile, pre-saturated with $CO_2$, and the anolytes investigated were 0.5 M $H_2SO_4$ (acid), 0.5 M $KHCO_3$ (neutral), and 0.5 M KOH (alkaline). Potenciostatic experiments were conducted for 30 minutes at -2.2 V (vs $Ag/Ag^+$) with a continuous $CO_2$ supply. After each experiment, the Pb electrode was dried by $N_2$ flow, and analyzed by SEM to investigate the surface of the plate. The pH anolyte influenced directly the $CO_2$RR, a higher current density was registered for the KOH electrolyte, and SEM images suggested that the pH also affects the corrosion mechanism on the surface of the Pb plate. Furthermore, for the $H_2SO_4$ and $KHCO_3$ anolytes, the Pb electrode undergoes structural changes due to partial dissolution and regeneration. XRD analysis of the Pb plate before and after each electrolysis demonstrated the absence of a new crystalline phase. Repeated cyclic voltammetry scans also showed that the electrode goes through activating over time, indicating that the corrosion could be related to the formation of the active phase in the $CO_2$ reduction. In summary, it was verified that the Pb plate suffers from erosion that's influences the catalytic performance for $CO_2$RR. In addition, the Pb electrode has better performance for $CO_2$ reduction with alkaline anolyte compared to the other evaluated anolytes.

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[2] SCHULER, E.; DEMETRIOU, M.; SHIJU, N. R.; GRUTER, G. J. M. *ChemSusChem*, v. 14, n. 18, p. 3636-3664, 2021.
[3] KÖNIG, M. et al. *Faraday Discussions*, v. 230, p. 360-374, 2021.

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**Área: ELE**

# Investigation of titanium|$BiVO_4$/FeOOH/NiOOH as Photoanode for light-assisted Oxygen Evolution Reaction

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Palavras Chave: *$BiVO_4$, photoanode, OER.*

## Highlights

$BiVO_4$ films, with controlled thickness, were deposited on titanium using a practical and affordable methodology based on a combination of Successive Ionic Layer Adsorption Reaction (SILAR) and thermal treatments. Photoelectrochemical measurements indicate that Ti|$BiVO_4$/FeOOH/NiOOH electrodes are promising photoanodes for solar-assisted oxygen evolution reaction in $NaHCO_3$ electrolyte.

## Resumo/Abstract

$BiVO_4$ is a n-type semiconductor that presents wide sunlight harvesting due its narrow bandgap energy ($E_g \sim 2.4$ eV). Furthermore, this is also very active for light-assisted Oxygen Evolution Reaction (OER) due its appropriate band edge positions. However, it presents short hole diffusion lengths and low carrier mobility.[1] The aim of this work is to investigate photoanodes based on $BiVO_4$ for OER in $NaHCO_3$ electrolyte, for application in the anodic compartment of electrolyzers for production of value-added chemicals from $CO_2$ reduction. $BiVO_4$ thin films were deposited on titanium foil by Successive Ionic Layer Adsorption Reaction (SILAR), a simple strategy for depositing high quality films[2]. This process was divided in three steps: 1) BiOI SILAR deposition → 2) Thermal treatment with 0.2 mol $L^{-1}$ $cm^{-2}$ $VO(acac)_2$/DMSO at 450 ºC/2h, and → 3) chemical etching with 0.5 mol $L^{-1}$ NaOH for 30 minutes. SEM images of the $BiVO_4$ films reveals a porous structure, inherited from BiOI, of interlinked nanospheres. Photoelectrochemical data were recorded in aqueous 0.5 mol $L^{-1}$ $NaHCO_3$ solution (pH 8.2), under 0.7 sun (homemade). $BiVO_4$ films synthesized with 30 SILAR cycles showed higher transient photocurrents densities at +1.23 V (vs RHE) ($J_{1.23}$ = 0.51 mA $cm^{-2}$), however this was unstable, probably due photocorrosion promoted by photogenerated holes. Further junctions with FeOOH/NiOOH[3] improved overall stability, probably due hole trap activity of $Fe^{2+} \rightleftharpoons Fe^{3+}$ fast reaction kinetics; and enhanced photocurrent density, because electrocatalytic activity of $Ni^{2+} \rightleftharpoons Ni^{3+}$ couple. So far, the Ti|$BiVO_4$/FeOOH/NiOOH photoanodes have showed good long-term stability of 7 hours under continuous polarization of +1.23 V (vs RHE), and appreciable photocurrent density (ca. $J_{1.23} = 0.75$ mA $cm^{-2}$) at 0.7 sun in 0.5 mol $L^{-1}$ $NaHCO_3$, an electrolyte frequently used in photoelectrochemical $CO_2$ reduction reaction.

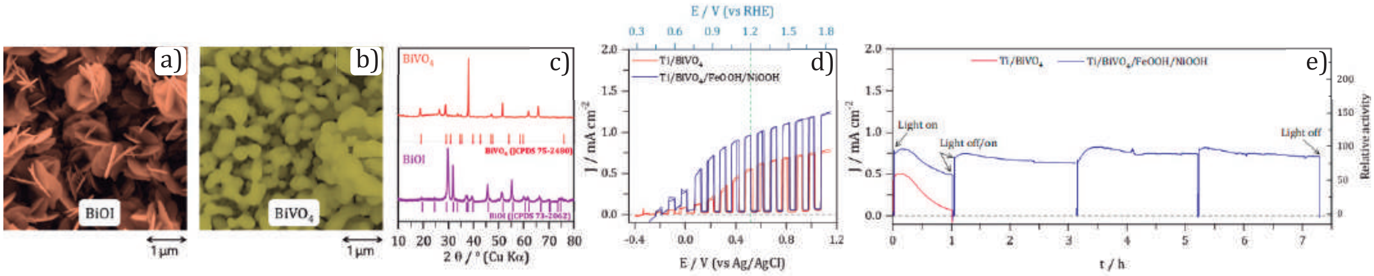

Figure 1 – SEM images of a) BiOI and b) $BiVO_4$; c) XRD of BiOI and $BiVO_4$; d) Chopped linear sweep voltammetry (20 mV $s^{-1}$) and e) chronoamperometry at +1.23 V (vs RHE). (0.5 mol $L^{-1}$ $NaHCO_3$, pH 8.2, 0.7 sun homemade)

[1] J.K. Cooper et al, Chem. Mater. 26 (2014) 5365 – 5373.
[2] S. Sfaelou, et al, RSC Adv. 5 (2015) 95813–95816.
[3] D.K. Lee, K.S. Choi, Nat. Energy. 3 (2018) 53–60

## Agradecimentos/Acknowledgments

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Área: ELE

# Laser-scribing generated gold nanoparticles paper-based BIA detection device for hypochlorite quantification

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**Keywords:** *Laser-scribing, ePADs, Gold nanoparticles, Batch-injection analysis, Hypochlorite.*

## Highlights

A low-cost kraft paper batch-injection analysis (BIA) cell with a fully integrated three-electrode system modified with gold nanoparticles was developed by the laser-scribing process for electrochemical selective detection of hypochlorite on a swimming pool samples.

## Abstract

Sodium Hypochlorite ($ClO^-$) is a widely used disinfectant in swimming pools, water treatment, and household bleaching agent[1]. In low concentrations, the disinfection effect is insufficient; however, high concentrations of $ClO^-$ can lead to adverse health effects in humans and create dangerous side products[2] as trihalomethanes. Therefore, the continuous online monitoring of $ClO^-$ in waters is necessary. In this context, coupling BIA electrochemical paper-based devices (ePADs) can provide a low-cost, portable, easy-to-use device to detect $ClO^-$ ions. In this work, we assembled two layers of kraft paper, which were laser scribed using a $CO_2$ laser to create a fully integrated three-electrode PAD (LS-ePAD). A 10 mmol $L^{-1}$ $HAuCl_4$ solution was then dropped cast onto the working electrode. A second laser-scribing procedure was applied, generating gold nanoparticles (LSAu-ePAD), which provides distinct sensing properties and enables hypochlorite selective detection. As seen in Figures 1-A and B, cyclic voltammograms of NaClO recorded in Britton Robinson (BR) buffer, pH 8, are shown, comparing the unmodified LS-ePAD performance to the LSAu-ePAD for $ClO^-$ ions detection, respectively. In addition, amperometric measurements were also performed on the modified BIA-ePAD, presenting good repeatability (RSD=4.73%), sample throughput (127 $h^{-1}$), and linearity (R=0.9966) for both increasing and decreasing NaClO concentrations (Figure 1-C), attesting the potential of the proposed LSAu-ePAD device coupled with BIA for hypochlorite detection in routine water samples.

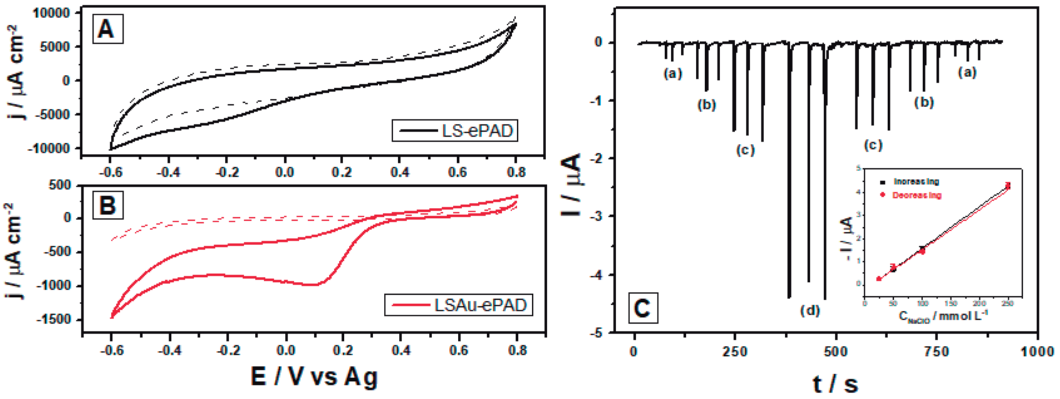

**Figure 1** – Cyclic voltammograms of 0.04 mol $L^{-1}$ BR buffer solution, pH 8, (dashed lines) with 5 mmol $L^{-1}$ NaClO (solid lines) at 50 mV $s^{-1}$ using (A) LS-ePAD and (B) LSAu-ePAD; (C) Amperometric detection using LSAu-ePAD of (■) increasing and (●) decreasing concentrations of NaClO (a) 25, (b) 50, (c) 100 and (d) 250 µmol $L^{-1}$ and its respective calibration curves (inset) at −0.2 V *vs.* Ag.

[1] Wang, B.; Anzai, J.I., Int. J. Electrochem. Sci., 10 (4), 3260–3268, 2015.
[2] Shanmugaraj, K.; Ilanchelian, M., New J. Chem., 41 (23), 14130–14136, 2017.

## Acknowledgments

The authors acknowledge FAPESP, CAPES, and CNPq for the financial support.

**Área: ELE** **Nº de Inscrição: 1412**

# Manganese-Cobalt Mixed Oxides for Oxygen Evolution Reaction

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Palavras-Chave:*(Bimetallic oxides, Water oxidation reaction, Oxygen evolution reaction, Electrocatalysis).*

## Highlights

Synergistic effect of Mn-Co bimetallic oxides significantly improves the water splitting process;
Oxides with a higher ratio of Cobalt showed lower values of the water oxidation overpotential.

## Abstract

Recently, much has been done to remedy the environmental damage caused by the use of primary sources of energy based on fossil fuels.[1] The interest in efficient technologies for converting and storing energy using renewable sources has been intensified, especially those related to the use of sunlight energy. The Bimetallic mixed oxides (BMOx) of transition metals have been used efficiently in multi-applications such as the improvement of the catalytic activities of new materials for their use in water splitting.[2] Water splitting is the chemical reaction in which water is broken down into $O_2$ and $H_2$, having as half-reactions of this process, the reactions named oxygen reduction reaction (ORR), oxygen evolution reaction (OER) and/or the hydrogen evolution reaction (HER). However, the half-reactions of the OER is a thermodynamically unfavorable process, besides it presents a sluggish kinetics and requires catalysts to lower the reaction overpotential, as it encompasses a complex reaction that requires the removal of four electrons and four protons from two water molecules to produce one oxygen molecule (see equation 1)[3].

$$2H_2O \rightarrow 2H_2 + O_2 \qquad \text{(equation 1)}$$

OER: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ $E_{anodo} = +1{,}23\ V - 0{,}059(pH)\ V\ (NHE)$

HER: $4H^+ + 4e^- \rightarrow 2H_2$ $E_{catodo} = 0\ V - 0{,}059(pH)\ V\ (NHE)$

In this regard, BMOx have demonstrated promising activity in respect to OER. Such effect may be related to possible synergistic effects of these metals in the materials. This work describes the preparation of mixed oxides with differing molar ratios of manganese and cobalt by hydrothermal synthesis, and their application in the electrocatalytic OER. The oxides were characterized by XRD, RAMAN, TG, SEM-FEG-EDS, AFM, XPS and electrochemical methods. BMOx (1:0, 0:1, 1:1, 1:4 and 4:1), were prepared from hydrothermal synthesis and tested in a potentiostat/galvanostat equipment, using a three-electrode system: FTO (fluorinated tin oxide) as working, Pt wire as counter and Ag/AgCl as reference electrodes, at different supporting electrolyte: $HNO_3$ (pH 1), $Na_2SO_4$ (pH 7) and KOH (pH 13), under ar atmosphere, by linear sweep voltammetry at 50 mV $s^{-1}$. The synthesized samples were deposited by drop casting on the FTO. It is possible to observe a positive effect in relation to the Mn-Co ratio of the catalyst in the onset overpotential ($j = 0.2$ and $j = 5$ mA $cm^{-2}$). The Mn-Co film (1:4) showed the best overpotential: 349 mV and 333 mV, at pH 1 and 7, respectively, and the second best 307 mV at pH 13, against 207 mV of the pure Cobalt film. Comparing the water oxidation processes of the prepared films, it was observed that there was a significant improvement in the Mn-Co ratio as the ratio of Cobalt increased. In conclusion, the prepared oxides showed promising results, since low overpotentials were obtained, especially in relation to tests in acid and neutral media, which have less favorable thermodynamic processes in relation to the tests in alkaline media. Also, a positive effect may be related to possible synergistic effects of these mixed oxides compared to the pure oxides.

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[2] OTHMANA, M. F et al. Renewable and Sustainable Energy Reviews, v. 80, p. 694-709, 2017.
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## Acknowledgments

The authors are grateful to the Fundação Carlos Chagas Filho de Amparo à Pesquisa do Estado do Rio de Janeiro, (FAPERJ), to the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) and to the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) for the research support.

**Área: ELE**

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

# Methylene blue/manganese(II) flow solar cell for high-performance energy production and storage

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Palavras Chave: *flux battery, photovoltaics, clean energy.*

## Highlights

A flow battery is a type of electrochemical cell where chemical energy is provided by two redox pairs dissolved in liquids that are pumped through the system on separate sides of a membrane. Solar cells produce direct current electricity from sunlight, which can be used to power equipment or recharge a battery using the photovoltaic effect, which is the conversion of light into electricity. A flow solar cell promises to combine these two technologies to obtain a single device capable to generate and store a large amount of energy.

## Resumo/Abstract

Despite the leverage of the use of renewable energy, there are still opportunities for improvement in both conversion, transport, and storage. In this sense, nanostructured devices hold great promise. However, the development of efficient devices ends up going through little green routes, resulting in the generation of waste whose destination is still uncertain. In this way, this project intends, with the use of techniques and methods innovators to produce new “greener” materials to produce energy converter and storage devices with high efficiency and performance, with excellent durability, and with low impact on the environment. In this way, the present work aims to combine the advantages of a photovoltaic cell with the properties of a flow cell, so that an organic photoactive redox pair absorbs sunlight and converts it into solar energy, while, in the absence of light, the battery can supply power efficiently. solar flow cell proposed in this work. As redox pairs, a 0.1 mmol $L^{-1}$ of methylene blue were be used as photoactive material (catholyte), while in the other compartment a pair of $Mn^{2+}/Mn^{3+}$ 10 mmol $L^{-1}$ will be used (anolyte). 0.5 mol $L^{-1}$ $H_2SO_4$ solution was used as electrolyte. The photoelectric properties of the device were tested in the dark and under lighting of 1 sun power (100 mW $cm^{-2}$). While flow battery properties were tested using charge and discharge cycles, also in dark and under light. The solution flow flux, and the concentration of active species will be optimized using factorial design. With this new device, was possible to obtain a high-performance and highly stable flow-through solar cell, which will automatically regenerate once the solutions are allowed to rest in the tanks outside the cell before being pumped again. Although the concept is simple, alias the two technologies has not yet been reposted in the literature and although it holds great promise.

## Agradecimentos/Acknowledgments

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**Área: ANA**

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

# Microchip electrophoresis with electrochemical detection for the determination of biological thiols and ascorbic acid

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Palavras-Chave: *Microchip electrophoresis; Electrochemical detection; biological thiols*

## Highlights

The electrochemical detection of biological thiols and ascorbic acid based on their reaction with menadione was performed using a microchip electrophoresis system with detection at +0.4V.

## Resumo/Abstract

Biological thiols such as glutathione (GSH) and cysteine (cys) and ascorbic acid (AA) are important for the protection of cells from reactive oxygen species. Besides, glutathione is the major intracellular antioxidant present at concentrations from 1–10 mM in microglia and other immune cells. Because of its key role in maintaining the redox status of the cell, the intracellular ratio of GSH/GSSG is often used as a quantitative measure of cellular oxidative stress. The small dimensions of the channels in microchip analytical systems and the small volumes involved make it possible to perform on-chip reactions in a controlled fashion as well as to monitor the contents of biological samples. Electrochemical detection has several advantages for microchip analysis. Electrodes can be fabricated directly on the chip using conventional microfabrication techniques. Herein we introduce a microchip electrophoresis device for the electrochemical determination of GSH, cys and AA. A PDMS/glass microchip with 5cm separation channel was employed and the BGE consisted of HEPES buffer (30mM, pH 8.5) with SDS 4mM. Sample was placed in the sample reservoir (Figure 1) and a voltage of 1.6 kV was applied to the sample reservoir and 1.9 kV to the buffer reservoir with the other two reservoirs at ground to generate a field strength of 222 V/cm along the separation channel. An electrokinetic gated injection of 1 second was used to introduce the sample into the separation channel.Thiols reaction with menadione enabled detection at +0.4V. The influence of TCEP, SDS and cyclodextrins were also evaluated. The separation of these species was achieved in less than 60s (Figure 2) and a good relationship between the concentration of analytes and the peak area was also achieved. The system will be employed for analytes determination in microdialysis samples.

**Figure 1**

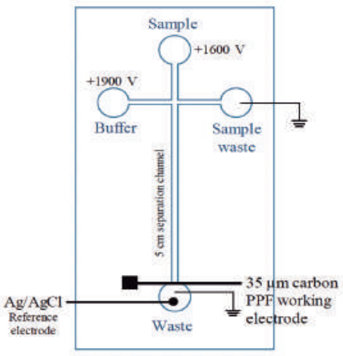
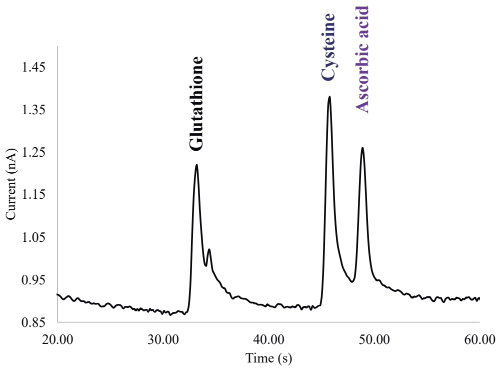


**Figure 2**



## Agradecimentos/Acknowledgments

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**Área: ELE**

# Micropipette tip-based miniaturized electrochemical device for analysis at microvolumes

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Palavras Chave: Microanalysis, Miniaturization, Electrochemical Sensors, Electroanalysis.

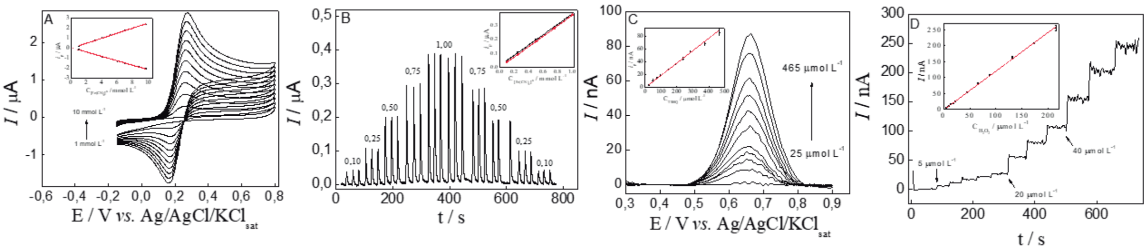
## Highlights

Inexpensive micropipette tip-based electrochemical device. Analytical performance was comparable with more sophisticated electrochemical sensors. Applicable in aqueous and aqueous:ethanol mixtures in static or flowing conditions.

## Resumo/Abstract

The miniaturization of analytical devices is a novel and the ultimate trend in analytical chemistry. However, most of the microfabrication techniques require sophisticated and expensive technologies making them inaccessible for researchers from developing countries. In this context, the objective of this study is to develop, characterize, and evaluate the analytical potentialities of a micropipette tip-based miniaturized electrochemical system designed as a versatile, robust, durable, and accessible device. The miniaturized electrochemical sensor was fabricated using micropipette tips and metallic wires recovered from a damaged combined glass electrode and a conductance cell. The analytical performance of this device was evaluated for some selected electroactive compounds, such as potassium ferrocyanide at static and hydrodynamic conditions, TBHQ in ethanol/aqueous solution, and hydrogen peroxide aqueous solution. Figure 1 shows the electroanalytical response of these species recorded in microvolumes of solutions.

**Figure 1: A)** Cyclic voltammograms recorded with the miniaturized device in 0.1 mol $L^{-1}$ KCl at different $[Fe(CN)_6]^{4-}$ concentrations, $\nu = 50$ mV $s^{-1}$. **B)** Amperometric response for injections of different concentrations of $[Fe(CN)_6]^{4-}$. The numbers correspond to $[Fe(CN)_6]^{4-}$ concentrations in mmol $L^{-1}$. Carrier solution: KCl 0.1 mol $L^{-1}$ Flow rate: 3 mL $min^{-1}$; sample volume: 100 µL; $E_{detection} = +0.6$ V. **C)** Baseline corrected differential pulse voltammograms recorded in ethanol:1.0 mol $L^{-1}$ $HClO_{4(aq)}$ (90:10; v:v) at different TBHQ concentrations. Voltammetric conditions: pulse amplitude: 50 mV; pulse width: 50 ms, $v = 10$ mV $s^{-1}$. **D)** Amperometric response of $H_2O_2$ in 0.1 mol $L^{-1}$ phosphate buffer pH = 6.8 at $E_{applied} = 0.7$ V. Inset: analytical curve.



The results presented in Figure 1 demonstrated that the proposed miniaturized device was extremely versatile once it could be used to determine diverse analytes using different electroanalytical techniques in different media, achieving a good linear relationship between the anodic ($I_{pa}$) or cathodic peak currents ($I_{pc}$) and analyte concentrations ($R^2$ close to 1). Thus, the proposed miniaturized device can find a wide range of applications. Moreover, its analytical performance was similar to that presented by other electrochemical sensors based on non-modified Pt electrodes. Thus, we believe that the approach described here is a promising way to produce versatile, efficient, and cost-accessible electrochemical sensors.

## Agradecimentos/Acknowledgments

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**Área: ELE**

# Modular electrochemical-peptide biosensor for determination of COVID-19 antibodies

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***Keyword:** Biosensor; Peptide; COVID-19; Antibodies; AuNPs.*

## Highlights

The simple and modular construction of electrochemical biosensors; Mimetic peptide thought in biorecognition systems; Point-of-care diagnosis and Mass Screening; Commercial development of technologies

## Abstract

The different areas of science have focused on creating, understanding, and applying biosensors to monitor the COVID-19 pandemic. Spike (**S**) and Receptor-binding domain (**RBD**) proteins have been used as a recognition element, but large-scale fabrication is complex and expensive.Thus, immunogenic peptides (IP) are a versatile, cheap, and sensitive alternative to use for this purpose.[1] In this work, we built an electrochemical biosensor using glassy carbon electrodes (GCE) modified with gold nanoparticles (AuNPs), previously functionalized with an IP (NNATN) (**P**) (Figure 1A). This compound was designed by bioinformatics and validated by ELISA and molecular docking.[2] We analyzed serum samples from healthy (n=15, **NS**) and convalescent patients with COVID-19 (n=30, **PS**) (CAAE:43139921.2.0000.5594). The AuNPs were synthesized by the Turkevich method with a hydrodynamic radius ($R_H$) of 17 nm and Zeta potential (ZP) of -29 mV ± 1.6 SD. After interaction with **P**, $R_H$ was enhanced to 20 nm, and ZP decreased to -13.8 mV ± 1.0 SD. Electrochemical data (Figure 1B) demonstrate that the method performs well for the **P** immobilization and target recognition. In Figure 1C, we can see that **P** has a better sensitivity when compared to **S**, but a weak improvement in relation **RBD**, which reinforces the idea that the size of the bioreceptor helps in the detection process. The modified electrode showed high specificity and sensitivity (detection limit of 1.28 μgmL$^{-1}$) and good stability (~30 days). In Figure 1D, the $R_{ct}$ values obtained for the healthy (green) and convalescent (pink) patients could be easily classified, considering the black line is the cutoff (8067 Ω). The heterogeneity observed in convalescents (pink) occurs due to factors such as age, gender, genetics, exposure to other coronaviruses that influence the patients' humoral response. These data show that **P** can be used as a biorecognition element in label-free immunosensors, capable of distinguishing healthy from convalescent patients in complex clinical samples in sensitive and specific ways. The results are promising in developing low-cost and miniaturized biosensors for monitoring COVID-19.

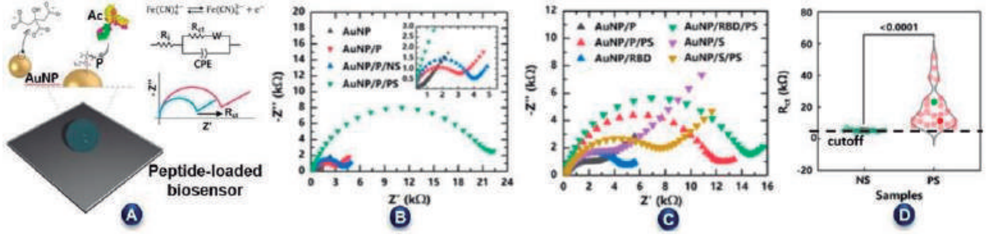

**Fig 1**. Functional principle of the biosensor for COVID-19. **(A)** A representative scheme using **P** (immunogenic peptide as a biorecognition element, and **Ac** as COVID-19 antibodies; **(B)** Nyquist diagram of GCE/AuNPs functionalized with **P** in the presence sera samples (1:500 v/v) from pre-pandemic (**NS**) and convalescent (**PS**) patients (convalescent patient with **high** levels of anti-SpiKe antibodies, translated by high optical density (OD) readings) **(C)** Nyquist plots for different biomolecules (**P**; **S**; **RBD**) in the presence of **PS** (convalescent patient with **low** OD on ELISA) **(D)** Violin curve with all sera **NS** (n=15) e **PS** (n=30), (highlight samples used in experiment B (green) and experiment C (red)), p<0.0001. The experiments were carried out in triplicate. Electrolyte: Solution of 5 mmol L$^{-1}$ $K_4Fe(CN)_6/K_3Fe(CN)_6$ in 0.1 mol L$^{-1}$ KCl.

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[1] *Nicoliche, CYN. et al. In situ Nanocoating on Porous Pyrolyzed Paper Enables Antibiofouling and Sensitive Electrochemical Analyses in Biological Fluids. ACS Appl. Mater. Interfaces **2022**, 14, 2522–2533.*

[2] *Castro, ACH. et al. Modular label-free biosensor loading nature-inspired peptide may enable the translation of accurate and fast COVID-19 antibody tests into the real world, ACS nano, **2022** - **submitted***

## Acknowledgments

FAPESP, CNPq, CAPES, INCT de Bioanalítica, Laboratory of Cell Culture Engineering at COPPE/UFRJ.

**Área: ELE**

# Molecularly imprinted electrochemical sensor on nanostructured surface with manganese nanoparticles and polyaminoacid for determination of 3-hydroxydecanoic acid obtained from agroindustrial guava waste

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Keywords: M*olecularly imprinted polymer, reduced graphene oxide, 3-hydroxydecanoic acid, manganese nanoparticles, polyaminoacid, guava waste*

## Highlights

A sensor was proposed for determination of 3-hydroxydecanoic acid. RGO combined with MnNPs increases the sensor sensitivity. The sensor displays high selectivity and affinity to the target molecule.

## Abstract

The guava cultivation in Brazil has increased considerably in last few years, showing a great economic importance for the country. However, the agroindustrial waste of this fruit, composed of peel, pulp and seed, are discarded irregularly, contributing to nutrients wastage and environmental contamination. This way makes it necessary to find an efficient alternative to reuse this waste. A class of compounds that this waste constitute are the fatty acids, that acts as an intermediary to other products, such as rhamnolipids (RHLs), that contains acid 3-hydroxydecanoic (3-HDCN) molecule in its structure. With application in several fields, the development of analytics methods for determination of 3-HDCN, which has great industrial interest, brings great relevance to the fruit refinery and it can promote an environmentally favorable destination. Currently, there is no analytical method in the literature using electrochemical sensors with MIP containing nanoparticles for the determination of 3-HDCN from agroindustrial guava waste. Therefore, the purpose of this work was the construction of an electrochemical sensor based on glassy carbon electrode (GCE), modified with reduced graphene oxide (rGO), manganese nanoparticles (MnNPs) e molecularly imprinted polymer (MIP) of L-serine (L-ser), which shows high selectivity, sensibility, stability, low instrumental cost, low limit of detection (LOD) and quantification (LOQ) for determination of 3-HDCN acid present in RHLs. Initially, on the construction of the sensor, a 0,4 mg $mL^{-1}$ rGO suspension containing 0,1 mol $L^{-1}$ $Na_2SO_4$ was deposited on the electrode surface through chronoamperometry, applying a -1,4 V potential for 500s. Then, the MnNPs were electrodeposited with a $5\times10^{-3}$ mol $L^{-1}$ $MnSO_4.H_2O$ and 0,1 mol $L^{-1}$ $Na_2SO_4$ solution on the GCE/rGO through chronoamperometry, applying a -0,7 V potential until the charge of 0,9 mC was reached. To the electropolymerization, a solution containing $1{,}0\times10^{-5}$ mol $L^{-1}$ L-ser and $1{,}0\times10^{-6}$ mol $L^{-1}$ 3-HDCN acid in PBS pH 7,0 was prepared and interacted under slow agitation for 20 minutes. After that, the GCE/rGO/MnNPs electrode was immersed in the prepared solution and modified through electropolymerization with cyclic voltammetry (CV), for 10 consecutive cycles in a potential range of -0,3V to 1,3V at 50 mV $s^{-1}$ scan rate. After that, the electrode was inserted in a 0,1 mol $L^{-1}$ NaOH solution for 6 consecutive voltametric cycles in a potential range of 0V to 1,5V, with a 50 mV $s^{-1}$ scan rate, to remove the 3-HDCN template from the polymer matrix and obtain the GCE/rGO/MnNPs/MIP electrode. For the rebinding experiment, the electrode was placed for 10 minutes in different concentrations of 3-HDCN in PBS pH 7,0. The developed method exhibited two linear ranges, from $2{,}0\text{x}10^{-12}$ to $1{,}0\text{x}10^{-10}$ mol $L^{-1}$, with LOD, LOQ and amperometric sensitivity of $8{,}3\text{x}10^{-13}$ mol $L^{-1}$, $2{,}7\text{x}10^{-12}$ mol $L^{-1}$ and $7{,}7\text{x}10^{5}$ µA L $mol^{-1}$ (n=3), respectively. This electrode was characterized by CV, electrochemical impedance spectroscopy, scanning electron microscopy and energy dispersive X-ray spectroscopy. Furthermore, tests were made with interferents that composes the sample, such as mono-rhamnolipid, di-rhamnolipid and fatty acids, oleic and linoleic acid. The proposed device presented high selectivity, repeatability, reproducibility and excellent stability. So, the GCE/rGO/MnNPs/MIP sensor was successfully applied for the selective determination of 3-HDCN acid obtained from agroindustrial guava waste, showing good analytical performance, precision and reliability for the determination of this molecule.

## Acknowledgments

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**Área: ELE**

# Nitrogen-doped graphene quantum dots-modified electrode for the determination of triclocarban

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Keywords: Nitrogen-doped graphene quantum dots, Chitosan, Modified electrode, Triclocarban.

## Highlights

Nitrogen-doped graphene quantum dots were synthesized by citric acid pyrolysis. The quantum dots improved the sensitivity of the electrode. Quantification of triclocarban was carried out in personal care products.

## Abstract

Triclocarban (3,4,4′-trichlorocarbanilide, TCC) is an antimicrobial agent frequently used in personal care products with potential activity for endocrine disrupting, and hence its monitoring is particularly important [1]. Thus, a sensitive analytical tool was developed for electroanalysis of triclocarban by modifying a glassy carbon substrate (GCE) with nitrogen-doped graphene quantum dots (N-GQDs) immobilized in chitosan (CS). For this, the N-GQDs were obtained by a one-step procedure involving pyrolysis with citric acid as a carbon source and tris(hydroxymethyl)amino-methane (tris-HMA) as a nitrogen dopant [2]. To develop the modified electrode, 200 µL of the N-GQD dispersion was added to 9.8 mL of a 0.25% (m/v) chitosan solution and kept at 60 °C for 30 min under stirring. After, 2.0 µL of the N-GQD-CS dispersion was dripped onto the previously cleaned GCE surface (geometric area = 0.07 $cm^2$). The electrochemical experiments were carried out on a portable potentiostat PalmSens 4 (Palm Instruments BV, The Netherlands). A cell containing three electrodes was used in the experiments: N-GQD-CS/GCE as the working electrode, Ag/AgCl (KCl saturated) as the reference electrode and a platinum wire as the counter electrode. Commercial bar and liquid soap samples were purchased in stores in Florianópolis, Brazil. For the assays, 0.5 g of the soap samples was subjected to an ultrasonic bath in 10.0 mL of ethanol for 40 min, filtered (25.0 µm), and diluted in ethanol in a 25.0 mL volumetric flask. Electron microscopy results showed that the synthesized quantum dots had a diameter of 4.5 nm. The doping with nitrogen in the graphene matrix was confirmed by attenuated total reflectance Fourier transform infrared (ATR FT-IR) by the presence of stretching vibration bands at 1640 $cm^{-1}$ (C=N) and 1380 $cm^{-1}$ (C–NH). The N-GQD-CS/GCE showed superior results of the $[Fe(CN)_6]^{3-/4-}$ redox pair when compared to bare GCE and CS/GCE using cyclic voltammetry and electrochemical impedance spectroscopy techniques, indicating to be promising for electroanalytical applications. The cyclic voltammograms of TCC at N-GQD-CS/GCE in 0.1 mol $L^{-1}$ Britton-Robinson (B-R) buffer (pH 7.0):ethanol (95:5 v/v) showed an oxidation peak at +0.97 V. The peak observed is attributed to the oxidation of –NH of one of the amide groups presented in the TCC structure [3]. The best response was provided by the electrode modified with the N-GQDs supported in CS with a four-fold increase in the oxidation current compared with the bare GCE. When compared to the CS/GCE electrode, the increase was two times. This response gain can be attributed to the greater adsorption of TCC on the chitosan film that covers the electrode, as well as the increase in the electroactive area of the modified electrode and the conductivity of the system provided by the use of N-GQDs. The calibration plot for TCC was constructed under optimized conditions by differential pulse voltammetry in 0.1 mol $L^{-1}$ phosphate buffer (pH 7.0):ethanol (95:5 v/v) in the range of 0.05 to 8.0 µmol $L^{-1}$ with limits of detection and quantification of 17.0 and 57.0 nmol $L^{-1}$, respectively. The modified electrode was effectively implemented in the quantification of TCC in personal care products with recoveries data in the range of 90 to 109%, and in accordance with data obtained by UV-vis spectrometry.

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## Acknowledgments

CNPq, FAPESC, Capes, and UFSC.

**Área: ELE**

# On the evaluation of electrochemical properties of carbon Printex L6 modified with a MOF for oxygen reduction reaction

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Palavras Chave: *hydrogen peroxide, eletrocatalysis, MOFs, Printex carbono L6*

## Highlights

Printex L6 modified with ruthenium MOF improves the activity to oxygen reduction reaction without decreasing the selectivity of pure carbon printex L6 matrix.

## Resumo/Abstract

Hydrogen peroxide ($H_2O_2$) is a strong oxidant widely used in industrial, commercial and environmental applications. As an improvement over the traditional methods, environmentally friendly methods for $H_2O_2$ production have been proposed. In this view, the electrochemical method has gained prominence due to its efficiency and versatility of scale-up for any size of plant, including being able to generate $H_2O_2$ *in situ*. $H_2O_2$ electrogeneration occurs through the oxygen reduction reaction (ORR), where no toxic products are formed during the electro-synthesis. However, due to the slow kinetics of ORR, it is necessary that the electrodes to act as cathodes presented layers of a catalytic material which favor this reaction with minimum energy costs [1]. Thus, carbonaceous materials, that possess a high surface area, have been widely used as electrocatalytic materials for ORR mainly due to their abundance and low cost. Although, in acidic media, they are selective for $H_2O_2$, but have low catalytic activity, requiring the application of high overpotentials or high current densities for attain reasonable amounts of $H_2O_2$, which led to a high energy consumption [2]. Thus, the aim of present study was evaluate the effect of modification of Printex L6 with Ruthenium-Metal Organic Framework, which is a hybrid compound, in a proportion of 3% (w/w). The tests were carried out in a rotating ring disk in acidic medium ($K_2SO_4$ 0.1M, pH = 2.5). Results obtained showed that MOF-modified carbon and pure carbon presented similar selectivity (Fig 2. CPL6 = 80% and CPL6/MOF Ru = 81%), corroborating the results that the modification didn't change the selective property of the carbon matrix, but there was a displacement of 736 mV, in which the reduction in the potential of ORR is an indicative of decrease in the energy consumption for production of $H_2O_2$ in technological applications

**Figure 1.** Linear Sweep Voltammetry of CPL6 and CPL6/Ru-MOF

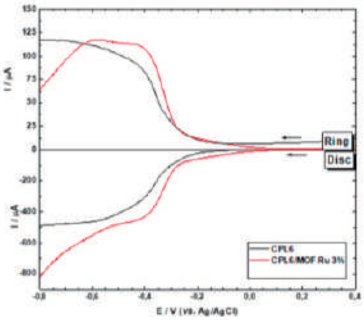
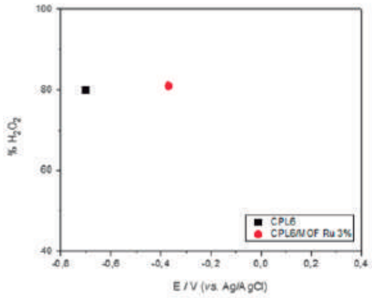


**Figure 2.** Selectivity for hydrogen peroxide



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## Agradecimentos/Acknowledgments

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**Área:ELE**

# Paper phenolic-based electrochemical sensors modified with multiple-walled carbon nanotubes by drop-casting for sulfanilamide determination

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keywords: *phenolic paper substrates, $CO_2$ laser, disposable sensors, carbon nanotubes, environmental samples, sulfanilamide*

## Highlights

Low-cost ecofriendly sensors produced onto phenolic paper with $CO_2$ laser. Electrode surface modification with carbon nanotube. Sulfanilamide quantification in environmental and pharmaceutical samples.

## Abstract

Phenolic polymers are typically used as substrates to fabricate printed circuit boards. They are inexpensive and robust materials, advantageous characteristics for sensor fabrication. Laser scribing is based on the carbonization of organic and insulating materials, generating carbon conductive tracks. The carbonization procedure is performed in a single step and has excellent reproducibility. Besides that, the electrochemical sensors can be easily modified by the drop-casting method, increasing the analytical method sensitivity and/or selectivity. Among the modifiers, carbon nanotubes have outstanding features due to their high surface area and efficiency in electronic transfer. As a result, electrochemical sensors were fabricated onto phenolic paper with laser $CO_2$. Recyclable phenolic papers obtained from old circuit boards were used as substrates, generating low-cost, eco-friendly sensors. The characterization studies were carried out using ferricyanide as an electrochemical probe. The sensors modified with multiple-walled carbon nanotubes functionalized by carboxylic acid (MWCNT) improved the electrochemical signal for ferricyanide ions (Figure 1A). Sulfanilamide was then selected as an analyte to evaluate the potential application of the sensors. Figure 1B shows that the modified sensors provided a better voltammetric signal for sulfanilamide oxidation than the non-modified electrode, demonstrating that carbon nanotubes are good modifiers for the electrochemical sensors. These results bring encouraging findings for sulfanilamide quantification. Consequently, different voltammetric techniques will be evaluated to develop an analytical method for this compound. Also, the next step will involve the study of the selectivity, pH range, calibration curve construction, and environmental/pharmaceutical sample analyses.

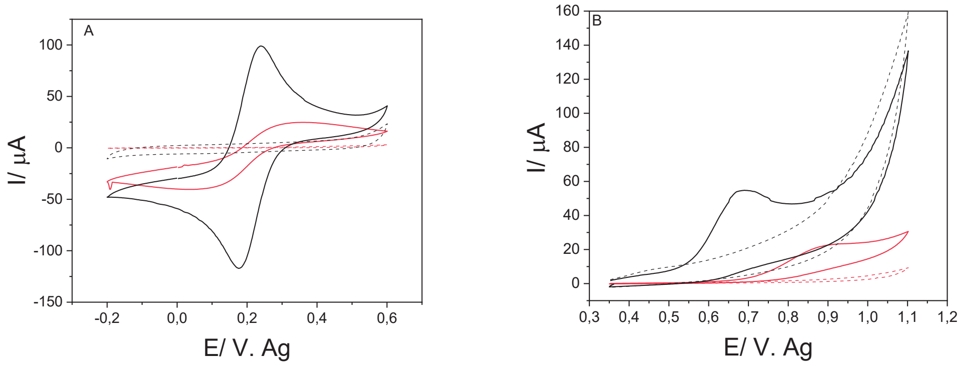

Figure 1- Cyclic voltammograms for untreated (Red lines) and MWCNT-phenolic-based electrodes (Black lines). (A) In 1.0 mol $L^{-1}$ KCl (dashed lines) + 5.0 mmol $L^{-1}$ Ferrocianate (solid lines). v = 20 mV $s^{-1}$.(B) In BR buffer pH 10 (dashed lines) + 1.0 mmol $L^{-1}$ Sulfanilamide (solid lines). v = 20 mV $s^{-1}$

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São Paulo Research Foundation - FAPESP (2021/00205-8, 2019/15065-7), Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - CAPES (PROEX 88887.341030/2019-00) and Conselho Nacional de Desenvolvimento Científico e Tecnológico - CNPq (140463/2021-6, 140462/2021-0).

**Área: ELE**

# Peach extract-based sensor containing graphene and gold nanoparticles for the detection of butylated hydroxyanisole

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Keywords: Peach extract, Gold nanoparticles, Graphene, Sensor, BHA.

## Highlights

Gold nanoparticles were synthesized and stabilized in peach extract (*Prunus persica*). Graphene was added to the dispersion of gold nanoparticles in the peach extract. The sensor was applied for the detection of butylated hydroxyanisole.

## Abstract

The butylated hydroxyanisole (BHA) is a synthetic phenolic antioxidant frequently used to prevent the oxidative rancidity of food, pharmaceutical, and other commercial products [1]. However, the presence of BHA has been linked to liver damage and carcinogenesis in laboratory animals [1]. Therefore, it is important to develop analytical tools capable of monitoring the presence of this agent. Thus, a peach extract-based sensor containing gold nanoparticles (AuNPs) and graphene (Gr) was developed for the electroanalytical detection of BHA. The peach extract (*Prunus persica*) served as a reducing agent and stabilizer for AuNPs and as a dispersing agent for graphene. The UV-vis spectrum of the AuNPs showed a single band at around 534 nm, which corresponds to an average particle diameter of around 50 nm [2]. The sensor was prepared by dripping a 2.0 µL of the modifying dispersion onto the surface of a cleaned glassy carbon electrode (GCE). The AuNPs-Gr-extract/GCE sensor showed superior results of the $[Fe(CN)_6]^{3-/4-}$ redox pair when compared to bare GCE in the cyclic voltammetry and electrochemical impedance spectroscopy studies, indicating to be promising for electroanalytical applications. Figure 1 shows a schematic diagram of the oxidation of BHA on the surface of the proposed sensor. The cyclic voltammograms of BHA at AuNPs-Gr-extract/GCE in Britton-Robinson (B-R) buffer solution (0.1 mol $L^{-1}$, pH 3.0) showed a peak at +0.51 V *vs.* Ag/AgCl, corresponding to the irreversible oxidation of BHA to tert-butylquinone (TBQ) [3]. Furthermore, the anodic current obtained was three times higher than bare GCE, showing the advantage of using the proposed sensor in the development of a sensitive methodology for the BHA quantification. The superior performance of the sensor can be attributed to the better conductivity provided by the presence of AuNPs and graphene stabilized in the peach extract. The calibration plot for BHA (Fig. 2) was constructed under optimized conditions in B-R solution (0.1 mol $L^{-1}$, pH 4.0) by differential pulse voltammetry in the range of 0.2 to 10.2 µmol $L^{-1}$ with limits of detection and quantification of 16.6 and 55.5 nmol $L^{-1}$, respectively. Thus, the proposed sensor represents a useful and sensitive analytical tool for the adequate determination of BHA and may help in food quality control.

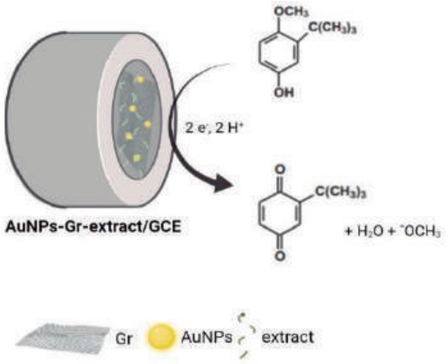

**Fig. 1.** Schematic representation of BHA oxidation on the surface of the AuNPs-Gr-extract/GCE.

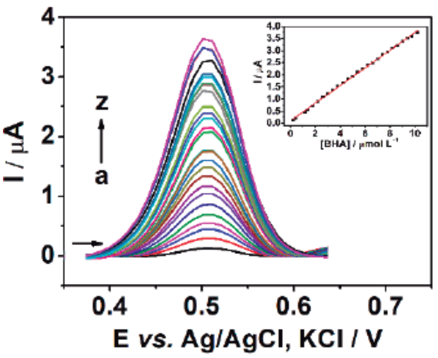

**Fig. 2.** Differential pulse voltammograms obtained with AuNPs-Gr-extract/GCE in B-R solution (0.1 mol $L^{-1}$, pH 4.0) containing different concentrations of BHA. Inset: Calibration plot for the BHA.

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CNPq, FAPESC, Capes, and UFSC.

**Área: ELE**

# Photoactive Gas Diffusion Electrodes in photoreactors for water decontamination and for solar fuels production from $CO_2$ reduction

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Keywords: Gas Diffusion Electrode, Photocatalysis, Oxygen Reduction Reaction, $CO_2$ reduction, solar fuels.

## Highlights

Photoactive Gas Diffusion Electrodes, assembled with different substrates and p-type semiconductors, were used as photocathodes for light-assisted $H_2O_2$ production from $O_2$ reduction and solar fuels production from $CO_2$ reduction.

## Resumo/Abstract

Gas Diffusion Electrodes (GDEs) have been considered an interesting approach for electrochemical reactions involving gases as reactants.[1] We have been investigating photoactive GDEs for $CO_2$ and $O_2$ reduction reactions (CO2RR, ORR) using p-type semiconductors and different porous conductive structures such as commercial carbon paper, graphite sintered with PTFE and also non-woven tissue with exfoliated and reassembled graphite. Photoactive GDEs prepared with the multiphasic $Ag/AgBiW_2O_8/Bi_2WO_6$ (Ag/ABW/BW), a photocatalyst for $H_2O_2$ production from ORR,[2] were used in a photoreactor for remediation of amoxicillin (AMX) aqueous solution. The GDE|Ag/ABW/BW photocathode under air flow (21 % of $O_2$) was associated with an FTO|$TiO_2$ photoanode and externally connected with a silicon solar cell (Fig. 1a). After 3 h under irradiation, 53% of AMX was degraded while with a bare GDE the AMX removal was 30%. Smaller values (< 15%) were obtained using GDE|Ag/ABW/BW under $N_2$ flow or with Pt as cathode, since these configurations preclude the $H_2O_2$ production from ORR. We are also investigating photoactive GDEs for application in a solar-driven electrolyzer to produce value-added chemicals from CO2RR (Fig.1b). Promising results were obtained using $Cu_2WO_4$ as photocatalyst[3] in irradiated GDEs under $CO_2$ flow and Pt counter-electrode in $NaHCO_3$ aqueous solution. Under E = -0.25 V (vs Ag/AgCl), the GDE|$Cu_2WO_4$ exhibited more intense cathodic photocurrent than the bare GDE (Fig. 1c). After 2 h, the GDE|$Cu_2WO_4$ produced ethanol and methanol (70 % of Faradaic Efficiency), while any product from CO2RR was identified in the electrolyte used with the bare GDE. Thus, photoactive GDEs can be used as cathodes in solar-driven photoreactors for water remediation and for solar fuels production from CO2RR.

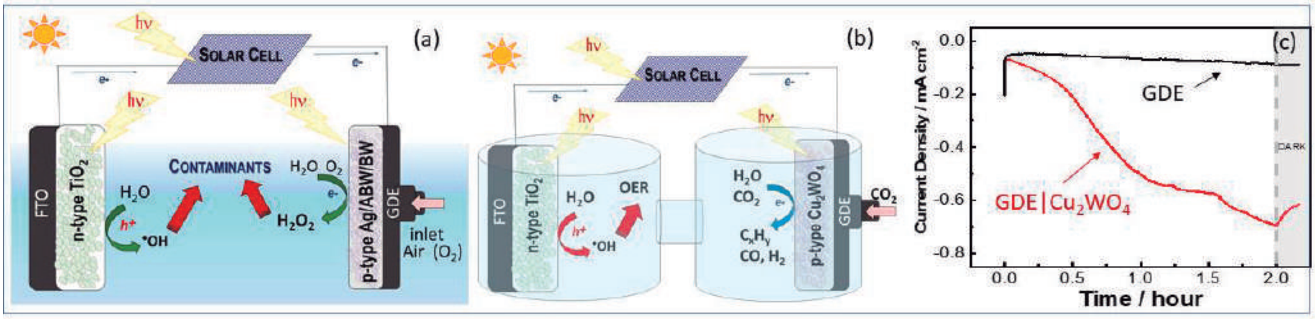

Fig. 1. Photoreactors for solar water remediation (a) and for $CO_2$ reduction (b) assembled with gas diffusion electrodes; electrolysis for CO2RR with irradiated GDE and GDE|$Cu_2WO_4$ under $CO_2$ flow at E = -0.25 V (vs Ag/AgCl) in aqueous $NaHCO_3$ solution (c).

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## Agradecimentos/Acknowledgments

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**Área: ELE**

# Photoelectrochemical conversion of glycerol aqueous solution to hydrogen and value-added chemicals using bismuth ferrite as photoanode

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Palavras Chave: Clean hydrogen, Glycerol, Water splitting, Bismuth ferrite

## Highlights

- Valuable chemicals from glycerol photo-electrooxidation and clean hydrogen are produced at the same time;
- Better PEC performance was achieved in alkaline media;

## Abstract

Replacement of oxygen evolution reaction by biomass derivatives is considered a favorable approach for photoelectrochemical (PEC) water splitting. With increase in global biodiesel production and consumption, efficient utilization of glycerol, which is one of its subproducts, becomes a necessary and highly profitable market. Glycerol has many oxidation products, like 1,3-dihydroxyacetone (DHA), formic acid, glycolic acid, glyceric acid, etc. In this work, we proposed the utilization of bismuth ferrite ($Bi_2Fe_4O_9$) as photoanode to promote the photoelectrochemical conversion of aqueous glycerol solution under different pHs to more value-added chemicals and clean hydrogen. $Bi_2Fe_4O_9$ thin films were prepared using chemical solution deposition (CSD) method. Photoelectrochemical tests were performed under AM1.5G irradiation (100 mW $cm^{-2}$). A three-electrode cell was used with a potentiostat/galvanostat (μAutolab III). The working electrode (WE) consisted of a $Bi_2Fe_4O_9$ photoanode, while the counter electrode was a Pt foil and the reference electrode was a Ag/AgCl 3M. HPLC measurements were performed in a Shimadzu LC-6AD chromatograph. The mobile phase was 0.5 mM $H_2SO_4$ with a flow rate of 0.6 mL $min^{-1}$, and the injection volume was 30 μL. The accumulation of hydrogen was measured via gas chromatography on an HP 6890 gas chromatograph equipped with a thermal conductivity detector (TCD) and Agilent CarboPLOT P7 column using $N_2$ as the carrier gas. In alkaline medium, we observed a higher photocurrent, larger number of glycerol oxidation products (glyceric acid, formic acid and glycolic acid) and greater amount of hydrogen produced. In neutral medium we did not observe any glycerol oxidation products or hydrogen formation. In acidic medium, we observed lower concentrations of hydrogen generated and less glycerol oxidation products (lactic acid and dihydroxyacetone). This strategy, in addition to making biodiesel more competitive and sustainable, also increases the efficiency of hydrogen production.

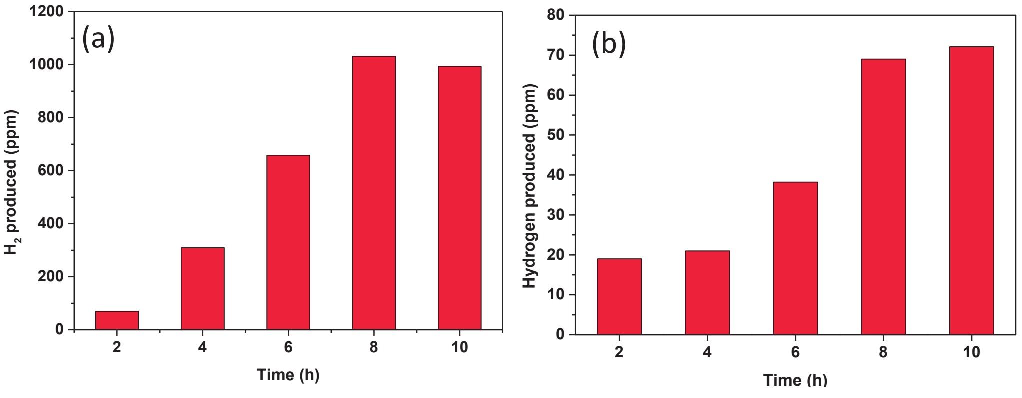

Figure 1. **Hydrogen produced in (a) alkaline medium and (b) acidic medium.**

## Acknowledgments

**Área: ELE** **Nº de Inscrição: 00830**

# Photoelectrochemical properties under ultraviolet light of a metal-organic framework structure based on cobalt obtained by precipitation synthesis

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Keywords: *Electrochemical properties, Metal-Organic Frameworks, MOF-Co, Precipitation method, Terephthalic acid, UV light.*

## Highlights

MOF-Co was easily synthetized by precipitation method. Its present very good electrochemical properties showing a high photocurrent under UV light.

## Abstract

Metal-Organic Frameworks (MOF) has attracted the attention of may researches once it has particularly properties. They are structurally based on the presence of a metal ion or clusters joined by an organic ligand in a highly ordered structure[1]. Its main characteristics are in its versatility and in its excellent physical-chemical properties, such as a high adsorption capacity, gas storage and catalytic activity, in addition to being able to present a semiconductor behavior[1,2]. In this work, a new MOF was obtained from the organic ligand terephthalic acid and Co(II) ions, giving rise to MOF-Co. The simple method used is based on a precipitation reaction at room temperature, with an environmentally harmless solvent with high yield[2]. Initially, the pH of the aqueous solution containing the organic ligand (in this case, terephthalic acid) was neutralized, followed by the mixture of the metallic precursor ($Co(NO_3)_2$). After 24 hours of stirring, the sample was centrifuged, washed with milli-Q water and taken to an oven for 15 hours at 100 ºC under vacuum, for the MOF activation step. Subsequently, the solid sample was characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and diffuse reflectance. Then, a photoelectrode of the material was constructed using the drop-casting method (5 layers of 20 µL each), on conductive ITO glass. As electrochemical characterization, cyclic scanning voltammetry (CV) and chronoamperometry ($Na_2SO_4$ 0.1 mol $L^{-1}$) techniques were used. With the DRX and FTIR techniques it was possible to prove the formation of MOF-Co, where the metalorganic framework is built by the interaction of the metal ion with the carboxyl groupings present in the acid structure, giving rise to a material with a low band gap, 2.09 eV (Fig. 1). The results of chronoamperometry (Fig. 2) and CV (Fig. 3), indicated excellent photoelectrochemical performance with a high current density when irradiated with UV light and by the application of +1.4 V potential. With chronoamperometry it was possible to observe a low tendency for electron recombination of the electron/hole pair, $h^+/e^-$, during electronic excitation with UV light, indicative of the excellent photoelectrochemical response of the material. From the CV, as the anodic scan progresses, (more positive potential values), an increase in the photoinduced current is observed, behavior typical of n-type semiconductor materials. Thus, with this work it was possible to demonstrate how a simple and inexpensive route for the preparation of MOFs can be used to obtain a material with electrochemical properties comparable to that of other materials commonly used, such ZnO, $BiVO_4$ and $TiO_2$ semiconductors.

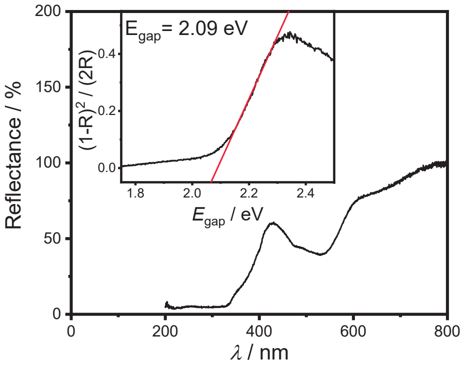

**Figure 1** – Diffuse reflectance spectra for MOF-Co obtained by precipitation method.

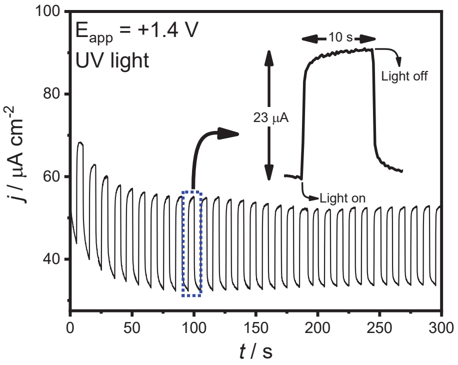

**Figure 2** – Effect of the electronic excitation with UV light on ITO/MOF-Co electrode.

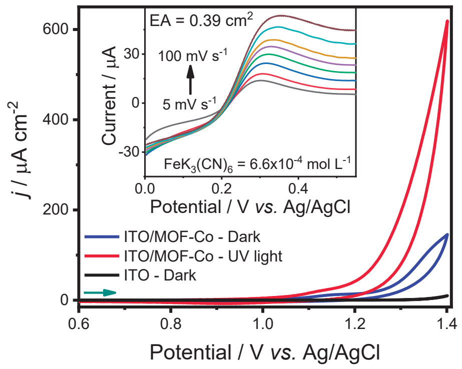

**Figure 3** – Cyclic voltammetry at different conditions. Insertion: electroactive area (EA) determination.

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[2]Ma, Z. et al. *J Mater Sci Technol.* **2019**, 35, 2132-2143.

## Acknowledgments

The authors thank the Fundação Araucária (38.647/12) and CNPq (465389/2014-7) for financial support. L.P.C. thanks to Capes for the Master scholarship. The authors would like to thank LMEM-UEL, LARX-UEL and LABSPEC-UEL.

**Área: ELE**

# Portable photoelectrochemical system for on-site clinical diagnostic

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Keywords: *Photoelectrochemical sensing, immunosensor, carbon nitride, $TiO_2$, prostate-specific antigen, 3D printed device.*

## Highlights

A miniaturized system for photoelectrochemical sensing was developed and applied for the prostate-specific antigen detection. This device can be used for photoelectroanalysis of other biomolecules.

## Abstract

Photoelectrochemical biosensing is a sensitive and low-cost analytical approach for use in clinical diagnosis[1,2]. Its main limitation is the use of high-power irradiation sources, which makes portability and application at the point of care impossible. In this work, we present a portable photoelectrochemical system that operates with a light-emitting diode (LED, 3 W) and is compatible with screen-printed electrodes. The system shown in Figure 1A was used for photoelectrochemical sensing of prostate-specific antigen under visible light (410 nm). The screen-printed electrodes were coated with nickel-graphitic carbon nitrides (Ni-$gC_3N_4$), titanium dioxide nanoparticles ($TiO_2$), and aryl diazonium salt. Aryl diazonium electrodeposited on Ni-$gC_3N_4$/$TiO_2$ decreased the recombination of photogenerated charge carriers, leading to a 3.1-fold increase in photocurrent compared to $TiO_2$, as shown in Figure 1B. This functionalization strategy also provides carboxylic groups to anchor antibodies through the carbodiimide bond, which can be extended to any other type of immunosensor. Under optimal conditions, the PEC immunosensor was able to detect PSA in human serum from $10^{-16}$ to $10^{-8}$ g mL$^{-1}$ with a limit of detection 0.06 fg mL$^{-1}$. The device can be used with any type of electrode modified to function as photoelectroanalytical (bio)sensors.

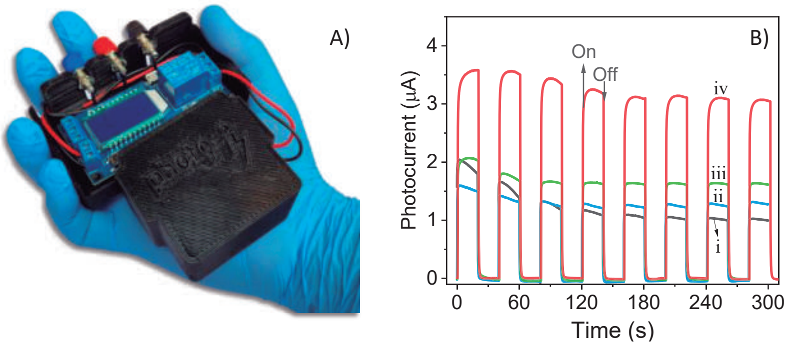

Figure 1. (A) Photoelectrochemical system. (B) Photocurrent curves for (i) $TiO_2$, (ii) $gC_3N_4/TiO_2$, (iii) $Ni_{10}$-$gC_3N_4/TiO_2$ and (iv) Amb/$Ni_{10}$-$gC_3N_4/TiO_2$ in PBS solution (pH 7.4) with 0.1 M AA at 0 V (vs. OCP).

Reference: [1]Low, S. S.; et al. TrAC Trends Anal. Chem. 2021, 145, 116454. [2]Wang, J.; Liu, Z. TrAC Trends Anal. Chem. 2020, 133, 116089.

## Acknowledgments

The authors are grateful for the financial support from the Brazilian agencies: São Paulo Research Foundation (FAPESP) (grants: 2018/22214-6, 2019/13514-9, 2019/01777-5, 2019/00101-8), CAPES (Finance Code 001, grant number 88887.334689/2019-00), and CNPq.

**Área: ELE**

# Potential bioreductive alkylating naphthoquinones: electrochemical and spectroelectrochemical investigation

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Keywords: *Cyclic Voltammetry, Reductive Elimination, Naphthoquinones, Quinonemethides, Redox Mechanism.*

## Highlights

The rationalization of the reduction mechanism of naphthoquinone derivatives shows the formation of quinone methides (QMs). The use of electrochemical techniques in medicinal chemistry is exemplified.

## Abstract

Quinone methides (QMs) are formed from either an direct 2-electron oxidation of 2- or 4-alkylphenols, by isomerization of *o*-quinones, or elimination of a good leaving group[1]. The action mechanisms of several drugs involve QMs formation, as key intermediates[2]. Three mono or dihalogenated naphthoquinone derivatives were studied electrochemically by cyclic voltammetry and differential pulse voltammetry in protic (acetate buffer, pH 4.21 + dimethylformamide, 20%) and aprotic (dimethylformamide + tetrabutylammonium hexafluorophosphate 0.1 mol $L^{-1}$) media, using glass carbon electrode (GCE) as working electrode, in order to obtain data regarding their reduction mechanisms. The complex voltammograms (Fig. 1) showed that reductive elimination, an EC type mechanism, which occurs after the reduction of quinone to a semiquinone radical anion, leading to the formation of the transient electrogenerated *ortho*-quinone methide (*o*-QM) (Fig. 3), a highly electrophilic species and that is capable of inducing cytotoxic and possibly cytoprotective responses *in vivo*, depending on the cell environments[1]. These electrogenerated intermediates were confirmed by in situ spectroelectrochemistry (Fig 2). To prove QMs generation is essential for the elucidation of the biological action mechanism of these compounds.

Figure 1 - Several inversion potentials in the CV of monohalogenated naphthoquinone in DMF + $TBAPF_6$ (0.1 mol $L^{-1}$), GCE, cathodic direction, $\nu$ = 100 mV $s^{-1}$.

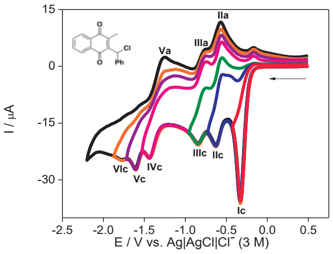


Figure 2 - *In situ* UV-vis spectroelectrochemistry in aprotic media.

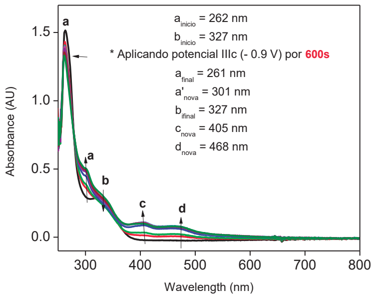
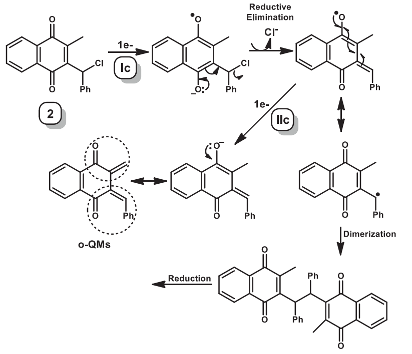


Figure 3 - Proposed mechanism for the reduction of compound 2.



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## Acknowledgments

FAPEAL, CNPQ, CAPES and INCTBIO.

**Área: ELE** **Nº de Inscrição: ________**

# Preparation of biochar from spent coffee grounds and its evaluation for lead ions determination.

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Keywords: Carbon paste modified electrode, *Spent coffee grounds, Biochar, Lead, Voltammetry.*

## Highlights

Biochar is a carbonaceous material has functional groups on its surface, which is very interesting from an analytical point of view because of its ability to adsorb inorganic compounds, like lead.

## Abstract

Biochar is a material that has received great attention due to its high capacity to pre-concentrate different species of interest. Chemical treatment can be used to improve adsorptive capacity of biochar towards metal ions when compared to biochar precursor. This enhancement is related to the increase of functional groups on the material surface. In the present work, biochar samples were prepared from spent coffee grounds at 300ºC and activated in nitric acid reflux. After, this material has been characterized and used as modifier for construction of carbon paste modified electrodes (CPME) aiming to development of an analytical method to lead ions determination. Modified carbon paste electrode with activated biochar (CPME-ACfB300) was evaluated in the spontaneous pre-concentration of lead ions and the voltammetric signal obtained was compared to the electrode unmodified (CPE) and modified with biochar without treatment (CPME-CfB300) (Fig 1A). It is possible to observe that there was the presence of well-defined faradic signals for CPME-ACfB300, indicating that the activation of the biochar surface contributed to the pre-concentration of lead ions on the electrode surface. After verifying the efficiency of the proposal, the most appropriate experimental conditions for the determination of lead were investigated and chosen, being possible to obtain an analytical curve (Fig 1B) with linearity from 0.01 to 2.44 µmol $L^{-1}$ (B), with limit of detection (LOD) and quantification (LOQ) of $4.5 \times 10^{-9}$ and $1.5 \times 10^{-8}$ mol $L^{-1}$, respectively. Finally, it was possible to perform the determination of lead in real samples, such as gunshot residues in simulated targets and hair dyes. Standard addition curves were performed for both samples, with 114 g $cm^{-2}$ of lead being determined in the simulated targets, showing an error of 8.8% in relation to the GFAAS comparative method, while for the hair dye sample, 0.0154 lead%, value in accordance with the specifications of the legislation (<0.6%).

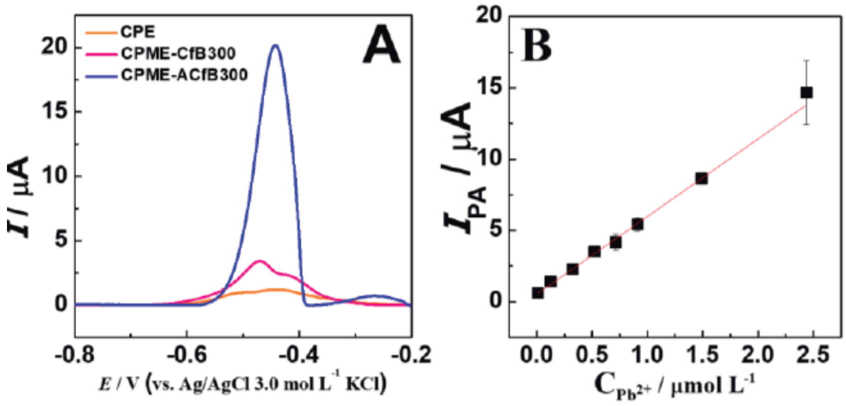

Fig 1: **(A)** DPV results recorded for CPE (orange line), CPME-CfB300 (red line) and CPME-ACfB300 (blue line) in buffer solution (absence of lead ions) after spontaneous accumulation step in presence of 5.0 µmol $L^{-1}$ of $Pb^{2+}$ (5 min). **(B)** Analytical curve obtained for CPME-ACfB300 using optimized set of experimental conditions.

## Acknowledgments

CAPES, CNPq and UFPR.

**Área: ELE**

# Printed immunosensor chip for label-free monitoring of 25-hydroxyvitamin D3 metabolite

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Keywords: *Electrochemical biosensor, Flexible, Disposable, Tree-like gold nanostructures,Vitamin D, On-site monitoring.*

## Highlights

- Immunosensor chip developed to monitor vitamin D, a nutrient relevant to the immune system.
- Detection performed on the immunosensor chip using a 100 μL sample volume.

## Abstract

The COVID-19 pandemic has highlighted the need to monitor nutrients relevant to the immune system and that provide protection against disease and pathogens. Vitamin D intake was particularly encouraged for its benefits: (i) absorption and regulation of calcium and phosphorus, (ii) functioning of muscles and brain cells, (iii) aid to the immune system, and (iv) in fighting viruses and bacteria [1]. The 25-hydroxyvitamin D3 metabolite is the most abundant form of vitamin D in the body because it has a longer half-life, and therefore an individual's vitamin D level is quantified through its detection [2]. In this work, we report a label-free flexible immunosensor chip with gold dendrite nanostructures, electrochemically formed by the selective desorption of L-cysteine on the (111) planes of gold. Electrochemical synthesis was used as it is cost-effective and allows for large-scale production of Au dendritic structures directly on the detection chip. The results of field emission gun–scanning electron microscopy and cyclic voltammetry show that electrocrystallization was easily manipulated by controlling the deposition potential and the molar ratio between $HAuCl_4$ and cysteine. The chip with the largest electroactive area was prepared with 1:40 $HAuCl_4$ to cysteine at −0.8 V for 900 s. Polarization modulation-infrared reflection-absorption spectroscopy and electrochemical impedance spectroscopy data confirmed the effective immobilization of antibodies and their interaction with the metabolite. The 25-hydroxyvitamin D3 metabolite was detected within 15 min in a linear range from 0.1 to 900 ng $mL^{-1}$ with a detection limit of 0.03 ng $mL^{-1}$. The detection of the metabolite was also performed in human serum and saliva samples with adequate recovery between 97 and 100%. The immunosensor chip also showed excellent reproducibility and stability, with RSD 3.7 and 0.7%, respectively. This performance in terms of detection limit and linear range is suitable for monitoring vitamin D, as the detection range of the immunosensor presented here is within the values of clinical interest.

References

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[2] N. Heureux, Vitamin D Testing—Where are we and what is on the horizon? (2017).

## Acknowledgments

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**Área: ELE**

# Reduced graphene oxide-based carbon paste sensor for voltammetric determination of 17α–ethinylestradiol in waste samples, tablets and synthetic urine

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Keywords: *Electrochemical sensor; Emerging pollutant; Hormone; Contraceptive; Estrogen.*

## Highlights

The modified sensor with reduced graphene oxide showed high sensitivity for direct detection 17α– ethinylestradiol. The proposed method presented LOD = 6.79 nmol $L^{-1}$ and LOQ = 22.60 nmol $L^{-1}$.

## Resumo/Abstract

The following study reports the development of modified electrode with reduced graphene oxide (ErGO) for the voltammetric determination of 17α–ethinylestradiol (EE2). These compounds can be highly dangerous to human health and the environment, even at ppb and ppt concentrations. The endocrine disruptors are substances having the ability to alter the functions of the human endocrine system and other organisms For the synthesis, powdered graphite and $KMnO_4$ were mixed in the proportion 1:3 (w:w) and the resulting mixture was put in an ice bath. 100.00 mL of sulfuric acid 98.1% was added dropwise, under constant stirring for 1 h. The product was removed from the ice bath and 400.00 mL of ultrapure water was added, under vigorous stirring. The solution was taken to the glycerin bath at 90 °C for 1 h under constant stirring. The product obtained was washed 3 times with ultrapure water and centrifuged for 5 min at 4000 rpm. The reduction of graphene oxide (GO) with ascorbic acid was performed by adding GO:ascorbic acid 1:10 (w:w) in 50.00 mL of ultrapure water. The suspension was kept under constant agitation for 48 h at room temperature. The suspension was centrifuged for 5 min at 4000 rpm and the rGO obtained was dried in an oven at 60 °C for 11 h. The CPEs were constituted by graphite and mineral oil (6.5:3.5)% (w:w). ErGO was composed of graphite, mineral oil and rGO in different proportions (2.5%, 5.0%, 7.5%, 10.0%, 15.0%, 20.0% and 30.0%). The mineral oil proportion remained constant. The mass variations were made in the graphite portion. The electrodes were macerated for 20 min with mortar and pestle. A homogeneous paste was obtained and inserted into a polypropylene tube ($\Phi_{int}$ = 4.8 mm), and the electrical contact was established through the insertion of a copper wire ($\Phi_{int}$ = 3.0 mm). At the end of each analysis, the surface renovation was made by hand-polishing on filter paper. The physicochemical characterizations of the synthesized rGO demonstrated properties similar to those observed in the literature.The TEM image of rGO shows few overlapping sheets, as well as a rough and transparent appearance. The SEM image shows a morphology with spaced separate structures. Those structures result from the decrease of functional groups generated in the reduction process, which weakens intermolecular interactions.In the FTIR spectra, a band referring to C=C of carbon *sp*$^2$ was observed. The UV-Vis characterization showed the presence of the most intense π-π* band transitions. The modified electrode with rGO (ErGO) demonstrated higher electroanalytical sensitivity for the EE2 detection when compared to unmodified electrode (CPE). Under optimized conditions, an analytical curve was generated for the sensor, which presented a linear dynamic range (LDR) from 0.04 to 8.28 μmol $L^{-1}$ ($R^2$ = 0.9999), with limit of detection (LOD) of 6.79 nmol $L^{-1}$ and limit of quantification (LOQ) of 22.60 nmol $L^{-1}$. ErGO15% was used to determine EE2 in wastewater, tablets, and synthetic urine samples with recovery values between 94.8% and 110.1%. The results obtained with ErGO15% show that the developed sensor can be used for the identification and quantification of EE2 in several matrices, due the excellent analytical performance presented. The electroanalytical methodology proposed was applied for EE2 determination in wastewater using the standard addition method by adding aliquots of spiked wastewater with EE2. Recovery levels obtained in this study were ranged from 92.53 to 111.29%, which demonstrates the ability of ErGO15% to detect EE2 in concentrations close to those added. For the determination of EE2 in synthetic urine and commercial contraceptives pills, the interpolation method of the analytical signal on the linear regression equation previously obtained was used. Recovery values between 94.80–104.00% were obtained for spiked synthetic urine sample, and 102.86 % for pills. The sensor was successfully applied for the EE2 determination in wastewater, synthetic urine, and tablets samples, where satisfactory recovery results were obtained. In view of the results obtained, the sensor demonstrated excellent electroanalytical characteristics for the detection of EE2, thus contributing to the studies of this emerging contaminant in several matrices.

## Agradecimentos/Acknowledgments

CNPq, CAPES, PETROBRAS, FAPITEC, Center of Chemistry Laboratories Multi-Users at UFS (CLQM), Corrosion and Nanotechnology Laboratory (LCNT), Sergipe Regional Competence in Oil, Gas and Biofuels (NUPEG), Associação Sergipana de Ciência (ASCi).

**Área: ELE**

# Removal of Bisphenol S via Photo electro-Fenton/$H_2O_2$ using modified gas diffusion electrode

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Palavras Chave: Bisphenol S*, Electrochemical Advanced Oxidation Processes, Photo electro-Fenton, Hydrogen Peroxide*

## Highlights

Cobalt-modified carbon-based GDE produced accumulated $H_2O_2$ value of 333 mg $L^{-1}$ via 2-electron oxygen reduction reaction.

The higher efficiency of bisphenol S degradation was Photo electro-Fenton/$H_2O_2$ reaching a mineralization rate of 80% in 360 min.

The residual organic matter was identified as short chain carboxylic acids.

## Resumo/Abstract

Bisphenol-S (BPS) is used as a substitute for bisphenol-A because of its excellent stability at high temperatures and resistance to sunlight [1]. Significant concentrations of BPS have been increasingly identified in surface water, groundwater, sewage and drinking water; In view of this, there have been growing concerns about the toxic effects of BPS on humans, animals and the environment [1]. The present work reports the application of a Printex L6 carbon-based gas diffusion electrode modified with 5% Co-Porphyrin in the removal of the contaminant Bisphenol S via different electrochemical advanced oxidative processes (EAOPs). The modified GDE with 5% Cobalt-Porphyrin allowed an electrochemical production of $H_2O_2$ from the oxygen reduction reaction (ORR) of 333 mg $L^{-1}$ in only 90 min, which represents 88% more generation of $H_2O_2$ compared to unmodified one. The investigated EAOPs techniques showed an increase in the kinetic rate constant of degradation in the following order: anodic oxidation (0.004 $min^{-1}$) < UV-C only (0.006 $min^{-1}$) < $H_2O_2$ (0.008 $min^{-1}$) < $H_2O_2$/UV -C (0.016 $min^{-1}$) < electro-Fenton (0.063 $min^{-1}$) < photo electro-Fenton (0.154 $min^{-1}$). The BPS was completely removed via the photo electro-Fenton (PEF) process after only 30 minutes of treatment and a value of ~80% mineralization was recorded after 360 minutes of treatment. Six aromatic BPS-derived intermediates were identified, the two main ones being: 4-(4-hydroxybenzene-1-sulfonyl)benzene-1,2-diol and 3,4-dihydroxy benzene-1-sulfonic acid, which were formed via attack of •OH, by hydroxylation. Our results show that after the formation of these two by-products, ring opening is the subsequent step of our proposed mineralization of BPS by PEF degradation with the production of short-chain acids, such as formic, acetic and oxalic acids. These results help confirm the excellent BPS decontamination efficiency via the PEF technique.

[1] Cordeiro-Junior, P.J.M.; Martins, A.S.; Pereira, G.B.S.; Rocha, F.V.; Rodrigo, M.A.; Lanza, M.R.V. Bisphenol-S removal via photoelectro-Fenton/$H_2O_2$ process using Co-porphyrin/Printex L6 gas diffusion electrode. **Separation and Purification Technology**, v. 285, p. 12299, 2022.

## Agradecimentos/Acknowledgments

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**Área: ELE**

# Simple and fast batch injection analysis method for monitoring diuron herbicide residues in juice and tap water samples using reduced grapheme oxide sensor

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Keywords: *Diuron, Herbicide, Batch injection analysis, Reduced graphene oxide sensor, Tap water, Juices food analysis*

## Highlights

First report of a batch injection analysis for monitoring diuron. Fast and sensitive method for diuron quantification. Good precision, accuracy and low limit of detection.

## Abstract

In this work, a new analytical method was developed using batch injection analysis with amperometric detection and reduced graphene oxide modified glassy carbon (GCE/rGO) electrode for the simple, fast, sensitive, and effective diuron (DIU) herbicide determination in tap water and food beverages (whole juice of grape and orange) samples. The GCE/rGO sensor provided a 7.6-fold increase in the DIU electrochemical oxidation current compared to the bare electrode (Figure 1A), which resulted in a method with good sensitivity and detectability. The developed method provided important analytical characteristics for the DIU quantification, such as detection limit of 0.36 μmol $L^{-1}$ (84 μg $L^{-1}$) below the maximum residual limit of U.S Environmental Agency, linear range from 5 to 50 μmol $L^{-1}$ (Figure 1B), good precision (RSD < 3.7 %), and accuracy (recovery levels ranging from 80.8–105.5 %) (Figure 1C). Furthermore, the minimal sample preparation (simple dilution in the supporting electrolyte) associated with a high analytical frequency (150 analyses per hour) stands out. In this sense, the proposed method proves to be an alternative analytical tool for applications in the environmental and food interest samples analysis[1].

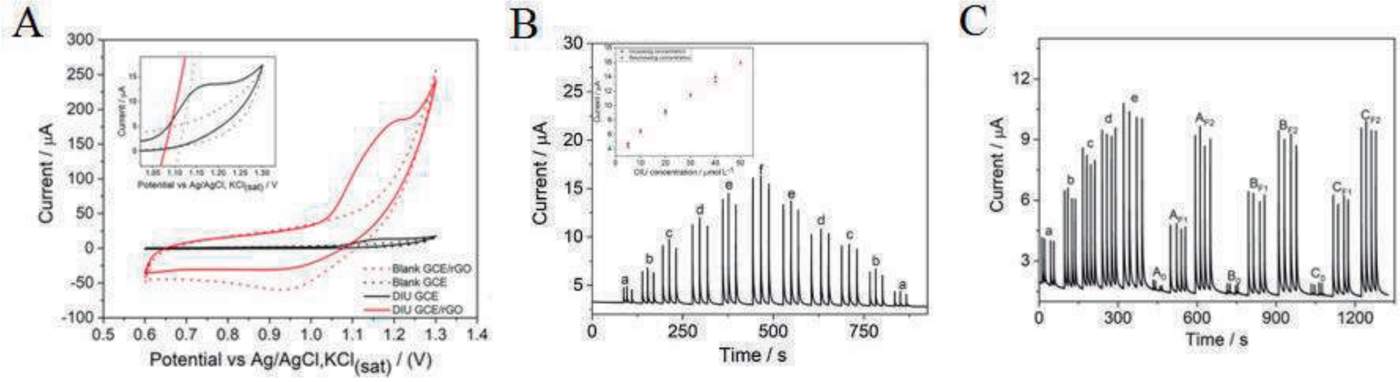

**Figure 1:** (A) Cyclic voltammogram of 312 μmol $L^{-1}$ of Diuron using GCE e GCE/rGO, (B) Calibartion curve for the method developed (a) 5, (b) 10, (C) 20, (d) 30, (D) 40 e (e) 50 μmol $L^{-1}$ e (C) Sample analysis of water, orange and grape whole juice ($A_o$, $B_o$, e $C_o$) and fortified samples in two levels (20 μmol $L^{-1}$ and 40 , μmol $L^{-1}$) respectivelty, of water ($A_{f1}$ e $A_{f2}$), orange ($B_{f1}$ e $B_{f2}$) and grape ($C_{f1}$ e $C_{f2}$) whole juice.

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## Acknowledgements

This research was supported by FAPEMIG (Research Support Foundation of the State of Minas Gerais) (process: APQ-00042-21), CNPq (National Council for Scientific and Technological Development, process: 307271/2017-0), CAPES (Coordination for the Improvement of Higher Education Personnel, financial code 001) and PROPESQ/UFJF.

**Área: ELE**

# Simultaneous determination of carbendazim and carbaryl using a biochar-modified electrode from *Moringa oleifera* pods husks

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*Keywords: Sensors, Carbamates, Voltammetry, Carbon paste electrode.*

## Highlights

- An easy-to-prepare electrode was modified with *Moringa oleifera* pods husks biochar (400 ºC);
- The developed electrode was used in the simultaneous determination of carbendazim and carbaryl.

## Abstract

*Moringa oleifera* (MO) is a plant of great industrial application due to its numerous properties. Recent studies have aimed to use the waste generated (husks and pods) during the process of obtaining seed oil and other products of interest. Due to their characteristics, these residues have potential for application as adsorbents for various organic and inorganic compounds, in addition to water treatment [1]. However, biomass modification processes, such as pyrolysis under specific conditions, are responsible for the formation of a solid carbonaceous material (biochar) with greater stability and functionalization in relation to the precursor biomass, which enhances its applicability, as in the interaction with pesticides, for example, which are chemical agents that need to be constantly monitored in crop environments and regions that may be affected by them, such as water bodies, due to their associated toxicity and potential health risks [2]. In this context, carbon paste electrodes modified with biochar from the moringa pods husks (MOB/E) obtained at 400 ºC were developed, which showed greater detectability (Figure 1) in the simultaneous determination of the pesticides carbaryl (CBR) and carbendazim (CBZ) when compared to the unmodified electrode (CPE). To obtain the data, the methodology of *ex-situ* analysis was used, which consists of carrying out the steps of preconcentration of the analyte and voltammetric measurement in different electrochemical cells, to minimize the effects of concomitant compounds [3]. In order to improve the sensitivity of the proposed electrode, the analysis parameters were optimized, making it possible to apply MOB/E to monitor these species in different matrices.

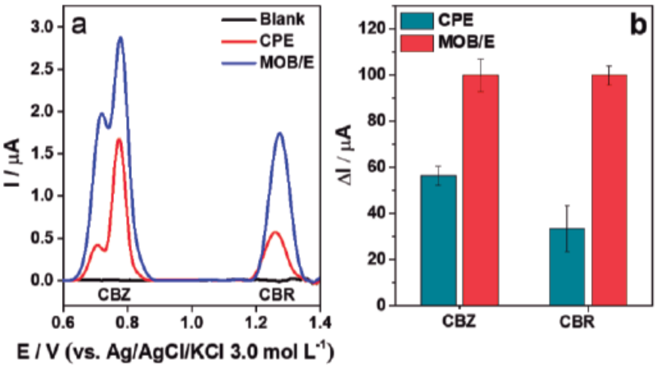

**Figure 1**: **a)** Representative differential pulse voltammograms (corrected baseline) obtained in the absence (blank) and presence of 200 µmol $L^{-1}$ of CBR + 10.0 µmol $L^{-1}$ of CBZ, using the modified electrode (MOB/E) and the unmodified (CPE) in *ex-situ* methodology, applying 1.2V for 15s before preconcentration. **b)** Relative current intensities between the MOB/E and CPE obtained for CBZ and CBR.

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## Acknowledgments

**Área: ELE**

# Study of Carbon matrix modified with benzophenone supported on carbon fiber as gas diffusion electrode for electrogeneration of $H_2O_2$

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Palavras Chave: *hydrogen peroxide electrogeneration, nanomaterial, gas diffusion electrode (GDE), electrocatalysis*.

## Highlights

Gas diffusion electrode (GDE) made of carbon matrix modified with organic compound results in higher efficiency for electrogeneration of hydrogen peroxide in alkaline medium

## Resumo/Abstract

The hydrogen peroxide ($H_2O_2$) is one of the most use oxidants in the advanced oxidated process (AOPs). This oxidant is formed by the oxygen reduction reaction (ORR), where one of the limitations of this reaction is the solubilization of oxygen in the reaction medium [1]. Thus, gas diffusion electrodes (GDE) of carbon matrix appear to overcome this problem due to its triple interface. For this reason, studies on modification of the carbon matrix aiming improvements on the electrogeneration of $H_2O_2$ has growing [2]. In this work, we evaluated the efficiency of $H_2O_2$ eletrogeneration in alkaline ($K_2SO_4$, 0,1 M, pH 11) using an GDE of carbon fiber with carbon Printex L6 unmodified (CPL6) and a modified with 2,0% benzophenone-3, 3, 4, 4, -tetracarboxylic dianhydride (CPL6/BTDA 2,0%). Electrolysis were conducted to both GDEs varying the current density (25, 50, 75, 100 mA/cm$^2$). As result, the GDE CPL6/BTDA 2,0% led to an increase in the $H_2O_2$ production when compared to the unmodified GDE (Figure 1). Thus, the modification brings advances to the carbon matrix, since resulted in more $H_2O_2$ electrogenerated applying the same current density. After that, other parameters were studied: the current efficiency (CE) and the energy consumption (EC) at the different current densities tested on the GDE CPL6/BTDA 2,0% (Figure 2). It's clear to note that both 50 mAcm$^2$ and 75 mAcm$^2$ presented the same current efficiency, but the energy consumption of the 75mA/cm$^2$ was a higher than 50mA/cm$^2$. So, it is possible to conclude that modification of the carbon matrix with the organic compound BTDA was successful and increased the generation of $H_2O_2$. Moreover, 50 mA/cm$^2$ was the most suitable current density in the alkaline medium showing a good CE and a low EC.

**Figure1**- Electrogeneration of $H_2O_2$ at different current densities

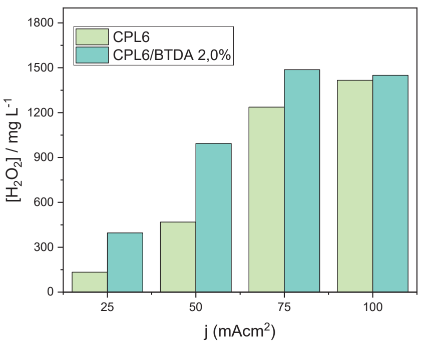
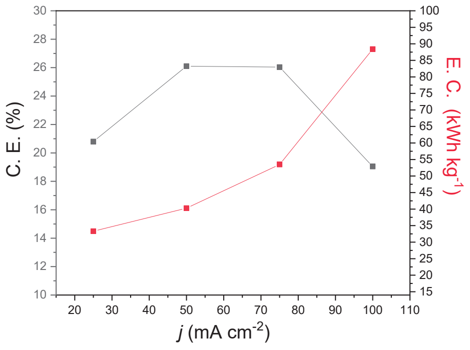


**Figure 2**- Current efficiency (EC) and energy consumption (EC) as a function of current density for GDE CPL6/BTDA 2,0%



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## Agradecimentos/Acknowledgments

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# Sulfur-functionalized graphene by non-thermal plasma process: A novel material with outstanding electroanalytical applications

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Keywords: *Sulfur-functionalized graphene; Plasma-assisted; Gold electrode; TBHQ, BPA.*

## Highlights

A novel graphene-based material was produced by a hybrid gas-liquid non-thermal plasma discharge. Sulfur-functionalized graphene shows strong interaction with gold electrode. An efficient voltammetric method was created to detect tert-butylhydroquinone and bisphenol A simultaneously.

## Abstract

An electrochemical sensor based on a gold electrode modified with sulfur-functionalized graphene was constructed. The graphene modification was carried out using a non-thermal plasma reactor with aqueous phase, which made the graphene sheets more hydrophilic and inserted sulfur in its edges. In what is of particular importance, there are thiol groups (-SH) present in the honeycomb-like structure of graphene. The modified material was hydrophilic and dispersed very well in solvents of high dielectric constant. The sensor was prepared by dripping 3.0 µL of the dispersion onto the surface of a cleaned gold electrode. The strong Au-S bond of graphene material and gold surface makes the modified electrode suitable and stable for electroanalytical applications. The presence of S-Graph facilitated the charge transfer in $[Fe(CN)_6]^{-4/-3}$ (0.1 mol $L^{-1}$ KCl solution) system providing higher current intensities and lower resistance to charge transfer when compared to bare Au electrode. The cyclic voltammograms of tert-butylhydroquinone (TBHQ) and bisphenol A (BPA) at S-Graph/Au in Britton-Robinson (B-R) buffer solution (0.1 mol $L^{-1}$, pH 7.0) showed peaks at −0.03 and −0.06 V, corresponding to reversible oxidation and reduction reactions of TBHQ, respectively, and a peak at +0.47 V, attributed to irreversible oxidation of BPA. However, these processes were not fully seen on the bare Au electrode, which only recorded peaks at +0.22 and +0.53 V, corresponding to oxidations of TBHQ and BPA, respectively, as can be seen in Fig. 1. This phenomenon can be attributed to the high electrical conductivity of graphene which improved the charge transfer in the redox system. The influence of the pH of the supporting electrolyte on the electrochemical reactions of TBHQ and BPA was examined in the pH range of 3.0 to 11.0 using 0.1 mol $L^{-1}$ B-R buffer solution. The highest current intensities were obtained at pH 7.0. In addition, linear shifts of the $E_p$ *vs.* pH plot were observed for all species analyzed with values close to the Nernst theoretical value (−59.2 mV $pH^{-1}$), indicating that the same number of protons and electrons were transferred in each reaction. The electrochemical behavior of TBHQ and BPA at the S-Graph/Au at different scan rates showed that the analyzed reactions were adsorption-controlled processes. In addition, the number of transferred electrons for all species was calculated to be approximately 2. According to the obtained results, it can be considered that the reversible reactions of TBHQ and the irreversible reaction of BPA involved 2 mol of protons and 2 mol of electrons each, as observed in schematic reactions in Fig 2.

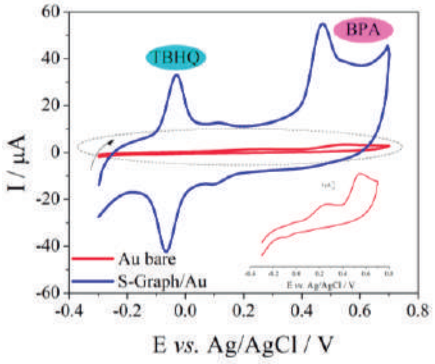

Fig 1. Cyclic voltammograms of 30 µmol $L^{-1}$ TBHQ and BPA using Au bare and S-Graph/Au electrodes in B-R buffer solution, pH 7.0.

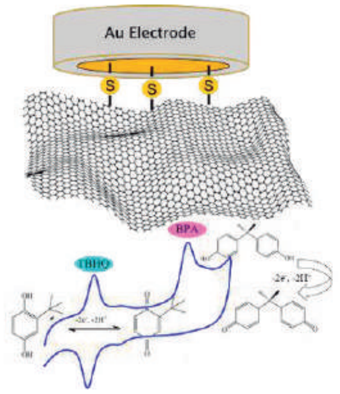

Fig 2. Schematic representation of TBHQ and BPA redox reactions on the surface of S-Graph/Au electrode.

## Acknowledgments

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**Área: ELE**

# Surface electrochemical treatment combined with laser scribing fabrication of paper-based electrochemical sensors for nitrite determination

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Keywords: *Paper substrates, $CO_2$ laser, Disposable sensors, Saliva, Environmental samples, Nitrite.*

## Highlights

Low-cost disposable electrochemical sensors produced on paper with $CO_2$ laser. Electrode surface activation with electrochemical treatment. Nitrite quantification in environmental and saliva samples.

## Abstract

Laser scribing is used to fabricate conductive carbon tracks by carbonizing organic and insulating materials. Paper is inexpensive, disposable, and flexible among the substrates, making this material promising to produce the sensors. Even though the electrochemical system can be easily engineered into different formats, the electrodes typically have low conductivity and slow electron transfer, affecting their analytical signal. As a result, electrochemical treatments have been studied to enhance the analytical performance of electrochemical sensors. A fast and straightforward strategy was developed to fabricate paper-based electrodes using $CO_2$ laser radiation. Different parameters were assessed for the electrochemical treatment, including the supporting electrolyte (acid, neutral and alkaline medium), applied potential, and application time. Ferrocyanide ion was used as an electrochemical probe for characterization studies. A remarkable enhancement in electrochemical responses was observed by applying -1.0 V vs. Ag in 1.0 mol $L^{-1}$ KCl. Under optimum conditions, the analytical performance of the treated sensors was also evaluated for nitrite oxidation, demonstrating significant improvement in the analytical signal (Figure 1A). Consequently, a calibration curve was constructed for nitrite (Figure 1B), and the proposed method was applied to analyze water, soil, and synthetic saliva samples.

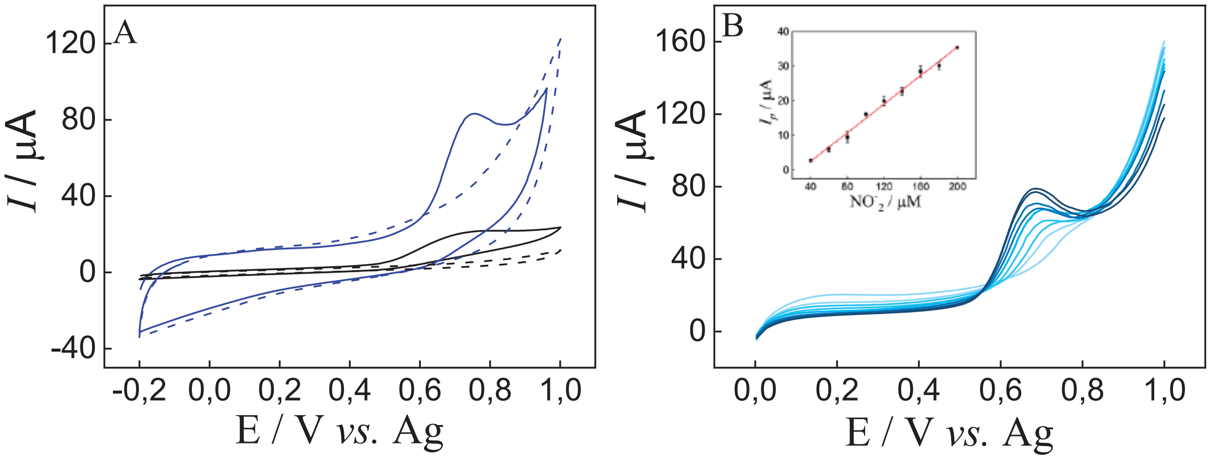

Figure 1 – A) Cyclic voltammograms for untreated (black lines) and treated paperboard-based electrodes (blue lines) recorded in phosphate buffer pH 7 (dashed lines) + 1.0 mmol $L^{-1}$ nitrite (solid lines). $\nu$ = 20 mV $s^{-1}$. B) Linear sweep voltammograms for treated paperboard-based electrodes recorded in phosphate buffer pH 7 with different nitrite concentrations. $\nu$ = 50 mV $s^{-1}$. Insert: calibration curve for nitrite.

## Acknowledgments

São Paulo Research Foundation - FAPESP (2021/00205-8, 2019/15065-7), Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - CAPES (PROEX 88887.341030/2019-00), and Conselho Nacional de Desenvolvimento Científico e Tecnológico - CNPq (140463/2021-6).

**Área: ELE**

# Ternary FeNiS as a bifunctional electrocatalyst for overall water splitting

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Palavras Chave: *hydrogen evolution reaction, oxygen evolution reaction, water splitting, alkaline medium, ternary sulfide materials, electrodeposition.*

## Highlights

Ternary nickel-iron sulfide films via one-step electrodeposition fabrication. Effective electrocatalyst for hydrogen and oxygen evolution reaction in alkaline medium.

## Resumo/Abstract

Hydrogen is a promising efficient and environmentally friendly alternative to traditional fossil fuels owing to its high calorific capacity and the formation of $H_2O$ as a byproduct of the combustion process. Electrochemical water splitting is an easy and eco-way to produce high-purity hydrogen and involves two half-reactions: the hydrogen evolution reaction (HER) in the cathodic compartment and the oxygen evolution reaction (OER) in the anodic side. Since the process suffers from sluggish kinetics, the development of high efficient bifunctional electrocatalysts for both HER and OER, made with abundant and low-cost elements, is highly desirable for practical applications. Transition metal-based materials have been found efficient to catalyze the HER and OER in the overall water splitting. Among them, transition metal sulfides have attracted considerable interest owing to their relatively lower electrical resistivity and the strategy of incorporating additional metal elements is an efficient way to optimize the surface active sites and increase their electroactivity. Based on the all mentioned above, this work shows the development of ternary nickel-iron sulfide films as a bifunctional catalyst for both HER and OER. This material was electrochemically synthesized on Ni foam substrate by cyclic voltammetry (CV), and the effects of precursor solution concentration and the number of cycles (5, 10, and 15 cycles) were studied. The optimized electrodeposition conditions were 10 cycles at 5 mV $s^{-1}$ in 25 mmol $L^{-1}$ $NiSO_4.6H_2O$, 25 mmol $L^{-1}$ $FeSO_4.7H_2O$ in 0.5 mol $L^{-1}$ $(NH_2)_2CS$. These optimized electrodeposition conditions were applied to obtaining FeNiS film on Ni foam substrate. After deposition, DRX, SEM, Raman, and EDX spectroscopies characterized the films. The catalytic activity of the electrode to HER and OER was explored by linear sweep voltammetry at 5.0 mV $s^{-1}$ in 1.0 mol $L^{-1}$ KOH solution. With the resulting polarization curves, the overpotential in 10 mA $cm^{-2}$ ($\eta_{10}$) for HER, 50 mA $cm^{-2}$ ($\eta_{50}$), and 100 mA $cm^{-2}$ ($\eta_{100}$) for OER were analyzed. The deposited film presents a high catalytic activity for both HER and OER processes, Figure 1, with $\eta_{10}$ equal to 164 mV and $\eta_{50}$ and $\eta_{100}$ equal to 280 mV and 300 mV, respectively.

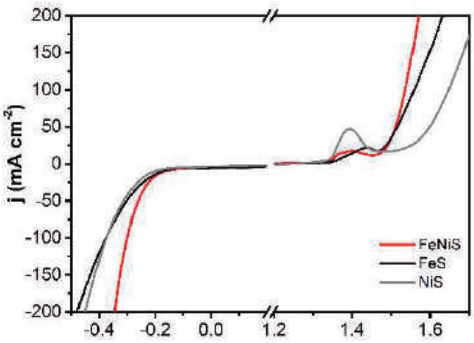

*Figure 1. Comparison of polarization curves for different materials in 1.0 mol $L^{-1}$ KOH at 5 mV $s^{-1}$.*

## Agradecimentos/Acknowledgments

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**Área: ELE**

# THE STUDY OF COMPOSITION OF POLYURETHANE DERIVED FROM CRAMBE OIL IN COATINGS TO PROTECT AGAINST CORROSION

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Palavras Chave: *Corrosão, Espectroscopia de Impedância Eletroquímica, Revestimentos Orgânicos.*

## Highlights

Organic coating based on cramble oil can be applied to aluminum alloy to corrosion protection. PEC2 and PEC4 samples supplied higher resistance against corrosion on NaCl 3.5% solution.

## Resumo/Abstract

Organic coating efficiency depends on the factor like mechanical properties, type and concentration of suspended inhibitors. Six polyurethane coats were obtained mixing prepolymer with hydroxylated polyesters obtained from the polyesterification of crambe oil with phthalic and maleic anhydride, at different proportions are shown in table 1.

Table 1: Molar ratio of compounds present in the coats.

| Sample / material | PEC1 | PEC2 | PEC3 | PEC4 | PEC5 | PEC6 |
|---|---|---|---|---|---|---|
| *Prepolymer* | 1:2 | 1:2 | 1:2 | 1:3 | 1:3 | 1:3 |
| *Crambe Oil* | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |
| *Trimethylpropane* | 3.0 | 5.0 | 5.0 | 3.0 | 5.0 | 5.0 |
| *Anhydride Phthalic* | 3.0 | 3.0 | 2.0 | 3.0 | 3.0 | 2.0 |
| *Anhydride Maleic* | | | 0.5 | | | 0.5 |

These coatings act as an alternative for the corrosion protection of an AA1200 alloy were studied by electrochemical impedance spectroscopy measurements in NaCl 3.5% solution. The measurements were acquired every 24 h until 816 h. The |Z| values at f=10 mHz, 24 and 816 h of immersion time are shown in table 2.

Table 2: The |Z| values at f=10 mHz, 24 and 816 h of immersion time in NaCl 3.5% solution for all samples.

| Sample / Time immersion | Substrate $|Z|$/kΩ cm$^2$ | PEC1 $|Z|$/GΩ cm$^2$ | PEC2 $|Z|$/GΩ cm$^2$ | PEC3 $|Z|$/GΩ cm$^2$ | PEC4 $|Z|$/GΩ cm$^2$ | PEC5 $|Z|$/GΩ cm$^2$ | PEC6 $|Z|$/GΩ cm$^2$ |
|---|---|---|---|---|---|---|---|
| *24 h* | 1.9 | 5.9 | 18 | 2.9 | 1.5 | 1.8 | 2.2 |
| *816 h* | 6.5 | 0.095 | 7.4 | 0.020 | 0.24 | 0.014 | 0.030 |

The total impedance values are on the order of magnitude of GΩ cm$^2$ for all coated samples at 24 h of immersion. Comparing the |Z| values at 24 h and 816 h for PEC1, PEC3, PEC5 and PEC6 samples, it is possible to observe a decrease of 3 orders of magnitude, while PEC4 and PEC2 samples present a smaller decrease behavior (1 order) were observed, indicating high resistance against corrosion. These decreases are related to the deterioration of the coating. The bode diagram phase angle *vs.* log f exhibit a time constant that remains as a plateau from 50 kHz up to 1 Hz at 90 degrees up to 96 h, 312h, 120 h, 288 h and 432 h to PEC1, PEC2, PEC3, PEC4 and PEC5, respectively and from 1 Hz until 10 mHz, the phase angle values decrease to 10º, 30º, 10º, 30º and 30º. The PEC6 sample presents 90 degree throughout the swept frequency range at 24 h of immersion, indicating that the electrolyte does not reach the substrate. After each immersion times, the plateau is separated into 2 times constants, with the maximum at 10 kHz and 1 Hz to sample PEC1; maximum at 0,1 kHz and 0,1 Hz to sample PEC2 and PEC4; maximum at 1 kHz and 1 Hz to samples PEC3, PEC5 and PEC6 (after 24 h). Bode diagram phase angle vs. log f of substrate shows two overlaid time constants, one for the oxide layer on the surface of the alloy and one for the charge transfer resistance and electrical double layer capacitance. For coated samples, the first time constant is attributed to the coating and the second one to the substrate corrosion. Even after 816 h of immersion in NaCl solution, it was not possible to observe the overlap of the peaks indicating that all coatings can protect AA1200 against corrosion. PEC2 and PEC4 samples are the ones that best protect the substrate.

## Agradecimentos/Acknowledgments

The authors thank CNPq, Capes, Fundect and Fapesp for their financial support.

**Área: ELE** **Nº de Inscrição: 809**

# The usage of polyacrylate hydrogel spheres as an electrolytic cell for electroanalytic applications.

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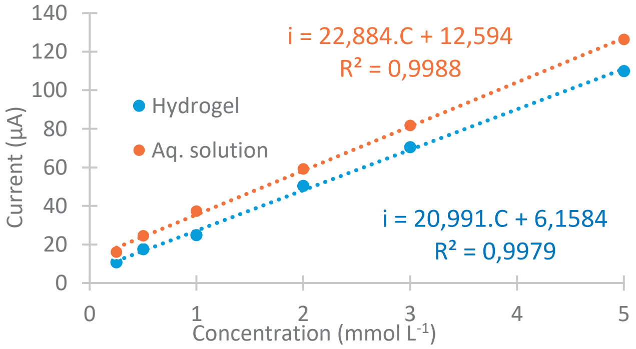
Keywords: *Hydrogel, Electrolytic cell, Cyclic voltammetry, Polyacrylate*

## Highlights

- Cyclic voltammetry studies taken inside the hydrogel showed that the redox reaction is reversible.
- Difusion is the main driving force of mass transfers inside the hydrogel.
- A calibration curve of $K_3[Fe(CN)_6]$ inside the hydrogel was statistically the same as in aqueous solution.

## Abstract

A hydrogel consists of a three-dimensional network of flexible polymers that are capable of absorbing a large amount of water in its swollen state. It can absorb more than a thousand times it's mass in water and it is also biodegradable.[1] These polymers are extensively used at the removal of heavy metals and organic pollutants in water treatments. The higher adsorption capacities in these materials are attributed to the presence of various groups, (such as: -OH, $-NH_2$, $-SO_3H$, -COOH, $-CONH_2$) and the removal of these pollutants is enabled by electrostatic interactions[2]. Therefore, the aim of this work is to show the possibility of using a hydrogel sphere as a electrolytic medium for the determination of metals and molecules by voltammetry. The hydrogel spheres made of polyacrylate were purchased by the commercially brand "Seven color crystal ball". Some parameters were studied such as: type of electrolyte, time of absorption, pH, concentration of both the electrolyte and $K_3[Fe(CN)_6]$ solution (used as a redox pair). It was observed that the best pH value was in the range of 6-8, the selected electrolyte was KCl in the concentration of 0,10 mol.L$^{-1}$ and the best adsorption time was 24h, that led to a constant volume of the sphere. An analytical curve was made using the technique of cyclic voltammetry by sticking a working electrode of graphite, a reference electrode of Ag/AgCl and a counter electrode of stainless steel inside the sphere with the adsorbed ferrocyanide solution in various concentrations. Another analytical curve using the same setup was made in aqueous solution and used as a comparison shown in Image 1. For a better understanding of the electrochemistry process taking place inside the hydrogel, a voltammogram was made by changing the scan rates and it revealed that the process is reversible and diffusional (Image 2). In a nutshell, this study is a proof of concept that voltammetry studies commonly made in aqueous solutions are also possible inside a hydrogel sphere. Moreover, as the studied hydrogel is anionic, it can adsorb cations efficiently. Therefore, it's also possible to preconcentrate an analyte and improve it's detection limits for several cationic species, such as metals and dyes.



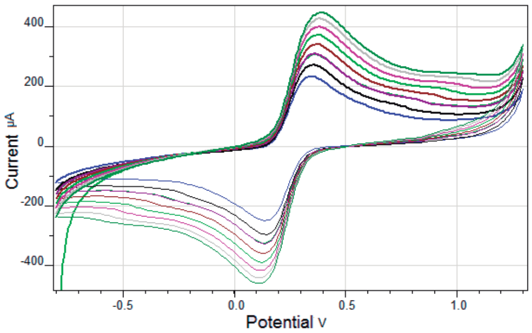


Image 1: Analytical curve in aqueous solution and inside the hydrogel

Image 2: Cyclic voltammogram in various scan rates inside the hydrogel

## Acknowledgments

The authors would like to thank CAPES, UFF and Peter Sorensen Laboratory

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**Área: ELE**

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

# Transition metal phosphide based on Co, Ni, and Fe for overall water splitting

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Palavras Chave: Transition metal phosphide, water electrolysis, NiP, CoP, FeP.

## Highlights

Obtaining CoFeNiP by electrodeposition without phosphidation step and using stainless steel as substrate. The use of this catalyst to alkaline water electrolysis exhibited promising outcomes.

## Resumo/Abstract

Nowadays, the change from fossil fuels to a renewable and sustainable primary source of energy passes through green hydrogen production. However, 96% of the hydrogen is produced by the Steam Methane Reforming process (SMR), which uses fossil fuel as the source, and only 4% is derivative from water electrolysis. During the water electrolysis, electrical power is used to split the water molecule in its components by its reduction on a cathode (where is produced hydrogen) and by its oxidation on an anode (where is produced oxygen). Nevertheless, the water electrolysis is expensive if compared to SMR, once it is necessary noble metals such as Pt, Ir, and Ru as catalysts to make the reactions faster and more efficient. Here, we propose the obtaining of transition metal phosphide catalyst based on Ni, Co, and Fe to its application for overall water splitting. The catalysts electrodeposition was investigated in a factorial planning design $2^5$ with the variables [$Co^{II}$] (0.1 and 0.5 M), [$Fe^{II}$] (0.002 and 0.01 M), [$Ni^{II}$] (0.5 and 1.0 M), current density to electrodeposition – $j_d$ – (-200 and -400 mA/cm²$_{geo}$), and charge of electrodeposition – $Q_d$ – (30 and 100 C/cm²$_{geo}$). Besides, the electrolyte contained 1.0 $NaH_2PO_2$ + 0.5 M $H_3PO_4$, while the electrodeposition was performed under 22 °C using a grade 304 stainless steel as substrate. The catalyst performance was evaluated in 1.0 M KOH at a three-electrode cell with the catalyst as working electrode, a Ni foam (for HER) or Pt mesh (for OER) as auxiliary, and Hg/HgO as reference electrodes. The overpotential to reach |10| and |100| mA/cm²$_{geo}$, $\eta_{10}$ and $\eta_{100}$, respectively, were chosen to evaluate the catalyst performance for hydrogen evolution reaction (HER) and oxygen evolution reaction (OER), without ohmic drop correction. The factorial planning design showed that the most important variables are the $j_d$, [$Co^{II}$], and [$Ni^{II}$] for HER. The $j_d$ had a positive effect at the $\eta_{10}$ and $\eta_{100}$, which means that the higher $j_d$, the higher $\eta_{10}$ and $\eta_{100}$. Regarding [$Co^{II}$] and [$Ni^{II}$] the effect was the opposite, the higher the precursor concentration, the lower $\eta_{10}$ and $\eta_{100}$. Significant interactions were observed to [$Co^{II}$] + [$Ni^{II}$] and [$Co^{II}$] + $j_d$, in which was observed the same negative effect. The lower $\eta_{10}$ (113 mV) and $\eta_{100}$ (189 mV) for HER were achieved by the catalyst electrodeposited at -200 mA/cm²$_{geo}$, with 100 C/cm²$_{geo}$, and electrolyte containing 0.5 M $Co^{II}$, 0.01 M $Fe^{II}$, 1.0 M $Ni^{II}$, 1.0 $NaH_2PO_2$, and 0.5 M $H_3PO_4$. Interestingly, in the OER, only $j_d$ shows a significant effect, which was the same that for HER, i.e., the higher $j_d$, the higher $\eta$. Thus, the best catalyst for OER could be obtained in the same conditions that for HER. We believe that the absence of significant effect of the variables in the OER is due to the oxidation of the catalyst with the formation of metal oxy-hydroxide. In these circumstances, the lowest $\eta_{10}$ and $\eta_{100}$ for OER were 301 and 380 mV. In addition, the catalyst showed stability over 24 hours at |10| mA/cm²$_{geo}$ for both reactions, HER and OER. The estimative to cell voltage in a two-electrode cell is around 1.65 V at 10 mA/cm²$_{geo}$, which is a promising and interesting calculus.

## Agradecimentos/Acknowledgments

FAPESP/Shell grant #2017/11986-5, FAPESP/CDMF grant #2013/07296-2 and grant# 2021/08614-4, Capes, and CNPq.

**Área: ELE**

# Understanding Mixtures of Ionic Liquids for Supercapacitors Improvements

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Palavras Chave: EDLC, Supercapacitors, IL, Ionic Liquids, Storage, Energy

## Highlights

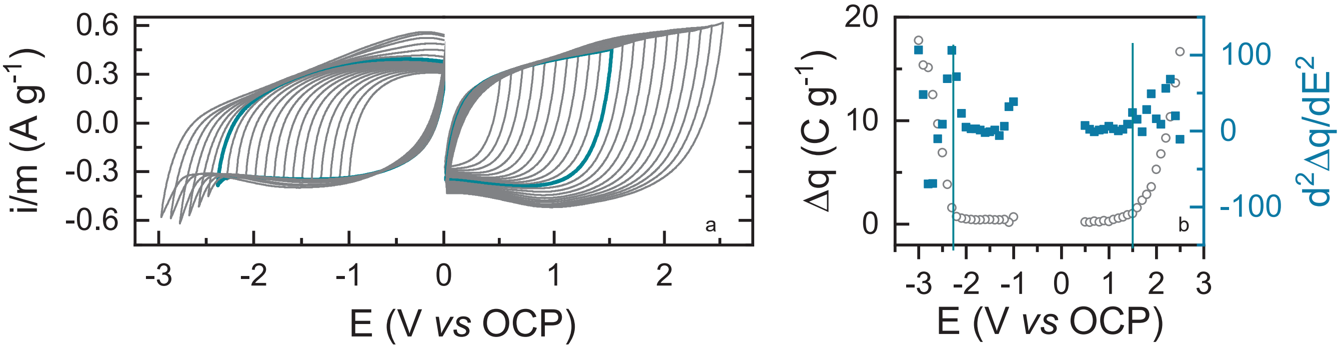
Understanding Mixtures of Ionic Liquids for Supercapacitors Improvements.

The main focus of the project was to select two commercial ionic liquids (Pyr1,4TFSI & Pyr1,4FSI) and choose different proportions for the anions, maintaining the same cation. In this case, the percentages chosen were 25%, 50% and 75%.

Characteristics of both anions were present at the results, showing that the electrolyte can be enhanced depending on the proportions of the ions, increasing stability of the electrolyte, for example.

## Resumo/Abstract

The Electrochemical Double-Layer Capacitors (EDLC) are capable to operate at high voltages for hundreds of thousands of cycles. Studies of these devices aims the same objective: enhance the potency and the energy stored. In this case, there is a need to analyze ways to increase the capacitance and the operating window of the cells. The focus must be given to the main material that the voltage depends: the electrolyte. Many Ionic Liquids (IL) has been and are still being studied with the intention to improve the characteristics mentioned before. IL are liquid salts at room temperature, giving the possibility to work without a solvent and, consequently, increasing the number of free ions at the environment, as well as raising the voltage of the device due the stability of this type of electrolyte.



## Agradecimentos/Acknowledgments

Acknowledgements for my supervisor, Roberto Manuel Torresi; for my college Vitor Lima Martins, that taught me most of what I know about storage devices and helped me during my scientific initiation; for FAPESP and CNPQ, that gave me the opportunity as student to work as a researcher, as well as many other students around the country; and finally, for SBQ to give me the opportunity to present this project.

# FIS

# Físico-Química

**Área: FIS** **Nº de Inscrição: 00185**

# A definição da termodinâmica nos livros didáticos de Ensino Superior: como aparecem?

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Palavras Chave: *Termodinâmica Clássica, Livros Didáticos, Ensino, Enfoque Macroscópico.*

## Highlights

The definition of thermodynamics in higher education textbooks: how do they appear?

The objective of the work was to analyze how the definitions of thermodynamics are expressed in seven textbooks of Higher Education. It was found that most works are based on approaches focusing on the macroscopic aspect.

## Resumo/Abstract

A termodinâmica, como ciência, começou a tomar forma com a publicação de Carnot (1824)[1], desde então houve uma série de avanços nessa ciência e o desdobramento em diversos tipos de termodinâmica, como a termodinâmica dos processos irreversíveis, termodinâmica dos meios contínuos e a termodinâmica clássica, por exemplo. Nessa perspectiva, o intuito desse trabalho foi de analisar e definições da termodinâmica clássica em sete livros didáticos do Ensino Superior[2]: (Atkins (1); Callen (2); Guggenheim (3); Levine (4); McQuarrie e Simon (5); Moran e Shapiro (6); Sonntag, Borgnakke e Wylen (7).

O quadro a seguir apresenta os resultados obtidos das sete obras analisadas.

**Quadro 1:** Análise da definição de termodinâmica dos livros didáticos selecionados

| Livro analisado | Definição de termodinâmica |
|---|---|
| 1 | O estudo das transformações de energia. Leva à discussão quantitativa de todos os efeitos envolvidos e propicia a antecipação deles. |
| 2 | Trabalha apenas com sistemas fechados em equilíbrio, do ponto de vista macroscópico. |
| 3 | Não define, apenas exemplifica onde a termodinâmica pode ser usada. Sempre a relaciona com troca de calor e variação de temperatura. Numa breve discussão, o autor informa que a termodinâmica não estuda a questão do átomo ou molécula, sendo uma ciência do mundo macroscópico. |
| 4 | É uma ciência do mundo macroscópico que estudas as relações entre várias propriedades de um sistema em equilíbrio e as mudanças nessas propriedades, nos processos entre estados de equilíbrio. |
| 5 | Não considera os efeitos de átomos e moléculas, ou seja, não considera o mundo microscópico. Ela estuda as relações entre várias propriedades de um sistema macroscópico em equilíbrio. |
| 6 | Trata basicamente da energia e das relações entre as propriedades da matéria. A termodinâmica clássica faz uma abordagem macroscópica, enquanto que a termodinâmica estatística faz uma abordagem microscópica. |
| 7 | A ciência da energia e da entropia, ou é a ciência que trata do calor, do trabalho e das propriedades das substâncias relacionadas ao calor e ao trabalho. É uma ciência experimental. O autor faz uma discussão sobre os pontos de vista macroscópico e microscópico, mas na obra foi considerado apenas o macroscópico. |

Fonte: Elaborado pelos autores

Pelos dados sumariados no quadro 1 foi possível observar que a maior parte dos livros analisados (2 a 7) propõem uma definição no contexto da termodinâmica clássica, pois apresentam como enfoque a abordagem macroscópica no estudo dos fenômenos e de forma sucinta.

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**Área: FIS** **Nº de Inscrição: 89**

# ANÁLISE TERMOGRAVIMÉTRICA DA INTERAÇÃO ENTRE TIROSINA (TYR) E ARGILA EM ÁGUA DO MAR ARTIFICIAL

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Palavras Chave: Química prebiótica, Argila, Interação, Água do Mar, Origem da vida, Termogravimetria.

## Highlights

Thermogravimetric analysis of the interaction between tyrosine and clay in artificial sea water.

The objective of this work was to evaluate the interaction of (Tyr) with clay by thermogravimetry.

## Resumo/Abstract

A química prebiótica é um ramo da ciência que investiga as reações que podem ter levado ao surgimento de vida na Terra. Conjunta-se que minerais podem ter desempenhado um importante papel em reações químicas prebióticas. Na Terra prebiótica, aminoácidos podem ter adsorvido na superfície de minerais, podendo ter sido essa uma condição determinante para a evolução molecular. A fim de avaliar essa hipótese, o objetivo desse trabalho foi avaliar a interação do aminoácido tirosina (Tyr) com a argila montmorilonita utilizando a termogravimetria.

O aminoácido Tyr foi dissolvido em água ultrapura (AU) e em água do mar artificial (AMA) de 4,0 bilhões de anos proposta por Silva e Carneiro (2020), na concentração de 450 μg mL$^{-1}$. Para cada ensaio, 500 mg de montmorilonita foram adicionadas em tubos Falcon (15 mL) contendo separadamente 9 mL de (a) AU ou AMA; (b) AU ou AMA com 450 μg mL$^{-1}$ de Tyr. Os ensaios foram feitos em triplicata. As amostras foram agitadas por 24 h, em temperatura ambiente (~25 °C) e em seguida centrifugadas durante 15 minutos a 3000 rpm. O sobrenadante foi utilizado para quantificação do aminoácido e o sólido foi liofilizado para ser usado nas análises termogravimétricas.

O perfil térmico da argila no sistema com Tyr em AU e AMA mostrou que para a argila pura, verificou-se um primeiro evento de perda de massa em 80°C, um segundo em 100°C, característicos de perda de água de hidratação, adsorvida na superfície da argila. Outro evento ocorreu a 600°C, atribuído ao processo de decomposição característico dos argilominerais, nos quais ocorrem rupturas das hidroxilas estruturais (desidroxilação), seguido de liberação de água e, por fim, colapso da estrutura.

Os termogramas da argila na presença de Tyr em AU e AMA apresentaram diferenças em relação a argila pura. A presença de Tyr deslocou a temperatura do primeiro evento de perda de massa para valores menores de temperatura. Em AU o segundo evento em aproximadamente 100°C não foi observado, quando comparado a argila pura. Infere-se que esse deslocamento para temperaturas inferiores possa ter sido provocado devido as interações eletrostáticas entre o aminoácido e a superfície da argila. Em AMA, ocorreu não só o deslocamento do pico para valores menores de temperatura para o primeiro evento, como também deslocou o segundo 24°C a mais quando comparado à argila pura. Esse deslocamento para uma temperatura maior implica em uma interação dos sais com o mineral e provável diminuição no quantitativo de moléculas de água. Concluiu-se que, possivelmente, a presença dos sais na AMA dificultou a saída das moléculas de água localizadas dentro das lamelas do mineral, justificando a necessidade de uma temperatura maior para eliminação dessa água.

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DOI 10.22533/at.ed.0732013016

## Agradecimentos/Acknowledgments

À Universidade Federal do Oeste da Bahia - UFOB

**Área: FIS**

# CATALYTIC PYROLYSIS OF THE SUGARCANE BAGASSE OF SECOND-GENERATION ETHANOL

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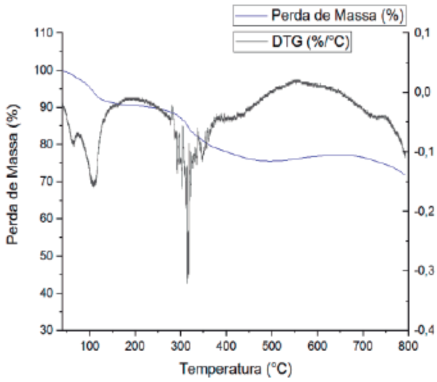
Keywords: *Lignocellulosic, Catalysis, Adsorption, Kinetics.*

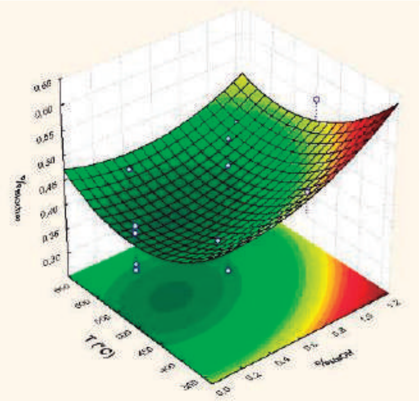
## Highlights

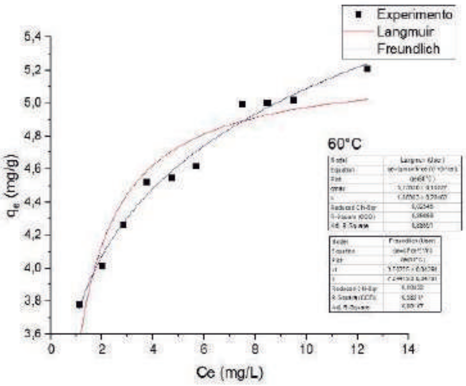
The reuse study of lignocellulosic residue generated by second generation alcohol; The technique of catalytic pyrolysis of lignocellulosic residue in the treatment of effluents by adsorption.

## Abstract

Second generation ethanol is one of the main technological innovations of the sugar and alcohol sector in the state of Alagoas. This process presents generation of waste rich in Lignin, which are intended for the generation of electricity through burning. This compound presents a chemical structure with a vast industrial applicability and due to this property is attributed to it the process of degradation by heating, called Pyrolysis. In this process part of the biomass is degraded into products in solid, liquid and gaseous phase, which evaluate quantitative and qualitative requirements. Aiming at higher yields related to solid (called biochar), the pyrolysis technique was performed with the addition of NaOH, which acts as catalyst. One of the main applications attributed to biochar is the use of biochar in the treatment of effluents from the adsorption phenomenon. For this, adsorptive studies with methylene blue were performed applying definitions formulated by Langmuir and Freundlich and also kinetic, in the modeling of pseudo-first order and pseudo-second order. The experiments were modeled using a Central Compound Planning, using temperature, NaOH fraction and biomass granulometry as independent variables to evaluate product yields. The analysis of biomass degradation was performed by thermogravimetric analysis (TGA). The results showed that the addition of catalyst contributed to biomass degradation at ~50ºC. Also showed that in high values of the dependent variables used there is higher biochar yield. When it comes to qualitative aspects, the biochar of 100 Mesh, with NaOH 1:1 produced at 400ºC and 115 Mesh, with NaOH 63:100 produced at 500°C showed better adsorptive behavior. The adsorption isotherm showed that the biochars have an extremely favorable adsorptive profile, with a curve fit tending to Freundlich's proposal (physissorption), and the adsorption kinetics showed a greater tendency to the pseudo-second order.







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**Área: FIS** **Nº de Inscrição: 00913**
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# Estudo teórico da degradação de compostos orgânicos voláteis em superfícies de $TiO_2$

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Palavras Chave: *TiO2, ondas planas, adsorção*

## Highlights

Theoretical study of volatile organic compounds degradation on $TiO_2$ surfaces. DFT-GGA and DFT-GGA + U approaches were used to optimize $TiO_2$ supercells with BTEX adsorption.

## Resumo/Abstract

Hidrocarbonetos aromáticos conhecidos por BTEX (benzeno, tolueno, etilbenzeno e isômeros de xileno) encontrados em reservas de petróleo e gás natural, cosméticos e solventes são contaminantes severos[1,2]. Desta forma, propiciar a fotocatálise desses poluentes seria uma boa forma de mitigar o impacto ambiental existente. É então fundamental alcançar catalisadores eficientes, estáveis e de baixo custo. Dentre os quais, a superfície (101) do dióxido de titânio ($TiO_2$), na forma anatase, se apresenta como opção conveniente[3]. Entretanto, a anatase possui suas limitações, como a perda da energia absorvida como recombinação do par e-/h[+4], e a ausência de atividade na presença de luz solar. Uma maneira de evitar tais imperfeições é a dopagem substitucional do catalisador. Assim, alterando suas características da forma desejada, seja por dopagem catiônica, aniônica, ou co-dopagem. Desta forma, este trabalho busca investigar a viabilidade de inserção de átomos de vanádio e nitrogênio como dopantes substitucionais, através da relação entre parâmetro de Hubbard (GGA+U) e band gap. Também é importante determinar o tipo de dopagem mais eficiente na adsorção de moléculas de tolueno e etilbenzeno.

Na calibração do parâmetro de Hubbard, ao variar o termo de interação elétron-elétron (U), altera-se o valor de intervalo entre banda de valência e banda de condução (gap). Correspondente ao intuito de corrigir para os valores experimentais da literatura. Foram calculadas as energias de adsorção de etilbenzeno e tolueno nas superfícies de TiO2 (101) “puro”, dopado com nitrogênio, dopado com vanádio, e co-dopado com nitrogênio e vanádio, pelo funcional PBE, num sistema de condições periódicas de ondas planas.

Os cálculos de adsorção mostraram que o tolueno adsorve com maior energia de interação na superfície de dióxido de titânio dopada com vanádio, enquanto para o etilbenzeno a superfície dopada com nitrogênio seria a mais indicada.

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## Agradecimentos/Acknowledgments

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**Área: FIS** **Nº de Inscrição: 822**

# Experimental factors that influence in the yield and reproducibility of gold nanorods synthesis and SERS spectroscopy performance.

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Palavras Chave: Surfactante, nanobastões de Au, SERS.

## Highlights

Gold nanorods synthesis yield is strongly influenced by surfactant origin and temperature control.
Removing surfactant excess by centrifugation/re-suspension is essential for SERS performance.
Optimal conditions for the SERS spectra of the cyanine dye IR-820 are reported.

## Resumo/Abstract

Os nanobastões de ouro (AuNR), devido à morfologia anisotrópica, apresentam duas bandas de ressonância de plasmon de superfície localizada (LSPR): uma longitudinal e outra transversal.[1] A modulação destas bandas LSPR torna-os promissores para aplicações do efeito Raman de intensidade por superfície (SERS).[2] Para o seu uso como substrato SERS é essencial que haja o controle da morfologia e tamanho de maneira reprodutível e com alto rendimento, além de pré-tratamentos do material obtido. No presente trabalho reportam-se alguns fatores críticos que influenciam na otimização da preparação dos AuNR e pré-tratamento para seu uso como substratos SERS. A partir da síntese de AuNR descrita por Nikoobakht e colaboradores,[1] diversos detalhes adicionais foram necessárias para que a formação dos AuNB ocorresse de forma eficiente. A tentativa de síntese realizada utilizando um surfactante brometo de cetiltrimetilamônio (CTAB) da marca Sigma, produto H5882, de alta pureza (>99%), levou à formação de outras nanoestruturas facetadas, com baixo rendimento de nanobastões, de acordo com resultados de SEM. O uso desse surfactante afeta a formação dos AuNR devido à presença de uma concentração iodeto superior a 50 ppm,[3] retardando a redução de $Au^{3+}$ à $Au^0$ e diminuindo o efeito do CTAB como molde macio. Dessa forma, verificou-se ser essencial o uso de CTAB com concentrações inferior de iodeto; a alternativa encontrada foi um CTAB Fluka (≥96%). Outro fator observado na influência do rendimento da síntese foi o controle preciso da temperatura. Observa-se na Figura 1(A), os espectros de extinção de AuNR sintetizados com controle da temperatura em 30,0 ± 0,1 ºC em comparação com controle com incerteza de 2 ºC (29 ± 2 ºC). Observou-se que a razão de intensidade LSPR longitudinal/transversal foi muito maior no primeiro caso, o que indica maior rendimento de AuNR. Essa mudança foi verificada por SEM, como apresentado na Figura 1(B), que mostra melhora no rendimento da síntese de AuNR com melhor controle de temperatura. Os AuNR em suspensão apresentam grande excesso de CTAB. Para obter o espectro SERS do corante IR-820 ($1{,}0\times10^{-5}$ mol $L^{-1}$) em AuNR, com $\lambda_0 = 632{,}8$ nm, foi retirado excesso de surfactante por ciclos de centrifugação. Observa-se na Figura 1(C), com a remoção do excesso de CTAB, a supressão da fluorescência e o aparecimento das bandas SERS do IR-820. Entretanto, mais que 4 ciclos causaram a diminuição do sinal SERS decorrente da perda de material plasmônico. A síntese de AuNR com alto rendimento necessita de cuidados experimentais específicos, como CTAB com controle de impurezas e controle preciso de temperatura. A melhor condição para obtenção do sinal SERS do IR-820 em suspensão foi realizar 4 centrifugações dos AuNR para a remoção do surfactante.

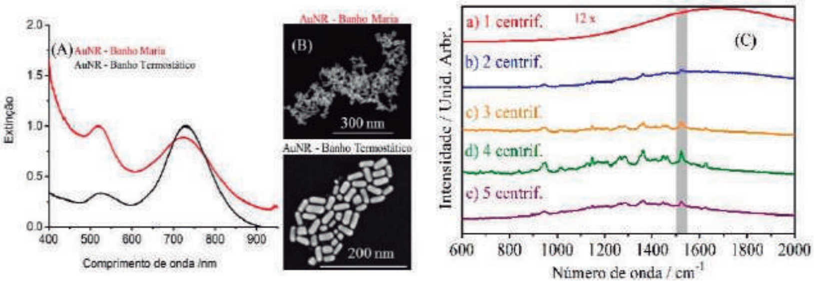

**Figura 1.** (A) Espectro UV-VIS e (B) Micrografia SEM dos AuNR sintetizados a 30,0 ± 0,1 ºC (banho termostático) e 29 ± 2 ºC (banho maria). (C) (a - e) Espectro SERS do IR-820 $1{,}0\times10^{-5}$ mol $L^{-1}$ obtido em AuNR em função dos ciclos de centrifugação *(Força-g 6.219)*, $\lambda_0 = 632{,}8$ nm.

## Agradecimentos/Acknowledgments

FAPEMIG, CNPq, CAPES, UFJF, UEMG.

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[1] B. Nikoobakht *et al.*, *Chem. Mater,* 2003, *15,* 1957.
[2] L.P.F. Peixoto et al., *Quím. Nova*, 2019, *42*, 1044.
[3] D.K. Smith. et al. Langmuir 2009, 25, 9518–9524

**Área: FIS**

# Kinetic study of chitosan thermal degradation under dynamic and isothermal conditions using artificial neural network

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Keywords: *Kinetic of thermal decomposition, Artificial neural network, Solid thermal decomposition, Biodegradable polymer decomposition.*

## Highlights

Chitosan is a biologically compatible natural polysaccharide chemically versatile. The study of its thermal behavior under isothermal and dynamic conditions allows us to predict applications.

## Abstract

Chitosan is a natural polymer derived from chitin, present in crustaceans and insects. Due to its biodegradability and thermal stability, chitosan is being employed in different technologies, which consequently requires it tolerates industrial process and storage conditions.[1] So, it is important to understand the chitosan thermal behavior to warranty the thermal stability in both, unit operations, which involves abrupt temperature variation and, in storage environments, where the storage temperature and lifetime has to be determined. Therefore, this work aims to study the chitosan thermal behavior using thermogravimetry data under isothermal and dynamic conditions. The thermal decomposition under isothermal condition was investigated at 256, 257 and 258°C and the curves are shown in Figure 1. For dynamic analyses, it was used four different heating rates 2.5, 5, 7.5, and 10°C/min, shown in Figure 2. For the isothermal treatment, a Multilayer Perceptron neural network (MLP) was adopted[2], and it was determined the two-dimensional contraction (R2) and Avrami-Erofeev (Am2) models presented higher contributions to describe the thermal decomposition. The activation energy (Ea) for isothermal case was determined as 90 to 103 kJ/mol, for R2 and Am2 models respectively, and for the dynamic analysis, it is shown in Figure 3. The results are coherent, suggesting the thermal decomposition mechanism in the initial stage does not vary for isothermal or dynamic processes, mainly due to the temperature is closer in both conditions. But as the temperature increases, above the isothermal case, the Ea assumes an increasing behavior, suggesting a variation in the decomposition mechanism with higher activation energy values.

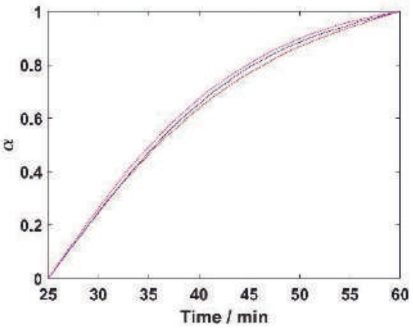

**Figure 1** Isothermal data

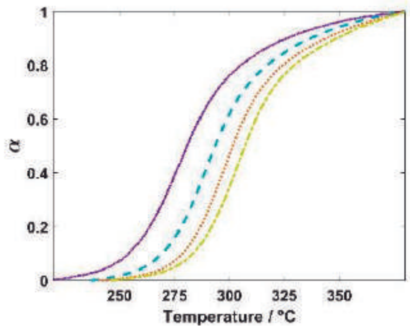

**Figure 2** Dynamic data

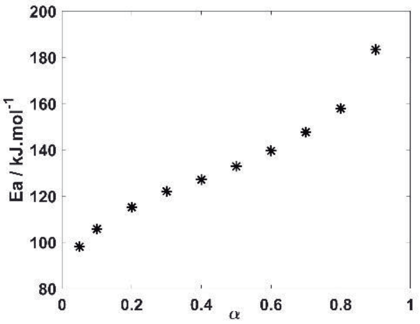

**Figure 3** Ea for dynamic data

[1] Riva et al., Adv Polym Sci **(2011)** 244: 19–44 DOI: 10.1007/12_2011_137

[2] Ferreira et al., J Therm Anal Calorim **(2018)** 134: 773–782 DOI: 10.1007/s10973-018-7568-1

## Acknowledgments

The authors would like to thank CNPq and UFMG/PRPq for financial support.

**Área: FIS**

# Morphological properties of pure and Fe, Co or Al doped anatase $TiO_2$ nanoparticles.

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Palavras Chave: Anatase, Crystallite size, Hydrotermal synthesis, *nanoparticles, Monocrystalline, Polydispersity*

## Highlights

Nanoparticles (NP) of pure $TiO_2$ and doped with Fe, Al or Co obtained by hydrothermal treatment of coloidal dispersions; Crystal structure parameters of the materials compared to the pure anatase.

## Resumo/Abstract

The colloidal dispersions were prepared by: (i) oxidizing $Ti_0$ with hydrogen peroxide in an alkaline medium and (ii) heating the resulting solution from (i) to 70°C, with ferric acetylacetonate or cobalt acetate or Al as a source of dopants. The samples were characterized by TEM, XRD, EDX and BET. Polycrystalline anatase NPs were obtained with different sizes depending on the synthesis conditions, from 18-25 nm and 8-107 nm, determined respectively by BET ($d_{BET}$) and MET ($d_{MET}$). Crystal structure parameters of the doped materials compared to the pure ones show evidence of inhibition of anatase nucleation by Co, and of induction of growth by Fe and Co. The measurements made it possible to obtain the polydispersity of the distribution degree ($\sigma_p/d_{MET}$) of each system and to compare them with a commercial sample. The influence of the treatment time was verified for samples without dopant, showing congruence of values in relation to $2\theta$ for the synthesized samples, however with values greater than the commercial one, with an increase of crystallite size ($t_C$) in relation to time, approaching to the $t_C$ of the commercial sample. For the samples with Fe, Co and Al, the crystalline deformations caused by the insertion of each contaminant in the titania lattice were analyzed, inferring a tendency of expansion or contraction of the crystalline lattice in relation to the ionic radius of the cation present as an impurity. There was a decrease in the value of $2\theta$ in relation to the increase in the ionic radius of the dopant, inferring lattice contraction by aluminum atoms and lattice expansion caused by cobalt and iron atoms. The effect of cobalt and iron as crystal growth inducers is verified. This effect can be further corroborated by comparing the ($d_{MET}$) and ($t_C$) data, so that the samples with cobalt show a preponderant presence of single crystals, while the samples containing iron preferentially polycrystalline behavior. Aluminum proved to be an inducer of nucleation, with the formation of a preferentially monocrystalline system. The degree of dispersion of the particle size distribution was estimated, verifying the highest degree of polydispersion for the cobalt-containing system, with $(\sigma_p/d_{MET})=0.50$, followed by the iron-doped system, $(\sigma_p/d_{MET})=0.41$ and aluminum, $(\sigma_p/d_{MET})=0.23$. It was also verified that the samples without dopant showed a degree of polydispersity similar to the system containing iron. For samples doped with cobalt submitted to heat treatment with a reducing atmosphere, phase segregation and the formation of cobalt metallic clusters were observed, when analyzing the results obtained by X-ray diffraction, corroborating the characterization by image and by XRD and by X-ray, close to the value obtained for samples of titanium dioxide without cobalt, indicating the diffusive process of cobalt leaving the anatase phase.

## Agradecimentos/Acknowledgments

Instituto de Química de Araraquara - UNESP

CAPES

**Área: FIS** **Nº de Inscrição: 00950**

*(Inserir o número de inscrição do autor que fez a submissão)*

# Problem-based learning: the use of prototypes operating in real thermodynamic cycles for teaching thermodynamics.

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[1] *Universidade Federal do Recôncavo da Bahia / Centro de Formação de Professores - Campus Amargosa*

Keywords: *Teaching, PBL, Thermodynamics, Thermal machine, Physical Chemistry*

## Highlights

Carnot and Stirling Thermodynamic cycles for teaching Physical-Chemistry. Stirling cycle as an example of a real thermodynamic cycle allowing students to calculate all state functions in each step.

## Abstract

The thermodynamics subject has been the precursor of research that aims to promote methods that improve the teaching-learning process in higher education courses, since its content requires a given abstraction in addition to show a difficulty in interpretation of its results [1]. The main reason is due to professors are concerned about theoretical information, such as formulas, inspections and mathematical deductions. This technical view makes it difficult to relate definitions to scientific phenomena [2]. Then, it is a good example why innovative methods are desirable to overcome Physical-Chemistry teaching. To solve this problem, this work deals with the active learning in Physical-Chemistry classes inviting students to build a thermal machine [3] in which they are free to choose the kind of machine and the best thermodynamic configuration based in Stirling cycle. Alternative materials (Figure 1) are proposed and the correlation among mathematics formulas, thermodynamics and real phenomena are achieved and well developed.

*Figure 1 - Thermal machine construction based on Stirling thermodynamic cycle.*

References: [1] TSAPARLIS, Georgios; FINLAYSON, Odilla E. **Physical chemistry education: its multiple facets and aspects**. Chemistry Education Research and practice: 2014, 15, 257-265; [2] NETO, Octavio Mattasoglio; SOSTER, Tatiana Sansone. **Inovação acadêmica e aprendizagem ativa**. Penso Editora, 2017; [3] CASTELLÓN, Erick. **Application of the Second Law of Thermodynamics To Explain the Working of Toys.** Journal of Chemical Education. 2014, 91, 687-691.

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The authors would like to thank UFRB and the students from GCPF 393 classes in Licenciature in Chemistry course located at CFP/UFRB.

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

**Nº de Inscrição: 01303**
*(Inserir o número de inscrição do autor que fez a submissão)*

# Regular corn starch treated by acid hydrolysis under electric field

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Palavras Chave: *Acid Hydrolysis, Starch, Electric Field, Crystallinity, SAXS.*

## Highlights

High starch crystallinity together with high gelatinization temperature range are achieved.
X-ray diffraction indicates the crystallinity degree on the granules and SAXS shows those surface fractality.
The obtained low amylose starches will present less tendency for retrogradation during the cooling of starch pastes.

## Resumo/Abstract

The main objective of the present work is the investigation of the acid hydrolysis of starch under the action of an external electric field. In the oriented acid hydrolysis (OAH) regular corn starch (18% amylose), solutions (5% (w/v)) were prepared by dispersion of powder starch in HCl 1.0 mol L$^{-1}$, followed by electric field application (500 V m$^{-1}$) in a 2 V fixed voltage. For this, a capacitor consisting of two semicircular gold electrodes parallel attached to a PTFE support was used. The gold electrodes have a fixed separation of 4 mm and a quartz cuvette was used as sample holder. Different electric field application times and number of cycles were evaluated. The results were compared to the free acid hydrolysis (FAH), which was performed in the absence of an electric field. After hydrolysis, the samples were centrifuged and washed several times with distilled water until neutral pH, then dried at 40 °C for 48 h. Finally, they were manually ground to powder in a porcelain grain.

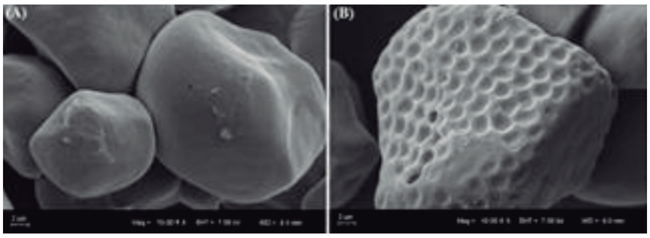

**Figure 1.** SEM images of (A) regular corn starch, (B) treated corn starch

The results obtained by treatment of regular corn starch having 18% amylose indicate that the best reaction conditions are related to the application of an electric field with large number of cycles in a minimum time. The new characteristics of the treated starch are mainly related to the loss of the amylose A relatively high crystallinity together with a high gelatinization temperature range of the treated starches are achieved.

## Agradecimentos/Acknowledgments

The authors would like to thank CNPq (Grant 405662/2016-5) for financial support and the Brazilian Synchrotron facility (LNLS/CNPEM – Proposal 20160060) for SAXS beam time. R. Zucatti and A. Vailatti thank PROPESQ – UFRGS and CNPq for undergraduate fellowships.

**Área: FIS**

# Study of the Kinects of Photodegradation of *Opuntia Dillenii* in different acids

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Keywords: *Anthocyanins, Photodegradation, UV-Vis spectroscopy.*

## Highlights

Obtaining extracts in aqueous and ethanolic medium from the fruit of the erect prickly pear (*Opuntia dillenii)* in different acids. Photodegradation kinetics in UVC radiation and analysis by UV-Vis spectroscopy.

## Resumo/Abstract

Anthocyanins are compounds of the family of flavonoids, which are a group of pigments responsible for the colors understood from the red color to blue color, present in flowers, fruits, leaves, stems and roots.[1] In an aqueous solution, anthocyanins are commonly found in the form of a mixture of different chemical structures in equilibrium: flavylic cation (red), anhydrous quinoidal base (blue), pseudo-base carbinol (colorless), and chalcone (colorless or slightly yellow).[1] Its use has been attracted a lot of interest due to its application potential, both industrial and medical because of its antioxidant properties.[2] However, the lack of a wider use of these dyes is mainly due to their poor stability. The anthocyanin color stability depends on a combination of several factors, such as anthocyanin structure and concentration, pH, temperature, the presence of complexing agents. In this study, the fruit of the erect prickly pear (Opuntia dillenii, figure 1, a species of flowering plant belonging to the *Cactaceae* family) was chosen as a plant source. The objective was to observe the degradation kinetics in aqueous and ethanolic extracts of anthocyanins under exposure to light in the presence of different acids (hydrochloric, citric, benzoic and ascorbic). The extraction method chosen was that described by Harborne[1], consisting in the extraction of pigments from small amounts of plant tissue immersed in the solvent under heating. Each of the extracts (in water and in ethanol, with and without acid) was submitted to UVC radiation at different exposure times and subsequent analysis in the UV-Vis spectrophotometer. Anthocyanins are known to follow first order degradation kinetics[2], and this was confirmed after analysis of the obtained spectra and their rate constants (Figure 2). The half-life times were obtained, and it is possible to observe different behaviors according to the solvent used in the extraction. In water, the best result of resistance to degradation was observed in the absence of acid. ($k = 3{,}8 \times 10^{-3}\ h^{-1}$, $t_{½} = 183$ h). In ethanol, the best results were observed with the use of ascorbic acid as a co-pigment ($k = 0{,}101\ h^{-1}$, $t_{½} = 6{,}8$ h) and with hydrochloric acid ($k = 7{,}2 \times 10^{-2}\ h^{-1}$, $t_{½} = 9{,}6$ h).

Figure 1 – *Opuntia dillenii*

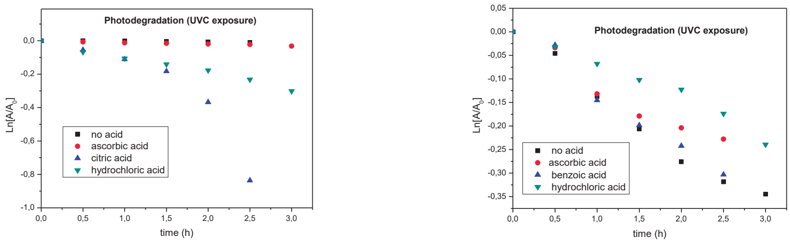

Figure 2 – Photodegradation (UVC light) of anthocyanins extracts in water (left) and ethanol (right)

[1] Harborne, J. B. *Phitochemical Methods* – A Guide to Modern Techniques of Plant Analysis, Chapman and Hall. London, 1973.
[2] Lee, S.V., Hadi, Z. H. Z., Abidin, Z., Mazni, N. A., Halim, N. A., Usop, R.Hassan, H.C., Majid, S. R., Arof, A. K. *Pigment and Resin Techonlogy,* **2015**, 44, 109.
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LQ/CA/UFPE and FACEPE

**Área:** FIS

# Tartrazine adsorption on biochar from residual biomass: a kinetic study

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Keywords: *biomass, adsorption, chemical kinetics, biochar.*

## Highlights

The best fit was obtained for the pseudo-second-order kinetic model, that suggests chemical adsorption. The highest adsorption capacity was shown for the temperature of 25 °C.

## Abstract

Biochar is one promising adsorbent for organic pollutants adsorption removal from water and soil.[1] The aim of this study was to determine kinetic parameters of the adsorption of tartrazine dye (TDY) in oat biochar (BCH). The residual biomass of oat, was pyrolyzed at 500 °C (± 5) for 30 min, generating BCH, that was crushed (≤ 0.01 mm), washed with distilled water and dried at 60 °C (± 3). The adsorption of TDY in BCH, were done in becker cups containing 50 mL of TDY solutions (6.2 to 74.3 mg/L), at 25, 40 and 55 °C, 100 mg of adsorbent for 30 min. Aliquots were collected every 5 min, centrifuged and the absorbance was determined in 420 nm.

**Table 1.** Adsorption of tartrazine in oat biochar: kinetic parameters.

| T | $q_e$ (exp.) | Pseudo first order | | | Pseudo second order | | | Intraparticle diffusion | | | Elovich equation | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $k_1$ | $q_e$ (teor.) | $R^2$ | $q_e$ (teor.) | $k_2$ | $R^2$ | C | $K_P$ | $R^2$ | α | β | $R^2$ |
| 25 | 6.05 | 0.04 | 0.42 | 0.25 | 5.86 | -0.21 | 1.00 | 6.81 | -0.14 | 0.41 | 3.87E-13 | -0.23 | 0.32 |
| 40 | 5.89 | 0.07 | 2.00 | 0.88 | 5.72 | -0.10 | 0.99 | 8.13 | -0.38 | 0.89 | 4.73E-06 | -0.66 | 0.81 |
| 55 | 2.89 | 0.09 | 6.85 | 0.84 | 2.62 | -0.07 | 0.95 | 8.99 | -1.08 | 0.91 | 3.01E-03 | -1.87 | 0.84 |

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$^{-1}$.

The best fit was obtained for the pseudo-second-order kinetic model ($R^2$: between 0.95 and 1.00) (Table 1). The highest adsorption capacity was shown for the temperature of 25 °C ($q_{e\ (exp.)}$: 6.05 and $q_{e\ (teor)}$: 5.86 mg/g)) (Table 1). The pseudo-second-order kinetic model suggests that the rate-limiting step is chemisorption rather than mass transport limitation.[2] Pseudo-second order kinetic model suggests that chemical adsorption of TDY by BCH is the dominant mechanism, involving electrostatic attraction.[3]

## Acknowledgments

LACOPPI, IFPR, PIBIC/CNPq, PIBIC/IFPR, CNPq.

### References

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[2]S. Saikia, A. Sinharoy, P.N. Lens, *Separation and Purification Technology*, **2022**, 120462.

[3]M.N. Alnajrani, O.A. Alsager, *Scientific Reports* **2020**, 10, 794.

# FOT

# Fotoquímica

**Área: FOT** **Nº de Inscrição: 01072**

# Avaliação dos fatores de Franck-Condon da transição eletrônica de menor energia permitida do ligante dpqQX via cálculos DFT

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Palavras Chave: Fatores de Franck-condon, estado excitado, DFT, TD-DFT.

## Highlights

Franck-Condon factors study of the lowest energy allowed electronic transition of the dpqQX ligand

TD-DFT calculations as a probe to study excited states

Vibronic transitions calculated at DFT level

## Resumo/Abstract

Cálculos computacionais combinados com experimentos permitem que diversas hipóteses para mecanismos fotofísicos e fotoquímicos sejam exploradas. Nesse panorama, cálculos TD-DFT tem desempenhado um papel importante pela possibilidade de se trabalhar com sistemas contendo centenas de átomos. No presente trabalho, está sendo apresentado um estudo teórico e sistemático do ligante de coordenação dpqQX,[1] ver Figura 1A. Os mecanismos fotofísicos de absorção e emissão foram estudados por cálculos TD-DFT (Ver Figuras 1B e 1C), onde foi verificado a influência dos funcionais B3LYP, PBE0, cam-B3LYP e M06-2X sobre os fatores de Franck-Condon (FC).

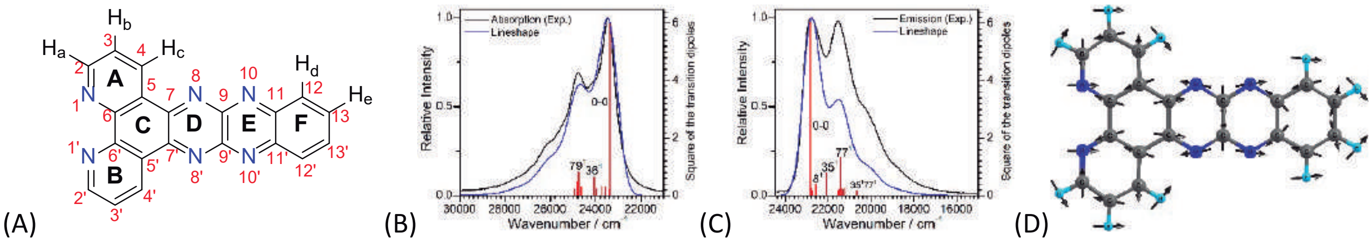

**Figura 1.** (A) Estrutura do ligante dpqQX; (B) e (C) Espectros de absorção e emissão experimentais e teóricos, respectivamente; (D) representação vetorial do principal modo de vibração envolvido nas progressões vibrônicas.

A análise dos resultados mostrou que as progressões vibrônicas envolvem os modos de vibração simétricos, tendo como principal característica a deformação axial da ligação C(9)–C(9'). Foi observado também que os funcionais B3LYP e PBE0 tiveram resultados mais consistentes que os funcionais de longo alcance, cam-B3LYP e M06-2X.

[1]Miranda, F. S.; *et. al*. Tetrahedron, 2008, 64, 5410 – 5415.

## Agradecimentos/Acknowledgments

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**Área: FOT** **Nº de Inscrição: 00549**

# Combining natural pigments to create new biocompatible dyes

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Keywords: *natural pigments, betalain, pyranoflavylium, pseudo-natural dyes*

## Highlights

The colors of plants, fruits and fungi are usually impaired by anthocyanins and betalains. Here we describe the semisynthesis and the photophysical properties of a new dye containing both pigments.

## Abstract

Pigments are vital compounds to animals, plants and fungi. However, their functions are far more complex than visual communication. Due to their conjugated structures and presence of auxochromic groups, natural pigments often show tend to interact with other chemical species via energy and electron transfer. The betalains and anthocyanins are water soluble vacuolar pigments pigmenting most angiosperms. Although their biological functions and colors are similar, they have completely different chemical structures. Betalains are alkaloids that contain the 1,7-diazaheptamethinium system, while anthocyanins are flavylium salts.[1,2] In red wine, anthocyanins are converted into their corresponding pyranoflavylium derivatives via oxidative coupling.[3] The resulting pigments are less sensitive to the pH of the medium compared to anthocyanins.

We semisynthesized PyFlavBeet, a pyranoflavylium betalain, by coupling a model flavylium compound and betalamic acid. After the reaction is complete, the color of the hybrid is green and the maxima absorption occurs at 710nm, in ethanol. After 24 hours, in open atmosphere, PyFlavBeet oxidizes and color turns magenta ($\lambda_{abs}$ = 540nm). Thus, we can form a biocompatible dye that is can show stability to hydration, color persistence through different pH's and applications as colorant and in solar cells. Furthermore, the chemical and photophysical properties will be investigated and compared with the starting reagents.

## Acknowledgments

We thank FAPESP (ELB 2019/06391-8, LFSH 2019/16606-1),CNPq and CAPES (Financial code 0001) for the financial support.

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**Área: ___FOT____**

# Insulin aggregation kinetics monitored by luminescent probe *cis*-$[Ru(phen)_2(ImAC)]^+$

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Keywords: *Insulin, Luminescent Probe, Amyloid Fibrils, Fibrillary Aggregates.*

## Highlights

The human insulin aggregation process was monitored using the complex *cis*-$[Ru(phen)_2(ImAC)]^+$, synthesized and characterized by the group, as a luminescent probe.

## Resumo/Abstract

Insulin was the first biopharmaceutical produced on an industrial scale for the treatment of insulin dependent diabetes. Insulin is an amyloid protein that in monomeric form undergoes a self-aggregation process, generating amyloid fibrils. Amyloid protein aggregation is one of the most common and problematic processes found in all stages of development, storage, transport and administration of biopharmaceuticals, because in the form of aggregates it is not bioavailable and any degree of amyloid formation during its manufacture reduces absorption, altering the effectiveness of the treatment. Therefore, knowledge of insulin fibrillation mechanisms is important both to improve pharmaceutical formulations used in the treatment of diabetic patients, as well as to contribute to the knowledge of the molecular characteristics of the formation of amyloid proteins.

A sensitive and selective strategy to identify insulin fibrils remains a challenge for researchers in amyloid protein research. Thus, it is critical to detect, *in vitro*, the species generated during amyloid aggregation, particularly the fibrillar species [1]. Here we monitor the human insulin aggregation process through spectrofluorometry, using the *cis*-$[Ru(phen)_2(4\text{-}ImAC)]^+$ complex (RuImAC; phen = 1,10-phenanthroline; 4-ImAC = 4-carboxylic acid) as a luminescent probe, in order to detect the stages of aggregation mainly regarding the formation of fibrillar species.

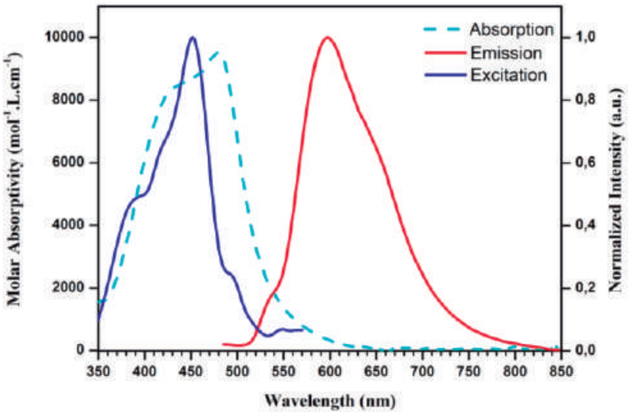

**Figure 1.** Electronic spectra of: excitation (blue, $\lambda_{em}$=600nm), absorption (cyan), and emission (red, exc= 450 nm) of the *cis*-$[Ru(phen)_2(4\text{-}ImAC)]^+$ complex in phosphate buffer solution (pH = 7,0; 33 mM) at a concentration of 42,2 µM.

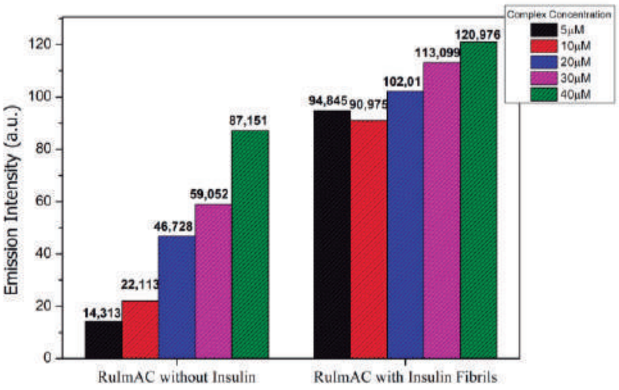

**Figure 2.** Study of the increase in the emission intensity of the RuImAC complex, at different concentrations, in the presence of insulin fibrils.

The RuImAC complex has a maximum emission intensity at 600nm, this intensity becomes greater when the complex is associated with insulin, allowing the monitoring of the stages of aggregation. Monitoring results using the RuImAC probe were compared with the standard Thioflavin T, a dye already used for this type of protein aggregation study.

## Agradecimentos/Acknowledgments

FAPESP CNPq CAPES

*[1] Pereira, L. M., Cali, M. P., Marchi, R. C., Pazin, W. M., & Carlos, R. M. (2021). Luminescent imaging of insulin amyloid aggregation using a sensitive ruthenium-based probe in the red region. Journal of Inorganic Biochemistry, 224, 111585.*

**Área: FOT**

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

# New Mn(II) complexes with *N*-heterocyclic carbenes as potential redox photocatalysts of CRP2 of acrylates.

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Palavras Chave: *Mn$^{II}$ complexes, NHC, Controlled Radicalar Photopolymerization, Redox photocatalyst*

## Highlights

Two NHCs ligands were synthetized according to the literature to give the two new Mn$^{II}$ complexes. The complexes were applied in the controlled radicalar polymerization of MA and BA. The polymerization studies showed they were good catalysts in the molar ratio of 200/1/0.02/1 using [MA]/[EBr]/[Mn$^{II}$]/[TEA].

## Resumo/Abstract

The monosubstituted imidazole ligand, mesethylimidazole was synthesized and characterized by FTIR and NMR following the procedure created by Gridnev (1994).[1] The second substitution of the monosubstituted imidazole with 2-bromopyridine/2-bromobenzene were synthetized according to the literature[2] and characterized with FTIR and UV-vis. The complexes [Mn$^{II}$(py-mesethylmidazole)$_2$](PF$_6$)$_2$ and [Mn$^{II}$(ph-mesethylmidazole)$_2$](PF$_6$)$_2$ were characterized by FTIR and UV-Vis. It was also possible to observe the behavior of the obtained complexes against irradiation at 365 nm, and its sensitivity to air. The synthesized complexes proved to be active as photocatalyst in the CRP 2 of MA and BA, using *α*-bromophenylacetate as an initiator and TEA as an electron donor, following the reductive pathway (Figure 1)[3] of the polymerization mechanism, obtaining a polymer with Mn = 144000 g.mol$^{-1}$ and Đ = 1.5; the preliminary test also indicated that there was control in the photocatalysis using the complex [Mn$^{II}$(py-mesethylmidazole)$_2$](PF$_6$)$_2$.

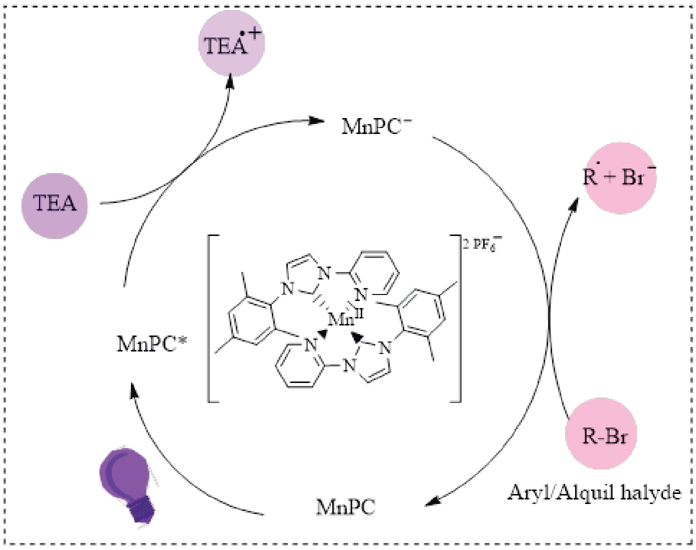

*Figure 1 - Reductive pathway mechanism for CRP 2.*

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## Agradecimentos/Acknowledgments

**Área:** FOT **Nº de Inscrição:** 00891

# Photochemical synthesis of a deep blue bithiophene dye from an old antiosporotic drug derived from strontium ranelate.

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Palavras Chave: *Antiosporotic drug, Dithiophene dye, Photodimerization reaction, Ranelate blue, Strontium ranelate*

## Highlights

A new bithiophene based dye has been generated by photodimerization of ranelate ion. It provides a new application of an old anti-osteoporotic drug. It behaves as a nontoxic species, performing as a light stable blue dye.

## Resumo/Abstract

Strontium ranelate is a well-known anti-osteoporotic drug used to treat postmenopausal osteoporosis[1]. In acid medium (HCl 6mol $L^{-1}$), the ranelic acid ligand undergoes a decarboxylation (Figure 1a), leading to a photo sensible molecule known as decarboxy ranelate (H5C).

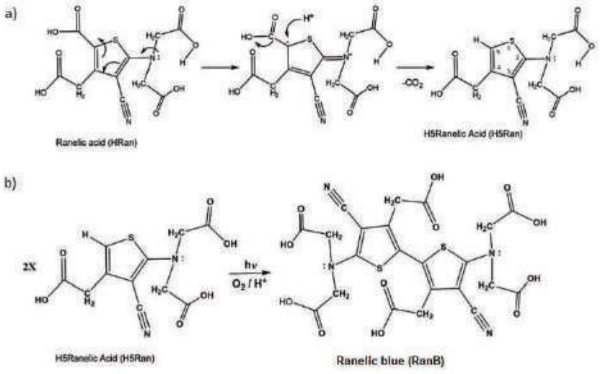

*Figure 1: a) Decarboxylation of ranelic acid [2] b) Photo dimerization of H5[2].*

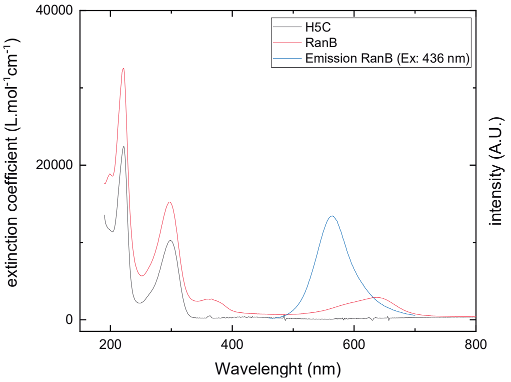

*Figure 2: absorption spectra of RanB and H5C and emission of RanB (Ex: 436 nm).*

In the presence of acid medium UV-Light and $O_2$, this molecule undergoes a photo dimerization reaction (Figure 1b).

This new bithiophene pigment, Ranelate Blue (RanB) has a strong absorption band at 637 nm (Figure 2), giving to the solution a vibrant blue color. It also exhibits a strong emission band at 564 nm.

RanB was isolated and fully characterized based on $^{1}H/^{13}C$- RMN, FT- IR, HS-MS and Ultraviolet-visible spectroscopy. Its emission characteristics have also been investigated, revealing very interesting photochemical properties for fluorescent dye applications.

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, in press.

## Agradecimentos/Acknowledgments

**Área: FOT**

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

# Photochemistry of methylene blue aggregates in styrene-divinylbenzene copolymer containing paired iminodiacetate ions and aprotic solvents

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Key-words: Methylene blue; Radicals; Polymeric matrix; Aprotic solvents; Stable radicals; Aggregation

## Highlights

Molecular aggregation modulates the photochemistry of methylene blue (MB). Leuco MB aggregates are stabilized in the polymer, Chelex 100®, and extracted by aprotic solvents forms new aggregates with stable free radicals.

## Abstract

Methylene blue (MB) has relevance in various applications covering photodynamic therapy, advanced materials, bioelectronics, and energy. Previous and ongoing studies in our laboratory have shown that photochemically-generated free radicals of phenothiazines are stabilized in aggregates. When the cationic thiazinic dye, MB, is irradiated in Chelex 100®, it is stabilized in the leuco two-electron reduced form (LMB). LMB removed from Chelex 100® by DMSO or transferred from DMSO to toluene forms new aggregates that stabilize free radicals of the dye photogenerated by the Type I mechanism [1]. The one-electron oxidized ($MB^{\bullet+}$) presents spectral contributions of a structured band at the 400 nm region and broadband at the 500 nm region (Figure 1A). The structured band at the 400 nm region is associated with an intense EPR signal from monomeric $MB^{\bullet+}$ (Figure 1B). When the DMSO or toluene solution of MB is put in resting, the structured band at 400 nm and the corresponding EPR signal decrease significantly whereas the band at 500 nm region increases. The broadband at 500 nm region is assigned to $MB^{\bullet+}$ stabilized in large aggregates in which EPR signal is suppressed by exchange interactions. Theoretical calculations are ongoing to unravel the mechanisms responsible for stabilizing these radical species in DMSO and toluene. The comprehension of the mechanisms underlying stabilization of MB leuco form and free radicals can be applied in many fields, for example, to enhance the efficiency of photodynamic therapy, since the photoactive molecule could show different properties in the low polarity zone of biological membranes. Furthermore, the free radicals of MB have the potential to be directly applied in energy transformation when associated with semiconductors the electron/hole transfers. Electrostatic interactions, pi-stacking, and formation of aggregates can modulate the formation and stability of MB redox states generated photochemically in mild conditions.

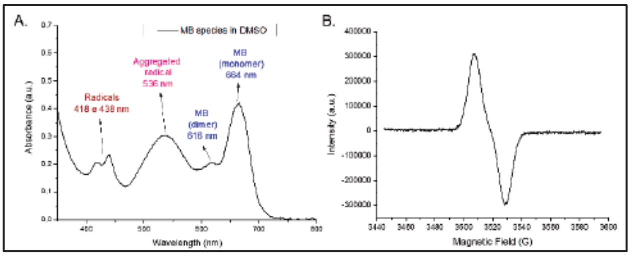

Figure 1. (A) UV-vis spectra and (B) EPR spectra of MB radicals in DMSO

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## Agradecimentos/Acknowledgments

Acknowledgments – FAPESP 2017/02317-2, 2019/26919-7, and NBB/UFABC, CNPq (309247/2017-9), for the financial support, CEM/UFABC for the access to facilities.

**Área: FOT**

# Photoinduced organometallic radical polymerization mediated by Ni$^{II}$(*Salen*) complexes

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Keywords: *Schiff bases, Ni(II) complexes, photopolymerization, photo-OMRP, copolymerization, on and off study.*

## Highlights

Ni(II) complexes coordinated to symmetric Schiff bases were evaluated as photo-OMRP mediators.
The copolymerization of vinyl acetate, methyl and butyl acrylate and the *on* and *off* study were evaluated.

## Abstract

Photomediated controlled radical polymerization is a versatile method to prepare, under mild conditions, various well-defined polymers with complex architecture. Organometallic mediated radical polymerization (OMRP) employs a weak bond between carbon and transition metal species[1]. In addition, various metal complexes are used to mediate OMRP including Co, Fe, Mn and Ni (metal used in this work). Therefore, the central idea was to select four Ni (II) complexes coordinated to symmetric Schiff bases and apply them in photo-OMRP. Firstly, it was performed the synthesis of tetradentate symmetric Schiff bases. In sequence, the complexes were synthesized giving the symmetric Ni (II) complexes coordinated with the Schiff base ligands (with substitute *tert*-butyl). In the vinyl acetate photo-OMRP, UV LEDs (390 nm) were used for the homolytic cleavage of the initiator TPO (2,4,6 - trimethyl-benzoyl-diphenylphosphine oxide) and visible LEDs (400 to 840 nm) were used for the homolytic cleavage of the Ni-C bond of the oxidized complex at 25 ºC. The reaction of photo-OMRP is represented in Figure 1, just as the chemical structures of compounds that were synthesized.

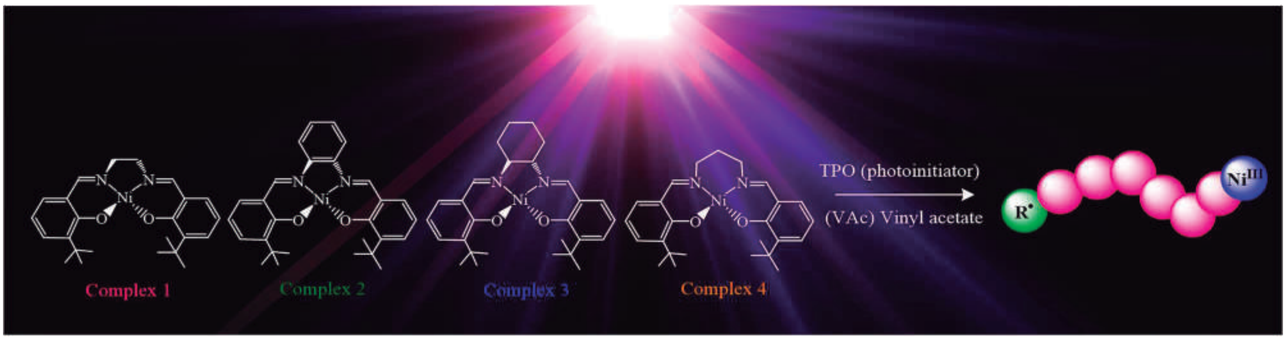

**Figure 1.** General scheme of photo-OMRP and structures of Ni(II) complexes synthesis.

The concentration of monomer and TPO were varied. The best molar ratios were of 600/1/0.5, 600/1.5/0.5, 900/1/0.5 and 900/1.5/0.5 ([VAc]/[M$^{II}$]/[TPO]). The conversions were between 40-80% in total time of approximately 22 hours. This investigation showed that the control of the polymerization was affected by the molar ratio between Ni$^{II}$ complexes and the monomer. Polymers with a controlled molecular weight and narrow molecular weight distribution (Đ =1.1-1.5) were obtained for the four complexes. In addition, copolymerization, *on* and *off* study and theoretical calculations were realized to the complexes with aim to study photo-OMRP mechanism.

## Acknowledgments

FAPESP Proc. 2018/19395-9, 2019/04297-4

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[1] Chen, M., Zhong, M., & Johnson, J. A. (2016). Light-controlled radical polymerization: Mechanisms, methods, and applications. Chemical Reviews, 116(17), 10167–10211.

**Área: FOT**

# Visible light oxidation of inorganic sulfide by modified Nb-containing photocatalysts

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*[1]Departamento de Formação Geral, CEFET-MG; [2]Departamento de Química, UFMG; [3]Departamento de Química, UFOP*

*Keywords: Inorganic sulfide, Modified Nb-photocatalysts, Visible light photoreactions, Inorganic pollutant.*

## Highlights

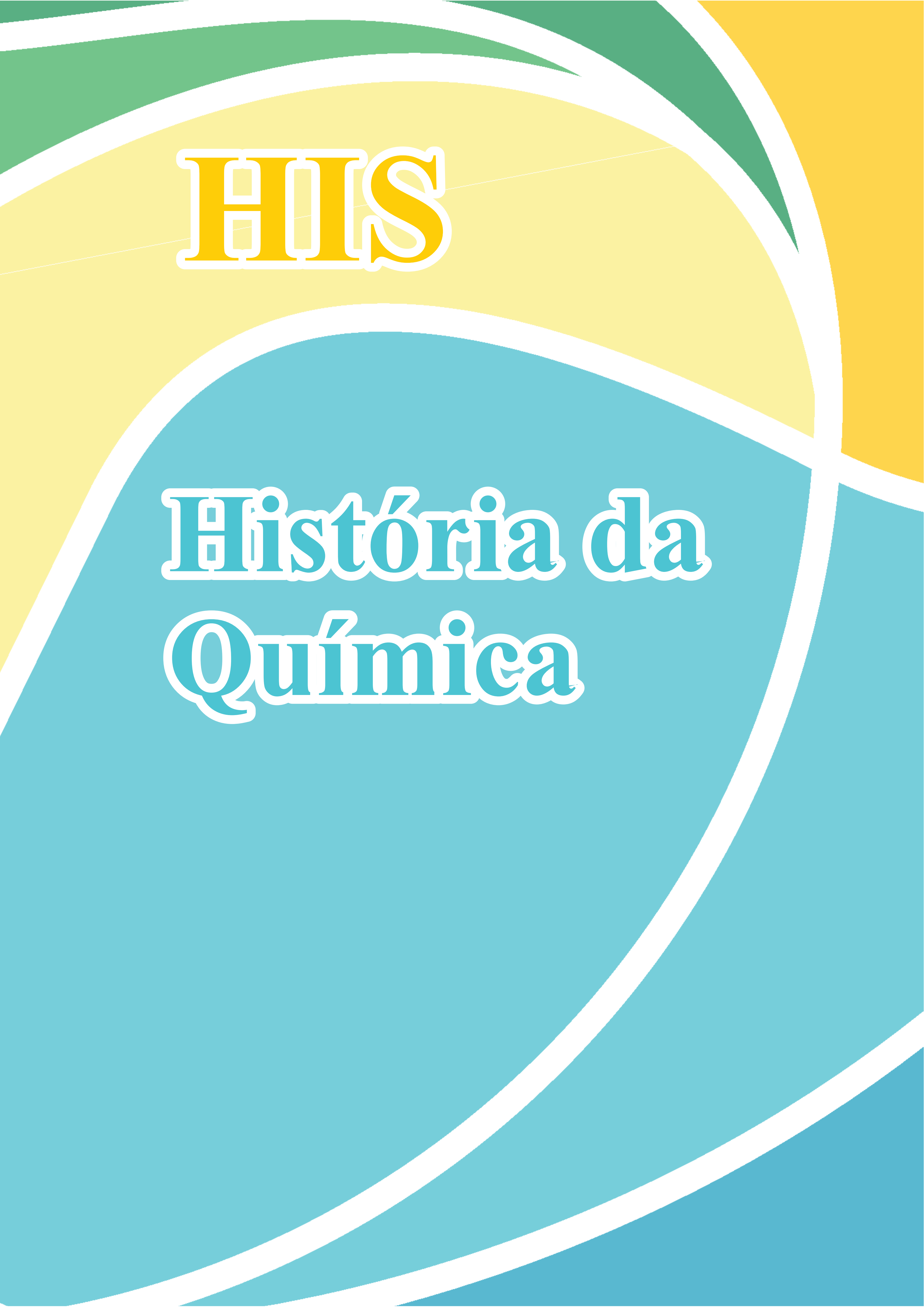
- Coupling niobium(V) oxide with cobalt species increases the photocatalytic capacity.
- The synthetic route drives the amount of Co(II)/Co(III) species.
- The amount of Co(III) enlarges the photocatalyst activity.
- The products formed in photoreactions are less toxic and hazardous sulfur species.

## Abstract

Brazil is the largest producer of niobium(V) oxide in the world, which makes its application very strategic for the country. It can be used as photocatalyst, however, it has low quantum yield and bang gap in the ultraviolet region. Such problems can be mitigated by incorporating some transition metals into their structure during synthesis. Another possible modification to solve the problem of high bandgap is to use a photosensitizer. The photosensitizer activates the material indirectly, since it is the one who absorbs the energy and transfers this excitation energy to the photocatalyst. In this work, we chose to use cobalt species and methylene blue to modify the materials in this both ways. All materials were synthesized by sol-gel route, by EISA method (Evaporation Induced Self-Assemble), producing mesopore materials. For the materials modified with Co, two types of synthesis were tested, with difference in the addition order of cobalt salt. The two resulted materials were called $mNb_2O_5/CoO$ and $mNb_{2-x}Co_xO_5$. The synthesis of the photosensitized material was through impregnation of the methylene blue on $mNb_2O_5$, resulting a material calling $mNb_2O_5/MB$. All modified materials synthesized in this work are capable of absorbing energy in the visible region. These materials were applied in the photooxidation of inorganic sulfide, a process not well studied. Sulfide ion is a pollutant present in large quantities in effluents from food processing, oil refining and paper industry. As it is corrosive substance, it causes several economic and environmental damage. According to the World Health Organization (WHO) and US Environmental Protection Agency (EPA), less than 200 ppm sulfide must be present in water used for human consumption. The wastewater from the oil industry by itself contains sulfide up to 25000 ppm! The objective of this work is to transform these species of inorganic sulfide into less toxic forms of sulfur, such as sulfate ($SO_4^{2-}$), polysulfides, among others. The reactions were made using a thermostatic water bath and a visible light lamp (white light, 150 W). Sulfide concentration was monitored by UV-Vis spectroscopy (Shimadzu), with main reading at 229.5 nm. Aliquots were collected at different reaction times for 4 h to assemble the kinetic trend and study some parameters, such as the apparent rate constant ($k_{ap}$), the reaction order and the activation energy ($E_a$). The results show that the reactions are all pseudo-first order and indicate that the modified material with cobalt that has the highest amount of $Co^{3+}$ presents higher $k_{ap}$, consequently, lower $E_a$, compared to the other material. The photocatalyst $mNb_{2-x}Co_xO_5$ presented the highest $L_{2,3}$ edge energies, according to EELS analyses (Electron Energy Loss Spectroscopy). The edge energy increases with the increase in the oxidation state. It occurs by the reduction of the shielding and the increase of the effective nuclear charge. The photosensitized photocatalyst presented lower $k_{ap}$ compared to the other modified materials, probably because of a slower activation of the material, because it was indirect. The pure material and blank reaction presented very low and close $k_{ap}$, indicating that in both cases only a slow photolysis occurs. Raman (LabRAM HR Evolution) analyses of the final products showed the presence of $SO_4^{2-}$ and $S_2O_3^-$ species, and elemental sulfur. Also, there was a reduction in the bands corresponding to inorganic sulfide. Furthermore, modified photocatalysts maintain up to 50% of catalytic capacity for 4 cycles.

## Acknowledgments

The authors would like to acknowledge CNPq, CAPES, FAPEMIG and INCT-Midas for financial support and to the Centre of Microscopy at the Federal University of Minas Gerais (http://www.microscopia.ufmg.br) for providing the equipment and technical support for experiments involving electron microscopy.



HIS

# História da Química

**Área: HIS Nº de Inscrição: 823**

# O livro de Sumner e Vieira – Peculiaridades da Prática I: Hidrogênio

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Palavras Chave: *Colégio Pedro II, Ensino de Química, Atividades experimentais, História da Química.*

## Highlights

**Sumner and Vieira's book – Peculiarities of Practice I: Hydrogen**. Pedro II College. Experimental Teaching of Chemistry. History of Chemistry. The experimental Chemistry in Brazil.

## Resumo

No ensino de Química, a necessidade e importância da experimentação são evidentes, pois além de motivar os alunos e despertar a curiosidade, auxilia para uma maior aprendizagem. Ainda hoje, com tantas tecnologias disponíveis, são muitas as dificuldades enfrentadas pelos professores de Química para a realização de aulas experimentais[1]. Neste contexto, estudar a estruturação das práticas de Química em uma época em que os livros, manuais e apostilas constituíam os principais recursos didáticos utilizados pelos professores e alunos, é um campo interessante, desafiador e ainda pouco explorado. Este trabalho configurou-se em uma análise documental exploratória e estudo qualitativo, cujo objetivo foi conhecer e compreender aspectos importantes da estruturação e forma de abordagem do conteúdo experimental proposto no livro Química Prática para os cursos Fundamental e complementar (Fig 1A). O livro teve, supostamente, sua primeira edição publicada em 1939 e pode ter sido o primeiro manual de aulas práticas utilizado no Colégio Pedro II, pois consta nos primeiros planos de ensino que continham a indicação de aulas práticas[2]. Aborda-se neste trabalho, apenas o primeiro experimento proposto no livro, que cita o uso de um metal e um ácido em uma reação de deslocamento para obtenção do gás hidrogênio. Os autores descrevem que o hidrogênio poderia ser obtido: "Pela reação de deslocamento entre o ácido sulfúrico e o zinco, podendo se utilizar alternativamente o ácido clorídrico; Pela decomposição da água pelo ferro aquecido ao rubro; Por meio da eletrólise da água; Pelo processo de Raul Pictet, que consiste do aquecimento de uma mistura de metanoato de potássio e hidróxido de potássio, obtendo-se carbonato de potássio e hidrogênio" (Fig 1B)[3]. Na Figura 1C são apresentados os aparatos, possivelmente, usados para a realização da aula experimental proposta.

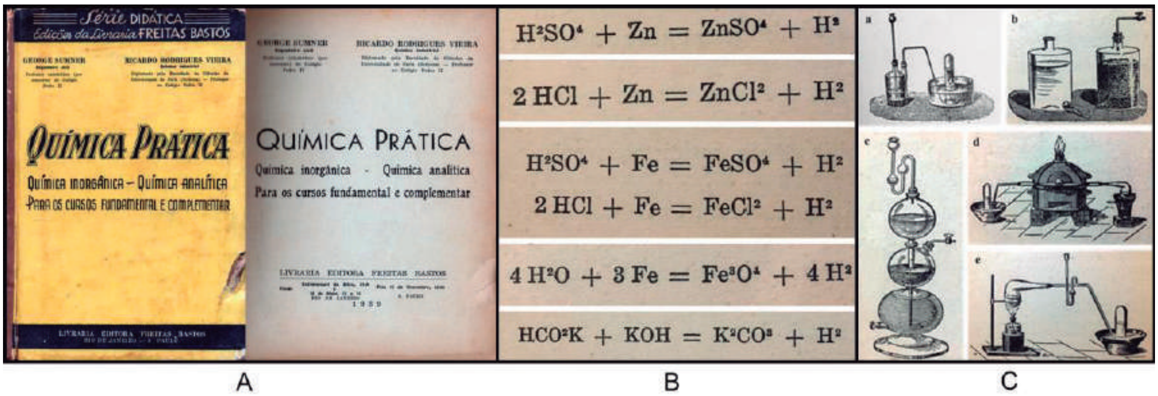

Figura 1 – Capa e contracapa do livro Química Prática de Sumner e Vieira (1939) (A); Reações citadas para obtenção do hidrogênio (B); Aparelhos empregados para a prática (C): a) Para a reação de deslocamento entre o ácido sulfúrico e o zinco; b) Preparação contínua do hidrogênio usando o aparelho de Sainte-Claire Deville; c) Aparelho de Kipp; d) Aparelho contendo tubo de porcelana aquecido ao rubro e feixes de fios de ferro; e) Retorna de vidro.

Apresenta-se neste trabalho, resumidamente, uma parte essencial da História da Química no Brasil. Ressalta-se ainda a importância dos manuais da época e a sua riqueza como fonte histórica.

**Referências**: [1]Stuart R. de C. Tópicos em ensino de química, São Carlos: Pedro & João Editores, p. 63-88, 2014; [2]Oliveira E. de Almeida F. O ensino Experimental de Química no Colégio Pedro II entre 1925 e 1942. 241 f., 2018; [3]Sumner G., Vieira R. R. Química prática para os cursos fundamental e complementar, 1939.

## Agradecimentos

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**Área: HIS**

# Reflections on the overvaluation of reason in Modern Science: what can we extract from Rousseau for Chemistry Teaching?

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Palavras Chave: *Ciência moderna, Iluminismo, J.J Rousseau, Ensino de Química.*

## Highlights

The scientism of the 17th and 18th centuries was something remarkable in the history of science, leaving marks for teaching. Therefore, we intend to discuss the reasons for overcoming such a vision.

## Resumo/Abstract

**Figura 1:** Tela “O alquimista em busca da pedra filosofal”.

A tela "O Alquimista em Busca da Pedra Filosofal", produzida em 1771, por Joseph Wright, representa a suposta descoberta da substância luminescente à qual foi atribuída o nome fósforo - do grego "portador de luz". As obras deste autor interessam aos estudiosos da História da Ciência para uma possível interação entre Arte e Ensino de Ciências; diante disso, a dispersão e intensidade da luz, na obra introduzida, parecem ser uma referência ao poder que o novo conhecimento (sobre a obtenção do fósforo no caso) poderia trazer[1]. Tal interpretação é possível diante da pintura que exprime o gesto de veneração religiosa da parte do alquimista, posto de joelhos diante do fenômeno observado, encantado com a luz emitida. Com efeito, a metáfora da luz alcança diversos contextos ao longo da história: no Velho Testamento não são raras as passagens que atribuem o conhecimento das coisas à iluminação divina, como no Salmo 36:9, onde “Graças a tua luz, vemos a luz”. Por outro lado, debruçando-se sobre os Princípios da Filosofia (1997), René Descartes defende que a faculdade de conhecer só é possível diante do esclarecimento dos objetos pela luz natural da razão. Percebe-se, portanto, a recorrência da analogia do ato de iluminar como possibilidade de atingir o conhecimento verdadeiro das coisas que pode estar presente na obra de Wright, mas que certamente está nos discursos iluministas que glorificavam a ciência enquanto *luz* que livraria os homens modernos da *escuridão* da ignorância. No entanto, quando vista sob a ótica de pensadores contemporâneos, aqui representados por Jean-Jacques Rousseau, a Ciência Moderna pode ter outra função que não a de tirar o homem da caverna platônica. Com a ousadia de censurar as ciências diante de uma das mais sábias companhias da Europa[2], o genebrino recebeu o prêmio da Academia de Dijon em 1750 por seu primeiro discurso em defesa de que a ciência empírico-indutivista da época estende “guirlandas de flores” sobre os ferros aos quais os homens encontram-se presos, por toda parte, desde que abriram mão de sua luz natural em favor de luzes artificiais que cegam por ofuscamento, pois as luzes produzidas pela Química, para Rousseau, deveriam acentuar a natureza problemática da essência da matéria e não revelar verdades ofuscantes e religiosamente veneráveis, como queriam alguns alquimistas[3], negando a validade daquilo que não é produzido na esfera operacional e estabelecendo um culto da razão. Diante disso, hoje, após diversas revoluções, as preocupações de Rousseau mostram-se caras aos professores de Química que pretendem romper com as visões simplistas de ciência resultantes da análise elitista, individualista, descontextualizada, aproblemática e ahistórica[4] do empreendimento científico que foi herdada dos métodos empírico-indutivistas dos séculos XVII e XVIII e ainda estão expressos pelo dogmatismo analítico sobre o “fazer ciência”. Nesse sentido, urge a necessidade de galgar discussões e (re)construir visões de ciência pautadas na reunião de veredas da História e Filosofia da Ciência que favoreçam o desenvolvimento de atividades teórico-práticas que tangenciam os interesses e conhecimentos sociais críticos, reflexivos e coletivamente construídos nos espaços formativos de professores(as) de ciências[5] de modo a dialogar com as utopias de um método universal de construção de conhecimento.

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# INO

# Química Inorgânica

**Área: INO** **Nº de Inscrição: 01045**

# Ability of Ru-nitrosyl complexes to inhibit tumor cell migration through metalloshielding of glycosaminoglycans (GAGs)

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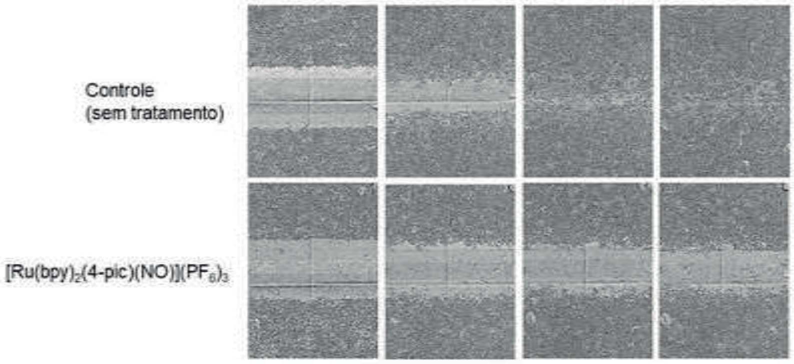
## Highlights

The present study shows the ability of Ru-nitrosyl compounds to bind glycosaminoglycans (GAGs) leading to an inhibition of tumor cells migration.

## Resumo/Abstract

GAGs, such as heparan sulfate (HS), when conjugated with proteins as heparan sulfate proteoglycans (HSPGs) have critical functions in cellular adhesion and migration. Recently studies have shown metallocompounds to block interactions between proteoglycans and binding partners, most notably inhibition of tumor migration, enzymatic cleavage, and growth factor binding.[1,2,3] In this work will be presented the ability of Ru-nitrosyl compounds to bind Fondaparinux (FPX, a pentasaccharide often used as a HS model) and the biological consequences of these interaction. The synthesis of nitrosyl ruthenium complexes *cis*-$[Ru(bpy)_2(L)(NO^+)]^{3+}$ (bpy = bipyridine; L = isonicotinamide, nicotinamide and 4-picoline) was conducted as previously described.[4] The FPX-binding were evaluated using methylene blue replacement assay. For this experiment we used 15.0 µM of FPX and 18.6 µM of Methylene Blue changing the concentration of the different Ru-NO complexes. The analyses were conducted in triplicate using an UV-Vis spectroscopy. In this study the compounds *cis*-$[Ru(bpy)_2(L)(NO^+)]^{3+}$ could inhibit FPX in the range of 25 µM to 51 µM. A wound healing study were developed using an IncuCyte with CHO-K1 cell line for confirm the ability of those compounds to inhibit the cell migration and the results showed an inhibition of cellular migration up to 60% when treated with *cis*-$[Ru(bpy)_2(L)(NO^+)]^{3+}$ compounds. The best activity were achieve by *cis*-$[Ru(bpy)_2(4\text{-pic})(NO^+)]^{3+}$, that was also the one that have had the better interaction with FPX. DNA-binding ability and cell viability assay were conducted showing that those compounds are not cytotoxic for this cell line. These results suggest that the *cis*-$[Ru(bpy)_2(L)(NO^+)]^{3+}$ compounds interact more favorably with heparan sulfate rather than DNA been able to shield GAGs without be cytotoxic. In this way, $[Ru(bpy)_2(L)(NO)]^{3+}$ are interesting candidates for an anti-metastatic agent and could be used in combination with other antitumor therapies in the fight against cancer.

Figura 1. Imagens obtidas a partir do equipamento IncuCyte® Live-Cell Analysis após diferentes períodos de tratamento (0, 12, 24 e 36h) com 500 µM do complexo *cis*-$[Ru(bpy)_2(4\text{-pic})(NO)](PF_6)_3$.



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**Área: INO**

# Activated carbon from soursop seed residue for adsorption of the Remazol Black B textile dye.

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Key words: *Activated carbon; Adsorption; Textile dye; Residual biomass; Point of Zero Charge.*

## Highlights

Activated carbon (SAC) produced from residual soursop pie. Use of SAC for adsorption of the Remazol Black B textile dye in aqueous medium.

## Resumo/Abstract

It is known that the textile industries discard a large amount of polluting waste in water, with dyes being one of the main polluting agents, which can generate serious environmental problems. One of the main processes studied for water treatment is adsorption. Studies with activated carbon produced from residual biomass have shown efficiency in the dye adsorption process. Activated carbon is considered an efficient adsorbent because it has a large surface area and microporosity, thus increasing its ability to remove contaminants. According to the Food and Agriculture Organization of the United Nations, the food industry discards about a third of the edible parts of food, and by not using these materials, they are called "waste", which if accumulated, can be harmful to the environment. In this context, the study of activated carbon from residual soursop biomass was proposed for application in the adsorption of the Remazol Black B textile dye in aqueous medium. Initially, the residual soursop pie was prepared by washing it with running water and drying it in a muffle, and characterized through immediate analysis, resulting in moisture and ash contents of 6.32% and 3.18%, respectively, which can positively influence the adsorption properties of the material; and for the content of volatile materials, an average of 75.7%, indicating that much of the material will decompose quickly in the combustion process. The preparation of activated carbon from soursoup biomass (SAC) was made from the carbonization of soursop seed residue in a muffle furnace and activated with $ZnCl_2$, and was characterized via XRD, FTIR and Point of Zero Charge (PZC), as well as the preliminary adsorption test against the removal of the Remazol Black B dye. XRD of SAC results showed a diffraction halo in $2\theta = 20^\circ$ at $30^\circ$, evidencing it as amorphous material, presenting disordered graphitic planes. FTIR spectra of SAC showed broad bands of stretching of -OH groups of carboxylic acids, around 3297 $cm^{-1}$ and absorptions at 2920 $cm^{-1}$, which can be said to be asymmetrical and symmetrical stretches -CH, in addition to the absorptions close to 1025 $cm^{-1}$ characteristics of -CO found in alcohols and phenols. Others, corresponding to C≡C at 2103 $cm^{-1}$ and C=C of aromatics at 1575 $cm^{-1}$. In Remazol Black B dye adsorption test, there was a removal of 55% in solution of pH=2, while in solutions of pH=6 and pH=10, 18% and 1%, respectively. These results are in agreement with the result of the PZC, since for pH values below 5.04, the adsorption is expected to be more effective than for pH values above 5.04.

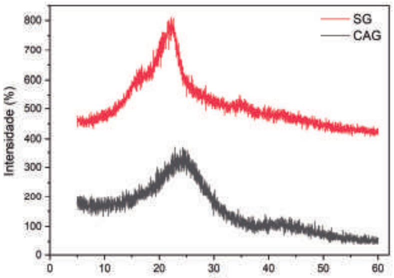

*Figure 1. X-ray diffraction spectra of activated carbons and in natura seed: "CAG" e "SG".*

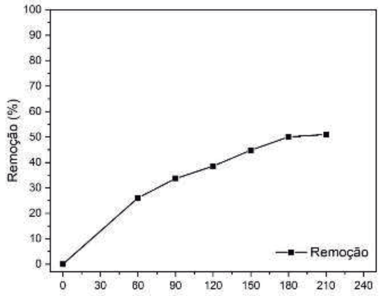

*Figure 2. Adsorption curve for removal of Remazol Black B dye at pH=2 using SAC.*

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## Agradecimentos/Acknowledgments

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**Área:______MAT_______ Nº de Inscrição:_00432______**

# A study of Pure Cu and Ag/Cu alloy nanoparticles as potential sensor components for optical fiber sensing

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Key words: LSPR, metal nanoparticles, fiber optics

## Highlights

- Pure Cu and Cu/Ag alloy NPs were synthesized via wet chemical reduction
- The NPs extinction spectra of light was characterized by UV-Vis absorption spectroscopy
- A simulation of the LSPR spectra, using the Finite Elements Method, was also done for the pure Cu nanoparticles

## Abstract

Metal nanoparticles (NPs) are present in a large array of interesting phenomena. One of those is the LSPR effect (Localized Surface Plasmon Resonance). An area in which they are largely applied is on optical fiber sensing. For instance, the metallic NPs are used in the detection of microorganisms, pollutants or even landslide prevention[1]. In this project, we have studied the synthesis of pure copper NPs and Ag/Cu alloy NPs to be applied as a sensor element in optical fibers sensors. In order to produce the pure copper NPs, copper(II) sulfate was used as copper precursor, the Polymer PEG was used as stabilizing agent, and $NaBH_4$ was used as reducing agent and water as solvent[2]. For the Bimetallic NPs, copper acetate and silver(I) nitrate were used as metal precursors, ascorbic acid was evaluated as stabilizing agent and again, $NaBH_4$ was used as reducing agent, the presence of sodium citrate was also evaluated in each test, a 3:1 mixture of water and isopropyl alcohol was used as a solvent[3]. Furthermore, the NPs were characterized by UV-Vis absorption spectroscopy to characterize the extinction spectra (absorption + scattering) of light due to LSPR effect (figure 1 for pure copper; figure 2 and 3 for bimetallic). A parallel simulation of LSPR in copper NPs was also done by using the Finite Elements Method to corroborate with the experimental results[4]. For the bimetallic ones, it was observed that the presence of sodium citrate in solution is determinant for its stabilization and the NPs obtained seemed to be more stable, as the extinction spectra for those NPs could still be detected after one week. Therefore, the pure Cu and Ag/Cu alloy NPs were successfully synthesized and the UV-Vis results show that they have potential for the fabrication of optical fiber LSPR based sensors.

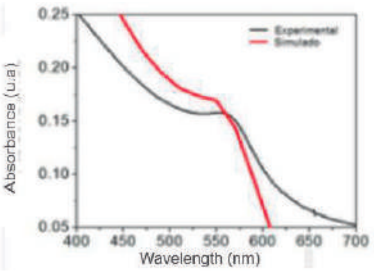

Figure 1 - Extinction spectra for pure Cu NPs and simulation

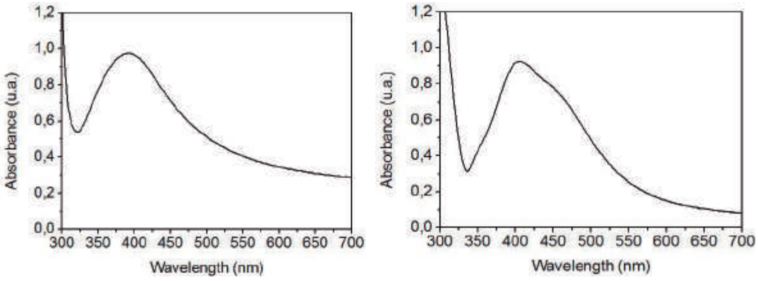

Figure 2 - Extinction spectra for Ag/Cu alloy NPs. a) right after synthesis. b) after 1 week

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**Área: INO**

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

**Nº de Inscrição: 01046**

*(Inserir o número de inscrição do autor que fez a submissão)*

# Avaliação da formação do complexo Cu(II)-Carbendazim em águas naturais por medidas eletroanalíticas

**Aymara da Silva Santos (IC),[1] Ana Layla Carvalho de Lima (IC),[1] Carolina Zeni Pires Mecca (PG),[1] Fabio Ruiz Simões (PQ), Lucia Codognoto (PQ), Eliana Maíra Agostini Valle (PQ),[1]**

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*Palavras Chave:* Carbendazim, complexo de cobre, águas naturais, voltametria de redissolução anódica.

## Highlights

Evaluation of the Cu(II)-Carbendazim complex formation in natural waters by electroanalytical techniques

Carbendazim (MBC) is an example of a harmful pesticide, which has atoms of nitrogen and oxygen in its structure that can form complexes with metal ions. Thus, in this work was studied the interaction between the copper (II) metal ion and carbendazim and its formation in natural water.

## Resumo/Abstract

O carbendazim (MBC) é um fungicida da família dos benzamidazóis, que inibe a formação de tubos germinais, agindo na mitose dos fungos [1]. A estrutura molecular do carbendazim apresenta átomos de nitrogênio e oxigênio que podem interagir com íons metálicos [2]. Estudos prévios denotaram uma possível interação entre o íon metálico cobre e o pesticida carbendazim em água ultrapura. Neste trabalho avaliou-se a formação do complexo em águas naturais.
As medidas foram realizadas a partir de soluções estoque de carbendazim $1{,}0\times10^{-3}$ mol $L^{-1}$, em etanol e $Cu(NO_3)_2$ $1{,}0\times10^{-3}$ mol $L^{-1}$, em água ultrapura. As medidas eletroquímicas foram realizadas em um Potenciostato/Galvanostato AUTOLAB PGSTAT128N, com três compartimentos. Eletrodo de trabalho: Carbono Vítreo (GC); Eletrodo de Referência: Ag/AgCl (KCl sat.); Eletrodo auxiliar: placa de platina; Eletrólito de suporte: solução de $KNO_3$ 0,1 mol $L^{-1}$ e em amostra de água da Represa Billings, situada no Bairro Eldorado - Diadema, próximo as dependências da Universidade Federal de São Paulo.
A partir de técnicas eletroquímicas, como voltametria cíclica, observou-se um pico de redução em 0,010 V e um pico de oxidação em 0,430 V, inferindo a interação entre as espécies. Por voltametria de redissolução anódica, observamos a complexação em uma proporção 1:1 e 1:2. Utilizou-se Espectroscopia de Impedância Eletroquímica (EIS) para avaliar o comportamento do complexo Cu-Carbendazim e a influência dos componentes da água natural (Billings), onde não foram observadas diferenças significativas na comparação dos resultados obtidos com amostras de MBC ou Cu-MBC, indicando que o efeito sinérgico observado na amostra de Cu-MBC, como o pico observado em 0,5 V, ocorreu devido à formação do complexo em solução sem afetar a superfície do eletrodo.

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CNPq, CAPES e FAPESP (2017/24235-8) pelo suporte financeiro.

**Área: INO**

# Benziloxychalcone copper(II) complexes: synthesis and solution stability.

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Chalcone, complexes, copper(II), solution stability.

## Highlights

New copper(II) benziloxychalcone complexes. UV-visible solution stability studies.

## Resumo/Abstract

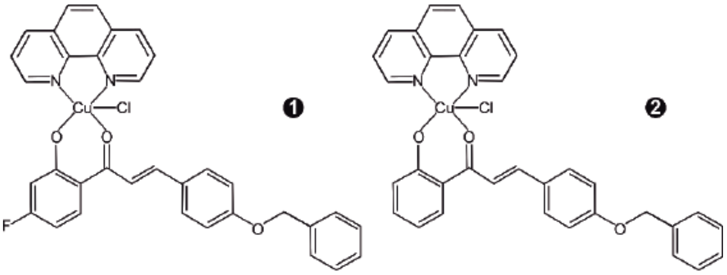

*Fig. 1 - Molecular structures of complexes [Cu($L_1$)(phen)Cl] (1) and [Cu($L_2$)(phen)Cl] (2).*

Chalcones are chemical precursors of flavonoids[1] and exhibit a range of biological properties, including anticancer[2], anti-inflamatory[3], antimalarial[4] activity. Transition metal complexes of chalcones show in vitro activities such as anticancer[5], antioxidant[6], and antibacterial[7]. Herein we report the synthesis and characterization of novel copper(II) complexes of benziloxychalcones of type [Cu(L)(phen)Cl] (L = deprotonated form of hydroxychalcones [3-(4-(benzyloxy)phenyl)-1-(4-fluoro-2-hydroxyphenyl)prop-2-en-1-one ($L_1$)[8] and 3-(4-(benzyloxy)phenyl)-1-(2-hydroxyphenyl)prop-2-en-1-one] ($L_2$)[9]; phen = 1,10-phenanthroline). The synthesis followed the methodology adapted from the literature[10]. Structure elucidation was carried out by elemental and spectroscopic methods (high-resolution mass spectrometry, infrared spectroscopy, and electronic spectroscopy), and single-crystal X-ray diffraction. The results indicate the coordination of one chalcone by the two oxygen atoms in the basal plane of the square pyramidal geometry complemented by the coordination of phenanthroline. In the axial position, a chloride is coordinated, carrying through the neutrality of the molecule. The UV-visible spectra of 1 and 2 show a broad band [420 nm (1) and 440 nm (2)] assigned to metal-ligand charge transfer besides ligand bands in 275 and 370 nm . Stability evaluation in solution indicates ligand exchange of both complexes in dimethylsulfoxide The MLCT decreases slowly in time, indicating discoordination. Lipophilicity of the complexes was determined, both approximately zero, indicating almost equal distribution between aqueous and organic layers. In vitro anticancer and leishmanicidal activities are to be performed.

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**Área: INO registration Nº 1360**

# Catalytic study of manganese porphyrins substituted dimethylamino and immobilized under SBA-15/APS for the oxidation of cyclohexane

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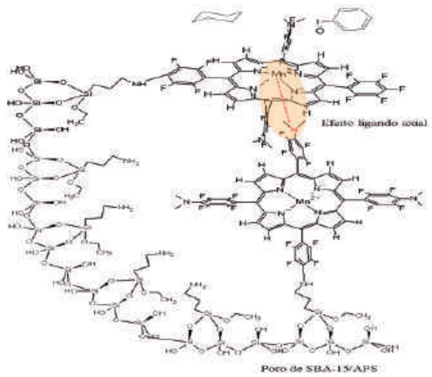
Palavras Chave: Biomimetic catalytic , manganese porphyrin, cyclohexane, MnPSBA-15

## Highlights



The exceptional results in catalytic performance of the MnP(F5)-SBA15 system indicate possible synergy between the two types of porphyrins inside the pore, positioned perpendicular to each other and close to the behavior of the MnP-imidazole system.

## Resumo/Abstract

The textural features of mesoporous silicate SBA-15 such as pore size (7.3 nm)[1] and wall thickness (4.9 nm)[1] prove to be a suitable matrix as supported in the immobilization of metalloporphyrins, as biomimetic of cytochrome P450. Three heterogeneous catalytic systems MnP supported on SBA-15/APS were synthesized and characterized. The synthesis of the material involved the insertion of the manganese ion in the center ring of the tetrakis-pentafluorophenyl porphyrin in DMF, in which three metallated fractions were obtained, MnP(F5), MnP(F6) and MnP(F3) with different degrees of nucleophilic substitution of -F by -$N(CH_3)_2$ (from the decomposition of DMF) in the *para* positions of the phenyl group. The samples were analyzed and characterized by UV-Vis and IR spectroscopy, mass spectrometry and cyclic voltammetry. On the other hand, the SBA-15 support was functionalized with APTES and characterized by IR, thermogravimetric and differential analysis, $N_2$ adsorption-desorption with the consequent "grafting" immobilization and characterization by diffuse reflectance spectroscopy, thus confirming the immobilization of MnP $\lambda_{max}$~460 nm in UV-Vis. Analysis by UV-Vis spectroscopy showed a loading of 5.7; 7.2; 3.8 μmol MnP/g catalyst for MnP(F5)-SBA15, MnP(F6)-SBA15 and MnP(F3)-SBA15, respectively..

**Table 1**. Cyclohexane oxidation with PhIO catalysed by manganeseporphyrins in a heterogeneous system.

| Catalyst | Selectivity (ciclohexanol) | Yield (%) |
|---|---|---|
| **MnTPFPP-SBA15**[2] | 80 | 46 |
| **MnP(F5)-SBA15** | 73 | 93 |
| **MnP(F6)-SBA15** | 78 | 66 |
| **MnP(F3)-SBA-15** | 89 | 26 |

Molar ratio 1 MnP:40 PhIO, Air atmosphere, 24 h, Room Temp, analyzed by GC-FID

The results of the catalytic tests of cyclohexane oxidation obtained in the reactions showed an exceptional performance for MnP(F5)-SBA15, with a yield of 93% higher than that obtained for MnTPFPP-SBA15. MnP(F5)-SBA15 consists of porphyrins di and tri substituted by –$N(CH_3)_2$ in which a possible synergistic effect occurs, in which one of the MnPs (-$N(CH_3)_2$ group) acts as an axial ligand in a second MnP, analogous to what occurs in the MnP-imidazole system. This process takes place inside the mesopore that acts as a nanoreactor.

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## Agradecimentos/Acknowledgments

The authors thank the Brazilian agencies CAPES (PG-Mestrado), CNPQ (PQ-2Proc.309143/2020-9), also thank Lucas Zanatta by SBA-15 synthesis

**Área: INO** **Nº de Inscrição: 00021**

# Cobalt(III) 1,1-dithiolate complexes: a DFT study of their spectroscopic and structural properties

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Palavras Chave: *Cobalt(III), Dithiocarbamates, Xanthates, Thioxanthates, DFT, TD-DFT*

## Highlights

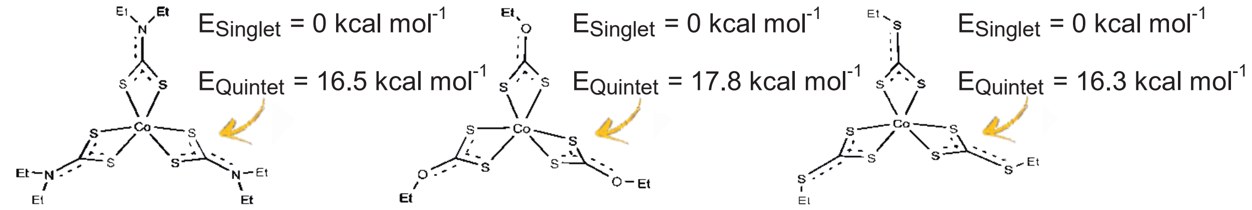
Cobalt(III) 1,1-dithiolate complexes are low spin. A slight difference in absorption wavelengths and an increase in oscillator strengths were observed from the dithiocarbamate to the thioxanthate one.

## Resumo/Abstract

Dithiocarbamates, xanthates and thioxanthates are some examples of a general class of monoanionic 1,1-dithiolate ligands[1]. Although they look very similar, the dithiocarbamates occupy a very special niche and has been studied in different fields, such as industrial applications and biological systems[1,2]. All of them form stable complexes with transition metal ions (e.g. cobalt(III)), due to the coordination ability of dithio ligands[2]. In this work, DFT (Density Functional Theory) and TD-DFT (Time-Dependent Density Functional Theory) calculations were performed in order to obtain a deeper insight into the structural and spectroscopic properties of tris(N,N-diethyldithiocarbamato-S-S')cobalt(III), tris(O-ethylxanthato-S-S')cobalt(III) and tris(ethylthioxanthato)-cobalt(III). The geometries in the gas-phase of the three studied complexes were obtained by optimizing the accessible experimental structures from the Cambridge Structural Database (CSD). Several functionals and basis sets were tested to find the best methodology to describe both geometry and electronic absorption spectra of the complexes. From these first results, CAM-B3LYP with 6-31G** basis set proved to be the most accurate methodology and was therefore used throughout this work. The geometry optimization was also carried out taking into account the effect of the solvent (chloroform), showing little increase in the bond lengths in relation to the experimental data.

Due to the configuration $d^6$ of Co(III), there are two possibilities for the complexes multiplicities (2S+1): singlet (low spin) or quintet (high spin). The energies and the bond lengths for each complex were compared for both cases after geometry optimization and they indicated that all of them were low spin (Figure 1). For the most stable structure was attributed an energy of 0 kcal $mol^{-1}$ and the energy difference for the less stable one was calculated in relation to this value. The bond lengths for the singlet complexes showed a relative error of up to 3% in relation to the experimental data and, for the quintet ones, this error increased for up to 11%.

Finally, the TDDFT calculations showed that the studied complexes had only slight difference in the absorption wavelengths, but the oscillator strengths of the monitored transitions increased in the order ETXACO01 < COEXAN < ETDCCO02.



$E_{Singlet}$ = 0 kcal $mol^{-1}$ $E_{Quintet}$ = 16.5 kcal $mol^{-1}$

$E_{Singlet}$ = 0 kcal $mol^{-1}$ $E_{Quintet}$ = 17.8 kcal $mol^{-1}$

$E_{Singlet}$ = 0 kcal $mol^{-1}$ $E_{Quintet}$ = 16.3 kcal $mol^{-1}$

**CSD refcode: ETDCCO02** **CSD refcode: COEXAN** **CSD refcode: ETXACO01**

**Figure 1.** Energy difference between the singlet (low spin) and the quintet (high spin) Co(III) 1,1-dithiolate complexes.

**References**: [1] Hogarth G. *Mini-Reviews in Medicinal Chemistry*. 2012, 12, 1202-1215.
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## Agradecimentos/Acknowledgments

**Área: INO**

# Complex of luminescent europium containing bis(diphenylphosphine)oxide ligands

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*Keywords: trivalent europium, β-diketone, luminescence, bis(diphenylphosphine)*

## Highlights

Novel kind of $Eu^{3+}$-β-diketonate complexes with phosphine oxide ligands have been successfully synthesized. The ligand-to-metal energy transfer processes in these complexes have been investigated.

## Abstract

Trivalent lanthanide coordination compounds are characterized by their long luminescence lifetime of emitting level, narrow emission band and high color purity, which makes them fascinate for application in LCMDs, OLEDs, immunoassay, bioimaging probes, luminescent sensors and in telecommunications systems etc. Among this class of compounds, those ones in which β-diketonate ligands act as luminescence sensitizers have found a prominent position. However, most of these systems are obtained in the form of simple molecular entities. Recently, interest in new polynuclear systems containing diketonate ligands has been growing significantly. Therefore, this work reports on the synthesis, characterization, and photophysical properties of the lanthanide compounds of general formula $[Ln_2(\beta\text{-dik})_6(dppeO_2)]$, where β-dik = tta, bzac, dbm, $[Ln(\beta\text{-dik})_3(dppeO_2)]$ where β-dik = btf and $[Ln(\beta\text{-dik})_3(dppeO_2)_2]n$ where β-dik = fod, $dppeO_2$ = 1,2-Bis(diphenylphosphino)ethane oxide, Ln = $Eu^{3+}$ and $Gd^{3+}$. These complexes were prepared by direct reaction among ethanolic solutions of the $[Ln(\beta\text{-dik})_3(H_2O)]$ complexes and $dppeO_2$ ligands in the molar ratios $[Ln(\beta\text{-dik})_3(H_2O)]$: $dppeO_2$ of 2:1. The FT-IR spectra of complexes show red-shifted of 20–41 $cm^{-1}$ for the band assigned to the ν(C=O) vibrational mode (Fig 1a), suggesting that β–diketonate ligands are coordinated to the $Ln^{3+}$ ion in chelating mode. Diffuse reflectance spectra of the $Eu^{3+}$-complexes show strong absorption bands in the range of 200–450 nm ascribed to the $S_0 \rightarrow S_n$ (ππ* or mixed nπ*) transitions from the diketonate ligands. The high relative intensities between excitation bands from ligand and 4f-4f transitions in the complexes with tta, btf and bzac indicates an efficient ligand-to-metal energy transfer process. On the other hand, for complexes with fod, dbm and bzac (Fig 1b) a lower intensity of the ligand bands is observed, suggesting that a luminescence suppression channel is operative. The emission spectra present the bands assigned to the $^5D_0 \rightarrow {}^7F_J$ (J = 0–4) transitions of the europium ion (Fig 1c). The $\Omega_2$ and $\Omega_4$ intensity parameters, lifetime (τ) and luminescence intrinsic quantum yield $\phi_{Eu}^{Eu}$ were calculated from the emission spectral data and luminescence decay curves of the compounds in solid state (Table 1). According with these data, the polymeric or dimeric investigated systems exhibit high luminescence intensities in the red region, which make them potential candidates for application as emitting layer in molecular light-converting devices.

Table 1. Experimental intensity parameters ($\Omega_\lambda$), lifetime (τ), radiative ($A_{rad}$) and non-radiative ($A_{nrad}$) coefficients, and intrinsic quantum yield $\phi_{Eu}^{Eu}$) of complexes 77 K.

| | τ (ms) | $\Omega_2$ ($10^{-20}cm^2$) | $\Omega_4$ ($10^{-20}cm^2$) | $A_{rad}$ ($s^{-1}$) | $A_{nrad}$ ($s^{-1}$) | $A_{tot}$ ($s^{-1}$) | $\Phi_{Eu}^{Eu}$ (%) |
|---|---|---|---|---|---|---|---|
| $[Eu(btf)_3(dppeO_2)]$ | 0.7938 | 23.41 | 7.14 | 897 | 669 | 1566 | 46.8 |
| $[Eu_2(tta)_6(dppeO_2)]$ | 0.6909 | 21.88 | 6.34 | 839 | 857 | 1697 | 40.7 |
| $[Eu_2(bzac)_6(dppeO_2)]$ | 0.6445 | 17.95 | 6.08 | 727 | 961 | 1688 | 38.0 |
| $[Eu(fod)_3(dppeO_2)_2]$ | 0.5209 | 17.28 | 8.49 | 773 | 1330 | 2103 | 30.7 |
| $[Eu_2(dbm)_6(dppeO_2)]$ | 0.4863 | 23.51 | 8.75 | 940 | 1406 | 2.346 | 28.6 |

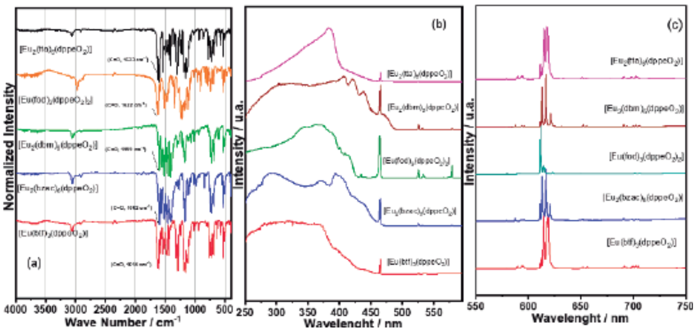

Figure 1. (a) Absorption spectra in the infrared region of the complexes. (b) Complex excitation spectra 77 K and (C) Complex emission spectra 77 K

## Acknowledgments

This work was supported by CNPq, FAPESP, FINEP, CAPES and UFPB.

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[2] Kitagawa, Y. *et al.* (2021) *Chemistry - A European Journal*, 27(1), pp. 264–269.
[3] Teotonio, E. E. S. et al. (2009) *Optical Materials*, 32, pp. 345-349.

**Área: INO**

# Computational Approaches of Metalloporphyrins Containing Pyrenyl Units: Influence of the Metal Center

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Keywords: Meso-porphyrins, Metallo-derivatives, TD-DFT.

## Highlights

Theoretical calculations were relevant to fully analyzed the structural parameters along with charges and molecular orbitals from TD-DFT methodology. Calculated Soret and Q-bands have a good agreement with experimental ones.

## Resumo/Abstract

Porphyrins applications can be explored in fields, such as catalysis, medicinal chemistry, photodynamic therapy, and biomimetic systems. Due to the importance of tetrapyrrole macrocycles, especially in the design of photosensitizers, time-dependent density functional theory (TD-DFT) provide a way to check on the assignments in the electronic transitions to analyze the photophysical behavior of free-base meso-tetra-(1-pyrenyl)porphyrin ($H_2$TPyrP) and its metallo-derivatives containing Zn, Cu, Ni, Co and Mn (Figure 1).[1]

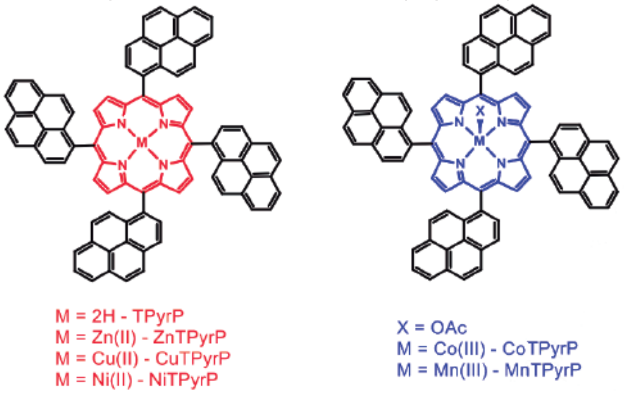

Figure 1. Molecular structures of meso-tetra-(1-pyrenyl) porphyrin derivatives.

The substitution of the inner hydrogens by metal ions changes the structure of the porphyrin in the planarity of the ring. For MnTPyrP and CoTPyrP the metals are above the plane formed by the nitrogen atoms, breaking planarity, which explain the long wavelength absorption bands. For Ni and Zn complexes, displacement of the metal ions were not observed, as well as in CuTPyrP. The main transitions can then be associated with the highest oscillator strengths (*f*). For $H_2$TPyrP the experimental main absorption band lies at 432 nm and appeared as the most intense band in the calculated spectrum. The *f* values indicated that this band have a contribution of four other bands, where HOMO-1, HOMO and LUMO are the most relevant orbitals for such transitions (Figure 2). This may be assigned from pyrenyl groups to pyrroles groups.

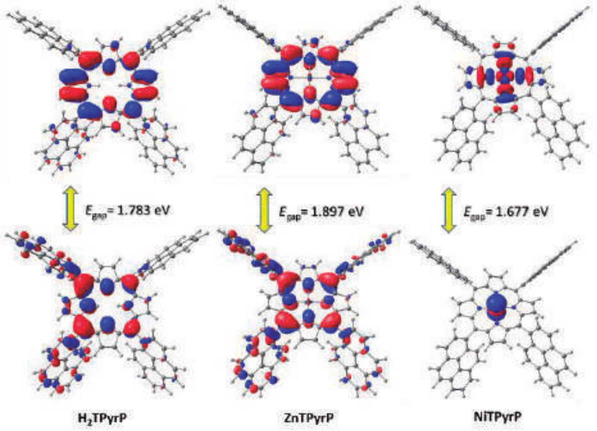

Figure 2. HOMO-LUMO gap for some pyrenyl-porphyrins.

For the metalloporphyrins, Soret bands are located in the range of 442 to 479 nm, which is in good agreement with experimental data. In these cases, LUMO+1 orbitals are also involved, receiving electrons from HOMO type orbitals, indicating metal-ligand charge transfer. The Q-bands were also in good accordance with experimental values (520-650 nm). For CoTPyrP and MnTPyrP the Q band appears in 720 nm.

1. *Eur.J.Inorg.Chem.* **2022**, doi.org/10.1002/ejic.202200075

## Agradecimentos/Acknowledgments

We thank the research funding agencies CNPq and CAPES, and UFJF.

**Área: INO**

# Copper (II) Complexes of Schiff Bases N,N,O and N,N,N,O as catalysts of the $CO_2$ to $HCOO^-$ reduction.

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Keywords: *(Carbon Dioxide Reduction, Copper Complexes, Schiff Bases).*

## Highlights

Perchlorate Cu (II) complexes were applied as catalysts in the electrochemistry reduction of $CO_2$. The formate ion was obtained as reduction product and the catalytic process depended on the ligand.

## Resumo/Abstract

The perchlorate copper (II) complexes synthesized for this work (Figure 1) showed catalytic activity in the $CO_2$(g) electroreduction carried out in acetonitrile/PTBA 0,1 mol $L^{-1}$ electrolyte solution. This catalysis was increased using the 2,2,2-trifluoroethanol (TFE) as proton source. According with de Cyclic Voltammetry (CV) performed in the cathodic way, after the $CO_2$ saturation there was appearance of cathodic peak attributed to adduct formation $CO_2$-copper complex evidenced by the small shift of Cu(I)/Cu(II) redox pair (around – 0.6 V vs Ag/AgCl), an increase of the current after this process and around -0.9 V vs Ag/AgCl.[1] After addition of the proton source, there were two processes in the metal region attributed to the Cu(I)/Cu(II) and Cu(0)/Cu(I) pairs and appearance of a anodic desorption process close to 0 V that would indicate the film formation of copper. The catalysis occurs in the region of the ligand, because after Controlled Potential Electrolysis (CPE) carried out in two potentials, -1.2 and -2.0 V vs Ag/AgCl, only in the second was possible observed a considerable increase in the current (catalytic current) which corresponds to the catalytic process. The confirmation occurred by the RMN $^{1}H$ and $^{13}C$ analysis of the electrolytic solution after CPE, where it was identified the 8.47 and 164.3 ppm peaks for the $^{1}H$ and $^{13}C$ in $D_2O$, respectively. So far, faradaic yield (FE %) and kinetic parameters (TOF and TON) calculation from the electrochemical experiments are being performed to the better comparison between the series of the complexes.

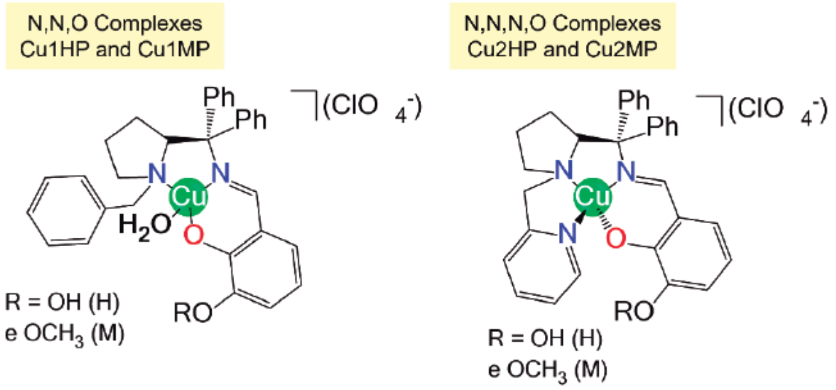

Figure 1. Structures of the series 1 and 2 copper (II) complexes.

Referências:

[1]M. Isaacs, J.C. Canales, M.J. Aguirre, G. Estiú, F. Caruso, G. Ferraudi, J. Costamagna. *Inorg Chim Acta*. 339 **(2002)** 224-232.

## Agradecimentos/Acknowledgments

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**Área: INO**

# Deep-red emitting heteroleptic iridium(III) complexes: promising optical oxygen sensors for medical diagnostics

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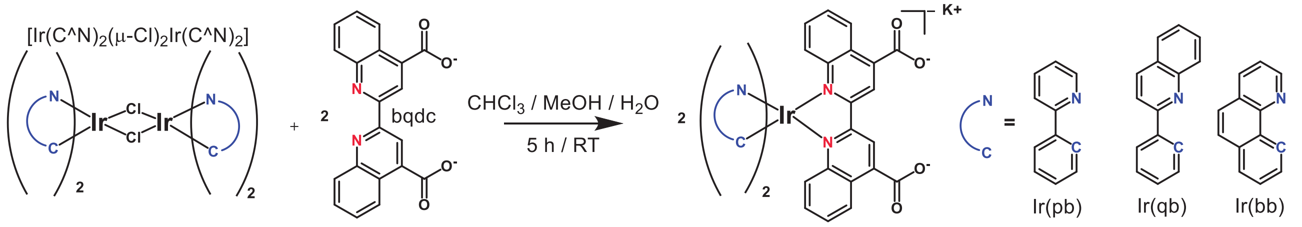
Keywords: *Ir(III), Phosphorescence, Probes, Spin−Orbit Coupling (SOC).*

## Highlights

Deep-red emitting Ir(III) complex as a promising oxygen sensing probe.

## Abstract

In this work we report a novel series of deep-red emitting Ir(III) complexes. Nowadays, iridium(III) complexes have emerged as viable alternatives as diagnostic probes [1], especially for the biological environment, due to their excellent photophysical properties. It can act as a luminescent probe to hypoxia and hyperoxia processes that may indicate some pathology [2], since its triplet-like emission state is very sensitive to oxygen. The Ir(III) heteroleptic complexes was designed and synthesized according to the routes shown in Scheme 1. Both synthesized Ir(III) complexes were characterized for structural elucidation by MALDI-TOF mass spectrometry, $^1$H-NMR, $^{13}$C-NMR and FTIR. The excited state had its photophysical properties studied by UV-Vis and Photoluminescence Spectroscopy. MALDI-TOF analysis confirmed the formation of complexes, calc./found (m/z): K[Ir(pb)]$^+$ 883.13/883.01, [Ir(qb)]$^+$ 944.20/944.91 and [Ir(qb)]$^+$ 944.20/944.91. By $^1$H-NMR it was possible to assign all the hydrogens to the chemical structures of all Ir(III) complexes.



**Scheme 1:** Synthetic route of heteroleptic Ir(III) complexes. The precursor dimer were synthesized by the Nonoyama route.

Absorption spectra in the UV-Vis of the Ir(III) complexes exhibit high molar absorptivity between 225 – 700 nm, Fig. 1(a). In the high energy region 225 – 300 nm is attributed to the spin-allowed Ligand-Centered singlet transitions $^1$LC $\pi\rightarrow\pi^*$. The medium energy region between 300 nm and 400 nm shows bands of lower intensity assigned to the spin-allowed singlet Metal-to-Ligand Charge Transfer $^1$MLCT (d$\pi$(Ir)$\rightarrow\pi^*$). Between 400 nm – 700 nm, transitions forbidden by spin selection rule are found, $^3$LC and $^3$MLCT. The strong Spin-Orbit Coupling (SOC) of Ir(III) relaxes these forbiddeness, making them more likely to occur, which also facilitates intersystem crossing between nominally $S_1$ and $T_1$ states. Emission spectra obtained for each Ir(III) complexes in aerated DMSO at 298 K are viewed in Fig. 1(b), where deep-red broad emission from the $^3$LC-$^{1,3}$MLCT hybrid states are observed. Complexes showed sensitivity to $O_2$, Fig. 1(c), while the quantum yield ($\Phi_{\%}$) increased under hypoxia conditions (aerated, $N_2$ saturated): Ir(pb) 8.7, 12.8; Ir(qb) 5.0, 16.1 and Ir(bb) 10.6, 17.8. The complexes exhibited long lifetimes with suitable $\Phi$ when compared to literature ($\mu$s): Ir(pb) 145.5; Ir(qb) 170.2 e Ir(bb) 66.8. Here we conclude, based on the results, that these Ir(III) complexes are promising to be used for intracellular and *in vivo* oxygen sensing.

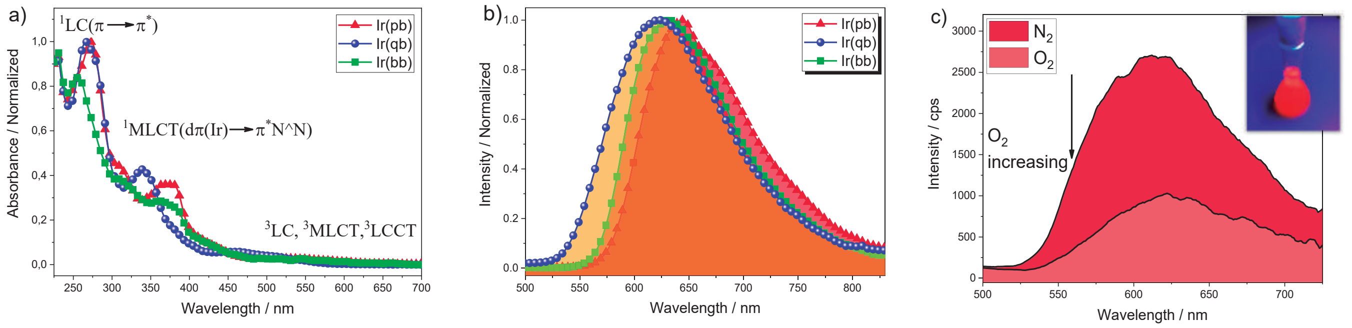


**Figure 1:** Absorption spectra in the UV-Vis in DCM solution 1.0x10$^{-5}$ mol.L$^{-1}$ (a). Emission Spectra ($\lambda_{ex}$ = 370 nm) in aerated DMSO solution 1.0x10$^{-5}$ mol.L$^{-1}$ (b). Emission of the Ir(qb) in aerated solution and after bubbling $N_2$ (c), inside: photographs of Ir(qb) solution under UV ($\lambda_{max}$ = 350 nm).

Reference: [1] Canisares, F.S.M. et al. Red-emitting heteroleptic iridium(III) complexes: photophysical and cell labeling study. Photochem. Photobiol. Sci (2022). [2] Zhang, K. Y. et al. Dual-phosphorescent iridium(III) complexes extending oxygen sensing from hypoxia to hyperoxia (2018).

## Acknowledgments

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**Área: INO**

# Desenvolvimento de sal complexo de Co(III) com hidroxiureia: potencial alternativa ao tratamento da Doença Falciforme

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Palavras Chave: *Cobalto, Hidroxiureia, Complexos, Doença Falciforme.*

## Highlights

Development of Co(III) complex salt with hydroxyurea: a potential alternative treatment for sickle cell disease

Synthesis and characterization of a Co(III) complex containing hydroxyurea as ligand. Obtention of a potential less aggressive drug for the treatment of sickle cell disease.

## Resumo/Abstract

A Doença Falciforme, de origem genética, acarreta quadros clínicos de falência de múltiplos órgãos e baixa expectativa de vida [1]. Substância utilizada no tratamento desta hemoglobinopatia, a hidroxiureia (HU) apresenta alta eficiência farmacológica, porém com vasta lista de prováveis reações adversas. Tal fármaco, do ponto de vista molecular, é capaz de se ligar a centros metálicos. Estudos têm revelado a alteração de propriedades de fármacos quando coordenados a centros metálicos [2]. Nesse sentido, a síntese de complexos contendo HU como ligante revela-se uma via interessante para a obtenção de medicamentos menos agressivos. Por conta disso, este trabalho visou a síntese e a caracterização inicial do complexo $Co(NH_3)_5(HU)]^{3+}(PF_6^-)_3$. O sólido obtido (rosa) e seu precursor $[Co(NH_3)_5Cl]Cl_2$, um sólido lilás, foram caracterizados por espectroscopia nas regiões do ultravioleta, visível e infravermelho, assim como foi avaliado o comportamento do novo sólido em água.

Comparando com o espectro de HU na região do infravermelho, o deslocamento da banda em 1644cm$^{-1}$ (associada à frequência de estiramento da carbonila, presente no fármaco [3]) para 1623cm$^{-1}$ é um indicativo da coordenação da hidroxiureia ao Co(III), via oxigênio da carbonila. Outro indicativo da coordenação de HU ao centro metálico é o deslocamento da banda na região do visível – de 530nm (precursor) para 517nm, atribuída à transição eletrônica envolvendo os orbitais d do centro metálico), sinalizando a substituição de ligante. Todavia, o aumento do pH do meio (5,5 para 6,2), após a adição do sólido em água, a uma concentração de 1,29mmolL$^{-1}$, é atribuído à atuação do sólido como base de Brönsted-Lowry frente à água, um indicativo de que sua fórmula química, na realidade, é $Co(NH_3)_5(HUd)]^{2+}(PF_6^-)_2$, onde HUd = hidroxiureia desprotonada. Assim sendo, os dados iniciais fundamentam a obtenção do complexo contendo HUd coordenada. Demais caracterizações contribuirão para elucidação estrutural, após as quais ensaios biológicos serão efetuados.

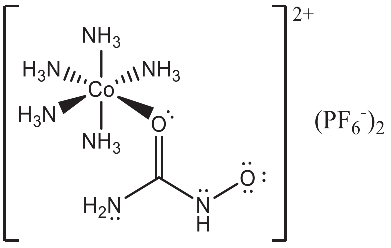

Figura 1. Estrutura do $Co(NH_3)_5(HUd)]^{2+}(PF_6^-)_2$

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**Área: INO**
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# Development of self-regenerating hybrid materials

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**Keywords**: *Hydrogel, Inorganic materials, Self-healing, Cell culture, Hybrid materials.*

## Highlights

Biomaterial-crosslinking chemistry;
Importance of the multifunctional hydrogels;
Hydrogel and inorganic materials, the ideal combination;

## Resumo/Abstract

Nowadays, there is an increasing concern with regards to the health of human beings. A considerable health concern is associated with the largest organ in the human body, the skin. It protects our interior from damage and microbial invasion and controls body fluids, electrolytes, and nutritional factors. The natural skin, which contains a great volume of water inside, is self-healing, elastic and detect any kind of environmental change. Cartilaginous tissue plays a very important role in living organisms in preventing dehydration and in protecting internal organs from chemical damage. However, the cartilaginous tissue can lose its protective capacity; in this case, there is some serious damage, such as burns, surgeries, skin diseases, among others, causing a wound. The self-healing is the ability of the material to restore its original shape and repair damages, restoring its mechanical and functional properties. The water-based materials, such as hydrogels, help to keep humidity in the damaged area, allow the permeation of oxygen and regulate the temperature in the injured surface, relieving the pain of patients. These biomaterials are obtained as wound dressings, which are used for the regeneration of cartilaginous and bone tissues. Therefore, the development of hydrogels using biomaterial-crosslinking chemistries has received a great deal of attention in the last decade. Although these materials offer a wide range of applications, their poor mechanical properties in the hydrated state, such as limited elastic response to stress and low absorbed energy per unit volume, is one of the major drawbacks that leads to early rupture of the structure. Furthermore, the mechanical proprieties of self-healed hydrogels are inferior those of the original materials, before undergoing some damage. The combination of a hydrogel with inorganic nanoparticles to form hybrid structure using specific crosslinking chemistries, which give the material a covalent character, is a response to this concern, besides being a step forward in the of production of sophisticated materials. In this work, we prepared a high-resilience hybrid hydrogel based on poly(vinyl alcohol) (PVA) and hydroxyapatite (HAp) with self-healing properties. HAp was previously prepared and subsequently vinyl-functionalized using a chemical approach. Vinyl groups on the surface of the modified HAp were observed using FTIR and XRD. The hybrid hydrogels rapidly swell to equilibrium at a pH of 7. The SEM images revealed the formation of a highly interconnected and porous structure, which play a critical role in water absorption and biocompatibility. The self-healing of the materials occurs entirely, and the mechanical properties are improved with addition of hydroxyapatite. The release mechanism from the hydrogels was found to be anomalous, indicating that a combination of Fickian diffusion and macromolecular relaxation is the main driving force for release.

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## Agradecimentos/Acknowledgments

The authors thank all involved in the work, Rinaldi Research Group, DQI/UEM, COMCAP/UEM and Brazilian Agencies for fellowship CNPQ, CAPES and Fundação Araucária/PR. (Proc. Grants. 202064/2014, 168778/2017-3, 113881/2018-5, 314220/2018-6, 434504/2018-1 and 830/2013).

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# Dinuclear Copper complexes with Thioether Ligands showing oxidase activity

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Palavras Chave: *Dinuclear Cu(II) complexes, Magnetic properties, X-ray crystallography, Catecholase activity, Funtional biomimetics.*

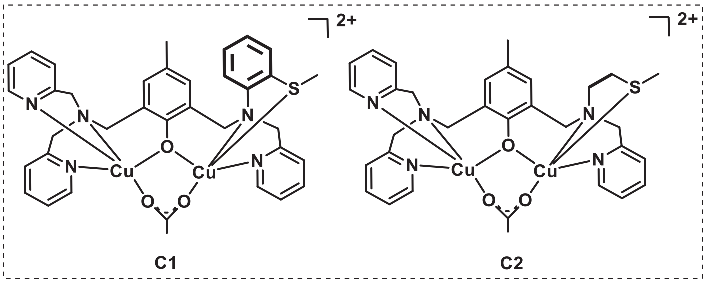
## Highlights

Synthesis and characterization of two dinuclear copper showing thioether aromatic or aliphatic chelate ring type;
Catecholase-like activity in the oxidation of the substrate 3,5-di-tert-butylcatechol.

## Resumo/Abstract

Copper is an element of extreme importance in the human biological cycle. It is present in several metalloenzymes, and type III involves binuclear copper (II) complexes, responsible for oxidation reactions present in the biological environment, among which is Catechol Oxidase, responsible for the oxidative catalysis of catechols to their respective quinones.[1]

In this work we present two binuclear copper complexes, C1 and C2, due to the design of the binucleating ligand, since two copper atoms do not have the same coordination or the same geometry. Interestingly, the phenolate oxygen of the bridge between the metals is distorted in both complexes, forming a slightly smaller Cu(1)-$O_{phenoxo}$-Cu(2) angle for C1 (117.597°) than for C2 (119.814°), as well as a smaller distance between the copper atoms of C1 when compared to C2 with distances of 3.5831Å and 3.701Å, respectively.



These structural differences are reflected on the magnetic properties of the complexes, C2 with a higher angle has a ferromagnetic behavior ($J$ = 5.72 $cm^{-1}$) while C1, with the ligand with greater rigidity, has an antiferromagnetic behavior ($J$ = -2.27 $cm^{-1}$).

The title complexes were adequately characterized by spectroscopic, electrochemical and kinetic studies. The catecholase activity and its kinetic parameters were obtained through the oxidation of the model substrate 3,5-DTBC. The kinetic data were determined spectrophotometrically by monitoring the increase of the 3,5-DTBQ characteristic absorption band at about 400 nm over time in methanol saturated with $O_2$ and aqueous buffer solutions (pH=9.0) at 25 °C.[2]

The dependence of the reaction rate on the 3,5-DTBC substrate concentration at pH 9.0 reveals a saturation behavior, so the data were treated using the Michaelis-Menten model and the kinect parameters. The catalytic efficiency shown C2 is more effective in of 22.85 L $mol^{-1}$ $s^{-1}$ compared to 11.33 L $mol^{-1}$ $s^{-1}$ found for C1.

## Agradecimentos/Acknowledgments

UFSC, CNPq, CAPES, INCT-Catálise.

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**Área: INO**

# Dual-emission CDots/EuDBC Nanocomposite incorporated in membrane to act as a ratiometric luminescent sensor of Cr(VI)

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Palavras Chave: *Dual emission, Europium (III), sensor, Chromium (VI)).*

## Highlights

High stability and facile preparation of red-light-emitting membrane based on europium coordination polymers and carbon dots for sensing chromium (VI)

## Resumo/Abstract

Fluorescent materials gaining prominence due to their promising characteristics in several areas of application, such as ion sensors. Chromium one of the most widely used metals in the industry, in its form of Cr(VI) it be toxic to the ecosystem, making it necessary to monitor[1]. The present work aims to synthesize and characterize a dual-emission nanocomposite based on carbon dots (CDots) and the coordination polymer EuBDC (BDC = disodium benzene-1,4-dicarboxylate) (CDots/EuBDC) to be incorporated into a membrane of cyanoacrylate (M_CDots/EuBDC) and act as a ratiometric Cr(VI) sensor. The structural analysis via XRD of the compounds CDots/EuBDC and M_CDots/EuBDC showed excellent correlation of the crystalline phase, being isostructural[2]. The spectrum of CDots/EuBDC, before and after incorporation into the membrane, showed emission bands characteristic of Europium ($^5D_0 \rightarrow {}^7F_{0-4}$), and CDots (**Fig.1A**). M_CDots/EuBDC is translucent and reasonably flexible (**Fig.1B**). The MEV (**Fig.1C and D**) of the CDots/EuBDC and M_CDots/EuBDC compounds revealed a lamellar morphology, and a smooth surface with the nanocomposite homogeneously distributed without agglomerates, respectively. When exposed to UV light (365 nm) M_CDots/EuBDC exhibits fluorescence (FL) in red, showing a decrease in FL intensity when in contact with the Cr(VI) (5mgL$^{-1}$) (**Fig.1E**). The M_CDots/EuBDC was explored for the detection of Cr(VI) in an aqueous system and exhibited a linear range from 0.03 to 0.15 mgL$^{-1}$ corresponding to the equation $[(I_{Cdots}/I_{Eu})_0/(I_{Cdots}/I_{Eu})] = 1.627\ (\pm\ 0.074)\ Cr(VI) + 1.133\ (\pm\ 0.007)$ with $R^2 = 0.9916$ (**Fig. 1F**). One of the proposed FL quenching mechanisms of the M_CDots/EuDBC was the internal filter effect, due to the overlap of the probe excitation and emission bands with the Cr(VI) absorption bands (**Fig.1G**). The M_CDots/EuBDC presents itself as a promising ratiometric sensor in the detection of Cr(VI).

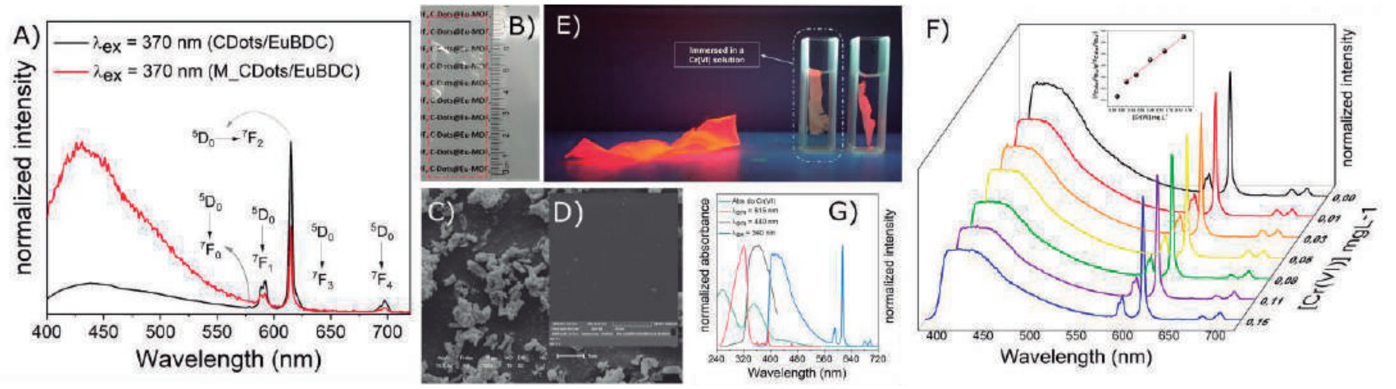

**Figure 1:** (A) Emission spectrum of CDots/EuBDC and M_CDots/EuBDC. (B) Image of CDots/EuBDC. MEV of CDots/EuBDC (C) and M_CDots/EuBDC (D). (E) M_CDots/EuBDC exports 365 nm UV light in the absence and presence of Cr(VI). (F) Emission spectrum of M_CDots/EuBDC at different concentrations of Cr(VI) ($\lambda_{ex}$ = 370 nm, Britton-Robidon pH buffer 9 and 1mM). (G) Cr(VI) absorption, excitation (monitoring emission at 440 and 615 nm) and emission ($\lambda_{ex}$ = 370 nm) spectrums from CDots/EuBDC.

## Acknowledgments

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**Área: INO** **Nº de Inscrição: 01004**

# Emission spectroscopy as a probe in the catalysis by EuMOF.

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Key words: Emission spectroscopy; europium; catalysis

## Highlights

Luminescence spectroscopy is an important probe in assessing the role of the europium ion as catalyst in carbonyl addition reactions.

## Resumo/Abstract

Coordination polymers of lanthanide ions or LnMOFs are of interest in several areas, including Lewis acid catalysts. Three europium networks were tested and used for aldehyde and ketone allylation reactions with potassium allyltrifluoroborate and allylboronic acid pinacol ester and in the cyanosilylation reaction, trying to understand the role of the catalyst through the luminescence spectroscopy of the trivalent europium ion. EuFum MOF was the first catalyst used in the aldehyde allylation reaction. The emission spectra of EuFum as prepared, after one catalytic cycle and after interacting only with each starting material revealed a strong interaction between EuFum and the allylating agent (potassium allyltrifluoronorate-ATB), as shown in figure 1A. Regarding the morphology, there is a change from a prismatic shape to spheroidal (figures 1B and 1C). These results suggest that the interaction between the catalyst and the allylating agent generates a more reactive species responsible for the formation of the product (homoallyl alcohol). When the allylating agent pinacol ester of alliboronic acid (PAB) is used, no catalysis is observed and the emission spectrum suggests that there is no interaction between Eu$^{3+}$ and PAB. Two other catalysts EuMand and EuFumOx were tested in the reaction of allylation with potassium allyltrifluoroborate. EuMand, tested with ketones, presented catalytic activity and the same behavior as EuFum regarding the photophysical and morphological properties. On the other hand, EuFumOx did not show catalytic activity or alterations in the morphology or the photophysical properties of Eu$^{3}$. These results corroborate the hypothesis of the formation of a more reactive species of the allylating agent, probably allyboronic acid, which is an unstable species. In the cyanosilylation reaction of aldehydes and ketones, using EuFum, no significant variations were observed in the emission spectra, which suggests that the catalysis occurs in a conventional manner, Lewis acid. These results indicate the importance of luminescence spectroscopy as a probe in assessing the role of lanthanide ions in catalysis.

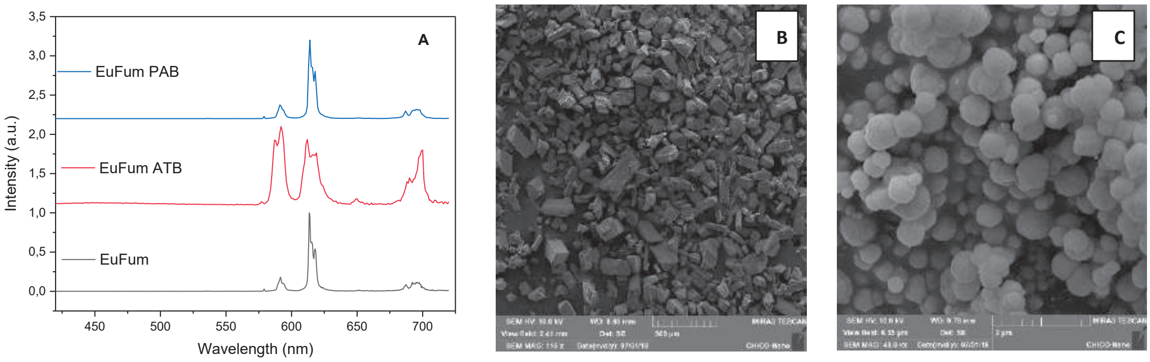

Figure 1: A) Eufum emission spectra as prepared and after treatment with ATB and PAB; B) MEV as prepared, and C) MEV after one catalytic cycle with ATB.

## Agradecimentos/Acknowledgments

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# Eu(III) *tetrakis* β-diketonate complexes dispersed in PMMA or PVDF films applied as coatings of UV-LEDs for application in lighting

**Ariane C. F. Beltrame (PG)*[1,2], Felipe S. M. Canisares (PG)[1,3], Airton G. Bispo-Jr (PQ)[4]; Ricardo V. Fernandes (PG)[5], Sergio A. M. Lima (PQ)[1,3], Ana M. Pires (PQ)[1,2,3].**

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*Keywords: Europium(III); DBM; Complexes; PMMA and PVDF Films; Red emitter; LEDs.*

## Highlights

Eu(III) *tetrakis* complexes dispersed in polymeric films applied as efficient red emitting coatings of LED prototypes.

## Resumo/Abstract

The interest of the scientific community in the search for luminescent materials is due to several possibilities of application such as LED and OLED lighting devices, in the biological area as cell markers, as well as in sensors and lasers[1,2,3]. Aiming the application in lighting devices, this study focuses on the synthesis and characterization of films produced by the drop-casting method containing the red-emitting *tetrakis* $[C_{26}H_{56}N^+][Eu(dbm)_4]$ complex (Hdbm = dibenzoylmethanate), using polymethyl-methacrylate (PMMA) or polyvinylidene fluoride (PVDF) as polymeric matrix. The $[C_{26}H_{56}N][Eu(dbm)_4]$ complex was synthesized free of coordinated water molecule and its structure and luminescence were elucidated by FTIR, TGA, MALDI-TOF, elemental (C, H, N) analysis, UV-Vis absorption spectroscopy, and photoluminescence. The $[C_{26}H_{56}N][Eu(dbm)_4]$ complex weight proportion was changed in the PMMA or PVDF films as 0.1, 0.5, 0.75, 1, 2 or 5 wt.%; PMMA films are completely transparent up to 1 wt.% and all PVDF films are opaque. All films displayed the characteristic $Eu^{3+}$ luminescence within the orange-red spectral region due to $^5D_0 \rightarrow {}^7F_J$ (J = 0-4) transitions whereas photophysical parameters (i.e., $^5D_0$ state lifetime, intrinsic and absolute emission quantum yield) depend on the doping concentration, but not uniformly, because at high concentrations, complexes tend to form agglomerates. Among the series of red-emitting polymeric films, both in PVDF and PMMA, those with a concentration of 1 wt% of the Eu(III) complex were considered as the most promising candidates for application as coatings for near-UV LEDs since they displayed overall emission quantum yields as large as 5.80% and 22.10% respectively. In the LED prototypes, those coated with the PMMA film presented the characteristic red emission due to the $Eu^{3+}$ complex while the device with the PVDF film generated yellowish white color emission, possibly due to the inhomogeneous scattering of light in the opaque film, and the refraction index. Therefore, by changing the polymeric matrix used to disperse the complex, it is possible to tune the emitted color of the device while the PMMA matrix is the best considering the optimization of the $Eu^{3+}$ complex red emission.

## Agradecimentos/Acknowledgments

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**Área: <u>INORGÂNICA (INO)</u>**
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# Europium activator ion acting as an efficient luminescent probe to identify local symmetry in $Li_2ZnSn_3O_8:Eu^{3+}$ materials prepared by the MASS method

**Matheus S.N. Saula (PG) [1*], Maria C.F.C Felinto (PQ)[2], Luiz A.O. Nunes (PQ)[3]; Oscar L. Malta (PQ)[4], Hermi F. Brito (PQ)[1].**

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Keyword:Luminescent materials – europium, stannates, microwave-assisted method, anti-counterfeiting probe.

## Highlights

$Eu^{3+}$ ion as the luminescent probe was used to investigate the local symmetry of ligand sites in $Li_2ZnSn_3O_8$ host matrix. $Li_2ZnSn_3O_8:Eu^{3+}$materials were synthesized by the domestic microwave oven (MASS method).

## Resumo/Abstract

Luminescent materials doped with rare earth ions (RE) have been intensely applied in several areas in the new photonic technologies, such as emergency lights, radiation detectors, biological markers, and anti-counterfeiting products. Stannate-based host matrices have attracted significant attention, as they are relatively inexpensive and have a favorable bandgap to allow the persistence luminescence phenomenon. In this work, $Li_2ZnSn_3O_8:Eu^{3+}$ was synthesized by the microwave-assisted solid-state method (MASS) using a domestic microwave oven after gridding $Li_2CO_3$, ZnO, $SnO_2$, $Eu_2O_3$ precursor oxides. Therefore, the as-prepared precursors were heated in a static air atmosphere at a preset configuration of 900W for 20 min. The material was characterized by powder X-ray diffraction (PXRD), scan electron microscopy (SEM), and diffused reflectance spectroscopy. The PXRD patterns indicate the formation of the desired $Li_2ZnSn_3O_8$matrix phase when doped with different concentrations of the $Eu^{3+}$ ion, showing a high crystallinity. The photoluminescence properties were determined based on the emission spectra of the $Li_2ZnSn_3O_8$:mol%$Eu^{3+}$ materials (**Fig 1**), showing intense yellowish-orange and reddish-orange emission colors under UV excitation at 282 and 336 nm, respectively. Moreover, both spectra show narrow emission bands characteristic of $^5D_0 \rightarrow {}^7F_{0-4}$ $Eu^{3+}$ transitions. Sinceeuropium ions are powerful spectroscopic probes for the symmetry of the first coordination sphere of these ions in a lattice, and the spectral profiles change with the incident radiation wavelengths, which demonstrates the presence of more than one site of symmetry around the chemical environment of the $Eu^{3+}$ion.Finally, it is noteworthy that these luminescent materials can be selectively excited in the UV range, leading to more than one specific emission spectral profile, which can be applied as efficient luminescent probes for anti-counterfeiting products.

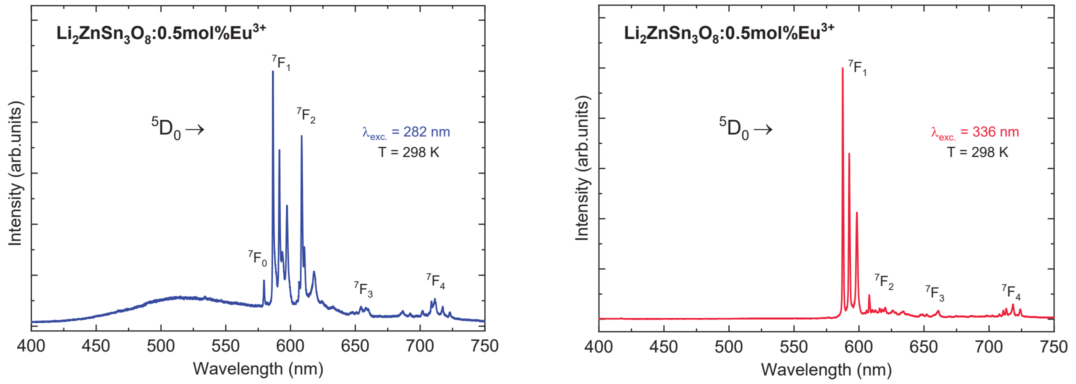

Fig. 1 – Emission spectra of $Li_2ZnSn_3O_8$:0.5mol%$Eu^{3+}$luminescent material prepared by MASS method under UV excitations at 282 (left) and 336 nm (right).

## Agradecimentos/Acknowledgments

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# Evaluation of the cytotoxicity of palladium/phosphine/curcumin complexes against tumor cells

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Keywords: *Cancer, Curcumin, Metallic Complexes, Palladium.*

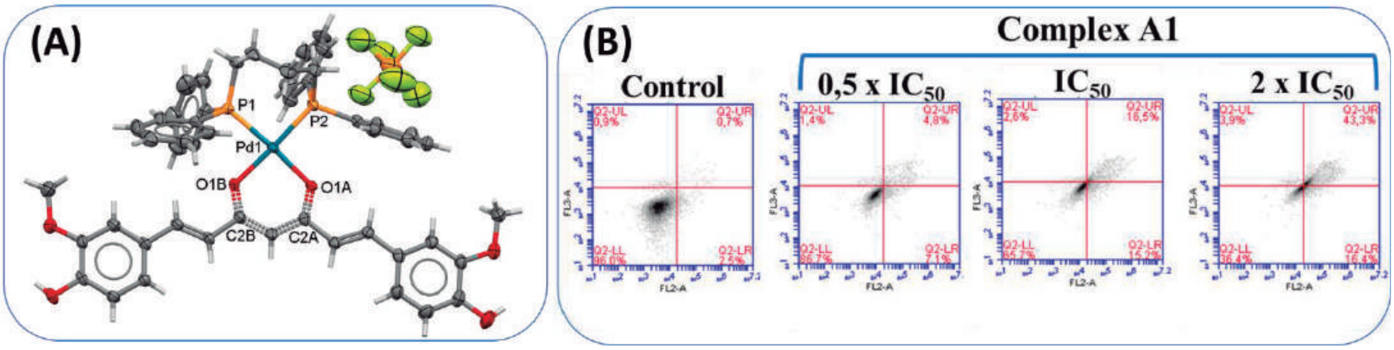
## Highlights

Five new palladium/phosphine/curcumin complexes were synthesized and characterized. The complexes showed good cytotoxicity against several cancer cell lines. The complex $[Pd(PPh_3)_2(cur)]PF_6$ stood out for its selectivity.

## Abstract

Curcumin (**cur**) has been known since antiquity, for its various medicinal properties, such as anti-inflammatory, antimutagenic, antimicrobial, antirheumatic, antioxidant, healing and digestive. However, only recently the mechanisms of action and bioactivity of its components are being investigated.[1] In this research, $Pd^{II}$ complexes employing cur and phosphines as ligands were synthesized and characterized, resulting in compounds of general formula $[Pd(PP)(cur)]PF_6$ (PP = **A1** - $(PPh_3)_2$; **A2** - dppe; **A3** - dppp; **A4** - dppb; **A5** - dppf) (71-80% of yield). The values of molar conductivity, in DMSO, show anionic complexes. The $^{31}P\{^1H\}$ NMR spectrum of the complexes shows just one singlet, indicating the magnetic equivalence of the phosphorus atoms *trans* to oxygens of **cur**. The other NMR experiments ($^1H$, $^{13}C\{^1H\}$, COSY, HSQC, HMBC) confirm the proposed structures for the planar square complexes. The mass experiments were performed adopting the MALDI-TOF/TOF technique, using dihydroxybenzoic acid as a calibrator. The theoretical values of the molecular ion mass are in agreement with the correspondent founded peak mass for the complexes, without contra ion: M-$PF_6$ = $[Pd(PP)(cur)]^+$. In FTIR the displacement of the bands $\upsilon$(C=O) to a region of lower energy in the complexes indicates the coordination of curcumin by the carbonyl group, where electronic delocalization decreases the double bond character, increasing the single bond character of the carbonyl group. The slow evaporation of **A4** in $CH_3OH/CH_2Cl_2$ (1:1) solution resulted in single crystals suitable for X ray diffraction, the structure is shown in Fig. 1(A). The cytotoxic activity of the complexes was evaluated in several cell lines. Improved activity for **A1** was observed in the A2780cis (cisplatin-resistant ovarian cancer cell line) with the $IC_{50}$ = 1.4 ± 0.4 $\mu$mol/L, and the high activity in the non-cancer lung cells (MRC-5), $IC_{50}$ = >40 $\mu$mol/L, gives this complex a remarkable selectivity index of 28.6 ($IC_{50}$ MRC-5/ $IC_{50}$ A2780cis). In order to investigate the mechanisms of death of the **A1**, we carried out the analyses by flow cytometry. The result shows that the percentage of A2780cis cells in apoptosis (early + late) increased considerably in a concentration-dependent fashion (Fig. 1(B)).

**Figure 1** – **(A)** Crystal structure of **A4** showing the atom labels and ellipsoids with 30% of probability **(B)** Induction of apoptosis in A2780cis cells after treatment with complex **A1** (incubation for 24 h).



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**Área: INO**

# Fast preparation of titania nanotubes using microwave assisted hydrotermal synthesis

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*Palavras Chave:* Nanotubes, titanium, microwave.

## Highlights

Titania nanotubes synthesis depends directly of the microwave irradiation time under autogenic pressure. SEM images shown the gradual formation of titanate nanotubes according to the increase of reaction time.

## Resumo/Abstract

Titanium is one of the most abundant elements in nature, present low toxicity when compared to other inorganic compounds and present higher photocatalytic activity when exposed to UV light. Frequently used in industry, present applications in the aerospace industry, in ceramic tiles, photocatalysts, solar cells, etc. Thus, in 1998, Kasuga and colleagues [2] discovered the alkaline hydrothermal route as strategy synthesis for TiO2 nanostructures in tubular format, based on carbon nanotubes [3]. Since then, various articles have been published about synthesis and characterization of titanium nanotubes. These titanium nanostructures are less popular than carbon nanostructures, however they have significant advantages such as: low cost and easy synthesis by conventional methods when compared to conventional titanium has a high surface area and capacity to transport charge [4]. Based on previous studies reported in the literature [1-4] we propose here the optimization of titania nanotubes synthesis using conventional hydrothermal synthesis that in general require high temperature and long reaction times reactions vs. the microwave-assisted process that is faster, cleaner, simpleer and energetically more efficient than conventional routes to synthesize titania nanotubes. In this work, the synthesis of titania nanotubes was evaluated using a kinetic approach, via alkaline hydrothermal method, optimizing the process using a high pressure microwave. For the nanotube synthesis, it was placed in the microwave vessels of 100 mL, 25mL of NaOH 10 M, 0.150g of TiO2, at 90°C, with 1600W potency, varying the times in 5, 15, 30, 60 minutes and autogenic pressure. After each interval time the material was washed using a diluted solution of 0.1 M HCl solution and water until it obtained a neutral pH, then dried and analysed by X-ray powder diffraction (XRD), infrared absorption spectroscopy (FTIR), and scanning electron microscopy (SEM). XRD shown the typical titanate reflections at 2θ angles of 25, 37, 38, 48, 54, 55, 63, 69, 70, and 75, and corresponding diffraction Miller index were identified as (101), (103), (004), (112), (200), (105), (211), (204), (116), (220), and (215), respectively, and the results can be readily indexed to anatase phases., SEM images shown the gradual formation of titanate nanotubes according to the increase of reaction time, at longer times (higher than 30 minutes) was possible identify the higher amount of titanate nanotubes obtained. This results is in agreement with previous discussed on XRPD. Thus the conclusion based on all characterization techniques, the irradiation time and pressure under sealed vessel promotes a reduction on required time to nanotubes synthesis , this effect was assigned to the pressure and temperature reached under microwave exposure, the conventional hydrothermal route require 72 hours counter 30 minutes under microwave, , was possible observe also the presence of anatase that according to several authors, the nanotubes will present good photocatalytic activity and higher specific surface area, with superior characteristics than presents conventional $TiO_2$

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## Agradecimentos/Acknowledgments

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**Área: INO**

# Hell's Gate globin I (HGbI) protein from an extremophile bacterium: cyanide and imidazole binding and peroxidase activity

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Keywords: *heme protein, ligand binding, peroxidase, pH dependence.*

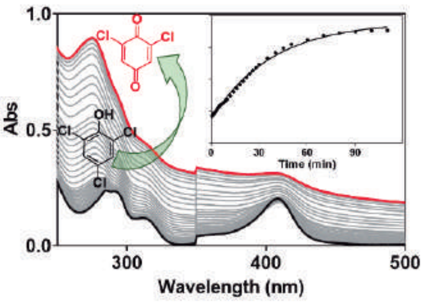
## Highlights

Association of cyanide to the heme protein HGbI is extremally slow, especially in basic medium.

2,4,6-trichlorophenol (TCP) is catalytically oxidated by HGbI.

## Abstract

Our understanding on how biomolecules function, especially proteins, has enabled enormous advances in medicine, pharmacology, food industry, catalysis, among other areas. The enzymes, for example, can be used to maximize enantiomeric selectivity, while providing an environmental friendly condition as compared to chemical catalysts[1]. Hell's gate globin I (HGbI) from the extremophile bacterium *Methylacidiphilum infernorum* is one exciting system to be investigated considering this microorganism lives under optimal conditions at 60ºC and pH 2.0. This heme protein exhibits a molecular weight of 15.9 kDa and binds well to $O_2$ as other globins. Some peculiar features of this protein are known, for example, extremely high oxygen binding, strong stability of the prosthetic group in acidic medium (pH 4.6) and its ability to bind acetate in the $Fe^{3+}$ state[2]. However, many other features are still unknown. In this work, cyanide ($CN^-$) and imidazole affinity to HGbI was investigated, highlighting a slow association rate of cyanide ($k_{on}$ = 0.06 $M^{-1}$ $s^{-1}$, at pH 7.4), only comparable to human neuroglobin[3], but more than 5,000 times slower than myoglobin[4]. Binding to imidazole occurs apparently fast, although spectroscopic changes are quite subtle indicating small changes in the chemical microenvironment of the heme. Both $CN^-$ and imidazole can act as a probe to investigate heme surroundings and their roles in the presence of a sixth axial ligand. Our results suggest that ligand-binding cavity in HGbI is indeed quite hydrophobic as shown by crystallography[2]. In addition, HGbI catalytical activity was investigated, where 2,4,6-trichlorophenol (TCP) was chosen as a substrate exploring peroxidase activity. TCP can be catalytically converted to the oxidized product (2,6-dichloroquinone), which was monitored by electronic spectroscopy[5]. Interestingly, it was found that HGbI can catalyze this reaction, which occurs faster and to a greater extent in acidic medium (pH 5.5) compared to a physiological pH (7.4). This kind of reaction can be exploited to degrade environmentally harmful organochlorine compounds, opening possibilities to investigate this and other potentialities of HGbI as a biocatalyst.



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## Acknowledgments

**Área: INO**

# Hidroxinitrato de zinco funcionalizado com ditiocarbimato

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*Palavras Chave:Hidroxissais lamelares, Ditiocarbimato, Compostos híbridos.*

## Highlights

- Uma matriz de composto lamelar foi funcionalizada com o ânion ditiocarbimato.

## Resumo

Compostos lamelares possuem sua estrutura organizada em camadas bidimensionais e, entre elas, há uma região chamada de espaço interlamelar, na qual esses compostos têm a capacidade de incorporar espécies químicas de interesse [1] e,assim, gerar materiais com diferentes funcionalidades. Desta forma, nesse trabalho estudou-se de modo preliminar a interação entre um hidroxinitrato de zinco (HNZ) e o ânion ditiocarbimato (ditio), com o intuito de gerar um material híbrido a ser estudado posteriormente em processos de vulcanização de borracha.Os dados obtidos por espectroscopia na região do infravermelho podem ser observados na Figura 1a, e mostram a interação entre o ânion e a matriz inorgânica, pois, bandas referentes ao ditiocarbimato aparecem no sólido sintetizado HNZ+ditio (curva em vermelho), são elas 1230 cm $^{-1}$, 1160 cm$^{-1}$, 1088 e 1032 cm$^{-1}$ e 829 cm$^{-1}$. Na Tabela 1, os valores das frequências das bandas são mostradas com seus respectivos modos vibracionais e nela é possível observar que a banda de estiramento assimétrico do grupo $CS_2$está deslocada para um valor de menor frequência (971 para 829 cm$^{-1}$) em relação ao espectro do ditiocarbimato puro (curva em azul), o que indica a possibilidade de interação do ânion ditiocarbimato com a matriz através desse grupo. Por sua vez, tais bandas não aparecem no espectro no sólido HNZ referente apenas a matriz inorgânica (curva em preto). Desse modo, fica evidente que houve a interação da matriz lamelar de hidroxinitrato de zinco com o ânion ditiocarbimato. As medidas de difração de raios X (Figura 1b) realizadas para a matriz sem a presença do ânion (HNZ) e com a presença deste (HNZ+ditio) indicou que não houve a intercalação do ânion ditiocarbimato, pois não houve alteração do espaçamento basal. Portanto, o ânion deve estar interagindo com a superfície externa da matriz, o que indica a possível funcionalização da matriz inorgânica com o ditiocarbimato.

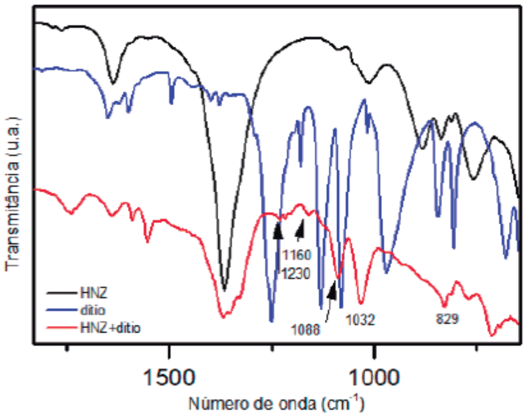


Figura 1a - Espectro na região do infravermelho ampliado na região de 650 a 1800 cm$^{-1}$ do ânion ditiocarbimato (azul), HNZ (preto) e HNZ interagindo com ditiocarbimato (vermelho).

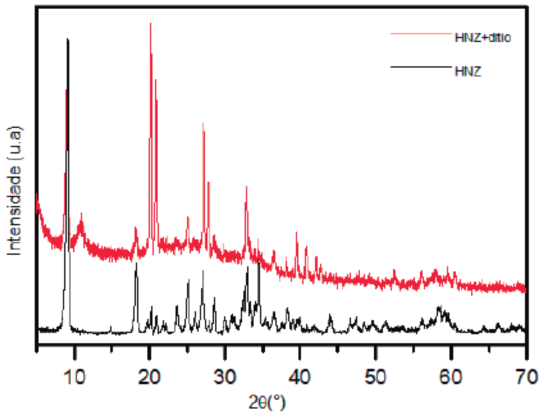
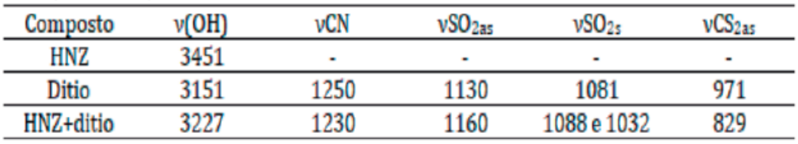


Figura 1b - Difratograma das amostras HNZ (preto) e HNZ interagindo com ditiocarbimato (vermelho).



| Composto | ν(OH) | νCN | $\nu SO_{2as}$ | $\nu SO_{2s}$ | $\nu CS_{2as}$ |
|---|---|---|---|---|---|
| HNZ | 3451 | - | - | - | - |
| Ditio | 3151 | 1250 | 1130 | 1081 | 971 |
| HNZ+ditio | 3227 | 1230 | 1160 | 1088 e 1032 | 829 |

Tabela 1 - Comparação dos modos vibracionais obtidos.

## Agradecimentos

Agradecimentos a Capes,aoCNPq, aUniversidade Federal de Itajubá - UNIFEI, aRede Mineira de Química de Minas Gerais, ao Laboratório de Caracterização Estrutural da UNIFEI - LCE, ao Grupo de Química de Materiais da UFPR – GQM/UFPR.

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**Área: INO**

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

# Highly cytotoxic organogold(III)-dithiocarbamate complexes: investigating the potential interactions with different biomolecular targets

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Keywords: *Organogold compounds, Dithiocarbamates, Antiproliferative effect, DNA, Albumin.*

## Highlights

A series of novel organogold(III)-dithiocarbamate complexes were assessed for their antiproliferative effect on cancer and normal cells, displaying activity in the submicromolar range and selectivity.

## Resumo/Abstract

Metal-based compounds, as cisplatin and auranofin, are widely known and used for biological applications, the latter being currently undergoing clinical trials. Organogold(III) complexes are a current focus of research due to their potential anticancer activity alongside with their monocationic analogs. The metal-carbene bond is efficient in stabilizing the metallic center, notably when stabilization is provided by cyclometallated C^N moiety. Dithiocarbamates are also capable of efficiently stabilize gold(III) centers and have been useful in the synthesis of drug candidates for their structural versatility and broad bioactivity. A wide spectrum of organogold compounds is being investigated, although their mode of action is not fully elucidated yet. [1,2]

In this work, we synthesized a series of five new organogold(III)-dithiocarbamate complexes (**C1**–**C5**) in high purity and stability under physiological conditions. Antiproliferative studies against B16F1 (mouse melanoma) and CT26wt (colorectal cancer) cells demonstrated that all compounds display impressive *in vitro* activity, specially **C3**, the most lipophilic compound, whose $IC_{50}$ = 0,7±0,1 μM. **C4**, however, seems to be the most promising compound against colorectal cancer since it showed remarkable cytotoxicity with a 15-fold selectivity ratio. The series will also be tested *in vitro* against a panel of human cancer cell lines. Addition of complexes **C1**–**C5** into an EtBr-DNA solution resulted in a significant quenching of the band, thus, complexes may displace EtBr from the adduct and intercalate to DNA, which translates to a possible biological target for the series to unravel its cytotoxic activity. Albumin (BSA) assays are currently under investigation, although preliminary studies revealed tight binding affinity to the protein.

*Figure 1. Cytotoxic profile of the complexes.*

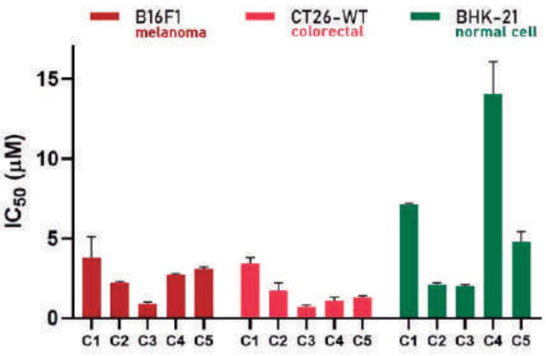
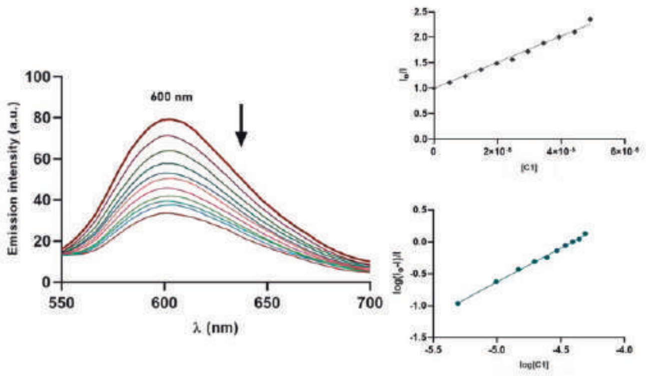


*Figure 2. Fluorescence emission spectra for EtBr-DNA vs. C1.*



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**Área: INO**

# Influence of different β-diketone ancillary ligands on the luminescence of [Eu(β-dkt)$_3$(AIP)] type complexes

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Keywords: Coordination, Lanthanoids, Photonics, Emission, Spectroscopy.

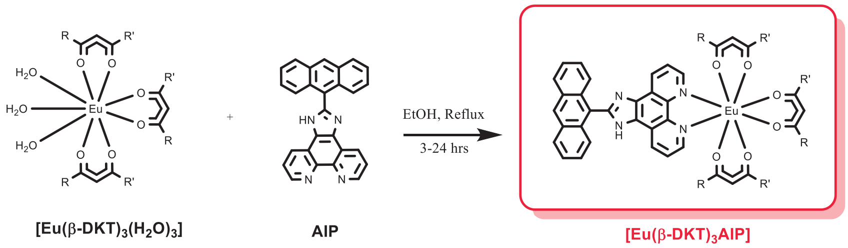
## Highlights

Three complexes were prepared and had their optical behavior studied. A comparison of their luminescence was made in terms of β-diketone excited states, using data generated by the LUMPAC software.

## Abstract

Lanthanoid ions have been used in several strategic areas, such as photonics, electronics, military industry, and biological sensing. Most of the applications occur by their well-defined optical properties related to their 4f-4f intraconfigurational transitions. However, due to the nature of these transitions (prohibited by the Laporte's rule), lanthanoid ions are weak energy absorbers. To overcome this problem, organic molecules can be coordinated to these ions, absorbing energy from the medium and transferring it to the lanthanoid emitter ion. This phenomenon is the so-called "antenna-effect", and different ligand classes have been used as sensitizers, like β-diketones (β-dkt), crown-ethers, carboxylic acids, phenanthroline derivatives, etc.[1] In this study, three new complexes were synthesized, having in common the presence of the AIP ligand (a phenanthroline derivative, also synthesized) and differing from each other by the choice of the ancillary ligand, in this case, a β-diketone (ACAC, DBM or BTFA). This class of ligand is well-known for acting as an excellent sensitizer for europium ions due to the energetic synergism between its singlet and triplet excited states and Eu(III) $^5D_{0,1}$ levels. Figure 1 shows a schematic representation of the proposed synthesis.[2] FTIR and Raman spectra of the synthesized complexes showed, in all cases, a displacement of the characteristic C=N stretching of the phenanthroline. In addition, via UV-Vis spectroscopy, a bathochromic shift of the n→π* transition, also assigned to C=N bound, is observed. Therefore, these data suggest that the phenanthroline was successfully coordinated to the Eu(III), and they are supported by mass spectrometry and thermal analysis. Finally, the optical profile of all complexes was monitored by PL spectroscopy, where the differences observed in their excitation and emission spectra are explained by the insertion of the AIP ligand on the coordination sphere of the initial β-diketonate complexes. By the LUMPAC theoretical approach, it was possible to correlate quantum emission efficiency with the expected values of the singlet and triplet energy states of each β-diketone. In conclusion, all Eu(III) complexes were successfully synthesized and exhibit promising luminescent properties that qualify them to be investigated for sensing applications, such as $^1O_2$ sensing.

Figure 1: Schematic representation of the synthesis of the complexes.



ACAC → R = R′ = $CH_3$

DBM → R = R′ = Benzo

BTFA → R = Benzo; R′ = $CF_3$

## Acknowledgments

CNPq (Proc. Nº 141081/2020-1).

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**Área: INO**

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

# Insights of new ruthenium-diphosphine complexes containing mercapto ligands: DNA-interacting studies and antitumor properties

**Marcos V. Palmeira-Mello (PQ),[1*] Analu R. Costa (PG),[1] Leticia P. de Oliveira (PG),[1] Nadija N. P. da Silva (PG),[1] João Honorato de Araujo-Neto (PQ),[1] Carlos Andre F. Moraes (PG),[1] Alzir A. Batista (PQ)[1*]**

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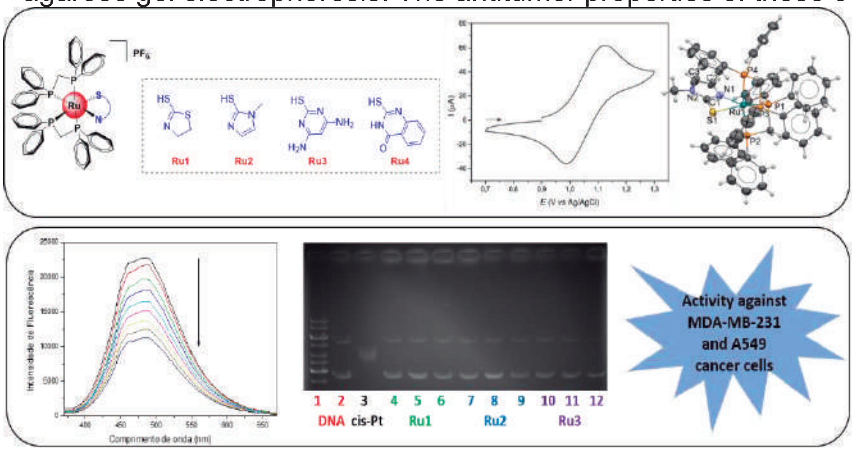
Palavras Chave: *metal complexes, ruthenium, DNA, antitumor drugs, cancer.*

## Highlights

Novel Ru-based complexes (**Ru1**-**Ru4**) were obtained and the structure of **Ru2** was determined by XRD. These complexes interact weakly with the DNA and are active against different cell lineages.

## Resumo/Abstract

Cancer is the second biggest cause of death worldwide.[1] Due the lack of selectivity and side effects exhibited by platinum complexes, ruthenium-based compounds arise like an alternative for the development of new chemotherapeutic agents.[2] In this context, we have investigated four novel ruthenium(II)-1,1`-*bis*(dimethylphosphine)methane (dppm) complexes (**Ru1-Ru4**) containing different mercapto ligands (N-S). The complexes $[Ru(dppm)_2(N\text{-}S)]PF_6$ (N-S = mtz: 1,3-thiazolidine-2-thione, mmi: mercapto-1-methylimidazole, dmp: 4,6-diamino-2-mercaptopyrimidine, 2mq: 2-mercapto-4(3H)-quinazoline) were obtained *via* reaction between the precursor $[RuCl_2(dppm)_2]$ and the respective mercapto ligand, under argon atmosphere and reflux during 12 h. The compounds were characterized by infrared and NMR spectroscopic techniques, mass spectrometry and the structure of **Ru2** was determined by X-ray diffraction. Conductivity measurements and elemental analysis are in accordance with the proposed structures. Cyclic voltammograms obtained for the complexes, in $CH_2Cl_2$, indicate *quasi*-reversible processes, corresponding to Ru(II)/Ru(III), which $E_{1/2}$ values in the range 1074-1321 mV *vs.* Ag/AgCl. Since DNA plays a key role on the development of metal-based compounds, DNA-interacting studies were also performed. Competitive binding studies using Hoechst 33258 indicate that the complexes interact with the DNA via the minor groove. The results are in accordance with viscosity measurements, pointing out week interactions between the complexes and the biomolecule. As expected, no cleavage property for these complexes was observed in agarose gel electrophoresis. The antitumor properties of these complexes were investigated in different cell lines, *via* MTT colorimetric assay. *In vitro* studies indicated the best performance for $[Ru(dppm)_2(mtz)]PF_6$ (**Ru1**) against MDA-MB-231 ($IC_{50}$ = 0.30 ± 0.13 μM) and $[Ru(dppm)_2(mmi)]PF_6$ (**Ru2**) against A549 ($IC_{50}$ = 0.04 ± 0.01 μM) cell lineages.



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## Agradecimentos/Acknowledgments

FAPESP, CNPq, UFSCar

**Área: INO**

# Interaction of the $[Ru_3O(OAc)_5(py)_2(dppzCl)]PF_6$ complex with enzymes of the cytochrome P-450 system by HPLC: a chromatographic and isomeric study

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Keywords: *in-vitro metabolism, Ruthenium, HPLC, Cytochrome*

## Highlights

The $[Ru_3O(OAc)_5(py)_2(dppzCl)]PF_6$ complex showed a 70% reduction of melanoma cancer cells viability
The complex was metabolized *in-vitro* by enzymes of the cytochrome P-450 system

## Abstract

The trinuclear ruthenium carboxylates (summarized in the molecular form $[Ru_3O(RCOO)_6(L)_3]^n$, where L is a N-heterocyclic ligand or a solvent molecule and n is the formal charge of the molecule), are compounds that have caught the researchers attention since 1930 due to their interesting spectroscopic and electrochemical properties,[1] although the literature focusing their biological activity is still scarce. Relevant to this work, we highlight the $[Ru_3O(OAc)_5(py)_2(dppzCl)]PF_6$ complex and its anticancer activity. This asymmetric compound was characterized by having a chloro-substituted-dipyridophenazine as a orthometalated ligand. This compound have shown a high rate of melanoma cancer cells viability reduction, decreasing it 70% at low concentrations, also not being cytotoxic to the healthy cell model (L929 fibroblasts).[2] Based in this previous result, this compound was chosen for this study.

The biotransformation route of most xenobiotics is mediated by phase I, phase II or a combination of both. The cytochrome P-450 (CYP) superfamily of enzymes plays a key role in phase I biotransformation and is present mainly in the liver. Many different CYP isoforms have been characterized and are categorized into families based on their sequences. Phase II enzymes also play an important role in the detoxification and excretion of many xenobiotics.[3]

The metabolism study was done by HPLC and, in order to establish the best chromatographic method for it, a total of 16 mobile phases were tested on two different chromatography columns: C18-agilent (250mm x 4,6mm x 5µm) and Sílica LiChroCART Si 60 (125mm x 4mm x 5µm). Among these, the one that generated the best chromatographic profile was the mobile phase of methanol:acetonitrile 80:20 (v/v) + 0.1% formic acid on a silica column. The other chromatographic parameters were an oven temperature of 30°C, pressure of 37 KGF/cm$^2$, flow rate of 0.6mL/min, injection volume of 10µL, and the wavelengths observed on the spectrophotometric detector coupled to the chromatography equipment were 250, 320 and 680nm. *In-vitro* metabolization was performed by incubating the complex with human liver microsomes (HLM) and rat liver microsomes (RLM) with NADPH for 50 minutes. The chromatographic profile after the incubation showed that the complex is metabolized by RLM, so that we had a decrease of the peak area of the complex by 29% (while the decrease generated by HLM was 8%). The next steps in this work are to evaluate the metabolic study of other biotransforming enzymes and to separate the positional isomers (and then the enantiomers) of this complex to assess whether there is a difference in biological activity.

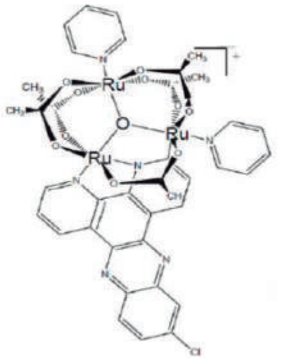

Figure 1. Structure of complex $[Ru_3O(OAc)_5(py)_2(dppzCl)]PF_6$

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## Área: INO

# Investigation of the solvatochromic effect in ruthenium complexes by multiparametric analysis

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[1-4] *Department of Chemistry, FFCLRP - USP*

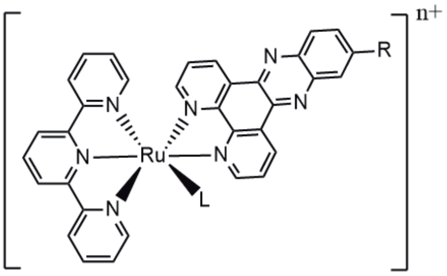
Keywords: *Coordination Chemistry, Ruthenium, Solvatochromism, Multiparametric Analysis*

## Highlights

The electronic spectra of two ruthenium complexes were recorded in as many solvents as possible.
Multiparametric analysis was performed using Catalán and Kamlet-Taft scales.
Both scales in the multiparametric analysis returned the result that the charge transfer transition is more dependent on the solvent acidity parameter.

## Resumo/Abstract

Since the discovery of the antitumor activity of cisplatin, several coordination complexes have been studied as possible candidates for metallodrugs, especially ruthenium complexes, which in addition to having biological activities of interest, can also act as photosensitizers or even catalysts.[1–3] Considering all their applications, the photophysics and photochemistry of these complexes is of great interest to the scientific community. One of the ways to study these aspects of a compound is through its electronic spectrum, since the charge transfer transitions present in the complexes generally tend to be sensitive to several factors, especially to the variation of the solvent used in the analysis.[4] With that in mind, this work aimed to analyze the solvatochromic shift of compounds **1** and **2** spectra (Figure 1) by the multiparametric approach using the Catalán and Kamlet-Taft parameters. Both compounds were synthesized and purified following literature adaptations and, for data collection, they were dissolved in as many solvents as possible (12 for compound 1 and 10 for compound 2) and the electronic spectra were recorded. After performing the multiparametric regression with the data obtained using both scales, it was observed that, for both compounds, there was a greater dependence of their transitions with the parameters SA of the Catalán scale and α of the Kamlet-Taft scale, which indicates a greater dependence of the transition with the acidity of the solvent, so that the formation of hydrogen bonds (including unconventional ones) in the case of protic solvents and the interaction between sites with a negative charge density of the complex with a positive charge density of the solvent in the case of aprotic solvents is the decisive factor for the stabilization of the ground state, since in both cases the sign found for these parameters was positive.



**1**: L = Cl ; R = H; n = 1
**2**: L = py ; R = $CH_3$; n = 2

Figure 1: Structure of compounds **1** and **2**.

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## Agradecimentos/Acknowledgments

The authors would like to thank Brazilian agencies Conselho Nacional de Pesquisa e Desenvolvimento Tecnológico (CNPq), Fundação de Amparo à Pesquisa (Fapesp) and Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) for the financial support for this work.

**Área: INO**

# Layered double hydroxides containing nickel and aluminum for removing tartrazine food coloring in aqueous solution

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Keywords :*HDL, Dye, Adsorption.*

## Highlights

Use of HDLNiAl as adsorbent for organic pollutants in aqueous solution. HDL-NiAl0,5 and HDL-NiAl0,67 performed better in removing tartrazine dye at acidic pH.

## Resumo/Abstract

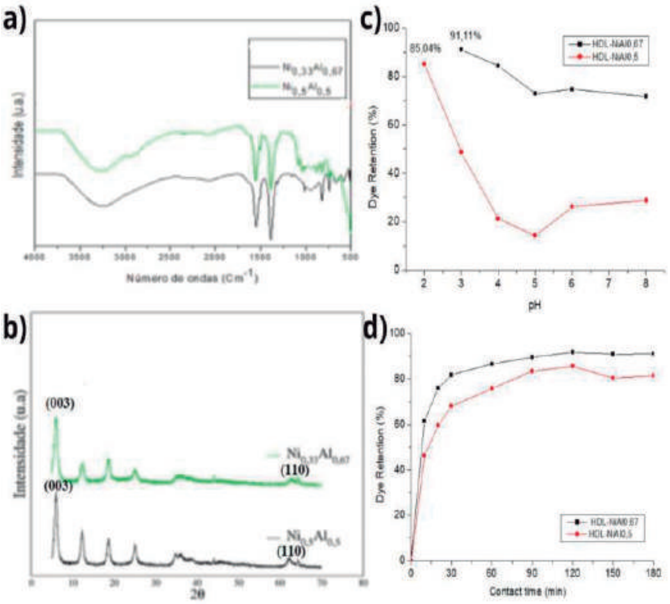

**Figure 1:** a) FTIR spectra; b) XRD spectra;c) Evolution of tartrazine retention as a function of pH**;** d) Evolution of tartrazine retention as a function of contact time (min).

The inadequate disposal of effluents by industries of different segments, such as in rivers and seas, has been causing great environmental impact. To remove these pollutants the adsorption process is recommended. In this perspective, layered double hydroxides were synthesized in metallic ratios Ni/Al= 1 and 0,5 containing the terephthalate anion intercalated, for the adsorption of the tartrazine food coloring in aqueous solution.The adsorbents named as HDL-NiAl0,5 and HDL-NiAl0,67 were obtained by the method of coprecipitation at controlled pH. XRD and FTIR results confirmed the formation of HDLsNiAl through the plans (110) and (003). FTIR data showed bands at 3000-3600cm$^{-1}$ related to the hydroxyls of the layer, as well as absorption at 1600cm$^{-1}$ and bands at 800-860cm$^{-1}$, responsible for the vibration of the benzene rings, confirming the intercalation of the terephthalate anion (Figure 1a;1b).The determination of the point of zero charge (PCZ) was performed using the method of the 11 points, resulting in the values of PCZ = 5.51 and 5.31 for HDL-NiAl0,5 and HDL-NiAl0,67. Adsorption tests found efficiency with removal rat e above 80% for the tartrazine dye at acidic pH, pH = 2 and pH =3 (Figure 1c), indicating agreement with the PCZs obtained, whereas for pH>PCZ values, the HDL surface tends to become more negative, and for pH<PCZ values, the surface tends to become more positive due to Sur-$OH_2^+$, Sur=surface, which will attract electrostatically the $Ta^{3-}$ anions of the dye, according to eq. Sur-OH + $H_3O^+$→Sur-$OH_2^+$ + $H_2O$.[1] Following this trend, there is a decrease in dye removal at alkaline pHs due to competition from hydroxyl ions by the active sites on the surface of the adsorbent forming the Sur-$O^-$ groups causing the repulsion of the tartrazine anion, according to eq. Sur-OH + $OH^-$→Sur-$O^-$ + $H_2O$. For the effect of the contact time, it was observed that the best time to HDL-NiAl0.5 and HDL-NiAl0.67 was 120 minutes, since after this time the adsorption equilibrium occurs, that is, the amount of solute in the liquid phase remains constant, as the maximum adsorption capacity has been reached. The rapid adsorption observed in the initial 30 minutes (Figure 1d) suggests that active sites are easily accessible by tartrazine dye ions in the initial step of the process. This way, HDLs can be considered promising adsorbents in the treatment of water contaminated with the tartrazine dye.

[1] OUASSIF, Hasna ; LAHKALE, Redouane. Zinc-Aluminum Layered Double Hydroxide: High efficient removal by adsorption of tartrazine dye from aqueous solution. Surfaces and Interfaces, 2020.

## Agradecimentos/Acknowledgments

UFRPE, LAQIS and LAQUIMAT for the support.

**Área: INO**

# *In Silico* Studies of Ligand Exchange of Drug Candidates Au(I) Complexes

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Palavras Chave:, Organometallic Au(I) complexes, DFT, ligand exchange.

## Highlights

Au(I) linear complexes are chemotypes for designing metallodrugs, and can exchange their ligands, affecting the biological outcome. We aim to use in silico methods to investigate those reactions.

## Resumo/Abstract

Aurothiomalate, aurothioglucose, and auranofin are approved drugs for the treatment of arthritis, and several experimental complexes have been showing significant anticancer, antiparasitic, antiviral, and antimicrobial activities[1]. In silico methods are growing in the pharmaceutical drug research area. In this study, we aim to use Density Functional Theory (DFT) to study the ligand exchange reactions of Au(I) compounds. Previously, Dos Santos and Goetzfried[2,3] studied Au(I)-NHC ligand scrambling reactions by DFT. The Nudged Elastic Band (NEB) is used to understand the minimum energy reactional path (MEP). In this work, we explored the kinetics and thermodynamics of ligand exchange between [Au(I)Cl(IMes)] and relevant molecules via NEB.

The calculations were performed using the ORCA software. Geometry optimizations of eight Au(I) compounds: [AuCl(IMes)], [AuIMes(S-DMSO)], [AuIMes(O-DMSO)], [AuIMes(Cys)], $[Au(IMes)_2]^+$, $[AuIMesDMAP]^+$ and [Au(PPh3)Cl], where IMes = 1,3-bis(mesityl)imidazole-2-ylidene, were carried out employing the PBE0 functional, def2-TZVP/BJ basis set, RIJCOSX approximation, using the ZORA method for relativistic corrections of the Au(I) cations, and CPCM (Conductor-like Polarizable Continuous Model) for DMSO. The harmonic vibrational frequencies of all structures were calculated at the same level of theory for minima verification. For the NEB studies, calculations were carried out for the $Cl^-$ substitution of the [AuCl(IMes)] complex for four different ligands: $H_2O$, DMSO, cysteine, and the NHC IMes itself, including geometry optimizations of the reactants and products of each reaction and the NEB-TS calculation itself with the same level of theory, with six intermediate images generated and optimized.

All the geometry optimizations converged and did not present imaginary frequencies. NEB computation with L = $H_2O$ and DMSO resulted in MEPs with TS confirmed by the optimization and vibrational frequencies, whereas the calculations, with L = cysteine and IMes found guesses for MEPs but failed to optimize the structure of the transition states, meaning there is a problem with the resulted MEPs. Figure 1 shows the MEP graphs of each reaction, where the exchange ligand is $H_2O$ (a) and DMSO (b). Also, Figure 1 shows the structures of the initial, transition, and final state of each calculation that succeed. The curves obtained are coherent, and both show that the reactions aren't spontaneous, where the Gibbs free energy change for L = $H_2O$ is 9,89 kJ/mol, and L = DMSO is 8,65 kJ/mol.

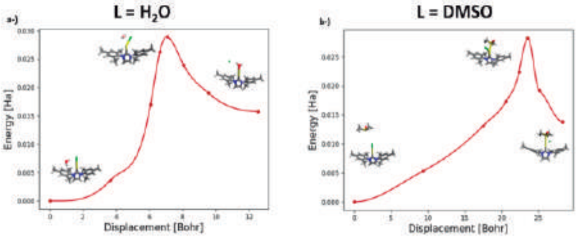

Figure 1. Curve of energy by reaction coordinate for the $Cl^-$ substitution for L = $H_2O$ (a) and L = DMSO (b).

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## Agradecimentos/Acknowledgments

We gratefully acknowledge financial support from CNPq 406444/2018-8, FAPESP 2020/11727-2 and 2019/16904-2, and CENAPAD-SP project#638 for computer time

# *In vitro* and *in vivo* studies of fluorescent Half-Sandwich Ru(II)/alizarin complexes

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Keywords: *Ruthenium, half-sandwich, alizarin, cancer, in vivo, zebrafish.*

## Highlights

Half-Sandwich Ru(II)/alizarin complexes shown to be suitable to treat triple negative breast cancer, in addition to very encouraging results in *in vivo* toxicological screening using the zebrafish model.

## Abstract

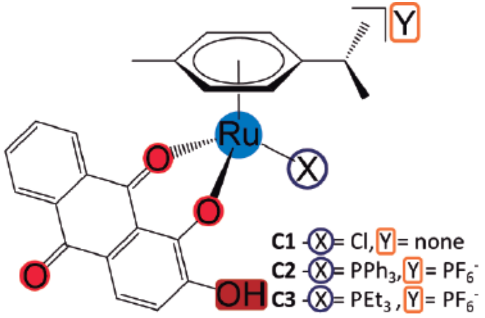

**Figure 1.** General structure of the new half-sandwich Ru(II)/alizarin complexes

The synthesis of metal complexes with natural products as ligands has attracted the attention of researchers, mainly due the possibility of reproduction of desirable characteristics belonging for both substances (complex and free ligands). Here we report the synthesis and characterization of Ru(II)-arene complexes (class of organometallic compounds with promising application in the treatment of cancer)[1] coordinated to alizarin (fluorescent anthraquinone), aiming to obtain a new potential fluorescent antitumor agent. This allow us to study the accumulation of these complexes in the tumor cells and their toxicities against Zebrafish *in vivo* model. So, three new Ru(II) half-sandwich complexes containing *p*-cymene (cp), alizarin (**L**) and different ligands in the X position were synthesized (Fig. 1). Compound **C1** was obtained from the precursor $[RucpCl_2]_2$ (**P1**), **C2** from $[Rucp(PPh_3)Cl_2]$ (**P2**) and **C3** from $[Rucp(PEt_3)Cl_2]$ (**P3**). All complexes were characterized by elemental analysis, molar conductivity, infrared, 1D/2D ($^{1}H$, $^{31}P$ and $^{13}C$) NMR spectroscopies and single crystal X-ray diffraction, confirming the proposed structures. The compounds were tested in human breast tumor and non-tumor cells, as shown in Tab. 1. Compound **C2** stands out, being the most active and the most selective to the non-tumor cell, inhibiting cell migration and clonogenicity. In the fluorescence assays, it was possible to follow the internalization of **C1** (ex. = 420 nm, em. = 700 nm). The image obtained (Fig. 2A) allows the observation of the accumulation of **C1** (red) inside the nucleus (blue / DAPI). **C2** showed quite encouraging outcomes in the *in vivo* toxicological screening at low concentration using the zebrafish model. Therefore, among all complexes, **C2** is the most suitable candidate for drug development to treat triple negative breast cancer.

**Table 1**. $IC_{50}$ (μM) data in breast tumor (MDA-MB-231) and non-tumor (MCF-10A) lines

| Complexes | MDA-MB-231 | MCF-10A | IS |
|---|---|---|---|
| **C1** | 42.27 ± 3.66 | 57.03 ± 0.58 | 1.34 |
| **C2** | 6.59 ± 0.06 | 10.00 ± 0.33 | 1.51 |
| **C3** | 45.45 ± 1.40 | 41.64 ± 0.07 | 0.91 |
| **P2** | 46.81 ± 0.61 | 18.24 ± 0.61 | 0.39 |
| **L, P1 and P3** | > 100 | > 100 | -- |

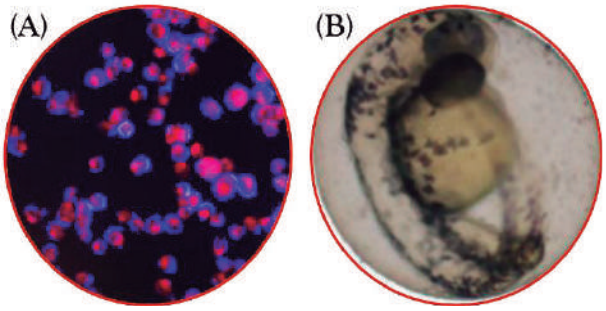

**Figure 2.** (A) Fluorescence microscopy image obtained after internalization of compound **C1** in MDA-MB-231 cells (B) Zebrafish embryos after 48 h exposure to **C2**.

[1] *Recent Considerations in the Application of RAPTA-C for Cancer Treatment and Perspectives for Its Combination with Immunotherapies*, Advanced Therapeutics, 2019, DOI 10.1002/adtp.201900042.

## Acknowledgments

The authors are grateful for the financial support from CAPES, CNPq (305190/2017-2, 151495/2020-3, 306329/2020-4) and FAPESP (2021/04876-4, 2020/14561-8, 2017/15850-0).

**Área: INO**

# *One-pot synthesis of protorphyrin containing ruthenium coordinated with europium(III) and dipicolinic acid for photodynamic therapy application*

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Keywords: *Photodynamic Therapy, Singlet Oxygen, Tumor Hypoxia*

## Highlights

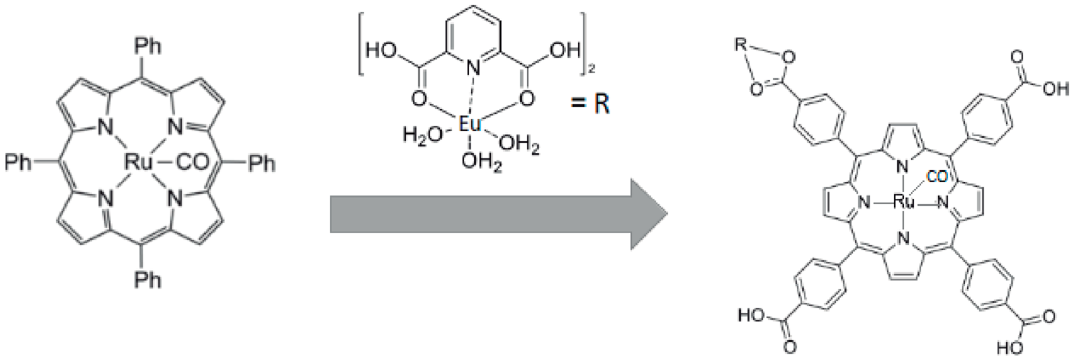
Luminescence activity after a metalloporphyrin was complexed with europium(III).

Europium(III) luminescence suppression as a mechanism with potential detection of tumor hypoxia.

## Resumo/Abstract

Porfirinas são uma classe de moléculas orgânicas com estrutura geral formada por 4 anéis pirrólicos. Suas aplicações são diversas das quais destacam-se aplicações direcionadas à terapia fotodinâmica. Sua importância para aplicações espectroscópicas se deve ao fato de tais estruturas possuírem espectros de excitação e emissão dentro da região do visível, além de serem boas produtoras de Espécies Reativas de Oxigênio (ERO's). A inserção via coordenação de alguns metais como rutênio na cavidade central da porfirina permite a formação de quelatos estáveis que potencializam o efeito na produção de ERO's. Neste trabalho, a inserção do rutênio ocorreu em um sistema de refluxo sob agitação e aquecimento a partir do reagente de partida cloreto de rutênio(III) dissolvido em etilenoglicol, com adição formaldeído como fonte de monóxido de carbono em atmosfera inerte de argônio. Após a redução do rutênio(III) para rutênio(II) confirmada a partir da alteração da coloração da solução para o amarelo, evaporou-se parte do solvente e adicionou-se a protoporfirina meso-tetrafenilporfirina, deixando o sistema sob refluxo por aproximadamente 30 horas. O sólido de coloração marrom obtido foi lavado em água e redissolvido em uma mistura de 20% de metano e 80% de etanol. Posteriormente, reduziu-se o volume para aproximadamente 30% da mistura adicionada, o sólido obtido foi filtrado e lavado diversas vezes com hexano. Como parâmetro de sucesso, serão apresentados os espectros emissão, excitação e absorbância, assim como os resultados obtidos em uma curva termogravimétrica.

Por final, serão discutidos os resultados obtidos com a inserção do európio coordenado ao ácido dipicolínico nas extremidades da protoporfirina via síntese *one-pot* desenvolvida conforme pode ser visualizado no Esquema 1. A importância do európio se deve a supressão de luminescência que este elemento sofre em presença de oxigênio, pois esta propriedade possui potencial para detecção do mecanismo de hipóxia tumoral, desta forma, atribui-se um potencial bimodal para esta sonda, podendo ser utilizada para detecção e tratamento em pacientes com câncer de pele.



Esquema 1 – Síntese proposta da metaloporfirina complexada ao európio(III) e ácido dipicolínico.

## Agradecimentos/Acknowledgments

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**Área: INO**

# Meaningful *in vitro* cytotoxic activity of ruthenium (II) complexes containing mercapto ligands

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Keywords: *Ruthenium complexes, DNA, Citotoxicity, Selectivity index, Cytostatic potential*

## Highlights

New ruthenium complexes with relevant cytotoxicity; Complexes of ruthenium (II) showed equal or more selectivity index than the cisplatin; Ruthenium complexes with good activity against triple negative breast tumor cell line.

## Abstract

Various researchers have been investing their efforts in the search on novel metal-compounds with potential antitumoral activity, which could have higher activity and minor side effects than the metallodrugs used in the chemotherapeutic regimes, such as cisplatin.[1] Thus, our research group has synthesized ruthenium complexes and investigated their cytotoxic activity *in vitro* in many cell lines. Thus, in this work, we synthetized three new Ru(II) complexes, of general formula [Ru(dppb)(phen)(NS)]$PF_6$, where dppb is 1,4-*bis*-(diphenilphosphino)butane, phen is 1,10-phenanthroline and NS is referent to mercapto ligands, more specifically, 2-mercaptopyridine **(complex A11)**, 2-mercaptothiazoline **(complex A12)** and 2-mercaptopyrimidine **(complex A13)**.The structures of the compounds were confirmed by several characterization techniques, including X-ray diffraction spectroscopy. On the cytotoxic evaluation, studies were conducted to analyze their interactions with DNA, which is a possible biological target. The results indicate a weak interaction between complex-DNA, that probably occurs in minor groove of the biomolecule.[2] The complexes are stable in aqueous media (DMSO/culture medium). Besides that, the biological experiments were carried out, and the $IC_{50}$ evaluation **(Table 1)** indicates that the three complexes showed good activity against all cell lines. The complex A12 was the most active in all tumor cell lines tested, being more active in MDA-MB-231 cell line, showing better selectivity index. When we compare this complex, it is almost 25 times more active than cisplatin and more selective (**Table 1**), In this course, advanced experiments were executed to analyze various aspects, as morphological damage, cytostatic potential, and others, that indicates greater damage in concentrations bigger than $IC_{50}$ value, cytostatic potential in concentration equal $IC_{50}$ and do not induce cell cycle arrest.

**Fig. 1-** General structure to complexes and ligands structures

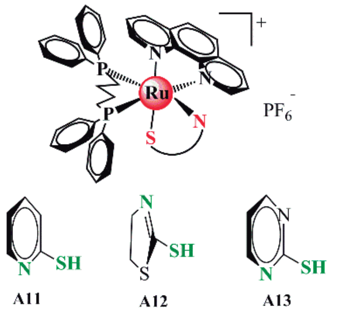

**Table 1-**$IC_{50}$ values to complexes and cisplatin

| COMPLEX | $IC_{50}$(μM) |  | Selectivity index |
|---|---|---|---|
|  | MDA-MB-231 | MCF-10A |  |
| **A11** | 0,19±0,09 | 1,59±0,05 | 8,4 |
| **A12** | 0,10±0,01 | 1,68±0,07 | 16,8 |
| **A13** | 0,24±0,01 | 2,14±0,22 | 8,9 |
| **Cisplatin[3]** | 2,44±0,20 | 23,9±0,70 | 9,8 |

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## Acknowledgments

**Área: INO/MAT**

# Mecanoquímica: alternativa sustentável para a síntese de hidrotalcita

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*Palavras Chave: hidróxidos duplos lamelares, hidrotalcita, mecanoquímica, química verde, moinho de bolas e moagem a mão.*

## Highlights

Mechanochemical: sustainable look at the synthesis of hidrotalcite. Simple, no-waste-producing and low cost methods was employed here to synthesize hydrotalcite. Products from ball-milling and manual grinding were compared. Ball-milling followed by ageing step increased hydrotalcite yield.

## Resumo/Abstract

Hydrotalcite is the best know among anionic clays, belonging to the class of layered double hydroxides, called LDH's. LDH's have a two-dimensional structure and their compositions are expressed by $[M^{II}_{L-x}M^{III}_{x}(OH)_2]^{x+}[A^{m-}_{A/m}.nH_2O]^{x-}$. The most common synthesis methods are co-precipitation, sol-gel, hydrolysis reactions, hydrothermal synthesis, vapor activation and microwave irradiation and, in this context, mechanosynthesis has a high potential still to be explored owing to characteristics such as green character, solvent-free, simplicity, low-cost and lack of waste production. Here we report the evaluation of mechanosynthesis to prepare Mg/Al- based layered double hydroxide, aiming at optimizing the product yield and comparing the performances of ball milling and manual grinding.

Manual grinding of mistures of MgO and Al(OH)3 was carried out in an agate mortar for 5, 10 and 20 minutes with and without addition of 0.5, 1.0 and 2.0 mL of water. Ball milling was performed using a Ball Mill Marconi at 350 rpm for variable times (between 16 and 220 hours). Analysis through scanning eléctron microscopy (SEM) images evidenced that grinding significantly reduces the particle sizes, causing also the particles to form compact aggregates and to exhibit the shape of hexagonal plates in the microstructure. Characterization by x-ray diffraction showed that formation of LDH phase from manual grinding depends on the presence of water and ball milling is more efficient to increase the product yield.

Manual grinding demonstrated trends in the formation of LDH Mg/Al and supports the improvement of ball milling. Howerer, the ball mil allows grater efficiency and effectiveness in the synthesis of hydrotalcite. This methods confirmsthe possiility of preparing lamellar double hydroxides Mg/Al with all their traditional advantages, being na attractive alternative for the future of green chemistry and making the optimization of synthesis parameters a reality.

## Agradecimentos/Acknowledgments

Nossos agradecimentos a Universidade Federal de Sergipe (FUFS), ao Programa de Pós-Graduação em Ciência e Engenharia de Materiais (P2CEM) e a Prof.ª DSc. Iara de Fatima Gimenez por todas as orientações. Agradecemos ao Centro de Laboratórios de Química Multiusuários (CQLM), ao Laboratórios Multiusuário do Departamento de Ciência e Engenharia de Materiais (LMDCEM) e ao Laboratório de Aplicações Nanotecnológicas (LAN.UFS) por toda a infraestrutura disponibilizada.

**Área: INO** **Nº de Inscrição: 01018**

# Mechanochemical synthesis of europium complexes.

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Key words: Acyclic imide, β-Diketone, Europium complex, Luminescence, Mechanochemistry.

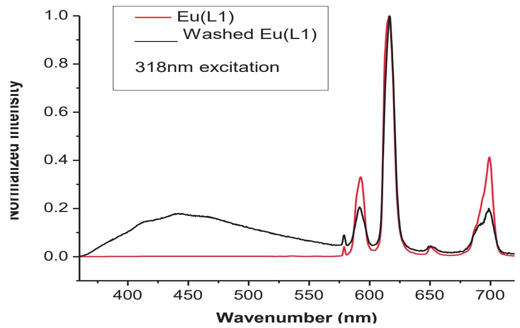
## Highlights

New europium complexes were synthesized with *N*-acetylbenzamide and 2-benzyl-1,3-diphenylpropane-1,3-dione as ligands by mechanochemical method, as new green synthetic route.

## Resumo/Abstract

Trivalent lanthanide complexes attract great interest due to their diversity of applications, which include photonics, catalysis, contrast agents for NMR imaging, diagnostics, photo and electro-luminescent devices. However, the low photo-stability under UV irradiation of several lanthanide complexes, especially with $Eu^{3+}$ and $Tb^{3+}$, hinders some of these applications. The syntheses of these complexes are not always trivial, so it is important to develop new green methods. Mechanochemistry is a technique that uses mechanical energy to enable chemical reactions, and allows them to occur in the absence of bulk solvents. In addition of reducing the use of solvents, it has other advantages such as: shorter reaction times, use of sparingly soluble or insoluble substrates, besides the formation, in some cases, of products different from those obtained in solution. However, there are few reports on the use of this method in the synthesis of lanthanide complexes. The present work uses mechanochemistry in the green and fast synthesis of trivalent europium complexes with the ligands *N*-acetylbenzamide (**L1**) and 2-benzyl-1,3-diphenylpropane-1,3-dione (**L2**). The choice of these ligands to form europium complexes is related to our interest in studying the photodegradation mechanisms of lanthanide compounds when exposure to UV light, a phenomenon well known for lanthanide β-diketonate complexes. The syntheses of ligands **L1** and **L2** were carried out based on adaptations of procedures described in the literature. The syntheses of the complexes were carried out with liquid-assisted grinding (LAG) in 10 mL Teflon jars, one 10 mm zirconia sphere and 25 Hz grinding frequency. For ligand **L1**, the synthesis was performed in a single step, with the addition of the ligand, base (NaOH) and $EuCl_3{\cdot}6H_2O(s)$ with water-assisted grinding for 90 min. The photophysical properties were evaluated for the solid after grinding and for the compound after washing with water, dissolution in acetone and dried. The excitation and emission spectra of the solids were acquired and they showed the $^5D_0 \rightarrow {}^7F_J$ (J = 0 to 4) transitions characteristic of $Eu^{3+}$. However, two distinct spectral profiles were observed (Figure **1**), indicating different chemical environments for $Eu^{3+}$.

**Figure 1**: Emission spectra of the europium complex and ligand **L1** as prepared and after washing with water and acetone.



These results suggest structural changes when the solid is washed with solvents, therefore, it is necessary to evaluate the conditions of synthesis and isolation of the complex. The synthesis with ligand **L2** was carried out in one-pot and two steps under ethanol assisted grinding: i) abstraction of the β-diketone proton with NaOH and ethanol (20 μl) for 30 min; ii) followed by the addition of $EuCl_3{\cdot}6H_2O(s)$ and another 60 min of grinding. The emission spectra of the solid showed the typical $^5D_0 \rightarrow {}^7F_J$ (J = 0 to 4) transitions of $Eu^{3+}$, with the same spectral profile being observed exciting at 286 nm (ligand) and at 394 nm ($Eu^{3+}$), which suggests the formation of a single coordination compound. These syntheses need to be optimized and the products are being characterized by X-ray diffractometry, infrared and Raman spectroscopies. The mechanochemical method has potential in the synthesis of new lanthanide complexes.

## Agradecimentos/Acknowledgments

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**Área: INO** **Nº de Inscrição: 00006**

# Mesoporous silica HMS as support of Mn-porphyrins for oxyfunctionalization of cyclohexane and n-heptane

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Palavras Chave: *heterogeneous catalysis, oxidation, mesoporous silica, metalloporphyrin, HMS*

## Highlights

Mn-porphyrins anchored on mesoporous silica *via* electrostatic or covalent bond. Supported catalysts able to oxidize cyclohexane and n-heptane. Heterogenized catalyst low MnP loadings (0.3% w/w) were selective for alcohol.

## Resumo/Abstract

Mn-porphyrins (MnPs) are quite employed as bioinspired catalyst in the Cytochromes P450 enzymes in oxidation reactions of organic substrate. Biomimetic systems, in homogeneous conditions, showed vulnerability, such as oxidative destruction and catalytic deactivation due bimolecular interactions between MnPs. The heterogenization of MnPs on chemical surfaces has been a strategy alternative for minimize theses effects. In the context, mesoporous silica HMS is promising platform, for showing high surface area and pore diameter of 3Å, which may to act in controlling the access of substrate and oxidant to the catalytic site, yielding a more efficient and selective catalyst. Herein, three catalysts were prepared (**Fig. 1**): (**1**) unmodified HMS electrostatically decorated with cationic Mn(**III**) *N*-methylpyridinium-2-ylporphyrin (**HMS/MnP2**) and chloropropyl-functionalized mesoporous silica HMS (HMS-Cl) covalently grafted with (**2**) Mn(**III**) 2-*N*-pyridylporphyrin (**HMS-Cl/MnP1**) or with (**3**) Mn(**III**) *N*-methylpyridinium-2-ylporphyrin (**HMS-Cl/MnP2**). Mesoporous silicas **HMS** and **HMS-Cl** were characterized by FTIR, TGA/DTA, elemental analysis, nitrogen adsorption-desorption, SEM, and TEM. DR-UV-vis spectra of the materials showed the characteristic MnP spectral profile.

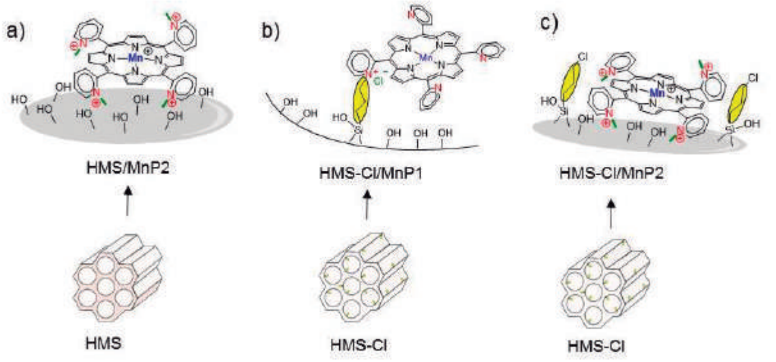

**Figure 1**. Schematic representation of the three classes of anchored catalysts: a) HMS/MnP2, b) HMS-Cl/MnP1, and c) HMS-Cl/MnP2.

The MnP loadings on the supports were determined by UV/VIS, with values of 2.6 for **HMS-Cl/MnP1**, 6.6 for **HMS/MnP2**, and 10.5 $\mu molg^{-1}$ for HMS-Cl/MnP2. The leaching of MnP from the materials was observed only for **HMS-Cl/MnP1** catalyst (*ca.* 50%). The three supported materials were evaluated as biomimetic catalysts for cyclohexane and n-heptane oxidation by iodosylbenzene (PhIO). For cyclohexane oxidation, the following effects were studied: **1**) support effect (HMS *vs.* HMS-Cl), **2**) influence of the Mn-porphyrin (MnP1 *vs.* MnP2), **3**) reaction time (of 90 min until 24 hr), **4**) oxidative stability toward increased PhIO/MnP molar ratio, **5**) reuse of heterogenized catalysts, **6**) influence of the water (4 µl and 40 µl), and **7**) influence of the temperature (~25 ºC *x* 40 ºC). All three heterogenized solids were able to catalyze the reactions of cyclohexane oxidation, being more selective (60%) toward cyclohexanol (C-ol). In the reused reactions, the materials showed decreased of 50% in the efficiency, indicating that there was some destruction of the catalysts. This also was observed when there was an increase of PhIO/MnP molar excess from 10 to 20. For n-heptane oxidation, **HMS-Cl/MnP1** (46% total yield) was more efficient than **HMS/MnP2** (18% total yield) and **HMS-Cl/MnP2** (27% total yield). All catalysts were equally regioselective for oxidations at positions ω-1, ω-2, and ω-2. All materials showed total yields of ketone equal to the total yield of alcohol (*ca.* 50%, *i.e.* low chemoselectivity). Catalytic performances of **HMS-Cl/MnP1** was maintained for at least two oxidation reaction cycles (reuse) with loss total yield of only 10%.

## Agradecimentos/Acknowledgments

UFPB; UFPR; FINEP; CNPq; CAPES; Fundação Araucária

# Nanoscintillators mediated X-ray inducible photodynamic therapy with a ruthenium-nitrosyl complex immobilized for cancer treatment

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Keywords: *Ruthenium-nitrosyl complex, Nanoscintillator, S-nitrosothiol, X-PDT.*

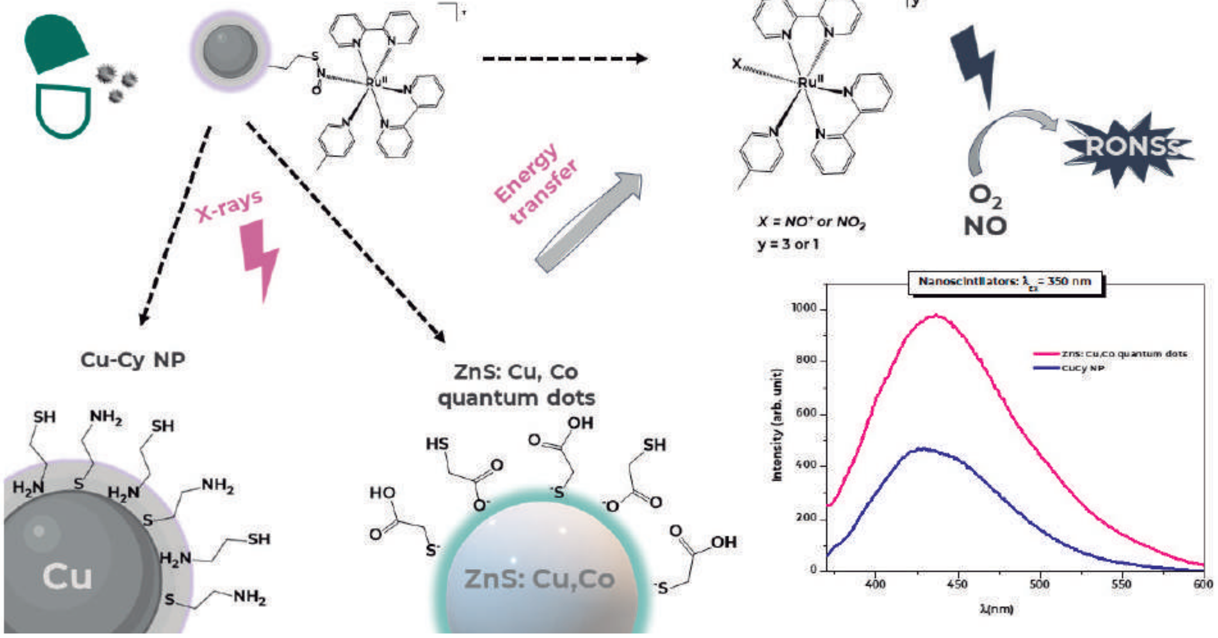
## Highlights

- Synthesis and characterization of two nanoscintillators for X-PDT in oncotherapy, Cu-cysteamine nanoparticles and ZnS: Cu,Co quantum dots;
- Immobilization of ruthenium nitrosyl complex in both nanomaterials and evaluation of their photoluminescence properties;
- The system could act as NO release platform, which functionalization in nanoparticles were viabilized by S-nitrosothiol bond formation.

## Abstract

The growing interest in Photodynamic Therapy (PDT) clinics, from oncotherapy to the treatment of bacterial diseases, is due to its high selectivity. Given the limited penetration of light into biological tissue, we are working on the possible use of X-rays to generate reactive nitrogen and oxygen species using compounds such as *cis*-$[Ru(bpy)_2(4\text{-pic})X]^{y+}$ with X= $NO_2$ or NO and y= 1 or 3, respectively. For this purpose, Cu-Cysteamine nanoparticles (CuCy NP) and ZnS: Cu, Co quantum dots were developed. Both NPs are water-soluble and showed high luminescence with $\lambda_{em}$ size-dependent. Similar results were observed when X-rays were used as an irradiation source. Based on the energy transfer process, ruthenium-nitrosyl complexes could produce nitric oxide by charge transfer process, which also allows its release, in a controlled manner and at specific locations. Those systems could be useful in cancer treatment, especially those tumors located in deep regions of the body. The synthesis of both NPs was carried out by the wet chemical method. The immobilization of the ruthenium complex to the NPs occurred *via* S-nitrosothiol bond (Figure 1), as demonstrated by FTIR and UV-vis spectroscopies.

**Figure 1.** Elucidation of functionalized systems of CuCy NP and ZnS: Cu,Co quantum dots with ruthenium-nitrosyl complexes and their luminescence properties.



In order to verify the potential of a NO release platform of the synthesized systems, it is intended to carry out photochemical and photophysical studies mediated by X-rays. In addition, the evaluation of its photocytotoxicity in tumor cells also will be studied.

## Acknowledgments

CAPES (88887.615169/2021-00), FAPESP (2019/19884-8) and CNPq (306243/2018-0)

**Área: INO**

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

# New Ru(II)-naphthoquinone complexes as potential anticancer agents

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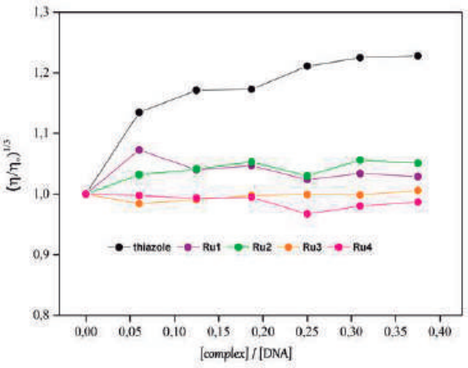
Keywords: *breast cancer, metallodrug, ruthenium complex and naphthoquinone.*

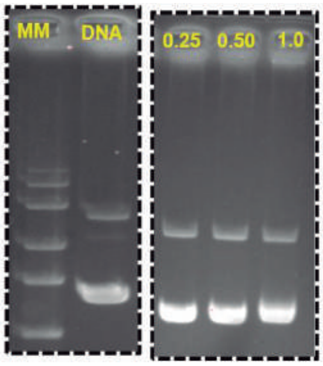
## Highlights

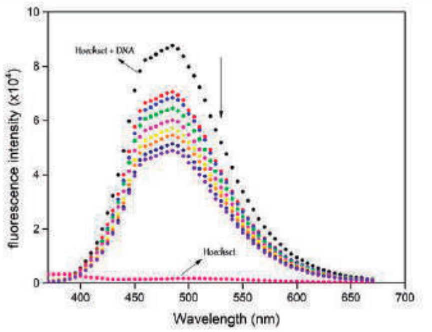
Development of new ruthenium compounds containing naphthoquinones and phosphine binders, possible candidates as new anticancer metallodrugs.

## Abstract

Bioinorganic and medicinal chemistry has benefited of metallopharmaceuticals as drugs and therapeutic agents. In this sense, many researchers are dedicated to synthesizing coordination compounds with potential medicinal application, searching for new drugs with biological activity and modeling the existing ones aiming the reduction of their side effects. In this sense, an interesting approach is to associate the biological activity of the free ligand with the metal ion, since studies have shown that the coordination of organic molecule with biological activity to the metal center has potentiated its cytotoxic action. Thus, the naphthoquinone derivatives, lawsone and lapachol exhibited a range of bioactivities and their metal complexes show the importance of this procedure[1,2]. Therefore, the objective of this work was to synthesize, characterize and evaluate the cytotoxicity of four new complexes with formula [Ru(Lau)(dppen)(bipy)]$PF_6$ (**Ru1**); [Ru(Lap)(dppen)(bipy)]$PF_6$ (**Ru2**); [Ru(Lau)(DPEphos)(bipy)]$PF_6$ (**Ru3**) and [Ru(Lap)(DPEphos)(bipy)]$PF_6$ (**Ru4**); dppen: 1,2-bis(diphenylphosphine)ethylene; DPEphos: bis[(2-diphenylphosphino)pheny]ether and bipy: 2,2'-bipyridine. The complexes were characterized by molar conductivity, FTIR spectroscopy, cyclic voltammetry, $^{1}$H, $^{13}$C and $^{31}$P{$^{1}$H} NMR and monocrystal X-ray diffraction. The cytotoxicity of the complexes against the tumor breast cell lines MDA-MB-231, MCF-7, SK-BR-3 and breast non-tumor cell line MCF-10A. All complexes were cytotoxic against evaluated tumor cell lines.The **Ru2** and **Ru3** complexes exhibited good selectivity, exhibiting values of 14.4 μM and 25.5 μM, respectively. The interaction studies with DNA performed by means of viscosity measurements, electrophoresis and competition assay with Hoechst, suggest the complexes interact with the DNA *via* minor groove. These results suggest that the complexes are potential candidates for breast cancer chemotherapy.







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**[2]** *Frontiers in oncology* 2021; 24 (11): 682-968.

## Acknowledgments

**The authors acknowledge the financial support of CNPq, CAPES and FAPESP.**

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

# New series of pentadecanuclear lanthanide compounds featuring a cage-like architecture

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Palavras Chave: *Lanthanide clusters, luminescence, crystallography, carboxylate ligands*

## Highlights

Synthesis and characterization of pentadecanuclear cage-like lanthanide-containing compounds. *In situ* formation of carboxylate ligand with multiple coordination modes. Distinct coordination symmetries of the metal ions.

## Resumo/Abstract

The reaction between trivalent lanthanides ions and the ligand pyridine-2-carboxylate (2-pic) gave rise to a series of isomorphic cage-like compounds of formula $[Ln_{15}Cl_5(\mu_3\text{-}OH)_{20}(\mu_2\text{-}O)_5(2\text{-pic})_{10}(H_2O)_{20}]$, in which Ln(III) stands for Eu(**1**), Tb(**2**), Dy(**3**) or Gd(**4**). The carboxylate-based ligand was formed *in situ* through the induced disproportionation of two pyridine-2-carbaldehyde molecules by tris(hydroxymethyl)aminomethane (tris). The crystal structures of all compounds were solved by single-crystal X-ray diffraction. The asymmetric unit of **1-4** revealed that three Ln(III) ions are octa-coordinated, while the five remaining are found at a nona-coordinated environment. Six different local symmetries were evaluated by SHAPE program[1] for the metal ions: i) $C_{4v}$, $D_{3h}$ or $C_s$ for the nona-coordinated ions and ii) $D_{4d}$, $D_{2d}$ and $C_{2v}$ for the octa-coordinated ones. The lanthanide ions occupy alternated vertices of a cubane-like architecture and are bridged by $OH^-$ ligands in a $\mu_3$ coordination mode (Fig. 1a). The carboxylate ligands in such compounds are coordinated to metal centers in a tridentate fashion, connecting three crystallographic independent ions from two cubane moieties (Fig. 1b). The luminescent properties for **1** were investigated. The intense emission observed at 579, 592, 614, 651 and 700 nm suggests that the pyridine-2-carboxylate ligand efficiently transfers energy to the metal centers through antenna effect. Remaining compounds are currently undergoing investigation of their emissive properties (**2** and **3**) and magnetic properties (**2**-**4**).

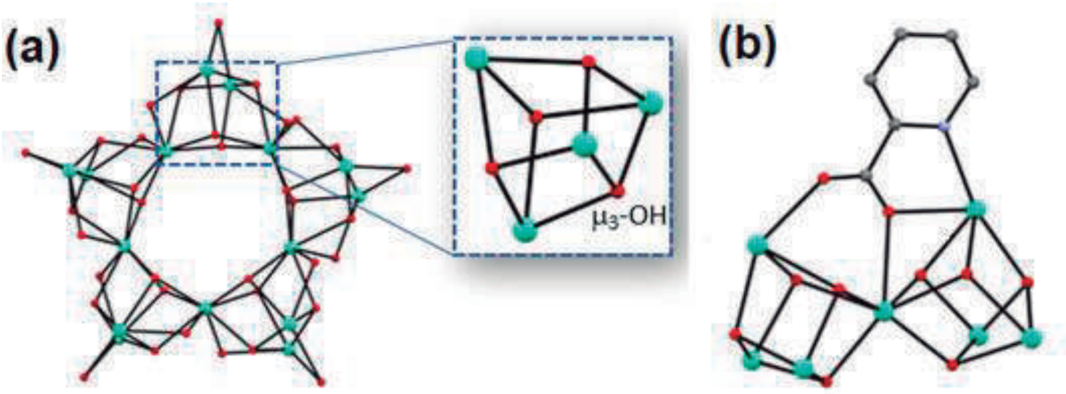

Figure 1. (a) Crystal structure of compounds **1-4**, highlighting the cubane-like architecture; (b) Coordination mode of pyridine-2-carboxylate ligand in **1-4**.

[1] M. Llunell, D. Casanova, J. Cirera, P. Alemany, S. Alvarez, SHAPE: Program for the Stereochemical Analysis of Molecular Fragments by Means of Continuous Shape Measures and Associated Tools, v2.1, Electronic Structure Group, Universität de Barcelona, 2013.

## Agradecimentos/Acknowledgments

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**Área: INO** **Nº de Inscrição: 01052**

# Nickel complexes containing PNP ligands: synthesis, structure and preliminary cytotoxic activity

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Keywords: *nickel, phosphine, cytotoxic.*

## Highlights

Nickel complexes containing amine-derived diphosphine ligands.
Molecular structure of [$NiCl_2(PN^{CH2Ph}P)$].
*In vitro* cytotoxic tests against B16F10 and A549 cell lines
Low $IC_{50}$ and high SI values.

## Abstract

Three novel nickel complexes with general formula [$NiCl_2(PN^RP)$] (R=$CH_2Ph$, $CH_2py$, Ph) were synthesized following the synthetic route summarized in Fig. 1. $^{31}P$ {$^1H$} and $^1H$ NMR, FTIR, and UV-Vis analyses were performed and results are in agreement with data reported for analogues species [1]. Furthermore, single crystals were obtained and DRX analysis was performed confirming the structure initially proposed. The molecular structure, represented in Fig. 2, presents a slightly distorted square planar geometry, with a bidentate PNP ligand coordinated to the metal centre and two chlorides *cis* positioned.

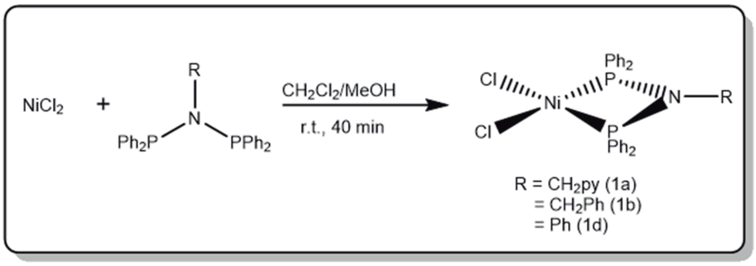

*Figure 1. Synthetic route for complexes with general formula [$NiCl_2(PN^RP)$].*

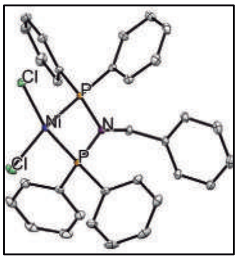

*Figure 2.ORTEP representation of [$NiCl_2(PN^{CH2Ph}P)$].*

In vitro cytotoxic assays were performed for two cancer cell lines and one healthy cell and the results are presented in Table 1. Complexes [$NiCl_2(PN^{CH2py}P)$] and [$NiCl_2(P\text{-}N^{CH2Ph}\text{-}P)$] were the most active against B16F10 and A549 cell lines, respectively. Both complexes presented very low toxicity against HACAT (healthy cells), resulting in good selectivity index.

Table 1. Cytotoxic results ($IC_{50}$ and Selectivity Index)

| ***Complex*** | | **HACAT** | **A549** | **B16F10** |
|---|---|---|---|---|
| ***$NiCl_2(P–N^{CH2py}–P)$]*** | $IC_{50}$ | 41.27 ± 1.23 | 65.60 ± 11.34 | 2.34 ± 0.53 |
| | SI | | 0.62 | 17.6 |
| ***$NiCl_2(P–N^{CH2ph}–P)$]*** | $IC_{50}$ | 9.01 ± 1.30 | 0.28 ± 0.04 | 16.56 ± 0.72 |
| | SI | | 32.1 | 0.54 |
| ***$NiCl_2(P–N^{p\text{-}tol}–P)$]*** | $IC_{50}$ | 42.39 ± 3.12 | 25.57 ± 5.48 | 28.05 ± 2.51 |
| | SI | | 1.65 | 1.51 |

1.Song, K., et al., European Journal of Inorganic Chemistry, 2009. 2009(20): p. 3016-3024.

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# Novel fluorescent Fricke dosimeter based on carbon dots

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Key words: *Ficke Dosimetry. Carbon Dots. Ionizing Radiation Sensor.*

## Highlights

Nitrogen-doped carbon dots (N-CDs) interacted with $Fe^{3+}$ ions produced after irradiation. Photoluminescence quenching is proportional to the absorbed radiation dose.

## Abstract

The carbon dots (CDs) are nanomaterials with fluorescent property made mainly of carbon. Synthesized from different precursors and synthesis routes, they allow their physicochemical properties to be adjusted. It has application capacity in several areas due to its high water solubility, biocompatibility, and low toxicity [1]. A new application is investigated in the production of ionizing radiation sensors that together with the Fricke solution, reported in the literature as radiation dosimeters for radiotherapy, this solution initially contains $Fe^{2+}$ ions and sulfuric acid, which, when exposed to ionizing radiation, oxidized to $Fe^{3+}$ ions and as it is used as a fluorescent sensor for $Fe^{3+}$ ions, the CDs were introduced into Fricke's solution for evaluation as a fluorescent dosimeter, keeping among them the characteristic of equivalent tissue [2,3]. In this work, nitrogen-doped CDs (N-CDs) were synthesized from citric acid and melamine via hydrothermal synthesis. Characterization techniques were also used to elucidate surface functional groups and optical properties. The concentration of $Fe^{2+}$ ions and N-CDs in Fricke's solution was optimized and irradiated with gamma-ray photons. The photoluminescence emission spectra and the respective dose-response curve are shown in Figure 1 (A-B). The best condition determined was prepared with 1.5 mmol $L^{-1}$ of $Fe^{2+}$, 8.0 mmol $L^{-1}$ of $H_2SO_4$ and 10.0 mg $mL^{-1}$ of N-CDs and irradiated in the range of 0.0 to 30.0 Gy. It was observed that the dose-response has two regions that perform linearly. For doses below 2.5 Gy, the coefficient of linearity, $R^2$, was 0.949 and the sensitivity, -40.07 ± 7.65 $Gy^{-1}$. The dose range that corresponds between 5.0 and 30.0 Gy presented $R^2$ = 0.991 and sensitivity, -12.76 ± 0.70 $Gy^{-1}$.

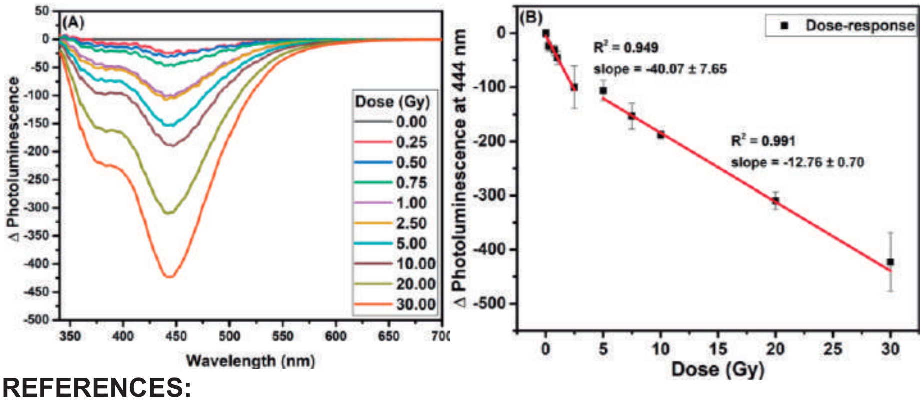

**Figure 1: A)** Photoluminescence emission spectra of the Fricke-NCDs solution irradiated with gamma-ray photons.

**B)** Dose-response curve Fricke-NCDs irradiated with gamma-ray photons in the range of 0.0 to 30.0 Gy

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## Acknowledgments

**Área: INO**

# Palladium-doped Cobalt and Manganese Oxides for Electrocatalytic Oxygen Evolution Reaction

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Palavras Chave: *Water oxidation reaction, Palladium, Electrocatalysis, Manganese and cobalt oxides*.

## Highlights

Pd/α-$MnO_2$ and Pd/$Co_3O_4$ were applied in the electrocatalytic oxygen evolution reaction
PdO were deposited on the surface of the oxides
Doped oxides showed superior activity and lower overpotential

## Resumo/Abstract

The development of efficient technologies for the conversion and storage of energy using renewable sources has been intensified, especially those related to the use of solar energy. The preparation of new materials for hydrogen generation, storage, and transportation, is still a challenge, and the bottleneck of the process is the uphill oxygen evolution reaction (OER) that has high thermodynamic and kinetic barriers. The Earth-abundant first-row transition metal oxides have been applied as catalyst for OER, as alternative less expensive materials in relation to the noble metal oxides that presented the highest efficiency reported for OER. Manganese and Cobalt oxides have been successfully applied in the electrocatalytic OER, although high stability is achieved, the OER activity is still below the reported for the Noble metal oxides. This work aims to combine the robustness and abundance of Manganese and Cobalt oxides with the high activity of the noble metal Palladium, to prepare more active and stable electrocatalysts. Palladium-doped α-$MnO_2$ and $Co_3O_4$ were prepared by Pd introduction during the synthesis of the respective oxide, by reflux for α-$MnO_2$ (3.7wt%) and hydrothermal synthesis for $Co_3O_4$ (8.9wt%). Characterization data revealed the formation of PdO nanoparticles well dispersed over the Mn- and Co-oxides, being responsible for the lower OER overpotential and higher turnover frequencies. At $j$ = 10 mA $cm^{-2}$, lower overpotential (636 mV) was obtained for Pd/α-$MnO_2$ in relation to α-$MnO_2$ (700 mV), what is in alignment with the lower charge transfer resistance of Pd/α-$MnO_2$ (4.9 kΩ $cm^2$) compared to α-$MnO_2$ (10.4 kΩ $cm^2$). Lower Tafel slope (73 mV $dec^{-1}$) and higher TOF ($2.87\times10^{-4}$ $s^{-1}$) at overpotential of 350 mV was obtained for Pd/α-$MnO_2$ in relation to α-$MnO_2$ (Tafel of 77 mV $dec^{-1}$ and TOF $1.94\times10^{-4}$ $s^{-1}$), indicating a faster electron transfer kinetics promoted by Pd. Pd/α-$MnO_2$ was stable at $j$ = 14 mA $cm^{-2}$ for 6 h. For Pd/$Co_3O_4$, the electrocatalysis was tested in pH 1, 7, and 13, where better performance was achieved in alkaline pH, although remarkable results were also found at pH 1. At $j$ = 10 mA $cm^{-2}$, lower overpotential (389 mV) was obtained for Pd/$Co_3O_4$ in relation to $Co_3O_4$ (435 mV) for pH 14, and 523 mV against 594 mV at pH 1, respectively. Lower charge transfer resistance was obtained for Pd/$Co_3O_4$ in all pHs. All materials showed long-term stability in the OER conditions. In conclusion, improvement was achieved for α-$MnO_2$ and $Co_3O_4$ by the introduction of small amounts of the noble metal Pd, due to a synergistic effect between the two metals, leading to lower overpotentials and higher turnover frequencies.

## Agradecimentos/Acknowledgments

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**Área: INO**

# Preparation of nanostructured systems by self-assembly of nanoparticles

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Palavras-chave: *automontagem, nanopartículas, modificação de superfície.*

## Highlights

Controlled nanoparticles self-assembling is a promising strategy to attain new materials. The surface of spherical and rod-like gold nanoparticles was modified to promote specific particle interactions.

## Resumo/Abstract

Nanopartículas de ouro (AuNPs) são consideradas materiais de grande interesse devido às suas propriedades que dependem fortemente de seu tamanho e forma. O ambiente em torno dessas partículas produz efeitos que ajustam ou alteram completamente suas propriedades, neste caso, solventes, moléculas, íons, pH, a proximidade com outras partículas etc. Nesse sentido, buscamos desenvolver metodologias para obtenção de materiais nanoestruturados via processos de automontagem, utilizando AuNPs com diferentes morfologias como blocos de construção. Para tanto, nanoesferas (AuNSs) foram sintetizadas pelo método de Turkevich (~13 nm de diâmetro) e nanobastões (AuNRs) foram obtidos pelo método mediado por sementes, conforme protocolo desenvolvido pelo grupo El-Sayed (45 x 15 nm). Os coloides obtidos apresentaram espectros de absorção de UV-vis característicos (Figura 1). Para induzir um processo específico de automontagem das AuNSs e dos AuNRs, modificou-se a superfície de cada tipo de nanopartícula com moléculas com grupos funcionais específicos, cisteamina (CYS) contém grupos amina e tiol e ácido mercaptoacético (AMA) contém ácido carboxílico e grupo tiol. Após a modificação da superfície, quando misturados os dois conjuntos AuNR / CYS e AuNS / AMA com EDC (1-etil-3-(3-dimetilaminopropil)carbodiimida) e NHS (N-Hidroxissuccinimida) permitem a formação da ligação C-N (Figura 2A). Após a mistura das partículas modificadas, o espectro de absorção UV-vis da combinação mudou radicalmente. Pode-se perceber também, através da imagem visualizada por Microscopia Eletrônica, que não houve interação seletiva como esperado, ainda que os bastões se ligaram preferencialmente às esferas, necessitando de um maior controle e organização dessas estruturas.

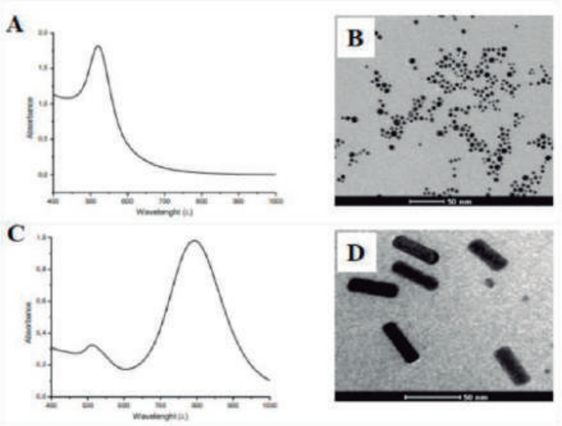

*Figura 1: Espectro de absorção UV-vis dos coloides contendo AuNSs (A) e AuNRs (B) e suas respectivas imagens de AuNPs pelo MET.*

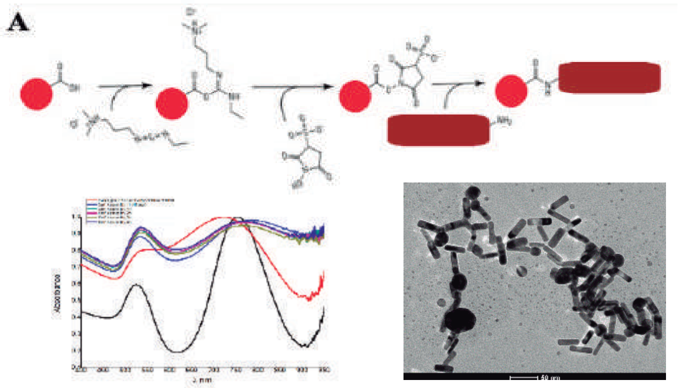

*Figura 2: Esquema que representa a estratégia de automontagem desejada (A). Espectros de absorção de UV-vis dos coloides antes e depois da mistura, respectivas imagens de AuNPs pelo MET.*

## Agradecimentos/Ackowledgments

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**Área: INO**

# Red-emitting europium(III) complex based on carboxylic acid ligand: photophysical, cytotoxic, and cell imaging studies

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Keywords: *Sensitization, bioimaging, europium, complex, red emission.*

## Highlights

A new water soluble Europium(III) complex was synthesized. The complex shows red emission, which is good for biological application. The complex has low citotoxy.

## Abstract

Red-emitting compounds are very attractive to be used in biological assays since biological components present blue and/or green fluorescence. In this scenario complexes based on europium(III) ion are one of the most investigated since its *f-f* transitions occur with emission in the red spectral region with high color purity; moreover probes based on Eu(III) have emerged as an alternative to conventional ones because they can minimize the natural fluorescence effects due to the long lifetime emission of their excited states, allowing the detection of emitted light after the cell autofluorescence has ceased[1]. Additionally, lanthanoid complexes may have high solubility in water, and generally low toxicity[2]. These characteristics of the lanthanoids allow them to be designed to act as viable sensors or as probes for microscopy images. Thus, in this work, a new red-emitting europium(III) complex, ($Na[Eu(Fmpc)_4(H_2O)_4]\cdot 3H_2O$)[3], based on a carboxylic acid ligand was synthesized and characterized by elemental analysis, MALDI TOF spectrometry, thermogravimetric analyses, UV-vis, FT-IR, and photoluminescence spectroscopies, and also a theoretical optimization was performed using the AM1 sparkle model. The gadolinium(III) complex, ($Na[Gd(Fmpc)_4(H_2O)_3]\cdot 4H_2O$), was synthesized and characterized to be used to determine the Fmpc ligand triplet excited state energy, concluding that the energy of the Fmpc ligand is suitable to sensitize the $^5D_0$ level of the europium(III) ion, in addition high sensitization rate was calculated with 98% efficiency. The luminescent properties of the europium(III) complex were investigated, its excited state lifetime was determined as 0.76 ms in acetonitrile solution, the relative quantum yield was estimated to be 27.9. Furthermore, the cytotoxicity tests were performed in CHO-k1 cell line by the MTT assay, no cytotoxicity was observed at 24 h of exposure within the tested concentrations (25 - 200 µg/mL). To evaluate the cell imaging application measures by fluorescence and confocal microscopies were performed. Our findings indicated that $Na[Eu(Fmpc)_4(H_2O)_4]\cdot 3H_2O$ complex exhibited great luminescence properties, it is non-toxic, and it has potential for bioimaging application as a luminescent dye.

## Acknowledgments

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**Área: INO**

# Relation between donor and acceptor energy state in sensitization of heterobimetallic Iridium(III)-Europium(III) complex.

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Keywords: *Sensitization, iridium, europium, UV-LED prototype, red emission.*

## Highlights

Efficient energy transfer between Ir(III) complex and Eu(III). The minimum triplet energy to sensitize the Eu(III) ion was determined by using a yellow heterobimetallic UV-LED prototype.

## Abstract

Imaging devices such as televisions, cell phones and computers, as well as public and domestic lighting, are responsible for a large part of energy consumption.[1] In this way, the search for materials with higher emission quantum yields (Φ) to safe energy has been incessant. Compounds with high values of Φ's have been reported based on metal complexes with high spin-orbit coupling constant (ξ), such as Ir(III), Pt(II), Os(II), and Re(I)[2]. However, these complexes exhibit MLCT or LC emissive states with broad emission bands, as consequence, compromising the *d*-metal complexes color purity, which is a problem for imaging devices, since the high color purity allows the production of images with better contour contrast. Therefore, the use of lanthanoid ions with low dependence with the chemical environment in which they are inserted exhibiting narrow emission bands configures a suitable strategy to enhance luminophores color purity. In luminescent devices, the combination of luminophores emitting red, green, and blue (RGB system) generates other colored lights in the electromagnetic spectrum, including the perception of white light. Among the luminophores emitting the three fundamental RGB colors, the red emitters have received great attention in relation to the others, as they exhibit lower Φ according to the Energy Gap Law. Although red emitters based on the Eu(III) ion have high color purity, their Φ is usually lower than that of red emitters based on the Ir(III) ion, despite the latter having low color purity. In this sense, our strategy here is the synthesis of heterobimetallic *d-f* complexes, to combine the high Φ of *d*-metal complexes with the high color purity of lanthanoid(III) ions, whereas systems based on Ir(III) and Eu(III) are the most investigated.[3] In a heterobimetallic complex of the Ir(III)-Eu(III) type, the Ir(III) complex acts as a ligand, that is, the excited state is overpopulated due to the high spin-orbit coupling of Ir(III) ($\xi = 4{,}430\ cm^{-1}$), transfers the absorbed energy to the Eu(III). As in monocentric Eu(III) complexes, in Ir(III)-Eu(III) heterobimetallics, the sensitization efficiency depends on the energy difference between D (donor) and A (acceptor), but for *d-f* systems the transfer processes energy still need to be further investigated. In this study, polymeric PMMA films doped with $\{[Ir(dfppy)_2(\mu\text{-}bpdc)]_3Eu_2\}Cl_3$ heterobimetallic complex (Ir-p-Eu) were used to coat a UV-LED chip to investigate the photophysical properties. The results obtained by modulation of the applied voltage to the Ir-p-Eu:LED prototype made possible to predict, for the first time, that 19,103 $cm^{-1}$ is the minimum energy needed to observe only the red emission from the Eu(III) ion, as a consequence of efficient energy transfer.

## Acknowledgments

Capes (88887.341772/2019-00), CNPq (304003/2018-1) and Fapesp (2019/26103-7).

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**Área: INO**

# Synthesis and Structural Analysis of a novel Copper(II) Complex with a Hydrazone Ligand

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*Palavras Chave: hydrazone, pyridoxal, copper(II) complex, crystal structure.*

## Highlights

Novel Cu(II) complex with a pyridoxal-hydrazone was synthesized and studied by crystallography.
The Cu(II) ion shows a distorted square-based pyramid geometry.
The hydrazone is coordinated through the *ONO* chelating system.

## Abstract

Hydrazones are organic compounds characterized as Schiff bases and are known because of a variety of coordination sites and show great interest due to their relevance in the pharmacological application as antibacterial, antifungal, antitubercular, antioxidant, and antitumor agents. Hydrazones are a class of compounds that have wide applications in areas like analytical chemistry, medicine, and coordination chemistry. Metal complexes with hydrazones are interesting in the bioinorganic area due to the antimicrobial, antitubercular, and antitumor potential that they can demonstrate.[1]

The $B_6$ vitamin has several forms, which demonstrate relevant abilities in coordinating with several metal ions. One of these forms is the pyridoxal, in addition to participating in enzymatic catalysis, is also responsible for vast biochemical functions, including direct antioxidant activity in fungi.[2]

Studies of copper(II) complexes with bioactive ligands have been increasing considerably, due to the application of these compounds in organic synthesis and their matter in many biological processes.[3] All these factors were the motivation for the production of this work, which unites the great biological importance of the hydrazones, pyridoxal and copper(II).

This work reports the synthesis and structural characterization of a new copper(II) complex $[CuBr_2(B_6Bh)]$ with a hydrazone-pyridoxal ligand ($B_6Bh$). The complex was elucidated by single-crystal X-ray diffraction and shows the ligand coordinated with the metal center in a tridentate form through the *ONO* chelate system. Furthermore, the copper(II) atom is coordinated with two bromide ions, providing a distorted square-based pyramid geometry ($\tau$ =0.095), Figure 1. Hydrogen bonds and π···π stacking interactions allowed a two-imensional organization of asymmetric units in the crystalline packing.

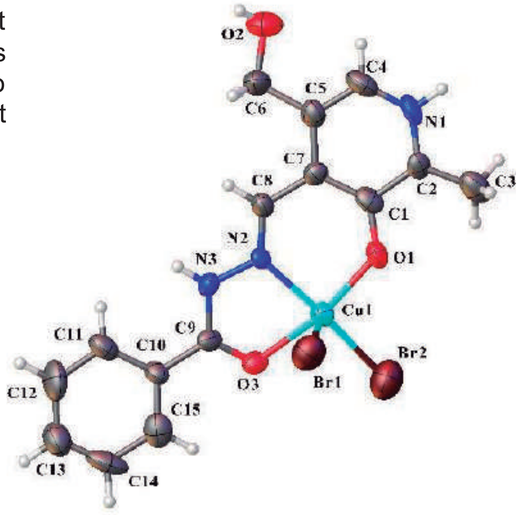

**Fig. 1.** X-Ray Crystal structure of $[CuBr_2(B_6Bh)]$ with thermal ellipsoids at the 30% probability level

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fapdf Fundação de Apoio à Pesquisa do Distrito Federal
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CAPES

**Área: INO**

# Síntese e caracterização de complexos de Co(III) contendo ureia e tioureia: potenciais anticâncer

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*Palavras Chave: Complexos, Cobalto, Tioureia, Ureia, Câncer*

## Highlights

Synthesis and initial characterization of Co(III) complexes, with potential anticancer action.

Two new water-soluble Co(III) complexes.

## Resumo

Dois novos potenciais agentes anticâncer foram sintetizados a partir do complexo precursor $[CoCl_2(phen)_2]Cl$[1]: *cis*-$[Co(phen)_2(L)_2]Cl_3$, em que phen = 1,10-fenantrolina, L = tioureia (Tu) ou ureia (Ur). Na síntese, os ligantes Tu e Ur substituem o cloreto ($Cl^-$) na esfera de coordenação do Co(III). Os compostos foram caracterizados por espectroscopia nas regiões do infravermelho (IV), do ultravioleta e do visível (UV-Vis) em água, bem como medidas de pH. Para o composto com ureia, no espectro vibracional, na região do infravermelho, foram verificadas bandas em 1627 $cm^{-1}$ atribuído ao modo vibracional da ligação C=O[2], 1454 $cm^{-1}$ à frequência de estiramento ($\nu$) da ligação $C\text{-}N_{amida}$, e 3306 e 3180 $cm^{-1}$ para $\nu$N-H[3]. Para o composto com tioureia, as bandas em 726 e 1425$cm^{-1}$ são atribuídas, respectivamente, a $\nu$C=S e $\nu C\text{-}N_{amida}$. Sabendo-se que a tioureia possui bandas em 727 e 1414 $cm^{-1}$, pode-se inferir que Tu está coordenada a Co(III). Nas regiões UV-vis, para o *cis*-$[Co(phen)_2(Tu)_2]Cl_3$ há bandas em 224, 270, 445 nm e, para *cis*-$[Co(phen)_2(Ur)_2]Cl_3$, 204, 220, 274 e 520 nm. As bandas na região do UV são atribuídas às transições eletrônicas intraligantes (IL-Tu: 224 nm; IL-Ur[2]: 274 nm]; IL-phen[4]: 204, 220 e 224 nm). As bandas no visível são atribuídas à transições eletrônicas centradas no centro metálico (d-d) e estão deslocadas em relação à do complexo precursor: 524 nm. As soluções aquosas dos complexos apresentam pH mais baixo que o da água que lhes deram origem. Isso indica ocorrência de reação química, com aumento da concentração de $H_3O^+$ no meio. Certamente, pelo menos um dos átomos de hidrogênio do grupo $NH_2$ deve ser doado pra água, em decorrência do poder polarizante do Co(III), frente aos átomos doadores da ureia e da tioureia.

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## Agradecimentos

**Área: INO**

# Síntese e caracterização inicial de complexos de Ru (II) e Co (III) contendo hidroxiureia para tratamento da doença falciforme e câncer

**Alexsandro Assis Lopes (PG),[1] Denise Santos de Sá (PQ),[2] Vanessa Miranda dos Santos (PG),[1] Carlos Daniel Silva da Silva (PQ).[2*]**

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Palavras Chave: *Cobalto, Rutênio, Hidroxiureia, Complexos, Doença Falciforme.*

## Highlights

Synthesis and initial characterization of Ru(II) and Co(III) complexes, containing hydroxyurea as ligand, with study of behavior in water and acid-base reaction. Compounds synthesized with the aim of being potential drugs for the treatment of sickle cell disease and cancer.

## Resumo/Abstract

A doença falciforme é uma comorbidade de origem genética associada a uma série de doenças e complicações, como crises de dor aguda, anemia, maior propensão a infecções, entre outras, dentre as quais algumas oferecem alto risco de vida. O principal tratamento utilizado atualmente para reduzir os efeitos da doença falciforme é através da hidroxiureia (HU), um antimetabólito utilizado também em tratamentos contra o câncer. Embora haja benefícios na utilização da hidroxiureia para combate às manifestações da doença falciforme, é relatado que o próprio composto causa uma série de efeitos adversos no organismo [1].

Buscando obter compostos com menores adversidades ao organismo e que mantenham/aumentem a atividade no tratamento das doenças supracitadas, foram sintetizados complexos inéditos *cis*-$[M(HU)_2(phen)_2]^{n+}(Cl^-)_n$, em que phen=1,10-fenantrolina e M = Ru(II) ou Co(III), a Figura 1. As amostras foram caracterizadas via técnicas espectroscópicas nas regiões do infravermelho e do ultravioleta-visível. Testes de solubilidade e análise do comportamento em água foram realizados.

Comparando os espectros no infravermelho da hidroxiureia com os dos sólidos obtidos, foram observados deslocamentos na banda associada à carbonila, o que pode ser indício da ligação da hidroxiureia a ao centro metálico: de 1643 $cm^{-1}$ para 1668 e 1628 $cm^{-1}$ (complexos de Co(III) e Ru(II), respectivamente). Em água, *cis*-$[Co(HU)_2(phen)_2]^{3+}(Cl^-)_3$ forma solução, que altera de cor ao decorrer do tempo, indicando possibilidade de reação, confirmada pelo teste cinético no espectrofotômetro UV-Vis, e também pela mudança de pH da solução, que variou para 4,46 a menos que a água pura antes da adição do sólido. O complexo de Ru(II) apresentou solubilidade parcial em água, com alteração de cor similar ao citado antes. Esses dados sugerem que há reação ácido-base entre os complexos e água. Logo, o pKa dos compostos deve ser determinado, a fim de se verificar como os complexos se apresentam em meio fisiológico.

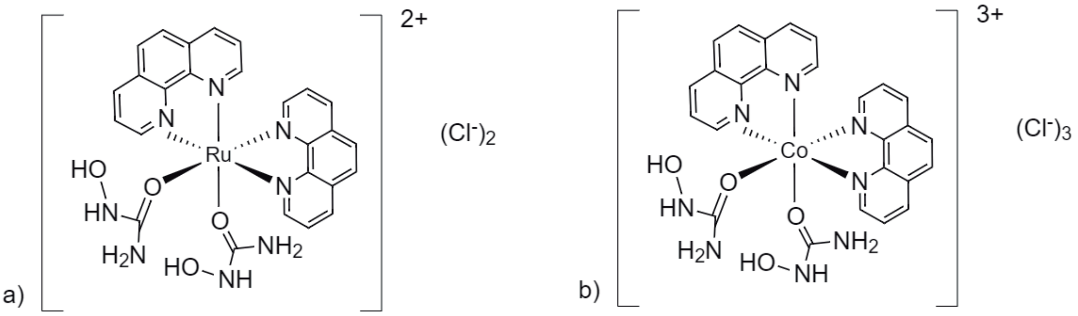

Figura 1. Estruturas propostas para os complexos sintetizados

Referências: [1] Brasil, M.S., Termo de esclarecimento e responsabilidade. Portaria nº 55, de 29 de janeiro de 2010 – Doença Falciforme, 2010.

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**Área: INO**

# Síntese e *design* via *docking* molecular de marcador químico, [Eu(DBM)$_3$.LAP], para inibição de superfungo *candida auris.*

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Palavras Chave: *Lapachol, candida auris, európio, docking, superfungos.*

## Highlights

**Synthesis and design via molecular docking of Chemical marker type, [Eu(DBM)$_3$.LAP], for inhibition of candida auris superfungs action -** We report in this work a simulation based on molecular docking of a lapachol based complex of europium.

## Resumo/Abstract

O recente surgimento de infecções causadas por *Candida auris* atraiu uma nova preocupação em todo mundo no sentido de minimizar os danos do mesmo. Isso reflete não apenas sua relativa facilidade de transmissão e alta mortalidade, mas também níveis crescentes de resistência as equinocandinas, azóis, e anfotericinas, considerados as principais classes de antibióticos usados nestas infecções. Portanto, no presente trabalho o objetivo é a extração, novo processo de purificação da molécula de Lapachol (LAP) a partir de sua fonte natural, a madeira de Ipê Roxo, além do emprego do material como ligante em complexo de $Eu^{3+}$ - HDBM (dibenzoilmetano), e o estudo *in silico* da aplicação do sistema como inibidor de super fungo, *Candida auris*. O sistema de partida, [Eu(DBM)$_3$.2H$_2$O], foi sintetizado a partir da reação estequiométrica,$EuCl_3.6H_2O$:3HDBM,em torno de pH=7.0, em meio aquo/etanólico. As moléculas de água foram substituídas na primeira esfera de coordenação do sistema inicial por uma molécula de LAP, que se coordena de forma bidentada ao $Eu^{3+}$, formando o complexo [Eu(DBM)$_3$.LAP]. Via docking molecular (resultados na Tabela 1), foi possível verificar a interação entre o complexo, [Eu(DBM)$_3$.LAP] e a polimerase, apresentando uma energia vinculante que varia de -8,6 Kcal/mol. Já o antibiótico usado como padrão positivo, posaconazole, mostrou uma energia de afinidade de -7,3 Kcal/mol.

Tabela 1- Correlação entre o complexo gerado através da afinidade energética do encaixe rígido e RMSD

| Complexo+ligante | Energia de afinidade (Kcal.mol$^{-1}$) | RMSD (Å) |
|---|---|---|
| Eu(DBM)$_3$.LAP + 6VSI | -8.6 | 1.069 |
| posaconazole + 6VSI | -7.3 | 0.162 |

Os dados (tabela 1) revelam que o sistema, [Eu(DBM)$_3$.LAP], é muito mais útil do que a o antibiótico posaconazole na simulação computacional. O desvio entre o ligante e o receptor variou com RMSD (desvio da média quadrática) de 0,162 a 2.380 Å. É importante notar que a variação ideal precisa ser próxima de 2.500 Å, dependendo do tamanho da lixiviação. Esses resultados mostram um melhor desempenho do complexo de európio na simulação de acoplamento. Ás interações observadas entre o receptores-ligante, no complexo de európio [Eu(DBM)$_3$.LAP] apresentaram uma capacidade inibitória baseada em suas aproximações hidrofóbicas no sítio proteico ativo. Os ligantes estudados apresentaram três fragmentos de aminoácidos em comum: Ile60, Trp63 e Tyr86. Assim, os dados iniciais apontam para a combinação efetiva dos ligantes com o centro metálico, o que possibilita a aplicação do novo material, especialmente como marcador/inibidor químico do superfungo *Candida auris*, face ao potencial farmacológico do ligante tipo Lapachol, além de estudos futuros *in vitro* que espera-se que ratifiquem o estudo i*n sílico* aqui proposto.

## Agradecimentos/Acknowledgments

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**Área: INO**

# Structural Design and Investigation of Noncovalent Interactions of New Copper(II) Complex with a Dithiocarbazate Ligand

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*Palavras Chave: noncovalent interactions, crystal structure, copper(II) complex, dithiocarbazate.*

## Highlights

A new Cu(II) complex with a dithiocarbazate was studied by X-ray crystallography.
The 3D Hirshfeld surface was analyzed to verify noncovalent interactions upon the molecular packing.

## Abstract

The dithiocarbazate are important ligands in bioinorganic and coordination chemistry and they are a class of Schiff bases with increasing interest due to their stereochemistry, binding modes, and therapeutic applications.[1,2] Their properties can be modulated by the introduction of different aldehydes or ketones, providing a variety of donor atoms with potentiated biological applications.[1] Additionally, these ligands can form stable metal complexes with an extensive variety of metal ions.[3,4] A considerable number of copper complexes with dithiocarbazate ligands have been intensively studied for their pharmacological properties and biological applications.[5,6]

The present work reports the structural elucidation and investigation of noncovalent interactions of new copper(II) complex [Cu(L)Br] with 2-acetylpyridine-S-p-bromobenzyl-dithiocarbazate ligand (HL). The Schiff base was found tridentate with *NNS*-donor atoms. The metal center shows a distorted square geometry including a bromide ion to complete the coordination sphere. A packing architecture analysis shows important and relevant noncovalent interactions, Figure 1 (a). The $\pi\cdots\pi$ stacking interactions and hydrogen bonds were analyzed using the Hirshfeld surface, Figure 1 (b).

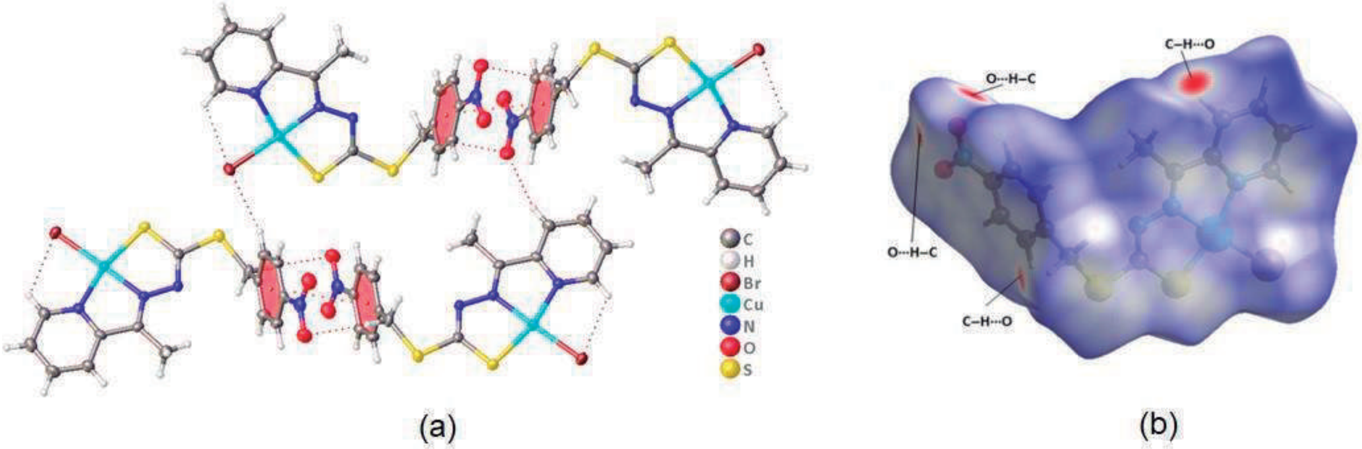

**Figure 1.** (a) View of [Cu(L)Br] showing the 1D chain made up of $\pi\cdots\pi$ stacking interactions and hydrogen bonds. (b) Hirshfeld surface mapped in $d_{norm}$ for [Cu(L)Br].

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## Acknowledgments

**Área: INO**

# Study of the properties of Biochar obtained from fast oxidative pyrolysis of sawdust biomass

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Keywords: *biochar; sawdust biomass; pyrolysis.*

## Highlights

Biochar synthesis from sawdust biomass through fast oxidative pyrolysis. The biochar formed presented as a predominantly amorphous and high carbon content material.

## Resumo/Abstract

The agro-industrial sector produces large amounts of waste as a by-product of its activities that has no defined destination results in an environmental problem due to idle accumulation. Examples of this are wood or sawdust residues which are lignocellulosic biomasses consisting mostly of hemicellulose, cellulose and lignin. The pyrolysis process can be an environmentally friendly alternative for the management of this solid leavings. Pyrolysis consists of thermal degradation under an inert atmosphere to convert biomass into a carbon-rich solid (biochar), liquid product (bio-oil) and biogas. In this work, the biochar is synthesized from residual sawdust biomass through fast pyrolysis in a bubbling fluidized beds reactor at temperatures between 450 and 500 °C. The physicochemical properties of the biochar were evaluated through immediate chemical analysis, thermal analysis (TG/DTG), Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD). Through the TG/DTG curves it was possible to observe about three mass loss events. The first takes place between 50 and 100ºC, being related to the moisture humidity of the sample. The second (250 to 380ºC) was attributed to volatile materials; the third event observed between 400 and 800ºC corresponds to the remaining residues. The results of TG/DTG obtained presented contents of 5% of humidity, 12% of ash, 32% of volatile materials and 51% of fixed carbon, typical of a solid material subjected to fast pyrolysis. By XRD it was possible to identify the presence of a diffraction halo at 2θ = 20 indicating that the material is predominantly amorphous, characteristic of biochar. In the infrared spectroscopy, vibrations were observed in the range of 3800 to 3100 cm$^{-1}$ corresponding to O-H bonds suggesting the existence of alcohols, phenols and/or organic acids, and from 2800 to 2600 cm$^{-1}$ was associated with C-H, pointing to structures of alkanes, probably aldehydes and/or aliphatic compounds. The range from 1800 to 1400 cm$^{-1}$ is about C=O groups and 1300 to 900 cm$^{-1}$ to the C-O groups, related to ketones, esters, ethers, organic acids and/or aldehydes [1]. These results confirmed the structure of the solid material obtained from pyrolysis as biochar. Taking this into consideration, there is optimism about the application of Biochar produced from residual sawdust biomass through rapid pyrolysis in heterogeneous catalysis.

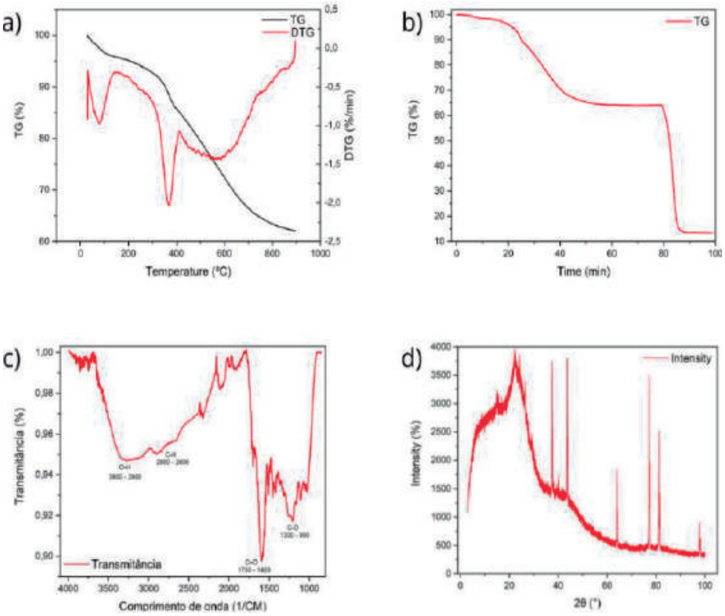

*Figure 1: Thermal analysis (TG/DTG) (a), immediate chemical analysis (b), Fourier transform infrared spectroscopy (c) and X-ray diffraction (d) of sawdust biochar.*

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**Área: INO**

# Synthesis and characterization of a new Iron(III) complex containing the ligands 1,4,8,11-tetraazacyclotetradecane (cyclam) e 2-mercaptopyrimidine.

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Palavras Chave: *Synthesis, Characterization, 2-mercaptopyrimidine, macrocyclic*.

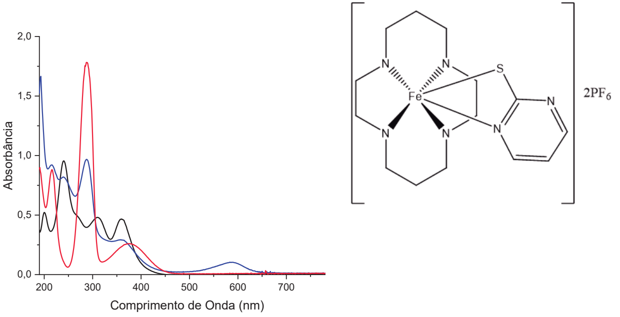
## Highlights

An iron(III) complex containing a macrocyclic and mercaptopyrimidine ligands was synthesized and characterized by spectroscopic techniques.

## Resumo/Abstract

Recent studies report the synthesis of complexes with 1,4,8,11-tetraazacyclotetradecane (cyclam) and 2-mercaptopyrimidine (Spy) ligands, suggesting them as having interesting photochemical properties [1]. Thus, the present work presents the synthesis and characterization of complex [Fe(cyclam)(Spy)]($PF_6$)$_2$. The synthesis of the complex was carried out in metanol under argon atmosphere. The desprotonation of the Spy ligand was achieved by adding $NaHCO_3$, followed by addition of the percursor complex cis-[Fe(cyclam)$Cl_2$]Cl in a shclenk flask. The reaction mixture was stirred for 60 min while protected from light. Both the percursor and the final complex were characterized by spectroscopic (FTIR and UV-visible) and voltammetric (CV) techniques. In the FTIR spectrum of the ligand, the frequency attributed to C=N is observed at 1608 $cm^{-1}$, while in the spectrum of the complex this stretching was observed at 1629 $cm^{-1}$. Similarly, the frequency related of the CS bond stretching, for Spy ligand is observed at 1188 $cm^{-1}$, while in the final complex it was observed at 1168 $cm^{-1}$ [2]. In the UV-visible spectrum for the [Fe(cyclam)(Spy)]$^{2+}$ in acetonitrile (Fig. 1) is observed absorptions bands at: 216 nm ($\varepsilon$ = 1,50 x $10^4$ $M^{-1}cm^{-1}$), 289 nm ($\varepsilon$ = 1,66 x $10^4$ $M^{-1}cm^{-1}$) and 361 nm ($\varepsilon$ = 3,75 x $10^3$ $M^{-1}cm^{-1}$) attributed to the $\pi$-$\pi$* transition of the Spy ligand, 239 nm ($\varepsilon$ = 1,32 x $10^4$ $M^{-1}cm^{-1}$) attributed to the $\pi$-$\pi$* transition of the cyclam ligand and the last one at 587 nm (1,62 x $10^3$ $M^{-1}cm^{-1}$) attributed to a ligand to metal charge transfer transition (LMCT) [3], being this one a strong suggestion of the formation of the proposed complex. The cyclic voltammogram of a solution containing the [Fe(cyclam)(Spy)]$^{2+}$ complex ion, in acetonitrile showed a redox potential centered at 97 mV, vs. Ag/AgCl, due to $Fe^{3+/2+}$ couple. This value is 48 mV more positive than the potential for the precursor, *cis*-[Fe(cyclam)$Cl_2$]$^+$, corroborating with the formation of the proposed complex.

**Figure 1.** UV-vis spectra for: [Fe(cyclam)(Spy)]($PF_6$)$_2$ (5,80 x $10^{-5}$ mol $L^{-1}$) (blue), free Spy ligand (1,20 x $10^{-4}$ mol $L^{-1}$) (red) and *cis*-[Fe(cyclam)$Cl_2$]Cl (4,70 x $10^{-4}$ mol $L^{-1}$) (black), and structure of the title complex



According with the spectroscopic data, the synthesis of the [Fe(cyclam)(Spy)]($PF_6$)$_2$ complex was obtained. In addition, as a perspective, photochemical experiments and activity assays against gram-positive and gram-negative bacteria will be carried out and presented further.

## Agradecimentos/Acknowledgments

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**Área: INO**

# Synthesis and characterization of a new red emitting Ir(III) complex aiming cell imaging

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Keywords: *iridium, cell imaging, red emission, spin-orbital coupling.*

## Highlights

New red-emitting irdium(III) complex. High intense red emission. Water soluble iridium(III) complex.

## Resumo/Abstract

Lately, many research groups are focusing their efforts on the creation of new iridium(III) complexes due to their different application possibilities, such as in optical materials, biological area, catalysis, and others. This attention to the iridium(III) ion in optical materials application is related to their large spin-orbit coupling (ξ), something around 4,430 cm$^{-1}$, which acts mixing the singlet and triplet excited states and creates an overpopulated emissive state increasing radiative emission decay and resulting in complexes with high emission efficiency[1]. The emission wavelength of iridium(III) complexes can be easily modulated by changing the ligand structure of the ligands, varying the color emission from blue to red. The use of luminescent iridium(III) complexes in the biological field has been gaining place in the recent years to visualize the cell shape and inner organization as *in vivo* as *in vitro* studies. Some important properties could be used to explain the interesting by cyclometallating Ir(III) complexes as biomarkers, such as large Stokes shifts reaching hundreds of nm, long excited state lifetimes in a range of 100 ns to 1 ms, suitable photostability and permeability to cell membranes[2]. In this scenario, red and/or infrared emitters are more desired than other color emitters to be used in cell imaging, since biological components such as skin, fat, and blood components present high absorptivity to photon emitted below 600 nm. In this way, fewer photons are absorbed by biological components and more photons are detected by the equipment if red/infrared light is used, resulting in more reliable images. Another factor is that biological tissue presents fluorescence in the blue/green spectral region; thus, the use of a red emitter to obtain images reduces the interference by bioautofluorescence. In this work, a new red emitting iridium(III) complex was synthesized aiming cell imaging application. For that, the precursor dimer, $[(Fppy)_2Ir(\mu\text{-}Cl)_2Ir(Fppy)_2]$, was synthesized according to the Nonoyama route[3], yielding 87.6%. Next, the $[Ir(Fppy)_2(bqdc)]$ complex was synthesized. A mass of 49.6 mg of bqdc ligand (2,2' biquinoline – 4,4' potassium carboxylate tri hydrated) was dissolved in 5 mL of water and kept under stirring at room temperature; then a solution of the dimer precursor was prepared by dissolving 63.9 mg in 5 mL of dichloromethane. The dimer solution was added to the bqdc ligand solution, and a biphasic system obtained; thus, methanol was added to obtain a monophasic system. The solution was kept at stirring at room temperature for 4 h. Then, the complex was precipitated by water addition, and put to dry in a desiccator. The complex formation was confirmed by FTIR, UV-Vis spectroscopy, and MALDI-TOF analyses. The complex present high intense red emission under UV excitation.

## Agradecimentos/Acknowledgments

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**Área: INO** **Nº de Inscrição: 00024**

# Synthesis, characterization and antitumor activity of terbium complex with 1,10-phenanthroline ligand

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Keywords: Complexes, Terbium, Characterization, Antitumor

## Highlights

The incidence of neoplastic diseases in recent years shows that the search for more effective and selective agents with lower toxicity, in addition to predicting the reduction of significant side effects and the intrinsic or acquired drug resistance is necessary.

## Resumo/Abstract

Terbium complex was synthesized from the aqueous solution containing 1 mol of ligand (1,10-phenanthroline) to 1 mol of metal ($TbCl_3.6H_2O$) to form a colorless solution. The resulting solution was stirred at 60 ° C until complete evaporation of the solvent. Acetone was added to yield a precipitate, which was filtered, washed with acetone, and dried under vacuum, yielding a white powder. The complex was characterized by solubility, elemental analysis, Infrared (IR) spectroscopy, melting point, molar conductivity and UV-Vis spectroscopy tests. The obtained complex presented solubility in water, ethanol, methanol and DMSO. Unlike its ligand which has to be insoluble in water. Through the melting point obtained for the complex, it was possible to observe significant differences between the melting point values of the ligand. The obtained complex decomposed while the ligand melted at 117 °C. Such a difference may be related to metal-ligand coordination. The conductivity was performed for the complex and for the ligand in 1 x $10^{-3}$ M concentration in order to obtain the number of counter ions present in the structure of the complex. The conductivity of the terbium complex was 57 μS, which when compared with the reference values for electrolytes cited by Geary (1971), it is observed that this value is close to the reference range for absence of electrolytes, indicating that the complex obtained presents no counter ions in its structure. Electron spectra were obtained in the visible ultraviolet region for the ligand and its complex using methanol as a solvent at room temperature, in order to obtain confirmation of the metal-ligand coordination. Through the obtained spectroscopic data it is possible to observe the emergence of a new band in the UV region of the complex, unlike the analyzed ligand. IR (KBr,$cm^{-1}$): 3750 (ν-OH), 1511 (ν-CC,CN), 853 (γ -CH), δ (CCN, CCC). Anal. Calc. for $C_{12}H_{10}N_2TbCl_3$ (%) (Mr = 447,51): C, 32.21; H, 2.25; N, 6.26; Found: C, 35.28; H, 2,25; N, 6,85%. The results of C, H and N suggest a compound of minimum formula $C_{12}H_{10}N_2TbCl_3$, according to the proposed formula $[Tb(Phen)Cl_3]$, in which the terbium (III) is coordinated with a 1.10-phenanthroline molecule and three ions chloride. The cytotoxic evaluation of the complex was evaluated against cisplatin, metal and ligand in the B16F10 tumor cell line. IC50 values were calculated from dose x response curves obtained after 72 hours of exposure to the compounds by the MTT test. From the data, it was found that the terbium complex is more active than the ligand, metal and cisplatin in the strain tested. The terbium complex is 15 times more active than free ligand and metal. When compared to cisplatin it was observed that the synthesized complex is about 60 times more active. That is, to inhibit 50% of cancer cells only requires a concentration of 3,898 μM, while cisplatin needs 176 μM. It is also observed that the complex obtained has higher activity than the commercial drug cisplatin.

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**Field: INO**

# Synthesis, characterization and DNA interaction studies of novel metal hybrid compounds containing both azole drugs and planar ligands

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Keywords: *Multi-target, Metal Hybrid Compounds, DNA.*

## Highlights

- Twelve copper(II) hybrid compounds containing either azole and planar ligands were synthesized;
- They were characterized using modern spectroscopic and analytical techniques;
- Preliminary DNA interaction studies are in progress;
- These metal compounds are currently under evaluation towards parasites and fungi.

## Resumo/Abstract

Concerning how aggressively parasitic diseases have been affecting thousands of people worldwide, mainly in non-developing countries from Asia, Africa, Latin America and Mediterranean regions[1] and the lack of vaccines to defeat these illnesses, our research group has been designing new metal-based compounds containing both antifungal drugs (Ketoconazole (KTZ), clotrimazole (CTZ), itraconazole (ITZ) and fluconazole (FLZ)) known as cytochrome P-450 (an essential enzyme present in the ergosterol biosynthesis pathway) inhibitors[2,3] and planar DNA intercalator ligands (1,10-Phenanthroline (phen); 1,10-Phenanthroline-5,6-Dione (phendione); dipyridophenazine (dppz)) [4,5], with higher efficacy, lower toxicity to the host and low-cost, using endogenous metal ions such as zinc(II) and copper(II). Based on the successful results obtained from these compounds, we decided to enhance their activity even more by combining both azole drugs and planar ligands linked by one metal ion yielding multi-target metal hybrid compounds that may act by either interacting with DNA parasites and inhibiting cytochrome P-450 simultaneously.

In this work, we will present a series of 12 promising metal hybrid compounds $[Cu(phen)(L)_2(NO_3)](NO_3)$ (**1-4**), $[Cu(phendione)(L)_2(NO_3)]NO_3)$ (**5-8**), $[Cu(dppz)(L)(NO_3)](NO_3)$ (**9-12**), L = KTZ, (CTZ), (ITZ), (FLZ) that was synthesized upon reaction of KTZ, CTZ, ITZ and FLZ with the corresponding copper(II) precursors under mild conditions and characterized using several analytical and spectroscopy techniques such as elemental analyses, infrared spectroscopies, UV-Vis, conductivity, etc. In order to investigate mecanisms of action of these metal hybrid compounds, preliminary DNA interaction studies were also performed using spectroscopic titrations and viscosity measurements with *Calf-timus DNA.* The very good biological results obtained in our latest papers demonstrated that the coordination of bioactive ligands to metal ions leads to very active antiparasitic compounds, therefore we hope these structurally modified metal-azole complexes will be even more effective and, consequently, great candidates for the treatment of not only Leishmaniasis but also other diseases, once the drugs available for their treatment are far from the ideal.

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UNIVERSIDADE FEDERAL DE JUIZ DE FORA
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**Área: INO**

# Synthesis, characterization and study of chiral complexes containing trivalent lanthanide ions exhibiting circularly polarized luminescence (CPL)

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Keywords: *Lanthanides, Complexes, Chirality, Circularly Polarized Luminescence.*

## Highlights

New chiral complexes of europium(III) showing circularly polarized luminescence (CPL) and high values of dissymmetric factor ($g_{lum}$) between 0.1-0.37 for transitions $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_3$.

## Abstract

Circularly polarized luminescence (CPL) is the emission of left and right circular polarized light with different intensities by chiral molecular systems in the excited state.[1] The CPL signatures is correlated with the excited state properties and can be used to evaluate structural information on chiral compounds. Furthermore, CPL has aroused much interest due to its promising applications in three-dimensional displays, spintronic devices, information storage, optical sensors, and security labels and anti-counterfeiting methods, for example. The chiral complexes of lanthanides(III) are highlighted because they have the highest values of luminescent dissymmetry ($g_{lum}$) between 0.1-1.45.[2,3] Aiming at this great potential, we propose the synthesis, characterization and photophysical study of new chiral complexes containing europium(III) ions. Chiral complexes are composed of sensitizing ligands, whose function is to transfer energy to the $Ln^{III}$ ion through the *antenna effect*, and chiral ligands, whose function is to induce chirality in the final complex and consequently in the $Ln^{III}$ ion. The sensitizing ligands chosen were β-diketonates 4,4,4-Trifluoro-1-(2-thienyl)-1,3-butanedione (tta), 1,1,1,5,5,5-Hexafluoro-2,4-pentanedione (hfa), 1-Phenyl-1,3-butanedione (bzac) and (+)-3-(Trifluoroacetyl)camphor (facam). The chiral ligands S-Bn-pybox (pyridine bis-oxazoline), S-Ph-pyox (pyridine oxazoline) and S-Ph-pzbox (pyrazine bis-oxazoline) used were synthesized using low-cost synthesis routes, while the ligand S-MeO-biphepo (bis-diphenylphosphinoxide) was synthesized by the oxidation of the ligand S-MeO-biphep (bis-diphenylphosphine - Merck). The ligands were characterized by nuclear magnetic resonance, FTIR and specific rotation $[\alpha]_D$. The chiral lanthanide complexes were characterized by FTIR and ultraviolet-visible absorption spectroscopy, specific rotation $[\alpha]_D$, thermogravimetric analysis, circular dichroism, photoluminescence and circularly polarized luminescence. The ligand structures were confirmed, and the data obtained by the different techniques indicate that the complexes were obtained as planned. In addition, circular dichroism spectra show bands with positive and negative signs in the region of achiral β-diketonates. Therefore, the chiral ligands successfully induced chirality in the final complex. The photoluminescence spectroscopy data indicate numerous evidence of the formation of the new complexes, as for example, changes in the profiles of the excitation and emission spectra and increase of emission lifetimes. All complexes show CPL as predicted. Among them, those with the highest $g_{lum}$ values for the $^5D_0 \rightarrow {}^7F_1$ transition were: $[Eu(hfa)_3(S\text{-}Bn\text{-}pybox)]$ (+0.2, $10^{-5}$ mol $L^{-1}$ in dichloromethane and 0.15 $10^{-4}$ mol $L^{-1}$ in acetonitrile), $[Eu(facam)_3(S\text{-}Ph\text{-}pyox)]$ (-0.37, $10^{-3}$ mol $L^{-1}$ in acetone and 0.12, $10^{-3}$ mol $L^{-1}$ in acetonitrile), $[Eu(bzac)_3(S\text{-}Bn\text{-}pybox)]$ (-0.12, $10^{-3}$ mol $L^{-1}$ in dichloromethane). In the literature, similar complexes of pybox with $Eu^{III}$, as well as other lanthanide complexes, usually have $g_{lum}$ values between 0.1 and 0.5. Values greater than +0.76 and +1.38 are rarely observed, and they assigned to the specific complexes of $[Eu(facam)_3]$ and $Cs[Eu((+){-}hfbc)_4]$, respectively.[1]

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## Acknowledgment

**Área: _______INO________**

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

# Synthesis, Hirshfeld surface analysis, magnetism and luminescent properties of mononuclear lanthanide-based compounds

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Palavras Chave: *Lanthanides, luminescence, single ion magnet, Hirshfeld surfaces, carboxylate ligands*

## Highlights

Synthesis and characterization of mononuclear lanthanide complexes exhibiting luminescent properties. Single-ion magnet behavior was observed for a Dy derivative. Intermolecular interactions evaluated by Hirshfeld surfaces.

## Resumo/Abstract

Two series of coordination compounds containing trivalent lanthanoid ions with potential application in the field of materials were obtained through complexation of the metal salts by carboxylate-based ligands. The first series consists of isostructural compounds with general formula $[Ln(NO_3)_2(4\text{-pic})_2](NO_3)_2$, in which $Ln^{III}$ = Eu(**1**), Tb(**2**), Dy(**3**), Sm(**4**), Er(**5**), Nd(**6**) or Gd(**7**), and 4-pic is the zwitterionic form of the 4-pyridinecarboxylic acid. The lanthanide ion in **1-7** lies on a square antiprismatic geometry, featuring a D4d symmetry. A more in-depth discussion about the intermolecular interactions observed in these compounds arose through a Hirshfeld surfaces analysis (Fig. 1b), which stated that hydrogen bonding is predominant. The characteristic visible emission of **1-4** derivatives was observed by spectroscopy techniques. The magnetic measurements of all complexes were carried out and fully interpretated considering the spin-orbit coupling effects (**1**) or the depopulation of the Stark levels (**2-6**). For **7**, since the metal ions are separated by a large distance in the crystal packing and the $Gd^{III}$ is isotropic ion, it was possible to fit the magnetic data taking into account a mean-field approximation, which afforded a very weak intermolecular ferromagnetic interaction of 0.01 $cm^{-1}$ AC susceptibility measurements (Fig 1c) revealed a field-induced slow relaxation of the magnetization and a single-ion magnet (SIM) behavior for **3**. A second series of mononuclear $Ln^{III}$ complexes with other heterocycle-substituted carboxylate ligands has been already synthesized and is currently undergoing characterization.

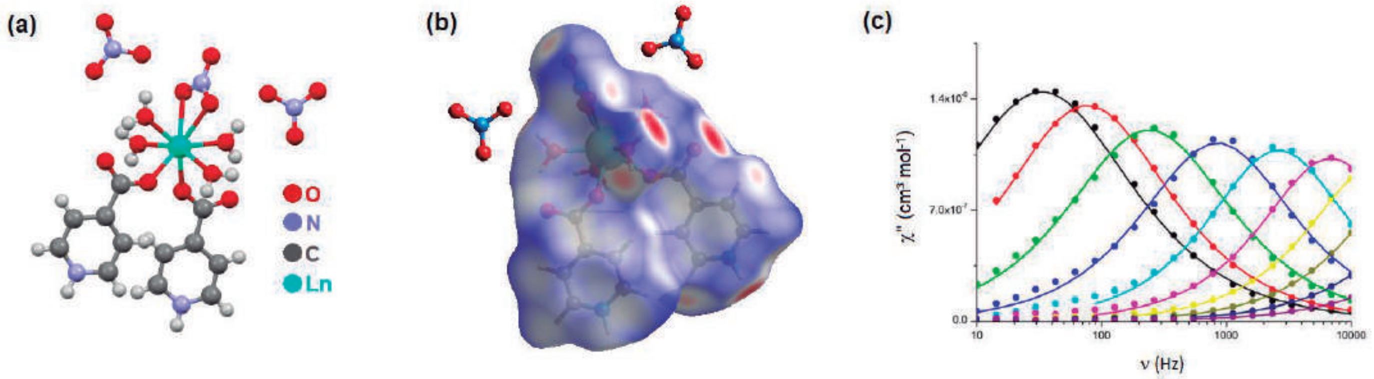

Figure 1. (a) Crystal structure of mononuclear $Ln^{III}$ complexes (**1-7**) containing the zwitterionic form of the 4-pyridinecarboxylic acid as ligand (b) Hirshfeld surface mapped for **3** (c) Out-of-phase ($\chi''$) susceptibility for **3**.

## Agradecimentos/Acknowledgments

We thank CBPF, LDRX-UFF and LAME-UFF for the use of their laboratory facilities, as well as CNPq, CAPES and FAPERJ for the financial support.

**Área: INO**
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# Synthesis of co-doped S,N-Carbon dots from aniline derivatives to evaluate the effect ofsubstituents on photophysical and structural properties.

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Key words: *Carbon Dots, Aniline derivatives, Hydrothermal, Amines, Sulfur, Fluorescence.*

## Highlights

- The Synthesis of C-dots in water was successfully achieved;
- Characterization by spectrofluorescence and FTIR;
- Influence of substituents on photophysical properties was analyzed.

## Resumo/Abstract

**Introduction**

*Carbon dots* (C-dots) are luminescent biocompatible carbon nanoparticles, which may be obtained from several precursors, including organic molecules[1]. The present work aims to synthesize C-dots from *o*-phenyldiamine (*o*-PD) and *o*-aminothiophenol (*o*-ATP) aiming to evaluate the effect of substituents on their photophysical and structural properties.

**Results and discussions**

The C-dots were obtained by hydrothermal synthesis from *o*-ATP and *o*-PD in different reactors. The products were centrifuged and filtered. Solutions were obtained with colorless (3.06 nm) nanoparticles from *o*-ATP and orange (3.62 nm) from *o*-PD (Figure 1a). The C-dots were characterized by FTIR, DLS, UV-Vis and fluorescence (Figure 1b and c). The C-dots of *o*-ATP showed characteristic bands of groups $S-CH_3$, C=S, C-S and S-S in FTIR, while those of *o*-PD, bands of aromatic and aliphatic C-N groups, in addition to N-H, from their precursors.

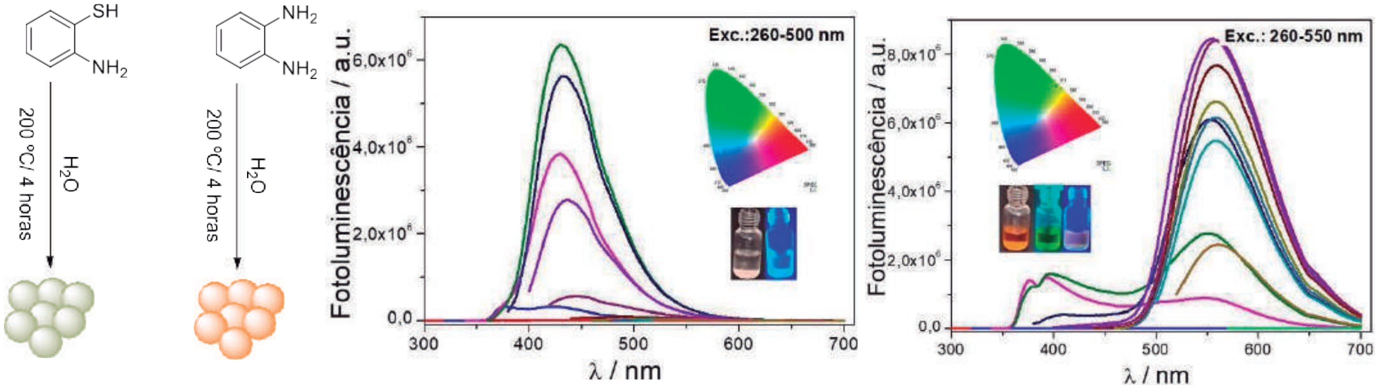

**Figure 1: a)** C-dots synthesis and emission scheme: **b)** *o*-ATP and **c)** *o*-PD with their CIE diagrams.

When analyzing the UV-Vis spectra of these C-dots, absorption bands were observed in higher wavelengths for the *o*-PD, corroborating the fluorescence spectrum that presented an independent emission, centered on the yellow-green region. For *o*-ATP C-dots, it was found that sulfur favored a hypsochromic displacement, with absorption and emission in shorter wavelengths, centered on blue.

**Conclusion**

The photophysical and structural properties of C-dots were affected by the presence of different substituents in the precursor molecules. These results are promising for multifunctional applications of these nanoparticles, as in optical applications.

**References**

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## Agradecimentos/Acknowledgments

CAPES; UFAL; IQB; IF; PPGQB; GCAR, LPqPNSO.

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# Synthesis & Photophysical Study of Ru (II) Mono-/Homo-Bimetallic Complexes with Possible Application as Dye Sensitizers for Solar Cells (DSSC)

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Palavras Chave: C*omplexos de Ru (II) 4,4´-dicarb(et)oxi-2,2´-bipiridínicos; Síntese, Ligantes de Alta Conjugação, Fluorescência, DSSC.*

## Highlights

Ru(II) complexes with 2,2´-bipyridine ligands present remarkable hydro-solubility, photophysical and fluorescence properties becoming themselves promising novel agents for DSSCs

## Resumo/Abstract

Ru(II) polypyridine complexes endowed with thiocyanate ligands (**N3**, **N719** or "*black dye*") described by Grätzel and O'Regan, in 1991 [1] have been extensively studied due to their enormous potential as fluorophores in photovoltaic devices for Dye-Sensitized Solar Cells (DSSCs) and Organic Ligth Emitting Diodes (OLEDs). These compounds have maintained a clear lead in performance and represent one of the most remarkable methodologies for large-scale, low-cost, efficient conversion of sunlight to electricity and power production from renewable energy sources even until today. The strong metal-to-ligands charge transfer allows these bipyridine cyclometals to have very unique redox, photophysical and electrochemical properties in the excited state. In the present work are reported the syntheses and the photochemical studies of three [Ru(**L**)(X$_2$-bipy)$_2$](PF$_6$)$_2$ complexes (**RuCBXFN** (**1a**), **RuCBEtFN** (**1b**) and **RuCBXDX** (**2**), **L**= 1,10-phenanthrolino-5,6-dione (**FN**); 2,3,7,8-tetraaminobenzo[1,4]-dioxin (**DX**); X$_2$-bipy = 4,4'-disubs tituted-2,2'-bipyridines; X =CO$_2$H (**CBX**), CO$_2$Et(**CBEt**)), and one homobimetallic complex of ruthenium(II) [Ru(**CBEt**)$_2$(**μ-FNDXFN**)**Ru**(**CBEt**)$_2$](PF6)$_4$ (**3**). It is noteworthy that **2** and **3** are novel in the literature. All complexes have been synthesized, in quite good global yields, starting from [Ru(COD)Cl$_2$]$_n$., and the ligands 4,4'-disubstituted-2,2'-bipyridines (X$_2$-bipy, X =CO$_2$H (**CBX**), CO$_2$Et (**CBEt**)), 1,10-phenanthrolino-5,6-dione (**FND**) and 2,3,7,8-tetraaminodibenzo[1,4]dioxine were also efficiently obtained through classical synthetic routes. All ligands, precursors, intermediates and final complexes have been characterized by spectrometric and physicochemical techniques. When the molar absorptivity coefficient (Ɛ) is analyzed, we notice that the effect of the substituent does not affect the values. When comparing the values of Ɛ and Φ, for complexes **2** and **3**, there is a predominance of increased absorptivity due to the presence of two metallic centers in the complex **3**. The complexes described in the present work demonstrate how changes in substituents of bipyridine ligands may lead to improvements in the photophysical properties of cyclometallates. However, the effect of bipyridine substituents seems to prevail in the emission, providing a higher value of quantum fluorescence yield for the complex **2**. The photophysical studies of all of the studied Ru(II) complexes were also investigated and it is remarkable the observed hydro-solubility and the fluorescence even in water and in other five solvents becoming themselves promising novel agents for DSSCs

## Agradecimentos/Acknowledgments

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**Área: INO**

# Termômetro luminescente baseado em um polímero de coordenação contendo Eu(III) e um derivado piridil(vinil)benzoico.

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Palavras Chave: *Lantanídeos,Termometria, Luminescência.*

## Highlights

**Coordination polymer based luminescent thermometer containing Eu(III) and pyridyl(vinyl)benzoic derivative.** The thermometric parameter of a coordination polymer containing europium and the **Hpvb** was determined by the analysis of the emission spectra in the 16.00 to 319.80 K temperature range.

## Resumo/Abstract

Devido às mudanças das propriedades luminescentes em função da temperatura, complexos trivalentes de európio são candidatos a serem aplicados na construção de termômetros luminescentes.[1] Com o objetivo de avaliar tal propriedade, um polímero de coordenação foi sintetizado contendo Eu(III) e o ligante ácido {4-[2-(4-piridil)vinil]}benzoico (**Hpvb**). A síntese foi realizada em temperatura ambiente, a partir de uma solução de um sal de Eu(III) em uma mistura de dimetilformamida e água e um derivado do **Hpvb** na forma de sal de potássio K(**pvb**). O sólido amorfo obtido a partir desta reação foi recristalizado, dando origem a monocristais incolores (**1**), que foram caracterizados por espectroscopia vibracional na região do infravermelho, difração de raios X de policristais, análise elementar de CHN e análise termogravimétrica.

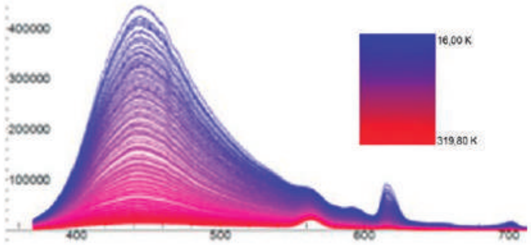

**Figura 1**: Espectros de emissão de **1** na região entre 16,00 (azul) e 319,80 K (vermelho).

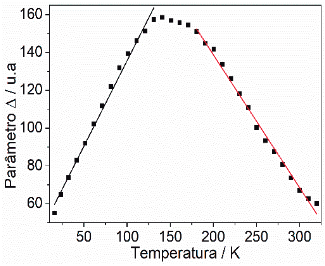

**Figura 2**: Parâmetro termométrico em função da temperatura.

Os espectros de emissão coletados na faixa entre 16,00 (azul) e 319,80 K (vermelho, **Figura 1**) mostram que há uma diminuição das intensidades de emissão com o aumento da temperatura. Foi realizado um tratamento matemático em toda a faixa de temperatura a fim de determinar a área referente à emissão do ligante (entre 380 e 550 nm) e a área da banda em 617,4 nm, referente à emissão do Eu(III). A razão entre as duas áreas deu origem ao parâmetro termométrico $\Delta$. Na **Figura 2** observa-se que as tendências lineares de $\Delta$ ($r^2$) em relação à temperatura nas regiões entre 16,00 e 130,91 K, e entre 180,72 e 319,90 K são iguais a 0,991 e 0,993, respectivamente. Portanto, **1** pode ser utilizado como um termômetro luminescente no estado sólido nessas duas faixas de temperatura. A sensibilidade térmica relativa (Sr) para **1** variou entre 0,23 à 2,50 % $K^{-1}$, o que está na mesma ordem de grandeza dos termômetros similares encontrados na literatura.[2]

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## Agradecimentos/Acknowledgments

**Área: INO**

# The possibility of repositioning bisphosphonates for the treatment of iron overload

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Key Words: *Bisphosphonates, Iron, Iron Overload, Chelation Therapy, Chelator.*

## Highlights

Bisphosphonates are a class of drugs widely used in osteoporosis. They are candidates for the chelation therapy of iron overload.

## Abstract

Despite being an essential trace element, excess iron is toxic due to the generation of reactive oxygen species (ROS). Long-term iron overload (IO) causes cardiac and liver damage, which can be countered by chelation therapy. Approved drugs for IO are desferroxamine (DFO), deferiprone, and deferasirox, all of them with adverse reactions such as visual and auditory toxicity, agranulocytosis, and renal and hepatic failure[1]. Therefore, the importance of searching for new iron chelators is evident. Drug repositioning proposes new applications for drugs approved in clinical trials. In this scenario, bisphosphonates (BPs), which are synthetic analogues of pyrophosphate[2] for the treatment of osteoporosis, present interesting coordination characteristics with iron[3]. Etidronate, alendronate, tiludronate, and zoledronate were submitted to competition tests with iron calcein (a model for high affinity biological iron binding)[4] and exhibited satisfactory chelating activity when compared to the DFO standard (Fig 1). Calcium did not prevent the chelation. In iron-dependent antioxidant activity assays in physiological conditions[5], it was observed that all BPs decreased the generation of ROS in a dose-dependent manner (Fig 2). None of the chelators was able to remove iron from transferrin, although iron from iron-loaded BPs were transferred to the protein. These data suggest that BPs are suitable candidates for reestablishing normal levels of iron in IO.

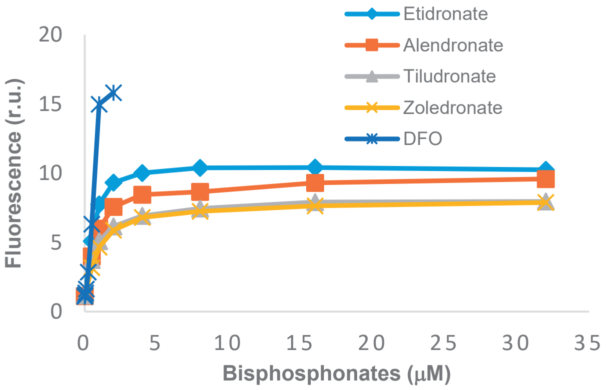

*Fig 1: **Competition studies**. BPs (up to 30 μM) were able to scavenge the metal from iron calcein (1 μM) at approximately half of the ability of the standard chelator DFO (1 μM). r.u.: relative fluorescence units*

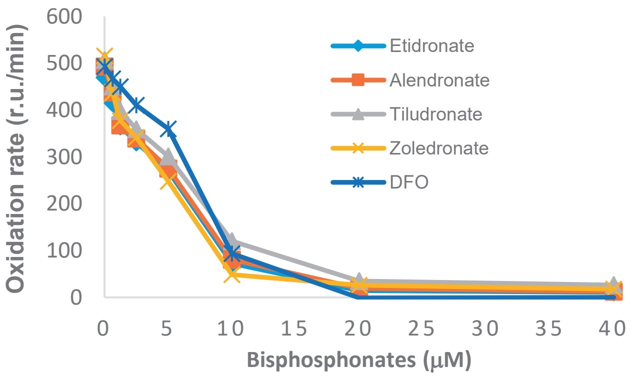

*Fig 2: **Antioxidant activity of BPs**. Iron- and ascorbate-mediated oxidation of dihydrorhodamine was inhibited due to iron chelation by BPs in the same dose-dependent manner as the standard DFO. r.u.: relative fluorescence units.*

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**Área: <u>INORGANICA (INO)</u>**

# The role of the $Eu^{3+}$ $^7F_1$ level in the direct sensitization of the $^5D_0$ emitting level through intramolecular energy transfer

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Palavras Chave: *Transferência de Energia, Európio, Equações de Taxas, Simulações, Transientes*

## Highlights

Through numerical solutions of rate equations for the $[Eu(tta)_3(H_2O)_2]$, we have performed simulations for the ligand and $Eu^{3+}$ excited states transients using two different models and showed that the $^7F_1$ thermal population is relevant for energy transfer processes.

## Resumo/Abstract

The understanding of intramolecular energy transfer (IET) processes in photoluminescent $Eu^{3+}$ chelates is of great importance in the design of new efficient emitting devices, sensors, optical thermometers, etc. Even though the theoretical models have been established, some considerations on the participation of the thermally populated excited state $^7F_1$ are necessary for experiments at room temperature. This work presents theoretical simulations of the transients related to the ligand and lanthanide excited states by employing two IET processes models, with and without the consideration of the $^7F_1$ thermal population at 298 K for the $[Eu(tta)_3(H_2O)_2]$ compound. The transients were obtained from a numerical method of the differential rate equations for each excited state, simulating a high-power density as in transient experiments. It is shown that all transients are considerably affected by the introduction of the $^7F_1$ state and the predicted curves, especially for the ligand $S_1$ state, can be experimentally measured. Therefore, the proposed model suggests that when considering energy transfer processes involving ligand and $Eu^{3+}$ states, the thermal population of the $^7F_1$ state should be taken into account at room temperature.

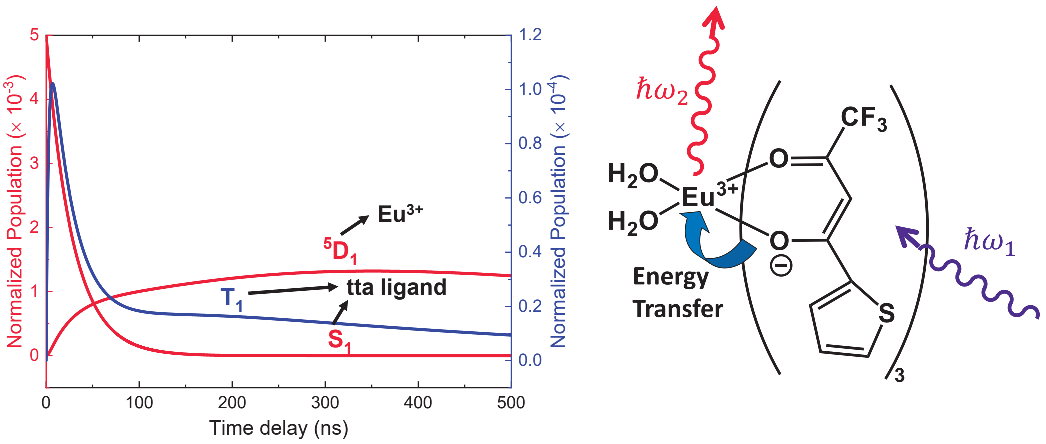

Figure 1: Example of the simulated transients (left) and an illustration of the energy transfer process (right)

## Agradecimentos/Acknowledgments

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Reference: L. Blois, A.N. Carneiro Neto, O.L. Malta, H.F. Brito, *J. Lumin.*, **247**, 118862 (2022).

**Área: INO**

# Trinuclear nickel(II) and cobalt(II) triple helicates with a multidentate bithiazole(bis)oxamato ligand as supramolecular nanomagnets

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Keywords: *Oxamate, Magnetic Properties, Metallosupramolecular Complexes.*

## Highlights

Nickel(II) and cobalt(II)-mediated self-assembly of the tris(chelating) *N,N'*-2,2'-(4,4'-bithiazole)bis(oxamate) ligand leads to a new metal-organic supramolecular nanomagnets featuring a unique linear triple-stranded trinuclear structure of the helicate-type.

## Abstract

The supramolecular coordination chemistry offers convenient tools for the current evolution from molecular magnetism toward molecular spintronics and quantum computation.[1] Our group have been recently working with the *N,N'*-2,2'-(4,4'-bithiazole)bis(oxamate)[2] ligand (L) and herein we report the synthesis and general physical characterization, molecular and crystal structures, as well as the study of the static and dynamic magnetic properties of the compounds of formula $Na_6Ni_3L_3\cdot 11H_2O\cdot MeOH$ (**1**) and $K_6Co_3L_3\cdot 8H_2O\cdot MeOH$ (**2**). **1** and **2** were obtained by the stoichiometric reaction (1:1 molar ratio) of the diethyl ester derivative of the ligand ($H_2Et_2L$) and either nickel(II) or cobalt(II) nitrate salt in basic aqueous media. The IR spectra of **1** and **2** show the occurrence of two strong intensity peaks at 1615 and 1590 (**1**) or 1616 and 1595 $cm^{-1}$ (**2**) [$\nu$(C=O)] show a significantly displacement when compared to the IR spectrum of the proligand suggesting a coordination of the oxamate groups. Furthermore, the shift of the thiazole skeleton bands from 1476, 1439 and 1302 $cm^{-1}$ in the IR spectrum of $H_2Et_2L$ to 1523, 1454 and 1325 (**1**) or 1521, 1450 and 1321 $cm^{-1}$ (**2**) is also indicative of the coordination by the thiazole groups. X-ray powder diffraction performed on crushed crystals of **1** and **2** suggests they are isostructural compounds and reproduce well the diffraction patterns calculated based on the crystal structures. **1** crystallize in the C2/c and **2** crystallize int the $P2_1/n$ both in the monoclinic space group. The asymmetric unit of both contains a triple-stranded trinuclear complex anion of helicate-type, $[M^{II}{}_3L_3]^{6-}$, formed by three $L^{4-}$ ligands wrapping around three $Ni^{II}$ (**1**) or $Co^{II}$ ions (**2**) in a linear array. Six crystallographically independent $Na^{I}$ (**1**) and $K^{I}$ ions (**2**) complete the asymmetric unit, together with water and methanol coordinated molecules that results in a crystal packing of an oxamato-bridged heterometallic $A^{I}M^{II}$ 3D structure with an intricate pillared double mixed triangular/rhombic layered architecture. The *dc* magnetic measurements reveal a very weak antiferromagnetic coupling between the $Ni^{II}$ ions for **1** which contrasts with the moderate antiferromagnetic coupling between the $Co^{II}$ ions through the amidothiazole bridges for **2** [$-J = 0.31$ (**1**)/1.80 $cm^{-1}$ (**2**); $\mathbf{H} = -J(\mathbf{S}_1\cdot\mathbf{S}_2 + \mathbf{S}_2\cdot\mathbf{S}_3)$ with $S_1 = S_2 = S_3 = 1$]. The *ac* magnetic measurements show a slow magnetic relaxation (SMR) at relatively low applied *dc* magnetic fields for **2**, whereas no SMR effects are observed for **1** regardless of the magnitude of the applied *dc* magnetic field. A simple analysis of the *ac* magnetic data through the Arrhenius model reveals a thermal-assisted Orbach mechanism for the spin relaxation dynamics of **2** with values of the energy activation and pre-exponential factor typical of field-induced cobalt(II)-based single-molecule magnets [$E_a = 6.1$ and 6.4 $cm^{-1}$ with $\tau_0 = 4.0$ and $5.4\times10^{-8}$ s at $H_{dc} = 2.5$ and 5.0 kOe, respectively]. These compounds are candidates to obtain a new class of magnetic metal-organic frameworks.

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## Acknowledgments

CAPES, CNPq, IFG, UFG.

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

**Nº de Inscrição: 97**
*(Inserir o número de inscrição do autor que fez a submissão)*

# Triplet excited state studies and application of cationic *meso*-tetra(cisplatin)porphyrins in aPDT

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Palavras Chave: *Platinum(II) porphyrins, Cisplatin, Singlet oxygen, Antimicrobial photodynamic therapy.*

## Highlights

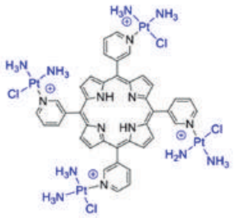
Cationic tetra-platinated porphyrins were used to photoinactivation of bacteria;

3-cis-PtTPyP presents higher photodynamic activity against bacteria;

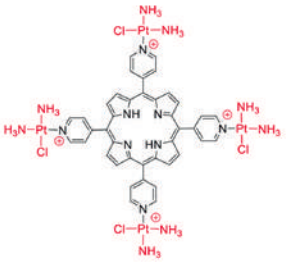
Bacterial photoinactivation was attributed to ROS generation with white-light irradiation conditions;

## Resumo/Abstract

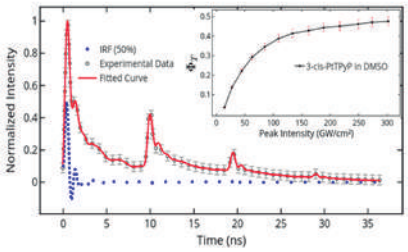
In this work, we report, the photophysical study of triplet excited states and antimicrobial photoinactivation of positively charged tetra-cisplatin porphyrin derivatives against Gram(+) and Gram(–) bacterial strains. Isomeric cisplatin-porphyrins were used and applied in aPDT assays in the bacilli *Escherichia coli*, *Klebsiella pneumoniae* and *Pseudomonas aeruginosa* (Gram negative) and a cocci *Staphylococcus aureus* (Gram positive) strain. The results show that compound substituted at meta position (**3-cis-PtTPyP**) is the more efficient photosensitizer against bacteria culture. In this way, tetra-cationic porphyrins containing cisplatin units might be promising aPDT agents with potential applications in clinical infections.

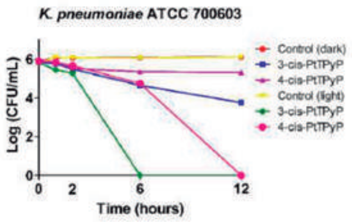


3-cis-PtTPyP



4-cis-PtTPyP





## Agradecimentos/Acknowledgments

The authors thanks to CNPq, FAPERGS, CAPES/PROEX – Finance code 001 and FAPESP for financial supporting.

**Área: INO** **Nº de Inscrição: 00011**

# Um novo polímero de coordenação de Gd(III) derivado de um ligante do tipo oxamato: síntese e caracterização.

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Palavras Chave: *Oxamato, EtH$_2$pcpa, Gd(III).*

## Highlights

**A new Gd(III) coordination polymer derived from a oxamate-type ligand : Synthesis and characterization.**

In this work, we present the preparation and structural results concerning the formation of complexe between the Gadolinium(III) ion with the N-(4-carboxyphenyl)oxamic acid (EtH$_2$pcpa).

## Resumo/Abstract

A preparação e compostos de coordenação com ligantes do tipo oxamato tem sido bastante explorada nas últimas décadas com inúmeros exemplos de onde a estratégia de síntese leva a diferentes topologias estruturais e propriedades físicas.[1,2] Neste trabalho, apresentamos os resultados estruturais relativos a formação de complexo entre o íon de gadolínio(III) com o ligante ácido N-(4-carboxifenil) oxâmico etil éster (EtH$_2$pcpa). O complexo foi obtido na forma de monocristal por difusão lenta em tubo na forma de H na estequiometria de 1:1 (ligante:metal) em água. Rendimento: 81%. A estrutura do complexo metálico de fórmula [Gd$_2$(Hpcpa)$_3$(H$_2$O)$_5$]$_n$ foi determinada por difração de raios X de monocristal. IR (KBr) v / cm$^{-1}$ 3421, 3358, 1653, 1603, 1536, 1411, 1310, 1181, 861, 785, 698. O complexo formou cadeias neutras de íons Gd(III) unidos por ligantes Hpcpa$^{-2}$, onde a unidade assimétrica contém dois íons de Gd(III) com geometria octaédrica. O Gd1 está coordenado a três moléculas de água, dois oxigênios-oxamato de um ligante Hpcpa$^{-2}$ e três oxigênios-carboxilato de três diferentes ligantes Hpcpa$^{-2}$, enquanto Gd2 está coordenado a duas moléculas de água, dois oxigênios-carboxilato de dois diferentes ligantes Hpcpa$^{-2}$ e quatro oxigênios-oxamato de outros dois ligantes Hpcpa$^{-2}$. A separação intracadeia entre os íons metálicos Gd1···Gd2 é de 5,061 Å.

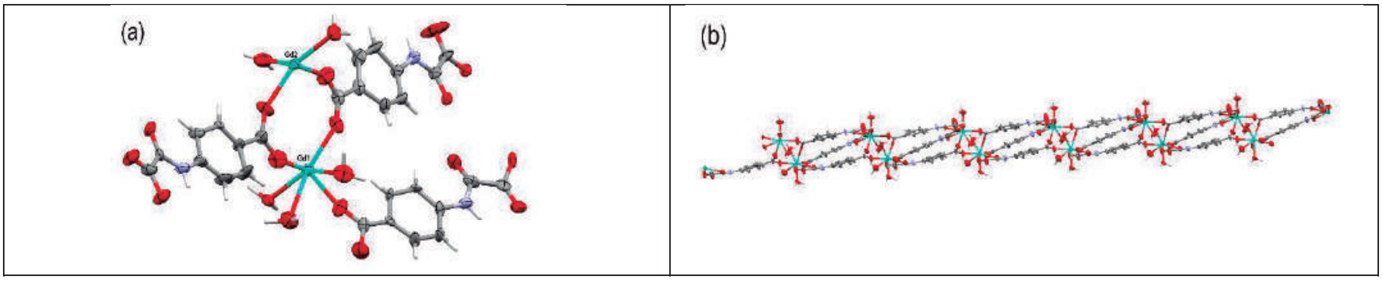

**Figura 1:** (a) Unidade assimétrica de [Gd$_2$(Hpcpa)$_3$(H$_2$O)$_5$]$_n$, (b) Fragmento de uma cadeia neutra de [Gd$_2$(Hpcpa)$_3$(H$_2$O)$_5$]$_n$. Os elipsoides estão desenhados ao nível de probabilidade de 50%.

Foi obtido um composto inédito que foi caracterizado por difração de raios X em monocristal e espectroscopia na região do infravermelho até o momento. Como perspectiva serão realizadas a caracterizações elementares e o estudo das propriedades magnéticas.

## Agradecimentos/Acknowledgments

CNPQ, CAPES, FAPEG e UFG.

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**Área: INO**

# Unexpected luminescent and thermal properties of novel tetrakis $Eu^{3+}$-indandionate complex: Experimental and theoretical studies

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*Keywords: trivalent europium, indandionate, luminescence, Judd-Ofelt parameters, molecular thermometers*

## Highlights

The highest value of Judd–Ofelt intensity parameter ($\Omega_2$) for the europium compound reported in the literature. The $Et_4N^+[Eu(isovind)_4]^-$ complex presents an abnormal phase transition changing $^5D_0 \rightarrow {}^7F_J$ luminescence profile.

## Resumo/Abstract

Luminescent coordination compounds based on trivalent europium ions ($Eu^{3+}$) have found wide range of applications in new technologies, such as optoelectronics, molecular thermometers, and biomedical devices. Applications of this materials may be associated with narrow emission bands, which are arise from intra-configurational Laporte forbidden 4f – 4f transitions ($^5D_0 \rightarrow {}^7F_J$). Furthermore, $Eu^{3+}$ ion can act as a powerful spectroscopic probe and the $^5D_0 \rightarrow {}^7F_2$ transition are strongly sensitive to small angular variations in the coordination polyhedron. However, the energy structures of the organic ligands in the complexes play the most important role on the $Eu^{3+}$ luminescence sensitization process[1]. In this context, this work reports about theoretical, syntheses, characterization, and photoluminescence studies of a series of tetrakis complexes containing tetraethylammonium, $Et_4N^+[Ln(L)_4]^-$ ($Et_4N^+$: tetraethylammonium cation, Ln: Gd and Eu, and L: 2-acyl-1,3-indandionate). The Judd–Ofelt intensity parameter ($\Omega_\lambda$), lifetime ($\tau$), radiative ($A_{rad}$) and non-radiative ($A_{nrad}$) coefficients, and intrinsic quantum yield $\Omega_{Eu}^{Eu}$) values were calculated for different temperatures (80 - 475 K) (Table 1). The $Et_4N^+[Eu(isovind)_4]^-$ complex, where isovind: 2-isovaleryl-1,3-indandonate) shows an extraordinarily high value of the intensity parameter ($\Omega_2 = 73.5\times10^{-20}$ cm$^2$, considering the index of refraction equal to 1.5) and radiative decay rate ($A_{rad} = 2.468\times10^3$ s$^{-1}$) at 300 K. These optical results show an abnormally high emission intensity of the $^5D_0 \rightarrow {}^7F_2$ transition (Figure 1), leading to the highest measured $\Omega_2$ value of the europium materials, to the best our knowledge, reported in the literature. In addition, this complex shows different solid phases at 367 and 460 K, leading significant changes in the band profile assigned to the $^5D_0 \rightarrow {}^7F_2$ transition. The spectroscopic study of luminescent systems has shown very interesting and promising results for applications, such as OLED devices and luminescent thermometers based on $Ln^{3+}$ ions.

Table 1. Experimental intensity parameters ($\Omega_\lambda$), lifetime ($\tau$), radiative ($A_{rad}$) and non-radiative ($A_{nrad}$) coefficients, and intrinsic quantum yield $\Omega_{Eu}^{Eu}$) of $Et_4N^+[Eu(isovind)_4]^-$ complex.

| Temperature K | $\Omega_2$ ($10^{-20}$) cm$^2$ | $\Omega_4$ ($10^{-20}$) cm$^2$ | $\tau$ (ms) | $A_{rad}$ (s$^{-1}$) | $A_{nrad}$ (s$^{-1}$) | $A_{tot}$ (s$^{-1}$) | $Q_{Ln}^{Ln}$ (%) |
|---|---|---|---|---|---|---|---|
| 80 | 63.6 | 7.9 | 0.371 | 2140 | 555.4 | 2695 | 79.4 |
| 200 | 68.4 | 8.8 | 0.358 | 2307 | 486.3 | 2793 | 82.6 |
| 300 | 73.5 | 8.9 | 0.330 | 2468 | 562.3 | 3030 | 81.4 |
| 375 | 77.7 | 8.8 | 0.172 | 2362 | 3452 | 5814 | 40.6 |
| 425 | 83.1 | 10.8 | 0.127 | 2791 | 10910 | 13700 | 20.4 |
| 475 | 90.5 | 13.1 | 0.018 | 3053 | 52500 | 55560 | 5.5 |

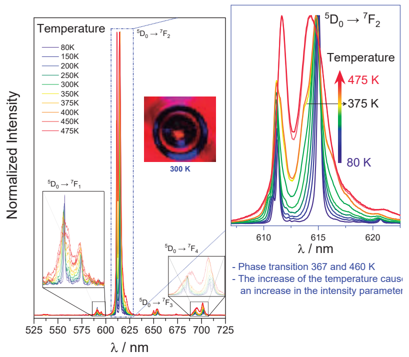

Figure 1. The emission spectra of $Et_4N^+[Eu(isovind)_4]^-$ complex at from 80 to 475 K. Insert: Photograph taken under the 365 nm UV lamp at 300 K.

## Agradecimentos/Acknowledgments

This work was supported by CNPq, FAPESP and CAPES.

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**Área: INO**

# Water absorption studies and characterization of a Co(II)-based coordination compound assembled from an aminoacid ligand

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*Keywords*: *Cobalt(II) complex, Water harvesting, Reversible water sorption*

## Highlights

A water harvester candidate composed of a Co(II) coordination complex was synthesized, characterized and had its absorption properties studied.

## Abstract

Safe and clean water scarcity is still a major problem in different regions around the world[1]. Sorbent-assisted atmospheric water harvesting can be used not only as an alternative water production method, but also as a dehumidifying agent[2]. The study of new compounds[2] to understand their water absorption mechanisms is important to improve their performance when compared to the widely used traditional sorbent, such as zeolites or silica gel. Herein, we report the absorption studies of a Co(II) coordination complex assembled using an aminoacid ligand[3] that presents as an atmospheric water harvester candidate. The complex was synthesized using and metal-ligand molecular ratio of 1:2, combining a MeOH solution of $Co(CH_3COO)_2.4H_2O$ and a 1:1 $MeOH:H_2O$ solution of the ligand. The single crystal X-ray diffraction analysis revealed a structure composed by a Co(II) metal center coordinated with two ligand molecules and two water molecules in a monoclinic $P2_1/n$ space group. There is also one uncoordinated water molecule in the asymmetric unit interacting with the complex unit through hydrogen bonding, responsible to the crystalline stabilization (Figure 1a). To investigate the water capture properties of the complex, thermogravimetric analysis (TGA) were performed. Initially to activate the material, single crystals were heated at 155°C for 30 min, resulting in a color transformation. Followed by three different water absorption tests using i) air humidity, ii) liquid water and iii) water vapor at 60 °C (Figure 1b). The absorption studies were monitored by TGA, indicating a maximum water uptake of 18 %. Powder X-ray diffraction (PXRD) showed the structure reversibility upon an absorption/desorption cycle (Figure 1c).

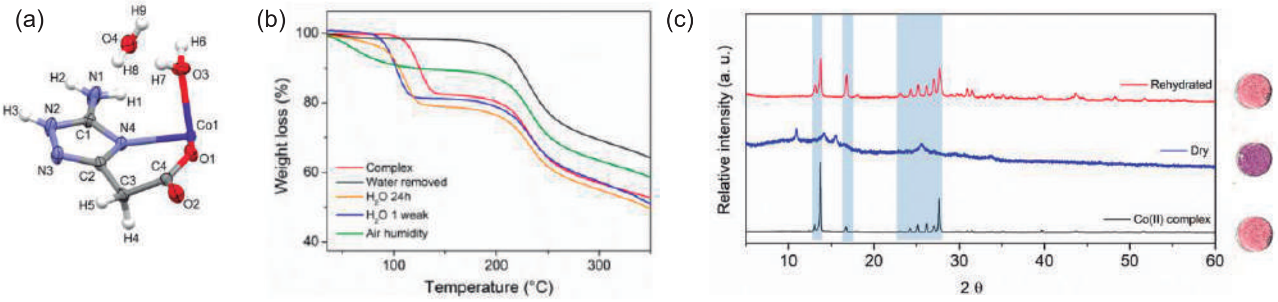

Figure 1: (a) Asymmetric unit of the Co(II) complex; (b) TGA for the complex; (c) PDRX of the complex dehydrated and after water capture.

## Acknowledgments

FAPERJ; CNPq; CAPES; UFF; LDRX; LaReMN; LAMATE; LAME.

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[3] Matos, C. R. M. O. *et al.*, Dalton Transactions, 49, 16359–16367 (2020).

# MAT

# Química de Materiais

**Área: MAT** **Nº de Inscrição: 00342**

# Adsorbents based on hydroxyapatite/tripolyphosphate/chitosan spheres

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Keywords: Hydroxyapatite, *Chitosan, Bioadsorbents*.

## Highlights

Amino hydroxyapatite/sodium tripolyphosphate/chitosan spheres were prepared.
Different mass proportions (10% to 75%) of organofunctionalized hydroxyapatite were employed.
The organofunctionalized HA samples presented high efficiency for dye removal.

## Resumo/Abstract

Substantial quantities of dyes contaminate certain aquatic bodies. Therefore, the treatment of dye effluent is necessary [1]. In this context, the use of bioadsorbents like chitosan/inorganic compound composites is an alternative for the remediation of river resources and/or ecosystems [2]. Among the inorganic matrixes, hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) is used due its high adsorption capacity for cationic and anionic species, availability and low cost, in addition to its high thermal stability. In this work, hybrid materials based on amino hydroxyapatite ($NH_2$-HA) and chitosan (CS) were prepared by reticulation in presence of sodium tripolyphosphate (TPP). HA was synthesized by reaction between ammonium hydrogen phosphate and calcium chloride with a Ca:P mol ratio of 1.67 at pH 10 in presence of NaOH. For organofunctionalization, 5 g of the activated HA reacted with aminopropyltrimethoxy silane under reflux of toluene and $N_2$ atmosphere for 72 h. The final solid (HA-$NH_2$) was separated by filtration, washed twice with ethanol and water and dried at 80 °C for 24 h. For nanocomposites. appropriate amount of chitosan (90, 75, 50 and 25 in wt%) was dissolved in 120 mL of a 2% (v/v) acetic acid/$H_2O$ solution. HA-$NH_2$ was added to the chitosan solution in 10, 25, 50 and 75% w/w proportions. The system reacted for 12 h under at 800 rpm. The gel was sonicated for 2 h and dropped in a 10% weight/volume TPP aqueous solution. Finally, the hybrid were washed with water until neutral pH and dried at 60 °C for 24 h. The resulting solids were used for the removal from aqueous solution of reactive violet 5R, an organic dye. Synergy between the properties of the precursors was observed for the hybrid biomaterials highlighted by X-ray diffraction (XRD), thermogravimetry, and CHN elemental analysis as well as infrared and $^{13}C$ nuclear magnetic resonance spectroscopies. XRD patterns indicated that after silylation, the relative intensity of the HA reflections decreased without alteration in the position of the $2\theta$ values. The XRD pattern of chitosan presented a broad peak in the $2\theta$ region 10-30°. In presence of 10% HA, the peaks of HA are hardly visible. With increasing HA amount, peaks attributed to HA are clearly distinguishable, and the broad peak of CS becomes broader. CHN elemental analysis (Table 1) showed the presence of 1.80 mmol $g^{-1}$ organic groups on HA, while for the pristine HA, the quantities were $C \leq 0.3\%$ and $N \leq 0.02\%$, possibly associated with the presence of carbonate as observed from the FTIR spectrum. For all hybrids, the quantity of organic content decreased with increasing HA content. The adsorption capacities of the resulting hybrid were proportional to the content of chitosan in the hybrids and the surfaces were positively charged at pH 1-7 as showed Zeta potential measurements. The best dye removal capacity was achieved at pH 3, with 350 and 365 mg $g^{-1}$ for the solids containing 10 and 25% silylated HA in 30 min, respectively. The present data indicated high dye removals by the prepared hybrids.

**Table 1**. CHN content for the pristine and silanized hydroxyapatites and their composites with chitosan(CS).

| Sample | % C | % H | % N |
|---|---|---|---|
| HA-$NH_2$ | 6.50 | 1.90 | 2.50 |
| CS | 39.82 | 6.73 | 6.78 |
| 10HA-$NH_2$/CS | 35.22 | 6.42 | 6.26 |
| 25HA-$NH_2$/CS | 32.11 | 6.07 | 5.95 |
| 50HA-$NH_2$/CS | 23.53 | 4.49 | 4.12 |
| 75HA-$NH_2$/CS | 18.90 | 3.74 | 3.22 |

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## Agradecimentos/Acknowledgments

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**Área:** MAT

# Amplification of the Azithromycin activity using keratin nanocarriers to control microbial resistance

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Palavras Chave: Keratin *nanoparticles, Bacteria, Biomaterials.*

## Highlights

Keratin nanoparticles extracted from human hair by acid hydrolysis were loaded with azithromycin to amplify antibiotic resistance against bacteria strains.

## Resumo/Abstract

According to the World Health Organization (WHO), antibiotic resistance represents a considerable global threat. Therefore, the scientific research aims are to develop new and non-susceptible controlling methods to prevent microbial resistance (1). Nanotechnology might be the path for solving this issue due to the unique physical and chemical properties of nanodevices applied as drug delivery systems (DDS). Nanocarriers can be engineered to internalize and interact with microbial cells, enhancing the antimicrobial activity of loaded drugs. Despite the massive efforts from the scientific community to develop and optimize new nanocarrier properties, there is a need for continuous improvement in the development of materials that amplify the activity of antibiotic drugs. Several studies indicate that keratin nanoparticles (KNPs) could be used as natural-based nanocarriers. KNPs are cytocompatible and biodegradable, being a fibrous protein of natural origin. Therefore, this project aims to obtain KNP nanocarriers loaded with the conventional azithromycin drug. Azithromycin was used to treat the SARS-Cov-2 virus, which may promote in the future, resistant bacterium strains. The KNP nanocarriers might be able to amplify the antibiotic activity against different bacterium cells (*S. aureus* and *E. coli*) to control microbial resistance. Preliminary data showed that the human hair hydrolysis with concentrated sulfuric acid provided spherical KNPs (average diameter of 70 nm, Figure 1). The as-prepared KNPS can act as a DDS toward azithromycin to prevent microbial resistance, enhancing its antimicrobial action.

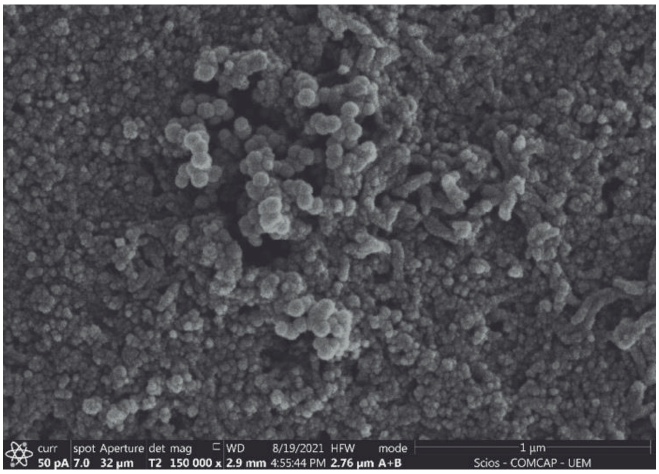

**Figure 1**. SEM image of the extracted KNPs from human hair using sulfuric acid.

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## Agradecimentos/Acknowledgments

We thank the CNPq and CAPES for the financial support in the form of fellowships.

**Área: MAT**

# Óxidos mistos de Zn/Co obtidos a partir de lauratos lamelares heterobimetálicos com centros de íons $Zn^{2+}$ e $Co^{2+}$.

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Palavras-chave: Compostos Lamelares, Carboxilatos de metais de transição, Óxidos mistos.

## Highlights

- Synthesis of heterobimetallic lamellar carboxylates with $Zn^{2+}$ e $Co^{2+}$ centers.
- The synthesized carboxylates were calcined to obtain the mixed oxides of $Zn^{2+}$ and $Co^{2+}$.

## Resumo

Os carboxilatos lamelares fazem parte do grupo dos compostos lamelares neutros, ou seja, suas lamelas não possuem cargas. Por meio da decomposição térmica desses compostos é possível obter óxidos mistos (Guo et al., 2009). Tais óxidos podem ser obtidos com tamanhos de partículas uniformes, pois o precursor utilizado tem como objetivo agir como um template. Esta pesquisa teve como intuito obter óxidos mistos por processo de decomposição térmica de carboxilatos heterobimetálicos, visando analisar a influência das variáveis temperatura e tempo de calcinação na formação desses óxidos. Na Figura 1 são apresentados os gráficos de DRX (A) e FTIR (B) do Laurato de Zinco e Cobalto e dos óxidos mistos obtidos à 800°C.

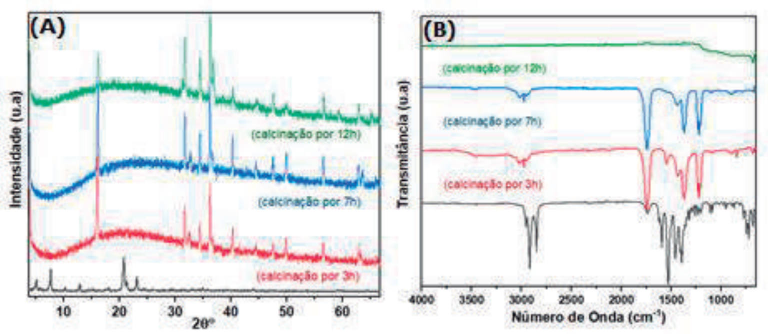

Figura 1 – (A) DRXP e (B) FTIR para o precursor laurato de zinco e cobalto e após aquecimento à 800°C em tempos de 3, 7 e 12 horas. As identificações das curvas do material calcinado estão presentes no gráfico.

Ao analisar os difratogramas de raios X, observa-se que ocorrem alterações significativas devido às diferenças na calcinação, pois, os picos na região de 3 e 20° (2θ) desaparecem e surgem picos característicos de óxido de zinco na região entre 30 e 40° (2θ), além de na região entre 10 e 20° de 2θ aparecer um pico referente a uma fase de hidroxissal duplo de zinco e cobalto, que, no entanto, necessita de maiores investigações. Observa-se nos espectros de infravermelho que as bandas características dos carboxilatos na região entre 1300 e 1500 $cm^{-1}$ desaparecem totalmente no experimento conduzido à 800°C no tempo de 12 horas de calcinação (YANG et al., 2019). Apesar da evidência de formação dos óxidos mistos, ainda há necessidade de estudar a formação das partículas com tamanho e forma uniformes.

## Agradecimentos

Os autores agradecem: à Rede Mineira de Química, Laboratório de Caracterização Estrutural da UNIFEI (LCE), Grupo de Química de Materiais da UFPR (GQM), UNIFEI, CAPES e CNPq.

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**Área: MAT**

# A novel method for obtaining a magnetic carbon nanocomposite with different selectivity for adsorption of organic emerging pollutants

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Keywords: *Magnetic nanocomposite, Adsorption, Activated carbon, Waste valorization, Cocos nucifera, PPCPs.*

## Highlights

A newly proposed method for obtaining magnetic carbon nanocomposite (**MNC**) is presented.
**MNC** has a higher surface area and adsorption capacity than the traditionally synthesized magnetic biochar (**MBC**).

## Abstract

Emerging contaminants are a great problem because of the possibility to bioaccumulate and potential risks to humans and the environment. The adsorption process shows great potential to mitigate this problem. In this context, activated carbons and biochars have been successfully applied as sustainable and efficient materials for that application. Magnetic materials can be easily retrieved from an effluent representing a way to reduce operational costs. Yet, the development of magnetic carbon composites for adsorption has one major setback. Introducing magnetic particles on the surface of the carbon matrix considerably lowers the surface area of the material, occupying pores that could otherwise be used as active sites for pollutant adsorption [1]. This work proposes a new methodology to obtain magnetic nanocomposite applied as an adsorbent for organic micropollutants, comparing it with a magnetic biochar, from a traditional synthesis.

**Table 1:** Textural & binary adsorption results

| Material | ACP | MNC | MBC |
|---|---|---|---|
| Surface area ($m^2/g$) | 1242 | 1019 | 474 |
| **CF** max. adsorption (mg/g) | 242 | 135 | 31 |
| **SA** max. adsorption (mg/g) | 208 | 128 | 86 |

The magnetic biochar (**MBC**) was synthesized by co-pyrolysis. Briefly, green coconut husk wastes were collected, dried, and shredded. The biomass obtained was then impregnated with a solution of $Fe^{3+}$ (1:3 $FeCl_3 \cdot 6H_2O$ mass ratio). The dried mixture was pyrolyzed (500 °C, $N_2$, 2 h) and afterward washed with water, dried, crushed, and sieved. For the preparation of the nanocomposite, the components were synthesized independently. The activated carbon (**ACP**) by the pyrolysis (500 °C, $N_2$, 2 h) of the coconut biomass was impregnated with $H_3PO_4$ (1:3 mass ratio) which was washed with water, dried, crushed, and sieved. To embed the support with magnetic properties, a stable colloid of magnetite nanoparticles was mixed with **ACP** at different proportions and several contact times until equilibrium was reached. The formed magnetic nanocomposite (**MNC**) was magnetically separated from the solvent and washed [2]. The materials were characterized via powder XRD; TEM; SEM; FTIR; PZC; $N_2$ adsorption surface measurements and SQUID magnetometry. Then the 3 materials (**ACP**; **MBC**; and **MNC**) were investigated for their adsorption capacities in isolated and binary solutions of salicylic acid (**SA**) and caffeine (**CF**), which were used as simulations of organic micropollutant effluents. Adsorption investigation was performed in fixed-bed experiments, kinetic, and isotherm batch studies at room temperature (293 K). The results obtained (**Table 1**) show that **MNC** retains the adsorptive behavior of **ACP** with a slight decrease in surface area and adsorption capacity. Moreover, the diverse surface chemistry promoted a completely different selectivity on the binary assays. While **ACP** and **MNC** favor the adsorption of caffeine, **MBC** adsorbs almost exclusively salicylic acid. Therefore, this study furnished a simple methodology to produce magnetic carbon materials with a high surface area, suitable magnetic response, and selectivity. The diversity of the pollutants require the constant development of new materials and methods such as the ones proposed in this work.

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## Acknowledgments

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**Área: MAT** **Nº de Inscrição: 03128**

# Bioavailability of macronutrient incorporated in nanostructures for application in agriculture

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Palavras Chave: *nanofertilizers; biodisponibilization, micropropagation, sugarcane, and biometry.*

## Highlights

- The macronutrients K, P, and N were incorporated within nanoparticles;
- *In vivo* experiments in sugarcane raised by tissue culture led to better results in comparison to commercial fertilizers.

## Abstract

The integration of biotechnology and nanotechnology can, in principle, lead to more efficient pathways to deliver macronutrients to plants. Plant physiology in their early growth stages is rather different and much more active than in adult plants. This opens room for the development of new technologies that can improve nutrient uptake and minimize losses. There have been estimates of losses of up to 50% of the total amount of phosphate added to some areas due to sequestration in the soil. On the other hand, nanomaterials can potentially deliver the nutrients through controlled release.[1] Nanomaterials have allowed a positive response in food production and an increase in fertilizer efficiency.[2] Recent research with nanoparticles is motivated by their expected benefits such as to reduce the amount of the nutrients to be supplied and to obtain an efficient system for nutrient delivery.[3] In this work, the macronutrients (potassium, phosphorus, and nitrogen) have been incorporated into chitosan and silica nanoparticles and delivered to sugarcane raised by tissue culture. Different nutrient loads were added to the nanoparticles. The chitosan nanoparticles present average sizes ranging from 150 nm to 697 nm and those based on silica, 106 – 400 nm, which are larger particles than the nanoparticles without nutrients, 50 nm and 63 nm, respectively. They were also characterized by transmission electron microscopy. These samples were tested on micropropagation *in vitro and in vivo* of seedlings of sugarcane plants at the bio-factory Gov. Miguel Arraes at CETENE. The results obtained so far showed that the amount of nutrient-loaded in the nanoparticles matrix is dependent on several factors including particle size, morphology, surface charge, and nature of the nanoparticle. The *in vivo tests* were carried out in triplicate on 120 plants. The biometry parameters such as height, stem diameter, leaf chlorophyll index (ICF) has been measured for seven months in acclimatized seedlings. The plant height, stem diameter, and chlorophyll content of plants treated with nanofertilizers (height: 62 cm, 13, 77 cm, and ICF A: 39,83) are higher compared seedlings where commercial fertilizers were used (height: 41 cm, 11,41 cm, and ICF A: 30,01). These results suggest that the N, P, and K were efficiently incorporated into the nanoparticles and efficiently delivered to the sugarcane plants.

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## Acknowledgments

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**Área: MAT**

# Biocompatible nanocomposite based on mesoporous silica and hydroxyapatite as a new potential gated keeper nanocarrier to cancer treatment.

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Palavras Chave: *Mesoporous silica nanoparticles, Hydroxyapatite, Nanocomposite, Drug delivery systems*

## Highlights

In the present work, we synthesized a nanocomposite based on mesoporous silica and hydroxyapatite to work as a new nanovalve for cancer treatment.

## Abstract

Mesoporous silica nanoparticles have been used as reservoir for the construction of nanovalves due to its high surface area (>1000 $m^2$ $g^{-1}$) and the possibility to lock inside their nanochannels cargo molecules[1]. Our research group have been already exploring this material using it as a gated keeper nanocarrier in nanovalves[2]. However, the biodegrability of silica are subject to discussion. Therefore, we proposed a new nanovalve using a previously described nanocomposite based on mesoporous silica and hydroxyapatite, the latter one being the inorganic phase of bone tissues, to improve biocompatibility. The nanocomposite synthesis was performed following a procedure described in literature[3]. The Figure 1 presents the transmission electron microscopy (TEM) images of the synthesized material MSN-HAP. As shown, its is possible to observe the presence of two different phases, one of hydroxyapatite, which has a rod shape like structure, and a second one, which is the hybrid material. The successful formation of the nanocomposite structure is the absence of organized tubular pore channels, which indicates that the silica structure had suffered modifications. However, some robust characterization techniques, such as energy dispersive X-ray spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS), will be further performed to confirm the presence of both silica and hydroxyapatite phases.

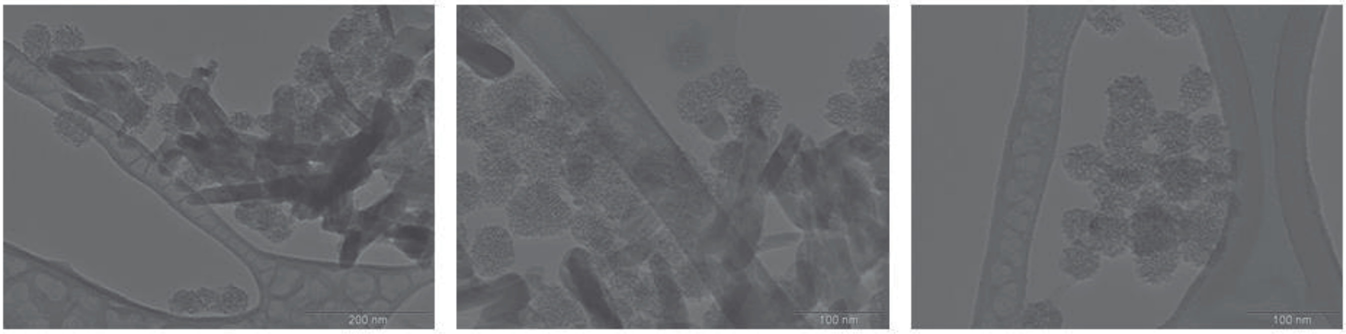

Figure 1: Transmission electron microscopy images of the hybrid MSN-HAP.

## Acknowledgments

UFF, CAPES, CNPq, FAPERJ, PPGQ-UFF, LQSN, LAME, LAMATE

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**Area: MAT**

# Biocomposites of $Eu^{3+}$-doped gellan gum and nanocellulose for 3D printing

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Keywords: Biomaterials; Luminescence; Cellulose nanocrystals; Scaffolds.

## Highlights

Biocomposites of $Eu^{3+}$-doped gellan gum reinforced with nanocelulose.
Hydrogels with 3D printing properties, for tissue engineering scaffolds.
$Eu^{3+}$ used as a probe to study the structure of the compound.

## Abstract

Biopolymers have attracted great interest in tissue engineering research, and the biodegradable scaffolds developed from these materials can be used as temporary substrates to induce the regeneration of newly developed tissues. Gellan gum (GG) is a natural polysaccharide that can be prepared as a hydrogel, and it is a versatile and functional biomaterial [1]. Several structural groups from this biomaterial are available as coordination site for lanthanide ions, well-known for their luminescent properties; in this case, the $Eu^{3+}$ ion was used herein as a luminescent probe and allowed us to obtain information about the coordination environment in which the ion was inserted in the GG matrix and, therefore, enabled a better understanding of the structure of the material. Obtaining GG hydrogels with the addition of $Eu^{3+}$ in their preparation showed that the lanthanide ion promoted the crosslinking of the polysaccharide chain and gradually changed the viscoelastic properties of the material. Oscillatory rheology studies indicated that the presence of the ion in the polymeric network decreased its reticular strength, but better maintained the behavior of the gel structure as shown in the tests with temperature variation (Figure 1 - a). Such properties are already favorable to generate three-dimensional structures from 3D printing [2]. This work also aims to reinforce these obtained materials with cellulose nanocrystals (CNC), which have the potential to improve the mechanical properties of polymer composites. The luminescence of the $Eu^{3+}$-doped GG and NCN composite was studied, showing that the ions were not sensitized by direct excitation in the matrix and the emission profiles (Figure 1 - b) match the $Eu^{3+}$ ion in a low symmetry environment [3]. Thus, the strategy in this work to avoid a quenching way for the luminescence was to use the ligand TTA (2-thenoyltrifluoroacetone), which acts as a sensitizer for $Eu^{3+}$ ions resulting in a material with strong emission. This study, already done with GG, is being extended to the composite of GG and CNC.

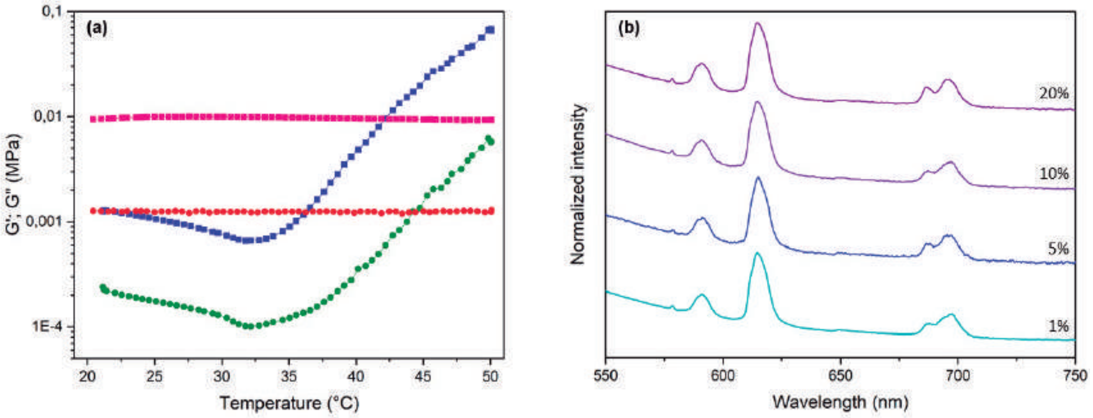

**Figure 1. (a)** Temperature sweep rheogram showing stability of the elastic (G') and viscous (G") modulus along the analysis of the 2% $Eu^{3+}$ doped GG sample (G' = pink, G" = red) comparing with the pure GG gel (G' = blue, G" = green); **(b)** Emission spectra ($\lambda_{ex}$ 394 nm) of 1% $Eu^{3+}$-doped GG + CNC films (% w/w, CNC/film).

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**Área:**
**MAT**

# Buparvaquone complexation on the surface of gold nanoparticles: a new possibility of drug delivery.

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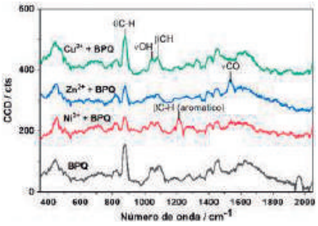
Key-words: *Leishmaniasis, buparvaquone, gold nanoparticles, transition metals, Raman SERS, complexation.*

## Highlights

Leishmaniasis, caused by protozoans of the genus *Leishmania*, is a disease that can be categorized as: cutaneous, visceral or mucocutaneous, transmited by insects and is part of the Neglected Tropical Diseases (NTDs). NTDs are more common in the tropical countries of Asia, Africa and South America and are obfuscated by other diseases such as malaria and tuberculosis. Medication is scarce due to the lack of investments, sanitary control and awareness. Buparvaquone (BPQ), a drug potentially usable in the treatment of leishmaniasis, is already well characterized and commercialized as *Butalex*®. A hydroxynaphtoquinone, composed of an aromatic ring, a semiquinone group and an aliphatic chain, the BPQ presents low solubility in water, which makes it difficult to act in the organism of infected individuals. The presence of the semiquinone group draws attention to the possibility of complexation by the molecule with transition metals, which may ease the drug's delivery in the organism. This study's goal is to investigate the likelihood of the usage of ranelate-gold nanoparticles (AuNp@Ran) as means of anchorage and drug delivery for the BPQ, based on its complexation with transition metals.

## Resumo/Abstract

**Results:** The pKa value, equal to 6.02, was determined by means of an acid-base titration and UV-VIS spectroscopic technique with the intention of setting the optimal working conditions, since the deprotonation of the hydroxyl is crucial for the complexation with the present metals. Following the addition of the metals to the nanoparticles' surfaces, on the other hand, a slight bathochromic shift was observed after the addition of BPQ, suggesting complexation on the surfaces of the AuNp@Ran. Nonetheless, the Raman spectroscopic analysis reveals that the interactions between the organic molecule and the particles are effective, since it is possible to identify signal intensification due to resonating light scattering (SERS) in the AuNp@Ran+BPQ spectrum. But not only that, this technique also unravels significant differences in the spectrum once the gold nanoparticles are modified with zinc and nickel previous to the addition of BPQ (Picture 1).



Picture 1: Raman-SERS spectra of the interaction between: BPQ and gold nanoparticles; and AuNp@Ran after the addition of of $Ni^{2+}$, $Zn^{2+}$, $Cu^{2+}$.

The AuNp@Ran+BPQ Raman-SERS spectra reveal multiple intense peaks tied to the semiquinone group, indicating the proximity between it and the nanoparticles' surfaces. In regards to the AuNp@Ran+BPQ+$Zn^{2+}$ spectrum, one can observe the intensification and definition of the peak related to stretch of the semiquinone's CO bond, apart from the mischaracterization of the peak tied to the hydroxyl group. On the contrary, the interaction between the nanoparticles and the BPQ, after the addition of $Ni^{2+}$, produces a spectrum that endorses the aromatic ring's plane distortion more than any other spectrum, hinting its proximity to the AuNp@Ran.

**Conclusions:** The presence of metal ions, such as $Zn^{2+}$ and $Ni^{2+}$, complexes BPQ before it even bonds to the nanoparticles' surface. As far as we know, this is the first study that tackles this subject and presents promising results that grant the possibility of the development of a new BPQ delivery system in the organisms of Leishmaniasis patients.

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## Agradecimentos/Acknowledgments

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**Área: MAT**

# Captopril as a possible marine pollutant: A detecting method by using gold nanoparticles

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Keywords: Gold nanoparticles, Localized surface plasmon resonance (LSPR), sensing applications.

## Highlights

- Synthesis and characterization of 8 and 20 nanometers gold nanoparticles;
- PVA films with gold nanoparticles for sensing captopril in different concentrations;
- Discussion about size influence in sensing applications.

## Resumo/Abstract

Drugs are indispensable for the human health care. However, after use, the active agents and their metabolites are excreted and impact the environment via different pathways. There is still a lack of knowledge concerning quantities of pharmaceuticals and the effects of the active substances on aquatic organisms. Of captopril, it is known that its toxicity may cause bone marrow suppression and proteinuria. Nevertheless, not much is known about the effect in aquatic organisms by direct disposal or in plants irrigated by drug-contaminated reused water. [1]

Being a subject of great interest to several researchers from different science areas, gold nanoparticles have, for example, chemical applications in catalytic activities and solar cells, biomedical applications in drug-delivery and disease diagnosis. From the property presented by metallic nanoparticles, the localized surface plasmon resonance (LSPR) occur within the visible region of the electromagnetic spectrum, which is interesting for other applications.[2] Since it presents a high sensibility for molecule detection, they are applied as chemical sensors and biosensors. When coupled in optical fibers, it creates the possibility to be applied in remote sensing.[3]

In this study, gold nanoparticles were synthesized with 8 and 20 nm by a classical route employing a gold(III) salt and reducing agents. A new sensor was developed using polivynil alcohol and gold nanoparticles to detect captopril by the interaction of sulfur present in drug molecules with the gold nanoparticles. To determine the detection, UV-Vis absorption spectra were measured and evaluated by the maximum absorption wavelength variation regarding the LSPR effect (Figure 1). Modifying the drug concentration, it was possible do determine the limit of detection. Lastly, the influence of gold nanoparticles size in the sensor was verified.

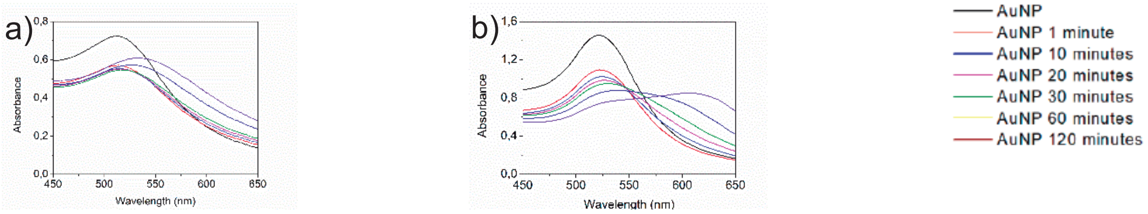

Figure 01: UV-Vis Absorption spectra peak shift by time from gold nanoparticles with (a) 8 nm and (b) 20 nm when interact with captopril.

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## Agradecimentos/Acknowledgments

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**Área: MAT**

# Castor oil-based polyurethane nanocomposites can increase the release control in granulated fertilizers by controlling nutrient diffusion

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Keywords: *Controlled release, Castor oil, Polyurethane, Montmorillonite, Hydrotalcite, Fertilizer.*

## Highlights

Small amounts of lamellar material are effective to control the N and P diffusion; PU-coatings modified with montmorillonite and hydrotalcite can delay the N and P release from urea and MAP.

## Resumo/Abstract

Despite the indispensable use of agricultural fertilizers to achieve current levels of productivity, chemical nutrients have their effectiveness limited by problems such as ammonia (NH3) volatilization, leaching and/or soil immobilization. One strategy to minimize these problems is to protect the fertilizer with nutrient-release barrier materials. Thus, 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 mechanical compromise (fracture) of the polymer. The permeation through a polymer can be significantly reduced by the presence of internal diffusional barriers such as finely dispersed nanoclays (in the nanocomposites form). Thus, we proposed a nanocomposite system based on castor oil-derived polyurethane (PU) for controlling the release of fertilizers by an ion-exchange mechanism. PU coatings modified with less than 5% (by weight) montmorillonite, a cation-exchange material, successfully retarded the nitrogen release from urea granules, with less than 50% of the nutrient released within 18 days of immersion, as confirmed by soil incubation experiments. The same profile was observed for the phosphate release from mono ammonium phosphate (MAP) granules coated with PU modified with hydrotalcite (less than 5% by weight), an anion-exchange material. The release times were proportional to the contents of the cation- or anion-exchange materials, which exhibited specific correlations with the kind of nutrient released (e.g., cationic or anionic), confirming the diffusion barrier promoted by the PU coating structures. Our results demonstrated that the use of PU nanocomposites can significantly reduce the coating thickness with improved nitrogen and phosphorus release control, opening a new field for the investigation of controlled-release fertilizers.

## Agradecimentos/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, #2019/18036-8 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. The authors also thank the National Nanotechnology Laboratory for Agribusiness (LNNA) for providing institutional support and facilities.

**Área: MAT**

# Cation exchange reactions in the new layered double hydroxide with the ideal composition $[Zn_6Al_6(OH)_{24}][(SO_4)_3(AOH)_2].nH_2O$ (A= $Li^+$, $Na^+$, $K^+$).

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Palavras Chave: *Layered double hydroxides, Exchange reactions, Intercalation, Alkali metal cations.*

## Highlights

New layered double hydroxide with the composition $[Zn_6Al_6(OH)_{24}][(SO_4)_3(KOH)_2]\cdot nH_2O$ was synthesized and intercalated $K^+$ ions have been partially replaced by $Li^+$ or $Na^+$, keeping $SO_4^{2-}$ and $OH^-$ constants

## Resumo/Abstract

In traditional layered double hydroxides (LDH) with the general chemical composition $[M^{2+}_{1-x}M^{3+}_x(OH)_2]\ (A^{n-})_{x/n}\cdot yH_2O$, part of the $M^{2+}$ in the brucite-like structure is replaced by $M^{3+}$, and the positive charge on the layer is compensated by intercalated hydrated anions [1,2]. New synthetic LDH with the composition $[M^{2+}{}_6Al_3(OH)_{18}(SO_4)_2Na(H_2O)_6]\cdot 6H_2O$ ($M^{2+}$=Mn, Mg, Zn) [3,4], have been recently obtained and it was demonstrated for the first time that this LDH can exchange cations, anions or both simultaneously [2]. To investigate the capacity of exchange cations in a new LDH having Zn/Al in a molar ratio of 1:1, this LDH was synthesized by coprecipitation at increasing pH. As described for the $Mn_3Al_3(OH)_{12}(SO_4)_2Na.nH_2O$ [4], a solution of 1.0 mol $L^{-1}$ KOH were slowly added to acid solution of $ZnSO_4$ (24.447 mmol), $Al_2(SO_4)_3$ (12.229 mmol), and $K_2SO_4$ (4.074 mmol) in 100 mL of Milli-Q water, until the pH= 9.55 and at 90 °C, under $N_{2(g)}$ flow. The mixture was treated at 90 °C for 120 h, repeatedly centrifuged at 4000 rpm after redispersing in Milli-Q water and dried in an oven at 45 °C for 48 h. In the exchange reactions, an aqueous dispersion of Zn/Al-$SO_4$/K was stirred with an excess of $Li_2SO_4$ (Zn/Al-$SO_4$/K-Li) or $Na_2SO_4$ (Zn/Al-$SO_4$/K-Na) (three times the amount of intercalated potassium) for 72 hours at room temperature under $N_{2(g)}$ flow. Subsequently the materials were centrifuged at 4000 rpm, washed, and dried in an oven at 60 °C for 48 h. XRD analyses of the synthesized sample indicated a basal spacing of 10.84 Å, consistent with the intercalation of sulfate ions in double layer arrangement. A small contamination of Gibbsite (~3-5%) was also observed, slightly increasing the amount of Al in the analyses. The distance of two metals in the layers of the hexagonal cell (a=b= $2d_{110}$ = 3.054 Å) obtained for all compounds is consistent with the proposed compositions. FTIR indicated the characteristic bands attributed to O-H and Zn/Al-O and S-O bonds which supported by ICP-OES analyses, confirmed the proposed formula (Table 1).

Table 1 – ICP-OES analyses of the synthesized LDH and after exchange reactions.

| Compound | $Zn^{2+}$ | $Al^{3+}$ | $SO_4^{2-}$ | Alkali metal | Exchange (%) |
|---|---|---|---|---|---|
| Zn/Al-$SO_4$/K | 0.490 | 0.510 | 0.251 | 0.185 | - |
| Zn/Al-$SO_4$/K-Li | 0.489 | 0.511 | 0.223 | K= 0.044; Li= 0.126; K+Li = 0.170 | 74.1 |
| Zn/Al-$SO_4$/K-Na | 0.494 | 0.505 | 0.246 | K= 0.049; Na= 0.130; Na+K= 0.179 | 72.6 |

Ideal composition: $[Zn_{0.5}Al_{0.5}(OH)_2][(SO_4)_{0.25}(KOH)_{0.167}].nH_2O$ or $[Zn_6Al_6(OH)_{24}][(SO_4)_3(KOH)_2].nH_2O$.

After the cation exchange reactions, XRD patterns indicated a slight change of the basal distances (10.92 Å for Zn/Al-$SO_4$/K-Li and 10.94 Å for Zn/Al-$SO_4$/K-Na) while a=b cell parameters were kept constant. Also, ICP-OES analyzes confirmed the partial replacement of $K^+$ by $Li^+$ (72.6%) and $Na^+$ (74.1%). The bands in the FTIR spectra were kept in the same position indicating that $SO_4^{2-}$ was maintained in the interlayer space as well as hydroxide anions, in the presence of the new alkali metal cations. This is the first time that LDH with the molar ratio of $Zn_1Al_1$, intercalated with sulfate and neutral alkali metal hydroxides were synthesized and characterized.

## Agradecimentos/Acknowledgments

This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – Brazil (CAPES) – Finance Code 001, Conselho Nacional de Pesquisas - CNPq (FW: 300988/2019-2) and FINEP. A.R.S. also thanks CNPq for the Postdoctoral fellowship (163817/2020-0).

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**Área: MAT**

# Cellulose nanomaterials from rubberwood obtained via enzymatic hydrolysis route

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Keywords: *Rubberwood Biomass, Enzymatic hydrolysis, Physicochemical characterization.*

## Highlights

Evaluation of fibers from natural rubber tree as feedstocks for the production of nanomaterials. Reuse of agro industrial waste. Value aggregation to the natural rubber production chain.

## Resumo/Abstract

Novel strategy for the production of advanced materials from the waste generated in natural rubber exploration can improve the whole production chain (PARASHAR and CHAWLA, 2021). Lignocellulosic biomass from rubberwood has the potential for several applications, being formed by cellulose, hemicellulose, lignin, and inorganic compounds in smaller amounts. In this context, this work shows the characterization of nanomaterials obtained via enzymatic hydrolysis from bleached fibers of rubber tree. The fibers were mercerized with 5% (w/w) aqueous sodium hydroxide solution for 2h at 80 °C. Afterwards, the fibers were bleached with a solution composed of equal parts (v/v) of acetate buffer (27% by weight NaOH and 7.5% (v/v) glacial acetic acid, in distilled water) and aqueous sodium chlorite (1.7% by weight $NaClO_2$ in water). Then, the fibers were bleached twice with a solution of equal parts (v/v) of 4% NaOH (w/w) and 24% $H_2O_2$ (v/v). The bleached fiber was submitted to enzymatic hydrolysis in sodium citrate buffer (0.1 M, pH 5), with a solids load of 15% (w/v) and an enzymatic load (Cellic Ctec 3 - Novozymes®) of 10 mg / g of biomass in a shaker incubator at 50 °C. and 200 rpm for 48h. The characterizations were made by AFM measurements (Dimension V microscope - Veeco); X-ray diffraction (XRD) using a Shimadzu 6000 diffractometer with CuK$\alpha$ ($\lambda$ = 1,54 Å), at room temperature and with 2$\theta$ angle between 5 and 40° (1° min$^{-1}$); thermogravimetric analysis (TGA) in an inert atmosphere, using TA Instruments equipment, model Q500 with a heating rate of 10 °C/min from room temperature to 600 °C. The X-ray diffractograms showed that the main peaks corresponding to the crystallographic planes of Type I cellulose. The Bragg angles (2$\theta$) were: 16.0°, 22.4° and 34.6°, with the highest intensity in the crystallographic plane (002). The crystallinity index, calculated according to the method proposed by Segal (1959), was 57.8% for *in natura* fiber, 75.1% for bleached fiber and 80.8% after hydrolysis. Analyzing the thermograms, it was observed that the $T_{onset}$ of the fiber *in natura* was 289 °C, that of the bleached fiber was 292 °C and after the hydrolysis it was 327 °C. There was a change in the maximum degradation peak, in the final temperature of the process and in the amount of residue after the treatment. The AFM images exhibited structures rod-like shapes, with mean length of 349.9±169.6 nm and the diameter of 4.0±1.7 nm, after 48h to enzymatic hydrolysis. Our results showed that the obtained nanomaterials can be effectively extracted from the studied lignocellulosic source using the enzymatic route. The nanostructures showed high crystallinity, excellent thermal stability and high aspect ratio. Thus, nanomaterials presented important characteristics for the use in several applications, including as reinforcement.

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## Agradecimentos/Acknowledgments

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**Área: MAT** **Nº de Inscrição: ________**

# Characterization of colloidal metallic nanoparticles by microwave-assisted decomposition platform

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Keywords: *Nanoparticles Characterization, Sample Preparation, Microwave-assisted Decomposition, Elemental Analysis.*

## Highlights

Evaluation of the metal concentration in colloidal metallic nanoparticles with a complex matrix. Development of a microwave-assisted decomposition platform. Quantification of gold by ICP techniques.

## Abstract

The unique properties of the metallic nanoparticles (MNP) have been stimulated their employment on a wide range of applications, such as nanomedicine, optical sensors, catalysts, biosensors, and electronics. The MNP is mainly characterized in relation to its morphology, composition, and crystal phase, and just recently the characterization based on the metal concentration in the colloidal metallic nanoparticles gained attention. Such type of characterization is interesting for the evaluation of some features of the MNP, as for example its stability over storage time, separation and sampling steps, and synthesis yield. Another potential application for this characterization is the speciation and monitoring of metals from nanoparticles in the environment. Therefore, we report the development of a microwave-assisted decomposition platform for the quantification of gold in gold nanorods (AuNR) colloid. The aim of the work is proposing a procedure to decompose colloidal nanoparticles with complex matrix and high content of organic matter, such as surfactants and polymers. AuNR with high size and shape homogeneity (length of 57 ± 11 and diameter of 19 ± 3 nm) were synthesized via a seed-mediated growth method, in which the surfactant hexadecyltrimethylammonium bromide (CTAB) is the stabilizer of the nanoparticles. The CTAB stabilizes the AuNR by a bilayer structure around the nanoparticle, making difficult the complete decomposition of the high amount of organic matter, preventing the gold quantification. For this, the AuNR colloid was separated into three fractions: AuNR-total is the fraction of the colloid after synthesis, AuNR-res is the AuNR resuspended in water after a washing step, and AuNR-sob is the supernatant fraction removed from the washing step. Thus, several microwave-assisted decomposition procedures were tested with different combinations of sample volume, acid mixture and microwave program to guarantee the release of the $Au^{3+}$ ions during the decomposition procedure in the acidic media. After the optimization of the microwave-assisted decomposition, it was performed the determination of gold content in the AuNR fractions by both ICP OES and ICP-MS, in way to check the accuracy of the results. For AuNR-sob, Au concentration in solution quantified was around 1%, and for AuNR-total and AuNR-res was found Au concentration respectively around 100 and 105%, demonstrating that the seed-mediated growth method of AuNR exhibits high yield. Statistical hypothesis tests demonstrated statistically equality between the values determined by both techniques. The proposed microwave-assisted decomposition procedure demonstrates high robustness, efficiency, reliability, and reproducibility.

## Agradecimentos/Acknowledgments

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**Área: MAT**

# Chiral Nanoparticles of Cobalt Oxide Produced with Peptide

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Palavras Chave: *(Cobalt Oxide Nanoparticles, Peptide, Chirality, Magnetic Circular Dichroism)*

## Highlights

Chiral peptide used as template to produce cobalt oxide nanoparticles. Magnetic circular dichroism confirmed the formation of chiral nanoparticles.

## Resumo/Abstract

Chirality is a very active field of study; it is present in chemistry, medicine, biology and has potential applications in chiral sensing, catalysis and optical devices. Cobalt oxide nanoparticles were produced using the peptide “CHA” as template. The peptide is formed by the aminoacids (Fig. 1) cysteine, histidine and alanine. Chiral peptides *D*-CHA and *L*-CHA were used, and the aim of this project was to produce chiral cobalt oxide nanoparticles. UV-Visible spectroscopy was used to see spectral absorbance of the bands corresponding to cobalt oxide, TEM images were acquired to confirm the formation of the nanoparticles and magnetic circular dichroism (MCD) spectroscopy was used to investigate structural aspects of optically active chiral molecules, and to confirm that the peptide bonded to the particles and produced chiral particles. Likewise, the opposite signals obtained at the MCD indicate that the electronic structure of the catalyst has chirality on it.

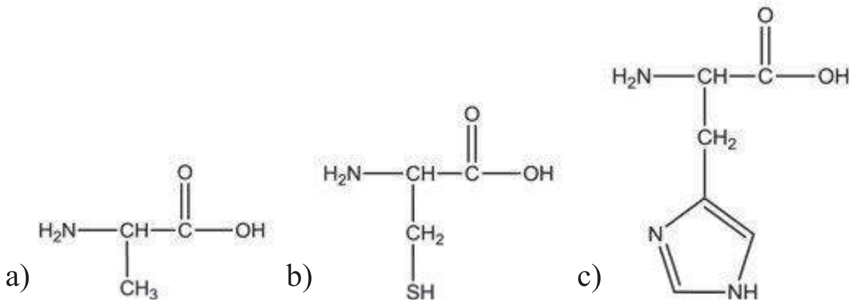

Figure1. Aminoacids that forms the peptide “CHA”: a) alanine; b) cysteine and c) histidine

## Agradecimentos/Acknowledgments

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**Area: _MAT_**

# CHITOSAN/POLYETHYLENE GLYCOL/LAPONITE NANOCOMPOSITES FOR SEED TREATMENT

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Keywords: Polymer/clay nanocomposites, Hydrogels, Argillominerals, Seed coatings.

## Highlights

Chitosan directly interferes in the maximum deformation supported. Nanocomposites formed a favorable for application as a coating. Preliminary tests showed the potential use of seeds.

## Abstract

Agriculture occupies one-third of the earth's surface, moving billions of dollars and generating countless jobs with the demand for new materials that do not cause adverse impacts to the environment. The commercial use of laponite and chitosan in an environmentally friendly manner and aiming at sustainable materials is a new challenge to consider in the bioeconomy. Polymer/clay nanocomposites are a class of organic/inorganic materials that have shown wide application in several areas, such as the coating of seeds that can be used in their protection, hydration, or release of agrochemicals. This work sought to synthesize and study polymer/clay nanocomposites based on polyethylene glycol (PEG), chitosan, and laponite. The samples were named PxQyLz, where z corresponds to the osmotic potential of the PEG solution used (MPa), y the mass amount (g) of chitosan, and z the mass (g) of laponite. The materials were characterized by infrared absorption spectrophotometry (FTIR), and the rheological was evaluated. In addition, Hanson lettuce seeds were coated, and germination was evaluated. The FTIR analysis (Figure 1) showed that all nanocomposites presented similar profiles, including samples P12Q0L06 and P08Q0L06, which do not present chitosan in their structure. Thus, it can be inferred, that they resemble the PEG spectrum. The band at 1,740 cm$^{-1}$ present higher intensity in sample P12Q0L06, can also be seen in sample P08Q0L06, and at a lower intensity in sample P08Q3L03 (dotted trace). This band can be attributed to the C-O bond of PEG and cannot be found in the other samples, probably due to the interaction PEG and chitosan. In Figure 2, the samples P12Q0L06 and P08Q0L06 did not present a linear viscoelastic region. This result suggests that the chitosan influenced the rheological of the nanocomposites. In this case, the sample flows and may like a viscous liquid, as the variation of G' as a deformation function is observed. The increase in chitosan concentration increases the mechanical strength due to the greater crosslinked polymeric networks. Such characteristics may favor seed coatings. They showed a well cross-linked, low-fluid system, conducive to an application to ensure uniformity during coating.

Figure 1: FTIR spectra

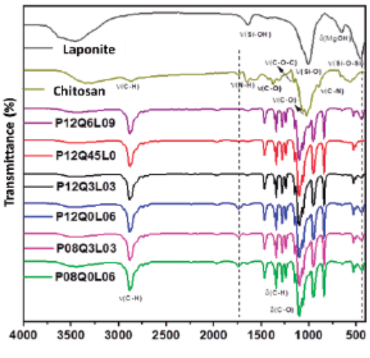


Figure 2: Strain Scanning Test

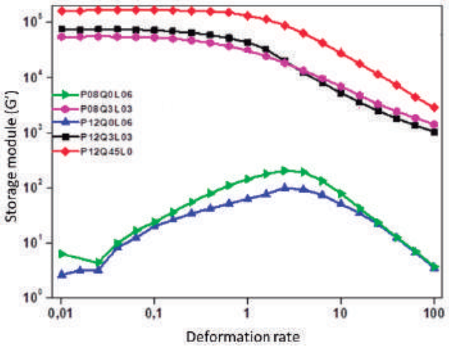
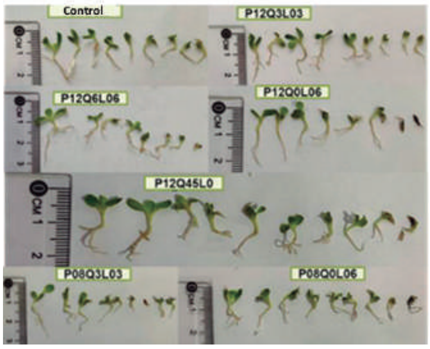


Figure 3: Germination tests



Hanson's lettuce seeds coated with the treatments showed reasonable germination rates, with emphasizing on samples P12Q6L09 and P12Q45L0 that showed 100% germination, exceeding the germination observed by the control. Except for one seed that received the P12Q0L06 coating, which has no chitosan, the seeds had no fungi visually detected (Figure 3). It is worth noting that chitosan has antifungal activity, and the coating showed promise in preliminary tests.

## Acknowledgments

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**Área: MAT**

# Comparison of synthesis methodology for the oxides $SiO_2$-$ZrO_2$ and $SiO_2$-$ZrO_2$-BaO for application in liquid chromatography

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Keywords: *sílica, Glycerol, HPLC, Pechini, chitosan.*

## Highlights

- Synthesis of silica-based oxides for use as a stationary phase.
- Development of new materials using Pechini's methods and metal-chitosan complexation

## Abstract

Silica is the most used material in liquid chromatography either as a chromatographic support or even as a stationary phase due to its characteristics, such as the high surface area. The modification of silica has been an alternative to improve some properties of this material, such as the insertion of other metallic oxides, providing greater chemical and mechanical resistance. In this work, the modification of silica was carried out, aiming its use in liquid chromatography, with the oxides $ZrO_2$ and BaO, by the modified Pechini method (MPE), using glycerol as polyol, and by the metal-chitosan complexation method (CMQ), in order to give better properties to the final material, such as a greater surface area, to increase its chromatographic efficiency, and greater chemical resistance. The oxides $SiO_2$-$ZrO_2$ (SZ) and $SiO_2$-$ZrO_2$-BaO (SZB) were synthesized by both methods. To elucidate the structural and textural properties of these materials, they were then characterized by thermogravimetric analysis (TGA), infrared absorption spectroscopy (FTIR), analysis of nitrogen physisorption at 77 K (BET) and X-ray diffraction (XRD). The TGA analyzes showed that the synthesized materials had an effective calcination, with the absence of organic matter and presented a good thermal resistance, without degradation and with mass losses between 4 and 8%, close to 100 °C, referring to the loss of adsorbed water. In the FTIR analysis, the loss of signal at 800 $cm^{-1}$ (Fig. 1) present in pure silica was observed in the spectra, showing that there is a change in the Si-OH groups with the insertion of metals in this bond. In the analysis of nitrogen Physisorption, by the BET method, a greater surface area was observed for the SZB oxide synthesized by the CMQ method (203 $m^2/g$), whereas the SZ oxide presented a greater area when synthesized by the MPE method (335 $m^2/g$) , however, the oxides synthesized by Pechini had a larger pore diameter, with bottle-shaped pores, as could be observed by the H2-type hysteresis (Fig. 2A) for these materials (SZ = 37 Å and SZB = 166 Å), while the materials synthesized by CMQ showed H1 isotherms (Fig. 2B), which characterize cylindrical pores. By XRD it was observed that the materials were amorphous. After the characterizations, the modification of silica with the oxides $ZrO_2$ and BaO was noticed, as well as a high surface area (335 $m^2/g$) and high thermal and chemical resistance, characteristics that are important for the application of these materials in liquid chromatography.

**Fig 1: FTIR analysis of oxides synthesized by Pechini and metal-chitosan complexation**

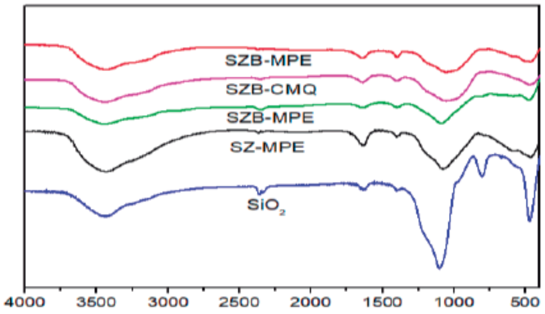
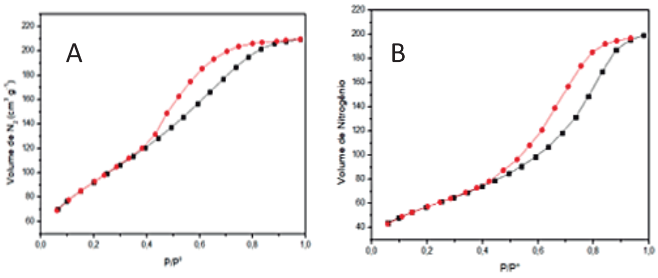


**Fig 2: Isotherms obtained by BET for $SiO_2$-$ZrO_2$ oxides synthesized by Pechini (A) and metal-chitosan complexation (B).**



## Acknowledgments

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**Área: MAT** **Nº de Inscrição: 00444**

# Controlled Release Study of Pharmaceuticals Adsorbed in Cellulose/Ionic Liquid Grafted Matrix

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Palavras Chave:*(Erythromycin, Cimetidine, Naproxen, Indometacin, Siepmann - Peppas kinetic model.*

## Highlights

*cell[(MeO)$_2$Sipmim]Cl* was used to desorb molecules with different types of structures under biological mimicked conditions; release profile occurs according to Siepmann – Peppas model.

## Resumo/Abstract

Cellulosic derived material grafted with ionic liquid - *cell[(MeO)$_2$Sipmim]Cl* was used to adsorb/desorb pharmaceuticals such as Erythromycin, Cimetidine, Naproxen, Indometacin, under biological mimicked controlled conditions. The material *cell[(MeO)$_2$Sipmim]Cl* was previously described in S.S.O.Santos; R.D.Sinisterra, M.G.Speziali; *Eur. Pol. J.*, Vol.124, 2020, 109490. Table 1 shows adsorption results for previously selected pharmaceuticals. Desorption experiments were done using a *phosphate buffer solution* (PBS) – pH 7,4. Reactors were kept under 37±1 ºC and constant stirring. At predetermined intervals, samples were taken and analyzed using UV-spectroscopy. Each molecule was read under a different wavenumber where it presented maximum absorption. The measures results were used combined with calibration curves to plot a cumulative release graph for each pharmaceutical, shown in Figure 1.

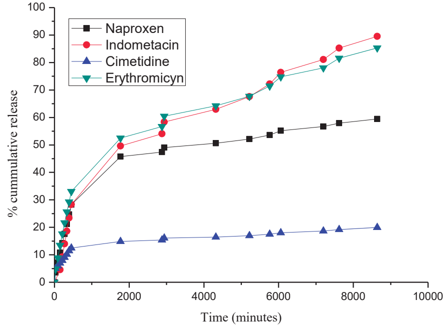

**Figure 1: Kinetics release profile for distinct pharmaceutical adsorbed in *cell[(MeO)$_2$Sipmim]pharmaceuticals***

**Table 1: Adsorption results for selected pharmaceuticals**

| Pharmaceutical / mass (g) | *cell(MeO)$_2$Sipmim]Cl* (g) | Pharmaceutical adsorbed (g) |
|---|---|---|
| Indometacin (1,1869) | 0,1869 | 1,3693 |
| Naproxen (0,9981) | 0,1820 | 0,0888 |
| Erythromycin (1,7620) | 0,0966 | 0,2584 |
| Cimetidine (1,1908) | 0,1850 | 0,6268 |

Cumulative release curves presented two distinct regions, namely: the first one from 0 ≈10hours characterized by a "*burst effect*" and the second one similar to a straight line. The linear regression for the second part of the curve was fitted according to Siepmann-Peppas kinetic release model: $\frac{M_t}{M_\infty} = k_0 t + b$ and the resulted equations were shown as follows: Erythromicyn $y = 44{,}1337 + 0{,}0048x$ $R^2 = 0{,}987$; Cimetidine $y = 0{,}1348 + 7{,}31.10^{-4}x$ $R^2 = 0{,}976$; Indometacin $y = 38{,}497 + 0{,}0059x$ $R^2 = 0{,}987$; $y = 42{,}16 + 0{,}00203x$ $R^2 = 0{,}986$ Naproxen. Obtained results have shown that *cell[(MeO)$_2$Sipmim]pharmaceuticals* can be used efficiently for controlled drug release with different pharmaceuticals with distinct chemical structures beyond that anionic species, as previously reported by authors.

## Agradecimentos/Acknowledgments

SSOS and BS thank to FAPEMIG for her scholarship and financial support; MGS acknowledges the financial support given by Research Pro-rectory UFOP.

**Área: MAT**

# Corrosion inhibitor for carbon steel in acidic medium from jatobá fruit shell extract (JFSE) – Mechanism and thermodynamic considerations

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*Keywords: Plant extract; Green corrosion inhibition; Electrochemical tests; Surface analysis; Thermodynamic data.*

## Highlights

The jatobá fruit shell extract (JFSE) acts as a corrosion inhibitor through the adsorption of organic molecules that effect a geometric block on the carbon steel surface.

## Resumo/Abstract

Corrosion is a thermodynamically spontaneous phenomenon for some metals and their alloys, especially steel [1]. The use of natural extracts as corrosion inhibitors is an alternative that shows effectiveness. This is an alternative that fits the concepts of green chemistry [2]. Aqueous JFSE was tested as an eco-friendly corrosion inhibitor for carbon steel in 0.5 mol $L^{-1}$ $H_2SO_4$. Electrochemical tests: potentiodynamic polarization (PDP) and electrochemical impedance spectroscopy (EIS) were performed to evaluate the extract as a corrosion inhibitor. The experiments were performed at 25 ºC, except for the temperature dependence study, which was conducted at 15, 25, 35, 45 and 55 ºC. The activation parameters of the corrosion process were acquired using Arrhenius and transition-state plots. Adsorption isotherms were plotted from PDP data. Surface analysis was carried out by scanning electron microscopy with energy dispersive spectroscopy (SEM/EDS). The potential of zero charge ($E_{pzc}$) was obtained from EIS experiments carried out at different applied potentials ($E_{appl}$). The value for $E_{pzc}$ in the absence and presence of the JFSE was -0.476 V. Antropov's rational corrosion potential ($E_r$) was calculated from $E_{pzc}$ and the corrosion potential ($E_{corr}$) and provides a numerical value for the relative electrode charge in a specified medium. Values of $E_r$ = +0.064 and +0.035 V were determined in the absence and presence of 1233.4 mg $L^{-1}$ JFSE, respectively, indicating that the electrode is positively charged in 0.5 mol $L^{-1}$ $H_2SO_4$ solutions. The SEM micrographs showed a reduction in the damage caused to carbon steel in acidic medium in the presence of JFSE, compared to the experiment in the absence of the extract. The EDS spectra has shown a decrease in the peak referring to the oxygen atom and an increase in the peak referring to the carbon atom, which confirms the hypothesis that the increase in the concentration of organic molecules from the adsorption of JFSE on the steel surface decreases the formation of oxides as corrosion products. The Langmuir isotherm model was adequate to explain the adsorption of the species contained in the JFSE to carbon steel. This indicates the formation of an adsorbed monolayer without the influence of lateral interaction between adsorbates. The effect of temperature on the corrosion of steel in the absence and presence of 1233.4 mg $L^{-1}$ JFSE showed an energy of activation ($E_a$) and enthalpy of activation ($\Delta^{\ddagger}H^{o}$) around 2.5 times higher than the value in its absence, which means that the energy barrier for the occurrence of the iron oxidation reaction becomes higher, and thus the corrosion kinetics is slowed with the use of the JFSE. The proposed mechanism support that organic molecules present in the JFSE replace water and $H_3O^+$ at the steel surface and adsorption occurs via polar groups such polyphenols. The hydrophobic part of the organic molecules forms a protective film that decreases the access of the corrosive solution to the steel surface.

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## Agradecimentos/Acknowledgments

The authors thank FAPESC, CAPES, CNPq, LCME-UFSC and UFMS-Campus Pantanal.

**Área: MAT**

# Degradation of ciprofloxacin by green cobalt oxide quantum dots

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Palavras Chave: *Cobalt Oxide, Quantum Dots, Ciprofloxacin, Green Synthesis, Emergent Pollutant.*

## Highlights

$Co_3O_4$ QDs produced by green synthesis promoted degradation of ciprofloxacin. $Co_3O_4$ QDs are activated by UV light. The inactivation of ciprofloxacin by $Co_3O_4$ QDs is assigned to oxidative processes.

## Resumo/Abstract

Ciprofloxacin (CIPRO) is a fluoroquinolone antibiotic extensively used to treat various bacterial infections. The extensive use of CIPRO has promoted its accumulation in diverse aquatic environments as an emergent pollutant. Concentrations of CIPRO found in surface and ground waters and seas vary from ng to mg/L and represent a real risk for the rise of new resistant bacterial strains. The complex and stable chemical CIPRO structure is not favorable for biological degradation. However, magnetic $Co_3O_4$ quantum dots ($Co_3O_4$ QDs) with 5 nm of mean diameter synthesized using biomolecules from tomato (Solanum lycopersicum L.) seed extract were efficient to promote photodegradation of this emergent pollutant under UV irradiation. CIPRO degradation was corroborated by UV-visible and Fourier Transform Infrared (FTIR) spectrophotometry. The photodegradation using UV-light in the presence of $Co_3O_4$ QDs was the more efficient strategy to impair the bactericidal action of CIPRO and, consequently, to avoid the development of bacteria-resistant strains. The $Co_3O_4$ QDs are a low-cost, efficient, and green option for CIPRO degradation.

## Agradecimentos/Acknowledgments

Supported by FAPESP 2017/02317-2 (ILN-C), 2019/01425-1 (JDB) and CNPq 313111/2021-9, NBB/UFABC, CEM/UFABC for access to facilities.

**Área: MAT**

# Desenvolvimento de fotocatalisadores à base de óxidos de metais para aplicação em conversão fotocatalítica de derivados da biomassa

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Palavras Chave: *Heterojunção, $SnO_2$/NiO, Fotocatálise.*

## Highlights

- Development of photocatalysts based on metal oxides for application in photocatalytic conversion of biomass derivatives;
- $SnO_2$/NiO heterojunction synthesis for photocatalytic activity.

## Resumo/Abstract

Nesse estudo, foi realizado a síntese pelo método de precipitação dos fotocatalisadores $SnO_2$ e NiO e pelo método de co-precipitação sintetizou-se a heterojunção $SnO_2$/NiO-5%. Os óxidos metálicos, $SnO_2$ e NiO - semicondutores tipo *n* e tipo *p*, respectivamente - são fotocatalisadores ecologicamente corretos, termicamente e quimicamente estáveis[1]. E, à saber, o acoplamento de semicondutores com diferentes elementos de *bandgap* produz fotocatalisadores com alta atividade e estabilidade[2]. Os materiais foram caracterizados por DRX, FTIR, DRS e a área superficial foi calculada usando o método desenvolvido por Brunauer, Emmett e Teller (B.E.T.). O DRX (Figura 1A) evidenciou a fase rutilo para o $SnO_2$ (ICSD – 9163) e padrões característicos da fase estrutural cúbica de face centrada para o NiO (ICSD – 9866). Para heterojunção $SnO_2$/NiO-5%, a análise de DRX revelou que a adição do NiO proporcionou alteração na rede cristalina do $SnO_2$, ocasionando uma diminuição na intensidade dos picos de difração. Na Tabela 1, notamos que a adição de NiO na estrutura do $SnO_2$ provocou uma diminuição na cristalinidade do material, evidenciada pela diminuição do valor do tamanho médio de cristalito em comparação aos óxidos puros. Pelo FTIR (Figura 1B) constatamos que os materiais apresentam bandas em torno de 3440 $cm^{-1}$ e 1620 $cm^{-1}$, 1700 $cm^{-1}$, 450-650 $cm^{-1}$ atribuídas à vibração de estiramento do grupo OH, vibrações de estiramento C=O e interações metal-oxigênio, respectivamente. O DRS (Figura 1C) evidenciou que o $SnO_2$/NiO-5% possui uma banda de absorção intensa em ~380-520 nm, que presume modificação nas propriedades eletrônicas na rede do $SnO_2$, pois a inserção de outro metal, nesse caso o níquel, pode ter favorecido o fluxo de elétrons entre os níveis eletrônicos do $SnO_2$ [3]. Os dados de reflectância foram usados na equação de Tauc e resultaram nos valores de *bandgaps* de 2,38 eV para o $SnO_2$, 3,37 eV para o NiO e 2,0 eV para o $SnO_2$/NiO-5% (Figura 1C-1). Nota-se que o valor de *bandgap* para heterojunção exibe um decréscimo se comparado aos óxidos puros, o que pode ser promissor para ativação deste material com comprimentos de onda na faixa visível do espectro eletromagnético. A heterojunção apresentou um valor de área superficial de 62,2 $m^2$/g (Tabela 1), superior aos óxidos individuais. Este resultado demonstra que a área superficial da heterojunção exibiu uma associação inversa com o tamanho do cristalito, pois sabe-se que quanto menor o valor do tamanho de cristalito obtém-se um material com cristalinidade pouco definida e consequentemente com mais defeitos estruturais e maior valor de área superficial [1].

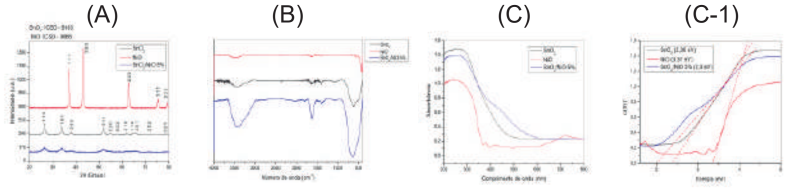

**Figura 1.** (A) Difração de Raios-X; (B) FTIR; (C) DRS; para NiO, $SnO_2$, e $SnO_2$/NiO-5%.

| Amostra | Tamanho médio do cristalito (nm) | $S_{BET}$ ($m^2$/g) |
|---|---|---|
| $SnO_2$ | 15,4 | 19,4 |
| NiO | 20,9 | 23,7 |
| $SnO_2$/NiO-5% | 9,0 | 62,2 |

**Tabela 1.** Tamanho médio do cristalito e área superficial dos óxidos sintetizados.

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**Área: MAT** **Nº de Inscrição: 1023**

# *DESIGN* DE UM NOVO MATERIAL CONVERSOR DE LUZ A BASE DE $Eu^{3+}$ COMBINADO COM O LIGANTE NATURAL LAPACHOL E $(EuDBM)_3.2H_2O$

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Palavras Chave:*Lapachol,Dibenzoilmetanato,Európio,Emissão,Luminescente.*

## Highlights

DESIGN OF A NEW CONVERTER OF LIGHT MATERIAL BASED ON $Eu^{3+}$ COMBINED WITH NATURAL LAPACHOL ON $Eu(DBM)_3.2H_2O$.In presente work, we carried out the synthesis of a $Eu^{3+}$-dibenzoylmethanate complex that integrates the natural ligand Lapachol, as an inexpensive alternative that potentially amplifies the emission.

## Resumo/Abstract

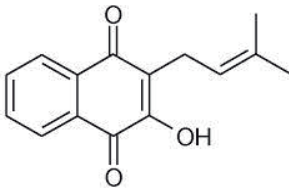

Figura 1: Lapachol-(LAP)

Neste trabalho, um novo complexo luminescente de Európio, $Eu^{3+}$, foi sintetizado utilizando o ligante natural Lapachol (LAP), [2-hidroxi-3-(3-metil-2-butenil)-1,4-naftoquinona] – figura 1 , como forma de amplificar a emissão final do material de partida, o sistema $[Eu(DBM)_3.2H_2O]$, com DBM=dibenzoilmetanato. O uso do lapachol é estratégico pois o comprimento de onda do seu pico de absorção no UV (280 nm) favorece o efeito antena. Ele pode ser utilizado como ligante em compostos de coordenação, pois sua função cetoenol garante um potencial quelante; além de ser um material de baixo custo e abundante no Brasil, pois pode ser obtido da serragem de madeiras como o Ipê Roxo, Ipê Amarelo e Pau d'Arco, o que também reduz o custo da produção do complexo final, uma vez que a serragem é descartada pelas serrarias onde as madeiras são beneficiadas. O lapachol foi extraído da serragem da madeira de Pau d'Arco em solução alcalina, e recristalizado em etanol (PF: 140°C). Fez-se uma cromatografia em camada delgada (CCD) com uma amostra do Lapachol extraído e recristalizado, utilizando-se-se como fase estacionária uma cromatoplaca de alumínio (Sílica Gel 60), c/indicador UV254, e fase móvel uma mistura de acetato de etila e hexano 3:7, contendo um único registro com fator de retenção ($R_f$) de 0,51, o que ratifica a pureza do material. O sistema de partida, $[Eu(DBM)_3.2H_2O]$, foi sintetizado a partir da reação estequiométrica, $EuCl_3.6H_2O$:3HDBM, em torno de pH=7.0, em meio aquo/etanólico. As moléculas de água que contêm osciladores de alta frequência (grupo, OH), inibidores de emissão foram substituídas na primeira esfera de coordenação do sistema inicial por uma molécula de LAP, que se coordena de forma bidentada ao $Eu^{3+}$, formando o complexo $[Eu(DBM)_3.LAP]$. O espectro no IV do lapachol puro mostra claramente bandas dos principais grupos funcionais como C=O (1651 $cm^{-1}$) e O-H (3351 $cm^{-1}$). O espectro no infravermelho do novo material revela que a banda atribuída ao grupo carbonila (C=O) é deslocada para um menor comprimento de onda, sendo o deslocamento provocado pela coordenação do oxigênio ao metal central que enfraquece o caráter da dupla ligação, tais dados indicam que o oxigênio fenólico do lapachol está coordenado ao $Eu^{3+}$. O espectro de emissão obtido a 298K na faixa de 500-720 nm, com o monitoramento da excitação em torno de 366nm mostra bandas correspondentes às transições do estado excitado $^5D_0$ para o fundamental $^7F_J$ (J = 0, 1, 2, 3 e 4). A amostra apresenta a emissão, $^5D_0\rightarrow{}^7F_0$, indicando que o centro metálico pode possuir uma simetria *Cnv, Cn,* ou *Cs*. A única linha de emissão na transição $^5D_0\rightarrow{}^7F_0$ em torno de 580 nm pode ser atribuída à existência de um único sítio de simetria em torno do íon $Eu^{3+}$, além de indicar o alto grau de pureza do novo material. A característica proeminente notada no espectro de emissão é a alta intensidade da transição $^5D_0\rightarrow{}^7F_2$, em torno de 612nm (a maior intensidade da transição $^5D_0\rightarrow{}^7F_2$ em relação à $^5D_0\rightarrow{}^7F_1$, em torno de 590 mm, indica a ausência de centro de simetria). Os resultados iniciais apontam para alternativas de novas combinações envolvendo ligantes de baixo custo para possível fabricação de novos materiais luminescentes, ou seja, a possibilidade da arquitetura de dispositivos fotoluminescentes baratos, com alta eficiência quântica o que possibilitaria maior competitividade em relação a materiais similares disponíveis no mercado e com melhor custo-benefício.

## Agradecimentos/Acknowledgments

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

# Detection of SARS-CoV-2 spike protein using polyclonal IgG attached to gold nanoparticles by dynamic light scattering (DLS): AuNP size effect

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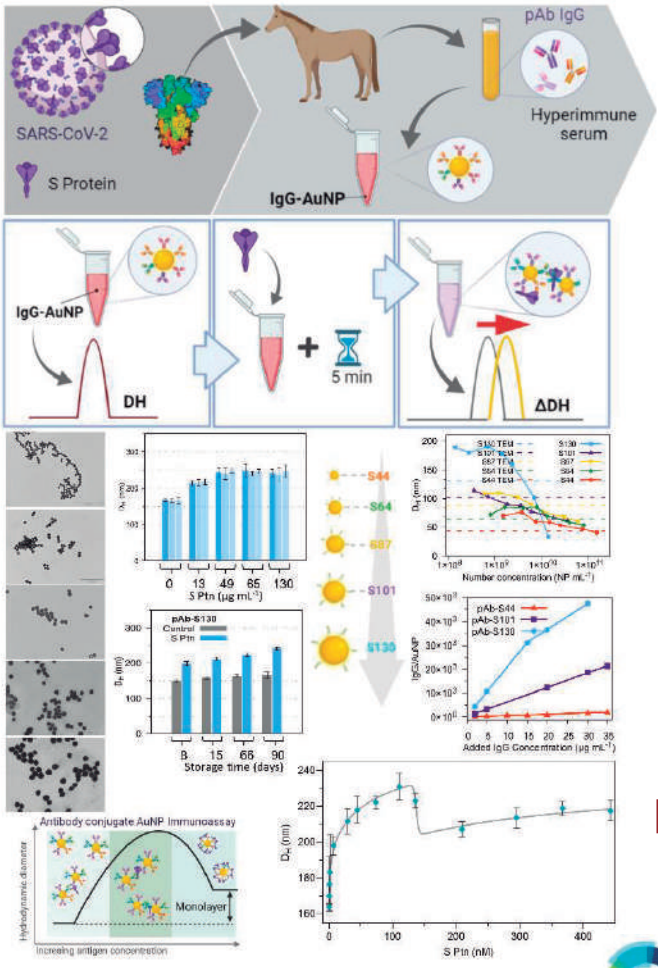
Palavras Chave:*( Immunoassay, Gold nanoparticles Size Effect, Dynamic Light Scattering, SARS-CoV-2 Spike Protein).*

## Highlights

Fast detection of S protein using polyclonal horse antibody attached to gold nanoparticles. Detection by dynamic light scattering. Detection limit 30 pM. Influence of AuNP sizes from 44 to130 nm.

## Abstract



Due to the unprecedented and ongoing nature of the coronavirus outbreak, the development of rapid immunoassays to detect COVID 19 (SARS-CoV-2) and its highly contagious variants is an important and challenging task. We report the development of polyclonal antibody-functionalized spherical gold nanoparticle biosensors (pAb-AuNPs) as well as the influence of the nanoparticle sizes on the immunoassay response to detect the SARS-CoV-2 spike protein (S protein) by dynamic light scattering (DLS). Monitoring the increment in the hydrodynamic diameter (ΔDH) by DLS measurements in the antigen-antibody interaction, S-protein can be detected in only 5 minutes. The larger the nanoparticles, the larger ΔDH in the presence of S protein. From adsorption isotherm, the calculated binding constant ($K_D$) was 83 nM and the estimated limit of detection was 13 ng mL$^{-1}$ (30 pM). The biosensor was stable up to 90 days at 4 °C. Therefore, the biosensor developed in this work could be potentially applied as a fast and sensible immunoassay to detect SARS-CoV-2 infection in patient samples.

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Sociedade Brasileira de Química
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FAPERJ Fundação Carlos Chagas Filho de Amparo à Pesquisa do Estado do Rio de Janeiro

**Área: MAT** **Nº de Inscrição: 00002**

# Development and characterization of materials involving Photoactive Tungstic Keggin Species on Faujasite Y Zeolite

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Keywords: *Tungstic Keggin Species, Faujasite Y Zeolite, Structural and Physicochemical Characterization.*

## Highlight

An extensive structural and physicochemical characterization showed the generation of new catalytic materials with better activity properties (lower band gap values and higher acidity).

## Resumo/Abstract

For a better future for humanity, chemical processes must be increasingly effective, causing less damage to the environment and generating products with high selectivity [1]. In this way, the research into new methodologies to increase the properties of catalysts materials is of vital importance [2]. Thus, the objective of this study was evaluated the effect of insertion of Tungstic Keggin Species ($H_3PW_{12}O_{40}$, HPW) on the structure of Faujasite Y zeolite, as well as the possible generation of more active materials to be use in photodegradation reactions. Synthesized by wetness impregnation method, the materials were characterized by several techniques: EDX-FRX, $N_2$ physisorption, XRD, FT-IR, SEM, MAS-NMR of $^{31}P$, $^{27}Al$ and $^{29}Si$, TG/DTG, DRS-UV-Vis, leaching test and pyridine gaseous adsorption. The results indicated that the state of the zeolitic structure after the process can interfere deeply in the properties of the final materials. The XRD revealed that the materials were formed by the deposition of nanoclusters of small units of Keggin (5 nm) on the surface of the zeolite and that even after such process, the crystallinity remained high (average of 75%). Morphological, textural parameters and results of MAS RMN $^{27}Al$ indicated that the zeolitic structure underwent slight modifications that resulted in the formation of materials of lower specific area but with more mesopores. The leaching test did not indicate losses of HPW suggesting good stability, a hypothesis confirmed by MAS RMN $^{31}P$ which demonstrated the maintenance of HPW on zeolite, with a strong interaction (-13.3 ppm). A decrease in the calculated band gap energies, and greater quantity and strength of available acid sites were observed with the addition of HPW, indicating that the modified materials would increase the capacity to absorb higher wavelength radiation, favoring photocatalytic processes.

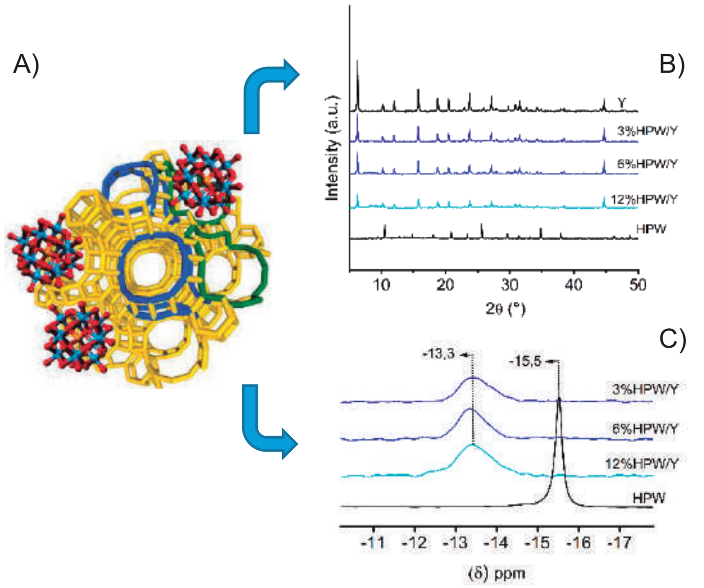

**Figure 1.** A) 3D graphic representation, B) XRD patterns and C) $^{31}P$ MAS-NMR of the developed materials.

**Table 1.** Specific surface area ($S_{BET}$), total number of acid sites obtained by adsorption of Pyridine ($n_{ads}$) and optical band gaps ($E_g$, calculated from DRS-UV-Vis) of the developed materials.

| Materials | $S_{BET}$ (m²) | $n_{ads}$ (mmol) | $E_g$ (eV) |
|---|---|---|---|
| Y | 907 | 0,7 | 5,2 |
| 3%HPW/Y | 666 | 0,9 | 4,5 |
| 6%HPW/Y | 564 | 1,1 | 4,3 |
| 12%HPWY | 460 | 1,2 | 4,0 |
| HPW | 5 | 1,0 | 4,1 |

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**Área: MAT** **Nº de Inscrição:** 01341

# Development of MCM-41-$NH_2$ with "green" iron oxide for Methyl Orange adsorption.

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Keywords: *Adsorption, MCM-41, functionalization, Iron, tea, dye.*

## Highlights

Mesoporous silica MCM-41 was synthesized and functionalized with amino groups; Iron oxide nanoparticles were synthesized from black tea extracts; Adsorbent capability was tested in the removal of azo dye in water.

## Resumo/Abstract

Adsorption is an efficient technique for removing micropollutants such as dyes. In order to produce a material with high adsorbent capacity, four different materials have been developed. The mesoporous silica was identified as MCM-41, and then aminated through reflux with toluene and APTES, named as MCM-41-$NH_2$. Iron nanoparticles were also synthesized through the reaction between $FeCl_3{\cdot}6H_2O$ and black tea extract (Dr. Oetker) in the presence of MCM-41 and MCM-41-$NH_2$. These materials were named as $^{BT}$Fe-MCM-41 and $^{BT}$Fe-MCM-41-$NH_2$, respectively. The catalysts were characterized by XRD, FTIR, thermogravimetric analysis, ASAP, AAS and SEM. The hexagonal tubular structure of the mesoporous silica was confirmed by XRD, while FTIR spectra confirmed the presence of the silanol groups at 3430 $cm^{-1}$, adsorbed water at 1630 $cm^{-1}$ and siloxane at 1110 $cm^{-1}$. The spectra of the material $^{BT}$Fe-MCM-41-$NH_2$ presented two bands at 1400 $cm^{-1}$ and 1500 $cm^{-1}$, associated with phenyl groups, confirming the incorporation of the organic compounds from the tea polyphenols. The TG curves showed the highest organic content for $^{BT}$Fe-MCM-41-$NH_2$, 25.9 wt%, while $^{BT}$Fe- MCM-41, MCM-41 and MCM-41-$NH_2$ results showed only 12.9, 5.7 and 14.2% wt, respectively, indicating that organic materials from tea and amino groups from the APTS were incorporated to the catalyst. ASAP analyzes showed a significant reduction in the specific surface area after functionalization, SEM images indicate the morphology of the materials as asymmetrical, highlighting the presence of some rounded particles and rods, and the atomic absorption spectroscopy results demonstrate a low incorporation of the iron nanoparticles to the silica, only 0.35% for $^{BT}$Fe-MCM-41 and 0.42% for $^{BT}$Fe-MCM-41-$NH_2$. The adsorption studies carried out towards the azo dye methyl orange were conducted at 25 °C, pH 4.0, the volume of the dye solution used was 100 ml in a concentration of $5.0 \times 10^{-5}$ M for 25 mg of adsorbent. The precursor materials did not show promising adsorption capability ($q_{e\ \mathrm{MCM\text{-}41}} = 5.85$ and $q_e$ MCM-41-$NH_2$ = 27.45), but the final material $^{BT}$Fe-MCM-41-$NH_2$, combining functionalized support with the green iron nanoparticles proved to be a material with a high adsorbent capacity (with $q_e = 64.99$) for the methyl orange dye. Removal increased from 8% to 85% when compared to pure MCM-41, at that same test conditions. The adsorption isotherms were determined for the material ($^{BT}$Fe-MCM-41-$NH_2$). It was observed that the Langmuir isotherm adjusted more accurately to the adsorption tests, exhibiting a higher correlation coefficient value ($R^2 > 0.99$) than the other studied models (Freundlich $R^2 = 0.93464$, Tempkin $R^2 = 0.92331$ e Dubinin- Radushkevich $R^2 = 0.82886$.) The $R_L$ equilibrium parameter was calculated (0.32) and a favorable adsorption was observed. In conclusion, very promising adsorbents for azo dye were prepared in a sustainable and green approach.

## Agradecimentos/Acknowledgments

Thanks to UERJ, CAPES, FAPERJ, CNPQ.

**Área: MAT**

# Discoloration of Indigo Carmine dye using titanium dioxide nanoparticles immobilized on cellulose membranes

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Palavras Chave: *cellulose, indigo carmine, titanium dioxide, catalysis, biopolymer*

## Highlights

Heterogeneous catalysts based on cellulose membranes; $TiO_2$ nanoparticles immobilized on cellulose membranes; degradation of indigo carmine dye; Photocatalysts based on cellulose and titanium dioxide.

## Resumo/Abstract

Titanium dioxide nanoparticles ($TiO_2$NP) are one of the most studied photocatalysts due to their capability to degrade different types of pollutants, such as dyes in aqueous media. Despite their established activity, the agglomeration of these nanoparticles during their use should be avoided to maintain their catalytic capability and to allow their reuse. In this sense, the immobilization of $TiO_2$NP in polymeric matrices is an attractive approach to circumvent these inconveniences. Among them, cellulose is one of the most fascinating matrices, since it is abundant, comes from renewable sources and it is insoluble in an aqueous medium. In this context, in this study, we show a new simple and fast method to prepare cellulose membranes containing $TiO_2$NP nanoparticles (commercial - P25 and synthesized ones – $TiO_2$NP). $TiO_2$ nanoparticles were synthesized from the slow hydrolysis of titanium (IV) isopropoxide in an acidic medium [1]. The cellulose membranes were prepared by mixing dissolved microcrystalline cellulose in chloride 1-butyl-3-methylimidazolium (BMImCl) and $TiO_2$NP or P25. The membranes were formed by the addition of the water (regeneration process) in the cellulose mixtures, according to a procedure already studied in our research group [2] (Figure 1). The membranes contain amorphous cellulose (Type-II) and nanoparticles distributed homogenously on the polymeric matrix (Figure 2). In the case of the membranes containing P25 bigger particles and agglomerated were seen. The membrane containing synthesized $TiO_2$ nanoparticles has anatase phase exclusively, while P25 has also the rutile phase. The content of titanium was lower in the membrane prepared with synthesized $TiO_2$ (7.5 wt %). than that with P25 (10 wt %). The membranes containing$TiO_2$ and P25 showed bandgap values around 3.05 eV e 3.84 eV, respectively. These values were higher than those found for the non-immobilized $TiO_2$ samples. The photocatalytic test was evaluated using 20 ppm indigo carmine (IC) solution with pH=2 under a mercury vapor lamp (125W). The discoloration of IC was twice faster for Cel_$TiO_2$NP when compared to Cel_P25 film and it was used at least 5 times without losing activity.

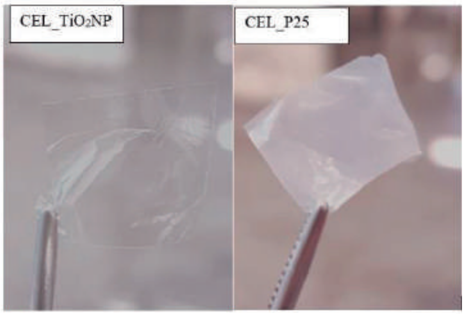

Fig. 1: Photos of the membranes

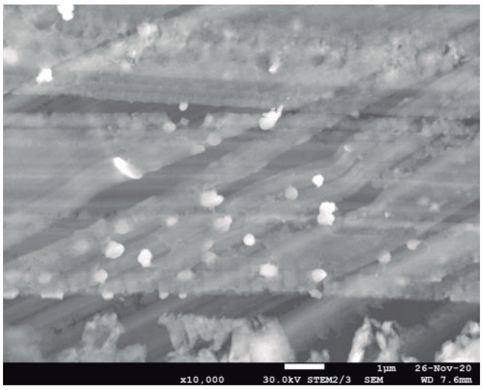

Fig. 2: STEM image of the Cel_$TiO_2$NP

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## Agradecimentos/Acknowledgments

*This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – Brasil (CAPES) – Finance Code 001. The authors gratefully acknowledge the financial support from FAPESP (Grant Numbers: 2018/20826-4; 2017/17844-8 and 2019/08582-5).*

**Área: MAT**

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

# Efeito do solvente de cristalização na temperatura de transição de spin do complexo bis(terpiridina)cobalto(II)

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Palavras Chave: composto de coordenação, transição de spin, magnetismo, spin crossover, molecular switch

## Highlights

The effect of guest solvent molecules in the spin crossover temperature of a bis(terpyridine)cobalt(II).

This work reports the synthesis, structural analysis and magnetic investigation of a bis(terpyridine)cobalt(II) complex, highlighting how reversible adsorption/desorption of guest solvent molecules affects the temperature dependence of spin transition process.

## Resumo/Abstract

Os interruptores moleculares têm sido buscados devido ao seu potencial de aplicação em dispositivos de armazenamento de informação e sensores, onde se destacam compostos que exibem o fenômeno de transição de spin (Spin Crossover - SCO). O fenômeno de SCO ocorre em complexos octaédricos, como, uma conversão reversível e controlada entre os estados de baixo spin e alto spin induzida pela ação de estímulo externo que pode ser variações de temperatura, pressão ou irradiação [1]. Esta transição leva a mudanças na cor, estrutura e no comportamento magnético. A observação de SCO em compostos octaédricos de cobalto(II) coordenados por ligantes derivados da terpiridina já foi relatada [2]. Devido às mudanças estruturais observadas durante o fenômeno SCO, estudos envolvendo formas de restringir o aumento do volume do complexo são desejados e uma forma de obter este comportamento é projetar solventes de cristalização na rede cristalina do composto.

Nesse trabalho serão apresentados a síntese, caracterização estrutural e espectroscópica e o estudo das propriedades magnéticas do complexo $[Co(pyterpy)_2](hfac)_2\cdot 2EtOH\cdot 2H_2O$, onde hfac, pyterpy e EtOH, são, respectivamente, hexafluoroacetilacetonato, 4'-(4"-piridil)-2,2':6',2"-terpiridina e etanol. A estrutura foi resolvida utilizando dados de difração de raios-X de monocristal. O composto cristaliza no grupo de espaço *Cc*. O íon de cobalto(II) apresenta ambiente de coordenação octaédrico distorcido, sendo coordenado por seis átomos de nitrogênio pertencentes a duas moléculas da pyterpy. Duas moléculas de $hfac^-$ atuam como contra íon, além de quatro moléculas de solventes de cristalização. A análise termogravimétrica e a espectroscopia de absorção na região do infravermelho foram utilizadas para estudar a remoção dos solventes de rede da estrutura. A dessolvatação ocorre lentamente em temperatura ambiente quando cristais do complexo são removidos do solvente de cristalização. O estudo da dependência da susceptibilidade magnética estática com a temperatura mostrou diferenças significativas na transição de spin do composto na ausência e presença do solvente de cristalização, evidenciando a importância do solvente na rede cristalina no fenômeno de SCO. O estudo das propriedades magnéticas sugere que o processo de dessolvatação e solvatação é reversível.

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FAPERJ; CNPq; LDRx-UFF.

**Área: _____MAT________**

# Effect of pH on LDH $Mg_2Al$ synthesis, aiming application in $CO_2$ capture

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Palavras Chave: *LDH, Hydrotalcite, Carbon Dioxide, Co-precipitation, Adsorption.*

## Highlights

The pH is one of the main parameters, that should be analyzed during the synthesis of Lamellar Double Hydroxides, as it can influence both the structure and the adsorption capacity of this material.

## Resumo/Abstract

The Lamellar Double Hydroxides (LDH) has a lot of properties, like a high surface area. Furthermore, it shows a low cost material, which allows your utilization on several areas, being the carbon capture one of them[1]. These materials displays a structure similar to the brucite and with general formula: $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}A^{m-}_{x/m}\cdot nH_2O$, being composed of layers made of a mixture of cations di and trivalent, surrounded by hydroxyl and intercalated by anions to neutralize the layer charge[1]. The pH plays a key role on our material quality[2], therefore, the aim of this work is to study the influence of pH on the formation of LDH, with $M^{2+}/Al^{3+}= 2$, intercalated with $CO_3^{-2}$ ions.The LDH were obtained by the coprecipitation method, made at the following pH: 8.5, 10, 11. The LDH synthetized were $Mg_2$-Al-$CO_3$ at 76°C during the precipitation, later submitted to the same temperature overnight. The product was filtered and washed until pH 7 reached and dried at 100°C over 24 hours and at 120°C over 4 hours.

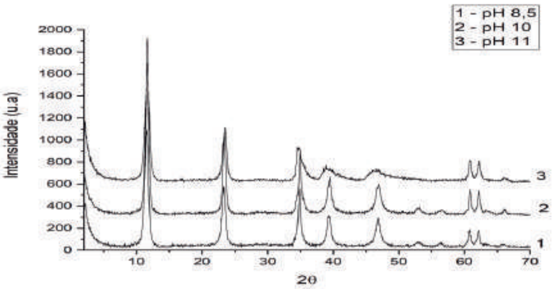

Figure 1. Difraction patterns of LDH $Mg_2Al$-$CO_3$: 1) pH 8.5; 2) pH 10; 3) pH 11

The product was characterized by X-rays diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). The diffraction patterns show reflections close to 12°, 23°, and 60°, relative to the (003), (006), and (110) planes, characteristic of LDH. It is observed that the diffractograms of the products synthesized at pH 8.5 present wider and less intense peaks than the products synthesized at higher pH. Note that for the synthesis carried out at pH 10, the peaks are more intense and narrower than the HDL produced at pH 11, demonstrating greater organization of the solid under these acidity conditions.

The absorption spectra in the IR region of the synthesized HDLs present bands in the region from 4000 to 2000 $cm^{-1}$ characteristic of O-H stretching, (s(OH) and as(OH)). In the region from 2000 to 400 $cm^{-1}$, bands at 1640 and 1372 $cm^{-1}$ are observed, attributed to the angular deformation of water (δHOH) and stretching of the carbonate ion (CO) respectively, and between 1000 – 400 $cm^{-1}$, the vibrational modes of $MgO_6$,$AlO_6$.

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## Acknowledgments

To LABTECH, LARHCO, and the Multiuser Laboratory of the Chemical Institute-UFRJ.

**Área: MAT**

# Effect of synthesis parameters in the textural properties of mesoporous carbons and its 17α-ethinylestradiol adsorption capacities

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Keywords: Mesoporous carbon, Emerging contaminant, Adsorption, Solvent-free, 17α-ethinylestradiol

## Highlights

Solvent-free method produces mesoporous carbon with mesoporous quality. Higher content of surfactant increases the pore size and area of the mesopores. Superadsorbent for 17α-ethinylestradiol.

## Resumo/Abstract

This work reports the synthesis of mesoporous carbons (MCs) produced from the solvent-free method and its application in the adsorption of the emerging contaminant 17α-ethinylestradiol (EE2).[1] Resorcinol was used as a carbon source, surfactant F127 as a template for the mesopores and terephthalaldehyde as a crosslinking agent.[1,2] A serie of synthetic parameters was evaluated: carbon precursor/surfactant ratio (p/s); heating rate; stabilization time and self-assembly temperature (Fig 1). The MCs were named according to the formula RF-a-c-b, where: a) p/s ratio (0.5 or 1); b) time that the temperatures remained constant (1 or 3 h); c) T100, for the two materials synthesized with an initial step at 100 °C, or LR (low rate) for the material synthesized with a rate of 1.5 °C/min.

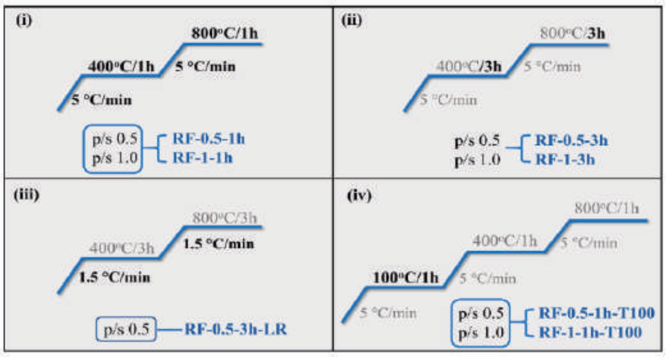
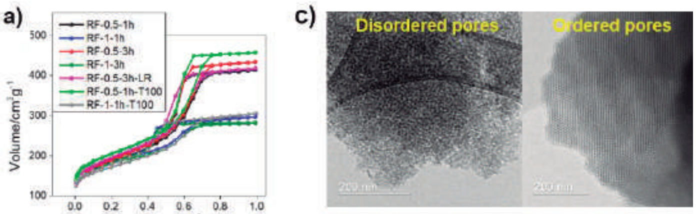


Fig 1: Summary of the synthesis steps used and materials nomenclature.

All MCs produced showed a type IV isotherm (Fig 2a) typical of mesoporous materials.[2,3] The MCs produced in p/s-0.5 presented larger average size and volume of mesopores in comparison to the MCs of the p/s-1 type (Fig 2b). The transmission micrographs indicated the formation of ordered and disordered pores (Fig 2c).[1]

We found that EE2 adsorption was more affected by diameter, volume and mesoporous content than by the type of pore ordering. Materials with high diameter and mesoporous content (series p/s 0.5) showed 99% EE2 removal.[1] For RF-0.5-1h, kinetic and adsorption isotherm studies were performed. The system reached kinetic equilibrium in 45 minutes indicating that the adsorption is fast. The maximum adsorption capacity for EE2 was equal to 157 mg/g. Furthermore, in the reuse studies, the adsorption capacity of the material remained almost 100% until the fourth cycle and above 85% until the tenth cycle.[1] Therefore, it was possible to produce MCs from a new methodology and, in addition to having textural.



b)

| | BET area/ $m^2g^{-1}$ | Pore diameter/ nm | Volume of mesopores/ $cm^3g^{-1}$ | Mesopor area/ $m^2$g |
|---|---|---|---|---|
| **RF-0.5-1h** | 640 | 5.6 | 0.492 | 462 |
| **RF-1-1h** | 650 | 4.8 | 0.223 | 308 |
| **RF-0.5-3h** | 666 | 5.6 | 0.504 | 453 |
| **RF-1-3h** | 667 | 4.9 | 0.205 | 253 |
| **RF-0.5-3h-LR** | 686 | 5.6 | 0.459 | 451 |
| **RF-0.5-1h-T100** | 716 | 5.6 | 0.525 | 445 |
| **RF-1-1h-T100** | 615 | 4.8 | 0.262 | 324 |

Fig 2: a) Physisorption isotherm; b) Texture parameters; c) Transmission micrographs;

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**Área: MAT**

# Electronic and structural study of $SrY_2O_4:Ce^{3+}(2\%),Eu^{3+}(x)$ (x = 1, 3, 5, 7, 9%) red-emitting phosphor for phosphor-converted LEDs.

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Keywords: WLEDs; Phosphors; Red-emitting; Solid-state lighting; Electronic properties; Density-Functional theory

## Highlights

The Pechini synthesis of $SrY_2O_4:Ce^{3+},Eu^{3+}$ with D-sorbitol complexing agent led to a single-phase red-emitting phosphor with high intrinsic emission quantum yield, displaying potential for WLED application.

## Abstract

Nowadays, phosphor-converted white light-emitting diodes (PC-WLEDs) are the main devices within solid-state lighting. However, some aspects still need improvement, such as the color rendering index (CRI) and the decrease of correlated color temperature, aiming the ideal application in night-lighting considering the regulation of human circadian rhythm[1,2]. Such drawbacks arises from the lack of red-emitting component in commercial hybrid PC-WLEDs; thus, we introduce here the $Ce^{3+}$(2 at. %), $Eu^{3+}$(1, 3, 5, 7, 9 at. %) co-doped $SrY_2O_4$ red-emitting phosphor produced by Pechini modified method[3]. All phosphor samples were synthesized by the annealing at 1100 °C upon CO reducing atmosphere of the precursor resin generated by the mixture of citric acid, D-sorbitol and metal ions solution, whose procedure was adapted from the reference [3]. XRD data confirmed that all obtained samples are single-phased $SrY_2O_4$ type. Rietveld refinement revealed the arrangement of two $Y^{3+}$ sites in the structure and, the higher the dopant concentration, the longer the length of the Y–O bond; in addition, Fourier density maps confirmed the preferential substitution of yttrium sites by both lanthanoid ions. However, X-ray photoelectron spectroscopy (XPS) data from samples doped with $Eu^{3+}$ (3 and 9 at.%) revealed the proportion of $Ce^{4+}$ and $Ce^{3+}$ being ≈70% and ≈30%, respectively, for both samples, regardless of the $Eu^{3+}$ doping percentage. Thus, the presence of cerium ions in the two oxidation states may be playing an important role in the stabilization of the $SrY_2O_4$ phase, since the proportion between them remains constant. Theoretical calculations of optimization and geometric relaxation at the DFT (Density Functional Theory) level suggest the positive variation in the lattice energy modulus when cerium ions are inserted into the matrix, confirming its important role in phase stabilization. Furthermore, density functional theory elucidated the electronic band structure of all samples. The results indicate the decrease of bandgap value with the increase of $Eu^{3+}$-dopant concentration, being a direct-gap transition on Γ high-symmetry k-point. Upon near-UV excitation (393 nm), the $SrY_2O_4:Ce^{3+},Eu^{3+}$ emission spectrum is a set of broad emission bands within the orange-red spectral region characteristic of $Eu^{3+}$ while the most intense band was assigned to the $^5D_0\rightarrow{}^7F_2$ transition in all samples, implying the insertion of $Eu^{3+}$ into low-symmetry sites lacking inversion center. The 3% $Eu^{3+}$-doped sample displays the highest intrinsic emission quantum yield (81%). The phonon spectrum was achieved by theoretical DFT calculations, displaying a higher quantity of low-frequency phonons, which corroborates with the large intrinsic emission quantum yield. In addition, the CIE 1931 chromaticity diagram indicates the high emission color purity of all phosphors. Thus, the red phosphor was successfully synthesized as proposed, and Ce-doping favors the single-phased system, while the combination of dopants ($Eu^{3+}$ and $Ce^{3+}$) yields a red-emitting phosphor upon near UV excitation. Therefore, both the theoretical and experimental data obtained suggest that this phosphor is a potential candidate for the development of warm phosphor-converted WLEDs prototypes.

## Acknowledgments

FAPESP (2019/13371-3) LACOM from FCT-UNESP, LACCEF from FCT-UNESP.

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**Área: MAT**

# Estudo da cinética de adsorção de azul de metileno utilizando hidrogéis do tipo IPN de alginato de sódio e sulfato de condroitina enxertados com poli(ácido acrílico)

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Palavras Chave: Biopolímero, Corante, Adsorção.

## Highlights

Kinetic investigations of the adsorption of methylene blue from aqueous solutions using IPN hydrogels of sodium alginate and chondroitin sulfate grafted with poly(acrylic acid)

IPN hydrogels exhibited a remarkable adsorption capacity higher than 1500 mg.g−1 within 15 min.
The interaction between the adsorbent and methylene blue ions was primarily based on a chemisorption phenomenon, as suggested by the pseudo-second-order kinetic model.

## Resumo/Abstract

Hidrogéis do tipo IPN de alginato de sódio (AS) e sulfato de condroitina (SC) enxertados com poli(ácido acrílico) foram sintetizados por polimerização em solução com interesse nestes sistemas como adsorventes do corante azul de metileno (AM), visando obter o modelo cinético mais adequado para descrição dos dados experimentais. Hidrogéis foram sintetizados de acordo com o procedimento a seguir, 0,5 g dos biopolímeros na razão de AS/SC (50/50 %m/m) foi solubilizada em 30 ml de água destilada à 70 °C sob agitação magnética e fluxo de $N_2$. Após a gelatinização, 2% m/m de $K_2S_2O_8$ foram introduzidos para gerar radicais livres nos biopolímeros. Dez minutos depois, 3,5g de AA (70% neutralizado com solução de NaOH 6 mol.$L^{-1}$) e 2% m/m de N,N'-metilenobisacrilamida foram adicionados.O produto resultante (50AS/50SC) foi resfriado à temperatura ambiente e, após 24 horas, lavado com água destilada, seguido de secagem em estufa a 70 ºC, e macerado até granulometria de 9-24 mesh (2,00-0,71 mm). Os ensaios de adsorção foram realizados utilizando as seguintes condições: 50 mg do adsorvente em 50 mL de solução de AM (1700 mg.$L^{-1}$); tempo de contato (5-480min) a 200 rpm; pH original da solução e temperature (25±1 °C). A concentração residual de AM foi determinada por espectrofotometria UV-Vis, utilizando o comprimento de onda máximo (670 nm) através de uma equação linear obtida a partir de uma curva analítica ($y = 0{,}0735x – 0.00299$, $R^2=0{,}9979$, sendo y a absorbância e x a concentração, respectivamente). Para melhor entendimento do mecanismo e investigar as etapas que controlam o processo de adsorção de AM por hidrogéis 50AS/50SC, os dados experimentais foram analisados e simulados utilizando-se os modelos cinéticos de pseudo-primeira ordem e pseudo-segunda ordem. Os parâmetros cinéticos obtidos estão listados na Tabela 1.

**Tabela 1.** Parâmetros cinéticos da adsorção de AM em hidrogéis do tipo IPN (50AS/50SC)

| Modelo | Parâmetros | 50AS/50SC |
|---|---|---|
| | $q_{e,exp}$ | 1647 |
| Pseudo-primeira ordem | qe,cal | 284 |
| | $k_1$ x $10^{-2}$ | 1,93 |
| | $\chi^2$ | 4,80 |
| | $R^2$ | 0,76155 |
| Pseudo-segunda ordem | $q_e$,cal | 1664 |
| | $k_2$ x $10^{-3}$ | 3,80 |
| | $\chi^2$ | 0,01 |
| | $R^2$ | 0,99998 |

Verificou-se que o melhor ajuste foi obtido no modelo de pseudo-segunda ordem, devido à proximidade do valor de $R^2$ a 1, além do valor experimental ($q_e$,exp) apresentar concordância com o valor calculado ($q_e$,cal). Portanto, estas evidências indicam que a quimissorção é a etapa determinante do mecanismo de adsorção[1].

## Agradecimentos/Acknowledgments

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

# Evaluation of photocatalytic activity of $TiO_2/SnO_2$ heterojunctions in methylene blue degradation.

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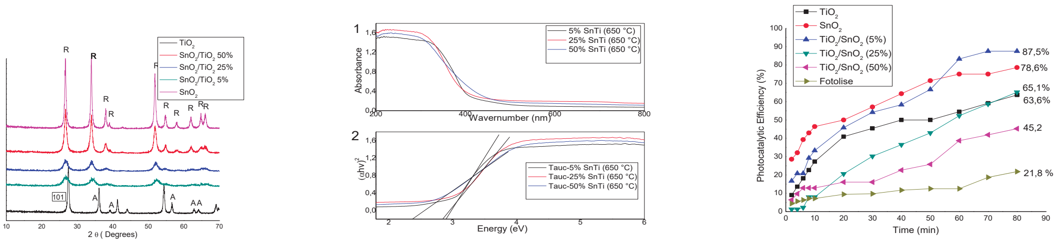
Palavras Chave: Heterojunction, $TiO_2/SnO_2$, heterogeneous photocatalysis, methylene blue.

## Highlights

- Photocatalytic degradation of methylene blue;
- Heterojunctions improve photocatalytic activity.

## Resumo/Abstract

Devido à alta taxa de recombinação interna, o $TiO_2$ possui atividade fotocatalítica limitada. No entanto tem-se investido em heterojunções semicondutoras do tipo *p-n*, como $TiO_2/SnO_2$, com intuito de melhorar as propriedades eletrônicas do $TiO_2$. Este trabalho teve como objetivo a síntese pelo método de coprecipitação de $TiO_2/SnO_2$ com 5, 25 e 50% de Sn, e caracterização pelas técnicas DRX, DRS e análise de fisissorção de $N_2$, e por fim, realizou-se testes na degradação fotocatalítica de azul de metileno. De acordo com a Figura 1A os picos de difração indicam a fase rutilo para $SnO_2$ (JCPDS Nº. 41- 1445), e para $TiO_2$' predominantemente anatase com frações da fase rutilo [2] (JCPDS Nº. 21-1272). Para as heterojunções observou-se que a medida que aumentou-se o teor de $SnO_2$ ocorreu um deslocamento dos sinais para ângulos menores. Esses resultados apontam uma modificação no $TiO_2$, pela inserção de íons $Sn^{4+}$ na rede do material [1]. Os espectros de DRS das heterojunções estão apresentados na Figura 1B-1 e indicam que aumento do teor de $SnO_2$ ocasionou um *redshift* das bandas para comprimentos de onda mais elevados, e tal fato pode ser devido à criação de níveis adicionais de energia no *bandgap* de $TiO_2$ pela presença dos íons $Sn^{+4}$. As energias de gap das heterojunções diminuíram com o aumento do teor de $SnO_2$, como mostrado na Figura 1 B-2, provavelmente devido à transição de carga entre os íons $Sn^{+4}$ e a banda de condução do $TiO_2$ [1-2]. A Figura 1C apresenta os testes fotocatalíticos sob luz-UV (365nm). Na fotocatálise heterogênea as propriedades superficiais podem influenciar na atividade do material, e o gap de energia é apenas um dos fatores que contribuem para atividade dos fotocatalisadores. Com isso, o melhor resultado foi atribuído ao $TiO_2/SnO_2$ 5%, esse efeito pode ser associado a maior área superficial, como mostrado na Tabela 1. Vale ressaltar que em comparação a fotólise direta os materiais investigados apresentaram atividade acima de 40%. Diante disto, conclui-se que heterojunções entre $TiO_2/SnO_2$ podem degradar com eficiência azul de metileno em meio aquoso.



A)

B)

C)

**Figura 1.** A) Difração de Raios-X do $SnO_2$, $TiO_2$, e heterojunções; B) DRS para $SnO_2$, $TiO_2$ e heterojunções; C) Testes fotocatalíticos.

| Amostra | $S_{BET}$ ($m^2g^{-1}$) | Bandgap (eV) |
|---|---|---|
| $SnO_2$ | 45,96 | 3,2 |
| $TiO_2$ | 16,06 | 4,2 |
| $SnO_2/TiO_2$ 5 % | 96,07 | 2,8 |
| $SnO_2/TiO_2$ 25 % | 77,92 | 2,7 |
| $SnO_2/TiO_2$ 50 % | 42,37 | 2,4 |

**Tabela 1.** Área superficial e bandgap dos fotocatalisadores.

Referências:
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[2] A. Kussior; L. Zych, et al**. Applied Surface Science**, 2019, 973-985.

## Agradecimentos/Acknowledgments

Agradecimento especial aos órgãos de fomento: CNPq, Finep, FAPEAL, INCT, UFAL e ao laboratório GCaR.

**Área: MAT**

# Evaluation of the effect of hydroxyapatite nanoparticle concentration in corn starch-based membranes for use in guided bone regeneration (GBR)

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Keywords: *starch, hydroxyapatite, guided bone regeneration, nanoparticle composite membranes, healing*

## Highlights

Membranes obtained from renewable sources based on starch/hydroxyapatite (HAp) nanoparticles. The increase of HAp concentration improved the functional properties of the membranes for guided bone regeneration.

## Abstract

Guided bone regeneration (GBR) is widely used to treat maxillofacial bone defects. However, the osteogenic responses are limited by the low availability of bioactive barrier membranes with suitable mechanical and biodegradability properties for the application. In this sense, the present study proposes the production and characterization of membranes based on corn starch, a cheap, renewable, and biocompatible material, added to different concentrations of hydroxyapatite nanoparticles (HAp), known for its osteogenic properties, the evaluation of its application as GBR. HAp was synthesized following an adapted protocol from Mota *et* al. [1]. The membranes were prepared by solvent casting from a 10 wt% starch aqueous suspension containing different amounts of HAp (0, 2, 5, and 10 g HAp/100 g starch). The membranes were named: Hap_0%, HAp_2%, HAp_5%, and HAp_10%, respectively. The membranes were evaluated in relation to the visual appearance, pH changes, biodegradability in PBS at different time intervals (0, 4, 24, 48, and 72 h), crystallinity by XRD, wettability, surface free energy, and healing assay evaluated by the MC3T3-E1 pre-osteoblasts cells migration to the closure of an injury at different time intervals (5, 7, and 24 h) [2]. The membranes were translucid and presented visible and homogeneously disperse white grains. The pH of the buffer solution was kept constant after the immersion of the membranes irrespective of the HAp concentration. The biodegradability assay revealed that the addition of HAp resulted in membranes more biodegradables (72 h: Hap_0%: 16% and HAp_10%: 22%). Peaks related to the HAp structure were present in the diffraction pattern of the membranes. The relative crystallinity increased as the HAp concentration increased revealing a better organization of the membranes that stans for higher rigidity. The addition of HAp promoted reduction of the hydrophilicity and increased the surface free energy which is beneficial for biomedical applications, as it allows adhesion of cells and proteins important for the osteointegration process. The healing assay revealed that the samples HAp_5% and HAp_10% promoted 50% higher cell migration than the other membranes. (Figure 1). Altogether, the results indicate that HAp_5% and HAp_10% membranes presented the best physical-chemical and biochemical properties to be potentially applied in GBR.

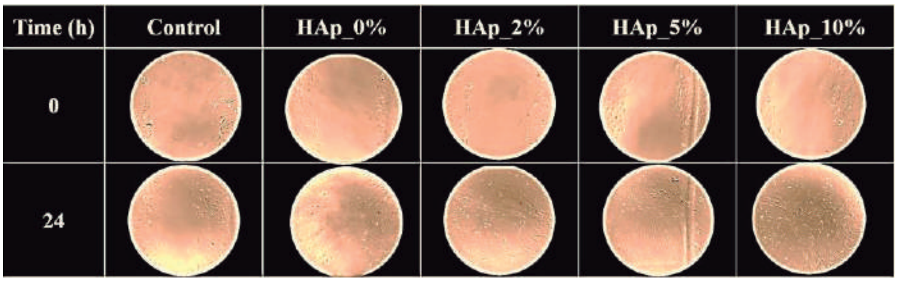

**Fig. 1**. ***Healing assays using pre-osteoblasts.*** Cells were cultivated for 0 and 24 h on the starch/hydroxyapatite (HAp)-based membranes, Hap_0%, HAp_2%, HAp_5%, and HAp_10%. The optical micrographs show the cell's migration after the cultivation period, in special for the Hap_5% and Hap_10% membranes. Cells cultivated in polystyrene discs were used as control.

[1] Mota et al. (2012) https://doi.org/10.1016/j.actbio.2012.06.040
[2] Jonkman et al (2014) https://doi.org/10.4161/cam.36224

## Acknowledgments

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**Área: MAT** **Nº de Inscrição: 00180**

# Extraction of the Glycoside from *Mimosa caesalpiniaefolia*

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Palavras Chave: *Glycoside, Mimosa caesalpiniaefolia, Sabiá.*

## Highlights

The obtained powder presents bands characteristic of a glycoside and had a yield of 7.8±0.5%. The obtained powder can be used in the production of polymeric matrices with different uses.

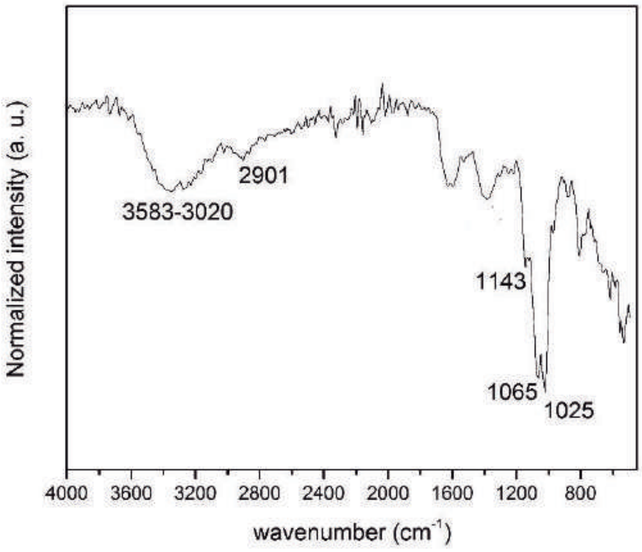
## Abstract

The present study aimed to extract galactomannan from the seeds of *Mimosa caesalpiniaefolia* (Figure 1), popularly known as Sabiá, a typical tree from northeastern Brazil. A white powder was obtained from the seeds, with a yield of 7.8±0.5%, considered low, but this yield is relative to the initial mass of the seeds in relation to the mass of powder obtained. The characterization by spectroscopy in the infrared region showed the characteristic bands of glycosides (Figure 2), therefore the material extracted is possibly a polysaccharide, however further analysis will be necessary for this confirmation. Thus, we will be able to use the powder in the production of polymeric matrices for the development of materials with different uses and, thus, use as raw material the seeds that would be discarded as a possibility of income for the region.

Figure 1. Photo of *Mimosa caesalpiniaefolia* seeds

Source: Author (2019).

Figure 2. Spectrum in the IR region for powder extracted from seeds.



Source: Author (2019).

## Acknowledgments

The authors thank the IFRN for the financial support.

**Área: MAT**

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

# Functionalized tellurite and fluorotellurite glasses with lanthanide metal-organic frameworks (Ln-MOFs) for optical gas sensing

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Palavras Chave: *Gas sensing, metal-organic frameworks, optical fibers, luminescence.*

## Highlights

- The work focuses on the development of optical fibers with a large transmission window for application in remote sensing of toxic, explosives and greenhouse gases and vapors.
- A facile in-situ growth of luminescent metal-organic frameworks (Ln-MOFs) on tellurite and fluorotellurite glasses is presented.
- Ln-MOFs were obtained MOFs with different crystalline structures depending on the glass composition, with different $ZnF_2$ concentrations.
- The hypersensitive emission of $Eu^{3+}$ at 615-630 nm was monitored and the quenching in the luminescence intensity indicates a great potential for its remote sensing of gases.

## Resumo/Abstract

The development of sensors for gases detections has been a hot scientific topic, especially for the control and monitoring of environmental pollutants. However, gas monitoring is hampered in many cases by difficult of access, high risk of on-site detection, or sampling in the case of explosive or toxic materials. In this context, sensors based on optical fibers become a promising alternative for remote sensing, allowing in-situ and faster responses, and excellent detection levels compared to semiconductor or electrochemical sensors. For gas sensing, optical fibers sensors can detect gases in real time and without degrading the samples. Another class of materials that shown great potential of chemical and gas sensing is the luminescent lanthanide MOFs ($Ln^{3+}$-MOF), especially for nitroaromatic explosive and other volatile organic compounds (VOCs). Thus, this work aims to the development of optical sensors based on optical fibers functionalized with luminescent $Ln^{3+}$-MOF for remote detection of gases. Initially, the pieces of tellurite glasses, a glass matrix suitable for optical fiber production due to their great thermal stability against crystallization, high refractive index and large transparency window, were functionalized by in-situ growth of $Ln^{3+}$-MOF. The functionalization with $Ln^{3+}$-MOFs have been made with Eu(III) MOF $\{[Eu(HPDC)(PDC)]\}_n$ (PDC = 2,6-pyridinedicarboxylate) by solvothermal method at 180 °C for 20 min. The MOFs synthesis is performed with the glass inside the reactor to promote the in-situ growth of MOFs crystals on the surface. The hybrid material obtained has been characterized by FTIR and Raman spectroscopies, X-Ray diffraction, Scanning Electron Microscopy (SEM) and Photoluminescence. The first results indicate the growth of different crystalline structures depending on the tellurite glass composition, with different amounts of fluoride ions. Chemical and VOC sensing trials, such as TNT, nitrobenzene, and chloroform, were carried with glass pieces containing Ln3+ -MOF on their surfaces and exposing the samples to analytes for different duration to evaluate selectivity and sensitivity parameters although Fluorescence Spectroscopy. The hypersensitive emission of $Eu^{3+}$ at 615-630 nm was monitored and quenching in the luminescence intensity was observed for different analytes, which indicates a great potential of application of this MOF for remote sensing of gases, coupling it to optical fibers of tellurite glasses

## Agradecimentos/Acknowledgments

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**Área: MAT**

# Gelatin-Carboxymethylcellulose bylayer films produced by continuous casting

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Keywords: Biopolymer, Films, Bilayer, Continuous casting, Carboxymethylcellulose, Gelatin.

## Highlights

Protein-polysaccharide bilayer films were produced in a continuous casting

Bilayer films have different hydrophilicity on each face

Decreasing permeability to water vapor

Increasing mechanical resistance

## Abstract

The elaboration and processing of materials based on biopolymers have been highlighted in recent years due to their potential for application in biological systems, to replace polymers from petrochemical sources, and because they come from renewable sources. Gelatin (GEL)-carboxymethylcellulose (CMC) bilayers films were produced by aqueous filmogenic solution contenting glycerol and, in the case of CMC, citric acid as crosslinker agent. The production of films was made in a continuous lamination system (continuous casting) composed of convective ovens in sequence. The GEL layer was made from filmogenic solutions at three different pHs; this is because proteins have their zeta potential altered as a function of pH. Apparently, the material presents a good adhesion between protein-polysaccharide layers that can contribute to improving their properties. Bilayer films containing the GEL matrix formulated at different pHs showed no significant differences in the properties analyzed. In this way, the electrostatic interactions between the matrix of GEL and CMC do not significantly influence the adhesion and, consequently, the final properties of the material. Contact angle measurements showed significant differences in the hydrophobicity of the two faces. The face composed of GEL presented values around 30°, while the CMC face, values around 80°. Water vapor permeability values show a considerable decrease in bilayers films, which is due to the increased thickness and components that promote the barrier effect. The mechanical uniaxial tensile test showed a 100% increase in the mechanical strength of the material. It is worth mentioning that no significant change was observed in the elongation at break and in the modulus of elasticity. The CMC layer helped in the formation of a self-supporting film since only the GEL layer does not present satisfactory handling. Regarding the possible applications, structures with anisotropic characteristics, such as bilayer films, allow the application, interaction, or detection of different systems simultaneously, since each face can present different characteristics.

## Acknowledgments

Process: 2019/26577-9

**Area: MAT**

# GRAPHENE-BASED MEMBRANES AS IONIC BARRIER FOR WATER TREATMENT

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*Keywords: Membrane, Stability, Swelling, Graphene Oxide.*

## Highlights

Herein we show how the reduction methods of the GO nanosheets strongly affect the nanostructuring and the performance of the lamellar membranes as ionic barriers for water treatment.

## Abstract

Water is one of the most valuable assets for the human development, and one of the main challenges is the growing demand and availability of clean/potable water. Currently, technologies for the treatment of seawater are explored due to its availability, however a high cost of operation is faced in processes like distillation and capacitive deionization. Despite revolutionizing the market, reverse osmosis technologies also present challenges to be overcome such as the low resistance of polymeric membranes to chlorine, used in most of the water/effluent treatments, and the surface fouling. Alternatives involving the use of 2D materials have been explored as new ways to manufacture membranes, highlighting the graphene oxide (GO) and reduced graphene oxide (rGO), which show higher chemical resistance to critical species such as chlorine when compared to the benchmark polymeric membranes. Despite the ability of restacked graphene oxide to form 2D nanofluidic channels with tunable porosity that is able to control the permeation of water molecules and other species, the instability of GO in water, due to its hydrophilic character, hinders the development of membranes. Different efforts have been made through modifications via functionalization or reduction of these materials to improve their properties for separation processes. In this work, different strategies have been evaluated to obtain rGO membranes, subsequently tested as an ionic barrier in a diffusion cell, as illustrated in Figure 1. The reduction methods were carried out using hydrazine in aqueous suspension (rGO) and by the steam (HGO), or by thermal treatment (TrGO). The samples were also reduced in two distinct steps when the combination of two methods was evaluated (HGO;HrGO;HTrGO). The obtained membranes were characterized by several techniques: (i) the X-ray diffraction data shows a significant variation in the interplanar distance of the 2D layers in the membranes depending on the reduction processes, from 8.73 Å for GO to 7.46Å for the HTrGO, (ii) the FT-IR data confirm that the reduction degree of the graphene oxide nanosheets can be finely adjusted by the developed methods and (iii) the ionic diffusion tests clearly pointed out the best strategy to obtain graphene-based membranes, with high performance as ionic barrier in aqueous solutions when compared to the benchmark polymeric membranes for reverse osmosis.

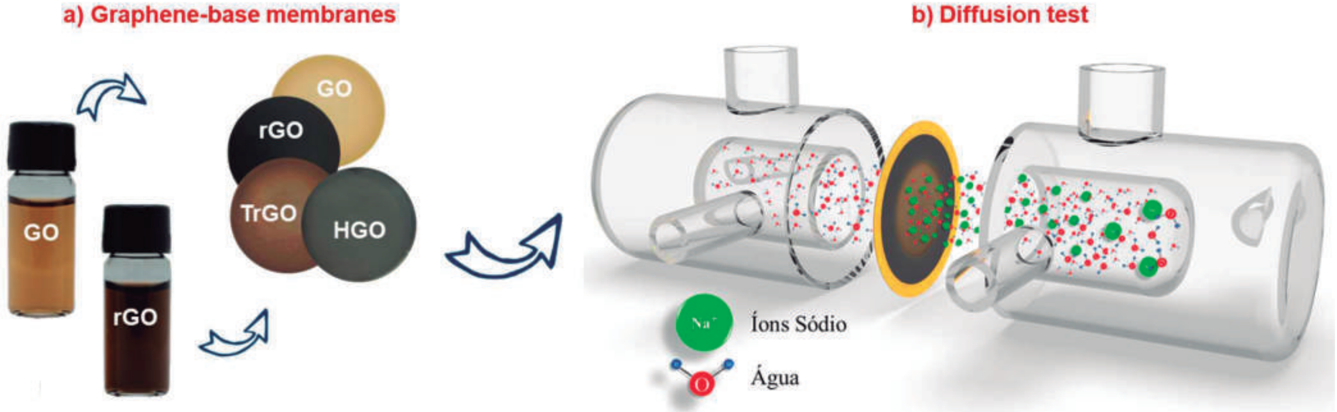

**Figure 1:** (a) Graphene-based membranes, (b) scheme of the diffusion cell setup test.

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**Área: MAT**

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# Green synthesis of calcium tungstate using eggshel as biogenic source

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Palavras Chave: *Synthesis, nanomaterials, characterization, waste, hydrothermal.*

## Highlights

*New approaches to obtain calcium tungstate nanoparticles; use of eggshell waste for the development of new materials for several technologies; structural and optical characterization; low-cost and facile sonochemistry method.*

## Resumo/Abstract

The development of new routes and processes for obtaining and processing materials, mainly nanomaterials, have been the focus of several studies in recent decades. In this context, residues derived from biomass (animal and plant) allows new routes of low cost and easy processing to obtain nanomaterials with technological applications. Calcium tungstate ($CaWO_4$) is a well-known semiconductor classified as scheelite minerals which exhibits tetragonal structure and excellent photoluminescent and semiconductor properties. Therefore, their properties have been studied, consequently, for several applications in the field of sensors, capacitors, catalysts, light emitting diodes and scintillators were confirmed. In this study, $CaWO_4$ nanoparticles were efficiently obtained using chicken eggshells as a biogenic source of calcium. Initially, eggshells collected from a supermarket in the Manaus city center (Amazonas), were dried in an oven for 24 h at 85 ºC. The eggshell was ground in a mortar, resulting in 65 g of material. Then, 10 g of these powder was solubilized in 100 mL of commercial vinegar, followed by vacuum filtration using filter paper with a mesh size of 200 microns. The calcium content was previously determined by gravimetry and then, 1 mmol of sodium tungstate dihydrate – $Na_2WO_4{\bullet}2H_2O$ and 1mmol of solution containing $Ca^{2+}$ ions were mixed under magnetic stirring and then subjected to ultrasound synthesis for 30 min at room temperature, using a Schuster ultrasonic washer machine, L100 model. The synthesized material was washed several times with distilled water and collected through centrifugation using 6,000 rpm, then dried at 65 °C for 12 h. The collected diffraction pattern and the Rietveld refinement plot of synthesized calcium tungstate are confirming that all diffraction planes are characteristics of the tetragonal structure of $CaWO_4$ with space group of *I41/a*. Moreover, agreeing with the crystallographic data contained in the Inorganic Crystal Structure Database (ICSD) nº. 18135 card. Therefore, showing the main XRD crystallographic planes in $2\theta = 17.6º, 28.2º$ and 28.6º, corresponding to planes (011), (112) and (013), respectively. In summary, high crystallinity degree and pure phase $CaWO_4$ nanomaterials were successfully synthesized using the alternative route and low-cost method adopting an easy sonochemistry route at room temperature.

## Agradecimentos/Acknowledgments

The authors would like to thank Samsung Electronics Company for financial support of this study. As well as to the Federal Institute of Education, Science and Technology of Amazonas (IFAM) for their support in the acquisition of measurements of diffraction patterns.

**Área: MAT**

# Hidrogéis de alginato de sódio/sulfato de condroitina enxertados com poliacrilamida assistidos por diferentes rotas

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Palavras Chave: Síntese, Aquecimento, Micro-ondas, Propriedades Hidrofílicas.

## Highlights

Sodium alginate/chondroitin sulfate hydrogels grafted with polyacrylamide assisted by different routes

The incorporation of chondroitin sulfate in the polymer matrix causes a decrease in the absorption capacity.
Microwave-assisted hydrogels showed higher capacity compared to conventional heating-assisted hydrogels.

## Resumo/Abstract

Hidrogéis do tipo IPN de alginato de sódio (AS) e sulfato de condroitina (SC) enxertado com poliacrilamida foram sintetizados por polimerização em solução por diferentes rotas de síntese: (i) por aquecimento convencional (AC) e (ii) por radiação de micro-ondas (MO), com interesse futuro no estudo desses sistemas, como adsorventes de corantes iônicos e/ou íons metálicos. O efeito da rota de síntese e da proporção dos biopolímeros AS/SC (100/0, 75/25, 50/50, 25/75 e 0/100) sobre as propriedades hidrofílicas dos hidrogéis sintetizados foram investigados. Os hidrogéis foram sintetizados de acordo com o procedimento a seguir, 0,5 g dos biopolímeros (AS/SC) em diferentes proporções (% m/m) foram solubilizadas em 25 ml de água destilada sob agitação magnética e fluxo de $N_2$. Após a gelatinização, 1% m/m de $K_2S_2O_8$ foi introduzido para gerar radicais livres nos biopolímeros. Dez minutos depois, quantidades específicas AM (3,5 g) e N,N'-metilenobisacrilamida (1% m/m) foram solubilizados em 5 ml de água destilada e adicionados ao sistema reacional. Em seguida, as sínteses foram assistida (i) por AC em banho de óleo a 70 °C por 2 horas, e (ii) por radiação de MO, utilizando um micro-ondas doméstico com frequência de 2450 MHz por 60 segundos. Os produtos resultantes foram resfriados à temperatura ambiente e, após 24 horas, lavado com água destilada, seguido de secagem em estufa a uma temperatura de 70 ºC e depois macerados até granulometria de 9-24 mesh (2,00-0,71 mm). Em relação a quantidade de água absorvida no equilíbrio ($W_{eq}$), observou-se que: (i) a incorporação de SC na matriz polimérica provoca uma diminuição da capacidade de absorção, indiferente da rota de síntese; e (ii) os hidrogéis assistidos por MO apresentaram um maior capacidade de absorção ($W_{eq}$ = 45,79 ± 2,77 g de água/ g gel) quando comparado ao hidrogel assistido por AC ($W_{eq}$ = 21,98 ± 1,75 g de água/ g gel). Esse aumento pode ser atribuído a maior quantidade de energia disponível uniformemente no material, provocando maior aproveitamento dos reagentes[1]. Por outro lado, hidrogéis assistidos por MO apresentaram um rendimento menor (aproximadamente 84 ± 2 %) que os assistido por AC (aproximadamente 93 ± 2 %), o que poderia indicar que as moléculas dos biopolímeros que não reagiram podem ser liberadas durante a lavagem dos hidrogéis assistidos por MO, em virtude do baixo tempo de exposição à radiação (60 segundos), resultando em um número insuficiente radicais livres formados, desfavorecendo a propagação da reação de polimerização, e proporcionando menor reticulação. Entretanto, o produto final é obtido de forma mais rápida e prática através da síntese assistida por MO necessitando avaliar um tempo maior de exposição afim de averiguar a obtenção de um maior rendimento reacional.

## Agradecimentos/Acknowledgments

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**Área: MAT**

# Hydrochar/Simonkolleite composites: Synthesis and characterization

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*Keywords: Hydrocarbon, Simonkolleite, Composite Materials.*

## Highlights

- Fabrication of Hydrochar/SK composites using different routes; - Investigation of the structural changes by several characterizations; - Improving natural features of the precursors.

## Abstract

The constant scientific and technological progress, as well as the need to develop environmentally friendly technologies, has driven intense work on obtaining composite materials with adsorptive and photocatalytic properties[1]. The properties of these new materials are often obtained from a synergistic combination or totally new, compared to the precursors. In addition, the possibility of controlling the morphology and physicochemical characteristics of these materials is an additional advantage.[2] Thereby, the present work aimed the preparation and characterization of new composites based on Hydrocarbon (HC) and Simonkolleite (SK ), in addition to evaluating the influence of synthesis routes on the materials morphology and structure. The composites were prepared by three different methods: Co-precipitation (CP), manual mixing of precursors (MM) and hydrothermal co-carbonization (HCC) and their characteristics were evaluated through SEM, FTIR, TG, XRD and $pH_{pcz}$ analyses. As a result, the efficiency of the different synthesis methods in the production of the HC-SK composite was verified. However, important variations in the properties of the materials produced were observed. The morphological profiles of the composites and their precursors obtained by SEM presented in Fig.1, shows that the surface of the HC was covered by hexagonal platelet structures, similar to SK, proving the formation of the composite, nevertheless differences in the disposition and structure of the SK more pronounced observed in the materials obtained by HCC. Changes in the surface charge of these materials were also noticed, the $pH_{pcz}$ of the composites, 6.86, 6.83 and 7.33 for CP, MM and HCC, respectively, were higher than that of HC (5.19) and closer to the SK (6.5), with emphasis on the high $pH_{pcz}$ value of the HCC, indicating synergy between the HC and SK. In the XRD patterns, Fig.2, variations in the average sizes of crystallites of the materials produced are observed when compared with the precursor SK, indicating that the presence of HC favored the reduction of the dimensions of the nanocrystalites, which is a very promising factor for the adsorptive process. Furthermore, a shift in the peaks of the composite obtained by HCC was observed, this fact is due to the conversion of SK into ZnO favored by the temperature (180 °C) required in this synthesis method and justifies the changes observed for this material in the previous characterizations. Changes in the surfaces and in the thermogravimetric properties of the materials were also observed by the FTIR and TG analyses. In this sense, it is observed that the different synthesis routes modify the properties of the materials, indicating that each route can directly influence the composition (generating ZnO), increasing the $pH_{pcz}$ and the surface area, directing the application of each composite.

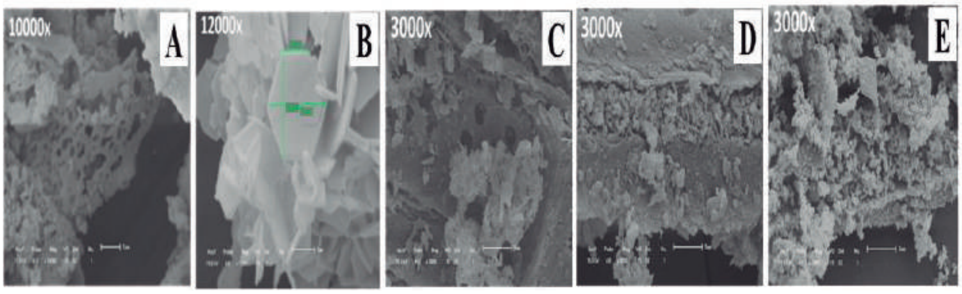

**Figure 1**: SEM of (A) HC; (B) SK; (C) CP; (D) MM; (E) HCC.

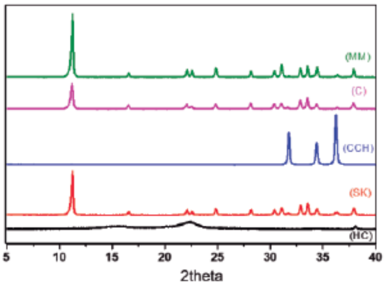

**Figure 2**: Diffractogram of materials.

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## Acknowledgments

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**Área: MAT**

# Immunogenic protein encapsulation into ordered mesoporous silica: analysis of incorporation methods

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Palavras Chave/Keywords: *SBA-15, Bovine serum albumin, Vaccine, Lyophilization, Evaporation, Adjuvant*

## Highlights

Ordered mesoporous silicas have attracted much attention due to potential applications as an immune adjuvant/vehicle.

Study about different incorporation methods is important to lead to the successful development of vaccines.

## Resumo/Abstract

Ordered mesoporous silicas (OMS) have been proposed as vaccine adjuvants due their properties such as high surface area (above 600 $m^2 g^{-1}$), pore volume (from 1 to 5 $cm^3 g^{-1}$), adjustable pores (2-50 nm) and narrow pore size distribution[1-2]. In the present study, we investigated the effect of solvent removal method (lyophilization and evaporation) on the intrinsic properties of the immunogenic materials (silica SBA-15: immunogenic protein). Bovine serum albumin (BSA), an immunogenic protein, was chosen as model antigen. The synthesis protocol for SBA-15 matrix is described in full detail in our previously published work[1]. The immunogenic material was prepared in the following way: SBA-15 was activated at 190 °C for 2 h, aiming to eliminate water molecules and then was added to the phosphate buffered saline (pH ~ 7.4) solution containing BSA. The resulting mixture was stirred at room temperature for 24 h, then divided into two parts (A and B). Part 'A' was frozen in a freezer at (− 25 ± 5) °C for 24 h and after lyophilized at − 52 °C, under vacuum (35 µmHg), for 48 h and the Part 'B' the solvent was evaporated in a Drying Oven at 35 °C for two days. The immunogenic materials (SBA-15:BSA_A and SBA-15:BSA_B) were characterized by several physical-chemical techniques including small-angle X-ray scattering (SAXS), nitrogen adsorption−desorption isotherms (NAI), scanning electron microscopies (SEM), Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), differential scanning calorimetry, fluorescence spectroscopy and circular dichroism (CD). By SAXS curves the characteristics reflections [(100), (110), (200), (210), and (300) from pure SBA-15 were observed which indicating that the silica mesostructure has been preserved after the incorporation of BSA. NAI measurements showed that for both samples, a decrease of surface area and of pore volume were observed, when compared to pure SBA-15, indicating that BSA was incorporated into the SBA-15 mesopores, corroborating with SAXS curves. Comparing the NAI data of the SBA-15:BSA_A and SBA-15:BSA_B samples, the evaporation process seems to be more efficient for the incorporation of BSA inside the SBA-15 pores. By TGA and DSC curves, both the samples exhibited higher thermal degradation temperature than pure BSA. The fluorescence spectrum of tryptophan residues in BSA incorporated into SBA-15 was quite similar to that of the pure BSA, showing the preservation of the aromatic residues, corroborating with the CD data. CD spectra of both samples suggest the preservation of protein secondary structure in the process of incorporation into the SBA-15 mesopores. These results evidenced the possibility to produce vaccines for oral vaccination.

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## Área: Química de Materiais - MAT   N° de Inscrição: 1079

# INCORPORAÇÃO DE NANOPARTÍCUAS DE PRATA EM PÓ DE POLIAMIDA 12 PARA APLICAÇÃO EM IMPRESSÃO 3D

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Palavras Chave: bactericida, poliamida, nanopartículas de prata.

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Keywords: bactericide, polyamide, silver nanoparticle.

## Highlights

INCORPORATION OF SILVER NANOPARTICLES INTO POLYAMIDE 12 POWDER FOR APPLICATION IN 3D PRINTING. Incorporation of silver nanoparticles in aqueous medium into polyamide 12 powder to obtain printed polyamide in various forms and with antimicrobial characteristics.

## Resumo/Abstract

Due to its various functions, 3D-printed pieces are relevant for the market, especially when it comes to producing systems with bactericidal action. Bearing such emerging market in mind, this project aims to incorporate silver nanoparticles (AgNPs) into polyamide 12 powder, a raw material for 3D printing. To this end, AgNPs will be reduced with sodium borohydride ($NaBH_4$) via a chemical route, in the presence of sodium citrate ($Na_3C_6H_5O_7$) as stabilizer, in the absence of organic solvent. This method allows AgNPs to be incorporated into polyamide 12 (PA12) powder, promoting new applications for 3D-printed pieces while maintainging the silver antimicrobial action. Briefly, the material was synthesized by preparing a colloidal AgNP solution from silver nitrate ($AgNO_3$), as precursor. Therefore, 10 mg of $AgNO_3$ was added to 75 mL of deionized water and 46 mg of $Na_3C_6H_5O_7$, under stirring. Then, a freshly prepared $NaBH_4$ solution (6 mg in 5 mL of water) was added dropwise, until a yellow solution typical of AgNPs was formed. AgNP formation was confirmed by UV-Vis absorption spectroscopy; the spectrum presented the characteristic AgNP plasmon band at 390 nm. Particle size was in the order of 10 nm. Next, 1 g of PA12 was added to the colloidal solution and stirred for 1 h, and the resulting powder was centrifuged and dried, to give a brown powder, shown in Figure 1.

**Figure 1:** Photograph of PA12 powder before (a) and after (b) AgNP incorporation.

The supernatant was analyzed by UV/VIS, which showed that all the AgNPs were incorporated into PA12. The brown powder presented plasmon band at 415 nm and was subjected to 3D printing at CTI Campinas and to antimicrobial and cytotoxicity evaluation, showing bactericidal action against *E. coli* and low cytotoxicity.

## Agradecimentos/Acknowledgments

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**Área: MAT**

# Influences on structural and photocatalytic efficiency of $TiO_2$ nanoparticles synthesis parameters.

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Key words: *Photocatalysis; Factorial planning; Sol-gel; Hydrothermal treatment.*

## Highlights

Influence of reaction parameters on $TiO_2$ nanoparticles synthesis. Evaluation of $TiO_2$ nanoparticle synthesis parameters for high photocatalytic efficiency.

## Resumo/Abstract

Obtaining $TiO_2$ through sol-gel process allows the control of parameters that influence its physical and chemical properties and, therefore, its application and efficiency as a photocatalyst. This work intended to study some of the parameters involved in the synthesis of $TiO_2$ nanoparticles and their influence in photocatalytic efficiency of the materials obtained through the sol-gel method and factorial experimental design. A complete $2^3$ factorial design was applied in duplicate to evaluate the following variables: molar ratio of water:ethanol:isopropoxyde, pH (HCl) and temperature (Table 1). $TiO_2$ nanocrystals were prepared via sol-gel hydrolysis precipitation of titanium isopropoxide followed by hydrothermal treatment using the different conditions described in table 1. The obtained materials were characterized by Scanning Electron Microscopy (SEM); X-ray Diffraction (XRD) and specific surface area and pore size (BET) measurements and their photocatalytic efficiency evaluated by monitoring the degradation of methyl orange dye in water solution.

**Table 1. Levels and variables factorial planning $2^3$**

| **Levels** | **Variables** | | |
|---|---|---|---|
| | **Molar ratio** | **pH** | **Temperature (°C)** |
| (+) | 150:02:01 | 6 | 180 |
| (-) | 150:04:01 | 4 | 80 |

Structural analysis showed that samples obtained at 80 $^0$C presented a lower crystallite sizes than samples obtained at 180 °C (media of 8,4 nm and 13,7 nm respectively). Although molar ratio and pH play a role in particle size the effects were not so significant as the observed for temperature. Effect of pH was observed in pore size (44 Å and 89 Å) for samples obtained at 80 $^0$C, Ratio 150:04:01 and pH 4 and pH 6 respectively. The effects of the studied synthesis parameters of $TiO_2$ in photocatalytic efficiency were obtained by factorial analysis. Changing the level from (-) to (+) in the molar ratio parameter, leads to 9,96% increase in photocatalytic activity, while an increasing the temperature level cause an efficiency decrease of 8,65%. Increase in pH also showed to be favorable to photocatalytic activity (increase of 7,32%). $TiO_2$ obtained using ratio of 150:2:1, pH 6 and temperature of 80ºC showed an photocatalytic efficiency of 66,6% while $TiO_2$ used as a control sample (PC500) showed an efficiency of 60,3%.

## Agradecimentos/Acknowledgments

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Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - CAPES

**Área:** MAT **Nº de Inscrição: 00475**

# Influência dos hidróxidos de magnésio e alumínio na ativação mecanoquímica do sistema $MgO – Al_2O_3 – SiO_2$

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*Palavras-chave: Ativação Mecanoquímica, Hidróxido, α-Cordierita*

## Highlights

**Influence of magnesium and aluminium hydroxides on the mecanochemical activation of $MgO$-$Al_2O_3$-$SiO_2$ system**

The influence of hydroxides as Al and Mg precursors was evaluated on the mecanochemical activation using two types of grinding elements. Three powdery formulations, according to stoichiometric composition of cordierite, were studied using X-ray diffraction analysis.

## Resumo/Abstract

Num estudo anterior, de ativação mecanoquímica do sistema $MgO$ - $Al_2O_3$ – $SiO_2$ em um moinho de bolas de baixa energia, observou-se que a presença de hidroxilas na superfície do precursor de sílica e a introdução de água ao meio de moagem contribuíram para o aumento da quantidade da α-cordierita ($Mg_2Al_4Si_5O_{18}$) formada. O objetivo deste trabalho é o de investigar a influência na ativação mecanoquímica da presença da hidroxila nos compostos precursores de Mg e Al, assim como, o efeito da variação do elemento de moagem utilizado. Para tanto, três grupos de compostos precursores de Mg e Al, mantendo-se a sílica-gel $HF_{254}$ tipo 60 (Merck) como composto precursor da sílica, foram ativados mecanicamente em meio aquoso por 72h e com a relação massa de reagentes/massa de elementos de moagem (M/C) igual a 1/100. Foram utilizados cilindros (Ø = 1cm e comprimento = 1cm) ou microesferas (Ø = 2mm) como elementos de moagem, ambos de zircônia ($ZrO_2$) estabilizada com ítria ($Y_2O_3$).
Na tabela 1 abaixo, estão relacionados os grupos de reagentes e os compostos formados durante a ativação mecanoquímica.

Tabela 1- Compostos formados durante a ativação mecanoquímica.

| sistema | precursores | amostras | compostos formados (observados no DRX) |
|---|---|---|---|
| $MgO – Al_2O_3 – SiO_2$ | $MgO$<br>$Al(OH)_3$ | Aq16 | $MgSiO_3$, $Mg_2Al(OH)_7$ |
| | | Aq16M | material amorfo |
| | $Mg(OH)_2$<br>$Al_2O_3$ | Bq16 | $Al_2O_3$, clinoenstantita ($MgSiO_3$) |
| | | Bq16M | $Al_2O_3$ |
| | $Mg(OH)_2$<br>$Al(OH)_3$ | Cq16 | clinoenstatita e enstatita (polimorfos do $MgSiO_3$) |
| | | Cq16M | $Mg_2Al(OH)_7$, $Mg_4Al_{12}(OH)_{14}.3H_2O$ |

O **M** após o nome da amostra indica a utilização de microesferas como elemento de moagem.

As análises por difração de raios X foram realizadas num difratômetro Shimadzu DRX 6000, 40Kv, 30mA, radiação Cu-$K_\alpha$ de 5º a 80º. Dos dados na tabela 1, podemos concluir:

1. A α-alumina (α-$Al_2O_3$), com dureza semelhante a da zircônia, não foi ativada.
2. Quando usado, o hidróxido de alumínio ($Al(OH)_3$), com dureza menor que a da zircônia, é ativado e forma hidróxidos mistos de Al e Mg.
3. Tanto o óxido de Mg ($MgO$) como o hidróxido de Mg ($Mg(OH)_2$) dão origem a uma solução sólida do Mg com sílica, formando, durante a ativação mecanoquímica, silicatos de Mg.
4. A utilização das microesferas leva a um maior grau de amorfização dos compostos formados.
5. Tanto a presença da hidroxila quanto a utilização das microesferas influenciam a ativação mecanoquímica do sistema $MgO – Al_2O_3 – SiO_2$.

## Agradecimentos/Ackowledgments

Ao Laboratório de Raios X do Instituto de Engenharia Nuclear (IEN/CNEN) pelas análises de difração de raios X.

**Área: MAT** **Nº de Inscrição: 01090**

# Influência dos ligantes de superfície em nanocristais de $ZrO_2$ na preparação e propriedades de nanocompósito acetato de celulose:$ZrO_2$

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Palavras Chave:*(Nanocompósito, Polímero, Óxido metálico, Funcionalização, Membrana).*

## Highlights

Influence of surface ligands on $ZrO_2$ nanocrystals in the preparation and properties of nanocomposite with cellulose acetate; Functionalization of nanocrystals to control interfacial region between phases; nanocomposite cellulose acetate membrane; Thermal properties of nanocomposite;

## Resumo/Abstract

Nanocompósitos são materiais que resultam da combinação de dois ou mais materiais em fases distintas, sendo que pelo menos uma das fases se encontre em dimensão nanométrica. Em muitos nanocompósitos as propriedades em aplicação se apresentam superior, quando comparado ao material da matriz individual. Um exemplo de nanocompósito é a combinação envolvendo polímeros e nanocristais inorgânicos, esse tipo de compósito apresenta como uma das vantagens a processabilidade, a qual se mantem da matriz polimérica. Na preparação de nanocompósito de matriz polimérica o sinergismo entre as fases é de extrema relevância sendo que esse sinergismo impacta nas propriedades do material final [1]. Para avaliar o sinergismo e a dispersão de nanocristais inorgânicos funcionalizados com uma matriz de acetato de celulose, foram sintetizadas nanoestruturas de $ZrO_2$ em três diferentes solventes orgânicos [2] os quais foram incorporados na matriz polimérica para obtenção de membranas. Os nanocompósitos obtidos foram caracterizadas por microscopias e técnicas de análises térmicas. A caracterização por microscopia, Figura 1, evidenciou duas características de interação dos nanocristais com o polímero, sendo que os nanocristais funcionalizados com ligante oleato (OAc) resultaram em dispersão mais uniforme, enquanto os ligantes benzoato (BnOH) e octanoato (OcOH) geram a formação de ilhas de nanocristais na matriz, quando na concentração de 20% (m/m) inorgânico/polímero. Uma segunda característica associada ao contraste obtido das imagens de microscopia ótica, indica que o benzoato promove uma melhor interação nas transições entre fases inorgânica/orgânica. Análises termogravimétricas e calorimetria exploratória diferencial indicaram uma elevação nas temperaturas de degradação ($T_d$) - até 17°C - e na temperatura de cristalização ($T_c$) - até 11°C - no compósito quando comparado ao polímero puro. Tal elevação está associado a redução de mobilidade da cadeia polimérica, pela presença dos nanocristais na matriz.

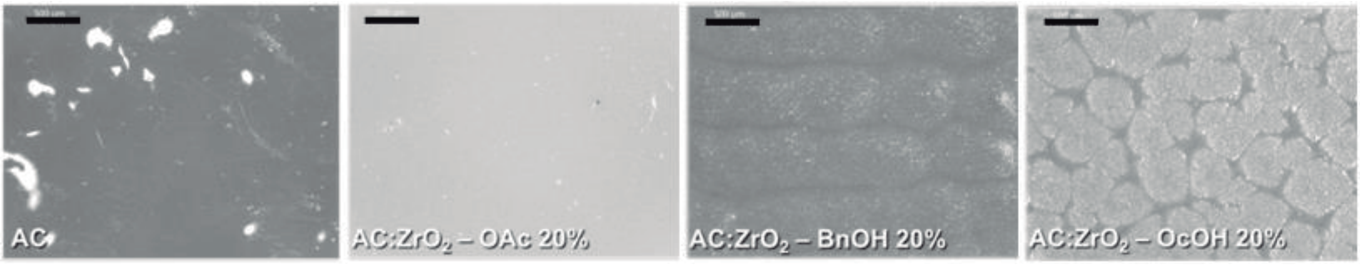

Figura 1: Microscopia ótica das membranas do nanocompósito (barra de escala 500 µm). Concetração (m/m)

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**Área:** ______________________

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

# Interfacial Self-assembly of Silk Fibroin Polypeptide and α-$NiCo(OH)_2$ Nanocrystals with Tunable Energy Storage Applications[1]

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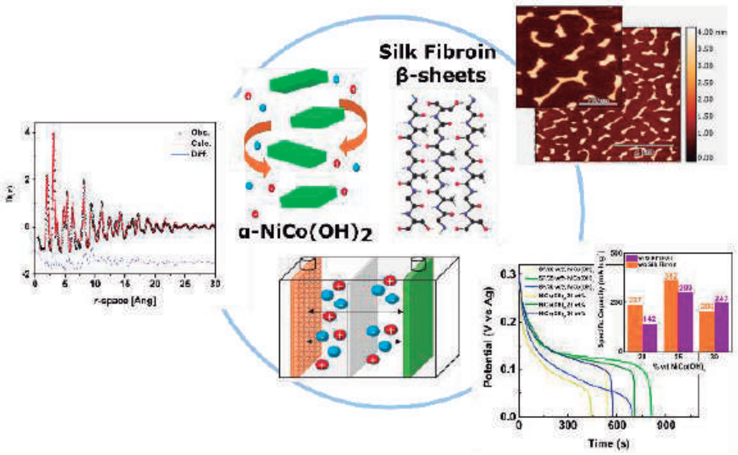
Keywords: Silk fibroin, nickel hydroxide, pair function distribution, β-sheets crystallinity, energy storage.

## Highlights

The silk fibroin stabilized the alpha polymorph of nickel-cobalt hydroxide nanoparticles. At the same time, the inorganic constituents induced the formation of a multi-domain network of β-sheets in polypeptide chains, making these structures suitable for applications as electrochemical energy storage.

## Abstract

There is an increasing interest in the self-assembly process from a bottom-up approach to synthesize functional structures for engineering applications. Silk fibroin is a protein extracted from the cocoons of silkworm Bombyx mori that can be processed into various materials generally stabilized by the induction of *β*-sheet formation through the use of solvents or by physical stretching. In our study, the introduction of cobalt-substituted nickel hydroxide nanoparticles on silk fibroin presented a dual effect causing the stabilization of the α polymorph of nickel hydroxide and promoting a highly connected network of the β-sheet crystalline domain in the fibroin chains. Electrochemical measurements were performed to examine silk fibroin (SF)/$NiCo(OH)_2$ hybrid materials. The optimized sample exhibits a high specific capacity of 362 mA h $g^{-1}$ at the current density of 1 A $g^{-1}$, maintaining steady electrochemical performance >75% of the initial value at higher current densities. The presented assembly provides a route for preparing monodisperse inorganic nanoparticles in the presence of SF as an organic matrix with potential energy storage properties.[1]



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## Acknowledgments

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**Área: ______________________**

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# Investigation of amphiphilic peptides as sensing elements for pesticide biosensors

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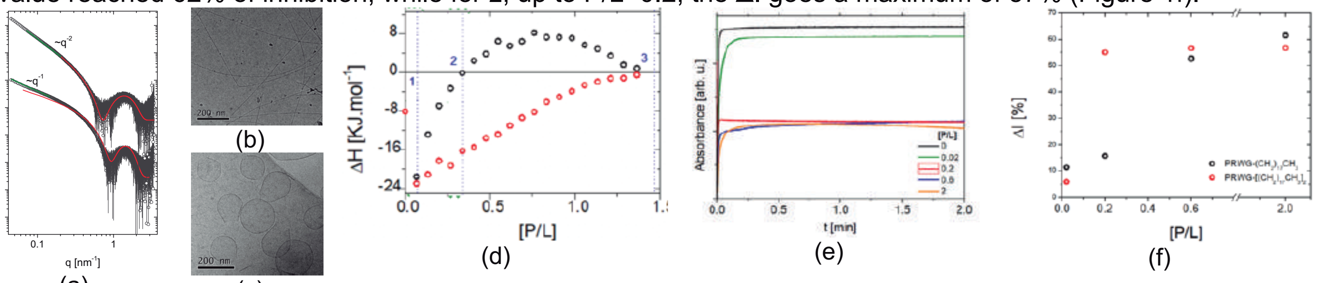
**Keywords:** *Lipopeptides; pesticide; SAXS; UV/Vis, Ellman's test.*

## Highlights

1) Acetylcholinesterase-mimetic system based on lipopeptide self-assembly; 2) Structural and thermodynamic study in the presence and the absence of pesticide; 3) Insights into the inhibition mechanisms involved in different self-assemblies.

## Abstract

The extensive use of pesticides in food production has attracted significant attention in the last years, mainly due to its impact on human health, ecological imbalance, and environmental contamination.[1] Million people are estimated to be poisoned by pesticides worldwide, of which over 300,000 die each year.[2] In this work, we synthesized new lipopeptides that can be used as functional models of the enzyme acetylcholinesterase (AChE) for future application as biosensors. These peptides contain the amino acids L-proline (P), L-arginine (R), L-tryptophan (W), and L-glycine (G), covalently linked to one (compound **1**) or two (compound **2**) long aliphatic chains. They were characterized using SAXS/SANS, Cryo-TEM, and Cryo-TEM techniques in an acidic medium. Also, we performed isothermal titration calorimetry (ITC) and UV/Vis experiments to analyze the pesticide and lipopeptide interactions. A considerable difference in the enthalpy and absorbance was observed between the system composed of one or two carbon chains in the pesticide presence. SAXS data allowed us to obtain some information on the morphology of the systems. In both cases, we can see core-shell forms. However, it is possible observed in the low q region, and the data have different behavior (see Figure 1a). For **1**, we observed an exponential decay $q^{-1}$ indicating the self-assembly of this system corresponds to a cylinder micelle core-shell structure. In the case of compound **2**, a planar core-shell structure ($q^{-2}$ exponentials decay). Figure 1d presents the ITC results for titration of glyphosate (PNG) in aqueous phosphate buffer at pH 7 of compounds **1** and **2**, respectively. The obtained enthalpogram for each system as a function of molar ratio pesticide/lipopeptide (P/L), obtained from the integration of each peak shown in the fluxogram, is different, translating distinct interactions. The kinetic experiments were performed to quantify the lipopeptide activity catalytic and inhibition ratio using Ellman's colorimetric procedure, as shown in Figure 1e. For **1**, we obtained a linear behavior, and for the higher pesticide amount, the value reached 62% of inhibition, while for **2**, up to P/L=0.2, the ΔI goes a maximum of 57% (Figure 1f).



(a) (b) (c) (d) (e) (f)

**Figure 1**. (a) SAXS data spectra of **1** and **2** with 0.2 wt%. The green line represents a decaying exponentially at low q values, corresponding to a cylinder ($q^{-1}$) and a planar ($q^{-2}$) system. The red line is the fitting using a cylinder core-shell and a bilayer as form factor. Cryo-TEM images (b) for **1** and (c) for **2** at PBS (pH=7.0). (d) ITC data for **1** and **2** and the SAXS data of the lipopeptides in the presence of PNG. The black and red dots correspond **1** and **2**, respectively. (e) Absorbance intensity as a function of the time with different lipopeptide amounts (for **1**). The inhibition rate as a function of P/L for **1** and **2**.

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## Acknowledgments

FAPESP, CNPq, CAPES, INCT de Bioanalítica

**Área: MAT**

# Investigation of novel hybrid titania-silica materials: improving surfaces for promising applications

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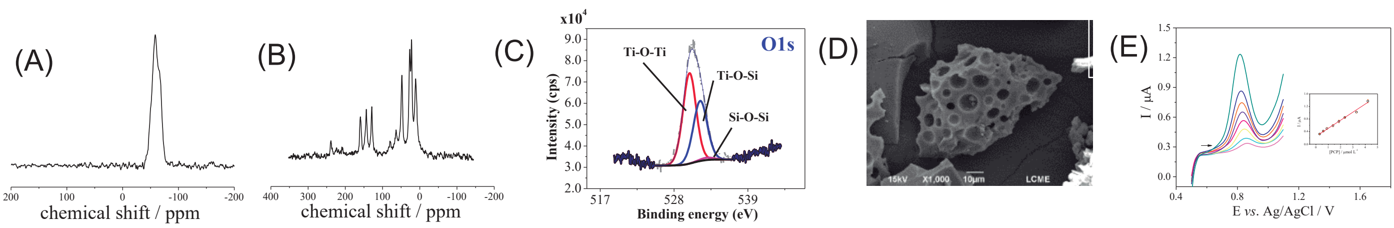
Palavras Chave: titania/silica, hybrid materials, electrochemical sensors, photoelectrochemisty

## Highlights

Synthesis and characterization of new titania-silica hybrid materials with successfull application to electroanalysis and promising results for photoelectroanalysis.

## Abstract

Titania-silica hybrid materials are a promising subject of research due to their combined properties that give the potential for its application in several technological fields. Chemical reactivity, thermic and mechanical proprieties provide interesting abilities to these materials to be applied in photocatalysis, adsorption processes, and electrochemical sensors[1]. This work proposes the synthesis and characterization of new hybrid titania/silica xerogels, the investigation of the influence on morphology and reactivity by altering the proportions of titanium and silicon precursors in amorphous and crystalline structures, and also by subsequent modifications with the organic group 4-methylpyridine in amorphous xerogels. The materials were characterized by spectroscopic techniques such as ATR-FTIR, DRS, XPS, solid-state $^{13}$C-NMR, and $^{29}$Si-NMR. The thermogravimetric, morphological, and surface profiles were investigated by the TGA, SEM, EDX, BET, and BJH methods. CHN elemental analysis and ion chromatography were performed to investigate the composition and ion exchange capacity of the new materials. The chemical structures of the material's surfaces were analyzed and compared according to the different proportions. The modification of amorphous xerogels with 4-methylpyridine was proven and the resulting positive charge associated with aromatic rings amplifies the electronic properties of these materials, achieved great potential for electrochemical applications. However, of the calcined xerogels, only the one with the highest proportion of Ti versus Si showed a significant improvement in the bang gap energy, ranging from 3.32 eV to 3.15 eV. The XRD results confirm that this material has a better-defined crystalline structure compared to the others. Electrochemical devices were built to quantify pentachlorophenol in river samples. Experiments for application in photoelectroanalysis are under development showing promising results.



Summarized results for TiSi30-4Pic: (A) and (B) $^{29}$Si-NMR, and $^{13}$C-NMR; (C) XPS Os1 spectra, (D) SEM image and (E) differential pulse voltammogram to PCP calibration curve.

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**Área: MAT**

# $Ln^{3+}$:YAG obtained via spray pyrolysis - particles and fibroin-based compounds, and its photonic applications

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Palavras Chave: *Luminescence Spectroscopy, Random Laser, Thermometry*

## Highlights

$Nd^{3+}$:YAG micropowder Random Laser was demonstrated;

All $Er^{3+}$ doped materials (YAG particles and Fibroin films) were exploited as luminescent thermometer.

## Resumo/Abstract

Advances in photonics are related to obtaining new materials and nanostructured systems, as well as studying non-linear effects. In this sense, laser emission resulting from the confinement of light in a disordered structure is a promising field of research[1], as well as the development of optical thermometers[2] and materials that can be applied as anti-counterfeiting devices[3], among others. In this work, YAG (Yttrium Aluminum Garnet, $Y_3Al_5O_{12}$) spheres doped with different lanthanide ions were obtained via Spray Pyrolysis, a methodology that provides high yield and can be used for large-scale production, without generating byproducts, and offering the advantage of not introducing impurities into the final product, since there is no external contact with the precursors, and each drop constitutes a homogeneous mini reactor that has the same chemical composition as the initial solution. During the synthesis and even after heat treatment at 1100 °C, the particles did not coalesce. All characterizations confirmed that the YAG phase was obtained in the presence of lanthanide ions ($Nd^{3+}$ or $Yb^{3+}/Er^{3+}$), which had their spectroscopic properties analyzed and explored for photonic applications. The $Nd^{3+}$:YAG particles were studied for their emissions in disordered environments[4], and the Laser threshold energy was depending of the $Nd^{3+}$ concentration. In addition, $Yb^{3+}/Er^{3+}$:YAG were intended for studies at different temperatures[5]. Furthermore, aiming for biological applications, these $Yb^{3+}/Er^{3+}$ doped particles were added to Silk Fibroin which is a biocompatible matrix that allows the insertion of different ions, molecules or nanoparticles; that shows good suitability in optical systems, mainly due to high transparency (> 95%) throughout the visible region of the spectrum; that is mechanically robust and moldable in the form of films[6], wires and particles. The same behavior observed in the particles was also observed in the film form.

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## Agradecimentos/Acknowledgments

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**Área: MAT**

# Low-dimensional $Co_3O_4$ as a plasmon free SERS substrate

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Key words: 2D nanomaterials, Semiconductor, SERS, Non-plasmonic substrate.

## Highlights

Semiconducting low-dimensional $Co_3O_4$ was employed to obtain a homogeneous and sensitive surface-enhanced Raman scattering (SERS) substrate for the non-plasmonic detection of rhodamine 6G.

## Abstract

**SERS** provides molecular fingerprints with high sensitivity, suitable for low-concentration biochemical detection. Apart from noble-nanoparticle substrates, semiconductors have emerged as promising (*e.g.*, lower cost, more homogeneous and specific, etc) materials for non-plasmonic SERS substrates, based on the charge-transfer (CT) mechanism. **$Co_3O_4$** is a highly porous semiconductor, with excellent stability and interesting electronic properties and, although being especially attractive, so far it has never been tested for this purpose. Thus, we have produced **$Co_3O_4$** and studied its properties targeting at a **SERS** substrate. Flower-shaped **$Co_3O_4$** nanostructures were obtained through a hydrothermal synthesis. The resulting powder was then exfoliated in ethanol (15 and 120 min), leading to the stable dispersions named **$Co_3O_4$-15** and **$Co_3O_4$-120**, respectively. Raman spectra confirmed the typical bands of the oxide and scanning electron microscopy (SEM) depicted highly porous materials in flower- and sheet-shaped structures for **$Co_3O_4$-15** and **$Co_3O_4$-120**, respectively (see **Figure 1A**). Atomic force microscopy attested thicknesses of ~15 nm for **$Co_3O_4$-120**. After morphological characterization, the oxides were investigated as **SERS** substrates with rhodamine 6G (**R6G**) as the probe molecule. Optimization studies showed that laser wavelength, **$Co_3O_4$** dispersion and proportion between **$Co_3O_4$** and **R6G** directly affect the **SERS** efficiency. Best results were obtained under $\lambda$ = 488 nm and 1:2 v/v mixture of **$Co_3O_4$-120** $1 \times 10^{-3}$ M /**R6G**, which detected down to $1 \times 10^{-8}$ M of analyte, while **$Co_3O_4$-15** could detect only down to $1 \times 10^{-5}$ M. Besides, Raman mapping attested the uniformity of the detection showing **$Co_3O_4$** sheets highly covered by **R6G** at $1 \times 10^{-8}$ M (**Figure 1B**). The more exposed surfaces of **$Co_3O_4$-120** may improve **R6G** adsorption and facilitate CT process. In fact, infrared spectra of **$Co_3O_4$-120/R6G** exhibited a new band, not observed for the separate components, suggesting a **$Co_3O_4$/R6G**-complex with enhanced CT process and, thus, **SERS** enhancement.

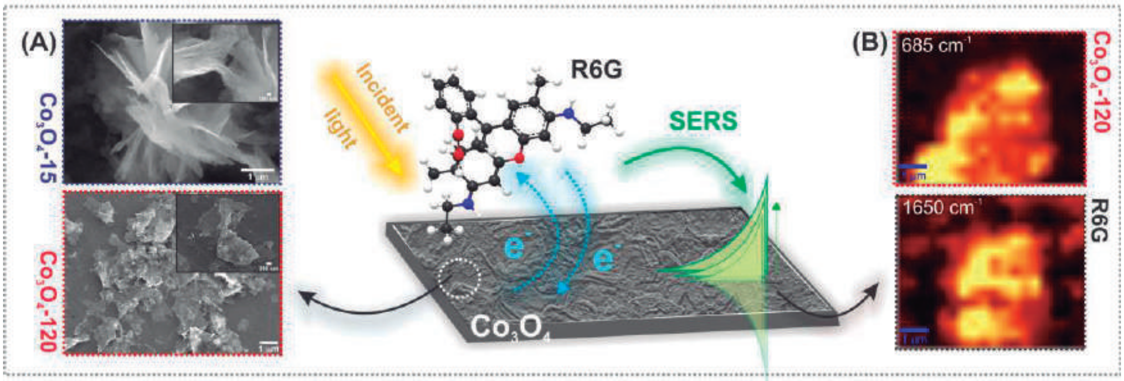

**Figure 1.** Overview of this work: (A) SEM images of the samples (B) Raman mapping of R6G $1 \times 10^{-8}$ M over $Co_3O_4$-120.

Overall, this work points to new possibilities towards the development of efficient, low-cost and homogeneous **SERS** substrates for the specific detection of a variety of analytes.

## Acknowledgments

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**Área: MAT** **Nº de Inscrição: _________**

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# Magneto-luminescent NaLnF$_4$ core@shell nanoparticles doped with Er(III), Yb(III), Nd(III) e Dy(III) as optical nanothermometer and magnetic field sensor

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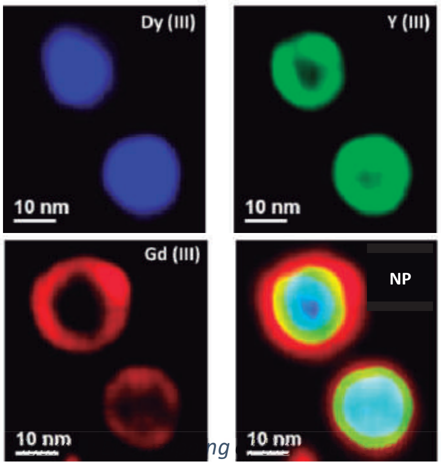
Keywords: *Lanthanide, upconversion, magnetic nanoparticles, core@shell nanoparticles.*

## Highlights

The nanoparticles may be excited at 980, 808 and 1550 nm, allowing their application in two different biological windows. Core@shell nanoparticles are paramagnetic systems, leading to a magneto-luminescent material.

## Abstract

Lanthanide-doped NaLnF$_4$ nanoparticles are a versatile system in the construction of multifunctional materials. A combination of optical and magnetic properties in a single system might lead to favorable synergistic effects for the construction of optical probe/sensors. Based on the intrinsic paramagnetism and the Stokes or anti-Stokes emissions of the lanthanide ions, this work presents the synthesis of NaLnF4 core@shell nanoparticles doped with Er(III), Yb(III), Dy(III) and Nd(III) ions. The core containing the Dy(III) ion will be the main responsible for the magnetic properties. The core is separated by both magnetically and optically inert shell from other shells that are co-doped with the Er(III), Yb(III) and Nd(III) ions, which are responsible for the photophysical properties of these systems. Results show the formation of nanoparticles with high crystallinity, well-defined morphologies and narrow size distribution. EDS mapping (Figure 1) indicates the core@shell hierarchical structure, which is corroborated by the systematic studies of luminescence and magnetization as a function of the applied magnetic field. The proposed nanoparticles show upconversion emissions, assigned to the Er(III) ion using excitation sources (lasers) at 808 nm, 980 nm and 1550 nm. It shows the versatility of the system in terms of its application as a biological probe imaging, where three different biological windows may be used. For thermometry measurements, 808 nm and 980 nm lasers were used for monitoring visible and infrared emissions, and it shows promising results over a wide temperature range from 87K to 327K (Figure 2). Photoluminescence measurements under applied external magnetic field show the applicability of the system as a magnetic field probe. The nanoparticles that make up this work are multifunctional showing magneto-luminescent characteristics. The results show their applicability as optical temperature and magnetic field probes.



*ng nanoparticles hierarchical structure*

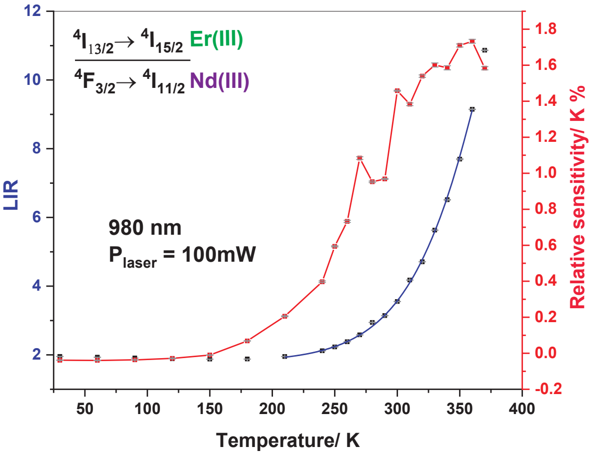


*Figure 2: Relative thermal sensitivity curve (red) and LIR (blue) as a function of the temperature of the core@shell nanoparticles monitoring the emissions in the NIR region.*

## Acknowledgments

This work was supported by CAPES, FAPESP, CNPq, INOMAT, LNNano and Multi-user Laboratory for Advanced Optical Spectroscopy.

**Área: MAT**
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# Materiais porosos à base de óxido de grafeno para o desenvolvimento de biocatalisadores

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Palavras Chave: *Grafeno, Mobilização enzimática, Celulose bacteriana, Biocatalisadores.*

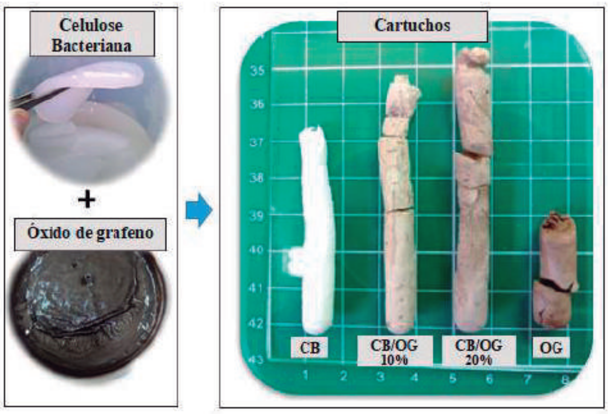
## Highlights

Porous materials based on graphene oxide for the development of biocatalysts

- Hierarchical bacterial cellulose and graphene oxide cartridges
- Porous immobilized material with potential in catalytic processes.

## Resumo/Abstract

A síntese de novos materiais tem sido objeto de crescente interesse por parte da comunidade científica, devido a escassez de recursos e a necessidade de práticas cada vez mais sustentáveis. Assim sendo, o uso de materiais porosos à base de carbono, que possuem propriedades únicas como alta resistência mecânica e alta área superficial, tornam-se potencialmente vantajosos para diversas aplicações, dentre elas, destacam-se os processos de imobilização enzimática, que podem conferir maior estabilidade às enzimas em condições de reação contra enzimas livres. Neste contexto, esta proposta visa desenvolver um novo biocatalisador com compostos de óxido de grafeno (GO) dispersos em uma matriz de celulose bacteriana, na forma de cartuchos e investigar seu desempenho em reações processadas em sistema de fluxo. O GO é o material ativo para imobilização enzimática com um profundo conhecimento de sua morfologia e propriedades estruturais. Os materiais foram preparados na forma de cartuchos a partir da síntese de óxido de grafeno, com posterior dispersão em uma matriz de celulose bacteriana. Em seguida, foram caracterizados por espectroscopia de absorção na região do infravermelho (FTIR), Análise Térmica (TG) e RAMAN. Posteriormente, a Enzima *Candida Rugosa* lipase será utilizada e os materiais obtidos deverão ser caracterizados por diferentes técnicas. O potencial dos materiais como suporte enzimático será avaliado por meio de um sistema de comutação com ativação eletrônica e detector de espectrofotometria UV-vis. Assim, os resultados iniciais demonstram a produção de um cartucho bem formado e espera-se com potencial em processos catalíticos.



## Agradecimentos/Acknowledgments

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**Área: MAT**

# Mechanochemistry and advanced nanomaterials: an environmentally friendly approach for bottom-up solid-state synthesis of noble metal nanoparticles

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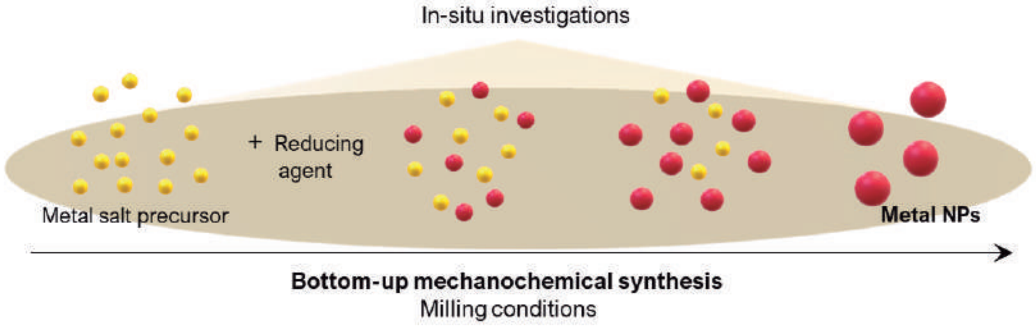
Keywords: *mechanochemistry, bottom-up approach, nanoparticles, ball-milling, in-situ investigation*

## Highlights

Bottom-up mechanochemical synthesis of mono- and bimetallic nanoparticles under ball-milling conditions. In-situ PXRD and XAS investigations of nanoparticle formation. Au and Ag plasmonic nanoparticles.

## Abstract

The interest in design of metal nanoparticles (NPs) continuously increase due to their exceptional properties, which make them suitable for applications in catalysis, energy, biomedicine, and sensing.[1] Solution-based synthetic protocols have succeeded in tuning the properties of metal nanostructures by controlling the nanoparticle architecture (size, shape, etc.). These techniques are, however, highly sensitive to the reaction conditions, and are either solvent and/or energy intensive. In the recent years, alternative environmentally friendly routes for the preparation of advanced materials have emerged. This is the case of solid-state mechanochemical synthesis,[2,3] which have been explored as a green alternative for the preparation of noble metal NPs from the chemical reduction of the metal precursors, i.e., through bottom-up approach.[4] Differently from simply particle size reduction by milling the bulk metals (top-down), bottom-up mechanochemical synthesis (BUMS) opens the possibility to control the reaction rate, nucleation, and growth, leading to a final controlled structure in terms of size, morphology, and composition. On the other hand, a fine tuning of the nanoparticle's properties is far from being reached through BUMS due to the limited information on the mechanisms of nanostructure formation.[4] Au NPs and Ag-Au nanoalloys have been the subject of our studies due to their exceptional plasmonic properties.[5,6] We have observed that the expected strength of the reducing agent based on solution chemistry is not replicated in the solid-state mechanochemical conditions. Conversely, the rate of reduction seemed not to affect the nucleation and growth in the same manner as in solution.[7] We have been using in situ X-ray absorption spectroscopy (XAS) and powder X-ray diffraction (PXRD) to study the BUMS of noble metal NPs to reveal the true mechanism of formation of the nanostructures, in an attempt to rigorously control their final size, shape and composition.[8] In our studies we have focused on the chemical reduction of the metal precursors, which it the first fundamental step for the construction of nanostructures and, consequently, to control their properties toward the target technological applications.



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## Agradecimentos/Acknowledgments

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**Área: MAT**

# Methylene blue adsorption process in arabic gum and *Araucaria angustifolia* seed coat bran hybrid hydrogels: Reuse and Isotherms

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Keywords: Methylene Blue Adsorption, Hydrogel, Arabic Gum, *Araucaria Angustifolia* seeds, Isotherms.

## Highlights

Our studies have shown that arabic gum hydrogels have a high adsorption capacity for the methylene blue dye. The presence of *A. angustifolia* seed (pinion) coat bran in these hydrogels, in addition to increasing the adsorptive capacity, also allowed their reuse, probably due to the non-saturation of its binding sites.

## Abstract

Hydrogels are three-dimensional polymeric networks capable of absorbing a large amount of water or other fluids. They can be synthesized from synthetic or natural polymers, such as the arabic gum.[1] Hydrogels have been studied aiming enviromental applications. Based on this, in this work we synthesized hybrid hydrogels based on gum arabic and pinion coat bran and applied them in the methylene blue dye removal from aqueous solution. This adsorption process was studied by Langmuir and Freundlich isotherms. The hydrogels were synthetized with 400.0 mg of arabic gum previously modified with glycidyl methacrylate, 1.04 mL of N,N-dimethylacrylamide, 1.0 g of sodium acrylate and different amounts of pinion coat bran (0.0, 50.0 and 100.0 mg, being called as G2P1, G2P2 and G2P3, respectively). Potassium persulfate (20.0 mg) was used as the polymerization reaction initiator.[2] The methylene blue adsorption experiment was carried out in triplicate with 200.0 mL of the dye at a concentration of 20.0 mg $L^{-1}$ over a period of 168 hours, while the reuse experiment was carried out in 24 hour cycles. For the dye removal experiments was verified that the G2P2 and G2P3 hydrogels, previously swollen in water, showed high removal capacity, reaching values close to 90% (Figure 01A). Furthermore, the G2P3 hydrogel showed a great reuse capacity since they maintained removal rates above 90% even after three cycles of use (Figure 01B). These results suggested a possible efficiency in removing methylene blue dye in concentrations above 20.0 mg $L^{-1}$. So, the isotherms were studied with different methylene blue concentrations (20.0; 40.0; 60.0; 80.0 and 100.0 mg $L^{-1}$). The plotted lines showed that the Freundlich model best represents the dye adsorption process (Table 01), since the $R^2$ has values closer than 1,000 when compared to the Langmuir model. These results demonstrates that methylene blue is adsorbed in several layers, which is consistent with the heterogeneity of the hydrogel surface.

**Figure 01:** (A) Methylene blue dye removal profile in 168 hours; (B) Reuse of hydrogels after 24-hour cycles; (C) Image of final staining of methylene blue solutions after 168 hours of removal (G2P1, G2P2 e G2P3, from left to right).

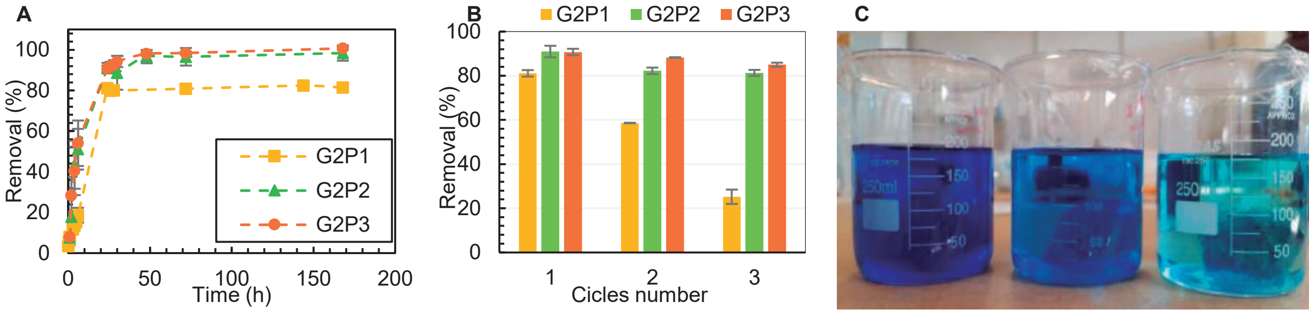

**Table 01:** Parameters found for the Langmuir and Freundlich models.

| Pinion Amount (mg) | Langmuir Isotherm | | | Freundlich Isotherm | | |
|---|---|---|---|---|---|---|
| | $Q_m$ | $K_L$ | $R^2$ | $n_F$ | $K_F$ | $R^2$ |
| 0.0 (G2P1) | 250,00 | 0,028 | 0,102 | 1,115 | 7,128 | 0,905 |
| 50.0 (G2P2) | 142,86 | 0,082 | 0,494 | 1,490 | 13,330 | 0,960 |
| 100.0 (G2P3) | 125,00 | 0,182 | 0,738 | 1,425 | 19,492 | 0,900 |

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## Acknowledgments

# $MgAl_2O_4:Eu^{3+}x,Mx$ (M = $Na^+$, $K^+$; x = 2, 3 %) red-emitting phosphor: Photoluminescence study aiming its application in WLEDs

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Keywords: WLEDs; Phosphor; Red-emitting; Co-doping; Electronic Properties.

## Highlights

The Pechini synthesis of $MgAl_2O_4:Eu^{3+}$ co-doped with alkaline metals aiming the reduction of electronic defects exhibited satisfactory photophysical properties, displaying potential for phosphor-converted LED application.

## Abstract

Nowadays, light-emitting diodes (LEDs) are widely used in different areas due to their low energy consumption and high efficiency [1], and they have been a recurring focus of several research to further improve their properties. Among the methods to produce white light-emitting diodes (WLEDs) the current one used commercially is the phosphor-converted hybrid-LED. It consists of a blue semiconductor that excites the yellow phosphor $Y_3Al_5O_{12}:Ce^{3+}$ (YAG:$Ce^{3+}$), although it suffers from a low color rendering index (CRI) and high color correlated temperature (CCT) due to the lack of red-emitting component [1]. Therefore, this study reports on the photoluminescence properties of $Eu^{3+}$-based $MgAl_2O_4$ co-doped with alkaline metals red phosphor synthetized by the Pechini modified method with D-sorbitol as a polymerizing agent. The resin was produced by adding, under heating and stirring, a stoichiometric amount of metal ion solution to the complexing agent, citric acid, and D-sorbitol, and fired at 350 °C, 3 h, yielding the so-called precursor charcoal. Thus, $Na^+$(2, 3 at. %) or $K^+$(2, 3 at. %), $Eu^{3+}$(2, 3 at. %) doped $MgAl_2O_4$ samples were formed by the charcoal annealing at 1000 ºC, 5 h, whose procedure was adapted from reference [2]. XRD data confirmed that all samples are monophasic, and their diffraction profile is assigned to $MgAl_2O_4$ spinel single-phased. From Rietveld refinement, the M-O bond length (M = $Mg^{2+}$, $Al^{3+}$), coordination number, and the sites assigned to each cation were estimated. XPS analysis was also performed and indicated the absence of surface contamination. Theoretical data obtained by density functional theory (DFT) also revealed the positive variation in lattice energy, explaining the easy stabilization of the phase. In addition, excitation spectra of samples recorded monitoring the $^5D_0\rightarrow^7F_2$ transition at 619.5 nm displayed the transition assigned to charge transfer band $O^{2-}\rightarrow Eu^{3+}$ as the most intense, while the narrow band attributed to $^7F_0\rightarrow^5L_6$ at 394 nm was the most intense one among *f-f* transitions. It can be highlighted that no shifts were noted in all excitation spectra. On the other hand, emission spectra recorded under excitation at the charge transference band at 250 nm revealed that the band assigned to the hypersensitive $^5D_0\rightarrow^7F_2$ transition exhibited the highest relative intensity, suggesting the insertion of $Eu^{3+}$ in low symmetry sites without inversion center [3]. Also, it was noticed that the $^5D_0\rightarrow^7F_1$ magnetic dipole transition has at least three components, suggesting $Eu^{3+}$ insertion into multiple non-equivalent sites. Concerning the relative intensity, the comparison of the ratio between 0-2 and 0-1 ($I_{0-2}/I_{0-1}$) intensity was performed, since 0-1 transition does not depend on the chemical environment [3], confirming that $MgAl_2O_4:Eu^{3+}(3\%),K^+(3\%)$ sample was the most intense one, being the best candidate for its possible application. The co-doping with potassium possibly decreased the holes and vacancies concentration, which decreases the phonon energy and thus, increases the radiative decay rate. Theoretical calculations by DFT will still be made to confirm this assumption. In conclusion, all analyzed results demonstrate that the red-emitting phosphor was successfully synthesized via Pechini modified method, and spectroscopic data confirmed that it is a promising candidate to develop a WLED prototype with a component in the red spectral region.

## Acknowledgments

CNPQ 128803/2021-5 Research group LaMaC and LCGRS - Prof. Dr. Silvio Rainho Teixeira.

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**Área: CAT**

# Microwave-assisted synthesis of metal semiconductors heterojunctions with photocatalytic applications

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Palavras Chave: *Titanate Nanotubes, Carbon Nitride, Bismuth Vanadate, Bismuth Niobate, Tungsten Oxide, Microwave-assisted syntheis.*

## Highlights

TiNT/g-$C_3N_4$, $BiVO_4/WO_3$ and $BiNbO_3/WO_3$ were prepared through microwave-assisted routes. The resulting photocatalyst were applied for dye degradation and $H_2$ production under sunlight irradiation.

## Resumo/Abstract

Using solar light in photo-induced processes is very attractive since it is a clean and practically limitless energy source. Recently research related to the development of new photocatalysts capable of use this kind of energy has been growing. Metal semiconductors have excelled in this field, however, the development of materials capable of utilize the visible component of the radiation (major portion of the Sun fallout) it is a contemporary challenge. The development of new heterojunctions of nanostructured metal semiconductors, whose synergic effect make it possible the use of the visible radiation, result in improved photocatalytic activity.

The talk will be focused on the following heterojunctions: titanate nanotubes/carbon nitride (Figure 1a), bismuth vanadate/tungsten oxide (Figure 1b) and bismuth niobate/tungsten oxide (Figure 1c). These catalysts were synthesized through microwave-assisted routes, an emergent technique that allows quickly obtaining of the desired products, with high selectivity, high yields and low energetic consumption, in comparison to conventional synthesis methods.These heterojunctions were characterized through several techniques and applied on photodegradation of organic species and photoelectrochemical generation of $H_2$.

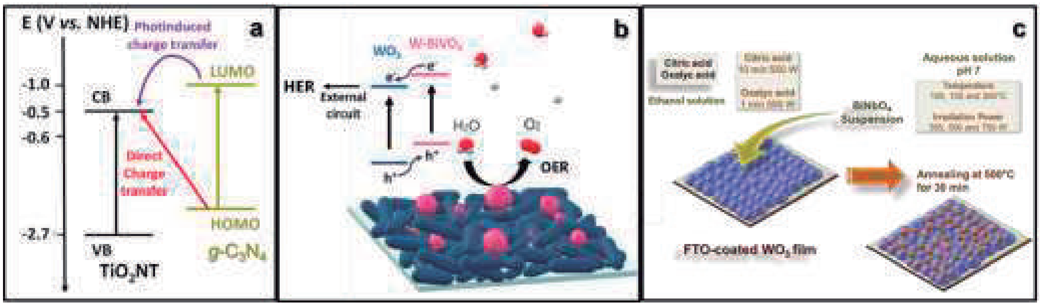

Figure 1. (a) Titanate nanotubes/carbon nitride. (b) bismuth vanadate/tungsten oxide and (c) bismuth niobate/tungsten oxide, studies.

## Agradecimentos/Acknowledgments

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**Área: MAT**

# Molecular fluorescence combined with theoretical models for the evaluation of copper - graphene oxide (GO) interactions

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Keywords: *Fluorescence suppression, metal, molecular interactions, nanomaterials.*

## Highlights

Copper suppressed GO fluorescence;
Ryan and Weber's mathematical model fitted better when compared to Stern-Volmer;
Controlling the oxidation of the nanomaterial can change the adsorption selectivity.

## Abstract

The water contamination by heavy metals such as copper has been the subject of many studies due to the increase in this metal concentration in the environment, associated mainly with human activities such as mining, industry, and agriculture. With this, researchers have sought to develop efficient materials and techniques for applications in treatments, remediation, and detection of pollutants. Thus, carbon nanomaterials become interesting, especially graphene-based materials, such as graphene oxide (GO), which has unique properties and distinct functional groups and has been widely tested as an adsorbent for metallic ions. However, studies are limited to understanding the efficiency and do not show how these interactions occur and whether GO is the best option for adsorption. Based on this, the present study aims to evaluate the ability of graphene oxide to bind by chemical complexation to metallic copper to identify and understand the mechanisms involved in these interactions. The analytical technique of molecular fluorescence was associated with Ryan and Weber's mathematical models and Stern-Volmer. Then, coarse-grained molecular dynamics simulations implemented with the Martini Force field were performed to observe the fundamental role of oxidized sites. Initially, synthesized GO was characterized by different experimental techniques.The GO used in this study is a few layered material with a lateral sheet size of up to 2 μm². The infrared spectroscopy technique proved that the GO presents the characteristics hydroxyl, carbonyl, carboxyl, and epoxy groups. The concentration of -COOH found by potentiometric titration was 1.83 mmol per GO gram. UV-Visible spectroscopy highlighted the typical GO spectra that present two characteristic bands, one at 300 nm and another at 228 nm. This GO showed fluorescence in the visible region, with better intensity at $\lambda_{em}$= 450 nm and $\lambda_{exc}$=520 nm. The suppression of the fluorescence signal was monitored by titrating the GO solution (1.8 mg.mL$^{-1}$) with increasing concentrations of $Cu^{2+}$ ranging from 0 mol.L$^{-1}$ to 7.18x10$^{-3}$ mol.L$^{-1}$. It was possible to notice a gradual attenuation in the intensity values according to the increase in copper concentrations, resulting from the interaction of copper with the aromatic structures and oxygenated groups. The mathematical modeling that best fitted the intensities was that of Ryan and Weber due to the non-linear fit. This same model showed an excellent interaction of GO with the metallic ion with values of Log K = 3.19 and CL of 5.93x10$^{-5}$ mol L$^{-1}$, very similar data for different species found in organic matter, indicating that the GO presents a behavior similar to these molecules in the complexation of copper. This is an important factor, as there is a growing search for materials for environmental remediation that mimic natural molecules. Another relevant aspect observed was the intensity 38.1; the fluorescence did not decrease further but fluctuated at very close values; this can be explained by the fact that copper is an intermediate Pearson's acid, thus complexing, but not highly stable, which leads him to get into his labile form quickly. Using the Molecular Dynamics simulations, it was possible to identify that all copper ions are close to the GO wall. This increase in the concentration of $Cu^{2+}$ in the GO sheet vicinity is accompanied by a decrease in the concentration of the $SO_4^{2-}$ anion. This shows how controlling the oxidation of the nanomaterial can change the adsorption selectivity of the material. Thus, GO may have an efficient approach to interacting with metals and maybe a new tool for sensing and controlling areas contaminated by copper ions; however, it may not be the most advantageous option when used as adsorbents of high concentrations of copper.

## Acknowledgments

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**Área: MAT__________ Nº de Inscrição: 1135___**

# Molecular orientation and charge transfer dynamics in transparent and conductive electrodes based on grafene oxide and PEDOT:PSS composites

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*Keywords: Organic solar cells, Conductive eletrodes, Grafene oxide, PEDOT:PSS, Morphology, Ultrafast charge transfer*

## Highlights

- The combination of PEDOT:PSS and GO is an efficient alternative structure for ITO in organic photovoltaics, due to the elimination of some drawbacks of ITO, such as high production costs and breakable structure under deflection.
- Spectroscopic results reinforce the synergistic effects found between GO and PEDOT:PSS nanocomposites.
- Application of synchrotron-based spectroscopic techniques.

## Abstract

The conducting polymer, poly(3,4-ethylenedioxythiophene):poly-(styrenesulfonate) (PEDOT:PSS), is certainly one of the most important substitute materials for indium tin oxide in organic devices. Its metallic conductivity and transmittance bring favorable perspectives for organic photovoltaic applications. Although graphene oxide (GO) is not a good conductor, it can form high-quality thin films and can be transparent, and additionally, GO is an inexpensive material and can be easily synthesized. This study investigated how the conductivity of a composite film of graphene oxide (GO) and different amounts of PEDOT:PSS can be modified. The effects of GO:PEDOT:PSS composites with several PEDOT:PSS proportions were analyzed in regards to the composite molecular structure and ordering, charge transfer dynamics (in the femtosecond range), electrical properties and morphology. For the best conductivity ratio, GO found with 5% PEDOT:PSS, a solvent treatment was also performed, comparing the resistivity of the film when treated with dimethyl sulfoxide (DMSO) and with ethylene glycol. Charge transfer times at sulfur 1s absorption edge were calculated by the core-hole clock method and the results demonstrate the faster electron delocalization process for the composite containing 5% of PEDOT:PSS with a value of 3.3 fs, which may be related to the higher homogeneity and ordering of this film, as probed by AFM, SEM and NEXAFS [1]. Additionally, the effect of thermal treatment of the nanocomposites was also evaluated by surface- and bulk-sensitive NEXAFS, resonant Auger spectroscopy and X-ray photoelectron spectroscopy [2]. GO:PEDOT:PSS 5% offers the best synergetic effect among the blends, a result that is in complete agreement with the electrical measurements.

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## Acknowledgments

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**Área: MAT**

# Nanocatalyst based on tridimentional graphene decorated with gold nanoparticles for contaminant degradation

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Keywords: *Nanocatalyst, Graphene, Gold nanoparticles, Degradation, Methylene blue.*

## Highlights

Porous three-dimensional nanocatalyst based on graphene decorated with gold nanoparticles synthesized in a green one-step way. Efficient catalytic degradation of methylene blue dye in aqueous media.

## Abstract

Due to the presence of pollutants in aquatic systems and the health impacts they can cause, the search for their remediation becomes inevitable. Aiming to mitigate or eliminate these contaminants, the use of nanoparticles of noble metals, such as gold, becomes an alternative precisely because of its catalytic potential. However, due to its instability, it is necessary to use support materials to maintain their properties[1]. Graphene materials are excellent support for metallic nanoparticles and have even more stability in their three-dimensional form.[2] In this context, the present work aimed at the preparation and graphene-based macrostructures decorated with gold nanoparticles (3DrGOAuNPs) and their evaluation as a nanocatalyst for the degradation of the contaminants molecules in aqueous media. Three-dimensional reduced graphene oxide decorated with gold nanoparticles were obtained from the thermochemical reduction of graphene oxide (GO) in the presence of the metal precursor; our group patented this method (BR10202001803). The materials were characterized by Scanning Electron Microscopy (SEM) and infrared spectroscopy (FTIR). In addition, the application and catalytic activity were evaluated through kinetic monitoring. The reactions were monitored by the Methylene Blue (MB) dye degradation. The catalytic degradation test consisted of mixing the solution with the MB molecule (30 $\mu$mol $L^{-1}$), containing a sodium borohydride solution (0.15 mol $L^{-1}$), maintained under controlled temperature and agitation in the presence of 20 mg of the nanocatalysts. The reaction from the beginning was monitored periodically using Ultraviolet-Visible Spectroscopy. In order to verify the nanocatalyst reusability, the same nanocomposite was used several times. SEM images showed that the synthesis methodology used provided the formation of well-defined porous rGO macrostructures uniformly decorated with AuNPs, with an average diameter of 68 nm. The FTIR spectra confirmed the reduction of the graphene oxide. The MB degradation reaction starts immediately. The materials were able to decrease the concentration of the MB solution in a range between 70% to 48% in just 30 minutes. In the control group, where there was no presence of AuNPs, there was a decrease of only 20%, probably due to the adsorptive property of graphene. These results are consistent with literature data for this type of material. The main advantage of our material is that it has a cohesive, stable structure with a high surface area for anchoring the nanoparticles, further facilitating the separation of the catalyst, preventing defragmentation during the application, and enabling prior adsorption of the molecules to be degraded. It was also possible to synthesize efficient nanocatalysts in a green, fast, and accessible way. Tests with other contaminants are already underway to prove the nanocatalyst's versatility.

## Acknowledgments

FAPERGS (scholarship and project term 21/2551-00007362), INOVAPAMPA, INCT-Nanocarbono, CNPq (proc. 424146/2018-5).

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

**Nº de Inscrição: 01361**
*(Inserir o número de inscrição do autor que fez a submissão)*

# Nanopartículas de prata suportadas em carvão ativado oriundo de Capim Annoni (*Eragrostis plana Nees*) para redução catalítica do 4-nitrofenol

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Palavras Chave: *Nanopartículas de Prata, Capim Annoni, Carvão Ativado, Contaminantes Emergentes, Catálise*

## Highlights

Silver nanoparticles supported active carbon from Capim Annoni (*Eragrostis plana Nees*) for catalytic reduction of 4-nitrophenol
This nanomaterials may be of interest in heterogeneous catalysis and used for removal pollutants from water.

## Resumo/Abstract

Para este trabalho utilizou-se o carvão ativado oriundo de Capim Annoni (*Eragrostis plana Nees*) via pirólise em forno micro-ondas e ativação química, com área superficial de 1030 $m^2$/g, como adsorvente para as nanopartículas de prata.[1] Esse nanocompósito foi caracterizado por MET, MEV/EDS, DRX, BET e aplicado como catalisador na reação de redução do 4-nitrofenol. Estudos de cinética e equilíbrio químico revelaram a capacidade de adsorção das nanopartículas (NPs) de Ag(0).

A solução coloidal de NPs de Ag(0) foi preparada pelo método de redução química utilizando $AgNO_3$, citrato de sódio e $NaBH_4$. A solução, com coloração amarelada, apresentou banda de plasma característica em torno de 400 nm e as nanopartículas apresentaram diâmetro médio de 8,5± 1,4 nm. Nesta solução foi adicionado 500 mg do carvão a temperatura ambiente por 40 minutos, obtendo assim Ag(0)/C (1,2%).[2] Através de MEV/EDS pode-se observar as NPs de Ag(0) na superfície do carvão e por MET pode-se visualizar nanopartículas com diâmetro médio de 12 ± 2,7 nm .

A cinética de adsorção atingiu o equilíbrio após 10 minutos, obtendo-se a adsorção de, aproximadamente, 80% das NPs de Ag(0) presentes em solução. O modelo de pseudoprimeira ordem foi o mais adequado para descrever o comportamento cinético. Além disso, o modelo de Langmuir foi o mais apropriado para representar as isotermas de equilíbrio. O estudo termodinâmico indicou que a adsorção de NPs de Ag(0) foi espontâneo, endotérmico e favorável entropicamente ($\Delta S>0$). Além disso, apresentou $\Delta H = 60{,}75$ kJ $mol^{-1}$ dando indício de quimiossorção.

O nanocompósito Ag(0)/C foi aplicado na reação de redução do 4-nitrofenol e se mostrou eficiente podendo-se observar a redução total em 10 minutos. Foi possível demonstrar a elevada potencialidade desse carvão em adsorver e estabilizar nanopartículas metálicas.

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## Agradecimentos/Acknowledgments

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# Nanopontos de carbono incorporados em sílica gel funcionalizada para recuperação seletiva dos elementos terras raras

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Os elementos terras raras (ETRs) têm sido cada vez mais utilizados na indústria moderna como os componentes essenciais de catalisadores, ímãs de alto desempenho, supercondutores, sistemas de telecomunicações. O desenvolvimento da energia limpa aumentará ainda mais a demanda, pois ETRs são usados na produção de baterias e painéis solares. Isso resultará em um aumento de lixo eletrônico. As tecnologias atuais para recuperação de ETRs baseadas na extração por solventes não são amigáveis ao meio ambiente e não são aplicáveis à reciclagem de ETRs a partir de lixo eletrônico. Portanto, novas tecnologias ambientalmente sustentáveis devem substituir ou complementar as existentes. As tecnologias de reciclagem e separação baseadas em adsorção é um passo essencial nessa direção. A adsorção é mais ecológica e econômica do que a extração por solvente, oferece altos fatores de enriquecimento, separação rápida de fases e a possibilidade de combinação com diferentes técnicas de detecção.

O objetivo do projeto atual é o desenvolvimento de metodologia baseada em adsorção para recuperação seletiva de ETRs a partir de resíduos eletrônicos. Recentemente sintetizamos os adsorventes a base de sílica gel com grupos funcionais de ácidos aminodifosfônico, piridinocarboxílico, etilenodiaminotetracético e hidroxâmico e mostramos suas vantagens para extração dispersiva em fase sólida e separação dos elementos terras raras [1–3]. Porém com a ideia de consolidar os benefícios de adsorventes inorgânicos com alta seletividade e cinética de adsorção com os benefícios de bio-adsorventes com alta capacidade foram preparadas as nanopartículas de carbono incorporadas na superfície de suporte inorgânico – sílica gel funcionalizada. As particularidades de síntese de nanopontos de carbono, e os materiais híbridos, suas caracterizações por vários métodos físico-químicos serão apresentadas junto com estudos preliminares da a metodologia de recuperação de ETRs.

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**Área: MAT**

# OBTENÇÃO DE BETUMES SINTÉTICOS (BINDERS) A PARTIR DE POLIOLEFINAS E ÓLEO LUBRIFICANTE AUTOMOTIVO PÓS-CONSUMIDOS

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Palavras Chave: Binders, Betume sintético, Sustentabilidade, Reologia

## Highlights

PRODUCTION OF SYNTHETIC BITUMEN (BINDERS) FROM POLYOLEFINS AND AUTOMOTIVE LUBRICANT OIL POST-CONSUMED

Sustainable synthetic bitumen from polyolefins; Binder for application in Pavement Asphalt Cement (CAP); Binder from polyolefins and automotive lubricant oil post-consumed; Rheological characteristics of synthetic bitumen.

## Resumo/Abstract

O betume é um dos mais antigos materiais de engenharia conhecidos[1]. No início de 1900, o betume refinado foi produzido primeiramente a partir do craqueamento do petróleo bruto nos EUA. Desde então, o consumo mundial de betume aumentou rapidamente, a maior parte usada na indústria da construção civil como aglutinante de agregados minerais do Cimento Asfáltico de Pavimentação (CAP) para produção de asfalto na construção de estradas[2,3]. Este material, porém, apresenta limitações durante a utilização em diferentes temperaturas. Considerando o apelo pela preservação ambiental e a sustentabilidade e tendo em vista o crescente aumento do passivo polimérico ambiental em resíduos sólidos urbanos (RSU) foram desenvolvidas formulações de betumes sintéticos (binders) a partir de misturas de óleo lubrificante automotivo e poliolefinas (Polipropileno - PP e Polietileno de alta densidade - PEAD) pós consumidos que, quando comparados ao betume tradicional e modificado, apresentaram melhor desempenho. Sendo assim, o trabalho objetivou, a obtenção de materiais coloidais multifásicos, similares ao betume do petróleo, provenientes de misturas entre PP e óleo automotivo pós consumidos e a mistura de PEAD e óleo automotivo pós consumidos, a fim de eleger o mais promissor para servir como um dos componentes do CAP. As massas dos polímeros e óleo lubrificante pós-consumidos foram calculadas de forma a se obter misturas com 5, 10, 15 e 20% de massa de polímero na composição. O presente trabalho apresenta as principais características termogravimétricas e reológicas de betumes sintéticos. Resultados da análise termogravimétrica sugerem que amostras que contêm maiores quantidades de polímeros na composição apresentaram melhora sutil na estabilidade térmica. Em relação ao ensaio de reologia, houve aumento do módulo de armazenamento (G') com o aumento da quantidade de polímero na formulação. Outro fator analisado foi a curva de fluxo, tendo em vista a aplicação como CAP. Em baixas taxas de cisalhamentos, amostras com maiores quantidades de material polimérico apresentaram viscosidades elevadas, comportamento importante para se manter os agregados suspensos. No entanto, à medida que a taxa de cisalhamento aumenta, observa-se uma diminuição na viscosidade. Essa diminuição é importante para facilitar a mistura do binder com os outros componentes, assim como para o escoamento e transporte da amostra e capacidade de espalhamento.

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## Agradecimentos/Acknowledgments

Os autores agradecem ao CNPq pelo suporte finaceiro dado pelas bolsas PCI DC e DD concedidas ao INT.

**Área:________MAT______________**

# One-pot functionalization of carbon dots with ecPis-4s antimicrobial peptide

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*Keywords: carbon dots, functionalization, peptide, ecPIS-4s, bionanostructure*

## Highlights

One-pot functionalization of carbon dots with ecPis-4s antimicrobial peptide. We report on the functionalization of carbon dots with the antimicrobial peptide ecPis-4s, in an aqueous medium, through activation reactions of oxygenated functional groups using 1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDAC) and Ethyl (hydroxyimino) cyanoacetate. The success in functionalization has been demonstrated by different techniques including $^1$H NMR and FTIR. We observed that functionalization does not impact the optical properties of CDs and maintains the ability of the peptide to organize itself in α-helical conformation in a mimetic medium of membranes. If, on the one hand, the bionanostructures did not show antioxidant activity on the other, they showed inhibitory capacity*, in vitro*, similar to the free peptide on the growth of gram-positive and negative cells, ie, *Staphylococcus aureus (S. aureus*), and *Escherichia coli (E. coli*).

## Resumo/Abstract

Carbon dots (CDs) were functionalized with the ecPis-4s peptide, with the objective of obtaining a (bio)nanomaterial with antioxidant and antibacterial properties and future applications related with peptide-cell membrane interactions, such as biomarkers. The CDs were prepared from acid dehydration and oxidation reactions of the cellulose biopolymer. This methodology was chosen because, it allows the obtainment of allows the obtainment of nanoparticles with a high concentration of oxygenated functional groups, which are be useful for the binding of the antimicrobial peptide ecPis-4s on the nanoparticle. The functionalization of the CDs was performed through the reaction of the carboxyl and hidroxil groups (CDs) with the amino group of the peptide through the activation of carboxyl and/or OH groups using 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDAC) and ethyl-2-cyano-2-(hydroxyimino) acetate (Oxyme Pure®). The materials obtained were characterized through different techniques, including proton Nuclear Magnetic Resonance of hydrogen ($^1$H NMR), Fourier Transform Infrared Spectroscopy (FTIR) and zeta potential. After the functionalization with the peptide, the zeta potential of the CD nanoparticles changed from -50.5 mV to -23.4 mV, suggesting the consumption of some negatively charged functional groups, such as carboxy, at a pH below 6. In the FTIR (figure1) spectra of the functionalized CDs, after purification, the in vivo, in vitro, showed that the functionalized nanoparticles are capable of inhibiting bacterial growth similary to ecPis-4s for *Staphylococcus aureus (S. aureus), and Escherichia coli (E. coli),* showing that they can inhibit growth with both Gram-positive and Gram-negative bacteria. This outcome is directly related to the α-helix conformation of the peptide covalently attached to the surface of the CDs, as shown by the results obtained with circular dichroism (Figure 2) in a membrane mimetic medium.

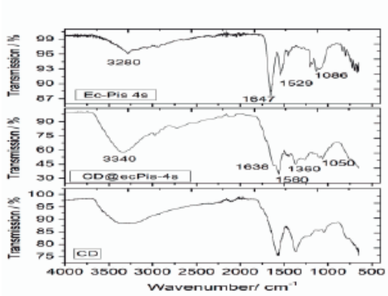

Figura1:FTIR spectra obtained for ecPis-4s, CD and CD@ecPis-4s.

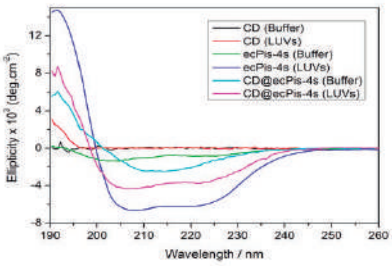

Figure 2:Circular Dichroism spectra obtained for samples in TRIS-HCl buffer (absence of LUVs) and in the presence of LUVs.

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## Agradecimentos/Acknowledgments

The authors are grateful: CAPES, UFVJM, UFMG, FAPEMIG, CNPq.

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

**Nº de Inscrição: 00183**
*(Inserir o número de inscrição do autor que fez a submissão)*

# Optical and structural study of cerium doped niobium oxides as photocatalysts under solar radiation

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Keywords: Niobium, Cerium, Titanium, Nanomaterials.

## Highlights

Nanostructured cerium doped niobium oxides were synthesized by hydrothermal method;
The effect of reactional pH was evaluated (pH = 1.0 and 3.0)
XRD and Raman patterns confirm the presence of monoclinic and orthorhombic phases;
Bandgap values (2.0 – 3.0 eV) for solar absorption was reached;
Materials are promising for photocatalysis.

## Resumo/Abstract

Photocatalysis is contextualized in a broad technological development environment, with applications ranging from the degradation of organic substances, sterilization of hospital utensils as an antibacterial agent and energy conversion processes solar cells[1]

When compared to other countries, Brazil is located in an intertropical zone, having the advantage of receiving high levels of solar radiation throughout the year. Therefore, developing of photocatalysts capable of using energy from the sun is desirable, and doping can cause changes in the range of semiconductor absorption[2]

The solid materials were synthesized by hydrothermal method employing ammonium niobium oxalate and cerium(III) nitrate as precursors, then the samples were calcined at 800 °C for 5 h. Cerium doped niobium(IV) oxides were characterized about their structure (FTIR, DRX, Raman and XPS) in Figure 1, morphological (SEM) in Figures 2 and optical (DRS) properties, and photocatalytic activity.

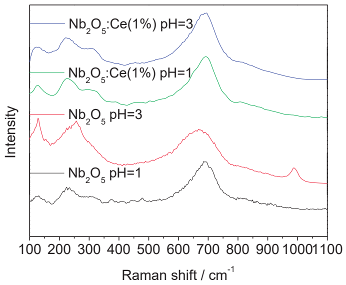

Figure 1: Raman spectrum of pure $Nb_2O_5$ and doped with cerium at pH=3.

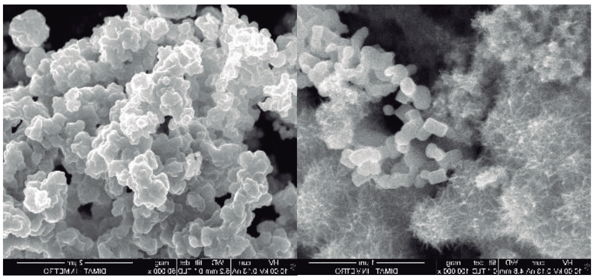

Figure 2: SEM images of $Nb_2O_5$:Ce(1%) at pH=1 and 3.

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## Agradecimentos/Acknowledgments

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**Area: MAT**

# Optimized polymeric carbon nitride/$TiO_2$-based photoanode for energy generation and pollutant degradation

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Keywords: *Photoelectrochemistry, MOR, Paraoxon, 4-nitro phenol.*

## Highlights

Potassium Poly(Heptazine Imide) increased photoanode response.

Methanol oxidation achieved up to 5 mA $cm^{-2}$ under solar simulated illumination.

4-NP and Pox presented good PEC degradation kinetics.

## Abstract

Heterojunctions constitute an approach that may improve the photo-generated charges separation and, consequently, the photoelectrocatalytic performance of the material. Materials such as titanium dioxide ($TiO_2$) and carbon nitride, besides being synthesized with relatively cheap and earth-abundant materials, present favorable band alignment for the obtention of a type-II heterojunction, which makes them promising candidates for photoelectrochemical studies.

In the present work, we added potassium poly (heptazine imide) (K-PHI), a polymeric carbon nitride with high structural order, a bandgap around 2.7 eV, to a commercial paste of $TiO_2$ nanoparticles (anatase), in a mass percentage of 5%, to obtain a photoanode applied for methanol oxidation reaction (MOR) and degradation of 4-nitrophenol (4-NP) and methyl paraoxon (Pox). While the first mentioned reaction is an alternative strategy for hydrogen generation, the degradation is also important from the environmental point, as long the 4-NP and paraoxon can be found in wastes from agricultural and pharmaceutical industries for example.

The paste of $TiO_2$/K-PHI was spin-coated over an FTO electrode and thermally treated at 400 °C. Then, the obtained $TiO_2$-K-PHI photoanode was evaluated by linear voltammetry, under chopped solar simulated irradiation with 100 mW $cm^{-2}$ of power, in 10% V/V methanol solutions at pH1 ($H_2SO_4$) for MOR. For PEC degradation the sample was evaluated by chronoamperometry under constant illumination, in $Na_2SO_4$ 0.5 mol $L^{-1}$ adjusted to pH 8, containing $1 \times 10^{-4}$ mol $L^{-1}$ of the target molecule (4-NP or Pox), polarized at 0.8 and 0.36 V vs RHE for 4-NP and Pox respectively.

In the MOR measurements were possible to observe a photocurrent of 500 μA $cm^{-2}$ at 0.2 V vs RHE for one layer deposited of $TiO_2$-K-PHI, with this value being about 5 times higher than pure $TiO_2$. Also, with further film thickness study (as a function of the deposited layers) the photocurrent was enhanced up to 5 mA $cm^{-2}$ for a $TiO_2$-K-PHI film containing 30 deposited layers. In the degradation studies, the PEC process has proven to be far superior to electrochemical or photocatalytic alone, achieving rate constants values of $6.02 \times 10^{-4}$ and $1.51 \times 10^{-4}$ $s^{-1}$ for 4-NP and Pox respectively. It leads to a catalytic increment in the order of $10^7$ times for Pox when compared with spontaneous degradation. This indicates that the here obtained photoanode is a promising material even for a clean fuel obtention (hydrogen), as well to environmental remediation (4-NP and Pox degradation).

## Agradecimentos/Acknowledgments

National Research and Development Council (CNPq), FAPESP, CAPES and Center for Innovation on New Energies (Cine – Shell) for the financial support.

**Área: MAT**

# Persistent luminescence glass composites based on $Sr_2MgSi_2O_7:Eu^{2+},Dy^{3+}$ materials

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Keywords: Persistent luminescent materials, Luminescent glasses, Glass composites, Phosphor-in-glass.

## Highlights

The persistent luminescent materials can emit light for several hours after ceasing an irradiation source, acting as luminescent batteries.

The development of luminescent glass composites allows the association of the particular PersL emission with the chemical/thermal stability of the glasses.

## Abstract

The persistent luminescent (PersL) materials have been called attention due to their single capacity of emission of light for several hours after ceasing an irradiation source. Due to this property, these materials are often applied in light storage systems, such as emergency signaling, anti-counterfeiting markers, luminescent paints, biomedical imaging diagnostics, etc. However, these materials are often obtained in powder form, which limits their application.[1] In order to extend the possibilities of applications, the PersL materials can be incorporated in host compounds, such as polymers and glasses. Besides the ease of processing of the polymers, the photodegradation under solar irradiation can reduce the duration of the composite. On another hand, a properly chosen glass composition can provide important characteristics, such as chemical/thermal stability and UV-Vis transparency.[2] In this work, we present a new persistent luminescent glass composite based on the incorporation of the $Sr_2MgSi_2O_7:Eu^{2+},Dy^{3+}$ (SMSO) luminescent guest on $NaPO_3$-$Ga_2O_3$ (NaPGaO) glass host. The PersL material was prepared by the rapid and energy-saving microwave-assisted solid-state (MASS) synthesis, in a 30 min single-step route. The glass composites were prepared by the well-known melt quench technique, using 2, 5, 10, and 20 wt% of SMSO at 900 or 950 °C. The results indicate a promising system with blue persistent luminescent emission ($\lambda_{em}$ = 460 nm) which can be excited with sunlight for emergency signaling and anti-counterfeiting marker applications.

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[2] R.F. Muniz, V.O. Soares, V.S. Zanuto, M.A.C. Melo, M. Sandrini, M.P. Belançon, A.N. Medina, M.L. Baesso, J. Non. Cryst. Solids. 574 (2021) 121169.

## Agradecimentos/Acknowledgments

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**Área: MAT**

# Phosphorus (P) release in water and biodegradation of composites based on natural polymers K-C/ALG/MAP/CNF

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Keywords: *Sustainable agriculture, Alginate, Carrageenan, Nanofibrillated cellulose, Biodegradation materials.*

## Highlights

- Composites based on natural polymers obtained through the “casting” technique
- Occurrence of “burst release” in the first 2 min of release
- The largest amounts of $CO_2$ released were up to the 30th day of biodegradation

## Abstract

The inappropriate management of plastic waste used in agriculture associated with the high need for soil fertilization has caused several negative impacts to the environment (REETZ, 2017) since up to 80% of the applied fertilizer is lost through leaching and/or runoff due to the low retention of nutrients and high hydraulic conductivity of Brazilian tropical soils (SILVA et al., 2013). To achieve the Sustainable Development Goals (SDGs), alternatives to reduce these problems have been carried out with materials that use fertilizer efficiently and without generating waste. The objective of this work was to evaluate a film based on natural polymers with biodegradable potentiality (Alginate – ALG, Carrageenan – K-C, nanofibrillated cellulose – CNF) added with phosphate nutrient considering the use as seedling wrapping. The films were obtained by casting, and the phosphorus release in water was evaluated at determined times (2, 4, 6, 8, 10, 15, 20, 25, and 30 min). Biodegradation was performed for 62 days using the Bartha respirometry technique. The properties of phosphorus nutrient release into water (not shown) and biodegradation were evaluated using a UV-Vis spectrophotometer and quantification by titration of $CO_2$ production, respectively (Figure 1). At the first point (2 min) of release, the “burst release” phenomenon occurred for all concentrations of the composites, where the most significant amount of $PO_4^{3-}$ was released into the water medium. After 30min the composites K-C/ALG/MAP/CNF(2%), K-C/ALG/MAP/CNF(3%), and (K-C/ALG/MAP/CNF(4%) still continued releasing small amounts of $PO_4^{3-}$. The composite K-C/ALG/MAP/CNF(0%) could not be evaluated due to complete solubilization in contact with water. Biodegradation showed the highest amounts of $CO_2$ released until the eighth day. Then we observed a progressive decrease in $CO_2$ quantity produced by the soil biota until the 30th day and remaining in the range of 10 mg of $CO_2$ until the end of the experiment (62nd day). Mechanical and thermal properties (not shown) also indicate the films based on polysaccharides is a potential candidate to be used as seedling wrapping.

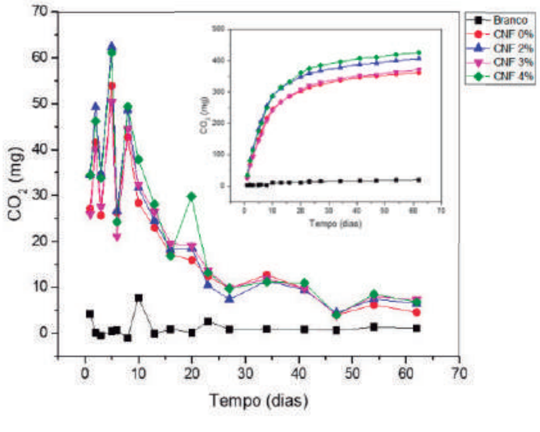

**Figure 1** Biodegradation of K-C/ALG/MAP/CNF composites at CNF concentrations of 0%, 2%, 3% and 4% (w/w).

## Acknowledgments

The authors thank the Federal University of São Carlos – UFSCar campus Araras – SP and the Graduate Program in Agriculture and Environment for making this research possible. The authors are also grateful for grants 2019/02535-5 from FAPESP for financially supporting this research.

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**Área: MAT**

# Plasma-Assisted Synthesis of Silver and Gold Nanoparticles

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Key Words: *silver, gold, nanoparticles, plasma jet.*

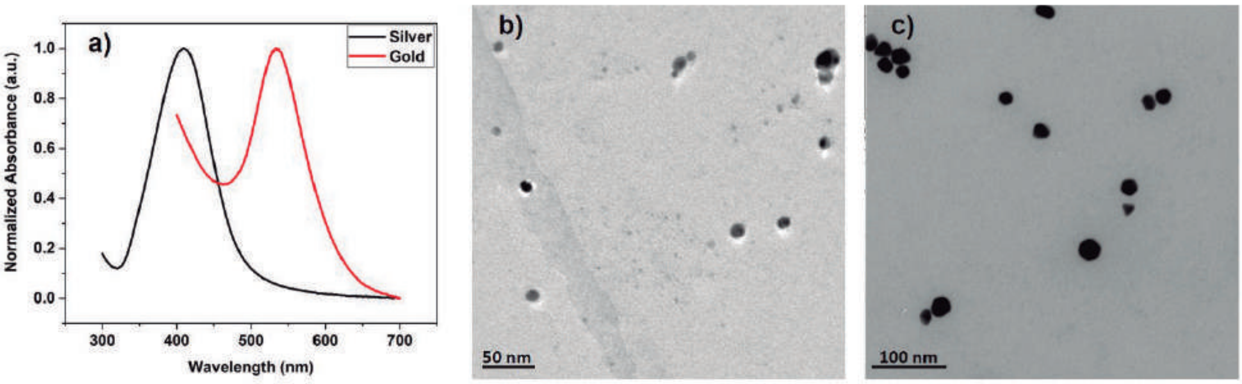
## Highlights

Silver and gold nanoparticles were successfully synthesized by a Helium atmospheric pressure plasma jet. Spherical and monodispersed nanoparticles were obtained within only 5 min of plasma exposure.

## Abstract

Plasma discharges of different configurations have attracted a lot of attention due to their various applications. In particular, plasma jet in contact with a liquid is a simple and cheap technique for the synthesis of metal nanoparticles. Its main advantage is the variety of species present in the plasma plume which can induce rapid chemical reactions in the solution. The optical emission spectrum of the plasma jet confirmed the reactive species present in the gas phase. Silver and gold nanoparticles are two of the most exploited nanomaterials due to their unusual physical, optical and chemical properties that are significantly different from their bulk counterparts as well as their promising applications in various fields.

This study shows that silver and gold nanoparticles can be successfully synthesized by a Helium atmospheric pressure plasma jet in a very fast and environmentally friendly way. Spherical and mono-dispersed nanoparticles were obtained within only 5 min of plasma exposure by using silver nitrate as a precursor and citrate as a capping agent for the AgNPs and $HAuCl4$ as a precursor and PVP as a capping agent for the AuNPs. The formation of these metal nanoparticles was firstly confirmed by UV-vis spectra. The surface plasmon resonance (SPR) band results in a strong optical absorption in the 400-450 nm range for AgNPs and in the 520-550 nm range for AuNPs. The size of the obtained nanoparticles was measured by DLS and their morphology was observed by transmission electron microscopy (TEM). The effects of different parameters such as the plasma discharge duration, the precursor's and capping agent's concentrations on the size and shape of these nanoparticles were studied.



**(a)** UV-vis normalized absorption spectra of the synthesized silver (black) and gold (red) nanoparticles. **(b)** and **(c)** TEM micrographs of the synthesized silver and gold nanoparticles respectively.

## Acknowledgments

The authors acknowledge the Brazilian funding agencies FAPESP (Proc. 2018/10172-7, Proc. 2019/18828-1) and Coordenacão de Aperfeiçoamento de Pessoal de Nível Superior – Brasil (CAPES) – Finance Code 001, as well as the University of São Paulo and Ministère de L'Enseignement Supérieur de la Recherche et de l'Innovation (France) for financial support.

**Área: MAT**

# Polyacrylamide hydrogels for adsorption of contaminants

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Keywords: *Nanocomposite Hydrogels, $TiO_2$ nanoparticles, Polyacrylamide, Heavy metal adsorption*

## Highlights

Adsorption efficiency of nickel (II) ions on the surface of nanocomposite polyacrylamide hydrogels with incorporation of $TiO_2$ nanoparticles (NPs).

## Abstract

Adsorption methods have been considered promising for the removal of heavy metals in aqueous streams, mainly due to the high efficiency that can be achieved, the easy application and the cost-effectiveness [1]. The efficiency of an adsorbent material directly depends on its properties, such as chemical composition, surface area, pore size distribution and also on the nature and concentration of the adsorbate [2]. Some authors have highlighted the use of polymeric hydrogels for heavy metal removal in water purification treatments [1]. These have the advantage of being easily reusable, biodegradable and environmentally benign [1]. For hydrogels to be successfully used, it is important that they have high mechanical strength and good rheological performance, being able to withstand high levels of stress and deformation necessary for water flow [1]. Due to the low cost and ease of preparation of the systems, polymers based on polyacrylamide are the most used in the preparation of gels. Polyethyleneimine (PEI) is currently the most investigated organic compound for crosslinking systems, mainly because it is ecologically correct and has a high nucleophilic character [3]. The incorporation of nanomaterials such as $TiO_2$ NPs in hydrogel matrices has been shown to be important in obtaining nanocomposite hydrogels with improved properties [4]. In this work, polyacrylamide nanocomposite hydrogels cross-linked with PEI, in the PAM/PEI 9:3 ratio, were obtained in saline solutions with ionic strength $\mu = 0.6$ from the incorporation of 1.0% (w/w) of NPs from $TiO_2$. The hydrogels were tested for adsorption of nickel (II) ions using a solution with an initial concentration of 20 mg $L^{-1}$ to which 50 mg of lyophilized hydrogel was added. Aliquots were taken at different times and atomic absorption measurements were performed to determine the nickel concentration.

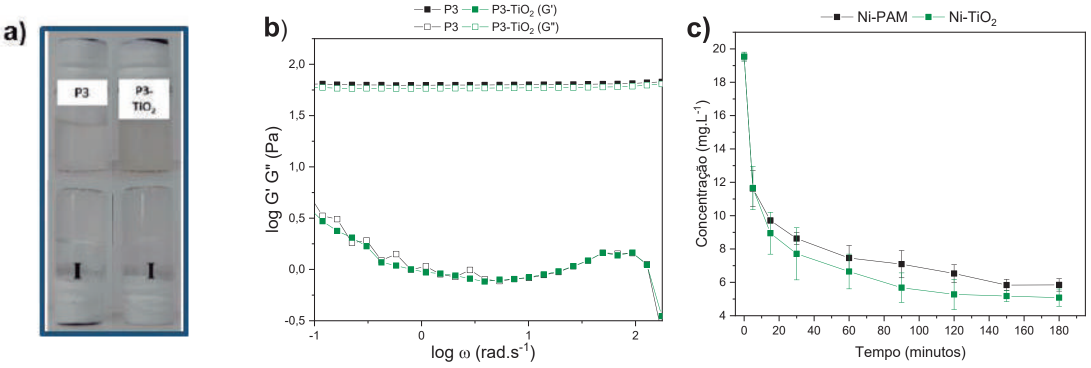

**Fig. 1a)** Sydansk gel strength codes of the gels used; **b)** Elastic (G') and viscous (G") modulus as a function of angular frequency for the gels; **c)** Nickel concentration by time in the tests with the different gels.

Fig. 1a shows a photo of the gels used before lyophilization, with Sydansk gel force code I representing rigid gels, where inversion of the tubes does not cause apparent deformation of the gel surface. Fig. 1b shows that after 40 days of storage in an oven at 70 ºC, the G' modules are superior to the G" modules in the entire frequency range analyzed, revealing the dominance of the elastic character for the gels under study. This result agrees with the codes strength-gel, where both gels have code I. Figure 1c shows the decrease in nickel ion concentration with time, showing the adsorption efficiency on the surface of the hydrogels used. The P3-$TiO_2$ nanocomposite hydrogel showed the highest adsorption efficiency on its surface. Thus, the incorporation of $TiO_2$ NPs in hydrogel matrices is interesting due to its adsorptive capacity for various contaminants and for showing an efficient structural reinforcement agent for hydrogels, promoting a double crosslinking system from interactions with the polyacrylamide and the crosslinking agent [4].

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## Acknowledgments

CAPES, FAPEMIG, CNPq and CTNano (UFMG).

**Área: MAT**

# Preparation and Characterization of Polyurethanes derivated from Castor Oil and MDI

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Palavras Chave: *Castor oil, MDI, Polyurethane, Polymerization, Infrared Spectroscopy, Morphological, Thermal analysis,*

## Highlights

This work demonstrated the results of polyurethanes synthesis derivated from castor oil and methylene diphenyl diisocyanate (MDI). The polymers obtained were characterized by FTIR, SEM and thermal analytical techniques (TG, DSC, DMA).

## Abstract

Polyurethane is a class of polymers synthesized from the polyaddition reaction of a polyol (soft segments) with a diisocyanate (hard segments) [1]. Urethane polymers are widely used in industry due to the versatility of their physicochemical, mechanical and thermal properties; however, most polyols used in synthesis are from fossil and non-renewable sources [2]. In recent years, vegetable oils and polysaccharides derived from plants and animals have emerged as low-cost sources, renewable materials in the preparation of polyurethanes [3]. Castor oil (CO) became attractive since it is made up of 90% ricinoleic acid, with three hydroxyl groups (OH) attached to carbon 12 of its fatty acids, which make up the triacylglyceride [4]. In the present work, polyurethanes were prepared by the direct 'one-shot' method, in which a polyol derived from CO, was mixed with methylene diphenyl diisocyanate (MDI) in a reaction flask at room temperature under stirring. The mixture was degassed and poured into a silicone mold to cure at room temperature. The polymers obtained were characterized by FTIR, SEM and thermoanalytical techniques (TG, DSC, DMA). The OH number determined for polyol was 304 mgKOH $g^{-1}$ and the % NCO was 38%. From these values, eight samples of PU were prepared varying the percentages of MDI in reaction. FTIR showed changes in the profiles of OH bands of polyol in the region of 3500-3200 $cm^{-1}$, the disappearance of N=C=O band of the MDI at 2189 $cm^{-1}$ and increasing the intensity of the bands of C=O and NH in the region of 1750 -1500 $cm^{-1}$ due to the formation of the urethane bond. According to SEM images in different magnifications, the morphology of PU showed roughness on the surface and inside, circular spots with diameters smaller than 200 μm, characteristic of the outflow of gases during polymerization. PU TG curves showed five events of mass losses attributed to loss of water, volatile molecules, decomposition of urethane, decomposition of ester of polyol and burning of the carbonized material, leaving a residue of about 0.5% at 1000°C. PU samples were thermally stable up to approximately 170°C. DSC curves revealed baseline variations in the regions from -10 to 30°C and from 45 to 115°C, with discrete broad endothermic peaks, which were attributed to the glass transition (T*g*) and curing of the samples, respectively, in agreement with DMA results. The results are relevant for the study of polyurethane obtained from renewable sources, new polyol derivated from CO, considering possible applications in the compatible biological materials area.

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## Acknowledgments

The authors thank the funding agencies CNPq and FAPESP for the support to develop the study.

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

# Preparation and photoluminescence properties of functionalized silica submicron-sphere materials decorated with $Eu(tta)_3{\cdot}FX$ complex (FX= fluoxetin)

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Keyword: Luminescent hybrid materials; Europium complex, Fluoxetine, Bioapplication.

## Highlights

The incorporation of $Eu(tta)_3{\cdot}FX$ complex into modified silica particles results in hybrid materials. 3D spectra for $Eu(tta)_3{\cdot}FX$ in the VUV region revealed a high emission band originated from $Eu^{3+}$ transitions.

## Resumo/Abstract

The development of functionalized silica particles containing luminescent materials has received special attention because of their biological applications such as optical markers in vitro and in vivo, clinical diagnosis and drug delivery. The incorporation of $Eu^{3+}$-complex into modified silica particles combines optical characteristics of $Eu^{3+}$-complex and properties of inorganic oxides, resulting in organic-inorganic hybrid materials.

In this work, we synthesize and characterize sub-microspheres of $SiO_2$ decorated with a new complex of $Eu^{3+}$ and fluoxetine, an antidepressant of the selective serotonin reuptake inhibitor (SSRI) class. The Eu-complex and the submicron-spheres ($\phi$~500nm) were characterized optically and photo-physical characteristics of these materials were examined spectroscopically. In emission spectra of complex (Fig 1.a), four characteristic peaks of $Eu^{3+}$ ion with the maximum at ~580 nm, ~595 nm, ~614 nm, and ~702 nm accredited to $^5D_0 \rightarrow {}^7F_J$ (J = 0-4) transitions appeared upon excitation in UV region. The most intense peak at 614 nm is accountable for the bright red emission of the ternary complex. For the $SiO_2$ nanospheres decorated with the complex these transitions are close to the complex but are identified the change in the symmetry around the $Eu^{3+}$ ion when analyzing the spectra. Experimental intensity parameters ($\Omega_\lambda$), lifetime ($\tau$), radiative ($A_{rad}$) and non-radiative ($A_{nrad}$) coefficients, and intrinsic quantum yield ($Q_{Eu^{3+}}^{Eu^{3+}}$) values were determined. 3D emission spectra for the $Eu(tta)_3{\cdot}FX$ complex in the VUV region (Fig. 1b) revealed a high emission band originated from ($Eu^{3+}$) $^5D_0 \rightarrow {}^7F_{2,4}$ transitions (centered around 614 and 702 nm) under excitation at near bandgap energy. Color purity and CIE parameters also suggest the red luminous behavior of complex. Thermal and morphological behavior of the Eu-complex and submicron-spheres decorated with the $Eu(tta)_3{\cdot}FX$ complex are also evaluated (Fig1c). Our investigation has revealed that the synthesized complex and inorganic hybrid materials could be used in preparing lighting systems, OLEDs, display devices and biological sensors owing to their luminescent characteristics

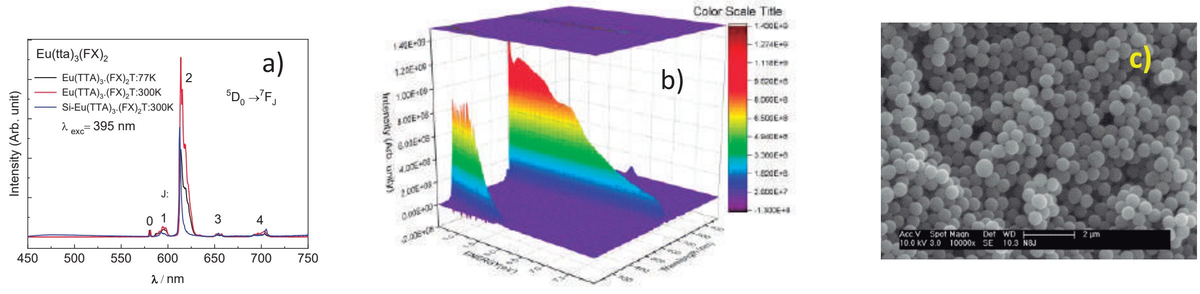

Fig 1. (a)Emission spectra of $Eu(tta)_3{\cdot}FX$ complex and $SiO_2$-$Eu(tta)_3{\cdot}FX$ hybrid materials, b) Synchrotron Vacuum-UV 3D spectra of $Eu(tta)_3{\cdot}FX$ and c)SEM image of $SIO_2$ submicron-spheres

## Agradecimentos/Acknowledgments

The authors are grateful to CNPq for the grants and to TGM-LNLS line for the X-ray UV-UVV measurements.

**Area: MAT**

# Preparation and spectroscopic study of Eu$^{3+}$-doped cellulose nanocrystals

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Keywords: *Luminescence; Cellulose nanocrystals; Europium.*

## Highlights

Obtaining Eu$^{3+}$-doped whiskers from bacterial cellulose.
Spectroscopic study of the material using the lanthanide ion as a probe.
Development of luminescent nanocomposite as reinforcement material.

## Abstract

Nanomaterials have been awakened great worldwide interest due to their peculiar properties, and it also being widely used as reinforcement materials in different polymeric matrices, as nanocomposites. On the other side, the cellulose is the most easily found biopolymer in nature, having an extended and highly rigid conformation [1]. By uniting the two interests, cellulose nanocrystals - also known as whiskers - bring together several of these characteristics as they are nanocrystalline domains that promote strong intermolecular interactions, presenting coordination sites and the functional groups could be change, which together build large structures of high applicability [2]. In this work, different routes of obtaining whiskers were studied followed by the interaction of lanthanide ions on the coordination sites, more specifically the Eu$^{3+}$ ion, that presenting a characteristic luminescence and aiming at the generation of a material that can be applied in photonic systems. From the photoluminescence analysis of the obtained materials, the study confirmed the characteristic Eu$^{3+}$ ion narrow bands from ff transitions in the excitation and emission spectra (Fig. 1a and Fig. 1b respectively). When analyzing the region of 300 nm in the excitation spectra, it was possible to notice a broad band possibly referring to the cellulose matrix under ff transitions, but with low influence on energy transfer on Eu$^{3+}$ sensitizing, while for the emission spectra, despite the bands being slightly widened, transitions related to the ff transitions were confirmed. By means of further analyzes such as lifetime and the emission parameters determination, it was possible to observe similar quantum efficiency values and the Judd-Ofelt parameters in the same order of magnitude with other Eu$^{3+}$ doped nanomaterials [3], providing information about the ion coordination and showing that it is possible obtaining Eu$^{3+}$-doped whiskers. Thus, the Eu$^{3+}$-whiskers interaction proved to be extremely interesting, however, there is a need to deepen the study of this compound and its interactions for possible changes of strategy in the extraction and doping procedure, aiming at a better coordination of the lanthanide ion on the whiskers surface and improving its spectroscopic properties.

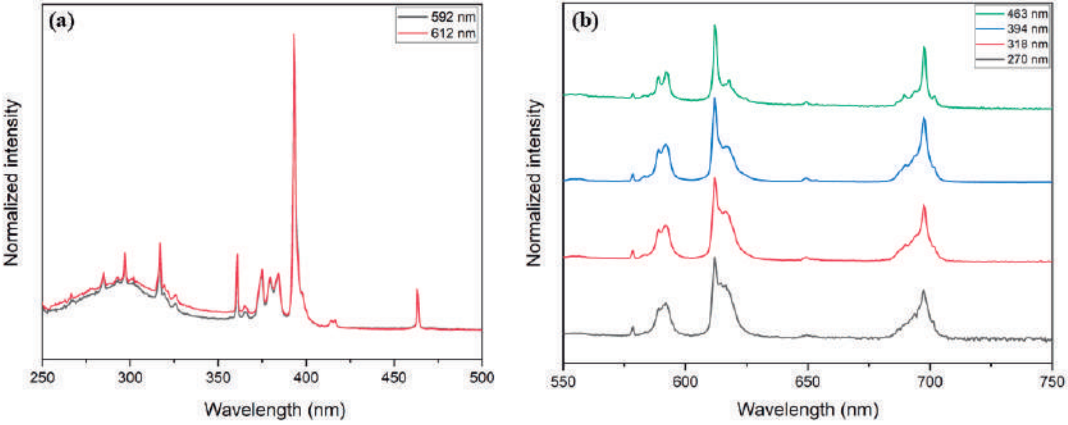

**Figure 1: (a)** Eu$^{3+}$-doped whiskers (0,0151 mmol/mg, Eu$^{3+}$/whiskers) excitation spectra monitoring at 592 and 612 nm. **(b)** Emission spectra of Eu$^{3+}$-doped whiskers excited at different wavelengths.

***References***: [1] Vasconcelos, N. F., et al., 2017. *Carbohydrate Polymers* 155: 425–31. [2] de Jesus Silva, D., et al., 2009. *O PAPEL vol. 70, num. 07*: 34–52. [3] Binnemans, K. (2015). *Coordination Chemistry Reviews*, *295*, 1-45.

## Acknowledgments

The authors acknowledge the Brazilian agency FAPESP (2019/18828-1) and the Universidade de São Paulo (USP) for financial support. In addition to Professor Dr. Hernane S. Barud, from the BioPolMat Group of UNIARA, for providing the bacterial cellulose membrane samples used.

**Área: MAT**

# Production of carbon-based mesoporous materials for heavy metal removal from aqueous media

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Keywords: *Porous carbons, Tommy Atkins, Persea americana, Adsorption, Heavy metals.*

## Highlights

- Production of mesoporous materials using different carbon sources;
- Characterization analyses confirm the creation of mesoporous carbons;
- Preliminary results indicate the obtention of homogeneous morphology, thermal stability, and elevated heavy metal capacity adsorption.

## Abstract

Heavy metals in high concentration in water bodies represents a serios dangerous to the environment, once it is intensively toxic for living organisms. Therefore, its removal is paramount.[1] Several techniques for the removal of heavy metal cations from aqueous media have been developed targeting the mitigation of wastewater contamination.[2] Among them, adsorption emerges as a prominent option given its easiness of operation, low cost, and the wide option of available adsorbents. Carbon-based materials present elevated superficial area, high adsorption capacity, and they can be obtained using agro-industrial wastes as carbon sources. In this context, the present work aims to develop porous carbons using seeds of mango *Tommy atkins* and avocado *Persea americana*. The seeds were purified, carbonized, and later oxidized. The materials obtained were characterized by infrared spectroscopy, thermogravimetric analyses, and scanning electron microscopy. The adsorptive potential of both samples was assessed via batch adsorption of representative toxic metals ($Cu^{2+}$, $Cd^{2+}$ , and $Pb^{2+}$). The results indicate the success in the preparation of porous carbons with composition, thermal stability, and morphology suitable to be employed as adsorbents in aqueous media. The adsorption tests showed a greater preference for adsorption of $Cd^{2+}$ ions, with maximum adsorption compactness values for the mango-based carbonized material (5.84 mmol $L^{-1}$). Thus, the synthesized materials present practical viability for the adsorption of toxic metals, mainly the $Cd^{2+}$ ion.

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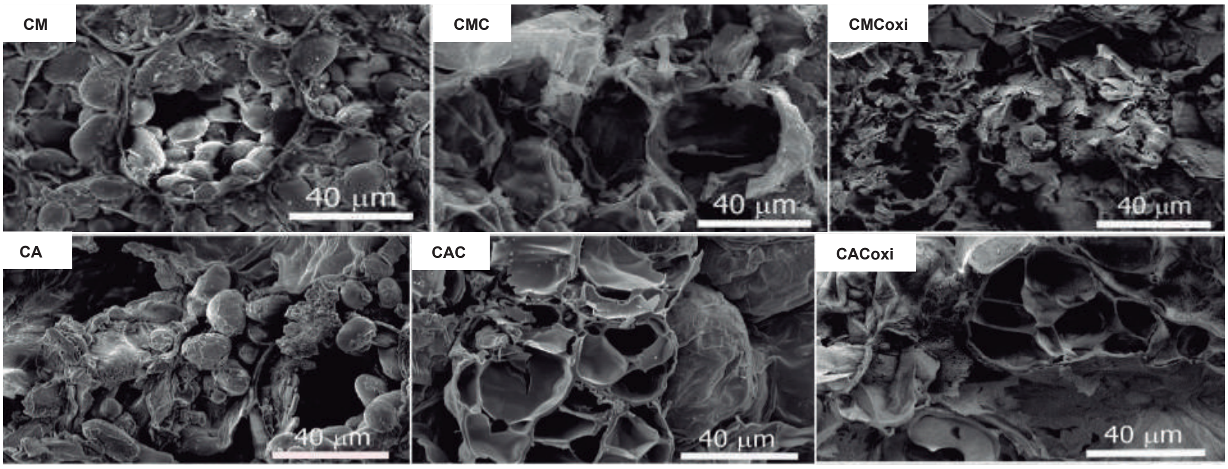
2. Chai, W., et al. **J. Clean. Prod.** 296 (2021) 126589.

Figure 1 - Scanning electron microscopy images for the samples of mango's cartridges freeze dried, carbonized and oxidized (CM, CMC, and CMCoxi), and for the avocado's cartridges (CA, CAC, and CACoxi).



## Acknowledgments

CNPq and Capes for funding this research, and Central Analítica (UFC) for SEM analyses.

**Área: MAT**

# PVA nanofibers/Cu nanoparticles as antiviral materials.

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Keywords: Electrospinning, Nanomaterials, Crosslinking, Green synthesis, Herpes simplex vírus, Biodegradable Polymer.

## Highlights

PVA nanofibers were produced using electrospinning; Cu nanoparticles were synthetized and added to the material; Fibers were crosslinked using temperature; Nanofibers were tested against HSV 1 virus.

## Resumo/Abstract

Applicability and sustainability are very important subjects with respect to the development of new and smart materials, so that, our research group has been trying to find smart alternatives to the conventional methodologies. Electrospinning is a versatile technique to produce materials applied in several areas. This technique is based in transporting a polymeric solution from the tip of a needle to a metallic collector (in this work we employed a rotative collector) with the help of a magnetic field which is generated by a high voltage application. The transport phenomena associated with another parameters of solution, method and environmental, are responsible to confer to the fibers a shape which varies from nm to mm of thickness, presenting different profiles of roughness. Electrospun PVA nanofibers (NF) (**Fig. 1**) were produced according to the methodology proposed by Ginestra (P. Ginestra *et al.*; 2020), employing 15 % wt. of PVA in water as solvent, an applied voltage of 20 kV, a needle-collector distance of 12.5 cm, a flow rate of 0.3 mL/h at 27 °C and about 30% of humidity. Copper nanoparticles (CuNPs) were added to those fibers in order to confer to the material antiviral and antibacterial properties. After this, NF were heated during 24h at 130 °C to enable crystallization of the PVA structure (Z. Wang *et al.*; 2021). With the help of the temperature, the PVA chains lost water molecules, so that, interactions become more stable and rigid leading to the crystallization and resistance to water solubility. Fibers are up to be tested against herpes simplex virus and be applied as covertures of the cold sores caused by the infection (**Fig. 2**).

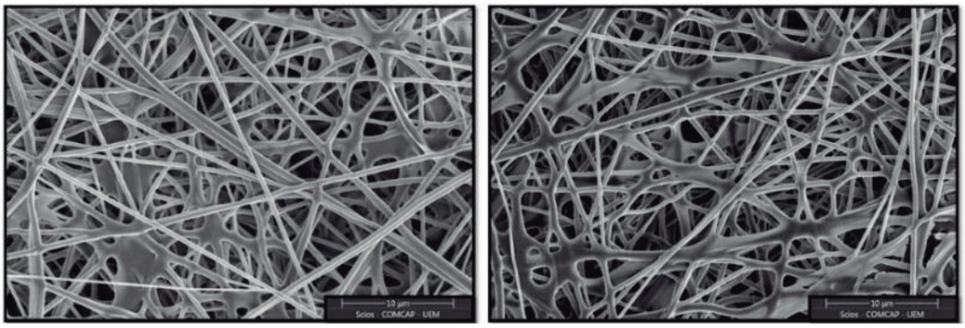

**Figure 1.** PVA nanofibers with CuNPs inserted in the bulk **a)** before and **b)** after crosslinking using temperature.

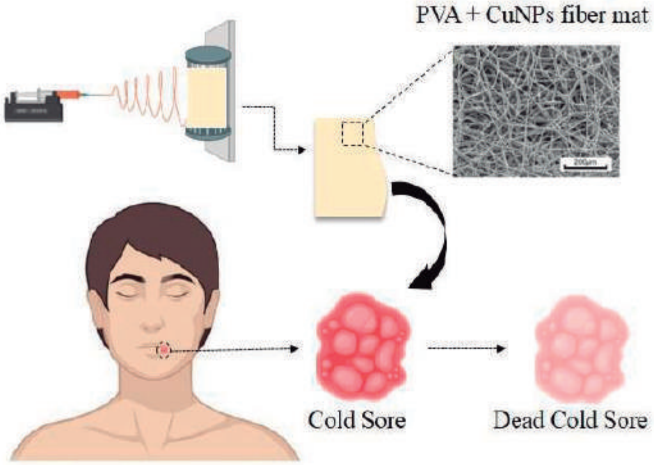

**Figure 2.** Electrospun CuNP-charged nanofibers applied against cold sores.

## Agradecimentos/Acknowledgments

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**Área: MAT**

# PVA/Starch as carriers for macro and micronutrients:spray-dryer microspheres & microcapsules

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Palavras Chave: *EEFs, Fertilizer, Microparticles, PVA, Spray-dryer, Starch.*

## Highlights

- ✓ Microspheres of starch/micronutrient were successfully obtained by spray drying;
- ✓ Microcapsules with macro and micronutrients release the nutrients according to the layer;
- ✓ The Peppas-Sahlin model mainly ruled the release kinetics.

## Abstract

To achieve sustainable agriculture and contribute to the second goal of the ONU agenda, the development of alternative materials to improve the efficacy of the agrochemicals in the soil and plant, reducing waste and environmental contamination, is necessary. Enhanced efficiency fertilizers (EEF) are materials that combine fertilizer with substances of interest resulting in a final product with advantageous properties. The primary advantage is reducing applied and lost fertilizer, minimizing the environmental problems. Moreover, as the final destination of EEF materials is the soil, it is significant to use products that do not damage the environment. The present work aims to develop EEF materials based on PVA, starch, and nutrients, considering few works address EEFs materials with micronutrients. Microspheres were spray-dried from the two-fluid nozzle (2FN) from monoelementary dispersions of gelatinized starch with micronutrients (Fe, Cu, Mn). Microcapsules were atomized from the three-fluid nozzle (3FN) with PVA/$KNO_3$ at the external and starch/micronutrient at the internal layer. The materials were thermally, structurally, and morphologically characterized. We evaluated water-medium nutrient release (Figure 1), release kinetics, and the swelling degree. Different micronutrients and microstructures affect morphology, size distribution, swelling degree, release, kinetics, and interaction between polymer-nutrient. Comparatively, microspheres fast release Mn and Fe (81.2 and 68.9 %), followed by macro/micronutrient-based microcapsules (72.4 and 66.1 %), and lastly, the micronutrient-based microcapsules (62.2 and 53.1 %). For Cu, the order is macro/micronutrient-based microcapsules (67.7 %), micronutrient-based microcapsules (61.5 %), and microspheres (46.7 %).

Moreover, the macronutrient was first released in the macro/micronutrient microcapsules due to assembly material. Concluding, microcapsules show enhanced release compared to microspheres. The nutrient release in water and microscopy results (not shown here) confirm that the macronutrient would be released before the micronutrient in microcapsule-type structures. The outer layer acts as a diffusion barrier. In addition, the materials are promising to be used as a multi-nutrient formulation in EEFs materials.

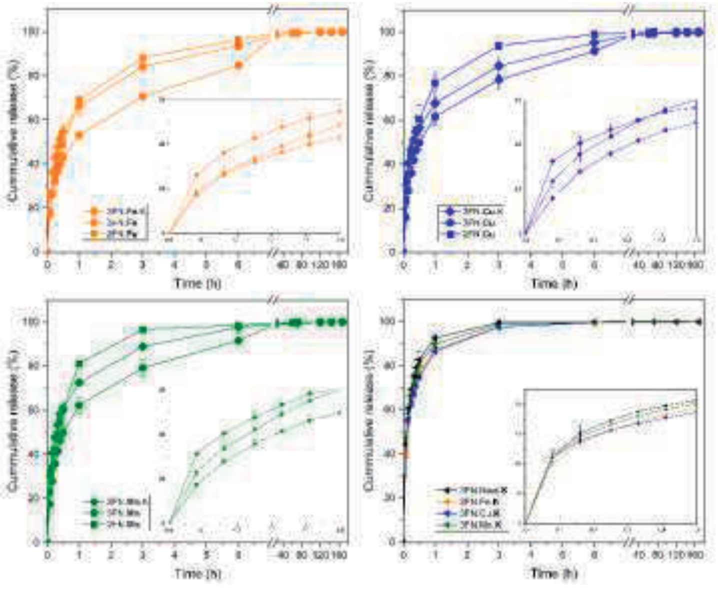

Figure 1. Nutrients release profiles in the water for microspheres and microcapsules produced with (i) Fe (2FN.**Fe**, 3FN.**Fe**, and 3FN.**Fe**.K), (ii) Cu (2FN.**Cu**, 3FN.**Cu**, and 3FN.**Cu**.K), (iii) Mn (2FN.**Mn**, 3FN.**Mn**, and 3FN.**Mn**.K), and (iv) K (3FN.Neat.**K**, 3FN.Fe.**K**, 3FN.Cu.**K**, and 3FN.Mn.**K**).

## Acknowledgments

The authors are grateful for grants 2019/02793-4 and 2019/02535-5 from FAPESP for financially supporting this research. This study was financed in part by CAPES - Finance Code 001. RF is a CNPq researcher.

**Área: MAT**

# Random lasing action in $Y_{1-x}Nd_xAl_3(BO_3)_4$ particles: synthesis, structural and spectroscopic characterization

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Keywords: *YAB, Neodymium, Random Laser*

## Highlights

Inorganic materials for random laser application
New synthesis route to prepare aluminum borate
The behavior of dependence of the $Nd^{3+}$ concentration at the properties of the random laser

## Resumo/Abstract

The search for efficient photonic materials for laser action has grown after the invention of the ruby laser. RLs presents several advantages over conventional lasers. They can be produced from low-cost material, feature diversity in size and shape, and simplicity in production and setup [1]. Among the elements that exhibit stimulated emission, $Nd^{3+}$ has received great attention for use in lasers because of their large emission cross-section [2]. Several host matrices have been developed for lanthanides ions, and YAB has proven to be excellent laser hosts due to their physicochemical properties [3]. In this work, we report a new synthesis route to prepare Nd-doped, based on the urea precipitation method. Structural characterization (Fig. 1a) confirmed that all the samples have trigonal symmetry with hexagonal space group. For the RL experiments (Fig. 1b) the normalized spectra of the sample with the high $Nd^{3+}$ concentration at three different excitation energies, from below to above the threshold, shows the emission peak is centered at 1063 nm. As expected for lanthanide-based RL, the linewidth decreases abruptly close to the threshold energy. We have successfully prepared yttrium aluminum borate with hexagonal phase by the urea precipitation methodology. The RL studies demonstrated the emission stimulated by the particles and the behavior of dependence of the $Nd^{3+}$ concentration.

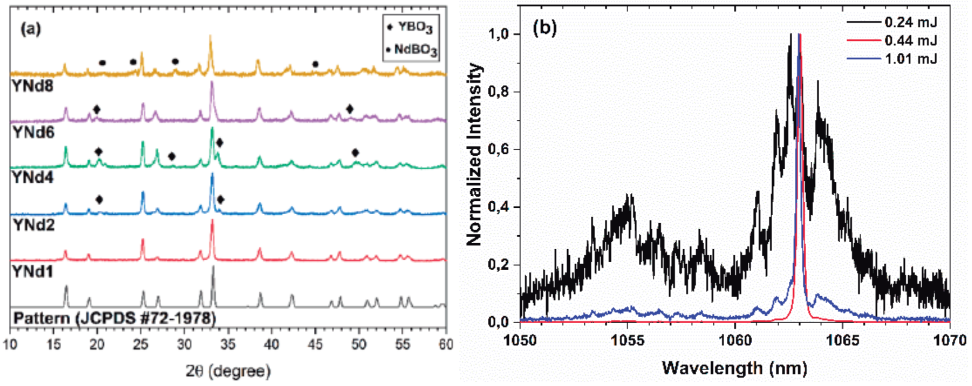

**Figure 1**: **(a)** XRD of YAB:$Nd^{3+}$ powders with hexagonal phase **(b)** Normalized emission spectra of $Nd^{3+}$ (transition $^4F_{3/2} \rightarrow {}^4I_{11/2}$) below to above threshold values.

*References*: [1] F. Luan, *et. al.*, *Nano Today*, 2015, **10**, 168–192; [2] S. Sharma, S. Kumar and R. K. Yadav, *Int. Jour. Eng. Res. Appl.*, 2014, **4**, 92–97; [3] L. J. Q. Maia, *et. al., Opt. Mater. (Amst).*, 2010, **32**, 484–490

## Agradecimentos/Acknowledgments

The authors acknowledge the agencies FAPESP (2019/18828-1), CNPq (141759/2019-4), Nacional Institute of Photonic (INCT – INFO) for the financial support and analysis, as well the University of São Paulo, Institute of Physic - UFG and Federal University of Pernambuco for carrying some analysis.

**Área: MAT** **Nº de Inscrição: 0772**

# RECICLAGEM QUÍMICA DE ARTEFATOS DE ACRÍLICO PÓS-USO PARA A PRODUÇÃO DE ADITIVOS ANTICONGELANTES PARA BIODIESEL.

**Arthur Hiroshi Matsuchita (IC)[1], Gabrielle de Souza (IC)[1], Ticiane Vieira de Paula Souza (PG)[1], Aline Silva Muniz (PQ)[1], Valéria Gonçalves Costa (PQ)[2], Angelo Roberto dos Santos Oliveira (PQ)[1], Maria Aparecida Ferreira César-Oliveira (PQ)[1]*.**

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*[1]LEQUIPE-Departamento de Química, UFPR; [2]Laboratório de Tecnologia de Materiais Poliméricos, INT.*

Palavras Chave:Poli(metacrilato de metila), *Reciclagem química, Metacrilato de dodecila, Aditivo anticongelante, Biodiesel, PMMA*

## Highlights

**Chemical recycling of post-use acrylic objects for the production of antifreeze additives for biodiesel.** Polymeric esters as cold flow improver additives for biodiesel. Chemical recycling of post-use PMMA. Production of methacrylic acid alkyl esters from chemical recycling of poly(methyl methacrylate).

## Resumo/Abstract

Metacrilatos de alquila são compostos utilizados na produção de polímeros de composição variada para diferentes aplicações. Ao contrário dos acrilatos de alquila que podem ter origem em uma fonte renovável, os metacrilatos são obtidos exclusivamente do refino do petróleo. Sendo assim, a reciclagem química de artefatos de poli(metacrilato de metila) (PMMA) pós-uso se mostra uma opção atraente para evitar o uso de matéria-prima virgem e também contribuir com a redução de resíduos plásticos descartados inadequadamente no meio ambiente. A proteção do meio ambiente passa também pela adesão ao uso de fontes de energia renováveis, como os biocombustíveis. Uma das inúmeras vantagens do uso do biodiesel se encontra na grande diversidade de fontes vegetais e de gorduras animais disponíveis para a sua produção. No entanto, por se tratar de uma mistura de ésteres graxos (saturados e insaturados), a redução da temperatura ambiente promove o aumento progressivo da viscosidade do óleo e do início da cristalização (o Ponto de Névoa, CP), seguida pelo progressivo crescimento dos cristais até atingir o Ponto de Entupimento de Filtro a Frio, CFPP) e, por fim, os cristais atingem tamanho suficiente para impedir seu escoamento (o Ponto de Fluidez, PP), conhecido também como temperatura de congelamento. O uso de aditivos anticongelantes visa afetar o processo de cristalização para reduzir a temperatura de solidificação do biodiesel, reduzindo as restrições de uso e comercialização, com consequente ampliação do mercado, inclusive no Brasil. Algumas classes de polímeros podem ser usadas para esta finalidade, como alguns polimetacrilatos. Os monômeros – matérias-primas para a produção desses polímeros – podem ser obtidos através de um processo de reciclagem de artefatos descartados após o uso. A degradação do PMMA foi estudada em diferentes condições, sendo os melhores resultados obtidos na degradação termo-oxidativa, sob fluxo de ar controlado, atingindo 93 % de eficiência na degradação do PMMA de alta massa molar, em apenas 90 minutos e em temperaturas cerca de 200 ºC mais baixas do que as relatadas na literatura para a decomposição térmica do PMMA. O metacrilato de metila (MMA), produzido em alto grau de pureza, foi diretamente utilizado na síntese dos monômeros de metacrilato de alquila através de reações de transesterificação, sob catálise ácida, utilizando diferentes álcoois (85 a 95 % de rendimento). O metacrilato de dodecila (DDMA) foi submetido à polimerização radicalar, em solução, produzindo homopolímeros e copolímeros em rendimentos superiores a 85 %. O desempenho dos aditivos poliméricos na melhoria das propriedades de fluxo a frio do biodiesel puro (B100) e de blendas B10 e B20 compostas por biodiesel metílico (Potencial Biodiesel/PR) e petrodiesel (Petrobras) é ilustrado pela Tabela 1 (médias de triplicatas (+/- 1 ºC) usando apenas 1000 ppm de aditivo).

**Tabela 1.** Resultados do desempenho do aditivo PDDMA em amostras de biocombustíveis.

| Biocom-bustível | Sem aditivo | | | Aditivado com PDDMA | | |
|---|---|---|---|---|---|---|
| | CP (ºC) | CFPP (ºC) | PP (ºC) | CP (ºC) | CFPP (ºC) | PP (ºC) |
| B100 | 2,0 | 0,0 | 1,0 | 2,0 | -4,0 | -7,0 |
| B10 | -7,0 | -5,0 | -15,0 | -8,0 | -9,0 | -30,0 |
| B20 | -7,0 | -5,0 | -12,0 | -7,0 | -12,0 | -23,0 |

Dentre os aditivos anticongelantes sintetizados, o que mais se destacou foi o PDDMA que reduziu o CFPP e o PP das três amostras de biocombustível. Além do ótimo resultado de redução do PP do B100 para -7 ºC, foi ainda mais eficiente para as blendas biodiesel-diesel, retardando a solidificação do B10 para -30 ºC e do B20 para -23 ºC, o que são excelentes resultados, considerando as temperaturas de inverno da região do sul do Brasil, e garantindo o aumento da participação do biodiesel na matriz energética brasileira.

## Agradecimentos

**Área: MAT**

# Reaproveitamento de resíduos pesqueiros para produção de nanofluidos voltados à recuperação avançada de petróleo.

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Keywords: *Nanoparticles, wetability, $CaCO_3$, interface, EOR.*

## Highlights

Reuse of fishing waste for nanofluids production turned to advanced oil recovery.

- Use of *Mytella falcata* shells as nanoparticle in a fluid mixture to oil recovery.

- Methodology based on milling and ultrasound dispersion.

- Results in a bench simulation indicated an oil recovery 30% higher than conventional methods.

## Resumo/Abstract

The oil industry is constantly looking for solutions that maximize its production in order to meet the high energy demand worldwide. On the other hand, there is also an environmental issue, a large and recurring generation of waste, arousing the interest in research aimed at sustainability to seek solutions that would minimize the negative effect of human action on the environment. To enhance oil production, recovery techniques are required turned to intervene in the reservoir's repressurization or in the alteration of the fluid-rock formation system's properties. Nanofluids, stable nanoparticles dispersed in fluid, are a recent resource investigated in advanced reservoir recovery due to their ability to preferentially alter the formation's wettability through action at the fluid-rock interface. It may probably seem like a stalemate on maximizing production in the oil industry and the concern to minimize the generation of waste. Thus, this paper proposes the reuse of shells from *Mytella falcata*, which tons of waste are generated in fishing activities developed on the lagoon shore from the Maceió city, to extract calcium carbonate ($CaCO_3$) and produce nanofluids from these components using a previous thermal treatment in three different temperatures, milling and submitting to a dispersion with ultrasound. The work evaluated the efficiency of oil recovery compared to water injection in a bench experiment that sought simulate a reservoir oil displacement, characterizing the materials through Fourier Transform Infrared Spectroscopy (FTIR), Optical Microscopy (OM), Scanning Electron Microscopy and Energy Dispersive X-ray Spectroscopy (EDX) in order to obtain information to help in the validation of the method recovery. All of the nanofluids evaluated presented an average recovery factor higher than that of the secondary recovery, with emphasis on those thermally treated at 300ºC, which showed a recovery factor greater than 40%. The characterizations indicated that nanoparticles are composed of almost 98% of Ca. From the nanoparticles FTIR spectrum, it can be seen that the material has transmittance bands to the presence of the CH bond of stearic acid in the molecule, and others referring to the asymmetric plane (OCO), vibrational bands referring to the $CO_3$ molecule out of the plane and asymmetric stretching of CO. The Microscopies indicated that although the material presents nanometric particles, many were agglomerated forming huge flakes up to 700 microns. From this work, it was possible to infer that the use of a natural material as nanofluids are a viable and advantageous alternative as an advanced oil recovery.

## Agradecimentos/Acknowledgments

The Authors thanks for the financial support of Fundação de Amparo à Pesquisa do Estado de Alagoas (FAPEAL) and to Federal University of Alagoas (UFAL).

## Área: Química de Materiais - MAT    N° de Inscrição: 1006

# SÍNTESE DE HIDROXIAPATITA CONTENDO NANOPARTÍCULAS DE PRATA COMO AGENTE ANTIMICROBIANO.

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*Palavras Chave: Biomateriais, Cerâmica de fosfato de Cálcio, Tecido Ósseo, Biocompatibilidade, Materiais Bioativos.*
*Keywords: Biomaterials, Calcium phosphate ceramic, Bone tissue, Biocompatibility, Bioactive materials*

## Highlights

Synthesis of hydroxyapatite containing silver nanoparticles as an antimicrobial agent. Synthetic hydroxyapatite (HA) for use as biomaterial. Addition of silver nanoparticles, as antimicrobial agents, to HA. Osteoinducing antimicrobial biomaterial.

## Resumo/Abstract

The search for biomaterials is increasing—such materials have been used in medicine to replace functions damaged by diseases and natural and accidental losses, so they have mostly been used as bone replacement. However, the use of certain materials as biomaterials requires caution: the materials must present special features so that they are not rejected by the organism, and they must be biocompatible, biodegradable, bioactive, and bioresorbable. In the field of biomaterials, HA has been an option for bone replacement. In the laboratory, HA can be obtained from precursors containing calcium and phosphate ions. Here, we obtained HA from calcium nitrate and phosphoric acid. Addition of silver nanoparticles (AgNPs) to HA may add antimicrobial action to the resulting biomaterial, enabling its use in open systems and preventing bacterial contamination during and after its insertion into the organism. The HA and HA+AgNP samples were characterized by infrared and UV-Vis absorption spectroscopy. HA formation was confirmed by infrared spectroscopy: the spectrum displayed the typical bands at 3570 cm$^{-1}$, due to hydroxyl O-H bonds, and 1054 and 1098 cm$^{-1}$, attributed to phosphate groups (P-O). The presence of AgNPs was confirmed by UV-Vis spectroscopy of the liquid and solid, which detected the plasmon band around 400 nm. Figure 1 shows the UV-Vis spectra of solid HA and HA+AgNPs. Figure 1 b shows the UV-Vis spectra of the colloidal HA solution before and after AgNP incorporation. The AgNP incorporated into HA inhibited the bacteria growth of the *S. aureus and E. coli*.

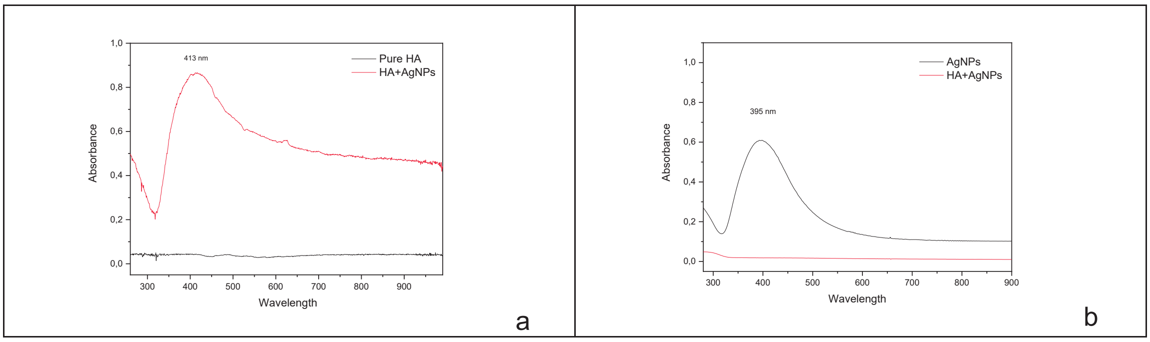

Figure 1: a) UV-Vis spectra of solid HA before and after AgNP incorporation and b) UV-Vis spectra of the colloidal HA solution before and after AgNP incorporation.

## Agradecimentos/Acknowledgments

CAPES, CNPq, and FAPESP

**Área: Materiais** **Nº de Inscrição:**

# Síntese e caracterização de nanopartículas de prata obtidas com alfa-hidroxiácidos.

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Palavras Chave: *nanotecnologia, prata, ácidos orgânicos, redução química, bottom-up.*

## Highlights

Synthesis and characterization of silver nanoparticles obtained with alpha-hydroxy acids.

Silver nanoparticles (AgNPs) were obtained via chemical reduction ($AgNO_3$/ $NaBH_4$) in the presence of different alpha-hydroxy acids. The (AgNPs) obtained showed average sizes between 17.3 and 4.73 nm.

## Resumo/Abstract

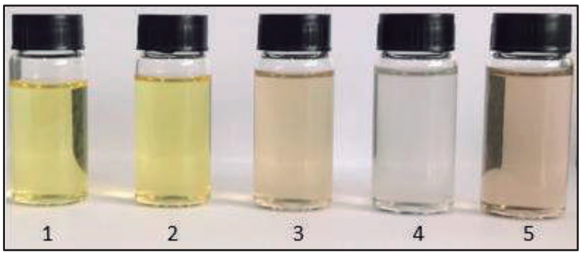

*Figura 1* – Aspecto visual das amostras obtidas com: (1) ácido cítrico, (2) tartárico, (3) málico, (4) lático e (5) caproico.

As nanopartículas de prata (AgNPs) são particularmente interessante, devido ao seu efeito bactericida a suas propriedades eletroquímicas, óticas e atividade catalítica. Existem diversas pesquisas em síntese de AgNPs buscando manipular suas características morfológicas e de tamanho, visto que, estas influenciam diretamente nas propriedades químicas e biológicas do material sintetizado. O objetivo do presente estudo, foi observar o efeito da presença de alfa-hidroxiácidos (AHAs) no preparo de AgNPs via redução química. Os AHAs são um grupo de ácidos naturais encontrados em alimentos e apresentam atividades antibacterianas. Para favorecer a redução química do material de partida $AgNO_3$, foi necessário adicionar ao meio reacional uma solução de $NaBH_4$. Foi possível notar que cada solução apresentou uma coloração específica, Figura 1. Os ácidos utilizados neste estudo foram os ácidos: cítrico (1), tartárico (2), málico (3), lático (4) e capróico (5). Para comprovação da formação de AgNPs os materiais foram avaliados por espectroscopia eletrônica na região do UV-Vis. Observaram-se bandas de absorção características de AgNPs em torno de 380-425 nm.[1] Posteriormente, a técnica *Dynamic Light Scattering*, foi utilizada para determinação do diâmetro hidrodinâmico das partículas obtidas. Observou-se que as AgNPs obtidas em presença dos ácidos: cítrico (**AgNPs-Cit**), tartárico (**AgNPs-Tar**), málico (**AgNPs-Mal**), lático (**AgNPs-Lat**) e capróico (**AgNPs-Cap**) apresentaram tamanhos hidrodinâmico médios de 17,3 ± 4,55 nm, 9,02 ± 2,15 nm, 6,31 ± 1,51 nm, 13,6 ± 1,42 nm e 4,73 ± 1,14 nm, respectivamente. Para avaliar a estabilidade coloidal das soluções foram realizadas variações do pH e medidas de seus respectivos potenciais zeta (ζ). No qual foi possível notar que à medida que o valor de pH da solução aumentava, mais negativos tornavam-se também os valores de ζ encontrados.[2] Os valores absolutos acima de 20 mV sugerem aumento da estabilidade coloidal.

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[2]SALEM, H. F. & MA, S. "Formulation and evaluation of silver nanoparticles as antibacterial and antifungal agents with a minimal cytotoxic effect". Int. J. Drug Deliv., 3: 293, 2011.

## Agradecimentos/Acknowledgments

**Área: MAT**

# Silica- and ceria-based nanosystems containing isotretinoin: Synthesis, physicochemical characterization and in vitro cytotoxicity study

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Key words: *Acne; sol-gel; nanocarriers; cytotoxicity.*

## Highlights

Synthesis of silica- and ceria-based inorganic nanoparticles by the sol-gel methodology in ammoniacal medium and capable of interacting with the drug isotretinoin provides materials with low toxicity and promising applications as nanoparticulate systems for drug administration.

## Resumo/Abstract

This work aims to synthesize and to characterize ceria- and silica-based nanoparticles for immobilization of the drug isotretinoin (ISO), evaluation of the chemical structure and biological properties, for applications as nano drug carrier systems. The nanoparticles were synthesized by the sol-gel methodology in ammoniacal medium and co-precipitation. At first, two materials were obtained: silica containing 10% of cerium III (SC2 10%) and ceria (C2), which were dried at 100 °C, incorporated with isotretinoin in DMSO, 1:1 (m/m) ratio, for 24 h, and named SC2 10%-ISO and C2-ISO, respectively. The SC2 10%, C2, SC2 10%-ISO, and C2-ISO nanoparticles were characterized by vibrational spectroscopy in the infrared region. The spectra presented the typical absorptions of silica bonds, ceria bonds, or the ISO functional group. Matrix-drug interaction was evaluated by indirect quantification in the supernatant by high-performance liquid chromatography (HPLC). Immobilization efficiency was 11% for SC2 10%-ISO and 16% for C2-ISO. Nanoparticle size, determined by light dispersion, ranged between 303 and 515 nm, with polydispersity index < 0.7 and positive zeta potential (+30.7 mV) for pure ceria and negative zeta potential (-33.0 mV) for silica containing cerium III. These values indicated homogeneous particle distribution and adequate electrical stability in the suspension, which prevented aggregation. For SC2 10%-ISO, the absolute zeta potential value decreased, and the hydrodynamic size increased as compared to SC2, whereas C2-ISO and C2 presented similar values. Cell viability results obtained in HaCat cell culture after incubation with nanoparticles at concentrations between 39.06 and 5000 ug/mL for 24 h showed that these concentrations were not cytotoxic even after drug incorporation, as revealed by XTT assays. Therefore, the nanoparticles are potential candidates as isotretinoin carrier.

## Agradecimentos/Acknowledgments

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**Área: MAT**

# Simple synthesis of hierarchically porous carbons from bio-oil to remove emerging contaminants.

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Keywords: *Hierarchical porous carbons, biomass; bio-oil, adsorption; emerging contaminants*

## Highlights

Synthesis of hierarchical porous carbon from bio-oil (biomass waste) for removal emerging contaminants (amoxicillin, ibuprofen, caffeine, paracetamol, 17α-ethinylestradiol) from water.

## Resumo/Abstract

In this work hierarchical porous carbons (HPC)[1] were prepared using bio-oil as carbon source and zinc chloride as activated agent.[2] The HPC were obtained by template-free route from biomass pyrolysis. The materials were characterized by the techniques of elemental analysis (CHNSO), XRD, TG, SEM, Raman spectroscopy, EDS, Physisorption analysis (BET) and zero charge point. The HPCs showed macro/meso/microporosity and specific surface areas of 764 – 836 $m^2.g^{-1}$, and total pore volume of 0.988 – 1.029 $cm^3.g^{-1}$. The materials presented high carbon contents (>80%) and presented a multimodal distribution with maximum 1nm and 3.3 nm, and average diameter of 0.614 nm. The Hierarchical porous carbon were applied in removal emerging contaminants (amoxicillin, caffeine, paracetamol 17α-ethinylestradiol and ibuprofen) from water. The materials showed removals above 70% for amoxicillin and above 85% for other contaminants in just 3 hours of contact. Kinetic and adsorption isotherms studies for caffeine and paracetamol demonstrated that most materials follow pseudo-second order kinetics. On the other hand, the adsorption isotherms adjusted better to the Sips model obtaining $q_{max}$ values of 183 $mg.g^{-1}$ and 520 $mg.g^{-1}$ of caffeine and paracetamol respectively.

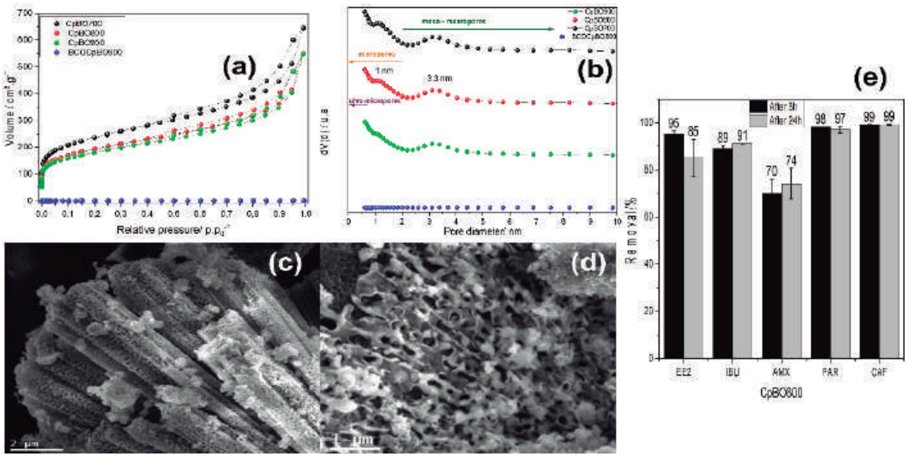

Figure 1: Isotherms of nitrogen sorption of HPC(a), Pore size distribution of HPC (b), SEM imagens of HPC (c) and (d), Adsorption tests for removal emerging contaminants from watter.

### References:

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2 J. Xu, B. Xue, C. Liu, C. Xia, M. Li and R. Xiao, *Sustain. Energy Fuels*, 2021, **5**, 3884–3894.

## Agradecimentos/Acknowledgments

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**Área: _____________ Nº de Inscrição: ________**

# Structural and Photophysical Properties of Lanthanide Coordination Frameworks with Pentafluorobenzoate.

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Keywords: luminescence, lanthanide, MOF, Ln-Ln interactions, energy transfer.

## Highlights

The unique photophysical properties of lanthanide-organic frameworks (LnMOFs) are relevant for many applications. A new LnMOF is a platform to study the interactions between $Ln^{3+}$ ions.

## Resumo/Abstract

Trivalent lanthanide $Ln^{3+}$ ions have unique photophysical properties and their organic frameworks (LnMOFs) are relevant for many applications. These and other properties are dependent upon the interactions between the $Ln^{3+}$ ions, which are ubiquitous in LnMOF. Therefore, they are interesting platforms to study these interactions. Pentafluorobenzoic acid (LH) is a strong acid ($pK_a$ = 1.48) that can yield coordination compounds (mono and dinuclear and MOFs) with $Ln^{3+}$ ions. Open synthesis at room-temperature and at 80 °C and liquid-assisted gridding (LAG) mechanochemical method were employed to synthesize the dimer $[Ln_2(L)_6(H_2O)_8](H_2O)_2$ (Ln = Eu, Gd, Tb) that is already described as well as a new mixed Eu-GdMOF $[Ln(L)_2(LH)(H_2O)_4](Cl)(LH)(H_2O)_2$. It structure, determined by crystallography, is quite unusual, because the Ln centers are connected by a single symmetric bridge ligand and a Ln-Ln distance of 6.865 Å, which has not been observed in frameworks of lanthanide-benzoates. The crystal asymmetric unit does not possess an inversion center, however, the crystal packing composed of four asymmetric units does present a center of inversion. Upon excitation at wavelengths larger than 277 nm, the emission intensity of the $^5D_0 \rightarrow {}^7F_2$ transition in the EuMOF is less intense than the $^5D_0 \rightarrow {}^7F_1$, transition suggesting the presence of an inversion center. However, for the heteronuclear Eu-GdMOF presents the typical $^5D_0 \rightarrow {}^7F_J$ ($J$ = 0 - 4) transitions, with $^5D_0 \rightarrow {}^7F_2$ being more intense than $^5D_0 \rightarrow {}^7F_1$. These changes in the relative intensities suggest that (i) the Eu-GdMOF was obtained and the inversion center in the unit cell is no longer present because the replacement of $Eu^{3+}$ by $Gd^{3+}$, and (ii) the interactions between the $Eu^{3+}$ ions are sufficiently strong for the four asymmetric units to behave as a single effective emission center. In the mixed Eu-TbMOF, the typical $^5D_0 \rightarrow {}^7F_J$ ($J$ = 0 - 4) transitions of $Eu^{3+}$ and $^5D_4 \rightarrow {}^7F_J$ ($J$ = 6 - 1) of $Tb^{3+}$ were observed upon excitation at the ligand states. The excitation spectra present a band due to the $^7F_6 \rightarrow {}^5D_4$ $Tb^{3+}$ transition when the emission were monitored at $^5D_0 \rightarrow {}^7F_2$ or at $^5D_4 \rightarrow {}^7F_5$, indicating energy transfer from $Tb^{3+}$ to $Eu^{3+}$ ions. The reverse energy transfer $Eu^{3+} \rightarrow Tb^{3+}$ was not observed either in the emission or the excitation spectra. The X-ray data as well as the luminescence results showed that the structure of the coordination compounds (dinuclear and MOF) depends on the synthetic method, that the $Eu^{3+}$ ions interact strongly even at distances of *ca*. 7 Å, and that $Tb^{3+}$ transfer energy to $Eu^{3+}$ ions. In addition to the novelty of the LnMOF and mixed LnLn'MOFs, their photophysical properties are being explored in several applications.

## Agradecimentos/Acknowledgments

FACEPE, CNPq, CAPES, Profs. Luís D. Carlos and M. Rute Ferreira (University of Aveiro) for the photophysical measurements, and Paula Brandão (University of Aveiro) for the crystallography.

**Área: MAT**

# Study of properties of Portland cement pastes modified with titanium dioxide nanoparticles - $TiO_2$

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*[2]Faculdade de Engenharias, Arquitetura e Urbanismo, Universidade do Vale do Paraíba – UNIVAP, São José dos Campos - SP*

Palavras-Chave: *Nanotechnology; Nanoparticles; Nanomaterials; Construction materials.*

## Highlight

$TiO_2$ nanoparticles ($TiO_2$NPs) acts as nano-filler accelerates the rate of hydration.

The chloride test indicated a reduction of porosity in the different samples.

## Resumo/Abstract

Nanoparticles have been applied in the production of construction materials to enhance the mechanical properties, reduce shirinkage and permeability, which contribute to extension of their service life.[1,2] In this work, nanomodified Portland cement paste with a water/cement ratio of 0,45 was prepared with the addition of $TiO_2$NPs, commercials, at 0,1, and 0,5% by mass of cement. The $TiO_2$NPs were heat-treated at a temperature of 400 °C for 4 hours, being later analyzed by UV-vis spectroscopy and transmission electron microscopy (TEM). As observed in Fig. 1a, TEM analysis confirmed the presence of spherical-like shape $TiO_2$NPs and their average size was 32.5 nm. The Fig. 1(b and c) shows the TEM image of the cement paste with the addition of 0.1%, and 0,5%, respectively, where can be observed dispersed $TiO_2$NPs into cement pieces. The samples prepared in this work are shown in figure 1d. The Fig. 1e shows the broken specimens after immersion in silver nitrate solution ($AgNO_3$). The purpose of this test was to verify the penetration depth of chloride ions for each sample and, thus, to evaluate the porosity of the samples. Mechanical properties data and other analysis will be presented in the final version of the poster in the congress.

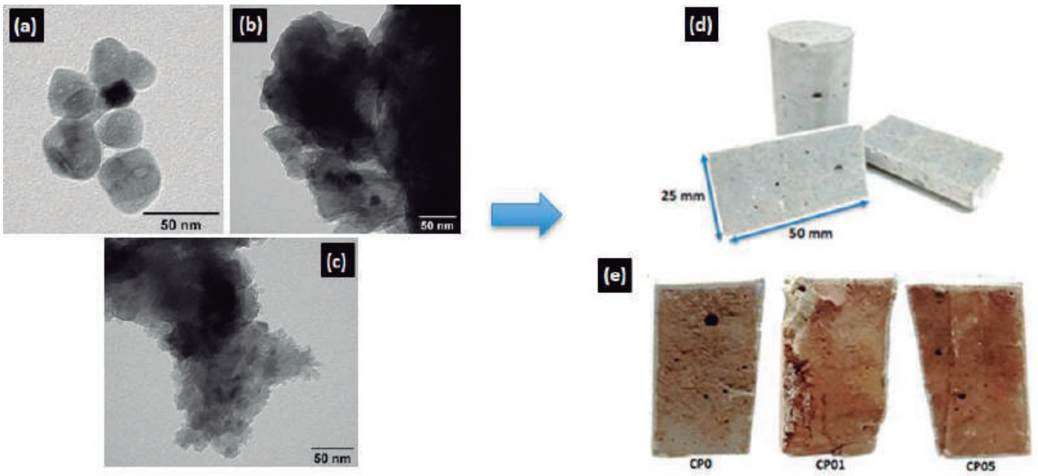

**Figure 1.** TEM images of $TiO_2$NPs (a), and Portland cement paste with nanoparticles (b and c). Specimens used to perform all tests and trials (d). Specimens after immersion in silver nitrate solution ($AgNO_3$) (e).

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## Agradecimentos/Acknowledgments

We would like to thank CAPES by Paulo's master's scholarship, IEAMar-UNESP for the TEM analysis, and FEAU-UNIVAP for mechanical tests.

**Área: ____MAT______**
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**Nº de Inscrição: __00634___**
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# Study of the influence of the application of compatibilizers on the production of polymer blends containing of PLA/PE

**Ana Paula Taveira Alves (IC)[1,*], Mariana Fernandes de Carvalho Lopes (IC)[1], Aline Lucas Ravagnani (IC)[1], Vivian Karina Bianchini (PQ) [1], Carlos do Amaral Razzino (PQ)[2], Katia Jorge Ciuffi (PQ), Liziane Marçal (PQ)[1].**

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*Palavras Chave: Biodegradable blends, Polylactic acid, Polyethylene.*

## Highlights

- PLA and PE showed a immiscibility polymer mixture, which were influenced by the use of compatibilizers.
- Different mechanical properties were observed for PLA/PE blends compared to PLA.

## Resumo/Abstract

The increasing consumption of synthetic polymers has created significant environmental concerns and impact. In this focus, specialists search for new recyclable technologies; that increase the use of plastic products that have renewable or biodegradable components. Therefore, is very important the study of polymer blends that consist a mixture of two or more polymers that have been blended together to create a new material with different physical properties. The main aim of the work was to develop biodegradable polymeric blends of poly(lactic acid) (PLA) and green polyethylene (PE) and to evaluate the influence of the addition of grafted compatibilizers. The compatibilizers used were the Lotader® product, which is a copolymer consisting of ethylene glycidyl methacrylate (GMA) and maleic anhydride (MA). The polymer mixtures were composed of PLA and PE, with a mass ratio of 70:30 with or without the addition of 3% of compatibilizer. Each composition was processed, at around 200°C, in a corrotational twin screw extruder, with two automatic feeders, exchangeable screw profile and degassing system. Injection molding at 200ºC was used to make specimens to evaluate the use of each blend in the manufacture of injection molded products. The materials obtained were characterized by x-ray diffraction (XRD), thermal analysis (TGA/DSC) and infrared absorption spectroscopy (FTIR), and the samples were applied uniaxial tensile tests and resistance to impact. The XRD results show that the semi-crystallinity of PLA and PE are maintained in the samples with the addition of compatibilizer. The results of thermal analysis of the blends show melting temperatures characteristic of each polymer (180°C for PLA and 140°C for PE); regarding the initial degradation, the polymers show maximum mass losses at 350°C for PLA and 475°C for PE. The blends were degraded in two main stages, with temperatures and proportions coinciding with the two polymers that compose them. The infrared spectra of PLA and PE have, in common, vibration modes of the CH bond (in, $cm^{-1}$) 2997-2965 ($CH_2$, $CH_3$), 1360-1450 ($CH_3$), 750 (CH) and in the case from PLA, the band at 1759 $cm^{-1}$ referring to C=O (carboxylic acid) was also observed, however in the blends spectra, this band shows a displacement presenting the interaction of the compatibilizer between PLA and PE. In the uniaxial traction tests, the values for the blends were found lower than the pure PLA values, indicating that less rigid materials were obtained. As with the module, the addition of polyolefins causes a decrease in the tensile strength of the blends compared to pure PLA. However, the impact resistance (R.I.) for all blends was higher than for pure PLA. Thus, as reported in the literature, most blends are presenting immiscible properties that are not suitable for industrial applications, that is, they are incompatible and it was proven that the conditions used in this work, resulted in an excellent cost/performance ratio of the studied polymer systems.

## Agradecimentos/Acknowledgments

CNPq, FAPESP, CAPES.

**Área: MAT** **Nº de Inscrição: 135**

# Supporting the Photocatalysts on commercial oxide: An Effective Way to Enhance the Photocatalytic Activity of $SrSnO_3$

**Luzia M.C. Honorio (PQ),[1,2] André Menezes (PQ),[1] Thalles M.F. Marques (PQ),[2] Edson C. da Silva Filho (PQ),[2] Josy A. Osajima (PQ),[2] Ary S. Maia (PQ),[1] Amer Hakki (PQ),[3] Donald E. Macphee (PQ),[3] Iêda M.G. Santos (PQ).[1*]**

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Palavras Chave: Perovskite, Strontium stannate, Pechini method, Azo-dye, Photocatalysis, Terephtalic acid

## Highlights

Photocatalytic activity of $SrSnO_3$ was improved by dispersion on $ZrO_2$, due to a smaller particle size and greater amount of $Sn^{2+}$

Band edge positions and feasibility of redox reactions were determined

## Resumo/Abstract

Photocatalysts based on $SrSnO_3$ and $SrSnO_3@ZrO_2$ were prepared by the modified-Pechini method at 800°C and applied in the photocatalytic degradation of Remazol Golden Yellow dye under UV radiation. The photohydroxylation of terephthalic acid and scavengers were employed in order to evaluate the participation of each active species, such as hydroxyl radical, and photogenerated electrons and holes on the photocatalytic process. The band gap structure was evaluated using the Mott Schottky method in combination with UV-visible spectrophotometry. According to the results of transmission electronic microscopy (TEM) and X-ray photoelectron spectroscopy (XPS), nanometric $SrSnO_3$ particles were obtained when supported on $ZrO_2$, associated to an increased amount of Sn(II). Results indicated that both samples had high photocatalytic activity, although $SrSnO_3@ZrO_2$ showed the best decolorization performance ranging from 32% to 98%, which was associated to the morphology of the particles and to the greater amount of oxygen vacancies. The participation of hydroxyl radicals in the reaction was confirmed when terephthalic acid was used as probe and by using isopropanol as hydroxyl radical scavenger, which resulted in the inhibition of the photocatalytic process. The photocatalytic activity was clearly related to surface redox reactions (Figure 1), as $H_2O$ oxidation, with different behaviors in relation to $O_2$ reduction depending on the pH of the solution.

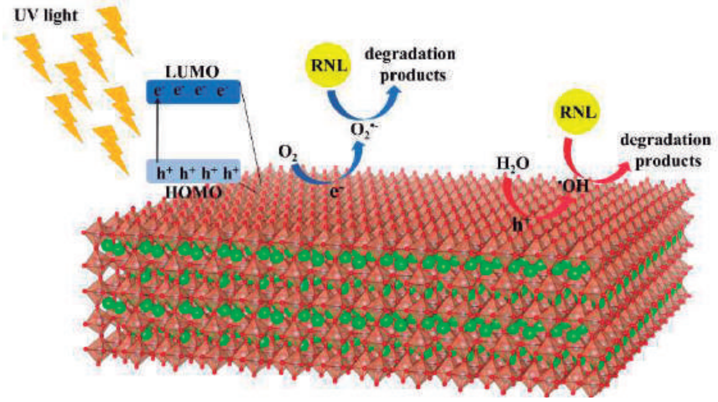

Figure 1: Schematic reactions during photocatalytic discolorization of an azo-dye in the presence of $SrSnO_3@ZrO_2$.

## Agradecimentos/Acknowledgments

This work was supported by grant 0012/2019, Paraíba State Research Foundation (FAPESQ), CT-INFRA/FINEP/MCTIC and CAPES/MEC (Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Finance Code: 001).

**Área: MAT** **Nº de Inscrição: 00222**

# SYNTHESIS AND CHARACTERIZATION OF CARBON DOTS SUPPORTED IN REDUCED GRAPHENE OXIDE.

**José Carlos dos S. Junior* (PG),[1] Jonatas O. S. Silva (IC),[1] José Felipe dos Santos (IC),[1] Eliana Midori Sussuchi (PQ),[1] Marcelo O. Rodrigues (PQ).[2]**

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*Palavras Chave: Ascorbic Acid, Carbon Dots, Graphite oxidation, Hybrid Material, Nanoparticle, Reduced Graphene Oxide.*

## Highlights

Hybrid material based on reduced graphene oxide/carbon dots as modifying on carbon paste electrode. Highly luminescent carbon dots.

## Resumo/Abstract

Carbon paste electrodes (CPE) have shown promise in the monitoring herbicide levels in different crops using electroanalytical techniques. In this work we synthesize a hybrid matrerial, based on reduced graphene oxide (rGO) and carbon dots (CD) to apply as modifier on CPE. The rGO was obtained by the synthesis of graphene oxide (GO) using the modified Hummers method, followed by reduction with L-ascorbic acid. To obtain the hybrid material, we synthesized carbon dots in situ in a matrix of reduced graphene oxide (rGO) through a hydrothermal route in an oven, at 180 ºC for 5 h, in a PTFE reactor with a stainless steel jacket. The raman spectra (Figure 1A) show the increase in the D/G bands ratio from GO to rGO follwed by decrease into CD-rGO material. This is related to defects like edges, ripples and folds, in main structure. In the FTIR spectroscopy, each spectrum (Figure 1B) shows several modes corresponding to functional groups containing oxygen. In the rGO spectrum, the reduced broad and weak signals at 3441 $cm^{-1}$ (O-H of phenol, diol and carboxylic group) and 1643 $cm^{-1}$ (C=O) show the decrease of presence of functional groups containing oxygen confirmed that the GO indeed was reduce into rGO. The signal at 1088 $cm^{-1}$ (epoxide C-O-C) is due the oxygenated functional groups that remain into CD-rGO hybrid graphitic structure. Additional application studies are underway to quantify glyphosate in food samples, as well as electrode stability.

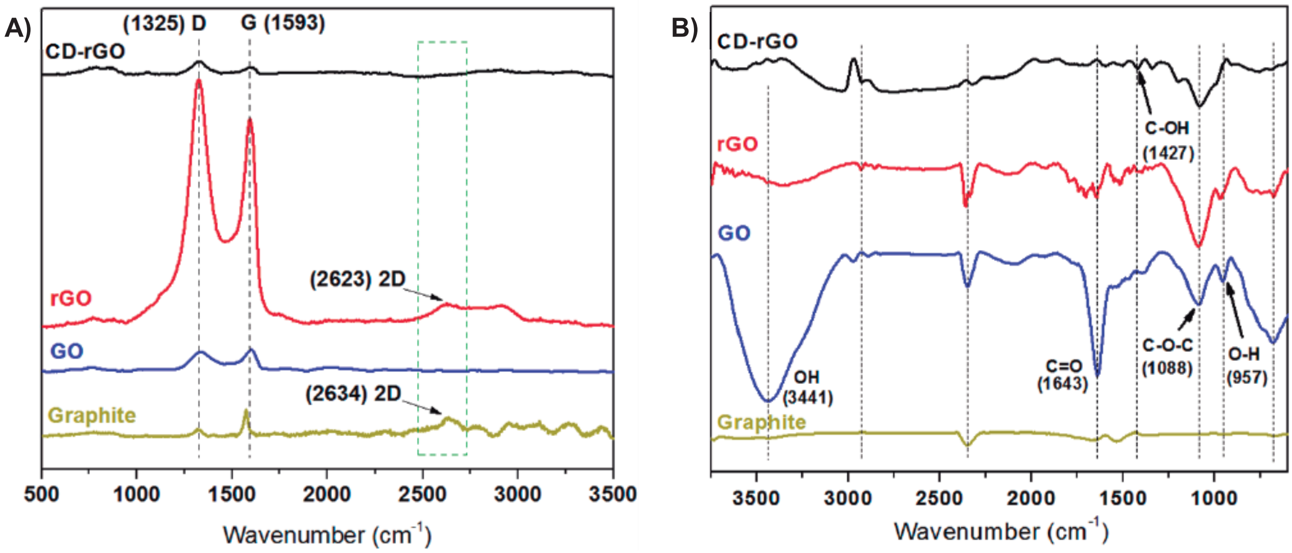

**Figure 1**. A) Raman and B) FTIR spectrum of graphite, GO, rGO and CD-rGO

## Agradecimentos/Acknowledgments

CNPq, CAPES, PETROBRAS, Center of Chemistry Laboratories Multi-Users at UFS (CLQM), Corrosion and Nanotechnology Laboratory (LCNT), Sergipe Regional Competence in Oil, Gas and Biofuels (NUPEG), Associação Sergipana de Ciência (ASCi).

**Área: ______MAT_________**

# Synthesis and characterization of kaolin and metakaolin geopolymers applied to Amoxicillin adsorption

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Keywords: *Geopolymer, $^{29}$Si NMR, Amoxicillin adsorption, CTAB*

## Highlights

Kaolin and metakaolin geopolymers were synthesized using CTAB as a structure-directing agent. NMR studies proved formation of geopolymer. Geopolymers presented excellent amoxicillin adsorption values.

## Abstract

In this study, geopolymers were synthesized using kaolin and metakaolin as precursors and CTAB as a structure-directing agent (Fig.1). These geopolymers were thermally treated at 300 °C for 2 hours and amoxicillin adsorption tests were performed for each synthesized material and its precursors. X-Ray diffraction patterns obtained for geopolymers are very similar to its precursors kaolin and metakaolin and indicated the presence of unreacted quartz, that might be incorporated as a filler in the geopolymer's structure. $^{29}$Si and $^{27}$Al NMR analyses (Fig. 2) indicated the formation of the geopolymers and also the presence of quartz, the latter corresponding to *ca.* 50% of the material's composition. For the geopolymer obtained using kaolin, it was also observed signals of this precursor, with indicates that the reaction was incomplete. For the amoxicillin adsorption tests, isotherms were obtained with solutions varying concentration from 50 to 300 ppm. As observed in Table 1, geopolymers presented excellent adsorption values in general, unlike its precursors, which presented no adsorption. The best adsorption value was 199 mg g$^{-1}$, obtained for Geo20, material made of kaolin with 20% w/w of CTAB. It is important to point out that CTAB's addition to geopolymer synthesis affected the absorption results more noticeably when kaolin was used as a precursor, which may imply CTAB has influenced greatly its structure, although it did not produce the expected increase in geopolymers' superficial area (values obtained were between 4 and 13 m$^2$ g$^{-1}$).

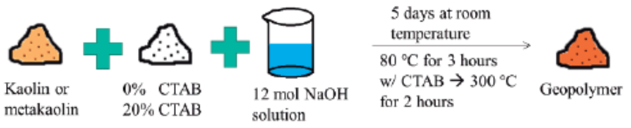

Fig. 1: Geopolymer synthesis scheme.

Table 1: Amoxicillin adsorption values.

| Material | Geo | Geo20 | MGeo | MGeo20 |
|---|---|---|---|---|
| Qmáx (mg g$^{-1}$) | 82 | 199 | 113 | 125 |

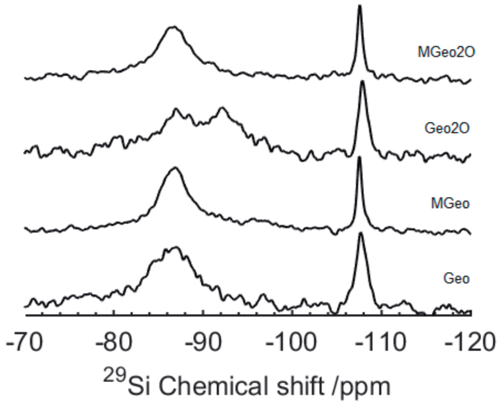

Fig.2: $^{29}$Si solid-state NMR analysis.

## Acknowledgments

**Área: MAT** **Nº de Inscrição: 00497**

# Synthesis and characterization of nanocomposites between graphene and zinc oxide nanoparticles doped with $Ag^+$ applied in photocatalysis

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*Departamento de Química, FURB.*

Key words: *nanoparticles, zinc oxide, graphene oxide, nanocomposites, $Ag^+$ doping, photocatalysis.*

## Highlights

ZnO-GO nanocomposites doped with $Ag^+$ were synthesized via a sol-gel method, resulting in nanomaterials with good morphological, structural and optical properties, as well excellent photocatalytic activity.

## Abstract

Zinc oxide (ZnO) nanoparticles (NPs) present great relevance for being important semiconductors of low toxicity and good chemical stability. It is very interesting to photocatalysis, since ZnO has a band gap of 3.37 eV and exciton binding energy of 60 meV. In the photocatalytic process, electron-hole pairs are formed in the semiconductor and react with water, oxygen and hydroxyl molecules to produce radical species responsible for photocatalysis. Moreover, the doping of ZnO with $Ag^+$ improves the separation of electron-holes and increases photocatalytic efficiency. Another material that increases photocatalytic activity is graphene oxide (GO) due to the high adsorption capacity, as well better charge separation and transportation. Considering those facts, this work aims to synthesize and characterize ZnO-GO nanocomposites doped with different $Ag^+$ ratios and to study their potential applications in photocatalysis. The sol-gel method was employed in the syntheses, using isopropanol as solvent. The nanomaterials synthesis had their growth kinetic followed by optical measurements, such as fluorescence and absorbance, increasing the intensity of fluorescence and the onset values for doped materials. Also, nanocomposites were analyzed by scanning electron microscopy (SEM), X-ray spectroscopy (EDS) and X-ray diffraction (XRD), which demonstrated the isolated presence of Ag species. In addition, higher Ag content increase the size of ZnO NPs from 14 to 9 nm for $[Ag^+]$ from $1\times10^{-3}$ to $10^{-5}$ mol $L^{-1}$, respectively. The nanomaterials were applied in photocatalysis of the methylene blue (MB) dye under the action of fluorescent light (59 W, 220 V, 0.3 A) for 240 min, resulting in excellent absorbance reduction at the maximum dye absorption wavelength of 655 nm. During the process, the formation of metallic Ag NPs was observed due to the appearance of a characteristic band at 410 nm, which is attributed to the plasmon band. This fact contributed positively to the rapid reduction of the AM absorption (< 10 min), in which NPs of ZnO-GO doped with $1\times10^{-4}$ mol $L^{-1}$ of $Ag^+$ presented the best results, achieving almost 100% reduction in absorbance at 655 nm in a period of just 70 min. Therefore, nanocomposites between GO and ZnO NPs doped with Ag are good candidates for application in photocatalysis.

## Acknowledgments

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**Área: MAT**

# Synthesis and characterization of nickel nanorods: effect of pH.

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Palavras-Chave: Nickel, Nanorods, Synthesis, effect of pH.

## Highlights

Preliminary results on the synthesis of nickel nanorods show that average length and diameter are not affected by pH (8 to 14). pH=14 provided nanorods with better length and diameter homogeneity.

## Resumo/Abstract

This work brings the preliminary results on the synthesis of nickel nanoparticles with differentiated geometries, studying the effect of the pH in the obtention of nickel nanorods. This synthesis aims to use the nanoparticles as an active phase in catalytic hydrogenolysis of hydrocarbons that present structure sensitivity. The synthesis was developed by modifying the method proposed by Wasiak et al. [1], using nickel nitrate and oxalic acid (1:1) to obtain nickel oxalate. Subsequently, polyethylene glycol and polyvinylpyrrolidone were added to the precursor in four different autoclaves, and the pH values were adjusted to 8, 10, 12, and 14 with sodium hydroxide. Hydrothermal treatment was performed at 180 °C for 24 h. The solids were reduced in $H_2$ atmosphere and characterized by scanning electron microscopy (SEM). SEM images, figure 1, show that pH does not significantly influence the average length (1750 nm) and diameter (500 nm) of the particles. However, it is possible to observe that the solids prepared at pH = 14 show a better homogeneity in the particle size distribution. Further studies on the synthesis parameters such as precursor, hydrothermal temperature and time, purification method are being performed to obtain smaller and more uniform particles to study the influence of geometric characteristics in hydrogenolysis reactions.

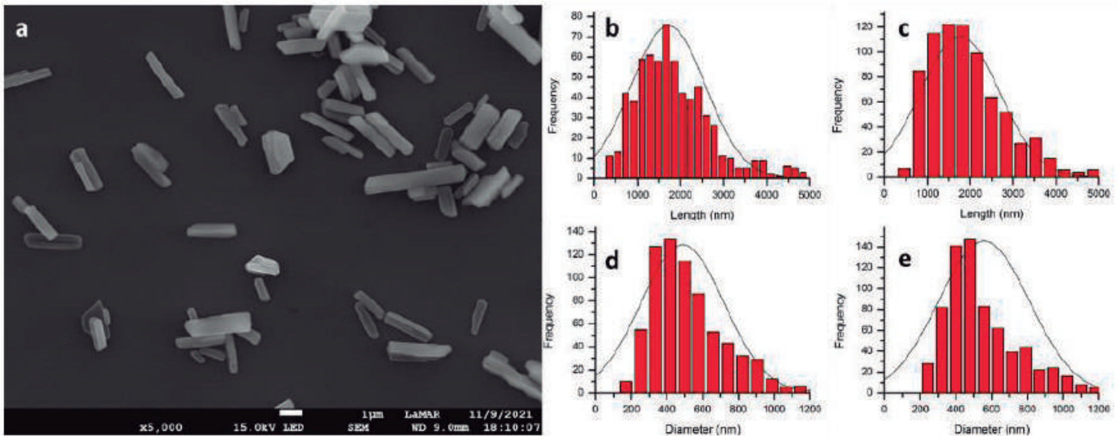

Figure 1-. a) SEM image of the solid obtained at pH=8, geometric characteristics: b) and d) pH=8, c) and e) pH=14.

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## Agradecimentos/Acknowledgments

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**Área: MAT**

# Synthesis and characterization of poly(vinylidene fluoride)/bentonite nanocomposite membrane for phosphorus adsorption

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Palavras Chave: *Nanocomposite membrane, poly(vinylidene fluoride), phosphorus, adsorption..*

## Highlights

The phase inversion method was used to prepare PVDF/modified bentonite membrane. The membrane showed good thermal stability and mechanical properties. The membrane showed excellent phosphorus adsorption capacity.

## Abstract

The removal and recovery of phosphorus (P) from wastewater is extremely necessary, as this nutrient is related to the eutrophication of water bodies. Furthermore, this non-renewable resource is an essential macronutrient for all forms of life and a key for global food security [1]. Adsorption is one of the most effective and selective methods to recover P from solution, and nanocomposite membranes are a new class of adsorbents studied in the literature that combine the advantages of both processes [2]. In this study, NT-25Fe/PVDF nanocomposite membrane was synthesized through the phase inversion method, using DMF as the solvent.

The addition of nanoclay adsorbent on poly(vinylidene fluoride) (PVDF) matrix resulted in the increase of porosity from 5% (pristine membrane) to 32% (nanocomposite). The modified membrane exhibited a higher thermal decomposition temperature (Figure 1) due to the incorporation of clay particles into the polymer chain. Furthermore, the membrane showed a tensile strength of 1.7 MPa, which is suitable for ultrafiltration processes. The membrane presented effective P adsorption during the kinetic study (Figure 2), removing 50% of the phosphorus in the aqueous solution in 8 h.

Figure 1 - TGA curves of pristine and modified membrane (25 °C to 850 °C – 10 °C $min^{-1-}$ $N_2$ atmosphere)

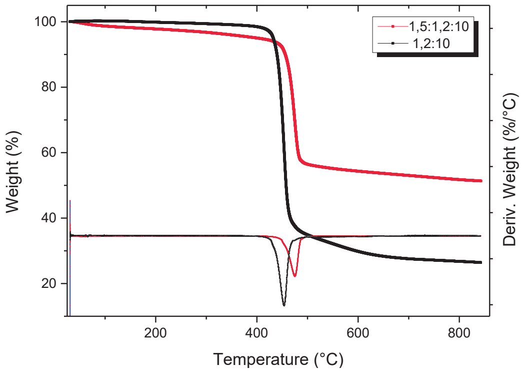
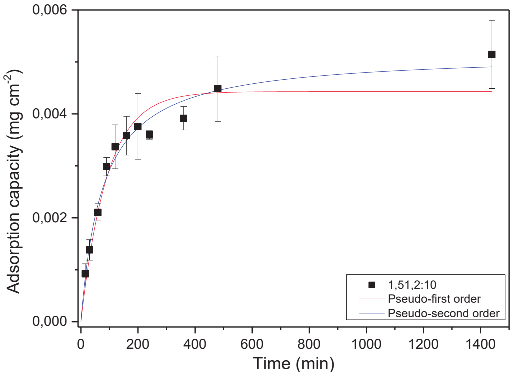


Figure 2 – Effect of contact time for NT-25Fe/PVDF membrane for adsorption capacity of P ($C_i$ – 5 mg-P $L^{-1}$, 24 h, memb. area - 25 $cm^2$)



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## Acknowledgments

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**Área: MaT**

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

# Synthesis and characterization of the $Fe_3O_4$ nanoparticles for application in controlled drug delivery

**Renata P. Neves (PG)[1], Erika S. Bronze-Uhle (PQ)[2], Pâmela L. Santos (PQ)[3], Paulo N. Lisboa-Filho (PQ)[1], Aroldo G. Magdalena (PQ)[1]**

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Palavras Chave: *Magnetic nanoparticles, Bovine serum albumin, Drug delivery, Salicylic acid, Nanoparticles.*

## Highlights

The incorporation efficiency of the SA was 91%; Most of SA was released within the first five hours; The concentration reached an equilibrium of about 0.265 mg $mL^{-1}$ of the SA.

## Abstract

In the past years, nanotechnology has advanced and its application in the clinical setting has become the object of research. Multifunctional nanoparticles can combine different therapeutic functions, image capability such as MRI. Remotely controlled and controlled drug delivery system and hyperthermia function[1]. Iron oxide ($Fe_3O_4$) nanoparticles (NPs) have superparamagnetic properties, responsible for the hyperthermia function, as well as high chemical stability, low toxicity, favorable biocompatibility, and biodegradability[2]. In this work, the synthesis and characterization of $Fe_3O_4$ NPs functionalized with bovine serum albumin (BSA) were carried out. The incorporation of salicylic acid (SA) into the nanoparticulate matrix and study of its release in vitro is also described in the present study[3]. Iron oxide NPs were obtained through the co-precipitation method and all samples were analyzed using Fourier transform infrared spectroscopy (FTIR), zeta potential, X-ray diffraction (XRD), fluorescence spectroscopy and transmission electron microscopy (TEM). The results showed in the DRX a large peak around 2θ equal to 20°, which is a characteristic of albumin. This can be observed in the functionalized NPs, leading to the conclusion that the protein coating was efficient. In the FTIR results, it was possible to identify new bands in the spectra of the coated NPs in comparison to pure $Fe_3O_4$. Those bands are attributed to surface modification with albumin. In the zeta potential results, it can be verified that the isoelectric point of pure magnetite is slightly higher than the one of albumin-functionalized NPs. The best pH value for good biocompatibility with blood plasma is in the range of 7.4 - 8.0. The data obtained in this analysis show that the zeta potential has a discrete variation over pH 7.5. These results indicate this system has good conditions to act as a carrier in the biological environment. The TEM results showed that with the addition of albumin, $Fe_3O_4$ NPs are agglomerated due to albumin crosslinking. In addition, the size of the NPs ranged from 20-30 nm. It is possible to analyze the intrinsic fluorescence of BSA and SA at emission wavelengths of 335 and 405 nm, respectively, when the samples are excited at 280 nm. Most of the SA was released within the first three to four hours and after five hours of release, the concentration reached an equilibrium of about 0.265 mg SA per mL. This result is promising because this is a slower release than that one obtained by Bronze-Uhle et al.[4] . About 91% of SA used in the synthesis was encapsulated by the NPs and the drug loading was approximately 30%. The release results of this study were above the one seen for the BSA-AS system[4].

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## Acknowledgments

The authors would like to thank FAPESP (n° 2017/25523-7).

**Área: MAT** **Nº de Inscrição: 00885**

# Synthesis and photophysical properties of core@multishell $NaYF_4$:Yb,Er@$NaYF_4$:Nd@$SiO_2$ upconversion nanoparticles

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Keywords: *Upconversion; Thin silica shell; Stöber method; Microemulsion.*

## Highlights

Upconversion nanoparticles hierarchically organized in a core multi-shell structure, $\beta$-$NaYF_4$:Er, Yb@$NaYF_4$:Nd@$SiO_2$. Evaluation of different methods for the synthesis of a thin silica shell.

## Abstract

Upconversion is a phenomenon in which the sequential absorption of lower energy photons leads to the emission of higher energy photons. The most common host lattice used for upconversion applications is the sodium yttrium fluoride in the hexagonal crystalline phase ($\beta$-$NaYF_4$), due to its low phonon energy, which decreases the possibility of nonradiative relaxation. Additionally, the matrix $\beta$-$NaYF_4$ is usually doped with $Yb^{III}$ and $Er^{III}$ ions, which act as sensitizers and activators, respectively. In this case, the $Yb^{III}$ ions are responsible for the near-infrared (NIR) absorption (when excited at 980 nm) and the $Er^{III}$ ions emit radiation in the green (510 - 540 nm) and red regions (630 - 675 nm). UCNPs present many applications, such as in bioimaging, photodynamic therapy and fluorescence intensity ratio thermometry. Furthermore, its use in plasmonic photocatalysis have been emerging, since coupling UCNPs with plasmonic and semiconductor nanoparticles leads to samples capable of harvesting UV-visible-NIR light. In plasmonic photocatalysis, the catalyst light absorption leads to the formation of active electrons and holes in the semiconductor, which can then participate in oxidation-reduction reactions. In this sense, a hierarchical construction of the components (UCNP, semiconductor, noble metal) is fundamental to enable the energy transfer processes between them. In this work, a hierarchical core@multhishell structure was designed in order to further obtain samples with potential application in plasmonic photocatalysis. First, $NaY_{0.80}Er_{0.02}Yb_{0.18}F_4$@$3NaY_{0.75}Nd_{0.25}F_4$ UCNPs (22 ± 3 nm) were synthesized, in the hexagonal crystalline phase, by the thermal decomposition method. The sample presented upconversion luminescence properties when excited both at 980 and 808 nm. Then, the particles were covered with a thin silica shell (< 7 nm) through different experimental procedures: (i) Stöber method using magnetic stirring (ii) ultrasonic-assisted Stöber method; and (iii) the microemulsion method. In the first two methods, the oleic acid, which acts as a capping agent, was removed through an acid treatment to guarantee the hydrophilicity of the UCNPs, however, even though the thin silica shell was formed, the NPs exhibited some aggregation. In the last method, the ligand density was increased in order to enhance the dispersion stability of the UCNPs in the hydrophobic medium, hence, disperse core@multishell structures were obtained.

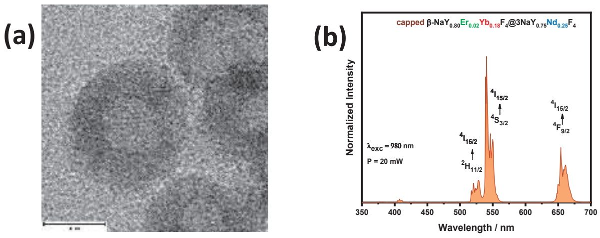

**Figure 1:** $NaY_{0.80}Er_{0.02}Yb_{0.18}F_4$@$3NaY_{0.75}Nd_{0.25}F_4$ UCNPs **(a)** TEM image and **(b)** upconversion luminescence spectrum.

Zhang et al, Nanoscale Horiz., 2019, 4, 579-591.

## Acknowledgments

**Área: MAT**

# Síntese, caracterização e estudo da solubilidade de oligômeros de quitosana e derivados base de Schiff

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Palavras Chave: *Quitosana, Oligômeros biopoliméricos, Bases de Schiff, Oligômeros anfifílicos.*

## Highlights

Synthesis, characterization and solubilitiy study of chitosan oligomers and derivatives Schiff base. Amphiphilic oligomers of Schiff bases derived from chitosan and salicylaldehyde were prepared. Results of preparation and characterization of depolymerized chitosan ($C_D$) and its derivatives with salicylaldehyde ($C_{DS}$) and glycidol ($C_{DSG}$) were presented.

## Resumo/Abstract

A quitosana é um polissacarídeo linear constituído de unidades 2-acetamido-2-desoxi-*D*-glicopiranose (GlcNAc) e 2-amino-2-desoxi-*D*-glicopiranose (GlcN), unidas por ligações glicosídicas do tipo $\beta$ (1→4), com maior quantidade de unidades GlcN[1]. Este trabalho teve como objetivo a síntese e caracterização de oligômeros obtidos a partir da despolimerização de quitosana. O biopolímero quitosana QP ($\overline{GD}$= 82,0%, $\overline{Mw}$= 60,2Da), foi purificado e submetido ao processo de despolimerização (QD, $\overline{GD}$= 80,0%, $\overline{Mw}$ = 6,34kDa). A determinação das $\overline{Mw}$ foi realizada por viscosimetria, revelando uma diminuição considerável no tamanho da cadeia polimérica, após a despolimerização. QD foi utilizado para a síntese do ligante base Schiff a partir de salicialdeído QDS ($\overline{GS}$= 57%). Na segunda etapa, a base de Schiff anfifílica QDSG foi produzida a partir da inserção do grupo hidrofílico glicidol ($\overline{GS}$. Representações das estruturas obtidas são apresentadas na Figura 1.

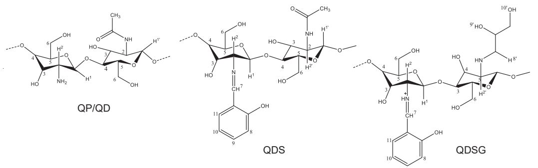
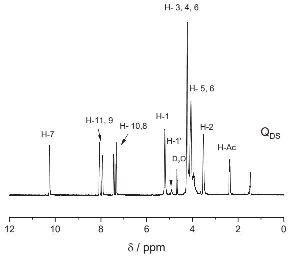
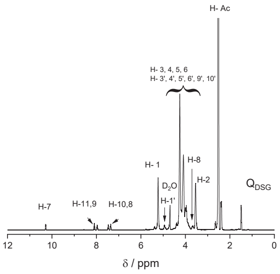
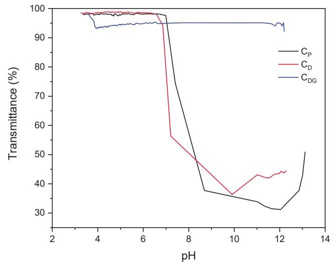


**Figura 1.** Representações estruturais da quitosana, quitosana despolimerizada (QP e QD, respectivamente) e os oligômeros de quitosana contendo a base de Schiff (QDS) os compostos anfifílicos (QDSG).

Os compostos sintetizados foram caracterizados por espectroscopia (FTIR, $^1$H RMN e UV-Vis). A formação de QDS foi confirmada pela presença da banda de C=N em 1630 cm$^{-1}$ (FTIR) e pelo sinal referente ao hidrogênio da imina na região de 10 ppm, bem como os sinais na região de aromáticos em 7-8 ppm ($^1$H RMN). Já a formação de QDSG foi confirmada pela presença dos sinais na região de 3,5 ppm. A solubilidade de QD e QDG foi estudada por Uv-vis, avaliando a transmitância em função do pH de meio. A modificação do oligômero com o grupo anfifílico levou a um aumento da solubilidade.







Foram obtidos o oligômero de quitosana, bem como seus derivados base de Schiff. A substituição com glicidol na ordem de 10 %, resultou em aumento da solubilidade em valores de pH acima do pKa da quitosana.

1. BARBOSA, H. F.G.; ATTJIOUI, M.; LEITÃO, A.; MOERSCHBACHER B. M.; CAVALHEIRO, E. T. G. Characterization, solubility and biological activity of amphihilic biopolymeric Schiff bases synthesized using chitosans. **Carbohydr Polym**. 2019.

## Agradecimentos/Acknowledgments

LATEQS, IQSC-USP e à CAPES.

**Área: MAT** **Nº de Inscrição: 1064**

# Synthesis, modification surface and characterization of tungstate/molybdate of zinc, doped with lanthanide ions [ $Zn_{1\text{-}x}RE_x(WO_4)_y(MoO_4)_z$] (y or z = 0, 0.5, 1)

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Palavras Chave: *Europium, Terbium, Rare Earth, tungstates, molybdates,).*

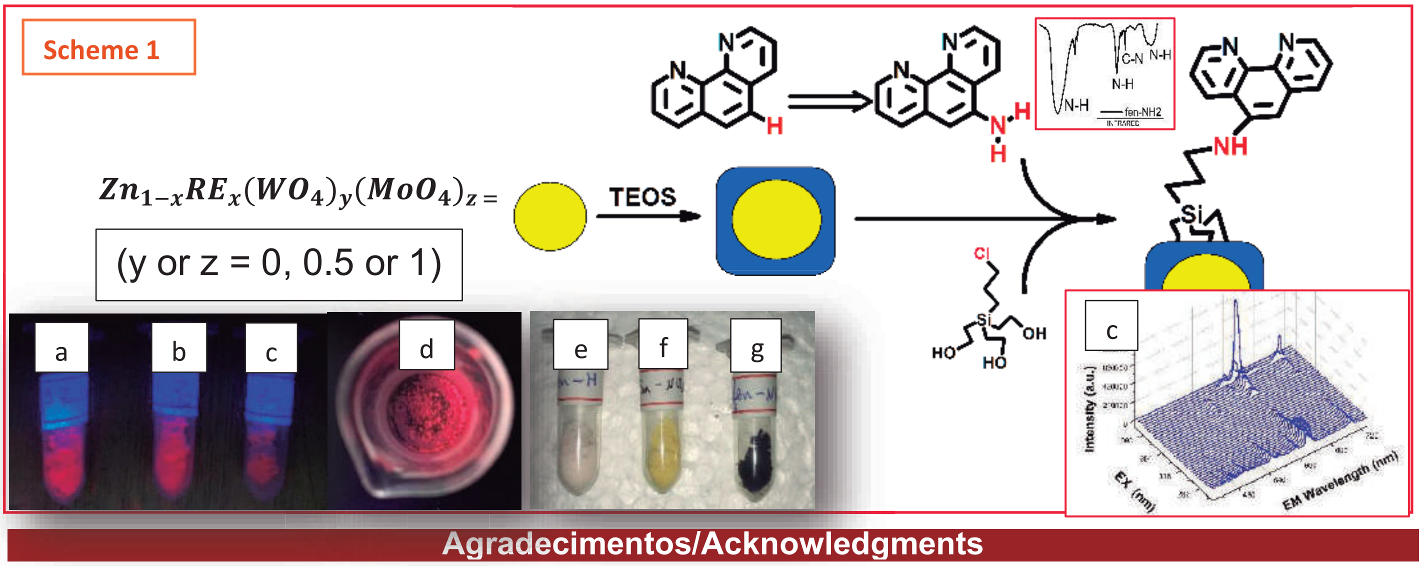
## Highlights

Was synthesized, using co-precipitation method, tungstates and molybdates of zinc doped with rare earth íons, and functionalizated with phenantroline ligand for aplications how luminescente sensors.

## Resumo/Abstract

A class of materials with the general formulation of $M^IM^{III}(XO_4)_2$ ($M^I$=Alkali metal, $M^{III}$ = trivalente metal and X = W or Mo) with structural importance and diferente properties exposed to the attention of researchers, especially when doped with rare earth ions, which give the material luminescent properties. These properties can make the material promisingly important for diverse applications, such as solar cells, light converting devices and sensors, depending only on the changes in its structure and surface. This work was synthesized using co-precipitation method from aqueous solutions tungstates and molybdates of zinc doped with rare earth íons (Scheme **1a** [ $Zn_{0.95}Eu_{0.05}WO_4$ ],**1b** [$Zn_{0.95}Eu_{0.05}(WO_4)_{0.5}(MoO_4)_{0.5}$],**1c** [ $Zn_{0.95}Eu_{0.025}Tb_{0.025}WO_4$ ]) and coated with a thin layer of sílica (scheme **1d**) using the hydrolysis and condensation of tetraethoxysilane (TEOS). For the phenantroline ligand functionalization, 3-(chloropropyl)triethoxy-silane (CPES) was grafted onto the particle surfaces in their aqueous suspensions, and bound to modified phenanthroline. For the synthesis of doped tungstates and molybdates, equivalent amounts of zinc, terbium, and europium chlorides were added under stirring at 70 °C for 1h. After drying, the material was ground with TEOS, water, ethanol and remained (with catalyze acid) for 3h at 70 °C under constant agitation. The 1,10-Phenantroline (scheme **1e**) has been nitrated ($H_2SO_4/HNO_3$) (scheme **1f**) and reduced (Sn/HCl) (scheme **1g** and infrared) to then be coupled to the modified particle. The final product was characterized. We are currently improving and studying synthesis conditions and aplications.

Scheme 1



## Agradecimentos/Acknowledgments

The Federal University of Sergipe (FUFSE) and the Education Secretary of State of Sergipe (SEED-SE) for licenses granted.

**Área: MAT** **Nº de Inscrição: 00000**

# Synthesis of core-shell Au nanorods@$Gd_2O_3$:Er,Yb@$Gd_2O_3$:Nd for biomedical applications

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Keywords: Gold nanorods, Core-shell structures, Up-conversion, Hyperthermia, Rare earth elements.

## Highlights

Heterostructures with potential applications for bioimaging and photothermal therapy treatments. Core-shell heterostructure based on Au nanorods@$Gd_2O_3$:Er,Yb@$Gd_2O_3$:Nd. System act as a thermal sensor and have potential applications as theranostic materials

## Abstract

Gold nanorods (AuNRs) are materials with two different absorption wavelengths (transverse and longitudinal modes), which can be modified depending on the aspect ratio of the nanoparticle. The combination of these nanomaterials with lanthanides in core-shell structures allows the phenomenon of up-conversion (UC) and gives them characteristics of interest, such as narrow emission bands, high chemical stability, low toxicity and tunable properties depending on the synthesis conditions. The purpose of this research is to carry out the synthesis of core-multishell structures, synthetizing AuNRs coated with $Gd_2O_3$: Er, Yb and $Gd_2O_3$: Nd, controlling the aspect ratio (between 4-5 and LSPR bands between 800-980 nm – Fig. 1a), in order to modulate the emission of the system to NIR region, taking advantage of the hyperthermia phenomenon. The concentration of Au in the final product was 0.37 mM, which was calculated from the normalized spectra (fig. 1a) at 400 nm, knowing that an absorbance of 1.2 correspond to [Au°] = 0.5 mM [1]. The AuNRs coating was realized by a surface exchange method with sodium oleate and the subsequently addition of the rare earth nitrates with hexamethylene tetramine at 85 °C for 5h. The product was calcinated at 800°C for 2h to guarantee the oxide formation (Fig. 1b). The amount of $Er^{3+}$, $Yb^{3+}$ and $Nd^{3+}$ in the shells was calculated to be 2, 18 and 20% respectively, because these are the optimal concentrations of the dopants to observe an enhancement of the UC phenomenon as was determined in previous works developed at the Functional Materials Laboratory at the University of Campinas. The presence of the ions of Yb, Er, Nd and Gd was confirmed by EDS mapping (Fig 1c), showing a homogeneous distribution of the ions along the shell. The contrast for $Er^{3+}$ it´s difficult to observe due to its low concentration (2%) compared with the other ions. The emission spectra was recorded on the NIR region showing two peaks located at ~980 and 1064 nm corresponding to the emissions of Yb and Nd respectively. This will allow the proposed system to act as a thermal sensor and have potential applications as theranostic materials. [1].Scarabelli, L *et al.* J. Phys. Chem. Lett. 2015, 6, 4270−4279.

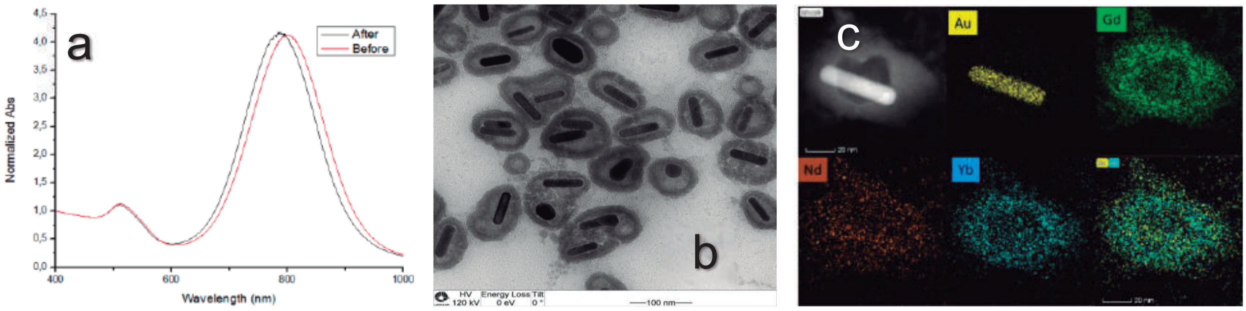

**Figure 1. a**. UV-vis spectrum normalized at 400 nm; **b** and **c**. TEM and EDS mapping of the AuNRs@$Gd_2O_3$:Er,Yb@$Gd_2O_3$:Nd nanoparticles.

## Acknowledgments

**Área: MAT** **Nº de Inscrição: 1234**

# Synthesis of non-stoichiometric $CeO_2$ hybrid nanorods for catalytic evaluation in the Water Gas Shift (WGS) reaction

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[2]*Instituto de Química, UFRGS, Porto Alegre, RS, Brazil.*

Keywords: Nanorods, Nanoparticles, Heterogeneous Catalysis, Cerium Oxide, Hydrogen, Carbon Monoxide.

## Highlights

Nanocatalysts based on $CeO_2$ hybrid nanorods were developed for catalytic evaluation in Water Gas Shift Reaction, under conditions similar to industrial reform reactors, obtaining values above 20% of CO conversion.

## Abstract

Hydrogen gas ($H_2$) stands out industrially for the potential for generating energy in fuel cells, with zero emission of pollutants, as $NO_x$ and $SO_x$. Produced, for the most part, from natural gas, by the processes of steam reforming, partial oxidation, dry reforming and autothermal. In general, the reactor output stream is a mixture composed of a higher concentration of hydrogen and different concentrations of carbon monoxide (CO), carbon dioxide ($CO_2$), water vapor ($H_2O$) and methane ($CH_4$ ) non-reactive. However, the presence of CO in these reaction beds is undesirable, as it can irreversibly poison most metallic catalysts. The WGSR (Water Gas Shift Reaction) has been widely used as an additional step to the reform, as a way to protect the catalysts and purify the $H_2$ produced ($CO + H_2O \rightleftarrows CO_2 + H_2$). The reaction is carried out in two steps: a high temperature shift (HTS) at 350-450°C and a low temperature (LTS) at 150-250°C. In the present work, we studied catalysts with nanorods morphology in ceria ($CeO_2$) doped with gadolinium (Gd) at 3, 5, and 7%molGd, or doped with gallium (Ga) at 16%molGa by different methodologies (M1e M2), and decorated with gold (Au) nanoparticles on the oxide surface, for application in the WGS reaction. Catalysts based on noble metals, such as gold, can enhance the catalytic activity of several reactions. Its presence improves the reducibility and the Oxygen Storage Capacity (OSC) of oxides with redox capacity. Smaller particles have greater activity for the WGSR, due to the increase of active sites at the metal-support interface, a nanostructured catalyst of Au-$CeO_2$ can be active in a temperature range up to 150 to 350°C. The catalytic results were satisfactory, carried out under conditions similar to industrial ones, with a gas mixture generated in a reforming reactor (10%CO/ 10%$CO_2$/ 20%$N_2$/ 60%$H_2$), at temperature of 300°C. So the two samples that presented the best performance were evaluated at 250°C, 12 catalysts tested in total. The highlight was the sample decorated with Au and doped with 5%molGd (Au/NBGdCeO-5), both at 300°C and at 250°C, reaching 25.2 and 14.4% of CO conversion, respectively. Au NPs anchored on oxide surface improved conversion results, allowing the CO concentration to decrease in the system, enabling the possibility of implementation in the industry after further studies.

## Acknowledgments

The financial support from CAPES is gratefully acknowledged, in addition for the collaboration, in front of the INOMAT project, by prof. Maria do Carmo Rangel from the Institute of Chemistry-UFRGS to carry out the catalytic tests. Finally, thanks to LNNano for the microscopy analysis.

**Área: MAT**

# The role of reaction time in Ni-rich cathode's morphological and microstructure properties for lithium-ion batteries.

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Keywords: *Lithium-ion battery, Co-precipitation,* $LiNi_{0.80}Co_{0.15}Al_{0.05}O_2$.

## Highlights

The reaction time showed a remarkable impact on $LiNi_{0.80}Co_{0.15}Al_{0.05}O_2$ microstructure and morphological properties.
The cathode was synthesized using the co-precipitation process.
The adequate reaction time was an important key to enhancing cathode performance.

## Abstract

At present, the main bottleneck in the Li-ion battery industry is overcoming significant performance challenges associated with electrical vehicles applications, such as their driving range. For this purpose, investigating microstructural and morphological properties of high energy density cathodes is crucial to present improvement paths[1]. Therefore, the work aims to assess the evolution of both microstructural and morphological properties of $LiNi_{0.80}Co_{0.15}Al_{0.05}O_2$ (NCA) cathode in the function of its synthesis reaction time. The precursors were synthesized by the co-precipitation method varying the reaction time of precipitation[2]. The molar ratio of metals were Ni:Co:Al = 0.8:0.15:0.05. The synthesized materials were calcined to achieve NCA cathodes. The properties were evaluated by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The XRD patterns of the final NCA cathode (Figure 1A) indicated that all materials achieved layered hexagonal structures. The intensity ratio between the highlighted peaks [R = (I(003)/I(104)] is often used as an estimate of cation mixing. The R values were 0.78, 1.35, and 1.17 for 1h, 3h, and 8h precursor reaction times, respectively. R values lower than 1.2 indicate high cation mixing that causes severe degradation in the electrochemical performance by blocking $Li^+$ migration. Besides, only 3h-material showed both split of the peaks (006)/(012) and (018)/(110), which is characteristic of the highly ordered layered structure. On the other hand, (006)/(012) split was not well defined in the both 1h and 8h-material, as can be shown by the enlarged graph areas. Furthermore, 8h-material showed impurities, indicating that long precursor reaction times developed undesired compounds in a final cathode. Figures 1B-D depicted SEM images of NCA precursors according to their reaction time of precipitation. In Figure 1B, the 1h-precursor showed fuzzy grains agglomerated into irregular particles shapes with a low degree of sphericity. In contrast, the 3h-precursor (Figure 1C) showed quasi-spherical regular morphology with primary particles agglomerated into secondary particles. In addition, the particles had better consistency in shape which is an effective way to improve the tap density and volumetric capacity. These morphological properties are important to develop high-quality electrodes. While in 8h-precursor (Figure 1D), the agglomerated spherical particles were transformed to larger particles and the degree of sphericity decreased when a long-time reaction was applied. According to the results, the reaction time remarkably impacted NCA microstructure and morphological properties. The precursor synthesized in 3 hours at laboratory scale developed a final cathode with excellent structural order without impurities and better shape particles.

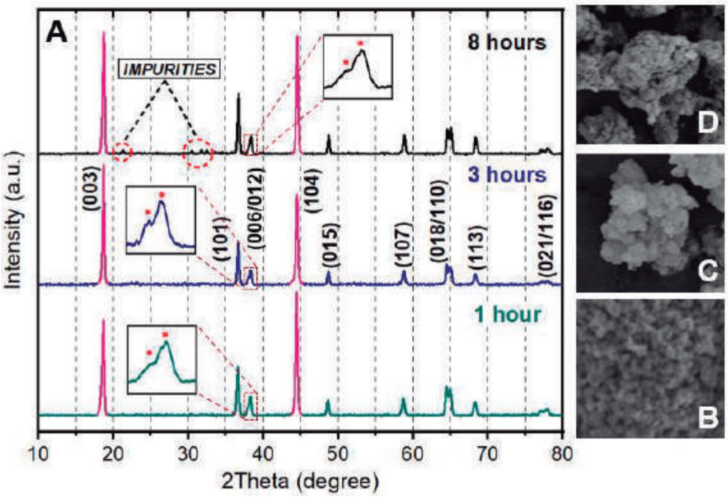

**Figure 1 –** (A) XRD patterns of final NCA materials in the function of precursor reaction time and SEM images of precursors in (B) 1h, (C) 3h, and (D) 8h of synthesis.

1. Kim, U. H. *et al.* Microstructure Engineered Ni-rich Layered Cathode for Electric Vehicle Batteries. *Adv. Energy Mater.* **11**, 1–11 (2021).
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## Acknowledgments

This work was financed by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) - Finance Code 001 and Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq).

**Área: Mat** **Nº de Inscrição: 01067**

# Titania doped with niobium ions immobilized onto Kaolinite and Bentonite clays as efficient heterogeneous photocatalysts for dye and Triaxon® removal

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Palavras Chave: *Clay minerals, titanium dioxide, niobium, drugs, contaminants*

## Highlights

Titania and niobium were homogeneously dispersed on clays. Hydroxyl radicals generated from clay-titania-niobium surfaces and from hydrogen peroxide promotes the degradation of Triaxon® and methylene blue.

## Resumo/Abstract

Several contaminants such as active pharmaceuticals, personal care products, hormones, industrial wastes are incorrectly discarded on environment and can results in adverse effects to the environment and consequently promotes damages to human health [1-2]. Conventional treatments not present efficiency for removal most of the contaminants present in wastewater, so it's necessary to search for new materials that can oxidize these substances of interest [1]. Among the different types of clays, the bentonite and kaolinite stand out due the lamellar structure, higher specific surface area, cationic exchange capacity that could be employed to immobilize different photoactive species. Various semiconductors have been tested in photo assisted techniques, among them, $TiO_2$ has been the most widely used because of its unique properties such as high chemical stability, non-toxicity and biocompatibility. Niobium based materials have received attention in the field of heterogeneous catalysis, being studied as catalyst and catalyst support in important chemical reactions [2]. Thus, the goal of this work was to evaluate the Kinect study of photodegradation of the dye MB and Triaxon® using nanocomposites using bentonite and kaolinite, titanium dioxide doped with niobium oxide. The nanocomposites named KaolNb400, KaolTiNb400, BentNb400 and BentTiNb400 was based on the work of Barbosa, et al [3]. In details, was kept under constant mechanical stirring for 24 hours, 1 g of bentonite (or kaolinite), 20 mL of isopropyl alcohol, 0.1 mL of acetic acid, 0.2 mL of titanium (IV) isopropoxide and ammonium niobate (V) oxalate hydrate (5% ratio of titanium). The nanocomposites were heated at 400 ºC. The kinetic degradation study was kept in photoreactor 10 mg from each material and 5 mL of methylene blue solution (10 $mg.L^{-1}$); the tests were performed in the presence and absence of ultraviolet irradiation ($\lambda$ = 394 nm and P = 15 W). X-ray diffraction showed that the materials have all the kaolinite and bentonite reflections that are between 20 and 40 $2\theta$°, and basal spacing of 7.14 Ǻ for Kaol, 7.09 Ǻ for KaolNb400, 7.19 Ǻ for KaolTiNb400, 14.91 Ǻ for Bent, 9.71 Ǻ for BentNb and 9.73 Ǻ for BentTiNb, indicating that the semiconductors are only on the surface of the clay particles. The bandgap energy of the $TiO_2$ is approximately 3.2 eV, while the niobium can vary from 0 to 2 eV when together with the titanium, and the materials have an average bandgap of 4.60 eV. Therefore, the support of clay minerals favored in all cases the increases the bandgap energy. On the other hand, it is evident that the semiconductor absorbs in a very wide region, up to 650 nm, which demonstrates that the presence of Nb ions plays a fundamental role in the construction of more efficient semiconductors for application in milder conditions. Through the kinetic study it was possible to conclude that all the materials presented a photodegradation profile, since the ratio between final and initial concentration was shown to be decreasing, with BentTiNb400 material being the most efficient, so these materials would just into to be used in photodegradation of other interest substances.

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## Agradecimentos/Acknowledgments

Grupo Sol-Gel, Grupo de Pesquisas em Materiais Lamelares Híbridos (GPMatLam), Capes (Código de financiamento 001), CNPq, Fapesp (2017/15482-1 and 2018/04706-9)

**Área: MAT**

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

# Titanium Suported on Functionalized MCM-41 Silica Containing S-Binol Ligand. A Hibrid Material in Chiral Synthesis.

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Palavras Chave: *Sílica mesoporo, material híbrido, MCM-41 Silica, Functionalized Silica*

## Highlights

Mesoporous silicas can be functionalized with chiral ligands through supported metals such as titanium. S-binol was used as a ligand. The results of obtaining functionalized silica will be presented.

## Resumo/Abstract

The MCM-41 mesopore silicas are materials with hexagonal pores and are obtained from an organic template, a quaternary alkylammonium surfactant, which interacts with the silica source, generating a structural framework that after undergoing calcination forms a bimodal structure. mesoporous. Among the various forms of mesoporous silicas used, a hybrid material can be synthesized from the bond between the silanols of the MCM-41 silica and a chiral chelating organic moiety. This material can be used in catalysis and is a challenge for several researchers looking for a solution for the reuse of extremely expensive transition metals in continuous processes in the synthesis of bioactive molecules. In this work we seek the synthesis of a hybrid material with MCM-41 silica and binol with defined absolute configuration to perform asymmetric synthesis. Silica synthesis was carried out with TEOS in basic medium and cetrimonium bromide. X-ray analysis of the crystalline material indicated a mesopore characteristic of the silica. TGA and infrared analyzes will be presented, both for silica and for the hybrid material. The first attempts to incorporate S-binol into mesopore silica occurred and will be disclosed at this meeting, as well as the way in which the chiral ligand was incorporated into the silica matrix.

## Agradecimentos/Acknowledgments

To the IFRJ for funding and space. To the Department of Inorganic Chemistry UFRJ for the X-ray analyses.

**Recomendamos fortemente o uso da língua inglesa nos resumos, uma etapa importante na internacionalização do evento.**

Área: MAT

# Use of bamboo as a renewable resource to synthesize silver nanoparticles and to obtain cellulose nanofibers

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Palavras Chave: Bamboo, Culm extract, Silver Nanoparticles, Nanocellulose.

## Highlights

Silver nanoparticles (AgNPs) were synthesized using bamboo culm extracts in aqueous medium.

Cellulose nanofibers (CNfs) were obtained from bamboo by alkaline hydrolysis method and using ultrasonication.

This study demonstrates the feasibility of using bamboo, which is a renewable resource, to obtain nanomaterials.

## Abstract

Bamboo is a rapidly renewable material that is available globally, which is an ideal characteristic for use in many applications.[1] Silver nanoparticles were synthesized using bamboo extracts obtained from three parts of the same bamboo culm and sodium borohydride as a reducing agent. All bamboo extracts presented pH equal to 4.5 and the same UV-vis spectra profile with absorption bands at 274 and 322 nm. All AgNPs colloids exhibited an absorption band at around 370 nm, characteristic of their plasmonic properties. As observed in Fig. 1(b), TEM analysis confirmed the formation of spherical-like shape AgNPs and their average sizes were 14.7, 14.9, and 18.0 nm for three different colloids. To obtain cellulose nanofibers, the bamboo culm was cut in small pieces and crushed using an industrial blender. The bamboo powder was hydrolyzed using alkaline solution to remove lignin.[2] After that, the hydrolyzed material was treated using an ultrasound for 1h and 2h, resulting two colloids, Fig. 1(c). TEM analysis confirmed the formation of CNfs with diameter below 100 nm for both samples. Take advantage of its great potential, this study demonstrated the feasibility of using bamboo culm, which is a renewable resource, to obtain two different types of nanomaterials. More results will be presented in the final version of the poster in the conference.

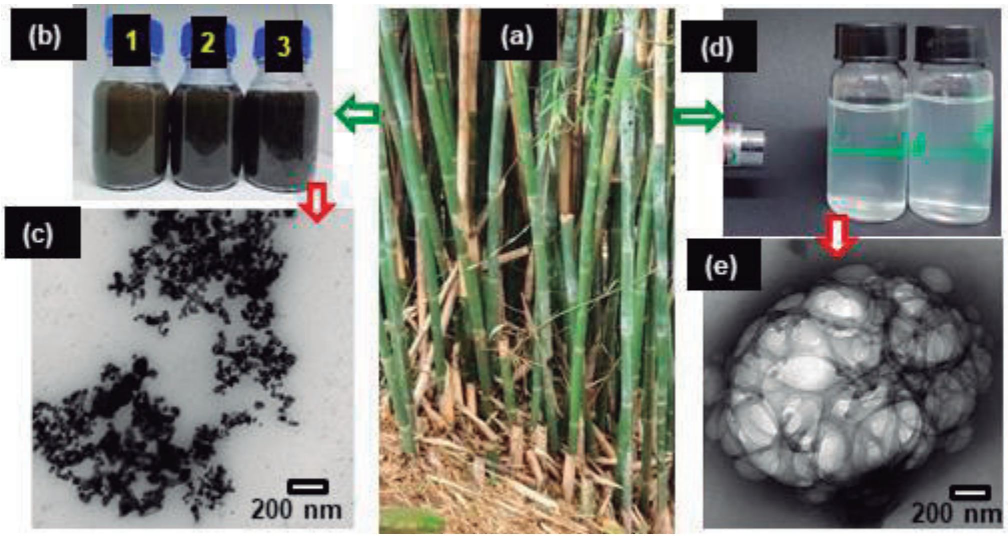

**Fig. 1.** Bamboo clump (a), AgNPs colloids obtained from the 3 culm extracts, TEM image of the colloid 1 (c), CNfs colloids obtained in different times 1h and 2h (d), and TEM image of the CNfs 1h (e).

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## Agradecimentos/Acknowledgments

We would like to thank IEAMar-UNESP for the TEM analysis.

**Área: MAT**

# Use of carbonyl index in monitoring polymer degradation: the case of polypropylene

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Palavras Chaves: *Polymer degradation, Carbonyl index, Polypropylene, Infrared.*

## Highlights

Diversity of reference bands prevent comparison between works on oxidative degradation.

Intensity instead area to calculate CI underestimate the diversity of carbonyl species formed during degradation.

## Resumo/Abstract

When following chemical changes using infrared spectroscopy, it is usual to calculate the ratio between the areas or intensities of a band that varies as a function of a stimulus to another that is not sensitive to the same stimulus (reference band). Perhaps the most common example of this approach is the carbonyl index (CI), which measures the oxidation over the polymers oxidative degradation. It is an important parameter to calculate, allowing inferences regarding lifetime prediction or methodologies to develop additives like stabilizers. The assessment of the way that CI is calculated to monitor the degradation of polypropylene is the starting point of this study. We carried out a systematic bibliographic search in the Web of Science database with the keyword "polypropylene" in the title and the keyword "carbonyl index" in the topics, from 2018 to 03/15/2022. The search resulted in 31 articles, which were evaluated by their titles, abstracts and, if necessary, by the full text to check the fit to this work, which is the reporting of CI analysis performed follow the degradation of polypropylene materials, homopolymers, composites or blends. After screening, articles that did not fit within the scope of this work were removed, totaling 27 articles evaluated. Figure 1A shows the percentage of articles that used the ratio between areas or between intensities and Figure 1B shows the reference bands used. Of the 27 studies considered, 33.3% used ratio between intensities, while 66.7% used band areas (Figure 1A). The use of peak intensity is simpler, since it uses only the intensity recorded at the wavenumber of the band peak, but this choice disregards that the carbonyl band in the oxidative degradation of PP is mainly populated by three distinct carbonyl species that predominate at different times of degradation (Rouillon et al., 2016) so choosing just one specific wavenumber might understimate the contribution of the other carbonyl species. Figure 1B shows the diversity of reference bands used in the selected works. The band at 2722 cm$^{-1}$ is the most used, followed by the band at the 1454 cm$^{-1}$. The variation of the bands used as reference prevents the comparison between the results in the different works since the molar absorptivity coefficient is different for each reference band is different. Another highlight is the fact that the reference bands are not necessarily inert or insensitive to the changing context, such as the $CH_3$ band at 1454 cm$^{-1}$ (Rouillon et al., 2016), which decreases in intensity due to the formation of volatiles containing the PP pending $CH_3$ groups. Beyond that, it is noteworthy to highlight that having such a diversity of reference bands in the literature prevent the comparison between different works.

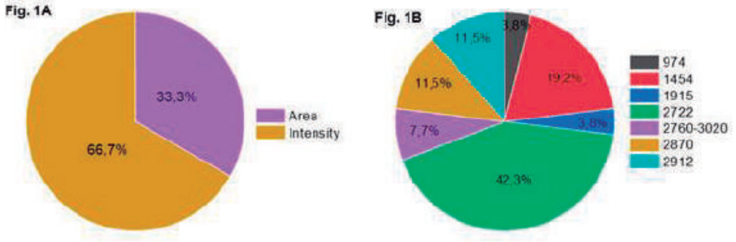

**Figure 1**- Distribution of studies that used (a) area or intensity and (b) main reference bands used

Rouillon, C., Bussiere, P.O., Desnoux, E., Collin, S., Vial, C., Therias, S., Gardette, J.L., 2016. Is carbonyl index a quantitative probe to monitor polypropylene photodegradation? Polym. Degrad. Stab. 128, 200–208.https://doi.org/10.1016/j.polymdegradstab.2015.12.011

## Agradecimentos/Acknowledgments

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**Área: MAT**

# Study of the efficiency of the algae extract Sargassum vulgare as a green corrosion inhibitor in carbon steel in acidic medium

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Palavras Chave: *Corrosão, Inibidor verde, Aço carbono, Sargassum vulgare.*

## Highlights

The ethanolic extract of the algae sargassum vulgare was evaluated as a corrosion inhibitor in carbon steel and presented as a good inhibitor reducing the corrosion parameters.

## Resumo/Abstract

**Introdução:** Novas propostas de inibidores de corrosão derivados de extratos vegetais, têm sido muito exploradas acerca do seu potencial. A alga marinha *Sargassum vulgare*, de coloração marrom, uma das espécies com maior biodisponibilidade no litoral brasileiro, ocorre tanto em costões rochosos protegidos como em costões expostos à ação das ondas[1]. Com relação as algas do gênero *Sargassum*, a literatura relata alguns estudos da sua utilização com inibidor de corrosão, como a *Sargassum muticum*[2]. **Objetivo:** Avaliar o extrato de *Sargassum vulgare* como inibidor verde de corrosão no aço carbono em HCl (0,5 M). **Metodologia:** O extrato etanólico bruto foi obtido por maceração das algas em etanol seguido de rotaevaporação. O efeito da concentração do extrato na taxa de corrosão e eficiência de inibição foi avaliada por técnicas eletroquímicas, Potencial de Circuito aberto (PCA), polarização potenciodinâmica e Espectroscopia de Impedância Eletroquímica (EIE), realizadas num Potenciostato Autolab PGSTAT 302N; e para compreensão do mecanismo de inibição realizou-se um estudo de adsorção. **Resultados e Discussão:** O PCA (Figura 1a) foi deslocado positivamente e negativamente com adição do extrato no sistema, com um deslocamento máximo de -28 mV. Essa variação de potencial sugere que o extrato atuou nas reações anódicas e catódicas. Na polarização potenciodinâmica (Figura 1b), o potencial de corrosão (Ecorr) deslocou-se com uma variação de 9 mV, quando a diferença de potencial é menor que 85 mV o inibidor pode ser classificado como inibidor do tipo misto. A adição do extrato ao meio corrosivo provocou mudanças nos potenciais de corrosão, obtendo-se uma eficiência máxima de 62,54 % de inibição da taxa de corrosão, no meio de 600 ppm de extrato. A EIS apresentou um diagrama de Nyquist (Figura 1c) em formatos de semicírculos, essa resposta está intimamente relacionada ao processo de transferência de carga, cujos valores variaram de 186,11 Ω para 229,87 Ω a 400 ppm, reduzindo, portanto, a transferência de carga. A isoterma de Frumkin apresentou o melhor ajuste, com um $\Delta G_{ads}$ de -13,96 KJ/mol. **Conclusões:** O inibidor proposto atuou como inibidor do tipo misto e se classifica como não tóxico, barato, disponível na natureza em abundância e de fácil extração, caracterizando-se como um inibidor verde de corrosão.

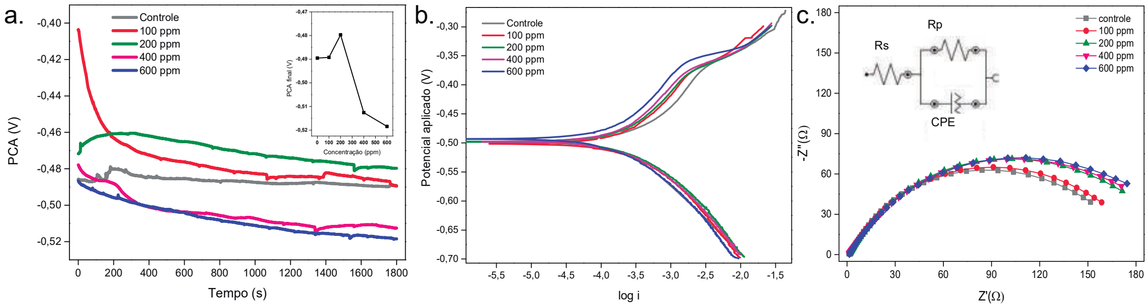

**Figura 1-** (a) PCA, (b) Polarização Potenciodinâmica e (C) EIE do aço carbono 1020 em solução de HCl e na presença do extrato de *Sargassum vulgare*.

## Referências

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## Agradecimentos/Acknowledgments

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**Área: MAT**

# Use of expired captopril drug as an environmentally friendly corrosion inhibitor for carbon steel in acidic environment

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Palavras Chave: *Corrosão, Inibidor verde, Captopril, Medicamento Vencido*

## Highlights

Efficiency study of expired captopril drug extract as a green corrosion inhibitor on carbon steel in acidic medium.

## Resumo/Abstract

**Introdução:** Existem vários tipos de inibidores de corrosão disponíveis, cada um com sua própria estrutura química e mecanismo de ação. No entanto, a natureza tóxica de alguns desses compostos, bem como o alto custo de seus métodos de síntese, levou à necessidade de inibidores de corrosão não perigosos, ambientalmente seguros e de baixo custo[1]. Uma das soluções é o reaproveitamento de resíduos, como é o caso de medicamentos vencidos, pois eles apresentam um grande potencial, devido ao fato de muitas moléculas de fármacos conterem heteroátomos como N, O, S, P, ligações π conjugadas e anéis aromáticos[2]. **Objetivo:** Avaliar o desempenho de inibição de um medicamento vencido, o captopril, na corrosão do aço carbono 1020 em 1,0 M de HCl. **Metodologia**: O medicamento foi pulverizado e solubilizado na solução ácida de HCl. O efeito da concentração do medicamento na taxa de corrosão e eficiência de inibição foi avaliada por técnicas eletroquímicas: Potencial de Circuito aberto (PCA), polarização potenciodinâmica e Espectroscopia de Impedância Eletroquímica (EIE), realizadas num Potenciostato Autolab PGSTAT 302N. **Resultados e Discussão:** O PCA (Figura 1a) foi deslocado negativamente com adição do extrato no sistema, com um deslocamento máximo de -29 mV. Essa variação de potencial sugere que o medicamento atuou nas reações catódicas. Na polarização potenciodinâmica (Figura 1b) o potencial de corrosão deslocou-se negativamente, com uma variação de 8 mV, assim, o inibidor pode ser classificado como inibidor do tipo misto, pois a diferença de potencial é menor que 85 mV. A adição do extrato ao meio corrosivo provocou mudanças nas taxas de corrosão, demonstrando eficiências que variaram entre 59,4 a 69,9%, no meio com 100 e 800 ppm do medicamento, respectivamente. A EIS apresentou um diagrama de Nyquist (Figura 1c) em formatos de semicírculos, essa resposta está intimamente relacionada ao processo de transferência de carga, o valor de resistência variou 59,5 Ω para 109 Ω a 800 ppm, reduzindo, desta forma, a transferência de carga. **Conclusões:** O captopril em todas as concentrações estudadas reduziu os parâmetros relacionados a corrosão, isso deve-se a presença de heteroátomos de N, S e O em sua estrutura que interagem com a superfície metálica formando uma barreira de proteção, protegendo, assim, da corrosão.

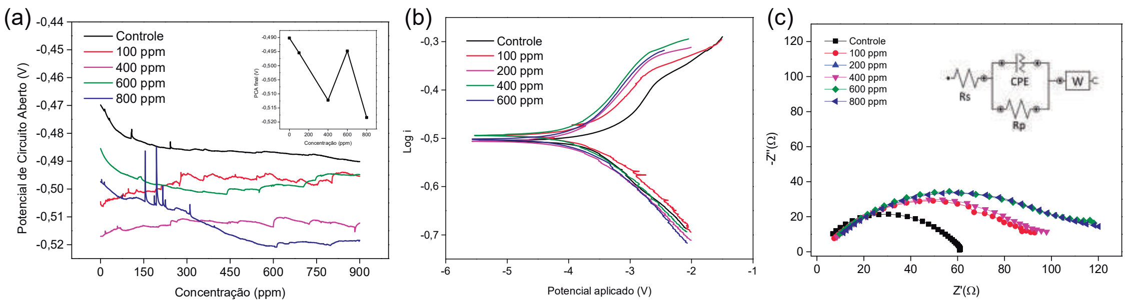

**Figura 1-** (a) PCA, (b) Polarização Potenciodinâmica e (C) EIE do aço carbono 1020 em solução de HCl e na presença do medicamento (captopril).

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## Agradecimentos/Acknowledgments

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**Área: MAT** **Nº de Inscrição: 633**

# Use of organofunctionalized montmorillonite to remove chromium in wastewater treatment

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Palavras Chave: *Adsorption, Potentially Toxic Metals, Montmorillonite*

## Highlights

The montmorillonite clay modified with 1- [3-(trietoxymethoxysilyl) propyl] urea. The modified clay was applied to adsorb potentially toxic metals. The main adsorption mechanism was ion exchange.

## Resumo/Abstract

Industrial activities have contributed greatly to a significant increase in the concentration of metal ions in water, representing an important source of contamination of aquatic bodies, which are a source of water supply for cities. Aqueous wastewater containing potentially toxic metals causes serious environmental problems due to instability. In this study, the montmorillonite clay was modified with 1- [3- (trietoxymethoxysilyl) propyl] urea (TMSPU) by the sol-gel methodology. The natural and organofunctionalized clay were characterized by the techniques of X-ray diffraction (XRD), molecular adsorption spectroscopy in the infrared region (FTIR), thermal analysis, determination of the cation exchange capacity (CTC), and specific area by the methylene blue (SE). Functionalized clay (Mont-TMSPU) was used as an adsorbent for chromium (III) ions, and its adsorption capacity was evaluated through the kinetic study. The characterization techniques revealed that montmorillonite was organofunctionalized with the alkoxide and from the FTIR technique it was possible to observe that the material presents the adsorption bands characteristic of urea, evidenced by analyzing at 3445 and 3342 $cm^{-1}$, which indicates the characteristic doublet of primary amides the $NH_2$ cluster; the band at 1685 $cm^{-1}$ is a characteristic of amide carbonyl; at 1626 $cm^{-1}$, another common fold in primary amides is observed, associated with the C=O bond of the urea molecule; and in 1457 and 1155 $cm^{-1}$ the bands are related to C-N axial deformation. X-ray diffraction (XRD) analysis showed an expansion of the interlayer space from 13.39 to 17.72 Å. The analyzed material has a CTC value corresponding to 25,53 $m_{eq}$/100 g and SE in 199,25 $m^2$/g. The adsorptive properties of the clay minerals through kinetic study with a removal of the order of 60%, which may be related to the capacity to remove potentially toxic metals due to the montmorillonite structure. Such structure allows the isomorphic substitutions of metallic cations such as $Al^{+3}$ for $Ma^{+2}$ or $Fe^{+2}$, which generate a negative charge on the layers. To compensate for this difficulty, the areas between the selected layers, which can be exchanged for other cations, adsorb the chromium ions present in the solutions. The Mont-TMSPU clay can be considered as a highly efficient alternative for the removal of chromium (III) metal because they showed high efficiency and benefits associated with its low cost and abundance.

## Agradecimentos/Acknowledgments

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**Área: MAT**

# Valence Tautomerism in a cobalt-dioxolene complex with the bmimapy ligand

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Palavras Chave: *Valence Tautomerism, Molecular Magnetism, Molecular Switches, Redox-active ligands*

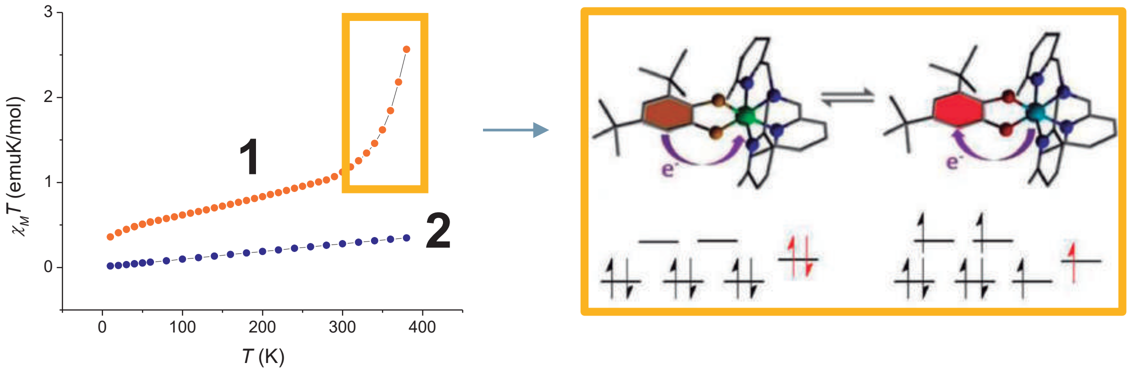
## Highlights

A temperature dependent change in intramolecular electronic distribution (Valence Tautomerism) has been found in a Cobalt-dioxolene complex featuring the bmimapy ligand.

## Abstract

Valence Tautomerism (VT) is an intramolecular charge transfer between two redox-active building blocks belonging to the same molecular context: a metal ion and an organic ligand.[1] The reversibility of the VT process, its possibility to be triggered by different stimula, like heat, light irradiation or pressure application, and the huge variations in structural, spectroscopic and magnetic features associated to it make VT systems promising materials for data storage at the molecular level or development of new sensors.

Even if found for several 3d transition metal complexes, in the vast majority of cases VT is presented by cobalt complexes coordinated by 1,2-dihidroxo-benzenes (dioxolenes).[1] In this case, an ancillary ligand is required to complete the first coordination sphere of the cobalt and to tune its redox potential, a necessary chemical requirement for the intramolecular electron transfer to take place.



In this work we investigated the charge distribution of complexes of formula [Co(bmimapy)L]($PF_6$), being bmimapy the ancillary bis(1-methylimidazol-2-yl)methyl)(2-(piridyl-2-yl)ethyl)amine ligand and L the 3,5-di-tertbutyl-catechol (**1**) or the tetrachlorocatechol (**2**) ligands. **1** displayed a VT transition above room temperature in the solid state, while **2** kept a temperature independent cobalt(III)-catecholate charge distribution. This behavior has been rationalized on the basis of cyclic voltammetry experiments.

[1] Tezgerevska, T.; Alley, K. G.; Boskovic, C., Coord. Chem. Rev. 2014, 268, 23-40.

## Acknowledgments

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**Área: MAT**

# Vibrational spectroscopy and intrinsic dielectric properties of $Sr_2RE_8(SiO_4)_6O_2$ (RE = rare earth) ceramics

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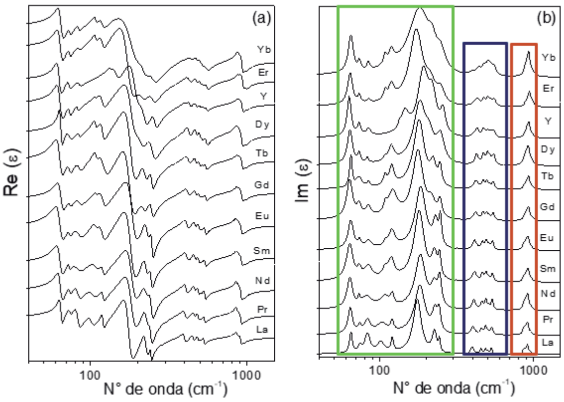
Keywords: *Apatites, rare earth, SOFC, microwave dielectrics, Raman scattering, infrared spectroscopy*

## Highlights

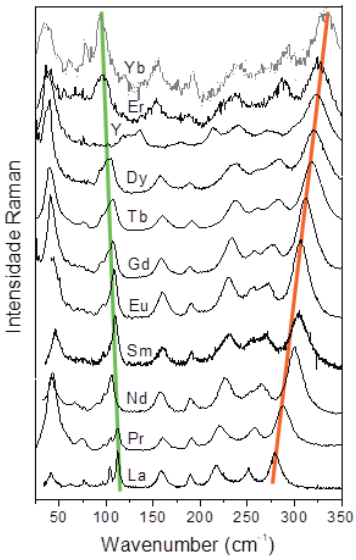
Vibrational and intrinsic dielectric properties of apatite-type strontium rare earth silicates ceramics were investigated by Raman scattering and infrared-reflectivity spectroscopy.

## Abstract

Apatite is a generic designation to nominate natural and synthetic materials with general formula $^{IX}A_4{}^{VII}B_6(^{IV}TO_4)_6X_2$, where the roman numerals indicate the ideal coordination number. The most common structure is the hexagonal *P6₃/m* space group. Apatites containing rare earth elements (*RE*) were discovered in 1959, and later it was proved that it is possible to obtain compounds with a combination of elements and charges. For strontium rare earth silicates $Sr_2RE_8(SiO_4)_6O_2$, the A-sites are equally occupied by $Sr^{2+}$ and $RE^{3+}$ cations, while B-sites are occupied exclusively by *RE*, T-sites are $Si^{4+}$ cations, and $O^{2-}$ anions are in the X-sites. Before 1995, the application research for silicate-based oxyapatites focused on their optical properties. After that, the materials were reported as high oxygen ion conductors. The technological importance of these materials allied to the lack of information related to the vibrational properties were the motivation to the development of this work. Raman scattering and infrared-reflectivity spectroscopy were employed under optimized conditions to determine the phonon modes in the $Sr_2RE_8(SiO_4)_6O_2$ series. The results showed good agreement with the theoretical predictions, in which all 33 Raman-active bands and 18 of the 20 predicted polar phonons were visualized and their positions evaluated as a function of the lanthanide ionic radii under investigation. Dispersion analyses were conducted in all $Sr_2RE_8(SiO_4)_6O_2$ ceramics using the Lorentz model and Kramers-Krönig relations to obtain the infrared optical functions and polar phonon characteristics of the materials, from which their intrinsic dielectric properties were calculated. The relationships between the intrinsic properties obtained by infrared spectroscopy and the extrinsic properties determined by direct microwave measurements, as well as with the values predicted by the Clausius-Mossotti equation were discussed. Some results are presented below.



Infrared optical functions for $Sr_2RE_8(SiO_4)_6O_2$ ceramics obtained from fitting by the Lorentz model. (a) real part of the dielectric function, Re(ε); (b) imaginary part of the dielectric constant, Im(ε). Boxes in green, blue and red show the characteristic region for lattice, bending and stretching modes of $SiO_4$, respectively.



Raman spectra for the $Sr_2RE_8(SiO_4)_6O_2$ ceramics obtained under different optimized experimental conditions (laser lines): La and Sm (660 nm); Pr and Tb (532 nm); Eu, Gd, Dy, and Y (514 nm); Nd (488 nm); Er and Yb (458 nm) from 40-350 cm$^{-1}$, showing the shifts of the bands when the RE is replaced.

## Acknowledgments

FAPEMIG, CNPq and CAPES are acknowledged for financial support.

**Área: MAT**

# Water-in-oil Pickering emulsions stabilized by Layered Double Hydroxides.

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Keywords: *Water-oil emulsion, Pickering emulsion, Layered double hydroxides.*

## Highlights

LDH intercalated with $SO_4^{2-}/Na^+$ were synthesized by co-precipitation and grated with Octadecyltrimethoxysilane (OTMS). The particles were used as stabilizers in water-in-oil Pickering emulsions.

## Resumo/Abstract

In recent years, layered double hydroxides (LDH) have been shown to be highly effective in stabilizing emulsions [1], mainly by versatile properties in terms of chemical composition, basicity, high charge density and surface area, possibility of controlling its characteristics of hydrophilicity/hydrophobicity and morphology [2]. We investigated the role of these particles in the stabilization of emulsions containing liquid paraffin. Na-shigaite with the ideal formula $[Mn_{0.666}Al_{0.333}(OH)_2][Na_{0.111}(H_2O)_{0.666}(SO_4)_{0.222}]\cdot 0.666H_2O$ was synthesized by co-precipitation with increased pH [3]. 1 g of Na-shigaite was dispersed in 25 mL of toluene (Synth, 99.5%) and 1 g of Octadecyltrimethoxysilane (OTMS, Sigma Aldrich, 90%) was added dropwise to the dispersion and kept under stirring at 80°C for 24 h, the resulting material was washed three times with toluene followed by centrifugation, and then dried at 80 °C. The XRD patterns (Fig. 1a) exposed a series of basal peaks, where the basal distances were calculated using the third basal peak as 11.03 Å and FTIR spectra (Fig. 1b) showed typical bands of LDH functional groups. The effect of the LDH particles as stabilizers from the mineral oil mixture (density = 0.874 $g\cdot cm^{-3}$ at 25 ºC) and Milli-Q water (density = 0.997 $g\cdot cm^{-3}$) was evaluated. Mass fractions ($\Phi_o$) of 0.7,0.5 and 0.3 of liquid paraffin in water and LDH concentrations of 0.1 to 1.0 wt% were evaluated, dispersed in the oily phase. These mixtures were ultrasonicated for 1 min and kept under air with constant temperature of 22 °C. Thus, a macro and microscopic study of the emulsions was conducted by obtaining photographs (Fig. 1c). The LDH particles were stained with rhodamine B (2.5 ppm) (red film around the dropletes), and water was stained with fluorescein (2.5 ppm) (green color inside the droplets). Oily phase appears in black. This is the first report of OTMS grafted LDH Na-Shigaite particles used to stabilize Pickering emulsions.

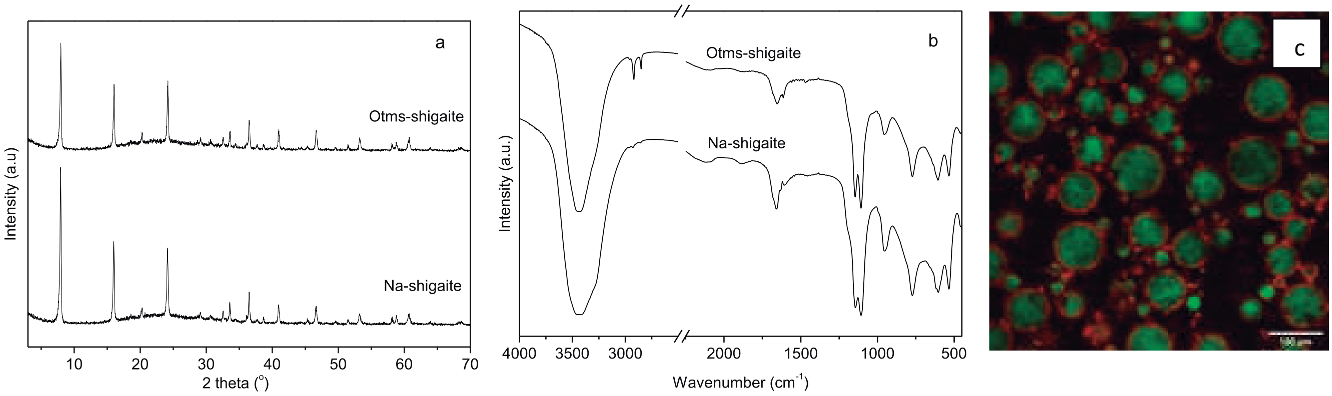

Figure 1: (a) XRD patterns, (b) FTIR spectra of Na-shigaite and Otms-shigaite and (c) Confocal fluorescence microscopic image of emulsions containing paraffin oil ($\Phi_{0.7}$) and water and 0.75 wt% of particles LDH OTMS-Shigaite after 24 h (200x magnification).

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## Agradecimentos/Acknowledgments

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

**Área: MAT**

# $WS_2$-$WO_3$/rGO nanocomposite as electrode: looking for the best combination

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Key Words: Nanocomposites, Energy storage, Tungsten disulfide, Tungsten trioxide, Reduced graphene oxide.

## Highlights

Nanocomposites based on tungsten disulfide ($WS_2$), tungsten trioxide ($WO_3$) and reduced graphene oxide (rGO), $WS_2$-$WO_3$/rGO, were synthesized and characterized aiming at studying their capacitive behavior.

## Abstract

Transition metal dichalcogenides (TMDs), transition metal oxide (TMO) and graphene derivatives (GO and rGO) are promising materials for energy storage systems. Individually, they face limitations such as instability of charge-discharge mechanisms (in TMDs and TMOs) and surface area dependence (rGO). Based on that, our main goal is to synthesize a nanocomposite based on these components and investigate its capacitive properties. With this in mind, we intent not just to mitigate their respectively drawbacks, but also to find the ideal combination of pseudocapacitance (TMOs and TMDs) and electrochemical double layer capacitance (rGO), aiming at finding a material with enhanced energy storage features. For this purpose, $WS_2$-$WO_3$ material was obtained by a one-pot hydrothermal method, by adding tungstein precursors into a Teflon-lined stainless-steel autoclave (200°C for 24 h). To further obtain $WS_2$-$WO_3$/rGO, the carbonaceous material was previously obtained by a modified Hummers method and reduced by hydrazine, in the following, it was added to the autoclave containing $WS_2$-$WO_3$ precursors. Products were collected by centrifugation, washed several times, dried, and fully characterized. Raman spectroscopy (Figure 1A) confirmed the successful synthesis of $WS_2$-$WO_3$ by exhibiting bands related to $E^1_{2g}$ and $A_{1g}$ modes of $WS_2$ and W-O modes of $WO_3$. Finally, the presence of rGO could be verified by the appearance of D and G peaks, fingerprints of this material. After the confirmation of materials nature, electrochemical characterization was carried out (Figure 1B).

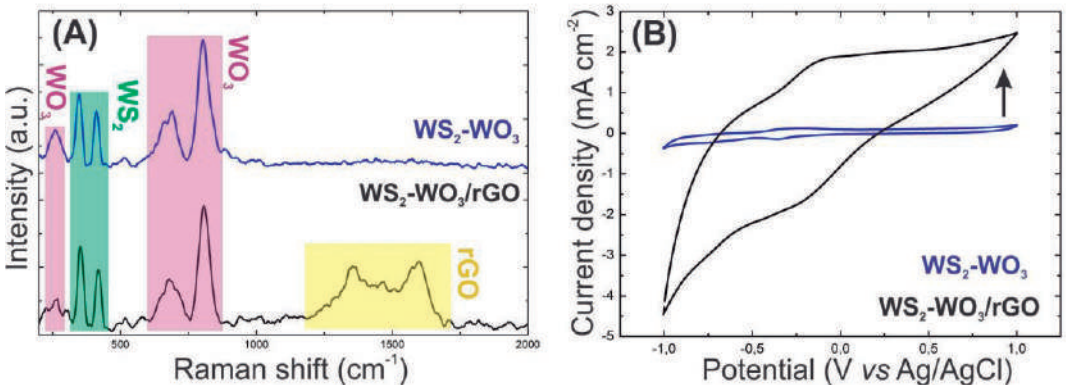

**Figure 01.** (A) Raman spectra (ʎ = 532 nm) and (B) cyclic voltammograms (10 mV $s^{-1}$, 1.0M $Na_2SO_4$) of the obtained materials.

So far, cyclic voltammograms and charge-discharge measurements results displayed superior responses in capacitance and stability for $WS_2$-$WO_3$/rGO when compared to neat materials (up to 3-fold more capacitive). Overall, we attested the production of a promising material through a simple one-pot route and demonstrated its boosted capacitive properties, demonstrating new possibilities suitable for supercapacitor electrodes.

## Acknowledgments

The authors acknowledge the Mackenzie Presbiterian Universisty (UPM), MackPesquisa, FAPESP (2020/13288-6), CNPq (306808/2020-0), CNPq/Universal, INCT of Carbon Nanomaterials, CAPES and Exército Brasileiro.

**Área: MAT** **Nº de Inscrição: 01220**

# Xerogel e criogel de gelatina-siloxano: Degradação e cinética de absorção em diferentes pHs

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Palavras Chave: *Gelatina, Colágeno, Hidrogel, Criogel.*

## Highlights

Gelatin-siloxane xerogel and cryogel: Degradation and absorption kinetics at different pHs
Géis de gelatina-siloxano com diferentes idades tiveram a absorção de água e degradação estudadas em diferentes pHs. Diferentes morfologias e idades impactaram o comportamento dos géis.

## Resumo/Abstract

O colágeno tem atraído interesse como biomaterial devido a sua biocompatibilidade, degradabilidade e, na forma de gelatina, sua capacidade de formar hidrogéis, aerogéis, criogéis e xerogéis, que podem ser utilizadas como arcabouços para crescimento celular, mediante a reticulação das cadeias peptídicas (ECHALIER et al., 2017). O presente trabalho teve como objetivo estudar a cinética de absorção de água em diferentes pHs de géis com duas diferentes morfologias e idades. Os géis foram obtidos previamente a partir da reticulação da gelatina pelo 3-glicidoxipropil trimetoxissilano (GPTMS) e tiveram a água removida em estufa, resultando em um xerogel na forma de filme, %gel=91%, ou por liofilização e posterior cura em estufa por 48 h, resultando em um criogel poroso, %gel=99%. Amostras do xerogel e criogel recém sintetizados e com 12 meses de idade (mantidos em condições ambientes) foram submersas em meio neutro (água destilada, pH 7), básico (NaOH pH 9) e ácido (HCl pH 2), por 48 h, e em determinados intervalos de tempo, a massa das amostras foi verificada para determinar a cinética de absorção de água nos diferentes meios. Verificou-se que todas as amostram, nos diferentes meios testados, apresentaram altos teores de absorção. Para os materiais recém sintetizados, o xerogel teve absorção de 219%, 197% e 183%% em pHs 2, 7 e 9, respectivamente, após 1 h de absorção, enquanto o criogel teve absorção de 182%, 212% e 169%; após 48 h de imersão, o xerogel teve absorção de 264%, 198% e 206% em pHs 2, 7 e 9 respectivamente, e o criogel teve absorção de 289%, 332% e 249%. Para as amostras com 12 meses de idade, o xerogel teve absorção de 85%, 279% e 109%% em pHs 2, 7 e 9 respectivamente após 1 h de absorção, e o criogel teve absorção de 278%, 176% e 229%; após 48 h de imersão, o xerogel teve absorção de 121%, 159% e 77% em pHs 2, 7 e 9 respectivamente, e o criogel teve absorção de 261%, 267% e 291%. Para os materiais com 12 meses de idade, diferente dos materiais recém sintetizados, houve início de perda de massa por volta de 24h de ensaio, isso mostra que tais amostras apresentavam menor teor de reticulação e, portanto, em condições ambientes, eles apresentam degradação, mas com uma cinética lenta, o que pode ser atribuído a umidade do ar, levando a hidrólise das ligações cruzadas Si-O-Si (LEE; KIM; JEONG, 2019) (SEGURA et al., 2017). A diferença no comportamento de absorção do material teve relação com a sua morfologia, criogéis apresentam microporos que permitem que eles absorvam água na matriz e ainda retenham água adicional nos poros. A idade do material também influenciou a absorção de água, uma vez que as amostras com mais idade tenderam a absorver mais água inicialmente, mas perder massa após 24h, um reflexo de um menor teor de reticulação e aceleração de sua hidrólise em meio aquoso. Para as amostras recém sintetizadas, com alto teor de rearticulação, pHs 2 e 7 foram os que, no geral, geraram maiores absorções, o que pode ser atribuído aos grupos protonáveis das cadeias de gelatina, permitindo um aumento de hidrofilicidade em pH neutro e inferiores. Neste trabalho, foi possível verificar a morfologia, idade e meio influenciam a absorção de água dos materiais e que eles são degradáveis. Ainda, eles se mostram promissores para a aplicação como biomateriais que tem boa capacidade de absorção de água e os criogéis, em especial, como arcabouços celulares, devido à presença dos poros.

ECHALIER, Cécile et al., **Materials Today**, v. 20, n. 2, p.59-66, 2017. LEE, Ho-yong; KIM, Hyoun-ee; JEONG, Seol-ha., **Colloids and Surfaces B**: Biointerfaces, v. 174, p.308-315, 2019. SEGURA, D. L. N. et al.,**Verano de la Investigación Científica**, v. 3, n. 2, p. 601–605, 2017.

## Agradecimentos/Acknowledgments

A UFABC, FAPESP, CNPq.

# MED

# Química Medicinal

**Área: MED** **Nº de Inscrição: 721**

# 2-Bromo-1,4-naphthoquinone regulates the collagen production and fibroblast migration through PKA/CREB pathway

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Palavras Chave: *Naphthoquinone*, *Wound healing, Fibroblasts, Migration, Collagen.*

## Highlights

2-Bromo-1,4-naphthoquinone increased fibroblast collagen synthesis.
2-Bromo-1,4-naphthoquinone improved fibroblast migration *in vitro*.
PKA/CREB signaling pathway is required for fibroblast migration induced by 2-Bromo-1,4-naphthoquinone.

## Resumo/Abstract

**Introduction:** Natural naphthoquinones such as lawsone, alkannin and shikonin, have been demonstrated to have wound healing properties, which may be due to anti-inflammatory and antioxidant properties [Res. J. Phytochem. 5 (2011) 123–129; Curr. Med. Chem. 15 (2008) 3248–3267; *Toxicol. Vitro 30 (2015) 364–372*]. Previous studies have been demonstrated the influence of electron-donating or withdrawing groups into structure of 1,4-naphthoquinones able to improving their pharmacological activities [*Biochem. Pharmacol. 35 (1986) 2587–2591; J. Mol. Cell. Cardiol. 39 (2005) 149–158*].

Fibroblasts are key players for maintaining skin homeostasis and for the wound healing process. Our previous work has found that the topical treatment with the naphthoquinone derivative, 2-Bromo-1,4-naphthoquinone, markedly accelerated diabetic wound healing [*Chem Biol Interact. 291 (2018) 55-64*]. However, the effects of 2-Bromo-1,4-naphthoquinone on fibroblast function have not been investigated yet. Thus, the aim of the present study was to evaluate the effect of 2-Bromo-1,4-naphthoquinone on collagen type 1 production and migratory response of fibroblast *in vitro*. **Methods:** NIH3T3 fibroblasts were culture in Dulbecco's Modified Eagle Medium (DMEM) supplemented with 10% fetal bovine serum, 2 mM-glutamine, and 40 µg/mL gentamicin, and cultured in a humidified atmosphere contained 5% CO2 at 37 °C. The effect of 2-Bromo-1,4-naphthoquinone on fibroblast viability, on collagen type I expression level and migration were assessed 24 h after treatment using MTT assay, immunofluorescence staining, and scratch assay, respectively. In another set of experiments, fibroblasts 2-Bromo-1,4-naphthoquinone-treated were exposed to specific inhibitors of PKA (6-22-amide) and CREB (KG-501) to explore the possible molecular mechanism involved in cell migration by using scratch assay. All assays were performed in three independent controlled experiments and statistical analysis performed using student's t-test or two-way ANOVA with post hoc Newman-keuls test. Differences at $p<0.05$ were considered significant. **Results:** At tested concentrations (1 to 50 µM) the 2-Bromo-1,4-naphthoquinone did not show any toxic effect on fibroblast. Our results also showed that 2-Bromo-1,4-naphthoquinone at 10 µM increased by 37.9% type I collagen expression as compared to untreated cells. Treatment with 2-Bromo-1,4-naphthoquinone at 10 µM accelerated fibroblast migration by 28.9% as compared with untreated cells. In addition, the 2-Bromo-1,4-naphthoquinone-induced fibroblast migration was completely abolished by pretreatment of cells with the PKA and CREB inhibitors. **Conclusion:** Our data suggest that the 2-Bromo-1,4-naphthoquinone stimulates the fibroblast activation by a mechanism involving PKA and CREB signaling pathways.

## Agradecimentos/Acknowledgments

The authors are grateful to the research team at the Laboratory of Cell Biology and LaSOM for helping them with some experimental protocols and CNPq and FAPEAL for financial support.

**Área: MED**

# [6]–gingerol Triazoles Derivatives and their Antibacterial Activities against *Staphylococcus aureus* (*S. aureus*) and *Escherichia coli* (*E. coli*)

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Key words: 1,2,3 – Triazoles, [6] – Gingerol, *Staphylococcus aureus*, *Escherichia coli.*

## Highlights

Isolation of [6]-gingerol; Obtaining of [6]-gingerol 1,2,3-triazoles derivatives; Activity of 1,2,3-triazoles compounds against *S. aureus* and *E. coli*.

## Abstract

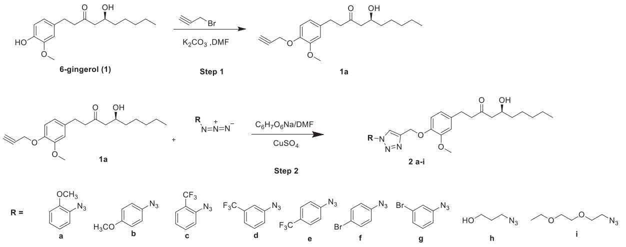
### Introduction

Recent research indicates the need to obtain new potentially useful compounds against bacteria, since these organisms have been increasingly resistant to available therapeutic treatments, corroborating severe infections in humans.[1]

In this context, natural products, such as [6]-gingerol, are the protagonists, as they have several related biological activities.[2] Therefore, aiming to obtain efficient and potentially useful structures, 1,2,3-triazole compounds from [6]-gingerol were synthesized and their antibacterial activities were evaluated against *S. aureus* and *E. coli*.

### Results and Discussion

The natural product [6]-gingerol (**1**) was isolated from the *Zingiber officinale* plant. From this, the preparation of **1a** and **2 a-g** derivatives was carried out by two steps in good yields as shown in Scheme **1**. A simple method was employed to obtain **1a** using potassium carbonate ($K_2CO_3$) 2.0 equivalents, commercial propargyl bromide, 1.5 equivalents in DMF at room temperature for 5 hours. To obtain compounds **2a-i** was used Click Chemistry reaction. All compounds were identified by IR, $^1$H and $^{13}$C NMR and HRMS.



**Scheme 1.** Synthetic steps

All compounds had their antibacterial activities evaluated and compound **2g** showed moderate activity against *S. aureus* (**Table 1**).

**Table 1**. Biological activities aganst *S.aureus* and *E. coli*.

| Compounds | CMI µg.mL$^{-1}$ | |
|---|---|---|
| | *S. aureus* (NEWP0023) | *E. coli* (NEWP0022) |
| **1** | ≥500 | ≥250 |
| **1a** | ≥500 | ≥250 |
| **2a** | ≥500 | ≥250 |
| **2b** | ≥500 | ≥250 |
| **2c** | ≥500 | ≥250 |
| **2d** | ≥500 | ≥250 |
| **2f** | ≥500 | ≥250 |
| **2g** | 15,6 | ≥250 |
| **2h** | ≥500 | ≥250 |
| **2i** | ≥500 | ≥250 |
| **Gentamicina** | ≤ 0.5 | ≤ 0.5 |

### Conclusion

We can conclude with the present work that the compound **2g** showed moderate activity against S. aureus, evidencing the importance of the 1,2,3-triazole ring as an excellent connector of molecules or pharmacophoric groups of biological interest. The data presented also suggest that new modifications need to be thought in order to potentiate even more the effects observed against the studied bacteria.

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[2]Ham, S.-Y., Han-Shin, K., Jo, J. M. & Lee, J.-H. Combined Treatment of 6-Gingerol Analog and Tobramycin to Inhibit Pseudomonas aeruginosa Infections. *ASM Journals* **9,** (2021).

## Acknowledgments

**Área: MED**

# ACTIVITY OF GUANYLHYDRAZONES AGAINST HUMAN GLIOBLASTOM (GBM02) *IN VITRO*

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**Keywords:** *cancer; synthetic compounds; guanylhydrazones; antitumoral activity.*

## Highlights

Guanylhydrazones have an antitumor effect against human glioblastoma cells, without toxic effects, against blood mononuclear cells.The compounds allowed a reduction in the number of GBM02.

## Resumo/Abstract

Cancer has a high impact on public health, being among the main causes of death worldwide. Among the various types of cancer, gliomas affect the central nervous system having a high mortality rate, which is associated with genetic mutations that makes the search for new drugs essential. In this context, guanylhydrazones represent a class of promising substances with widely reported tumor effects. The guanylhydrazones were designed from modifications in the LQM 14 prototype biphenyl. Thus, the changes involved substitutions involving aromatic groups (aniline and diphenylamine) and non-aromatic groups (pyrrolidine, pyrrolidine, 1-methylpiperazine and morpholine). Derivatives were obtained from two reaction steps that involved nucleophilic aromatic substitution or Buchwald reactions followed by condensation with aminoguanidine. The compounds showed varied reaction yields, but with a high degree of purity. In this work, we evaluated the effects of seven guanylhydrazones on glioblastoma cells (strain GBM02). The cytotoxic evaluation in monocytes and lymphocytes showed that none of the guanylhydrazones were toxic up to 100 µM concentration. Temozolomide (TMZ) was used as standard drug. However, it displayed antitumor effects lower than tested guanylhydrazones, except for LQM 242 (Table 1). Moreover, the guanylhydrazones exhibited great selectivity indexes for GBM02 cells. Further morphological investigations detected modifications in cells treated with LQM 14 and LQM 240 (Figure 1), confirming its ability to induce the death of tumor cells. Finally, the results so far are quite promising and deserve additional *in vivo* evaluation for a better characterization of their pharmacological properties.

**Table 1: Effect of guanylihydrazonic derivatives on GBM02 with 95% confidence index**

| Code | $IC_{50}$ (µM) | $CC_{50}$ (µM) | Selectivity Index (SI) |
|---|---|---|---|
| **TMZ** | >100 | >100 | >1 |
| **LQM 14** | 1,94 | >100 | >48,54 |
| **LQM 239** | 5,07 | >100 | >19,72 |
| **LQM 240** | 3,54 | >100 | >28,24 |
| **LQM 241** | 6,30 | >100 | >15,87 |
| **LQM 242** | >100 | >100 | >1,0 |
| **LQM 243** | 4,15 | >100 | >24,09 |
| **LQM 244** | 22,74 | >100 | >4,39 |
| **LQM 245** | 8,85 | >100 | >11,29 |

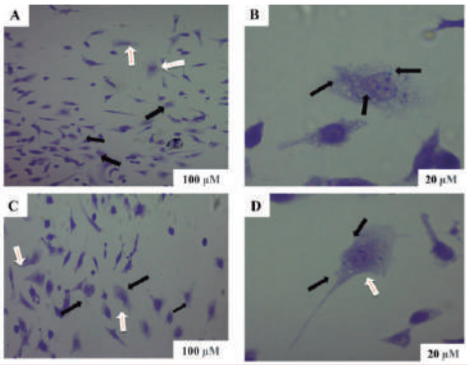

**Figure 1: GB02 morphology before (A and C) and after treatment with LQM 14 (B) and LQM 240 (D)**

## Agradecimentos/Acknowledgments

Proc INCT INOFAR/ CNPq Nº 573.564./2008-6 and Proc INCT RENNOFITO/CNPq Nº 465536/2014-0

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

**Nº de Inscrição:__ 00534__**
*(Inserir o número de inscrição do autor que fez a submissão)*

# Advanced glycation end products inhibition and in silico ADME properties of natural alkaloids from *Ocotea paranapiacabensis*

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Palavras Chave: *Swiss ADME, Collagen, skin aging.*

## Highlights

Natural alkaloids from *Ocotea paranapiacabensis* were identified as advanced glycation end products inhibitors, promoted a decrease in dermis contraction and had ADME properties predicted revealing a valuable potential for the prevention of skin aging.

## Abstract

The process of skin aging is associated with advanced glycation end products (AGEs), and strategies inhibiting their formation have been addressed by pharmaceutical companies for the development of novel anti-aging formulations. A bioassay-guided study aiming at identifying inhibitors of glycation process afforded four benzylisoquinoline alkaloids from the leaves of *O. paranapiacabensis*. The alkaloids were evaluated for their potential to inhibit AGEs formation and two of the compounds (6,7-dihydroxy-1-(4'-hydroxybenzyl)-2,2-N,N-dimethyl-1,2,3,4-tetrahydroisoquinoline (**1**) and 6,7-dihydroxy-1-(4'-hydroxybenzyl )-2-N-methyl-1,2,3,4-tetrahydroisoquinoline (**2**)) showed inhibition of 63% and 98.2% respectively (150 µM), compared to control aminoguanidine (92% inhibition, 10 mM). The anti-aging potential of these two alkaloids were further evaluated in the reconstructed human skin model in vitro and results showed a decrease in dermis contraction (8.7 and 4.2%) when compared to glycated control (57.4%), evidencing the activity of these compounds in preventing AGEs dependent collagen cross-links. The assessment of absorption, distribution, metabolism and excretion (ADME) and toxicity properties in the early phases of active compounds development increases the rate of success in later development phases. In silico methods constitute a useful approach in the early stages of the studies of a biologically active compound, reducing development costs, and eliminating possible candidates with deficient bioavailability. Permeability coefficient was determined for both alkaloids using Swiss ADME, and the predicted Log Kp values were -6.19 and -6.11 cm/s indicating low skin permeation. Modifications of the compounds' structures can increase absorption, or specific formulations can be used to increase skin permeation, so they could reach the dermis for bioactivity. Additionally, good oral bioavailability was predicted for both compounds that afforded suitable values for logP ($-0.7 < \log P < 5$), size (150 g/mol < molecular mass < 500 g/mol), polarity (20 $Å^2 <$ TPSA $< 130$ $Å^2$), insolubility ($0 <$ LogS $< 6$), insaturation (0.25 < fraction of Csp3 < 1) and flexibility (0 < nRotb < 9).

## Acknowledgments

FAPESP grants #2013/07600-3 (CIBFar-CEPID), #2014/50926-0 (INCT BioNat CNPq/FAPESP), CNPq and CAPES. MV acknowledge Fapesp scholarship #2019/05967-3.

**Área: MED**

# Anti-chikungunya activity of Cu(I)-N-heterocyclic carbenes

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Palavras Chave: *(Antiviral, Chikungunya, Copper, N-Heterocyclic-carbenes).*

## Highlights

Chikungunya is a neglected tropical disease of concern for the public health system. A systematic series of copper(I)-N-heterocyclic carbenes (Cu(I)-NHC) bearing -N-R groups with R = mesityl and 2,6-diisopropylphenyl (IPr) had their properties in solution, lipophilicity analyzed and correlated to their inhibition of viral replication (CHIKV). The results indicated that the compound [Cu(IPr)Cl] presented the lowest lipophilicity, and the highest stability in solution was the most active in the replication inhibition of CHIKV.

## Resumo/Abstract

### INTRODUCTION

Chikungunya fever is a Neglected Tropical Disease (NTD) caused by Chikungunya virus (CHIKV, arbovirus), transmitted by a vector, mainly the insect Aedes *aegypti*. One major drawback in CHIKV control is the lack of drugs for treatment or vaccines for prevention. Patient care is based on symptoms relief, which reinforces the need for effective treatment against CHIKV[1]. Although there are some metal complexes[2] with described antiviral activities for CHIKV, the use of organometallics is a promising and still unexplored area. Organometallic complexes of Cu(I) with N-heterocyclic carbenes (NHC) are promising candidates. NHCs are ligands that exhibit low toxicity and a high possibility of structural variations that allow lipophilicities and reactivities adjustment[3]. In this work, we investigated the anti-CHIKV activity of three Cu(I)-NHC complexes. The systematic series allowed us to correlate chemical properties and antiviral activities.

### MATERIALS AND METHODS

All syntheses were carried under air. Compounds [Cu(IMes)Cl] (1), Cu(IPr)Cl] (2), and Cu(IMes)$_2$]BF$_4$ (3) were synthesized according to reported methodologies[4,5]. $^1$H and $^{13}$C Nuclear magnetic resonance (NMR) spectra were obtained on 250 MHz. Octanol-water partition coefficient (Log P) was measured using the shake flask method and copper was quantified by ICP-OES[6]. Cell viability assays to assess the cytotoxicity of the compounds in BHK-21 cells were performed using MTT methodology. The antiviral assays were preformed using CHIKV-*nanoluciferase*, where virus replication was quantified by measuring Nanoluciferase activity (Promega)[2].

### RESULTS AND DISCUSSIONS

All complexes exhibited chemical shifts, multiplicity, and coupling constants in agreement with values reported [4,5]. The time-dependent $^1$H spectra of compound (1) in DMSO-d6 reveal an equilibrium of the neutral complex [Cu(IMes)Cl] (A) and its ionic species [Cu(IMes)$_2$][CuCl$_2$] (B), in a ratio of approximately 3:1 (A:B) at room temperature[7]. The compounds (1) (-0.713±0.173) and (2) (-0.684±0.055) exhibited a close log P value (an essential quantity for the accessibility of the drug to the active site), with compound (1) exhibiting the lowest logP value. The compound (3) (0.168±0.001) was the only one that showed a log P>0. These data demonstrated that [Cu(IPr)Cl] **(2)** presented the lowest lipophilicity and the highest stability in solution.

The results of viability e antiviral activity assay indicated that the compound [Cu(IPr)Cl] **(2)** was the most active on CHIKV inhibition of replication (91.9%), and the lowest cytotoxicity for the cells (cell viability=100%). These results suggest a direct correlation between the lipophilicity, and speciation in the biological activity of Cu(I)-NHC compounds.

### CONCLUSIONS

The syntheses of complexes of [Cu(I)(NHC)X] were well succeeded confirmed by $^1$H NMR. The best anti-CHIKV activity of the compound (2) indicates its inertness in solution, its least lipophilic of the series, demonstrating they are crucial properties for the design of novel anti-CHIKV. Compound 2 is an excellent chemotype for novel metallodrug design.

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## Agradecimentos/Acknowledgments

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**Area: MED** **Nº de Inscrição: 00836**

*(Inserir o número de inscrição do autor que fez a submissão)*

# Antiglioblastoma potential of *N*-benzyl-naphtylamines: synthesis, biological evaluation and molecular modeling.

**Thais Batista Fernandes (PG),[1] Rosania Yang (IC),[2] Glaucio Monteiro Ferreira (PQ)[3], Priscila Oliveira de Souza (PQ),[2] Gabriela Roliano (PG)[2], Elizandra Braganhol (PQ)[2], Mario Hirata (PQ)[3], Roberto Parise Filho (PQ)[1].**

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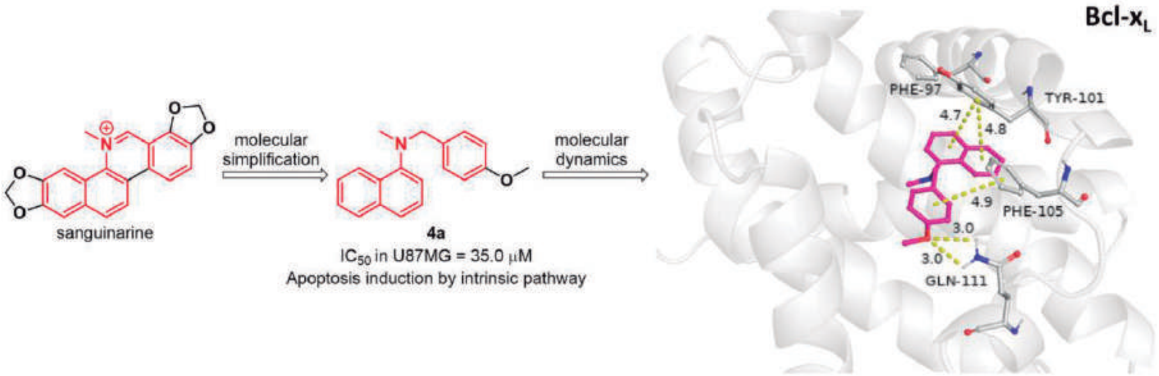
Keywords: *Glioblastoma; Bcl-x$_L$; Sanguinarine; Molecular simplification; N-benzyl-naphtylamines; Molecular dynamics.*

## Highlights

*N*-benzyl-naphtyl-amine (**4a**) was cytotoxic to U87MG and selective to tumor cells;
Biological assays and *in silico* data suggested that **4a** may induce apoptosis by inhibition the antiapoptotic protein Bcl-x$_L$.

## Abstract

Sanguinarine is an alkaloid able to inhibit Bcl-x$_L$, an antiapoptotic protein which is overexpressed in tumor cells and related to their resistance against antineoplastic chemotherapy. The aim of this work was the synthesis of sanguinarine analogues designed by molecular simplification and evaluate their antitumoral properties. Ten N-benzyl-naphtyl-amines were synthesized in two or three reaction steps through reductive amination. All compounds were characterized and analyzed by NMR $^1H/^{13}C$, melting point and HPLC. Cytotoxicity evaluation against U87MG glioblastoma cell line showed that *N*-benzyl-naphtylamines were more active than temozolamide. Tests against astrocytes indicated that the most promising analogue, **4a** (IC$_{50}$ > 100 μM), was significantly more selective than sanguinarine (IC$_{50}$ astrocyte = 5.8 μM; IC$_{50}$ U87MG = 3.0 μM). Compound **4a** also induced cell death by apoptosis and mitochondrial membrane depolarization, indicating apoptotic death by intrinsic pathway. Furthermore, **4a** provided cell cycle arrest at G$_2$/M phase, suggesting that it is a specific cell cycle agent. Molecular dynamics suggested that **4a** and sanguinarine interact with Bcl-x$_L$ mainly by hydrophobic interactions, although some polar interactions were verified for alkoxyl groups. Both compounds had similar affinity to the protein, which were verified by the root mean square flutuation. *In silico* pharmacokinetics analysis indicated that **4a** is able to cross blood-brain barrier and is not substrate for P glycoprotein. Molecular simplification was successful to provide cytotoxic compounds and *N*-benzyl-naphtylamines represent a relevant scaffold to be explored by medicinal chemists to the development of potential antitumor agents.



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## Acknowledgments

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**Área: MED**

# Biophysical studies of urease inhibition and interaction with imidazopyridine and imidazopyrimidine derivatives

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*Palavras chave: inibição enzimática; heterocíclicos de nitrogênio; fluorescência molecular; solos e bactérias.*

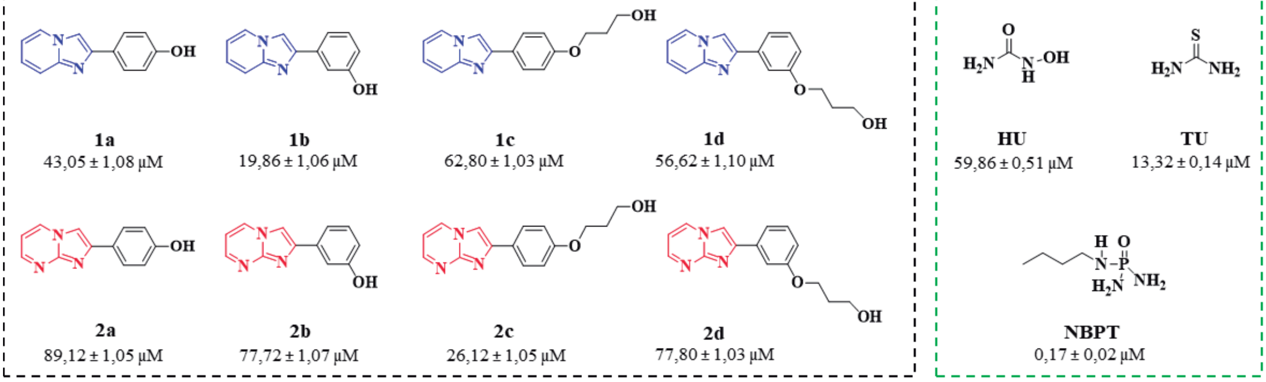
## Highlights

Imizadopyridine (**1a-d**) and imidazopyridine (**2a-d**) derivatives inhibited the ureolytic activity *in vitro*, and **1b** was the most active compound, interacting with the enzyme with a $K_b$ of $5,4\times10^4$ $M^{-1}$, mainly through hydrogen bonds and Van der Walls forces.

## Resumo

A hidrólise da ureia catalisada pela urease tem gerado problemas econômicos e ambientais, uma vez que ocorre degradação de fertilizantes N-ureia levando a perdas na agricultura, além de problemas de saúde decorrentes da colonização da *H. pylori* no estômago, a qual utiliza a enzima como sistema de defesa e permanência no organismo[1,2]. Devido a diversidade de atividades biológicas, incluindo inibição de ureases, descritas para compostos obtidos a partir da fusão entre os núcleos imidazol e piridina/pirimidina[3], os derivados de imizadopiridina (**1a-d**) e imidazopirimidina (**2a-d**) (Fig. 1) foram selecionados para o presente trabalho. Portanto, se avaliou por meio de estudos biofísicos a capacidade inibitória dos derivados frente a urease de *Canavalia ensiformis* (modelo), assim como, parâmetros de ligação entre o composto mais ativo (**1b**) e a enzima. Utilizando o método de referência para produção do azul de indofenol (reação de Berthelot)[4], comprovou-se que todos os compostos testados foram capazes de inibir a atividade ureolítica com valores de $IC_{50}$ (concentração inibitória relativa a 50% da atividade inicial) no intervalo de 19,86 a 89,12 µM (Fig.1). Todos os valores de $IC_{50}$ obtidos foram superiores ao do inibidor clássico NBPT ($IC_{50}$ = 0,17 µM usado em solos) e da tioureia (TU, $IC_{50}$ = 13,32 µM), porém o composto **1b (**$IC_{50}$ = 19,86 µM) apresentou valor próximo a TU. Por outro lado, os ligantes **1a**, **1b**, **1d** e **2c** apresentaram valores de $IC_{50}$ menores que a hidroxiureia (HU, 59,86 µM). De forma geral, o composto **1b** foi o mais ativo, devido ao menor valor de $IC_{50}$ (19,86 µM). Por fim, no estudo de interação realizado com este composto por fluorescência molecular, pôde-se observar que houve formação de um complexo supramolecular enzima-inibidor, com constante de ligação igual a $5,41(\pm 0,02)\times10^4$ $M^{-1}$ (29°C), sendo as ligações de hidrogênio e forças de Van der Walls as principais forças que estabilizam o complexo, o que é coerente quando se avalia a estrutura do ligante a qual possui átomos e grupos passiveis de realizar estes tipos de interações. Diante da capacidade inibitória dos compostos avaliados frente a urease, tem-se como perspectivas avaliar o modo e o sítio de ligação preferencial, além de aplicar o composto mais ativo (**1b**) em sistemas complexos, como amostras de solo e em cepas de *H. pylori*.

**Fig.1.** Estrutura química dos compostos avaliados e inibidores padrão com seus respectivos valores de $IC_{50}$ (µM).



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## Agradecimentos/Acknowledgments

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**Área:** MED

# CHALCONES SYNTHESIS AND EVALUATION OF CYTOTOXIC ACTIVITY AGAINST HCT116 AND HEPG2 CELLS

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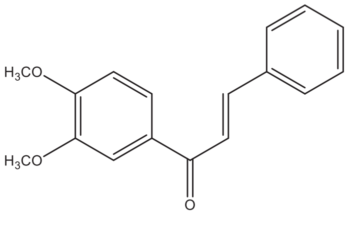
*Keywords*: *Bioatives molecules*, *Chalcones*, *Cytotoxic activity.*

## Highlights

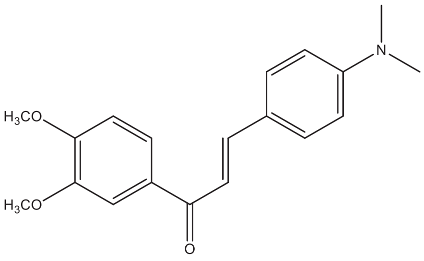
Use of bioactive molecules is efficient in cancer treatment. This study were synthesized and characterized two chalcones to evaluate their cytotoxic activity against HCT116 and HepG2 cells.

## Abstract

The chalcones were synthesized via the Claisen-Schmidt condensation reaction in excellent yield (80 to 85%) by treating 3,4-dimethoxyacetofenone with benzaldehyde and *p*-dimethylaminobenzadehyde. The reaction is performed with magnetic stirring for 3 hours in basic medium using ethanol as the solvent at room temperature. After this time, the reaction mixture is stored in a refrigerator for 24 hours and in the next day is vacuum filtered. The obtained compounds (E)-1-(3,4-dimethoxyphenyl)-3-phenylprop-2-en-1-one (CH-1) and (E)-1-(3,4-dimethoxyphenyl)-3-(4-(dimethylamino)phenyl)prop-2-en-1-one (CH-2) were characterized using FTIR, GC/MS, $^1$H-NMR and $^{13}$C-NMR (COSY, HMBC, HSQC). The chalcones were subjected to evaluation of cytotoxic activity against HCT116 (human colon carcinoma) and HepG2 (human hepatocellular carcinoma) cells in order to contributed to the diversity of synthetic molecules with effective pharmacodynamic potential in the treatment of câncer. The chalcone CH-2 showed a low ability to inhibit tumor cells and chalcone CH-1 showed a percentage inhibition of cell proliferation of 71.68 ± 0.32/ $IC_{50}$ 7.60 µg/mL (HCT116) and 70.21 ±0. 50 / $IC_{50}$ 9.18 µg/ml (HepG2).



CH-1



CH-2

## Acknowledgments

**Área: MED**

# Chemical space exploration and machine learning models for discovering multi-target anti-Alzheimer agents

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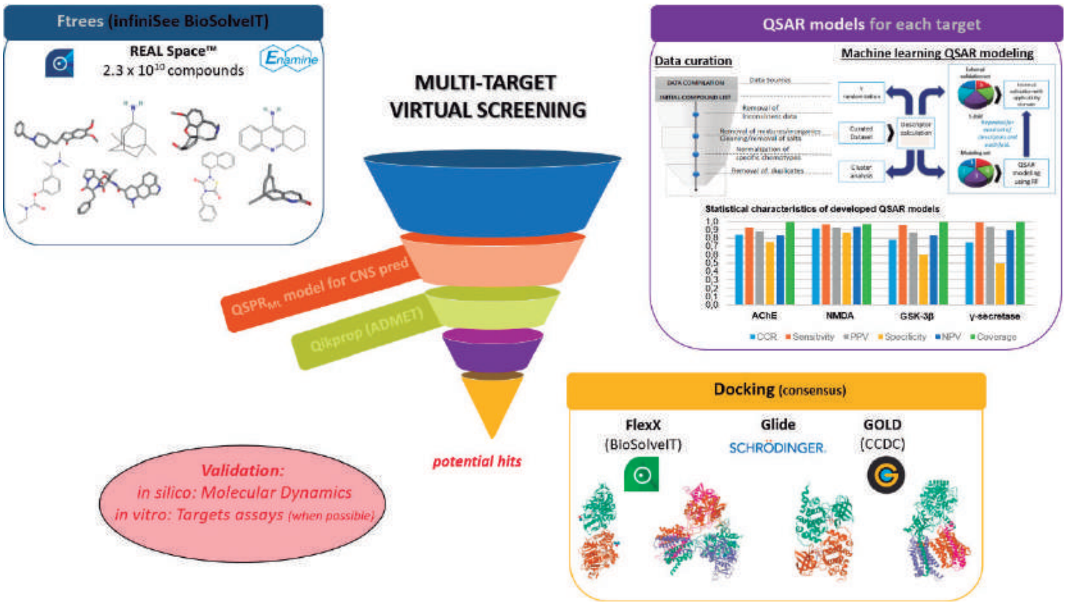
Keywords: *Alzheimer's disease, Drug discovery, Multi-target virtual screening, Chemical space, QSAR, Machine learning*

## Highlights

- Multi-target virtual screening for discovering anti-AD agents
- Exploring 23 billion compounds chemical space
- ADMET and CNS-like filtering
- 4 QSAR machine learning models
- Potential hits discovered

## Resumo/Abstract

Alzheimer's disease (AD) is a multifactorial neurodegenerative disorder that causes memory loss and affects more than 35 million people. Current pharmacotherapy is limited to slowing the disease's progress, despite recent advances. Therefore, it has been hypothesized that, due to the multifactorial characteristic of AD, drugs targeting multiple targets may improve the clinical outcome of the treatment. In view of this, we propose to apply an ensemble set of innovative in silico methods to discover multi-target molecules towards the treatment of AD. First, we selected four well-validated targets and eight AD drugs as probes for our virtual screening campaign. Next, we explored the REAL chemical space (>23 billion compounds) using BioSolveIT FTrees, thus obtaining 100 molecules for each of the eight probes. These were subsequently filtered using ADMET and CNS-like properties. We then predicted their potential to act, simultaneously, as inhibitors of four AD-targets by using four predictive and robust QSAR machine learning models - developed by us, using corresponding datasets of targets AChE, NMDA, GSK-3β, and γ-secretase, with correct classification rate (CCR) of 84, 92, 78 and 75%, respectively. This furnished us 39 hits with an enriched structural diversity and potential to act as modulators of all AD-targets here investigated. We will execute molecular docking and dynamics studies, as well as experimental assays, whenever possible, to confirm their multi-target anti-AD activities.



## Agradecimentos/Acknowledgments

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**Área: MED**

# Cytotoxic activity and cellular mechanism of action of new simplified gedatolisib analogues

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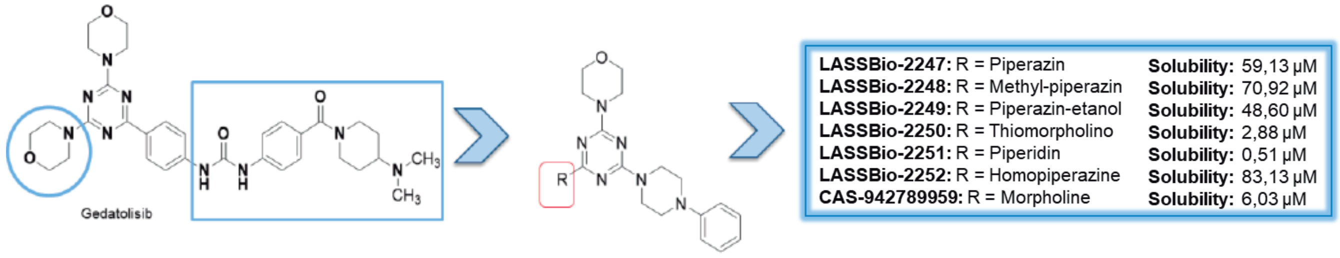
Keywords: *Cancer, PI3K inhibitors, Gedatolisib, Structural analogues, Phenotypic assays*

## Highlights

We described here the evaluation, by phenotypic assay, of seven new gedatolisib analogues and the comparison of their cytotoxic activity against different human tumour cell lines and their cellular mechanism of action. The cytotoxic profile was evaluated by the MTT assay, LASSBio-2252 were the most promising compound, being able to inhibit the growth of CCRF-CEM and MOLT-4 leukemic strains. The cytotoxic potency of LASSBio-2252 and the gedatolisib standard was restudied by flow cytometry where for the CCRF-CEM and MOLT-4 strains, gedatolisib showed a potency loss greater than 100x and the potency loss for LASSBio-2252 did not exceed 10x. In the annexin V assay, gedatolisib and LASSBio-2252 in their $CC_{50}$ values are able to reduce cell viability by about 50% and cause about 50% of total apoptosis of the CCRF-CEM strain. In the cell cycle assay, LASSBio-2252 promotes cell cycle arrest in the G0/G1 phase at the highest tested concentration of 50 µM for CCRF-CEM strain. Finally, the modulation of the PI3K pathway was studied by enzymatic kit by flow cytometry and we found that LASSBio-2252 promotes inhibition of the phosphorylation capacity of the target in the leukemine strains CCRF-CEM and MOLT-4.

## Resumo/Abstract

Studies on cancer biology have pointed to the role of the phosphatidylinositol-3-kinase (PI3K) in the development of solid tumours and hematologic malignancies. The main objective of the project is to contribute to the discovery of new antitumor prototypes, acting by inhibiting the enzyme PI3K. Therefore, we described here the design, synthesis, and pharmacological activity by phenotypic assays of seven new gedatolisib analogues. Compounds were designed by molecular simplification on gedatolisib structure. The new analogues were synthetized, and the relative purity was determined by HPLC. The cytotoxic profile of the new analogues was evaluated by the MTT assay. None of the evaluated compounds displayed better cytotoxic activity against the selected tumor cell lines than gedatolisib. LASSBio-2252 were the most promising compound among the series, being able to inhibit the growth of CCRF-CEM MOLT-4 and K562 leukemic strains with $CC_{50}$ of 6,25 µM; 9,76 µM and 23,41 µM, respectively. The cytotoxic potency of LASSBio-2252 and the standard drug (gedatolisib) was restudied by flow cytometry. The comparison between the MTT and cytometry methodologies revealed a loss of potency greater than 100x to gedatolisib against the CCRF-CEM strains ($CC_{50}$= 6,15 µM) and MOLT-4 ($CC_{50}$= 1,15 µM), while the potency loss of LASSBio-2252 did not exceed 10x for the CCRF-CEM and MOLT-4 strains. In the annexin V assay (performed by flow cytometry), gedatolisib and LASSBio-2252, in their $CC_{50}$ values, reduced cell viability by about 50% and cause about 50% of total apoptosis of the CCRF-CEM strain. In MOLT-4 cells, there was an increase in initial apoptosis at the lowest tested concentration of gedatolisib, which does not occur for LASSBio-2252. In the cell cycle assay, LASSBio-2252 promotes cell cycle arrest in the G0/G1 phase on CCRF-CEM strain like gedatolisibe. Finally, the ability of LASSBio-2252 to modulate PI3K pathway was studied by enzymatic assay kit, using flow cytometry. The results revealed that LASSBio-2252 inhibited the phosphorylation capacity of the target in the leukemic strains CCRF-CEM and MOLT-4, similarly to gedatolisib.



**LASSBio-2247:** R = Piperazin **Solubility:** 59,13 µM
**LASSBio-2248:** R = Methyl-piperazin **Solubility:** 70,92 µM
**LASSBio-2249:** R = Piperazin-etanol **Solubility:** 48,60 µM
**LASSBio-2250:** R = Thiomorpholino **Solubility:** 2,88 µM
**LASSBio-2251:** R = Piperidin **Solubility:** 0,51 µM
**LASSBio-2252:** R = Homopiperazine **Solubility:** 83,13 µM
**CAS-942789959:** R = Morpholine **Solubility:** 6,03 µM

## Agradecimentos/Acknowledgments

FAPERJ, CNPq, CAPES, INCT-INOFAR, LASSBio®.

**Área: MED** **Nº de Inscrição: 01352**

# Design and synthesis of new hybrids from a 1,2,4-triazole, prepared from piperine, and known nitroimidazolic drugs

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Key words: *Trypanosoma cruzi, Molecular hybridization, Piper nigrum, Antiparasitic chemotherapy, Chagas desiase.*

## Highlights

Chagas disease is a parasitosis that affects mainly developing countries. In this work we report the molecular palnning and the synthesis of novel hybrids of a 1,2,4-triazole derived from natural piperine and known nitroimidazole drugs.

## Resumo/Abstract

Chagas disease (American trypanosomiasis) is a parasitosis caused by the protozoan *Trypanosoma cruzi*. The vectorial transmission route has the insect known as "kissing bug" (*Triatoma infestans*) as the main agent. According to WHO data, this parasitosis is part of a group of diseases called neglected tropical diseases, which is the most neglected.[1] Currently, the therapeutic arsenal for the treatment of chagasic patients is very limited, with only two drugs, both of which are nitroheterocyclic derivatives, Nifurtimox and Benzonidazole; These two drugs are very limited and inefficient in the chronic phase of the disease, causing severe side effects, Our research group reported the trypanocidal effects of natural piperine and several of its derivatives. Recently, piperine's heterocyclic derivatives bearing a 1,2,4 triazolic ring (**<u>1</u> Figure 1**) were described as having important anti-*T. cruzi* effects.[2]

The molecular planning developed herein is based on the molecular hybridization of 1,2,4-triazole (**<u>1</u> Figure 1**) and the nitroimidazole portion of the know nitroheterocyclic drugs benzonidazole and metronidazole, present in both with well-described antiparasitic activity; aiming to enhance its activity through the synthesis of two novel hybrids that may act through two distinct mechanisms of action on parasite's cell. The new hybrids (**<u>2</u>** and **<u>3</u> Figure 1**) were prepared in good yields from natural piperine and and they were characterized by the methods of analysis; The main signals observed in NMR $^{1}H$ and $^{13}C$ spectra, which confirm the synthesis of these hybrids were $\delta$ 3,62 ppm (t, 2H); $\delta$ 45,22 ppm and $\delta$ 3,63 ppm (t, 2H); $\delta$ 48,59 ppm, which characterize the bond formed between $CH_2$ and Sulfur for hybrids <u>2</u> and <u>3</u>, respectively. The assessment of toxic effects of the novel hybrids <u>2</u> and <u>3</u> against *T. cruzi* amastigotes (Tulahuen C2C4 LacZ strain) is underway in our laboratory.[3]

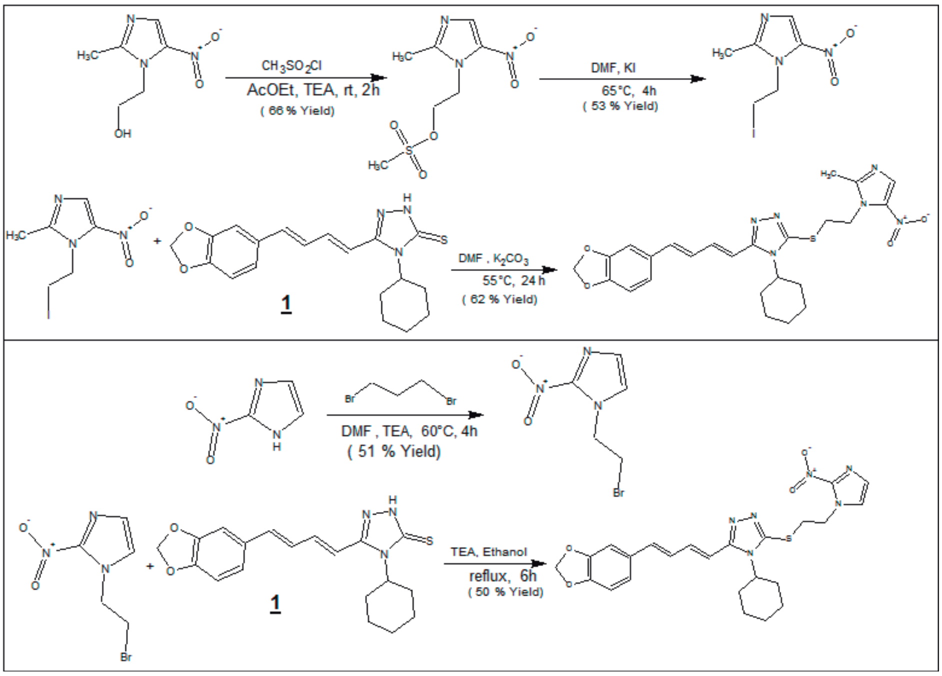

**Figure 1.** Synthetic route for the preparation of the new hybrids.

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## Agradecimentos/Acknowledgments

**CNPq, CAPES, FAPERJ**

**Área: MED** **Nº de Inscrição: 01346**

# Design and synthesis of novel *alfa*-mangostin-nitroimidazole hybrids with toxic effects on amastigotes of *Trypanosoma cruzi*

**Douglas Chaves Alcântara-Pinto (PG),[1] Afonso Santine M. Mesquita-Velez (PG),[1] Gabriella Calheiros-Magalhães[1] (IC), Paulo Pitasse-Santos (PG), Debora Decoté-Ricardo (PQ),[2] Marco Edilson F. de Lima (PQ).[1]***

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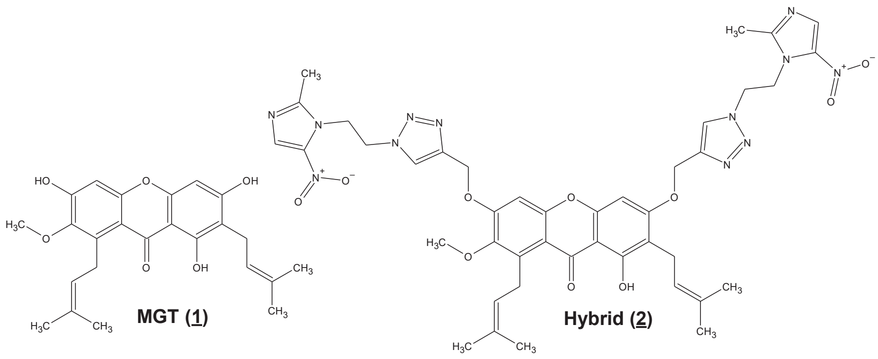
Keywords: *Chagas disease, Molecular hybridization, Click reaction, Antiparasitic chemotherapy, Garcinia mangostana.*

## Highlights

*alfa*-Mangostin (MGT) is the main product isolated from the the fruit pericarp of *Garcinia mangostana*. This xanthone exhibits important toxic effects on *T. cruzi* amastigotes. We describe herein the synthesis of new hybrid derivatives of MGT and nitroimidazoles using click reaction as the key-step. Toxic effects on intracellular amastigotes of *T. cruzi* (Tulahuen C2C4 LacZ).

## Resumo/Abstract

Mangosteen is a type of fruit that grows in the Asian region such as Malaysia, Myanmar, Thailand, Philippines, Sri Lanka and India. In 1855, MGT (**1**, **Figure 1**) was found among the major xanthones taken from the pericarps of the mangosteen fruit. This compound has been discovered to possess a wide range of biological activities, with anti-inflammatory, anti-tumor, cardioprotective, antidiabetic, antibacterial, antifungal, antiparasitic, antioxidant and anti-obesity agents.[1] American trypanosomiasis (or Chagas disease) is a parasitic illness that results from infection by the hemoflagellate protozoan *Trypanosoma cruzi*. The transmission of Chagas disease occurs primarily through the bite of an infected triatomine bug on an individual. Transmission can also occur via the placenta or breastfeeding or less commonly by oral contamination due to the consumption of fresh infected food. Although the acute phase of the infection is asymptomatic, some individuals get the chronic phase. This stage of the infection is characterized by the appearance of severe degenerative disorders in the host´s vital organs including megacolon, megaesophagus and cardiomegaly, usually culminating in death. Only two almost-100-year-old drugs are used to treat Chagas disease, namely the nitroimidazolic derivatives benznidazole and nifurtimox. However, neither of these drugs is effective during the chronic phase of the disease, and both cause numerous toxic side effects.[2] Using the molecular hybridization strategy[3] and having the Cu(I)-catalysed azide-alkyne cycloaddition (CuAAC) “click” reaction[4] as main synthetic tool, we were able to prepare the hybrid structures as shown below (**2**, **Figure 1**). The preparation of other derivatives is underway in the synthesis laboratory, as well as the evaluation of the *in vitro* anti-amastigote activity of the new hybrids obtained. In preliminary evaluation (at a concentration of 100 $\mu$M) the new hybrid (**2**) showed an inhibition of about 30% against intracellular amastigotes of *T. cruzi*. However, the biological results must be refined and repeated at lower concentrations of the inhibitor due to its low solubility under the test conditions.



**MGT (1)** **Hybrid (2)**

**Figure 1.** Structures of *alfa*-mangostin (**1**) and the novel *alfa*-mangostin-nitroimidazole hybrid (**2**).

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## Agradecimentos/Acknowledgments

**CNPq, CAPES, FAPERJ**

## Área: MED

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

# Design of new potential PI3Kδ and HDAC6 hybrid inhibitors for cancer treatment

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Palavras Chave: *molecular hybridization, histone deacetylase 6, phosphoinositide 3-kinase, anilino-purines, benzyl-hidroxamates, cancer.*

## Highlights

Pharmacophores of known PI3Kδ and HDAC6 inhibitors have been hybridized into a single entity. They were synthesized and evaluated for anticancer activity, blocking multiple signaling pathways at once.

## Resumo/Abstract

Cancer is a disease characterized by abnormal cell growth and proliferation, that can overcome treatments based solely on monotherapies. Hybrid inhibitors have the potential to overcome cancer resistance, by blocking multiple signaling pathways at once[1]. Both PI3Kδ (phosphoinositide 3-kinase δ) and HDAC6 (histone deacetylase 6) are commonly mutated on tumors and their inhibition has been shown beneficial for treatment[2,3]. To construct hybrid PI3Kδ/HDAC6 inhibitors, pharmacophores of known PI3Kδ and HDAC6 selective inhibitors bearing anilino-purines and benzyl-hydroxamates (idelalisib and nexturastat A) have been connected through a linker and hybridized into a single entity (Figure 1).

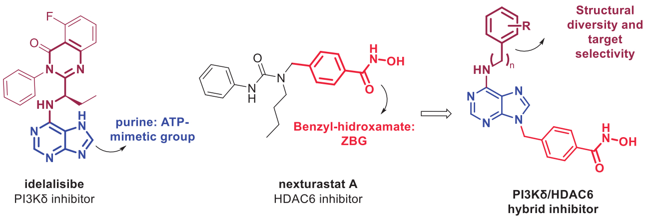

**Figure 1**: Design of idelalisib and nexturastat A hybrid inhibitors

These compounds have been synthesized in four steps and characterized by $^1$H, and $^{13}$C NMR. Their biological activity is being evaluated by cytotoxicity and mechanistic assays in solid and hematological cancer cells lineages. The results obtained for the most successful compounds are summarized in Table 1.

**Table 1**: Yields, purity and cytotoxic activities of hybrid compounds.

| Compound | Yield (%) | Purity (%) | IC$_{50}$ (µM) | | | |
|---|---|---|---|---|---|---|
| | | | HCT116 | MCF-7 | Jurkat | Namalwa |
| 4d | 53 | 98,2 | 9,30 | 9,30 | 0,02 | 0,04 |
| 4e | 60 | 97,8 | 21,7 | 31,7 | 0,03 | 0,04 |
| 4f | 50 | 95,2 | 8,30 | 19,5 | 0,05 | 0,01 |

These results are being rationalized by molecular docking simulation to propose structure-activity relationships and better understand the structural determinants for target selectivity.

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## Agradecimentos/Acknowledgments

The authors are grateful to Faculty of Pharmacy of University of São Paulo, which allowed the development of this work, Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES), for financial support and grant #2021/08260-8, from São Paulo Research Foundation (FAPESP).

**Área: MED**

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

# Evaluation of synthetic chalcones as anti-*Helicobacter pylori* and antitumoral agents and iNOS docking studies

**Jessica R.P.O. Borlot (PG),[1] Luna S. Santos (PG),[2] Guilherme J.S. Sampaio (PG)[3], Ricardo P. Rodrigues (PQ)[3], Reginaldo B. Santos (PQ),[2] Rodrigo R. Kitagawa (PQ). [1,3*]**

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Palavras Chave:*(Chalcones, iNOS enzyme, AGS cells, Molecular docking).*

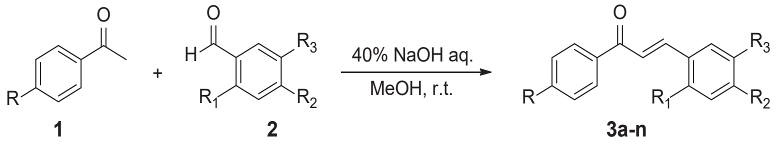
## Highlights

Five compounds showed strong to moderate anti-*Helicobacter pylori* activity;
All compounds evaluated in this study inhibited the NO production in LPS-stimulated macrophages;
Chalcones docking studies on the active site of the iNOS enzyme showed potential interactions;
Compounds **3b** and **3h** showed the highest selectivity to the cancer cell line and significant cytotoxic activity on AGS cells.

## Resumo/Abstract

*Helicobacter pylori* is a Gram-negative bacterium that colonizes the gastric epithelium of 50% of world population and the main etiological agent of human chronic gastritis and peptic ulcer. *H. pylori* infection, which is also associated with gastric cancer, induces pathological alterations and inflammatory responses. Problems in the current treatment like patient adhesion, high cost, side effects, and increase of resistant strains have boosted the search for new substances to control this infection. In this study, a series of 14 chalcones (**3a-n**) were evaluated for anti-*Helicobacter pylori*, NO inhibition, and AGS cells cytotoxic effects. We evaluated the interaction potential of chalcones at iNOS by *in silico* studies. The most active compounds showed minimal inhibitory concentrations ranging from 8 to 64 µg/mL. We observed structure-activity relationships, mainly related to the influence of methoxyl substituent at C-2 (**3b**) and the nitro group at C-4 (**3h**) in chalcone scaffold. The fourteen chalcones inhibited the NO production in LPS-stimulated macrophages and showed potential for interaction on the active site of the iNOS enzyme. Finally, **3b** and **3h** showed the highest selectivity to the cancer cell line and significant cytotoxic activity on AGS cells compared to cisplatin and the other compounds. Thus, ours results suggest **3b** and **3h** as potential candidates for design of new and effective agents against *H. pylori* and related diseases.

| Chalcone | R | $R_1$ | $R_2$ | $R_3$ |
|---|---|---|---|---|
| **3a** | H | H | H | H |
| **3b** | H | $CH_3O$ | H | H |
| **3c** | H | H | H | $CH_3O$ |
| **3d** | H | H | $CH_3O$ | H |
| **3e** | H | $CH_3O$ | $CH_3O$ | H |
| **3f** | H | H | H | Cl |
| **3g** | H | H | H | Br |
| **3h** | H | H | $NO_2$ | H |
| **3i** | H | H | H | OH |
| **3j** | H | H | $CH_3O$ | Br |
| **3k** | $NO_2$ | H | H | H |
| **3l** | $NO_2$ | H | $CH_3O$ | H |
| **3m** | $NO_2$ | H | H | Cl |
| **3n** | $NO_2$ | H | H | Br |



R = H; $NO_2$

$R_1$ = H; $CH_3O$
$R_2$ = H; $CH_3O$; $NO_2$
$R_3$ = H; $CH_3O$; Cl; Br; OH

Synthesis of substituted chalcones by *Claisen-Schmidt* condensation

## Agradecimentos/Acknowledgments

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**Área: MED** **Nº de Inscrição: 238**

# Evaluation of the urease inhibition mechanism of julolidines using biophysical studies

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*Palavras-chave: urease, julolidinas, inibidor enzimático, espectroscopia molecular.*

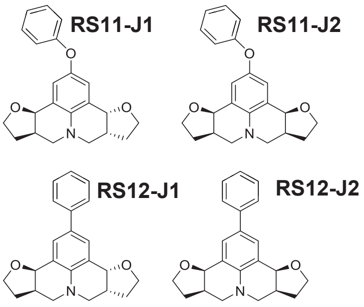
## Highlights

*In vitro* interaction between julolidine derivatives and urease. The interaction process leads to changes in the secondary structure of the enzyme and **RS12-J2** was promising urease inhibitor.

## Resumo/Abstract

As julolidinas constituem uma classe de compostos de *N*-heterocíclicos que têm em comum o anel quinolizina, uma subunidade estrutural comum em vários corantes fluorescentes. A propriedade de fluorescência permite aplicação desses compostos como sonda, em células solares, materiais fotocondutivos e como sensores para bioimagem.[1] Porém ainda não foi explorada a capacidade dos derivados de julolidinas como inibidores da atividade enzimática da urease. Nesse contexto este trabalho teve como objetivo avaliar o processo de interação *in vitro* entre derivados da julolidina (Fig. 1) e urease (*Canavalia ensiformis*, Jack bean) por espectroscopia molecular.

**Figura 1**. Estruturas dos derivados da julolidinas.



Na avaliação do processo de interação notou-se diminuição na fluorescência intrínseca da urease (2 μM) usando excessos das julolidinas (20 - 200 μM), caracterizando ocorrência de *quenching.* O mecanismo preferencial de *quenching* foi avaliado com base nos valores de constante de velocidade bimolecular difusional ($K_q$) os quais variaram de 5,91 a $7{,}60\times10^{11}$ $M^{-1}$ $s^{-1}$ para os compostos **RS11**, e de 1,49 a $3{,}41\times10^{12}$ $M^{-1}$ $s^{-1}$ para os compostos **RS12**. Uma vez que $K_q > 2{,}0\times10^{10}$ $M^{-1}$ $s^{-1}$, foi possível inferir que o mecanismo de *quenching* é preferencialmente estático com formação de complexo supramolecular. Os valores da constante de ligação ($K_b$) obtidos com base no seguinte modelo matemático de Scartchard variaram de 1,16 a $25{,}94\times10^{4}$ $M^{-1}$ para os compostos **RS11,** sendo menores quando comparados com o par de enantiômeros dos compostos **RS12** (0,01 a $7{,}33\times10^{6}$ $M^{-1}$) para o intervalo de 22 a 38ºC, sugerindo que os derivados **RS12** possuem maior afinidade pela urease. Os estudos cinéticos (método de Berthelot)[2] mostraram que valores das constantes de inibição ($K_i$) foram estatisticamente similares ao valor médio de 980 μM, no entanto apenas o **RS12-J2** atuou como inibidor estritamente competitivo. Dessa forma, os demais ensaios foram realizados com **RS12-J2**. O ensaio por UV-vis com níquel confirmou que **RS12-J2** interage com o íon metálico presente no sítio catalítico. Empregando fluorescência sincronizada foi possível verificar que **RS12-J2** interage preferencialmente próximo ao resíduo de tirosina (Tir), provavelmente devido à presença de Tir nas posições 410 e 544 próximos aos principais resíduos de histidina (posições 409 e 545), as quais são responsáveis por coordenar átomos de Ni no sítio ativo da enzima. O estudo de transferência de energia ressonante mostrou que a distância entre doador (urease) e receptor (**RS12-J2**) foi 3,96 nm. O estudo por fluorescência 3D comprou mudanças na estrutura secundária em relação a proteína nativa. Além disso, foi avaliada a influência de alguns inibidores clássicos na interação por ensaio de competição. A relação constante de ligação da urease ($K_b/K_b'$), na qual $K_b$ e $K_b'$ referem-se à constante de ligação na presença e ausência de um competidor, respectivamente, foi utilizado para comparação. A formação de complexos é favorecida quando a razão é maior que 1. Assim, foi possível observar que os valores da razão foram de 0,31; 0,06; 0,52; 0,12 e 0,13 na presença dos inibidores hidroxiureia, omeprazol, tioureia, NBPT e ácido acetohidroxâmico, respectivamente, indicando que o composto está competindo pelo sítio ativo. Portanto, é possível concluir que o composto **RS12-J2** apresenta capacidade inibitória da atividade enzimática da urease, podendo ter uma aplicação promissora do ponto de vista agrícola e/ou clínica.

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## Agradecimentos/Acknowledgments

PPGQB-IQB-UFAL; FAPEAL, Capes-Procad; CNPq, FAPEMIG.

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

# Exploring Synthetic Approaches on Pyrrolobenzodiazepines Structures to Discovering New Drugs with Anticancer Activities

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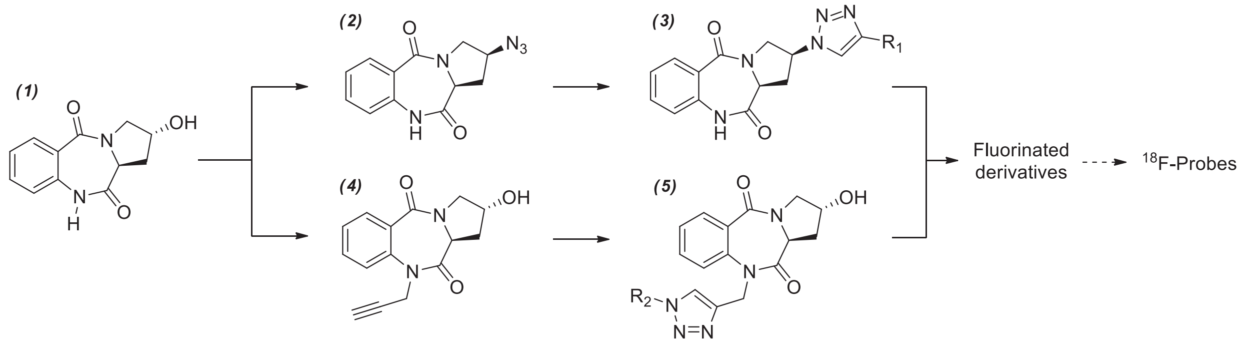
Keywords: *Pyrrolobenzodiazepines, Drug-discovery, Deoxyfluorination, Radiochemistry, PET-scan.*

## Highlights

Exploring Synthetic Approaches on Pyrrolobenzodiazepines Structures (PBD) to Discovering New Drugs with Anticancer Activities. PBD's are known as potential structures to act against cancer cells. The general activities occur through *minor groove DNA* interactions acting as a Michael acceptor. Some variations on PBD structures can find new modes of action and reveal specifics activities and applications such as introducing radiolabeling $^{18}F$ to treat cancer lines and shows high-resolutions images by *PET-scan*.

## Resumo/Abstract

Pyrrolobenzodiazepines (PBDs) are known since 1960's. These structures have natural occurrence and figure like a class of antitumoral substances, acting as DNA minor groove binding agents, with good prospect, considering low possibility to drug resistance, once the action mechanism can occur directly on the DNA helix. Our substances will be checked throw the activities against cancer cell lines such as SNB-19 (glioblastoma), HCT-116 (colorectal), PC-3 (prostate) and HL (leukemic). To modulate the biological activity and enhance the PBD promoted growth inhibition of cancer cells, were introduced different substituents linked with a triazole via a CuAAC reaction. Structural modifications were made, such as the introduction of fluorinated moieties which can not only modulate the lipophilic character of the synthesized compounds (enhanced metabolic stability), but also allow further exploration of the molecular interactions (by way of $^{19}F$ NMR and affinity photolabeling) by deoxyfluorination on hydroxyl groups with *SulfoxFluor* as well as development for *in vivo* imaging using positron emission tomography using $^{18}F$.



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CAPES-PrInt, CAPES, CNPq, CNRS

**Area:** MED

# Fast and inexpensive assay to monitor ornithine decarboxylase activity through benzoylation reactions

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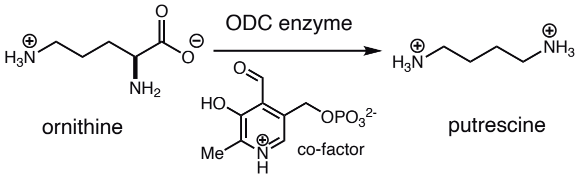
Keyword: *ornithine, putrescine, screening assay, NMR analysis*

## Highlights

Ornithine decarboxylase (ODC) is a target for several diseases, mainly cancer. Herein we intend to develop a suitable protocol to monitor ODC activity through the generation of benzoylated forms of ornithine and putrescine making it possible to easily differentiate them by chromatography and spectroscopic techniques.

## Abstract

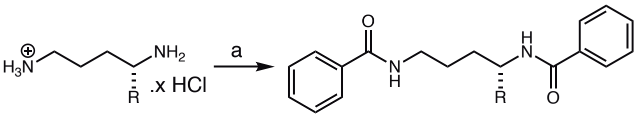
Enzymes are important therapeutic targets for drug discovery. The identification of new, specific, and potent modulators of enzyme function depends on the development of reproducible and efficient *in vitro* assay methods, which allow the rapid screening of small molecules that can act as enzyme inhibitors. Ornithine decarboxylase (ODC) is an important enzyme of redox metabolism. It catalyzes the decarboxylation of ornithine to putrescine with the help of a co-factor pyridoxal 5'-phosphate (Scheme 1). This enzyme is of great importance for the development of drugs for various diseases, especially cancer and parasitic diseases.[1]



**Scheme 1.** Ornithine decarboxylation by ODC

Currently, the methods used to monitor ODC in activity assays are complex, with several steps, or involve radioactive elements or expensive reagents for fluorescence analysis. In this work, we intend to develop a faster and lower-cost method to be used in the screening of many molecules.

We started the studies with the synthesis of benzoyl-ornithine and benzoyl-putrescine standards by the reaction with benzoyl chloride, NaOH, $Na_2CO_3$ in water at room temperature for 2 hours providing the desired products in quantitative yields (Scheme 2).[2]



R = $CO_2H$, x = 2 (L-ornithine)
R = H, x = 1 (putrescine)

R = $CO_2H$, (L-benzoyl-ornithine)
R = H, (benzoyl-putrescine)

a. NaOH (4,5 equiv), $Na_2CO_3$ (2 equiv), $H_2O$, rt, 2h

**Scheme 2.** Benzoylation of ornithine and putrescine

The enzymatic reaction is performed with the recombinant *Leishmania donovani* ODC (*Ld*ODC), expressed and purified by our group. To validate the protocol, we prepared the enzymatic reaction medium adding *Ld*ODC (50 μg/mL) to a mixture containing β-mercaptoethanol (2.5 mM), EDTA (1.5 mM), pyridoxal phosphate (75 nM) and L-ornithine HCl (3 mM) in 150 mM phosphate buffer (pH 7.1). Then, the pH of the medium was adjusted to 14 with 4M NaOH solution before 2.5 equivalents of benzoyl chloride were added. After stirring for 5 min, 20 min, and 2 hours, the reactions were diluted with acetone and analyzed by $^1H$ NMR. We also performed a blank control experiment following the same protocol with a reaction medium without L-ornithine, as well as a positive control experiment, using a reaction medium with a 1:1 molar ratio of L-ornithine and putrescine.

We were able to observe the complete consumption of ornithine and putrescine followed by formation of benzoylated products in all experiments where the reaction was carried out for 2 hours, through both the absence of starting materials signals in the region of 2.5-2.9 ppm and the presence of clear and characteristic signals of the products in the region of 2.4-2.8 ppm, 3.3-3.4 ppm and 7.65-7.75 ppm in $^1H$ NMR analysis.

As perspectives, we intend to analyze this protocol by HPLC and employ it in different enzymatic reactions.

## Acknowledgments

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**Área: MED** **Nº de Inscrição: 1164**

# Formulation and Evaluation of a Novel Itraconazole-Clotrimazole Topical Emulgel for the Treatment of Sporotrichosis

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Keywords: *Emulgel; Sporotrichosis; Itraconazole; Clotrimazole; Topical drug delivery systems*

## Highlights

A new stable formulation was prepared, fully characterized and had its *in vitro* antifungal activity evaluated. The emulgel was considered an optimal vehicle for the topical administration of itraconazole and clotrimazole against *S. brasiliensis*.

## Resumo/Abstract

Sporotrichosis is a subcutaneous mycosis caused by the thermodimorphic *Sporothrix* fungi.[1] The therapy for sporotrichosis includes itraconazole, the first line treatment for humans and cats. However, failure cases in human and feline treatment have been reported in recent years. Since epidemiological trends associated with the emergence of drug resistance have been identified, the development of new drugs for the treatment of sporotrichosis have been encouraged.[2] In this sense, the present work aimed to developed a new emulgel containing two highly active drugs against this widespread disease: clotrimazole and itraconazole. The new stable emulgel was prepared, fully characterized and had its *in vitro* antifungal activity evaluated. The results of this work confirm the great potential of emulgels as an alternative for topical delivery of hydrophobic drugs, as evidenced by its potent inhibitory activity *in vitro*. To our delight, is was proved that itraconazole and clotrimazole can be successfully combined and delivered topically in the form of an emulgel, which could be a complementary therapy to oral administration for sporotrichosis. We have observed that the newly developed emulgel displays all the required physicochemical properties for such application, also being capable of maintaining the drugs content over time.

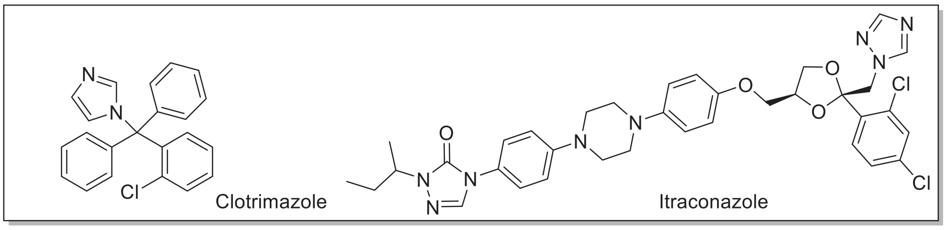

**Figure 1.** Structures of the clotrimazole and itraconazole.

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## Agradecimentos/Acknowledgments

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

# Fragment-Based Drug Design (FBDD) Approach to Develop Antiviral Compounds Targeting NS2B/NS3 from Zika and Dengue Viruses

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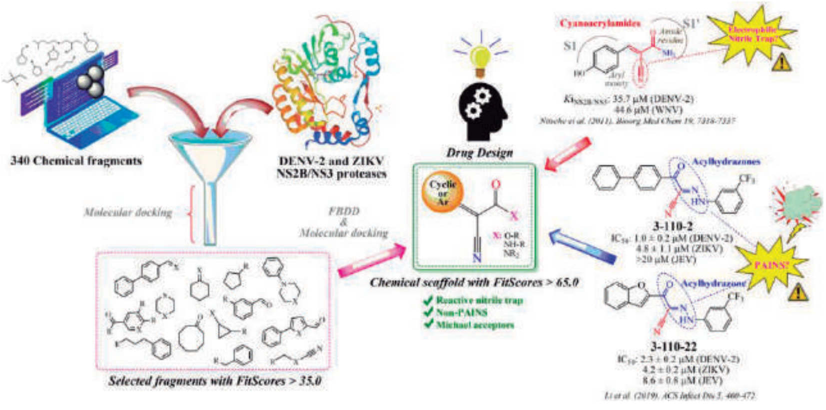
Keywords: NS2B/NS3; Serino protease; Synthesis; Drug design; molecular dynamics; MM/PBSA.

## Highlights

- α-Cyanoacrylamides via Knoevenagel condensation;
- $K_i$ value of 7 μM against DENV-2 NS2B/NS3 protease;
- Dixon plot showed a mixed activity on NS2B/NS3;
- MM/PBSA corroborated the experimental results.

## Resumo/Abstract

Dengue (DENV) and Zika (ZIKV) viruses are flaviviruses transmitted by *Aedes* sp. mosquitoes, being responsible for severe cases of infections worldwide. Up to date, there is still no specific and effective treatments of these infections. Thus, the search for new antiviral alternatives is an unmet need. In the present work, 340 chemical fragments were virtually screened on NS2B/NS3, via FBDD. Then, 5-phenyl-2-cyanoacrylamides were synthesized and evaluated against NS2B-NS3 protease from ZIKV and DENV. Thus, it was verified that two derivatives were able to act as inhibitors targeting both serine proteases, with $K_i$ values of ~ 7 μM. In addition, their selectivities were evaluated against other proteases from trypsin-like family. Finally, dynamics simulations and MM/PBSA studies were used to analyze their interactions, corroborating the experimental data. The figure below exhibits the workflow used in our work.



## Agradecimentos/Acknowledgments

**Área: MED** **Nº de Inscrição: 1426**

# INDOL-THIAZOL DERIVATIVES: DNA INTERACTION AND DOCKING STUDIES

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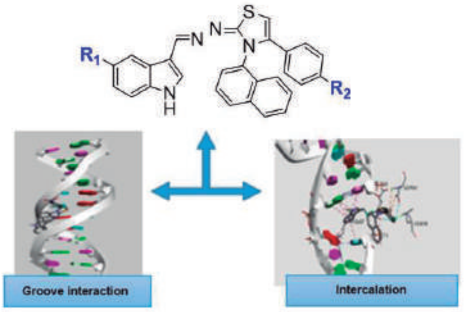
Keywords: Thiazole, DNA, Molecular Docking, UV-Vis.

## Highlights

Agents that can act on DNA are object of study in the development of chemotherapic agents. In this context, eight indole-thiazoles were evaluated *in silico* and *in vitro* as DNA ligands. *In silico* and spectroscopic studies have shown satisfactory results, making this series promising as antitumor agents.

## Abstract

DNA is a key receptor in the investigation of many cancer therapies. The binding of small molecules with DNA in a covalent or non-covalent manner can affect key steps of the cell cycle, intervening in the stages of transcription, replication and in the expression of genetic information in cells, causing inhibition of tumor cell growth (LAFAYETTE et al., 2017). In this context, a series of indole-thiazoles that are candidates for antitumor agents were evaluated through interaction with DNA using UV-vis spectroscopic assays, accompanied by molecular docking (Scheme 1).



**Scheme 1.** Thiazole-DNA interaction study

The docking study was done in Autodock and two modes of non-covalent interaction were analyzed. The interaction with the minor groove was observed through docking with the rigid crystallographic structure of DNA. Binding energy values below -9.00 kcal mol$^{-1}$ suggested the formation of thiazole-DNA complexes. In the 3D complexes, hydrophobic interactions were observed with the adenine and thymine bases. The intercalation was analyzed through the crystallographic structure of the TOPO IIα enzyme complexed to DNA. The formation of ternary complexes with binding energies lower than -10.00 kcal mol$^{-1}$ indicated intercalation with DNA base pairs through the aromatic portion of thiazole or indole.

In the UV-vis absorption spectroscopy assay, the compounds' spectra were plotted from experiments involving free compounds in a 30 μM concentration, complexed with ct-DNA in different concentrations, which led to significant hyperchromism (19-65%).The experimental data for each compound was used to obtain an intrinsic binding constant (Kb) (Table 1).

**Table 1.** Kb values of thiazole-DNA complex formation

| **R1: R2** | H:H | H:F | H:$NO_2$ | H:Ph | Br:$NO_2$ | Br:H | Br: F | Br:F |
|---|---|---|---|---|---|---|---|---|
| **Kb ($M^{-1}$)** | 6,4x $10^4$ | 1,4x $10^5$ | 3,6x $10^4$ | 2,1x $10^5$ | 2,8x $10^5$ | 2,1x $10^5$ | 2,0x $10^4$ | 1,5x $10^5$ |

The constant value is useful to indicate the non-covalent binding modes with DNA (intercalation: $10^4$ to $10^6$ $M^{-1}$; groove interaction: $10^5$ to $10^9$ $M^{-1}$) (RESCIFINA et al., 2014). The values in Table 1 show, in their majority, intermediate values in the order of $10^5$. The presence of unfused rings with torsional degrees allows a certain flexibility for the two connection modes. Based on the obtained results combined with docking, it is possible to predict that the analyzed ligands interact with the DNA sequence in a way that is most susceptible to the molecule in the physiological environment.

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RESCIFINA, A.; ZAGNI, C.; VARRICA, M. G.; PISTARÀ, V.; CORSARO, A. European Journal of Medicinal Chemistry, v. 74 , p. 95-115, 2014.

## Acknowledgments

CNPq-UFPE, LaSC- UFRPE, LIKA-UFPE, CCS-UFPE

**Área: MED___________ Nº de Inscrição: 01166_____**

# Integrative docking, machine learning models and experimental evaluation for identifying new Zika envelope glycoprotein hits

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Keywords: Zika virus, Envelope Glycoprotein, Virtual screening, Docking, Machine Learning.

## Highlights

Virtual screening against Zika virus (ZIKV) envelope glycoprotein (E) revealed seven promising virtual hits. Biophysical and enzymatic assays validated the computational strategy and showed that two compounds inhibited ZIKV protein E activity in nanomolar range. Cell assays will be performed to evaluate the antiviral activity.

## Abstract

ZIKV rapidly spread and caused a massive epidemic in 2016[1]. Despite causing mild symptoms, the major concern about ZIKV regards the severe neurological disorders, such as microcephaly and Guillain Barre syndrome[2]. Currently, there are still no approved antivirals to treat the infection. The envelope glycoprotein (E) is responsible for the virus entrance and represents one of the main antibody binding sites, being a promising target for drug and vaccine development[3]. In this study, we performed a virtual screening of the ChemBridge dataset against ZIKV E protein. The E binding sites are not described in literature. Thus, first, we predicted the druggable binding sites using the FTsite and PockDrug servers. We identified two binding sites: between the DI-DIII domains and in the dimerization interface. The screening based on docking at the DI-DIII site prioritized 1,361 compounds with binding affinity energy $\leq -7.0$ kcal·mol$^{-1}$. Thereafter, we used a phenotypic machine learning (ML) filter to predict active compounds which prioritized 43 molecules. We also used ML Bayesian Zika models, PAINS and blood-brain barrier permeability filters, as well as visual inspection of docking poses, prioritizing seven virtual hits to be evaluated experimentally. Biophysical and enzymatic assays were performed and two compounds inhibited ZIKV protein E activity in nanomolar range. Cell assays will be performed to evaluate their antiviral activity.

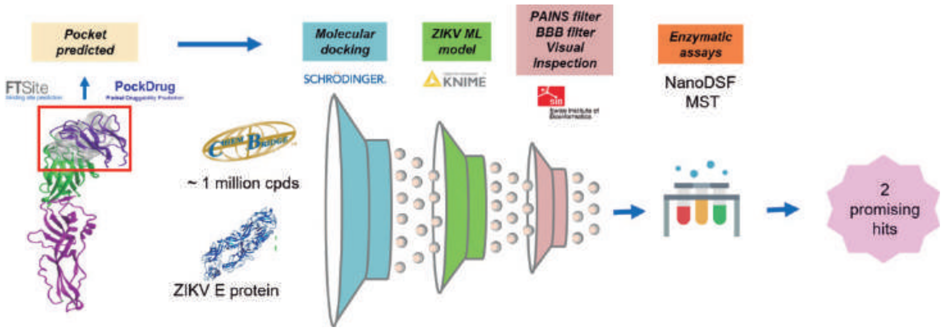

**Figure 1.** Workflow of ZIKV envelope protein virtual screening

## Acknowledgments

CNPq, FAPEG, Collaborations Pharmaceuticals, IBM, World Community Grid.

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**Área: MED**

# Interactions between tanshinones and derivatives with PAI-1, a possible new class of anticoagulants

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Palavras Chave: *Tanshinone, Salvia hispanica L., PAI-1, Anticoagulants, Docking*

## Highlights

- Warfarin is behind ~30% of preventable adverse hospital events;

- Tanshinones are natural lipophilic abietane diterpenes;

- Tanshinones are the most active anticoagulants in *Salvia hispanica* L. (chia).

## Resumo/Abstract

Hypercoagulation disorders, such as venous thromboembolism, are characterized by the production of clots, usually in the walls of deep veins, which, when detached, are carried by the bloodstream to the smaller vessels of the lungs. In the lungs, they interrupt blood flow and cause the so-called pulmonary embolism, a clinical condition that is usually asymptomatic and associated with a high risk of death. Aiming to develop effective and safer oral anticoagulants, this work proposes the synthesis of compounds capable of blocking the action of the plasminogen activator inhibitor type 1 (PAI-1), whose high plasma levels are correlated with thrombolytic disorders, such as myocardial infarct and other diseases linked with coronary arteries. To this end, tanshinones, lipophilic compounds, which are the main compounds responsible for the anticoagulant properties of *Salvia hispanica* L. (chia), will be used as starting compounds, which, when consumed *in natura*, unfortunately, show low efficacy in reducing risk factors for cardiovascular diseases. Therefore, the *in silico*-identified target compounds, with two promising lead compounds discovered so far, will be synthesized, characterized, and tested against PAI-1 before running *in vitro* anticoagulant tests. Our lead compounds show great similarities with cryptotanshinone, so, in the second part of this research, natural tanshinones isolated from the *S. hispanica* extracts are going to be tested against PAI-1 *in vitro* as well. The structural modification with fluorination of cryptotanshinone and its derivatives might ameliorate the physical-chemical features of these compounds, their solubility, bioavailability, and add-to anticoagulant properties.

## Agradecimentos/Acknowledgments

I thank the computational biology research group at Embrapa Agricultura Digital, for all the digital resources that enabled me to run *in silico* analyses of this project, CAPES for the scholarship, the faculty of pharmaceutical sciences, and the biological chemistry laboratory at the Institute of Chemistry, University of Campinas, for having welcomed me during these difficult times.

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

# *In vitro* biological evaluation of novels phthalimide-thiazole derivates Against *leishmania spp.*

**Fabiano Amaro de Sousa (PG)[1,2,*], Aline C. Santos (PG)[3], Juliana M. Conceição (PG)[2], Ignes R. Santos (PG)[2], Mabilly C. Holanda (IC)[2], Valéria Pereira (PQ)[3], Ana Cristna L. Leite (PQ)[2.]**

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Palavras Chave: *Medicinal Chemistry, Leishmania, Phathalimide-thiazole.*

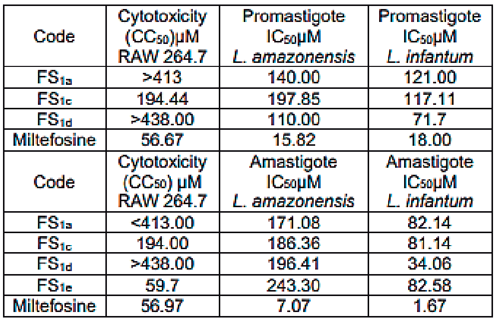
## Highlights

The biological activity of the novel compounds was tested Against *Leishmania amazonensis* and *infantum*. As 1result, three showed activities against the promastigote form and four against the amastigote form.

## Abstract

The compounds were based on the works of SILVA, 2013, and ALIANÇA et. al., 2017, Two of them are demonstrated in Figures 2a and 2b respectively. These compounds showed the best biological activity in their work. All structures of the synthesized compounds are shown in **figure** 1 and the biological activity is present in table 1. Therefore, this paper aims to synthesize other phthalimide-thiazole derivates as building blocks and to evaluate their biological activity. As result, just **FS$_{1d}$ (IC$_{50}$ 110.00µM)** and **(IC$_{50}$ 71.7µM)** showed relevant activity against the promastigote form of *L. amazonensis* and *L. infantum* respectively, to the amastigote form also **FS$_{1d}$ (IC$_{50}$ 34.06µM)** showed relevant activity against *L. infantum*. A possible justification for the low activity presented on the compounds is that whether the compound has a small group in the middle of the phthalimide-thiazole core the biological activity should increase, it can be demonstrated by SILVA, 2013 in **figure 2a,** their best compound has a hydrazine group and showed an **IC$_{50}$ 7.0µM**. Beyond that, ALIANÇA, et. al., 2017 also demonstrated in figure 2b that a secondary amine in the middle of phthalimide-thiazole core most increase the activity, their best compound showed an **IC$_{50}$ 13,9µM**. Both compounds were evaluated to the same target.

Table 1: biological activity of the compounds



| Code | Cytotoxicity (CC$_{50}$)µM RAW 264.7 | Promastigote IC$_{50}$µM *L. amazonensis* | Promastigote IC$_{50}$µM *L. infantum* |
|---|---|---|---|
| FS$_{1a}$ | >413 | 140.00 | 121.00 |
| FS$_{1c}$ | 194.44 | 197.85 | 117.11 |
| FS$_{1d}$ | >438.00 | 110.00 | 71.7 |
| Miltefosine | 56.67 | 15.82 | 18.00 |
| Code | Cytotoxicity (CC$_{50}$) µM RAW 264.7 | Amastigote IC$_{50}$µM *L. amazonensis* | Amastigote IC$_{50}$µM *L. infantum* |
| FS$_{1a}$ | <413.00 | 171.08 | 82.14 |
| FS$_{1c}$ | 194.00 | 186.36 | 81.14 |
| FS$_{1d}$ | >438.00 | 196.41 | 34.06 |
| FS$_{1e}$ | 59.7 | 243.30 | 82.58 |
| Miltefosine | 56.97 | 7.07 | 1.67 |

Figure 1: Structures of the active compounds

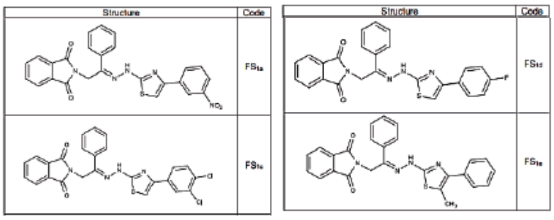
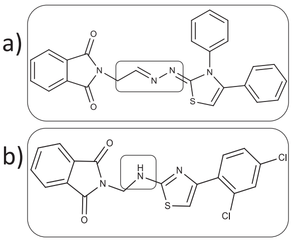


Figure 2: structure of compounds



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## Acknowledgments

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# LASSBio Chemical Library: characterization and molecular repositioning studies.

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*3 Instituto Nacional de Ciência e Tecnologia de Fármacos e Medicamentos (INCT-INOFAR; http://www.inct-inofar.ccs.ufrj.br/), CCS, Universidade Federal do Rio de Janeiro, Cidade Universitária, Rio de Janeiro, RJ, Brasil*

Keywords: *Medicinal Chemistry, Chemical Library, Repositioning, Repurposing, Screening.*

## Highlights

Studies of the LASSBio Chemical Library highlighted its adherence to pharmacokinetic parameters. A molecular repositioning study led to identification of SARS-CoV-2 Main Protease ($M^{PRO}$) hit.

## Abstract

**BACKGROUND:** The LASSBio Chemical Library (LCL) contains *ca.* 2300 compounds and the library content selection has been driven by medicinal chemistry concepts. In this work, content characterization of the LCL, and virtual screening of this library against SARS-CoV-2 $M^{PRO}$ is presented.[1]

**METHODS:** *In silico* preparation steps of LCL were performed in KNIME platform. Preliminarily pharmacokinetic (PK) and pharmacodynamic (PD) profiles were determined using Percepta (ACD/Labs, 2012) and Clarivate Analytics – Integrity, respectively. Docking-based virtual screening was performed using GOLD 2020.

**RESULTS:** Cluster-based analysis led to the identification of 6 main chemotypes (1-6) of the LCL (Figure 1). PK profile analysis of this library showed that 85% of its compounds are compliant with Lipinski's Ro5, and 95% with Veber's rules. PD profile analysis showed that compounds of this library target the main families of molecular targets modulated by FDA-approved drugs. Virtual screening allowed the identification of LASSBio-1945 (7) as a $M^{PRO}$ hit ($IC_{50}$ = 15.97 μM), among 8 compounds assayed (Figure 1).[2]

**CONCLUSIONS:** Characterization studies of the LCL highlighted its adherence to PK and PD trends of the drug discovery and development process. A molecular repositioning study led to identification of a $M^{PRO}$ hit, which represents an interesting starting point for subsequent hit-to-lead optimization steps.

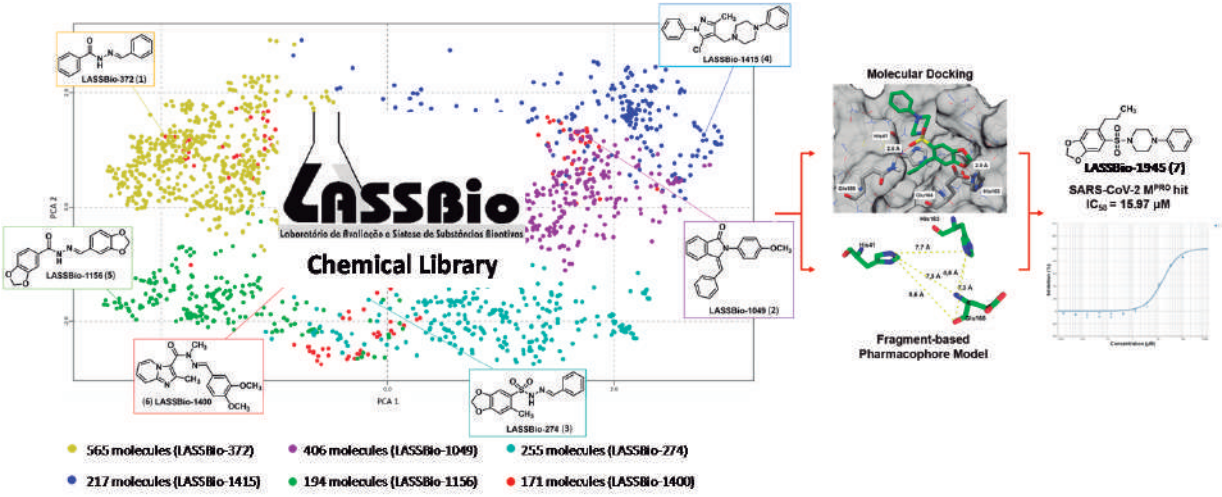

Figure 1. Main chemotypes of the LCL, and virtual screening leading to LASSBio-1945 (7) identification.

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## Acknowledgments

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**Área: MED**

# Ligand-Based Drug Design Studies for a Series of Oxazole and Oxadiazole Derivatives with Antileishmanial Activity

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Keywords: *QSAR, leishmaniasis, Leishmania, oxadiazoles, oxazoles, AutoQSAR.*

## Highlights

A robust and predictive 2D Quantitative Structure-Activity Relationship (QSAR) model was developed for a series of oxazole and oxadiazole derivatives with antileishmanial activity.

## Abstract

Leishmaniasis is a neglected tropical disease (NTD) that affects 12 million people worldwide. Visceral leishmaniasis, caused by *Leishmania donovani* and *Leishmania infantum*, is the most serious form of the disease, causing high mortality rates if not treated properly. The available treatment is complex, long, and presents high toxicity. Therefore, the development of novel, safe and effective drugs for visceral leishmaniasis is highly urgent. In this study, a ligand-based drug design (LBDD) approach was conducted. Two-dimensional Quantitative Structure-Activity Relationship (QSAR) models, using the AutoQSAR method, were developed for a series 62 compounds that are active against *L. infantum* ($IC_{50}$ values from 2.38 to 52.59 μM).[1,2] The best models, generated after clustering analyses, had high internal consistency and external predictive power. $R^2$ values of 0.90 and 0.82, and $Q^2$ values of 0.82 and 0.80 were obtained for the top two AutoQSAR models. Additionally, the 2D contribution maps indicated key structural features most closely related with the biological activity of the compounds (**1**-**2**, **Figure 1**). These findings demonstrate the usefulness of the AutoQSAR models to guide the design of novel antileishmanial agents structurally related with the investigated data set.

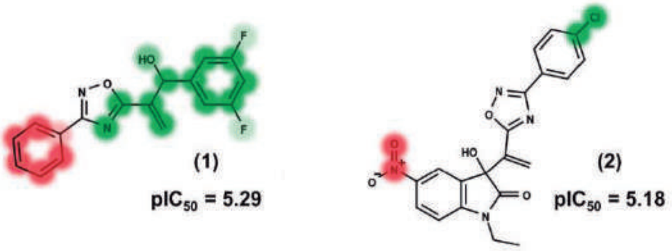

**Figure 1**. Contribution maps generated for two dataset compounds. Green represents positive contributions to the biological activity and red represents negative contributions.

### References

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## Acknowledgments

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**Área: MED**

# [$^{89}$Zr]Zirconinum radiolabeling antibodies and minibodies for molecular imaging in a preclinical model of A549 non-small cell lung cancer

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Palavras Chave: *Antibody, [$^{89}$Zr]Zirconinum, Radioisotope, Positron emission tomography, Molecular imaging, Autoradiography.*

## Highlights

DFO conjugated antibody and minibody anti-Tn antigen were radiolabeled with [$^{89}$Zr]zirconium. In vivo biodistribution in mice bearing lung A549 tumor showed intense antibody uptake in the tumor and lower concentration for the minibody.

## Abstract

Cancer diagnostic and therapy has handled billion dollars in drugs discovery, including small synthetic molecules, biomolecules, and gene therapy. Antibodies and their fragments are powerful molecules for therapy since they are selective to antigens on the tumor cells. Nowadays, antibodies have been labeled with radioactive compounds allowing to localize it by imaging or, using beta emissior, improving therapeutic efficacy. At this work, antibody and minibody produced at Institut Pasteur de Montevideo, were conjugated with *p*-SCN-Bn-DFO under pH 9 buffered solution and purified in a PD-10 gel size exclusion column. [$^{89}$Zr]zirconium was produced by nuclear reaction $^{89}$Y(*p*,*n*)$^{89}$Zr in a 16,5 MeV cyclotron, installed at Hospital das Clínicas-FMUSP. $^{89}$ZrCl$_4$ was purified by solid-phase hydroxamate column, transformed in oxalate salt, and complexed by DFO chelator conjugated in the biomolecules. Radiochemical purity was assessed by planar chromatography. Lung A549 tumors bearing nude mice were injected with $^{89}$Zr radiolabeled biomolecules and imaged in a small animal dedicated positron emission tomograph (PET) in a longitudinal study of the hour for the minibody and days for the antibody. After the final image, animals were euthanized, tumors were removed and submitted to autoradiographic imaging, exposing 30 μm sliced sections to a phosphor imaging plate, and scanned in the Typhon scanner. Radiolabeling efficiency was 90 % for the antibody and 85 % for the minibody.Standard value uptake (SUV) for [$^{89}$Zr]-DFO-Bn-Tn antibody changed from 0.5 at the first hour after injection to 1.3 at 24 h, remaining constant at 48 and 72 h. For [$^{89}$Zr]-DFO-Bn-Tn minibody SUV was 0.5 at the first hour and remained constant for 24 h. Autoradiographic analysis showed the concentration of radiolabeled compound mainly at the peripheric region of the tumor. The results allow to conclude that antibody was more efficient in binding Tn antigen than minibody. Furthermore, we have established a platform to produce radiolabeled biomolecules and performe pre-clinical trials.

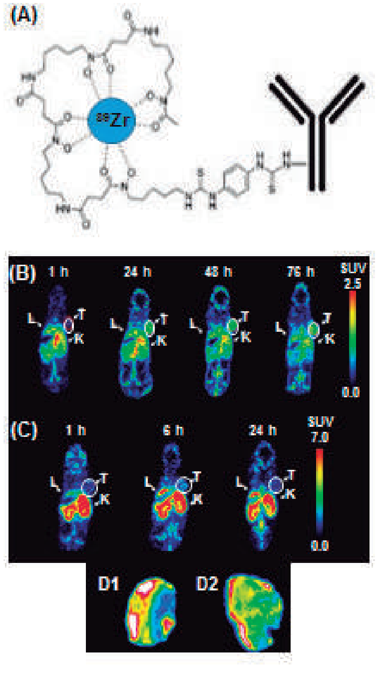

**Fig. 1: (A)** $^{89}$Zr-DFO-Bn-biomolecule. **(B/C)** Biodistribution imaging of the $^{89}$Zr-DFO-Bn-Tn antibody and $^{89}$Zr-DFO-Bn-Tn minibody. **(D1/D2)** Autoradiographic image of tumor slices labeled with $^{89}$Zr-DFO-Bn-Tn antibody and $^{89}$Zr-DFO-Bn-Tn minibody.
L = liver, K = Kidney, T = Tumor.

## Acknowledgments

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**Área:** MED

# Luminescent nitrogen-doped graphene quantum dots for biomedical applications

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Palavras Chave: graphene quantum dots, luminescence, cytotoxicity

## Highlights

N-GQDs with up to 7.2% of nitrogen have planar topology with about 1.0 - 1.5 nm of height and 35±10 nm of lateral size and photoluminescence emission at 510 nm. N-GQDs are re-dispersible in physiological solution. N-GOQDs exhibit high compatibility with Vero cells.

## Resumo/Abstract

Rational synthesis and simple methodology for purification of large (35-45 nm in lateral size) and flat (1.0 – 1.5 nm of height) nitrogen-doped graphene oxide quantum dots (GQDs) are presented. The methodology allows robust metal-free and acid-free preparation of N-GQDs with a yield of about 100% and includes hydrothermal treatment of graphene oxide with hydrogen peroxide and ammonia. It was demonstrated that macroscopic impurities can be separated from N-GQDs suspension by their coagulation with 0.9% NaCl solution. Redispersible in water and saline solutions particles of N-GQDs were characterized using tip-enhanced Raman spectroscopy (TERS), photoluminescent, XPS, and UV-VIS spectroscopies. The procedure proposed allows to obtain nitrogen-doped GQDs having 60-51% of carbon, 34-45% of oxygen, and up to 7.2% of nitrogen. Application of TERS allows demonstrate that the N-GQDs consist of graphene core with an average crystallite size of 9 nm and an average distance between nearest defects smaller than 3 nm. Nitrogen dopants in N-GQDs are mainly allocated in the graphene basal plane, while oxygen ones are on the particle edges in form of carboxylic groups that ensure the particle solubility in water and physiological solutions. Due to essential variation in the particle size and chemical composition, samples of N-GOQDs demonstrate excitation-dependent photoluminescence with emission at 460 – 520 nm that can be excited by visible light. The N-GOQDs have exhibited outstanding compatibility with the monkey epithelial kidney cells (Vero), which are used in COVID-19 research, resulting in almost 100% viability. This fact proves the effectiveness of the applied techniques to prepare stable luminescent dispersions of GOQDs for further relevant uses.

## Agradecimentos/Acknowledgments

Authors are grateful for financial support received from FAPERJ (grants E-26/010.155/2020, E-26/010.978/2019 and E-26/010.1556/2019) and CNPq (grants 306992/2018-3, 438450/2018-3). This research used facilities of LNNano (CNPEM). The Spectroscopy and Scattering staff of LNNano is acknowledged for their assistance during the experiments (XPS-20220035). The AFM staff of LNNano is acknowledged for their assistance during the experiments (AFM-27716). The authors thank INMETRO and UFMG for the PTTPs nanoantennas used in the TERS experiment. We also acknowledge the help of Professor Ricardo Queiroz Acélio (PUC-Rio) in obtaining and interpreting fluorescence spectra.

**Área: MED**

# Mechanistic Studies of Licarin A Derivatives on *Leishmania (L.) infantum*

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Key words: *Leishmaniasis*, *Natural Products, Licarin A, Mechanism of Action, Therapy*

## Highlights

Licarin A derivatives presents a potent anti-*L. (L.) infantum* activity.
Compound 1c increases calcium levels and alkalinize the acidocalcisomes.
Compound 1c induces hyperpolarization of parasite mitochondria.
Compound 1c promotes protein mass spectrum alterations.

## Resumo/Abstract

Natural metabolites from plants represent an extraordinary source of compounds with a high chemo-diversity and have been widely used as inspiration for the design of new drug candidates. Considering the need for new treatments against the neglected parasitic disease leishmaniasis, three semi-synthetic derivatives of natural neolignane licarin A were prepared: O-acetyl (1a), O-allyl (1b), and 5-allyl (1c). Using an *ex vivo* assay, compounds 1a, 1b and 1c showed activity against the intracellular amastigotes of *Leishmania (L.) infantum*, with $IC_{50}$ values of 9, 13 and 10 μM, respectively, similar to the standard drug miltefosine. Despite no induction of hemolytic activity, only compound 1b resulted in mammalian cytotoxicity, with a $CC_{50}$ value of 64 μM. The most potent compounds (1a and 1c) resulted in selectivity indexes >18. Considering the potency in both parasitic forms, based in the results of $IC_{50}$ and SI the compound 1c was selected to investigate the mechanism of action in extracellular promastigotes by fluorescent/luminescent flow citometry and mass spectrometry techniques. After a short-time incubation, increased levels of the cytosolic calcium were observed in parasites, with alkalinization of the acidocalcisomes. The compound 1c also induced hyperpolarization of mitochondrial membrane potential, resulting in decreased levels of ATP, without alteration of the reactive oxygen species (ROS). Neither plasma membrane damages nor DNA fragmentation were observed after treatment, but a reduction of the cellular proliferation was detected. By MALDI-TOF/MS analysis, mass spectral alterations of promastigote proteins were observed when compared to untreated and miltefosine-treated groups. This chemically modified neolignan induced lethal alterations of the bioenergetic and protein metabolism of *Leishmania (L.) infantum*. Future PKPD and animal efficacy studies are needed to the optimization of this promising natural-derived compound.

## Agradecimentos/Acknowledgments

This work was supported by the São Paulo Research State Foundation (FAPESP, Projects 2021/02789-7, 2021/04464-8, 2017/50333-7, 2020/03637).

**Área: MED** **Nº de Inscrição: 00379**

# Molecular docking and fluorescence based enzymatic inhibition assay: a study of *T. cruzi*'s CYP51 inhibition by heterocyclic compounds

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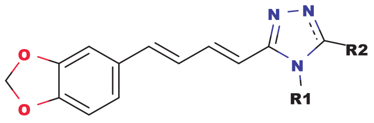
Palavras Chave: *Trypanosoma cruzi, Chagas disease, CYP51, molecular docking, fluorescence enzymatic assay.*

## Highlights

The *T. cruzi* CYP51 inhibition capability of heterocyclic compounds was evaluated by docking and a fluorescence-based enzyme inhibition assay, with promising results for triazole piperine derivatives.

## Abstract

Chagas disease is a neglected tropical disease caused by the *Trypanosoma cruzi* parasite. The lack of treatment options, which is restricted to the use of benzonidazole and nifurtimox only, and their low effectiveness in the disease's chronic phase, indicate that the search for new drugs is imperative. A target for this purpose is a *T. cruzi*'s enzyme, 14α-sterol demethylase[1] (CYP51), which is essential for its survival, that can be inhibited by heterocyclic compounds capable of complexing with the iron atom in the heme group of CYP51. On this project, a study of the inhibition by structurally different heterocyclic compounds was made using molecular docking and a fluorescence-based enzyme inhibition assay[2]. We evaluated the inhibition capability of two heterocycles compounds series using molecular docking and a fluorescence-based enzymatic inhibition assay. The first series[3] of triazole piperine derivatives was designed based on the CYP51's active site, using a theoretical model of activity prediction; the second series also presented heterocycles, but with a different structural pattern (Fig. 1). The molecular docking was made using ChemPLP function (chosen after redocking) of Gold 5.6 (CCDC). All solutions presented the ligands near the heme group in the active site with good scores values (Tab. 1); however, for the 1st series, good interactions between the iron atom and the ligands' nitrogen atoms were observed, while for the 2nd series compounds no such interactions were observed. To validate these results, a preliminary enzymatic inhibition reaction was carried out with bactossomes of *T. cruzi*'s CYP51 and the inhibition detection was verified indirectly by the decreasing fluorescence, as the fluorogenic substrate (Vivid BOMCC) was no longer converted into product by the enzyme[2]. A considerable decrease in fluorescence was observed during the reaction in the presence of compounds from series 1, while compounds from series 2 caused lower changes in the fluorescence response. These results indicate that the compounds designed based on the CYP51 active site have best inhibitory activity. Both methodologies results indicate a more effective inhibition by the compounds with less steric hindrance around the heterocyclic ring (series 1), allowing an effective N-Fe interaction between the ligand and the heme group. Currently we are performing more inhibitory enzymatic reactions with the compounds in order to build a dose response curve and obtain the $IC_{50}$ value for them.



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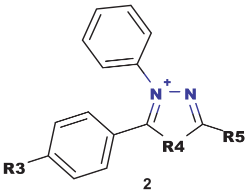

**2**

**R1: phenetyl, cyclohexyl**
**R2: =S, -S-$CH_3$, -S(=O)-CH3 e -S(=O)$_2$-$CH_3$**

**R3: -Cl, -$CCl_3$; R4: -$S^-$, -N-Ar; R5: -S-, -NH-Ar**

**Fig.1** structures of series 1 and 2 of heterocyclic compounds.

**Table1.** Docking scores and interaction distance between the compounds N atom and Fe atom of CYP51's heme group

| Compound | Distance (Å) | Docking Score |
|---|---|---|
| 1a | 2,61 | 91,79 |
| 1b | 2,61 | 96,28 |
| 1c | 2,61 | 81,44 |
| 1d | 2,67 | 87,07 |
| 2a | 9,96 | 67,01 |
| 2b | 4,08 | 59,45 |
| 2c | 6,50 | 84,58 |
| 2d | 6,40 | 87,96 |

## Acknowledgments

Capes, CNPq, PPGQ, UFRRJ, York University.

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**Área: MED** **Nº de Inscrição: 01016**

# Molecular Docking and Quantum Studies of Lawsone Dimers Derivatives: New Investigation of Antioxidant Behavior and Antifungal Activity

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Key words: Antifungals, Antioxidant, *C. albicans,* Lawsone, Molecular Docking.

## Highlights

Verification of the antioxidant potential using different techniques: *in vitro* tests, DFT and cyclic voltammetry. Rationalization of data obtained in antifungal tests through molecular docking.

## Abstract

In general, fungal species are characterized by their opportunistic character and can trigger various infections in immunocompromised hosts. The emergence of infections associated with high mortality rates is due to the resistance mechanisms that these species develop. This phenomenon of resistance denotes the need for the development of new and effective therapeutic approaches. In this work, we report the investigation of the antioxidant and antifungal behavior of dimeric naphthoquinones derived from lawsone whose antimicrobial and antioxidant potential has been reported in the literature. Seven fungal strains were tested, and the antioxidant potential was tested using the combination of the methodologies: reducing power, total antioxidant capacity and cyclic voltammetry. Molecular docking studies (**PDB ID 5V5Z** and **1EA1**) were conducted which allowed the derivation of structure-activity relationships (SAR) (Figure 1). Compound **1-i**, derived from 3-methylfuran-2-carbaldehyde showed the highest antifungal potential with an emphasis on the inhibition of *Candida albicans* species (**MIC = 0.5 µg/mL**) and the highest antioxidant potential.

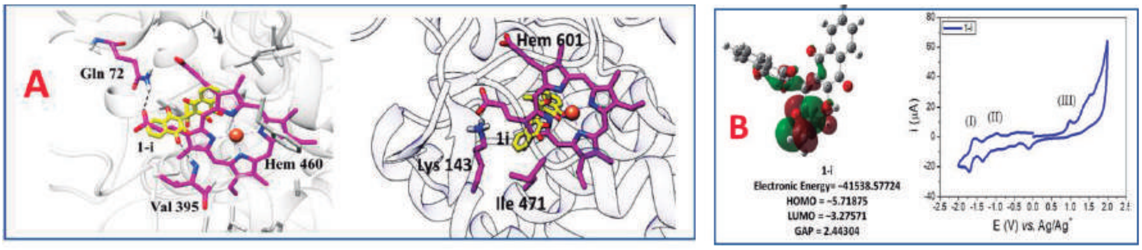

**Figure 1:** A) Best score docking poses for **1-i** (PDB 1EA1) (left) and best scoring docking poses for **1-i** (PDB 5V5Z) (right). B) Molecular orbital energy level and HOMO shapes. Cyclic voltamomgrams from **1-f** and 1-i obtained at glassy carbon electrode in 0.1 M $TBAPF_6$ in acetonitrile at a scan rate of 100 mV $s^{-1}$.

A combination of molecular modeling data and *in vitro* assays can help to find new solutions to this major public health problem.

## Acknowledgments

The authors acknowledge CNPq, CAPES and the Sao Paulo Research Foundation (FAPESP, CIBFar grant 2013/07600-3), Brazil, for financial support.

**Área: MED**

# Molecular dynamics of nitazoxanide and its metabolite tizoxanide with the main protease (M$^{Pro}$) of SARS-CoV-2

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Keywords: *nitazoxanide, tizoxanide, SARS-CoV-2, protease, molecular dynamics, MM/PBSA*

## Highlights

Nitazoxanide inhibits SARS-CoV-2 *in vitro*.

The Main Protease (M$^{Pro}$) of SARS-CoV-2 is a putative target of nitazoxanide

Molecular dynamics of the metabolite of nitazoxanide, tizoxanide, showed important structural fluctuations which may affect dimer stability and, therefore, M$^{Pro}$ function

## Abstract

The prodrug nitazoxanide (NTZ), present in the circulation as tizoxanide (TIZ), its active metabolite, has been studied for its multitarget actions due to a broad antimicrobial and antiviral activity. Among others, NTZ inhibits SARS-CoV-2 *in vitro*[1]. In addition, NTZ modulates the production of pro-inflammatory cytokines related to the so-called cytokine storm, of special interest in COVID-19 disease course[1,2]. Although clinical trials have not shown the clinical benefits of the use of NTZ to treat COVID-19, there is no doubt that this drug deserves to be investigated by structure-based methods, since its cellular target has not been revealed yet, to propose further molecular modifications. So, in this work, target fishing using *in silico* chemogenomics, with PIDGIN v.2, pointed to the main protease (M$^{Pro}$) of SARS-CoV-2 (PDB ID 6LU7)[3] as a putative target of NTZ/TIZ. Docking with GOLD v. 5.8.1 and molecular dynamics and MM/PBSA with GROMACS v. 2020.2 were performed, to investigate putative interactions of NTZ/TIZ with M$^{Pro}$. Analysis of intermolecular interactions were achieved with Pymol v.0.99, Discovery Studio 2016 and VMD. Firstly, the effect of the ligands on the monomeric structure of M$^{pro}$ was evaluated and a significant change could be observed with TIZ binding, which was supported by large fluctuations in Root Mean Square fluctuation (RMSF) analysis, in comparison to the apo form, and an affected region is the loop that connects domain II to domain III of M$^{pro}$. In addition, the co-crystallized ligand and TIZ were able to promote fluctuations in the α-carbons of chain B compared to the apo form, mainly in the *N*-finger region, which is likely to affect the stability at the dimer interface and, consequently, M$^{pro}$ function. Finally, although MM/PBSA energies of NIT/TIZ were not comparable to the observed values for the co-crystallized ligand, this study may give support to further design of better M$^{pro}$ inhibitors.

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**CNPq, FAPERJ**

**Área: FIS** **Nº de Inscrição: 815**

# Molecular modeling study of naftoquinone derivatives as potentials of *Leishmania* target

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Palavras Chave: Molecular modeling, Leishmania, Naftoquinones, Molecular docking.

## Highlights

Naftoquinone derivates presents anti-Leishmania potential

Trypanothione reductase is important target to find new drugs against Leishmaniasis

Molecular docking and toxicity risk prediction were applied for the development of new inhibitors

## Resumo/Abstract

Leishmaniosis is a disease caused by protozoans from the *Leishmania* genus, which is transmitted to humans through the bite of infected sand flies. According to the World Health Organization (WHO), leishmaniosis is an endemic disease in over 98 countries and about 350 million people are at risk. The disease is one of the so-called neglected tropical diseases, with little interest of clinical researches, there is no vaccine and the therapeutic arsenal is very inadequate. Trypanothione Reductase (TR) is an essential enzyme in trypanosomatids that have a unique role in trypanothione-based redox metabolism and oxidant defense. Lack of this enzyme in mammalian host is one of the reasons that turned it to attractive drug-target molecules. In the present work, molecular modeling studies with naftoquinone derivatives, obtained from *Eleutherine plicata* extract, were used to evaluate potentials inhibitors of TR enzyme. According to the molecular docking results, obtained with Gold 5.5 program, and subsequent visual inspection, ten compounds were selected. The selected ligands interact with the enzyme mainly through hydrogen bonds with Ser14, Lys60 and Thr198. Furthermore, the ligands also performed hydrophobic interactions with Gly56, Cys57, Thr198 and Ile199. Kumar colleagues demonstrated the importance these residues with TR enzyme. After, the OSIRIS Property Explorer program was used to estimate the risks of side effects, such as mutagenic, tumorigenic, irritant and reproductive effects of these ten naftoquinones. From this, the *in silico* prediction by OSIRIS showed that seven molecules do not have undesirable side effects, besides highest drug-likeness and drug-score values. Therefore, based on molecular docking and side effects prediction results, it was possible to perform a screening of compounds for further study of Molecular Dynamics simulation in the TR enzyme.

## Agradecimentos/Acknowledgments

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

# Putative *in silico* binding modes of nitrile-based peptoids as cysteine protease inhibitors

**Thiago K.B. Matos (PG), Luana Alves (PG), Deborah A. Santos (PQ), Rodrigo Cendron (PG), Fernanda R. Rocho (PG), Carlos A. Montanari (PQ), Andrei Leitão (PQ)*.**

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Keywords: Molecular docking, Peptoids, Nitrile warhead, Cysteine protease inhibitors.

## Highlights

Covalent docking was used to determine putative binding modes for novel cysteine protease inhibitors.
These chemicals were tested *in vitro* using enzymatic kinetic assays to obtain the constant of inhibition.

## Resumo/Abstract

Dipeptidyl nitrile analogs known as peptoids were synthesized as inhibitors of cysteine proteases of the papain superfamily. The new analogs differ from peptides due to the side chains of their P3 position being attached to the peptide backbone's nitrogen atom, not to the α-carbons. These derivatives lack the hydrogen amide at P2-P3 responsible for many of the secondary structural elements in peptides and proteins, making them resistant to proteolysis. The designed peptoids lose a hydrogen bond with the macromolecular targets, decreasing the enzyme's overall affinity. Cross-class cathepsin activity was observed for some of these novel compounds against cruzain and cathepsins B, K, L, and S. Besides, the putative mode of binding was determined using covalent docking, which aided in describing the structure-activity relationship (SAR) for the novel chemicals. Compounds **4a** and **4g** were docked to analyze their mode of binding (MoB) with cruzain. It was concluded that the presence of a methoxy moiety in the P3 position was detrimental to the affinity, corroborating the experimental pKi obtained via enzymatic assays. The same approach was taken to analyze the MoB of compounds 4a and 4d in CatL and compounds **4c** and **4e** in CatK. Interestingly, none of the peptoids inhibited CatB to any appreciable extent. These results provide guidance to identify novel bioactive nitrile-based peptoids for further drug design efforts.

## Agradecimentos/Acknowledgments

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**Área: MED**

# Quantitative Structure-Activity Relationship studies of a heterocyclic amine series with *in vitro* antidepressant activity

**Gustavo H. M. Sousa (PG),[1*] , Renan A. Gomes (PQ), Gustavo H. G. Trossini (PQ),[1]**

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Palavras Chave:*, Depression, Ligand-Based Drug Design, QSAR, Cheminformatics, Machine Learning*

## Highlights

Making use of the quantitative structure-activity relationship (QSAR) tools and methods, based on state-of-the-art statistical and computational techniques, is possible to predict a compound's physicochemical property or even its biological activity, driving the drug design process towards a more rational approach. From compounds showing *in vitro* activity against three major depression targets: dopamine, norepinephrine and serotonina transporters, we developed a typical quantitative strucutre-activity relationship workflow, in order to predict the ligands' biological activity. After proper treatment of the data, linear and non-linear algorithms were used to predict the response variable, measured in pKi, achieving best results with the non-linear methods such as *Random Forest* and *Support Vector Machines* for the dopamine and norepinephrine transporters and the models were able to predict accurately the test groups.

## Resumo/Abstract

Major depression is a central nervous system disabling disorder that affects people all over the world, from all ages and socioeconomic background and is characterized by a series os symptoms such as an exacerbated feeling of sadness, lack of interest in daily activities and recurrent suicidal thoughts, among other related symptoms[1]. The antidepressant therapeutic arsenal was supported by drugs that resulted in a increase of biodisponibility of monoamines (norepinephrine, dopamine and serotonine) at the synaptic cleft, like the tricyclics inhibitors and monoamine oxidase inhibitors[2]. One alternative is the use of triple reuptake inhibitors, which have the property to inhibit simultaneously the norepinephrine, dopamine and serotonine transportes, and a series of this kind of compounds were used in this work[1,2,3]. The current therapeutic arsenal has undesirable characteristics, such as the delay in the action time, in addition to several adverse effects and in this context, chemoinformatics is a promising field that can be applied in the discovery and optimization of hit molecules in the treatment of depression and several other diseases, using methodologies such as the Quantitative Structure-Activity Relationship (QSAR). The objective of this work was to explore techniques supported by the literature and obtaining models capable of predicting antidepressant activity observed *in vitro*. An usual QSAR workflow was used, with random partitioning of the test and training series, internal and external validation of data and relevant metrics ($R^2$ - correlation coefficient; RMSE – root mean square error) in the evaluation of the performances. Linear and non-linear methods were used, exploring some of the algorithms used in the literature such as *Partial Least* Squares (PLS), *Random Forest (RF)* and *Support Vector Machines (*SVM*)*, using the R programming language. The non-linear models obtained by RF and SVM presented a much higher performance when compared to the linear models, especially those that were built from simpler descriptors and with chemical meanings that are easily translated. The metrics obtained for the models related to the inhibition of dopamine and norepinephrine transporters were adequate for a QSAR study, all of them well above significant values of performance metrics. The best models were achieved for the dopamine receptor, with the performance metrics depicted below:

| Model | Receptor | $R^2$ (training) | RMSE (training) | $R^2$ (test) | RMSE (test) |
|---|---|---|---|---|---|
| RF | Dopamine | 0,863 | 0,362 | 0,817 | 0,398 |
| SVM | Dopamine | 0,811 | 0,395 | 0,799 | 0,418 |

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## Agradecimentos/Acknowledgment

**Área: MED** **Nº de Inscrição: 01407**

# Repurposing human cathepsin D inhibitors for fighting schistosomiasis

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*Key words: Schistosoma mansoni , aspartyl protease, cathepsin D*

## Highlights

Aspartyl proteases are promising targets to search for new antischistosomal drugs. The repurposing of human cathepsin D inhibitors was assessed and compounds with low micromolar potency against SmCD1 were identified.

## Abstract

Schistosomiasis is caused by trematodes of the genus *Schistosoma*. Aspartyl proteases are essential in the life cycle of these parasites and are under investigation as drug targets[1]. These enzymes play an important role in the digestion of haemoglobin obtained from ingested host erythrocytes, which is the parasite's source of nutrients. Recombinant cathepsin D-like aspartyl protease from *S. mansoni* (r*Sm*CD1) has been expressed and purified by our group[2]. SmCD1 shows 51% similarity with human cathepsin D (hCD), an enzyme that is considered an interesting target in anti-cancer therapy, and in Alzheimer's disease[3]. Knowing that the development of new drugs is a long and expensive process, drug repositioning becomes an interesting alternative, since it aims to use in the treatment of a disease a drug already commercialized, or a candidate in the phase of clinical study. In partnership with Merck's GHI we had access to a set of 22 compounds previously investigated as hCD inhibitors. An experimental screening was performed on the adult worm aqueous extract (WAE) and on rSmCD1 using a synthetic FRET peptide (Abz-AIAFFSRQ-EDDnp) as a substrate. The screening results on r*Sm*CD1 are shown in Figure 1. Compounds inhibiting more than 60% of the enzyme activity at 10 μM had their $IC_{50}$ determined and were also assayed for selectivity against mammalian (bovine) CD (Figure 2). Some of these compounds presents an acyl-guanidine group, that interacts with the side chains of the catalytic site (D33, D231) of SmCD1. Besides, hydrophobic groups, mainly benzene rings with or without substituents, interact preferentially in the subpocket S1 (Y78, T125) and S3 (F131), while benzene rings with halogen substituents interact with the subpocket S2' (M309) and S3' (I320). Thermodynamic parameters for the interaction between *Sm*CD1 and the most potent inhibitors will be studied by isothermal titration calorimetry (ITC) and microscale thermophoresis (MST).

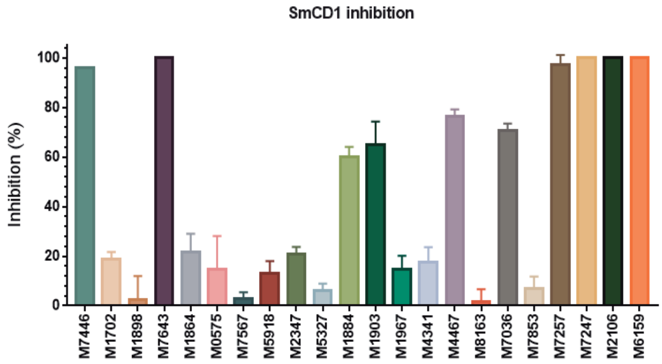

Figure 1: Inhibition obtained when screening compounds at 10 μM.

| Compound | $IC_{50}$ | | |
|---|---|---|---|
| | SmCD1 (μM) | hCD (μM) | bovine CD (μM) |
| M6159 | 0.73 | 0,013 | 0,56 |
| M7446 | 0.26 | 0.059 | 0,33 |
| M7643 | 0.80 | 0.0086 | 0,59 |
| M1903 | 17.3 | 5.3 | - |
| M4467 | 1.2 | 0.41 | - |
| M7036 | 3.2 | 0.045 | - |
| M7257 | 0.40 | 0.017 | 0,2 |
| M7247 | 0.41 | 0.011 | 0,06 |
| M2106 | 0.18 | 0.015 | - |

Figure 2: Comparative $IC_{50}$ determination for the most active compounds.

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## Acknowledgments

CAPES, CNPQ, FAPERJ, FIOCRUZ, NEWTON FUND, RES. ENG. CONNECTING CAPABILITY FUND

**Área: MED**

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

# Scientific and Technological Prospecting of Chemical Antiseptics to Prevent the Spread of SARS-CoV-2

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Keywords*: Prospecting, Pandemic, Antiseptics, SARS-CoV-2*, *Patents.*

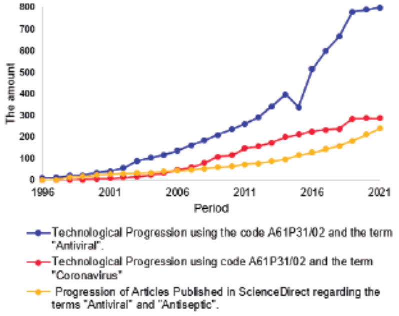
## Highlights

Quali-quantitative analysis of articles and patents from the stage of studies on the development of chemical and antiseptic formulations to control the spread of viruses, especially COVID-19.

## Resumo/Abstract

In 2020, the Health Organization (WHO) declared, because of the spread of SARS-CoV-2, a global pandemic. This situation, because in evidence the importance of the development of safe and determined prophylactic and therapeutic measures against its agent, and also requested actions to prevent the transmission of this vírus [1]. The use of antiseptics against COVID-19, among the adoption of other preventive measures, is very important [2]. This study searched for patents and scientific articles on the development of antiseptic formulations to control the spread of viruses to show prospects for application against human coronaviruses. The search for scientific articles related to the topic was performed in the ScienceDirect database. The inventory was performed using the keywords in the title search, abstract, individually with the words "Antimicrobial; Antiviral; Virus; Corona; COVID-19; SARS-CoV; Decontamination 'human skin'; Chemical formulations". For the patent search, the code "A61P31/02" was identified regarding the classification of antiseptics, and the combination was made with the keywords "Antimicrobial" and "Antiviral". The patent search was performed through the Espacenet portal of the European Patent Office (EPO) and Excel® software was used for data analysis in February 2021. The results of the article analyses showed that the development of antiseptics focusing on viruses accounts for 1.5% when "antiviral" is the search term and about 3.2% when the search term is "viruses". However, only 0.4% have studies focused on SARS-CoV, the first virus of the Coronaviridae family identified. Considering the term "chemical formulation" and "antiviral" the result is also 7.7% of the present in the searched database. The indicators showed a marked growth in the development and research of scientific information with the discovery of MERS-CoV in 2012 when compared to publications with the identification of SARS-CoV in 2002. In the analysis of patents, analyzing the combination of the search term "Antiseptic" with "Antiviral" it is possible to see that until 2016 this was not the object of publication when compared to what was observed for the period after, as expressed in figure 1. For this search, quantitative data indicating interest in the protection of patented technologies were found in Brazil. The prospection of patents indicated that there is 38% number of patents relating to substances intended for application in humans while 16% are for veterinary use and also about 46% without specific definition. The area of natural product chemistry stands out as a major sector of technologies with more related patents, corresponding to 24.97% of the references. As for the applying sectors, it is observed the business one seeking more to protect technologies, with 39.76% of the contributions. The patented data indicate that the development of this technology was associated with the growth of social demand observed with the case of MERS-CoV and there is an indication of growth prospects for the SARS-COV-2 group and others of the coronavirus group.

**Figure 1 -** *Number of patents and articles published cumulatively in the ESPACENET database.*



**Source:** Authors (2021)

**References:**

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## Agradecimentos/Acknowledgments

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**Área: MED** **Nº de Inscrição: 00179**

# Synthesis and Anticholinesterasic Evaluation of Substituted Aromatic Carbamates and Betaines

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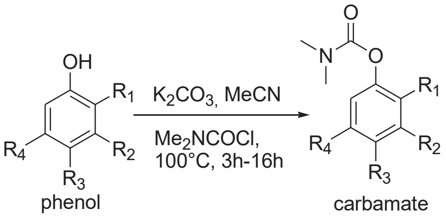
Palavras Chave:*(Acetylcholinesterase, Alzheimer, Betaine, Carbamate*).

## Highlights

Synthesis and Anticholinesterasic Evaluation of Substituted Aromatic Carbamates and Betaines. Anticholinesterasic compounds are used to treat Alzheimer's disease. Carbamates are potential anticholinesterasic agents. Compound **8** showed the best anticholinesterase activity at $IC_{50}$ 8.5 µM.

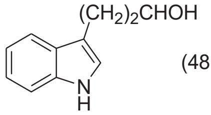
## Abstract

Alzheimer's disease (AD) is a neurodegenerative disease and, it is considered the most common dementia in the world. Part of the disorders developed during AD are related to failures in the cholinergic system. One of the most promising approaches for treating this disease is the use of acetylcholinesterase (AChE) inhibitors in order to increase the life-time of ACh molecules in the synaptic cleft leading to an increase in cholinergic neurotransmission. As new candidates for cholinesterase inhibitors, 15 compounds were synthesized, 10 carbamates (**Sch.1**) and 6 betaines (**Sch.2**). Betaines were not active at the tested concentrations, and among the synthetized carbamates, compound **8** was the most active ($IC_{50}$ = 8.5 µM) (**Tab.1**). *In silico* analyzes of the carbamates (**Fig.1**) were performed to seek for the main interactions of the carbamates with the amino acid residues in the AChE active site. Compound **8** showed the highest number of interactions with amino acid residues. These analyzes corroborates with the biological test outcomes.



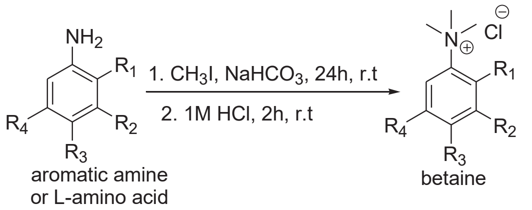
**1:** $R_1$=OMe; $R_2$=$R_3$= H; $R_4$= $NO_2$ (61%)
**2:** $R_1$=OMe; $R_2$=$R_3$= H; $R_4$= $NH_2$ (28%)
**3:** $R_1$=H; $R_2$=$R_4$=H;
$R_3$= $CH_2CH(NHCONMe_2)(COOMe)$ (95%)
**4:** $R_1$=$NH_2$; $R_2$=$R_3$= H; $R_4$= Cl (25%)
**5:** $R_1$=$R_2$=$R_4$= H; $R_3$= $NO_2$ (36%)
**6:** $R_1$=$R_3$=$R_4$= H; $R_2$= $NO_2$ (33%)
**7:** $R_1$=$R_2$=$R_4$= H; $R_3$= COMe (90%)
**8:** $R_1$= COMe; $R_2$=$R_3$= H; $R_4$= $OCONMe_2$ (95%)

**9:**



(48%)

**Scheme 1.** Reaction to obtain carbamates **1-8**.



**10:** $R_1$= Me; $R_2$=$R_3$=$R_4$= H (93%)
**11:** $R_1$=$R_2$=$R_4$= H; $R_3$= Br (80%)
**12:**$R_1$=H; $R_2$=$R_3$= H=$R_4$= OMe (96%)
**13:** phenylalanine (94%)
**14:** leucine (97%)
**15:** glycine (98%)

**Scheme 2.** Reaction to obtain betaines **9-15**.

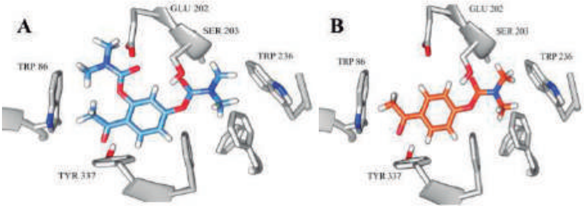


**Figure 1.** Intermolecular interactions of compounds **8** blue) and **7** (orange) and, amino acid residues at the active site of AChE.

**Table 1**. Results of anticholinesterase evaluation of compounds **1-15**.

| Compd[a] | $IC_{50}$(µM)[b]±S.E.M[c] |
|---|---|
| 1 | 585.7±0.6 |
| 2 | NI[d] |
| 3 | 89±0.06 |
| 4 | 64.5±0.16 |
| 5 | 803.9±0.99 |
| 6 | 956.4±1.05 |
| 7 | >1000 |
| 8 | 8.5±0.06 |
| 9 | >1000 |
| 10 | NI[d] |
| 11 | NI[d] |
| 12 | >1000 |
| 13 | NI[d] |
| 14 | NI[d] |
| 15 | NI[d] |
| NEO[e] | 2.0±0.04 |

[a]Compound. [b]$IC_{50}$ is the concentration inhibiting 50% of acetylcholinesterase enzyme activity. [c]Standard error of mean. [d]Not inhibition. [e]Neostigmine: positive control.

## Acknowledgments

The authors owe a debt of gratitude to the following Brazilian research agencies: FUNDECT-MS, CAPES and, CNPq for financial support and scholarships. This study was financed in part by the Fundação Universidade Federal de Mato Grosso do Sul – UFMS/MEC – Brazil.

**Área: MED**

# Synthesis and application of resveratrol analogues and their lipoic acid hybrids based on imine and amine scaffold

***Ari Souza Guimarães** (PG)[1], **Josué Carinhanha Caldas Santos (PQ),[1] Dimas José da Paz Lima (PQ),[1] Isis Martins Figueiredo (PQ)[1]**

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Palavras Chave: *Schiff* base, Amines, FPS-UVB, Antioxidants, tirosinase inhibittion, in sílico studies.

## Highlights

Derivatives **1-4** showed significant SPF-UVB. The compounds showed antioxidant activity against DPPH, ABTS, FRAP and CUPRAC methods. The **7** inhibited tyrosinase in a mixed manner, with an $IC_{50}$=180±0.6 $\mu$M

## Resumo/Abstract

Reactive species (RS) from exogenous sources are associated with several disorders, including the rise of inflammatory processes, skin pathogens, cancer and others.[1,2] In this context, considering the importance of multipotent antioxidant compounds, the synthesis and evaluation of the ultraviolet B solar protection factor (SPF-UVB), the antioxidant capacity ($C_{AO}$), the inhibition of tyrosinase enzyme and the in sílico study of iminic and aminic derivatives analogues to resveratrol and hybrids to lipoic acid were carried out.The synthesized compounds showed yields from 49 to 98% (**Fig. 1A**). In the SPF-UVB studies (**Fig. 1B**), the iminic derivatives showed considerable SPF, 2 having the highest result of the series (23.4 ± 1.0), comparable to the standard BZF-3 ($p \geq 0.05$, *Tukey* test). In the $C_{AO}$ evaluation, piacetannal (PIA), lipoic acid (LA), caffeic acid (CA), ferruic acid (FA), quercetin (Q) and Trolox (TR) were used as positive control. Among the compounds evaluated, the imine derivatives (**1-4**) showed an important response to the DPPH radical (**Fig. 1C**), with results comparable to FA and CA ($p \geq 0.05$, *Tukey test*). To the $ABTS^{\bullet+}$ method (**Fig. 1D**), the compounds showed comparable results to all standards ($p \geq 0.05$, *Tukey test*), with highlight to **2** ($IC_{50}$=1.69 ± 0.09 $\mu$mol $L^{-1}$). Besides, in front of the FRAP method (**Fig. 1E**), the amine derivatives demonstrated $A_{593}$ = 1.382 ± 0.015 - 1.422 ± 0.012, demonstrated as more efficient than their previous imines ($p \leq 0.05$, *Tukey test*). In addition, **2** reduced $Cu^{2+}$ ($TE_{CUPRAC}$=1.03 ± 0.01) similarly to PIA ($p \geq 0.05$, *Tukey test*) (**Fig. 1F**). Additionally, the compounds showed no complex $Fe^{2+}$ ions. These results are associated, probably, with the presence of electron-donating groups and hydrogen bonding donor centers present in these compounds (OH, NH, -C=N-). For the in vitro tyrosinase enzyme inhibition results, amine derivative **7** showed the lowest $IC_{50}$ of the evaluated series (180 ± 0.6 $\mu$M), as well as, a mixed type of enzyme inhibition (**Fig. 1G**). From docking studies it could be noted that the compound performs $\pi$-alkyl type interactions with the ALA286 residue, $\pi$-$\sigma$ with the VAL283 residue and $\pi$-$\pi$ stacking type interaction with HIS263, a residue that is coordinated with the cofactor copper atom in the active site of the enzyme. Therefore, theoretical calculations demonstrated a preference of the compounds to interact with the enzyme via hydrophobic interactions. Also, in silico ADMET assays demonstrated that the compounds have a low skin permeability (log Kp < -5.20 cm/s), as well as, log P of the compounds showed a higher hydrophilic character of the compounds, corroborating with the antioxidant studies. Finally, these results highlight the bioactive potential of the compounds evaluated, demonstrating their ability to act against multiple targets.

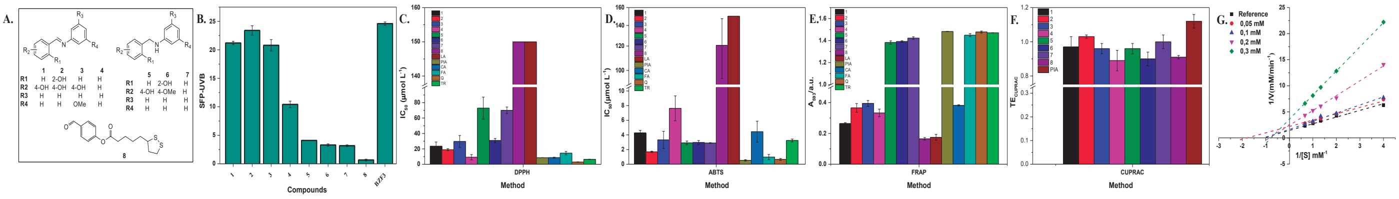

**Figure 1. a)** Imines and amines and hybrids with lipoic acid; **b)** Compounds FPS-UVB; **c)** Scavenging DPPH; **d)** Scavenging ABTS; **e)** FRAP; **f)** CUPRAC; **g)** Type of enzymatic inhibition compound **7**.

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## Agradecimentos/Acknowledgments

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**Área: MED**

# Synthesis and evaluation of the antiproliferative activity of phosphorylated, phosphonylated and sulfonylated derivatives of goniothalamin and piplartine

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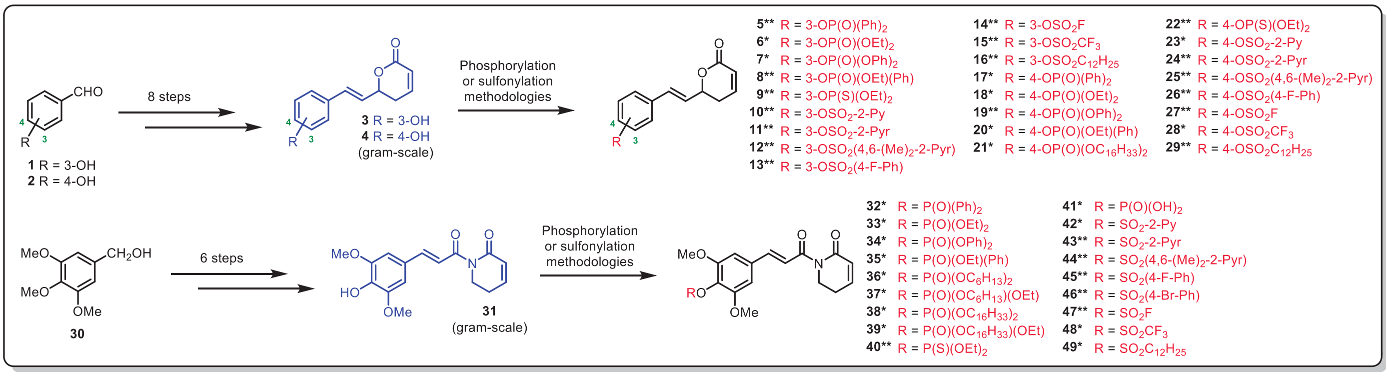
Keywords: *Goniothalamin, Piplartine, Phosphorylation, Sulfonylation, Cytotoxicity.*

## Highlights

Forty-three novel phosphorylated, phosphonylated and sulfonylated derivatives of goniothalamin and piplartine were synthesized. Sulfonylation with PyFluor increased cytotoxicity and selectivity towards breast cancer cell line.

## Abstract

*rac*-3-Hydroxygoniothalamin (**3**), *rac*-4-hydroxygoniothalamin (**4**), and 4-hydroxypiplartine (**31**) were prepared on gram scales according to our previously reported procedures.[1] Using reported methodologies for the phosphorylation or sulfonylation of phenols,[2] we synthesized a series of forty-three novel goniothalamin (**5**–**29**) and piplartine (**32**–**49**) derivatives (Scheme 1).



**Scheme 1.** Synthesis of the novel goniothalamin and piplartine derivatives. *Tested on MCF-7, MCF-10A, and PC3 cell lines. **Not tested on MCF-7, MCF-10A, PC3, and PNT2 cell lines.

The forty-three novel compounds are being tested *in vitro* on human cell lines MCF-7 (breast cancer), MCF-10A (normal breast), PC3 (prostate cancer), and PNT2 (normal prostate) using CCK-8 assay. The derivative of goniothalamin **23** exhibited a 4-fold increase in cytotoxicity towards MCF-7 cells ($IC_{50}$ = 3.5 μM, SI = 6.2) and also an approximately 4-fold higher selectivity for MCF-7 cells when compared to goniothalamin ($IC_{50}$ = 13.7 μM, SI = 1.6). When compared *in vitro* to its parent compound **4** ($IC_{50}$ = 108.9 μM, SI = 0.9), **23** was 31-fold more cytotoxic and also approximately 7-fold more selective for MCF-7 cell line. Among the piplartine derivatives tested, **42** showed a slightly lower potency than piplartine towards MCF-7 cells ($IC_{50}$ = 7.4 μM) with a selectivity index (SI = 10.3) ca. 10-fold higher than piplartine against MCF-7 cells ($IC_{50}$ = 5.0 μM, SI = 1.0). When compared *in vitro* to its parent compound **31** ($IC_{50}$ = 7.6 μM, SI = 0.6), **42** showed similar cytotoxicity and was approximately 17-fold more selective for MCF-7 cell line. *In vitro* studies to evaluate the cytotoxicity of all synthesized derivatives are ongoing in our laboratory. We expect that these derivatives may be even more cytotoxic and selective against cancer cell lines than sulfonates **23** and **42**.

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## Acknowledgments

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**Área: MED** **Nº de Inscrição: 01081**

# SYNTHESIS OF BIS-CHALCONES BY CLAISEN-SCHMIDT CONDENSATION: A STUDY OF THE ANTI-INFLAMMATORY POTENTIAL IN MICE.

**Cassia Sousa Ferreira (IC)[1*], Gabriella B. Souza (PG)[1] Fabiula F. de Abreu (PQ)[1], David N. Palmeira (IC)[1], Morgana S. Araújo (PG)[2], Péricles B. Alves (PQ)[1], Enilton A. Camargo (PQ)[1], Emmanoel V. Costa (PQ)[2]**

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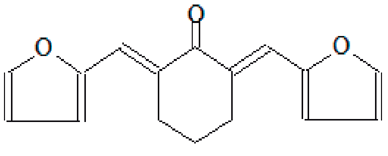
*Keywords*: *Bioatives molecules*, *Bis-chalcones*, *Anti-inflammatory potential.*

## Highlights

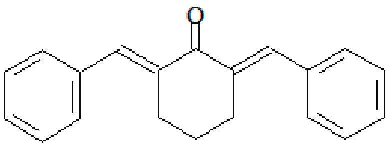
Use of chemical agents bioatives is efficient in the control of topical inflammation. This study synthesized and characterized two bis-chalcones for anti-inflammatory activity evaluation.

## Abstract

Symmetrical bis-aryl-α,β-unsaturated ketones were synthesized via the Claisen-Schmidt condensation reaction in excellent yield (77 to 85%) by treating cyclohexanone with aldehydes (furfural and benzaldehyde)[1]. The compounds obtained were characterized using FTIR, HRMS, $^{1}$H-NMR and $^{13}$C-NMR (DEPT 135°). Although called promising prototypes in the treatment of various diseases, these substances are little explored. In this context, bis-chalcones B1 *(2E, 6E)*-2,6-bis(furan-2-ylmetthylene)cyclohexanone and B2 *(2E,6E)*-2,6-dibenzylidenocyclohexanone were subjected to evaluation of the anti-inflammatory potential in mice[2]. Adult male Swiss mice (25-30 g) were used and the protocols were approved by the Ethics Committee for Animal Research (Ceua n° 8869010719). The topical anti-inflammatory activity was evaluated in the ear edema induced by 12-O-tetradecanoylphorbol-13-acetate (TPA). Treatment with B1 and B2 (1 and 3 mg/ear) or dexamethasone (0.05 mg/ear, control) was administrated 5 minutes after TPA (1 μg/ear) in the ipsilateral ear. After 6 h, edema (weight of ipsilateral subtracted from contralateral ear) and myeloperoxidase (MPO) activity were measured. Results were expressed as mean ± S.E.M. and were evaluated by one-way ANOVA followed by Tukey's test, with $p < 0.05$ considered as significant. Administration of TPA induced ear edema and elevated MPO activity (17.6±1.9 mg and 57.7±11.1 UMPO/site respectively). The topical administration of B1 and B2 reduced edema (5.2±1.3 and 7.9±1.7 mg for B1 at 1 and 3 mg/ear respectively; $p<0.001$ and $p<0.05$, respectively and 9.1±3.1 and 4.7±1.1 mg for B2 at 1 and 3 mg/ear respectively; $p<0.05$ and $p<0.001$ respectively) induced by TPA. B1 and B2 also reduced MPO activity in the same model (11.1±3.3 and 20.5±4.5 UMPO/site, respectively for B1 1 and 3 mg/ear; $p<0.001$ for both and 29.7±7.8 and 22.8±3.2 UMPO/site respectively for B2 1 and 3 mg/ear; $p<0.05$ and $p<0.01$, respectively) when compared to vehicle-treated group. Treatment with dexamethasone significantly reduced all parameters evaluated (2.95±0.87 mg and 4.10±1.68 UMPO/site).



B1



B2

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2. Bonfim, R. R. et al. Basic Clin. Pharmacol. Toxicol**. 2014**, 115, 237–243.

## Acknowledgments

# Synthesis of Morita-Baylis-Hillman Adducts as Larvicides against *Aedes aegypti* Mosquito Larvae and Morphological Analysis

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Palavras Chave: *Morita-Baylis–Hillman reaction, Biological action, Aedes aegypti, Morphology, Medicinal Chemistry.*

## Highlights

- ✓ A series of MBH adducts were synthesized.
- ✓ Four adducts exhibited larvicidal activity.
- ✓ The microscopic analysis indicates degenerative response in the abdomen region of the mosquito larvae.

## Resumo/Abstract

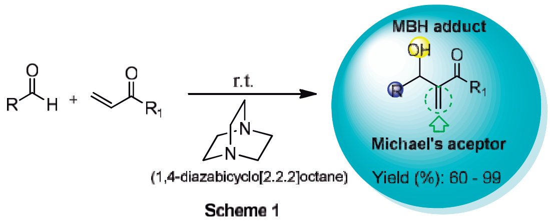
### Introduction

*Aedes aegypti* is a severe public health problem for spreading pathogenic arboviruses, such as Zika, Chikungunya and Dengue, which are responsible for 440,012 cases in Brazil, highlighting insecticide resistance as one of the factors of its expansion. Therefore, this study aimed to synthesize and evaluate the larvicidal action of Morita-Baylis-Hillman adducts against larvae of this vector and further microscopic analysis of morphological alterations.

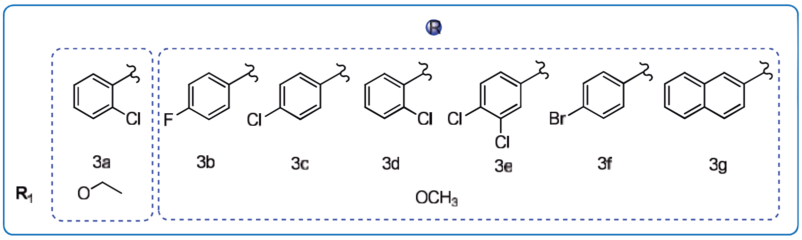
### Materials, Methods, and Results

### Morita-Baylis-Hillman Reaction

Aromatic aldehydes and methyl and ethyl acrylate (1:0.5) were reacted in the presence of 1,4-diazabicyclo [2,2,2] octane as catalyst, at room temperature under magnetic stirring, solvent-free (Scheme 1).



Scheme 1



### Evaluation of Larvicidal Action

The mortality rate was assessed in 24 and 48h at concentrations of 100 µg/mL, 50 µg/mL and 5 µg/mL, with fourth-stage larvae. It ranged from 26% to 87% in 48 hours, being **3a** and **3c** the most promising compounds.

### Light Microscopic Analysis

Morphological observations were performed with an Olympus CX40 microscope (10X magnification) equipped with a Redmi Note 10 (inch Full HD+ Amoled display48MP camera). It was observed the region of the larva' s abdomen undergoes severe injury. It is suggested that there might be a degenerative response in the cells of the digestive tract.

## Agradecimentos/Acknowledgments

CNPq, UFAL, Organic Chemistry Laboratory applied to Bioactive Materials and Compounds (LCM).

**Área: MED**

# The potential anti-inflammatory profile of 4-aminoquinoline and NSAIDs hybrids

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Keywords:*4-Aminoquinoline, Non-steroidal anti-inflammatory drugs, Hybrid molecules, Inflammation.*

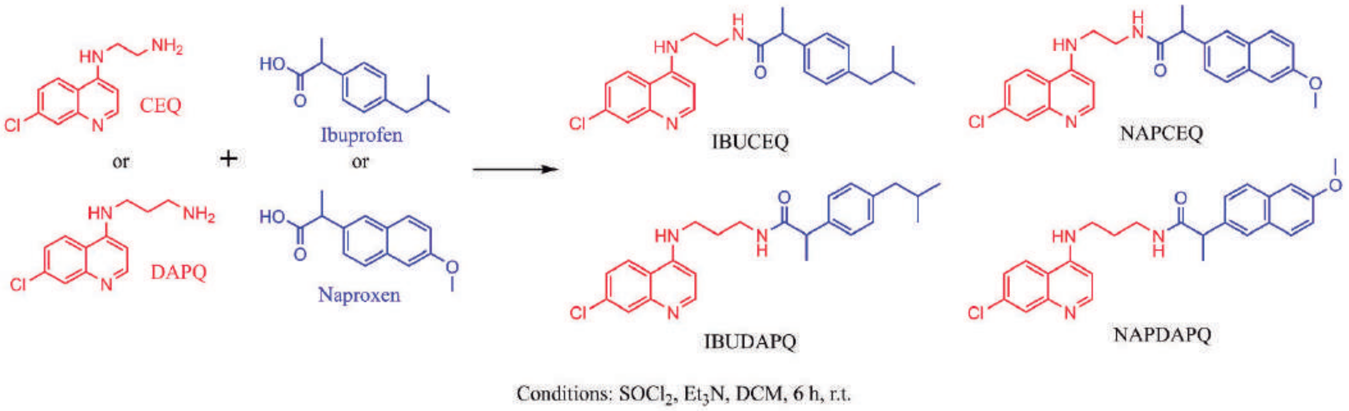
## Highlights

Hybrids of 4-aminoquinoline derivatives and NSAIDs were successfully synthetized and well characterized by spectroscopy techniques. New compounds with potential anti-inflammatory activity.

## Abstract

In chronic inflammatory diseases, such as rheumatoid arthritis, the inflammatory process induced by a noxious stimulus cannot be repaired. The usual treatment consists in non-steroidal anti-inflammatory drugs (NSAIDs) and glucocorticoids, as well as disease-modifying antirheumatic drugs (DMARDs), such as chloroquine – a 4-aminoquinoline derivative. In order to achieve a better treatment efficacy, chloroquine and NSAIDs are usually associated. Molecular hybridization is a ligand-based drug design (LBDD) approach that may result in compounds with different pharmacophoric groups and synergistic action. Thus, the aim of this study was to synthetize hybrid molecules of 4-aminoquinoline derivatives with ibuprofen and naproxen (NSAIDs), which may present an anti-inflammatory potential, followed by their structural characterization and biological evaluation.

**Fig. 1** – Synthesis design of hybrids **IBUCEQ**, **IBUDAPQ**, **NAPCEQ**, and **NAPDAPQ**.



The hybrids synthetized are new compounds, which presented an easy route of synthesis through a one-pot methodology. They were well characterized by $^1$H and $^{13}$C NMR, FTIR, and mass spectroscopy, which validated the planned structures. The first one, IBUCEQ, was chose to evaluate a preliminary anti-inflammatory profile. In the biological evaluation, the MTT assay showed that IBUCEQ presents significant cytotoxic effects only in concentrations ≥ 10 μM. Then, the secretion of pro-inflammatory cytokine IL-1β was evaluated in macrophages along with the treatment of IBUCEQ. The hybrid was able to statistically reduce the pro-inflammatory cytokine without interfering in the cell viability in all tested concentrations (0.3, 1.0, and 3.0 μM). Based on that, it can be inferred that this hybrid presents an anti-inflammatory profile, although further studies are necessary to evaluate the real anti-inflammatory potential of all synthesized hybrids.

## Acknowledgments

We would like to acknowledge the financial support from CNPq, CAPES, and FAPEAL, as well as IQB and UFAL.

**Área:______MED_________**

# Use of machine learning tools to enhance fitness functions on GOLD software

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Keywords:*(Machine learning, Fitness function, Molecular docking, GOLD).*

## Highlights

The results showed that machine learning tools can help to improve fitness function on GOLD software using parameters based in the structure of experimental ligands, allowing a better discrimination among active and inactive compounds.

## Resumo/Abstract

GOLD (Genetic Optimization for Ligand Docking) is one of the most used protein-ligand Docking Software. It is employed by expert on drug discovery for virtual screening through to lead optimization step. The extensively validated scoring functions in GOLD are trusted by scientists globally for pose prediction and virtual screening. The scoring functions in GOLD can predict the pose of ligand co-crystallized with a target protein by considering the Root Mean Square Deviation (RMSD) as a main validation parameter. However, there are multiple examples in the literature in which the predicted score value does not correlate with the ligand activity value being, therefore, unable to distinguish active from inactive compounds. Therefore, some docking tools like GOLD and Maestro allow to consider constraints criteria based on ligands similarities, scoring the way of interactions according to chemical properties from ligands used as templates models. Even so, in the literature, there are no specific protocols about how we can use these constraints since these data only can be extracted considering experimental results. In this way, the machine learning tools appears as an option, to allow the building of models able to get information about a variety of experimental data. The aim of this work is the use of machine learning tools to enhance fitness functions on GOLD software. To enhance these fitness functions, constraints criteria were used by scaffold similarity and scaffolds considering the data with 192 isocitrate dehydrogenase-1 (IDH1) mutant inhibitors, described in the literature. The choice of chemical structures was made according to IC50 values and structural similarity between them. All the ligands were chosen using machine learning tools unsupervised as a Hierachical Cluster and K-medoids. The tools were used through of Knime Analytics Platform 2022 v. 4.5. The docking results were analyzed by GoldMine, a component of the GOLD suite. Starting from the comparison between the docking of compounds with constraints and without constraints, it was possible to see that the functions considering similarity and scaffolds criteria, based on unsupervised machine learning, allowed to discriminate all compounds described as active and inactive, unlike of the same functions without constraints. These results show that the machine learning tools can help improving fitness functions, being one more tool for docking validation of experimental ligands.

## Agradecimentos/Acknowledgments

**CAPES, CNPQ, INCT- INOFAR, FAPERJ, LASSBio and UFRJ**

**Área: ____MED__________**

# VALIDATION BY ENSEMBLE DOCKING OF THE PLANNING OF NEW PI3K INHIBITORS

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Key words: *kinases, PI3K, Ensemble docking, Cancer, molecular planning.*

## Highlights

The abstract describes the application of the ensemble docking strategy to validate the molecular design of new structural analogues of gedatolisib, allowing to understand the impact of changes in the comparative mode of interaction between the analogues and gedatolisib with the PI3K target protein.

## Abstract

Phosphatidylinositol-3-kinase (PI3K) belongs to the family of lipid kinases, whose signaling pathway is altered in different malignant tumors. PI3K is a validated target for the treatment of cancer, with the arrival in the medical clinic of the drugs idelalisib, copanlisib, duvelisisb and alpelisib. Inserted in a line of research aimed at the discovery of new antitumor agents, acting through the modulation of kinases, this work aimed to validate the molecular design of new structural analogues of gedatolisib, through an ensemble docking approach. For that, 10 PI3K$\gamma$ proteins deposited in the Protein Data Bank (PDB) were selected, using as a criterion for choosing the co-crystal resolution ≤ 3 Å. To build the ensemble docking model, an overlap was made between each of the structures with a PI3K protein used as a reference (PDB code: 3DBS), in order to ensure greater conformational variability between the proteins to be used in the model. Seven of the ten proteins were used, all of which were prepared using the standard configuration protocol of GOLD, which performs the addition of charges and hydrogen for all amino acids considering the physiological pH (7.4). All ligands were geometrically optimized using the PM7 semi-empirical method, using the MOPAC 2016 software, and the protonation states of each ligand were previously determined using the MarvinSketch v.21.14 program. After choosing the 7 proteins, the model was validated by re-anchoring the co-crystallized ligands with each chosen protein (3DBS, 4ANU, 4ANW, 4URK, 6XRN, 7JWZ and 7JWE). All scoring functions (ChemPLP, GoldScore, ChemScore and ASP) were able to predict the poses of the co-crystallized ligands, and the ASP function was chosen because of the lower RMSD values for all proteins evaluated and due to its ability to discriminate compounds described as inactive (baits) in relation to ligands described as active. Considering the interaction modes presented by the 8 planned ligands, it was possible to observe interactions similar to those described for gedatolisib, such as the interaction of hydrogen with the residue VAL 882 for 3 of the 8 planned ligands. It is noteworthy that all ligands showed additional electrostatic interactions with residues of ASP 836, ASP964 and with residue of ASP 841. The results show that the introduction of a fragment containing an amine group to the planned ligands resulted in a complementary cation-anion interaction, due to the high probability of protonation of the fragment at physiological pH, which interacts with negatively charged ASP residues. Therefore, the ensemble docking model allowed us to evaluate, albeit theoretically, the impacts promoted by each fragment introduced in the structure of the new analogues of gedatolisib.

## Acknowledgments

FAPERJ, CNPQ, CAPES, INCT/INOFAR, LASSBio e UFRJ

# ORG

# Química Orgânica

**Área: ORG** **Nº de Inscrição: 00077**

# 3-[(*E*)-(4-hydroxyphenyl)iminomethyl]phenol and its reduced form as urease inhibitors: Synthesis, anti-urease activities and molecular modeling studies

**Breno G.F. Oliveira (PG),[1]* Caroline D. da Silva (PG),[2] Edjan C.D da Silva (PG),[4] Camila P. Pereira (IC),[1] Luzia V. Modolo (PQ),[3] Ângelo de Fátima (PQ),[1] Gisele A.C. Goulart (PQ),[2] Thiago M. de Aquino (PQ),[4] Júlio C.S. da Silva (PQ)[4].**

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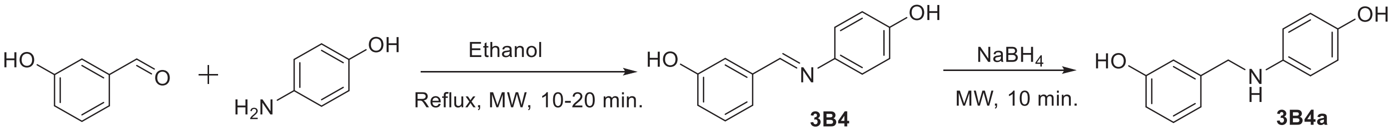
Keywords: *Schiff Bases, Amines, Urea, Nitrogen fertilizers, Molecular Docking.*

## Highlights

►Urea is the most used nitrogen (N) fertilizer in the world. ►Up to 70% of urea is lost due to ammonia volatilization due to the enzymatic action of urease. ►Both urease inhibitors, prepared in excellent yields, showed as potent as the positive control, hydroxyurea. ► The amine **3B4a** is the most promising urease inhibitor.

## Abstract

Nitrogen (N) is essential for plant survival, growth, and crop production. In agriculture, it has been recognized as the single most vital nutrient for increasing crop yields across the globe [1]. The use of N fertilizers is essential to maintain agricultural productivity, which is essential to provide sustenance to the human population. Urea is the most worldwide nitrogen fertilizer used; however, its enzymatic hydrolysis leads to losses through ammonia volatilization causing economic and environmental problems [2]. To prevent this loss, urease inhibitors have been used [2]. Among the new inhibitors synthesized by our research group, the Schiff bases have excelled results [3]. In this work two substances, a Schiff base (**3B4**) and its amine derivative (**3B4a**), were synthesized (Scheme 1) and their *in vitro* antiureolytic activities were also determined. Additionally, the interactions of these substances with the urease enzyme was studied by using a molecular docking approach. The **3B4** and **3B4a** were prepared with 72% and 76% yields, respectively (Scheme 1) The *in vitro* antiureolytic activity of **3B4** and **3B4a** (22.62 ± 6.87 and 24.16 ± 9.56, respectively) showed that both substances inhibited the urease in the same level to the positive control hydroxyurea (HU) (23.45 ± 11.95). However, it is important to mention that, differently from **3B4a**, the imine **3B4** is unstable in presence of water and this can restrict the use of **3B4** as additive in N fertilizer. The molecular docking studies for **3B4** and **3B4a** showed that the orientation of the hydroxyl group 3-OHPh of **3B4** and 4-OHPh of **3B4a** plays an important role in the biding orientation of such subtances with the 2 nickel atoms of the urease catalytic site. Furthermore, the complex urease-**3B4a** showed to be more stable than complex urease-**3B4**, in part, due to an additional hydrogen bonding interaction between His593 with amine group and two hydrogen bonds involving hydroxyl group and the residues Ala436, Arg439 and Asp633. As a conclusion, this work have disclosed substances **3B4** and **3B4a** as promising urease inhibitors, particularly amine **3B4a** that is as potent as **3B4** and it is stable in aqueous medium - an important requirement for potential urease with agriculture interests.



**Scheme 1**: Synthesis of imine **3B4** and the amino derivative **3B4a**.

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## Acknowledgments

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**Área:** ORG

# 5'-deoxy-5'-methylthioadenosine phosphorylase in ligand fishing assays with crude extract from a marine sponge

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Keywords: *Schistosomiasis, MTAP, Enzyme immobilization, Ligand fishing, LC-HRMS*

## Highlights

In the search for a ligand screening model in complex samples such as extracts of marine natural products, the MTAP enzyme was immobilized and applied in the ligand fishing assay, which revealed selective ligands for the enzyme.

## Abstract

5'-Deoxy-5'-methylthioadenosine phosphorylase (MTAP) from Purine Nucleoside Phosphorylase family is present in many organisms. Schistosomiasis is considered a neglected disease and the Praziquantel, drug available to control the disease is ineffective against the larval stage of *Schistosoma mansoni*, raising concerns about drug resistance. In the parasite, MTAP is vital to the organism[1]. Enzymes have been targets for the discovery of new drugs due to their biological importance. The ligand fishing assay is convenient and efficient to accelerate the screening process. There is a variety of these assays and usually, the difference in the procedure relays on the immobilized target. For enzymes, magnetic beads (MB) have been the most widely used solid support because the preservation of enzyme activity and handling practicality[2]. MTAP was immobilized on to magnetic beads (MTAP-MB) by a modified protocol[3]. Marine natural products library affords diverse molecular frameworks through their metabolites, herein a ligand fishing assay for MTAP-MB is described for prospecting ligands in methanolic extract of the marine sponge, *Topsentia ophiraphidites*.

Prior to affinity-based assays, the fingerprint chromatogram for *T. ophiraphidites* was recorded. Chromatographic conditions were acquired with an Acquity HSS T3 column (100 x 2.1mm x 1.7 µm) using acetonitrile and water with 0.1% formic acid. The LC system was coupled to a high-resolution mass spectrometer containing a quadrupole time-of-flight mass analyzer (LC-HRMS) and operated in positive full scan mode. The ligand fishing assay was performed for active (ac) and control (co) MTAP-MB. The steps were carried out according to the previously described procedure[3] with some modifications. The acquired LC-HRMS data were processed in the MZmine 2 software. The table with the aligned data was imported into Excel®. Subsequently, two steps were performed separately: At the first, affinity ratio (AR) were calculated in accordance with the following equation: $AR = (\text{molecular feature}_i)_{(ac)} / (\text{molecular feature}_i)_{(co)}$. For the ion to be considered as a ligand for MTAP, it was established that AR ≥ 1.3. To discard artifacts in the ligand mixture, comparison with the chemical profile of *T. ophiraphidites* and blank samples were carried out. In the second step, the table with the MZmine in the excel data was submitted to processing with the Ichthus software, which is being developed in a partnership work with collaborators from UFPE. The software, in Python language, is an easy-to-use tool for aligning molecular features and AR calculations. The same treatment was performed with the ions with AR ≥ 1.3.

After this inspection process, 16 ligands for MTAP with AR between 1.3 to 8.03 were identified, which are being subjected to dereplication processes using platforms such as GNPS and databases such as Dictionary of Marine Natural Products, Human Metabolome Database, KNApSAcK Core System, MassBank, PubChem and SciFinder.

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**Área: ORG**

# 6-(1*H*-1,2,3-triazol-1-il)-4-(trifluormetil)quinolinas Alquil(aril)-Substituídas: Síntese, Fotofísica, Biointerações Seletivas (DNA/HSA) e *Docking Molecular*

**Yuri G. Kappenberg (PG),[1]* Helio G. Bonacorso (PQ),[1] Isadora Tisoco (IC),[2] Bernardo A. Iglesias (PQ),[2] Pablo A. Nogara (PG),[3] João B. T. Rocha (PQ).[3]**

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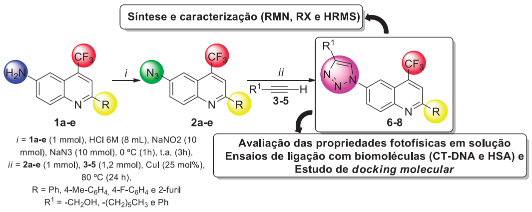
Palavras Chave: *Quinolina; 1,2,3-triazol; Propriedades fotofísicas; Biointerações; Docking Molecular.*

## Highlights

"*Alkyl(aryl)-substituted 6-(1H-1,2,3-triazol-1-yl)-4-(trifluoromethyl)quinolines: Synthesis, Photophysics, Selective DNA/HSA Bio-Interactions and Molecular Docking*": A new series of 4-Trifluoromethyl-(1,2,3-Triazol-1-yl)quinoline scaffolds was synthesized, the photophysical properties in solution and a selective interactions with DNA and HSA has been investigated.

## Resumo

Uma das abordagens mais comumente empregadas no desenvolvimento de novos compostos consiste em estratégias de hibridização molecular baseadas na combinação de dois ou mais núcleos farmacofóricos, visando produzir uma estrutura com perfil biologicamente aprimorado,[1,2] onde heterociclos, têm atraído atenção para o seu desenvolvimento.[3] Sendo assim, estratégias de hibridização molecular a partir da combinação de compostos heterocíclicos, como quinolinas e 1,2,3-triazóis tem sido pesquisada. A combinação destes dois núcleos via fusão ou conjugação, resultando em uma molécula híbrida, demonstram enorme relevância dada sua ampla possibilidade de aplicações farmacêuticas e terapêuticas.[4,5] Desta forma, com base nas propriedades biológicas significativas de quinolinas e 1,2,3-triazóis, este trabalho apresenta a síntese, análise estrutural e avaliação das propriedades fotofísicas de doze novas 2-aril(heteroaril)-6-(4-alquil(aril)-1*H*-1,2,3-triazol-1-il)-4-(trifluormetil)quinolinas (**6-8**), sendo aril(heteroaril) = Ph, 4-$MeC_6H_4$, 4-$FC_6H_4$ e 2-furil e, 4-alquil(aril) = $-CH_2OH$, $-(CH_2)_5CH_3$ e Ph. Os compostos **6-8** foram sintetizados com rendimentos de 77-95% via reação de cicloadição regiosseletiva de azida-alcino catalisada por cobre (*CuAAC*) entre 6-azido-4-(trifluormetil)quinolinas (**2**) e alcinos terminais selecionados (**3-5**). Os azido-intermediários **2** foram obtidos a partir da reação de 6-amino-4-(trifluormetil)quinolinas (**1**) com azida de sódio em 78-87 % de rendimento. Os sistemas híbridos **6-8** foram caracterizados estruturalmente por de RMN de $^1H$, $^{13}C$ e $^{19}F$, e RMN-2D $^1H$-$^{13}C$ (HSQC, HMBC), difração de raios-X em monocristal (SC-XRD) e HRMS (Esquema 1).



**Esquema 1.** Rota sintética para obtenção das (1*H*-1,2,3-triazol-1-il)-4-(trifluormetil)quinolinas (**6-8**).

Além disso, as propriedades fotofísicas, experimentos de ligação seletiva com DNA e HSA (biointerações) e estudos de *docking molecular* para compostos **6-8** foram realizados. Constatou-se também que, todos os derivados **6-8**, independente do solvente, apresentaram transições eletrônicas na região do ultravioleta; e na presença de biomoléculas, apresentaram efeitos hipercrômicos de bandas de transição, com leves deslocamentos batocrômicos, indicando assim, um possível modo de ligação externa, o qual foi também observado em simulações de *docking molecular*. Em resumo, foi possível obter e caracterizar espectroscópica e espectrometricamente uma nova série triazolil-quinolinas (**6-8**), com bons rendimentos. Investigações preliminares mostraram propriedades fotofísicas promissoras em solução, com fluorescências dependentes dos solventes. Simulações de *docking molecular* apresentaram dados consistentes com os ensaios experimentais, fornecendo informações estruturais importantes sobre as interações seletivas dos compostos **6-8** com DNA e HSA.

## Agradecimentos

CAPES, CNPq, FAPERGS.

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**Área: ORG**

# Aggregation-induced emission (AIE) of 2,3-bis(4-methoxyphenyl)quinoxaline-6-carboxylic acid

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Keywords:*(Aggregation-induced emission, AIE, Quinoxaline, Luminescent materials, Microwave synthesis)*

## Highlights

A compound containing a quinoxaline ring and a carboxylic acid is reported as a new AIE-luminogen. Restricted intramolecular motions of phenyl groups and H bonding give rise to aggregation which boosts emission efficiency.

## Abstract

Luminescent materials with aggregation-induced emission (AIE) have attracted much interest since the first report of the AIE concept, showing that some molecules poorly emissive in solution are highly emissive when aggregated.[1] The most acceptable mechanism for AIE is the restriction of intramolecular motions (RIM) in the molecule that prevents self-quenching aggregates.[2] AIE-luminogens have potential applications in chemosensors, bioimaging, and optoelectronic devices.[3] This work reports the synthesis and optical studies of compound **1**.[4] This compound is an interesting candidate for AIE since its structure possesses an H-bonding site (COOH), a luminescent moiety of electron- deficient quinoxaline linked to aryl groups with steric rotation restrictions, and also containing electron donor methoxyl groups, a potential intramolecular charge transfer is then achieved. **1** was prepared by the reaction between 3,4-aminobenzoic acid and 1,2-bis(4-methoxyphenyl)ethane-1,2-dione in acetic acid. The synthetic protocol has been highly improved by reactions in a microwave reactor. The chemical structure was fully characterized by IR, $^1$H and $^{13}$C NMR spectra. The optical properties were investigated by UV and fluorescence spectroscopy in solution and in thin films. **1** shows a moderate blue luminescence ($\lambda_{max.}$ 462 nm) in solution ($10^{-5}$M, MeCN). Gradual increase in the volumetric fraction of water (5 and 10%) in the MeCN/water mixtures more than doubled the emission intensity, a piece of evidence for AIE. The 50% water solution still shows a significant increase, though less than that of the 10% solution. Above 50% there is a decrease in luminescence efficiency, where part of aggregates is likely to precipitate. This compound also exhibits a strong blue emission in the solid phase. The preliminary studies corroborate our hypothesis that the AIE in **1** is occurring due to H bonding and the RIM mechanism. Thus, this material does not show the typical aggregation-caused quenching, instead, it aggregates with an increased emission. Nonetheless, this is a very accessible molecule by readily simple synthesis when compared to those complex examples of AIE-luminogens from literature.

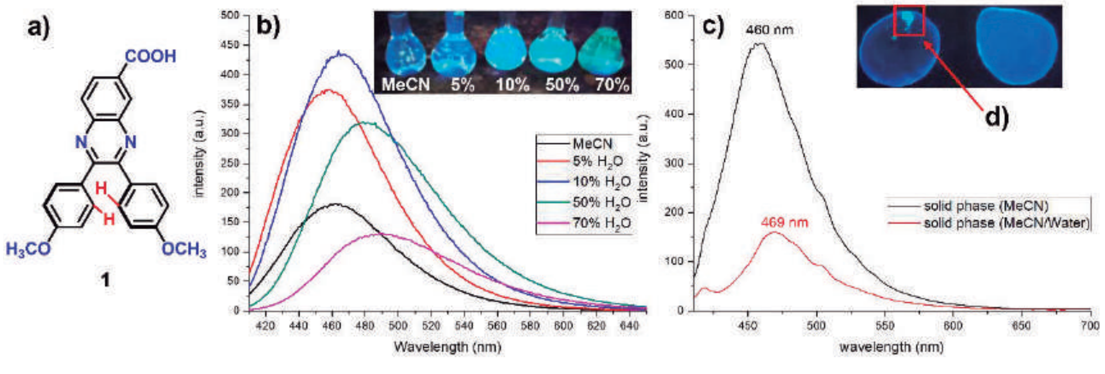

Figure 1: a) compound **1** *spotting the rising of RIM*; photoluminescence of **1** b) in solution; and c) in thin films; d) area with concentration of aggregates with increased emission. Unfortunately, a region not caught by the spectrum

## References

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**Área: ORG**

# Alkylation of α-carbonyl sulfoxonium ylides

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Key Words: *Sulfur Ylides, Sulfoxonium Ylides, Sulfur Bis-Ylides, Alkylating Agents, Michael Additions*

## Highlights

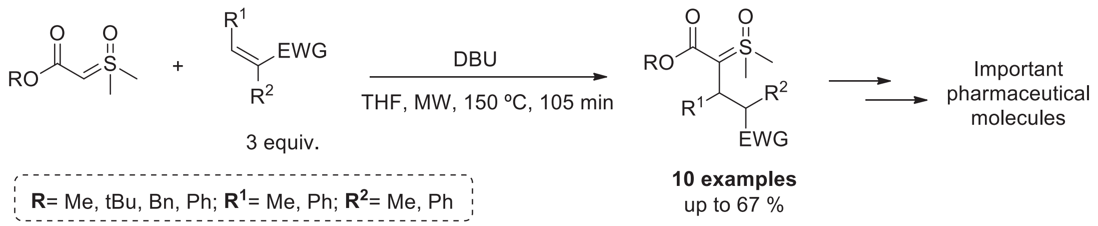
Evaluation of alkylating agents to obtain prochiral sulfoxonium ylides

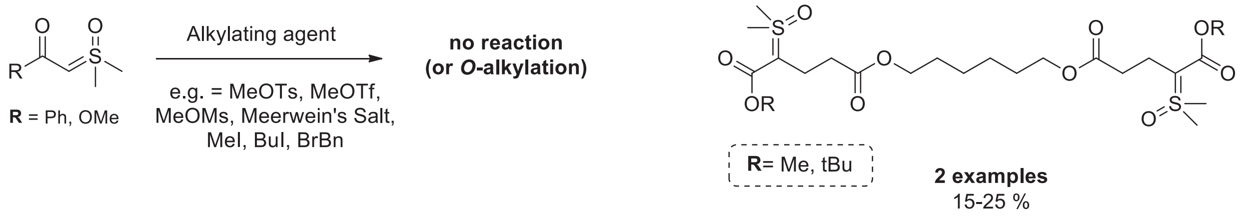
Synthesis of prochiral sulfoxonium ylides and sulfoxonium bis-ylides via Michael Additions

## Abstract

Sulfur ylides represent an important synthetic tool for organic chemists since they are used as building blocks in total synthesis, in material chemistry, and in the production of drugs, for example. However, there is a great difficulty associated with the alkylation of these compounds, mainly of the stabilized ones, as is the case of the α-carbonyl sulfoxonium ylides. For this reason, obtaining prochiral sulfur ylides without the use of diazo compounds is still a synthetic challenge. No method describes the insertion of any group different from aryl and this limits the application of these important platforms.[1,2]

In this context, in order to obtain prochiral molecules, a series of alkylating agents were investigated, mainly those that have unreactive counterions, such as oxonium salts. However, this strategy was not effective, since *O*-alkylated products were obtained instead of *C*-alkylated ones. The only alkylating agent that showed a promising result was a hypervalent iodine reagent, which resulted in the product in 8 % yield. Furthermore, the synthesis of prochiral ylides via Michael Addition reaction was studied. In this case, 10 prochiral sulfoxonium ylides were obtained in 2-67 % yields. In addition, a diacrylate was used in the studied condition furnishing sulfoxonium bis-ylides in 15-25 % yields. Also, these bis-ylides were employed in S-H insertion reactions, providing the corresponding β-ester di-thioethers in 25-40 % yields.





## Acknowledgments

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**Área: ORG** **Nº de Inscrição: 001435**

# ANALYSIS OF THE CHEMICAL PROFILE OF THE EXTRACTS OF THE AERIAL PARTS OF *Peperomia pellucida*

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Palavras Chave: *Peperomia pellucida, Perfil químico, CCDAE.*

## Highlights

The research addressed the analysis of the chemical profile of the extracts of the aerial parts of Peperomia pellucida, using chemical developers and verification of the antioxidant potential of the extracts.

## Resumo/Abstract

Medicinal plants are used by humanity in the treatment of various diseases. Among the species used for such use, select it in the species *Peperomia pellucida*. Within the *Peperomia* genus, *P. pellucida* is one of the most studied plants due to its applications in folk medicine, its wide distribution, chemical production and biological potential. Taking into account these facts, this study used High Performance Thin Layer Chromatography (CCDAE) for simultaneous analysis of extracts of the aerial parts of *Peperomia pellucida* to verify the chemical profile of the species. The extract was obtained from 50 mg of dry vegetable matrix, according to the method used by Freitas (2017) which consisted of an ultrasonic bath for 10 min. at a temperature of 25 ° C. the procedure was repeated 4 times and the residual volumes were collected and dried for further pre-treatment by SPE. After application and elution, the chromatographic plates were subjected to revelations with VAS (Vanillin Sulfuric Acid) used to verify the presence of terpenes, steroids and phenolic compounds in the extracts of P. pellucida. In addition, DPPH staining was performed to check the antioxidant activity, NP / PEG (Diphenylboryloxyethylamine/Polyethylene glycol) to check for the presence of flavonoids, Dragendorff to check for alkaloids and FBS (Fast Blue Salt) to check for phenolic compounds. Table 1 shows the standard substances used in the disclosure of each class. The results obtained through the revelations showed the presence of terpenes, steroids and phenolic compounds in the extracts of *P. pellucida*, in addition to signs that indicate the presence of flavonoids, as previously noted by Silva et al. (2013). In the verification of antioxidant activity, the method that eliminates the stable free radical (DPPH) used to detect the presence of antioxidant compounds was used (Oliveira, 2015), however the results were negative, as can be seen in Figure 1 only the fluorescent staining of the pattern Ascorbic acid. This is related to the conditions under which the extraction of *P. pellucida* was carried out, such as the low amount of mass used to produce the extracts. Therefore, studies of this nature are necessary because it is important to bring chemical information about plants, especially medicinal ones, in view of the therapeutic effects provided by these types of vegetables, as is the case of *P. pellucida*. In addition, this information is a relevant contribution to phytochemical studies of this species and is data that can be used for future research of a similar nature.

**Table 1.** Standards used in chromatographic plate development.

| STANDARDS | CHEMICAL CLASSES |
|---|---|
| β-amyrin | Phenolic compounds, steroids and terpenes |
| Brucine | Alkaloids |
| Rutin | Phenolic compounds |
| Rutin and Quercetin | Flavonoids |
| Ascorbic Acid | Antioxidant compounds |

**Figure 1**. Chromatographic plate with DPPH.

**Source:** Research data.

## Agradecimentos/Acknowledgments

A Universidade Federal do Pará pelo apoio financeiro.

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**Área: ORG** **Nº de Inscrição: 00565**

# Appel Reaction with Tribromoisocyanuric Acid/Triphenylphosphine: a Mild Methodology for Preparation of Nitriles from Aldoximes

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Palavras Chave: *Nitriles, Aldoximes, Tribromoisocyanuric acid, Triphenylphosphine, Appel reaction*

## Highlights

- New methodology for preparation of nitriles via Appel Reaction
- Easily available reagents
- Mild reaction conditions

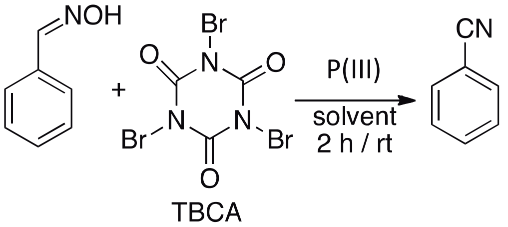
## Resumo/Abstrac

The Appel reaction is an important route for halogenations under mild and neutral conditions using a phosphorus(III) compound along with an halogen source. Several useful synthetic transformations are easily accomplished using Appel conditions, such as the conversion of alcohols to alkyl halides as well as aldoximes and amides to nitriles.[1] Among several reagents developed and applied as electrophilic halogen sources to the generation of the Appel reagent ($[Br\text{-}PPh_3]^+$), the tribromoisocyanuric acid (TBCA) is one of the most advantageous, due to its easy and inexpensive preparation and high atom economy.[2]

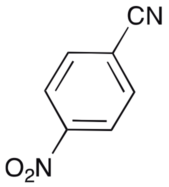
Herein we present the study of the TBCA/ P(III) system for the synthesis of nitriles via Appel reaction.

Initially, it was done an optimization of the reaction using benzaldoxime as a model substrate, forming benzonitrile in 20 – 75% chromatographic yield. Although phosphites can also be used, the best conditions were obtained using $PPh_3$ in $CH_2Cl_2$ at room temperature, 1/2/0.5 (PhCH=NOH/$PPh_3$/TBCA) mol ratio.

| PhCH=NOH/P(III)/TBCA | P(III) | Solvent | Yield (%) |
|---|---|---|---|
| 1/1,5/0,5 | $PPh_3$ | $CH_2Cl_2$ | 68 |
| 1/2/0,5 | $PPh_3$ | $CH_2Cl_2$ | 75 |
| 1/2/0,5 | $PPh_3$ | MeCN | 20 |
| 1/2/0,5 | $P(OPh)_3$ | $CH_2Cl_2$ | 35 |
| 1/2/0,5 | $P(OMe)_3$ | $CH_2Cl_2$ | 52 |
| 1/2/0,5 | $P(OBu)_3$ | $CH_2Cl_2$ | 42 |



Using these optimized conditions, we extended the methodology to other aldoximes. The Appel reaction was performed under mild conditions (rt, fast reaction, no special equipment) and furnished the corresponding nitriles after chromatographic column ($SiO_2$, hexane).



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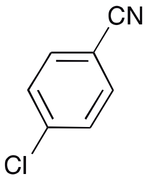

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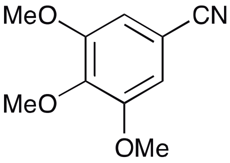

(66%)

However, the presence of an unreacted $PPh_3$ in many cases resulted in an inconvenient and tedious purification process. Therefore, a different approach was tested, consisting in a new mol ratio (1:2:1, PhCH=NOH/$PPh_3$/TBCA) with an excess of TBCA that oxidized the remaining $PPh_3$ to $O{=}PPh_3$, facilitating the purification process.

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## Agradecimentos/Acknowledgments

CNPq / PIBIC

**Área: ORG**

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

# Archicarbons: Carbon Allotropes using the Circular Arch as Building Block

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Palavras Chave:*carbon, allotrope, DFT, cyclo[18]carbon*

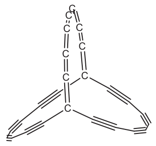
## Highlights

Novel family of carbon allotropes based on arches of the cyclo[18]cabon, a carbon-made molecular wheel, have been proposed. Several molecular carbon allotropes, as well as extended solids, have been investigated and DFT calculations have shown that these materials are viable structures.

## Resumo/Abstract

The wheel is one of the greatest human inventions. Another amazing human invention was the arch, which appeared in Mesopotamian brick architecture circa 2000 BC, and was fully explored by the ancient Romans, who employed it to erect structures such as bridges, aqueducts, domes, and gates. The arch revolutionized humanity so much in terms of construction, that it became the prefix to the word architecture. Recently a wheel entirely made from carbon (**1**) has been experimentally reported. A question that arises to us is if it is possible to use the arches extracted from cyclo[18]carbon (**1**) to build other carbon allotropes. If arches are extracted from cyclo-[8]carbon, they could be bonded to other carbon scaffolds, affording various interesting structures. Some of these structures are shown below. This contribution is an essay exploring some possible arch-based carbon structures, which will be called archicarbons. High-level DFT calculations (M11/def2-TZVP+GrimmeD3 and PBE+GrimmeD3 for extended solids) were employed for proving the viability of such molecules, their structures, and some key properties. Herein we report the outcome of such adventures in the structural chemistry of these exquisite carbon forms.

**1**



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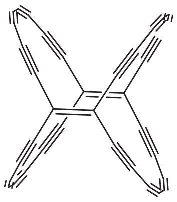

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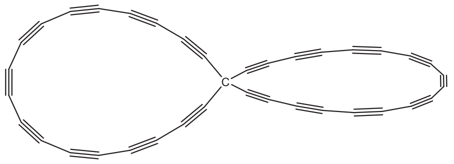

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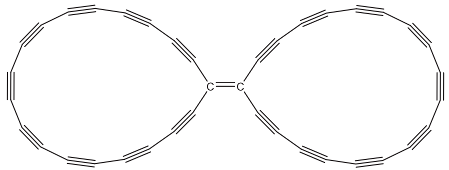

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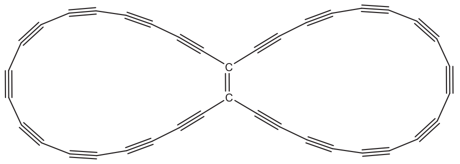

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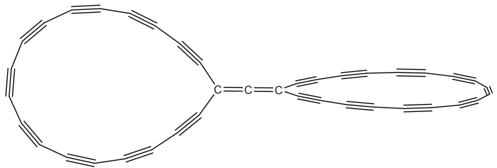

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## Agradecimentos/Acknowledgments

FAPERJ, CNPq, CAPES

**Área: ORG** **Nº de Inscrição: 00519**

# Artificial Neural Network hybridized with Genetic Algorithm in Solid State Fermentation for the production of lipase from *P. roqueforti* ATCC 10110

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**Key words: Artificial Intelligence, Biotechnology, Enzyme, Optimization.**

## Highlights

**First application of RNA-AG to optimize the lipase production of *P. roqueforti* ATCC 10110 by FES; 5.0 x $10^7$ artificial experiments from 28 bank experiments and triple lipase production.**

## Resumo/Abstract

**In this work, a Genetic Algorithm (GA) was used to optimize the lipase production of *Penicillium roqueforti* ATCC 10110 in solid state fermentation (SSF), modeled by Artificial Neural Network (ANN) to obtain greater enzymatic production. A multi-layered feed-forward neural network architecture was used. For ANN training, the *Levenberg-Marquardt* (LM) algorithm was selected due to its ability to reach training speeds in second order proportions. The architecture presented a polynomial configuration with 3 neurons in the input layer, 49 neurons in the hidden layer and 1 neuron in the output layer (Figure1). The input variables optimized by the RNA-GA were fermentation time, temperature and humidity (Table 1) in the optimized theoretical conditions: 1 day, 31 ºC and 72%, whose theoretical lipolytic activity was 72 U $g^{-1}$. The validation was performed considering the optimal condition and those of the central point. The lipase activities of the central and optimum points obtained were 10.25 U $g^{-1}$ and 48.00 U $g^{-1}$, respectively, representing a 78% recovery of activity, tripling the lipase production in relation to literature data[1], which makes the application of the model in other systems for enzyme production by SSF attractive. The use of AG allowed 5.0x$10^7$ artificial experiments to be simulated from a matrix with 28 bench experiments, enabling a high saving of time and reagents.**

**Figure 1. Network architecture used with the input layers (*Input*), (*Hidden*) and (*Output*).**

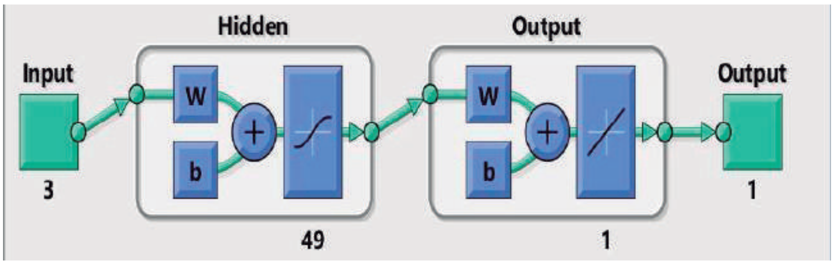

**Table 1. Variables and their levels for the planning used in the RNA-GA.**

| | Real Variables | | |
|---|---|---|---|
| **Levels** | **Time (day)** | **Temperature (ºC)** | **Moisture (%)** |
| -3 | 1 | 16 | 40 |
| -2 | 2 | 19 | 48 |
| -1 | 3 | 22 | 56 |
| 0 | 4 | 25 | 64 |
| 1 | 5 | 28 | 72 |
| 2 | 6 | 31 | 80 |
| 3 | 7 | 34 | 88 |

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## Agradecimentos/Acknowledgments

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**Área: ORG**

# A Selective C-C Bond Cleavage Strategy Promoted Only by Visible Light: C-C Insertions of 1,3-Diketones into Aryldiazoacetates

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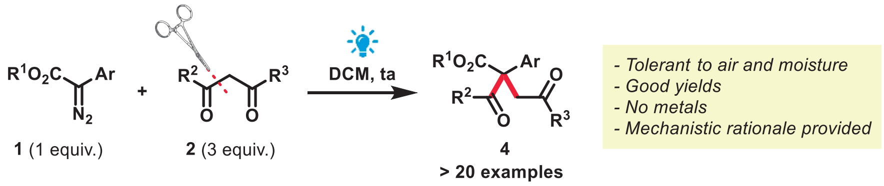
Palavras Chave: *visible light, aryldiazoacetates, 1,4-dicarbonyl compounds, C-C bond insertions.*

## Highlights

A new visible light-promoted reaction between aryldiazoacetates and 1,3-diketones allows good yields and selectivities for C-C bond insertions leading to the corresponding 1,4-dicarbonyl compounds. This transformation is straightforward and highly practical; it tolerates air and moisture and does not require the use of any metals. Mechanistic investigations support the involvement of a key cyclopropanol intermediate derived from an intramolecular rearrangement.

## Resumo/Abstract

We have developed a low energy photochemical transformation based only on the use of visible light allowing the C-C bond insertion of 1,3-diketones **2** into aryldiazoacetates **1** to afford the corresponding 1,4-diketones **4** in general good efficiency and selectivity. Mechanistic investigations suggest the involvement of a cyclopropanol derivative as a key reactive intermediate, leading to a formal C-C bond insertion reaction via an intramolecular rearrangement. The protocol reported herein is robust, practical, and cost-effective. In addition, our work showcases the reactivity and selectivity "truly" accessed by free carbene intermediates (C-C insertions), as opposed to a number of other previously reported metal-based approaches displaying a different selectivity (C-H insertions). Furthermore, our study also demonstrates that the generation of free carbenes under blue light irradiation can be used as an additional mechanistic tool for the interrogation of the more accurate role of metal catalysts when reacting with aryldiazoacetates.



**Scheme 1.** Resume of the C-C insertion of 1,3-diketones **2** into aryldiazoacetates **1** under blue light irradiation.

## Agradecimentos/Acknowledgments

Financial support is greatly appreciated from Fapesp for a Post-Doctoral fellowship to R. D. C. G. (2020/00144-6), and Fapesp for a Research Grant to I. D. J. (2019/01235-8).

**Área: ORG**

# Avaliação da capacidade antioxidante, investigação eletroquímica e espectroscópica de novas nitronitronas

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Palavras Chave: *Nitronas. Nitroaromáticos. Eletroquímica orgânica. Voltametria cíclica. Mecanismo redox. Capacidade Antioxidante.*

## Highlights

The electrochemical and spectroscopic investigation of new nitronitrones was conducted, along with the evaluation of the antioxidant capacity. In the redox study of nitronitrones, the nitro group reduces first and also the antioxidant capacity is affected by its presence. We report the trend of forming charge transfer complexes by the nitrone with DDQ.

## Resumo

As nitronas são conhecidas por reduzir o estresse oxidativo[1], por isso são úteis para o tratamento de diversas patologias[2,3]. O mecanismo molecular de ação biológica desse grupo de compostos ainda não está completamente elucidado[4]. O presente trabalho apresenta como objetivo investigar o comportamento eletroquímico, antioxidante e espectrofotométrico de nitronas sintéticas, seus derivados e precursores. Voltamogramas cíclicos (VCs) e de pulso diferencial (VPDs), em eletrodo de carbono vítreo (ECV), foram registrados em meio prótico (DMF (20%) + tampão acetato pH 4,17) a fim de mimetizar os ambientes hidrofílicos biológicos. Avaliou-se a capacidade antioxidante dos compostos, pelos métodos espectroscópicos de FRAP (poder antioxidante de redução de íons ferro) e capacidade antioxidante sequestradora frente ao radical DPPH$^\bullet$ (2-2-difenil-1-picril-hidralazina) (%RSA). Como também, a fim de avaliar a reatividade e constatar a função doadora de elétrons das nitronas foi investigada a interação entre nitronas e DDQ, usando a espectrofotometria no UV-Vis. Os VCs e VPDs registrados mostraram que as nitronitronas LQB-303 (Fig. 1) e LQB-304 foram eletroquimicamente ativas em redução. Na investigação da capacidade antioxidante, os valores de %RSA variaram entre 10,14 – 37,25% de inibição, já os valores de FRAP variaram entre 126,86 - 196,84 mg de equivalentes de trolox (ET)/mol do composto. Nos dois ensaios realizados, observou-se a redução do poder antioxidante dos compostos nitrados, quando comparados aos não nitrados. A interação entre a nitrona LQB-109 e DDQ resultou na formação de um complexo de transferência de carga (CTC) intermolecular, porém, o mesmo parece não ter sido observado com a nitronitrona LQB-303 e o DDQ (Fig. 2). Técnicas eletroquímicas e espectroscópicas foram úteis na obtenção de dados relativos ao comportamento redox das nitronitronas e seus precursores e foram correlacionados a atividades leishmanicidas, principalmente para as nitronitronas LQB-303, LQB-304 e LQB-484, que foram significativamente leishmanicidas, com baixa toxicidade[4].

REFERÊNCIAS: [1] DURAND, Grégory et al. **The Journal of Organic Chemistry**, 82, 135-142, 2016. [2] COSTA, Débora S. S. *et al*. **Bioorganic & Medicinal Chemistry**, 23, 2053-2061, 2015. [3] ROSSELIN, Marie *et al*. **Electrochimica Acta**, 193, 231-239, 2016. [4] PACHECO, Juliana et al.,ACS Med. Chem. Letters, 2021.

Figura 1. VCs para LQB-303 em tampão acetato, pH 4,17 + DMF (20 %), ECV, direção catódica. (A) Varreduras sucessivas e (B) em diferentes velocidades de varredura.

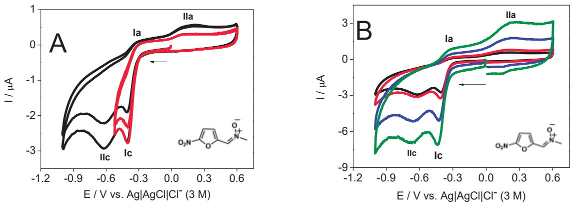
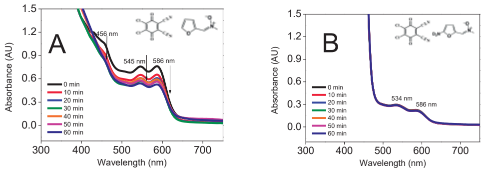


Figura 2. (—) Espectros iniciais na região do UV-Vis para a interação entre LQB-109 (c = 3,95.10$^{-2}$ mol L$^{-1}$) e DDQ (c = 1,322.10$^{-4}$ mol L$^{-1}$) (A). (—) Espectros iniciais na região do UV-Vis para a interação entre LQB-303 (c = 3,95.10$^{-2}$ mol L$^{-1}$) e DDQ (c = 1,322.10$^{-4}$ mol L$^{-1}$) (B). Espectros em função do tempo: (—) 10 minutos, (—) 20 minutos, (—) 30 minutos, (—) 40 minutos, (—) 50 minutos e (—) 60 minutos, em acetonitrila, caminho óptico de 1 cm



## Agradecimentos

FAPEAL, CNPQ, CAPES, PIBIC/UFAL e PET QUÍMICA da UFAL – Campus de Arapiraca.

**Área: _ORG_**

# Bifunctional-Squaramide Catalyzed Asymmetric α-Sulfenylation of Azlactones: Mechanism and Origin of Enantioselectivity

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Keywords: *Azlactone, Thiolation, DFT, Münchnone.*

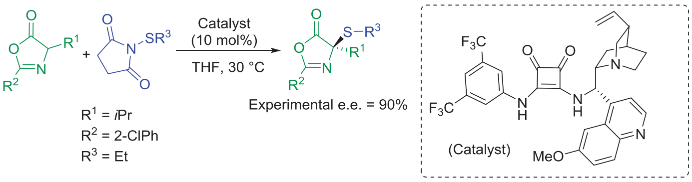
## Highlights

The mechanism and enantiosselectivity of the asymmetric α-sulfenylation of azalactones was investigated using DFT calculations. A Münchnone-type activation mode was found out as the enantiodiscriminating step.

## Abstract

Azlactones are versatile building blocks in organic synthesis, which have been employed in the preparation of a diversity of α,α-amino acid derivatives, heterocycles and natural products.[1] Although the asymmetric α-thiolation of azlactones employing a squaramide bifunctional catalyst (Scheme 1) appears as one of the most important transformations involving this heterocycle,[2] its mechanism and the origin of enantioselectivity of this transformation has not been investigated. Thus, the most plausible reaction pathway and the key interactions responsible for the asymmetric induction were investigated using Density Functional Theory (DFT) calculations.

**Scheme 1.** Asymmetric azlactone α-sulfenylation.



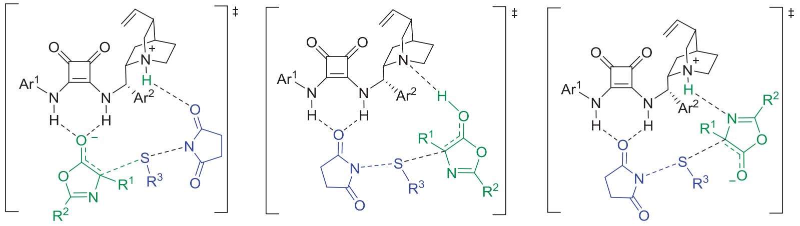
The results reveal that the reaction occur in two steps. Initially, the α-deprotonation of the azlactone by the catalyst tertiary amine moiety affords an ion pair intermediate containing the ammonium salt of the catalyst and the azlactone enolate ($\Delta G^{\ddagger}$ = 8.27 and 7.67 kcal mol$^{-1}$ for the (*R*) and (*S*)-azlactone, respectively).

The second step involves the formation of the carbon-sulfur bond and is responsible for the stereochemical outcome of the reaction. Three different proposals of activation modes were evaluated (Scheme 2). The first involves the squaramide interaction with the azlactone enolate, associated with interactions of the thiolating reagent and the catalyst ammonium hydrogen. The second involves a classical proposal for azlactones, with formation of an azlactone enol tautomer through an acid-base interaction between the enolate and the ammonium proton, and presents interactions between the thiolating reagent and the squaramide scaffold. The last proposal involves the interaction between the azlactone nitrogen and the ammonium salt, in a Münchnone-type activation.[3]

The last proposal presented considerably lower barriers than the others and also predicted the correct enantiomer with the lower relative error (experimental data: 90% e.e., $\Delta\Delta G^{\ddagger}$ of 1.75 kcal mol$^{-1}$). The prediction led to a calculated $\Delta\Delta G^{\ddagger}$ of 1.17 kcal mol$^{-1}$ and a theoretical e.e. of 75%.

Next, the generality of this model was tested by the prediction using a different reaction condition, in which the azlactone and thiolating reagent were simultaneously altered. The major enantiomer was correctly predicted, suggesting that the model is adequate.

**Scheme 2.** Possible activation modes.



| | | | |
|---|---|---|---|
| **(*R*)-product pathway** | **$\Delta G^{\ddagger}$ = 11.07 kcal mol$^{-1}$** | **$\Delta G^{\ddagger}$ = 10.77 kcal mol$^{-1}$** | **$\Delta G^{\ddagger}$ = 6.74 kcal mol$^{-1}$** |
| **(S)-product pathway** | **$\Delta G^{\ddagger}$ = 10.95 kcal mol$^{-1}$** | **$\Delta G^{\ddagger}$ = 13.19 kcal mol$^{-1}$** | **$\Delta G^{\ddagger}$ = 7.91 kcal mol$^{-1}$** |
| **Energy gap (*S* – *R*)** | **$\Delta\Delta G^{\ddagger}$ = -0.12 kcal mol $^{-1}$** | **$\Delta\Delta G^{\ddagger}$ = 2.42 kcal mol $^{-1}$** | **$\Delta\Delta G^{\ddagger}$ = 1.17 kcal mol $^{-1}$** |

References: [1] *Chem. Eur. J.* **2016**, *22*, 10294–10318; [2] *Org. Lett.* **2014**, *16*, 672–675. [3] *J. Org. Chem.* **2021**, *86*, 13169–13174.

## Acknowledgments

The authors are grateful for the generous financial support from CAPES (Finance Code 001), CNPq (150082/2020-7), UFJF, FAPEMIG and Rede Mineira de Química.

**Área: ORG** **Nº de Inscrição: 01314**

# Caracterização fotofísica e efeito da adição de TFA na fluorescência de derivados de 6-amino-4-quinolona

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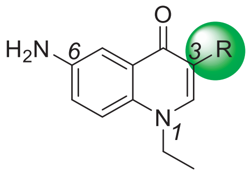
Palavras Chave: *quinolona, estudos fotofísicos, caracterização fotofísica*

## Highlights

"Photophysical characterization and effect of TFA addition on the fluorescence of 6-amino-4-quinolone derivatives". Fluorescent quinolone derivatives. Emission profile modulated by acid/base equilíbrium. pH dependent fluorescente sensors.

## Resumo/Abstract

O interesse contínuo da comunidade científica por derivados 4-quinolônicos decorre de sua grande versatilidade sintética e de suas variadas aplicações, que vão desde a Química Medicinal à Química de Materiais. As 6-amino-4-quinolonas do tipo **1** foram sintetizadas e tiveram suas estruturas elucidadas por espectroscopia na região do Infravermelho e por Espectroscopia de RMN de $^{1}H$ e $^{13}C$. A caracterização fotofísica dessas substâncias foi realizada em diferentes solventes sendo possível observar um efeito batocrômico na absorção e na emissão com o aumento na polaridade do solvente. As propriedades fotofísicas das substâncias, em acetonitrila, encontram-se na Tabela 1.



**1a:** R= $CO_2Et$
**1b:** R= COOH
**1c:** R= CONHPh

| Substância | $\lambda_{abs}$ (nm) (log ε) | $\lambda_{em}$ (nm) | $\Phi_f$ | $\lambda_{em\text{-}TFA}$ (nm) | $\Phi_{f\text{-}TFA}$ |
|---|---|---|---|---|---|
| **1a** | 226 (4,40); 265 (4,21); 325 (4,06) | 416 | 0,09 | 505 | 0,43 |
| **1b** | 242 (4,32); 264 (4,33); 326 (3,95) | 441 | 0,25 | 497 | 0,39 |
| **1c** | 229 (4,42); 280 (4,37); 330 (4,21) | 415 | 0,10 | 500 | 0,27 |

Na presença de TFA, os espectros de absorção de todas as amostras sofrem alterações indicando a formação de uma nova espécie em solução. Foi também observado um decréscimo na intensidade da banda de emissão original, o aparecimento de uma nova banda de emissão em maior comprimento de onda, e um considerável aumento no rendimento quântico de fluorescência, sendo o mais pronunciado na substância **1a** que aumenta de $\Phi_f$ = 0,09 para 0,43. Essa variação no perfil emissivo é dependente da concentração de TFA e um ponto isosbéstico foi observado (cerca de 460 nm para **1a**), indicando o estabelecimento de um equilíbrio termodinâmico. Além disso, **1a** se mostrou 1000 vezes mais sensível à adição de ácido do que os derivados **1b** e **1c**. Um análogo estrutural de **1a** sem o grupo -$NH_2$ em C-6 não demostrou qualquer alteração na absorção ou emissão com adição de TFA, demostrando a importância do grupo amino nas propriedades fotofisicas de **1a-c**. Estudos adicionais para compreender o equilíbrio de protonação em TFA de **1a-c** e o perfil emissivo das espécies protonadas estão em andamento. Com este trabalho espera-se que, no futuro, sensores óticos derivados desta classe de substâncias possam ser desenvolvidos.

## Agradecimentos/Acknowledgments

CNPq, FAPERJ, PPGQ-UFF, PROAP-UFF, CNPq -PIBIC. This study was also financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) - Finance Code 001.

**Área: ORG**

# Cellulose crosslinking by $S_N2$ reactions in DMSO/DBU/$CO_2$ system

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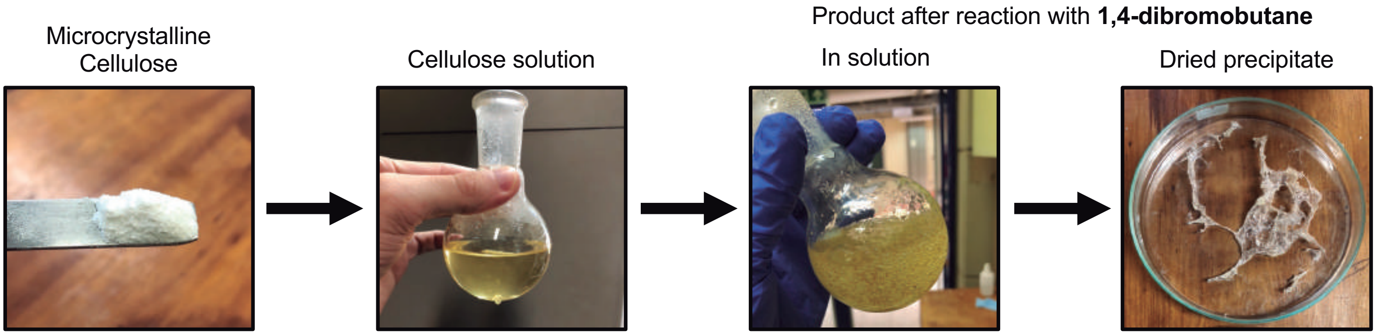
Keywords: *cellulose solubilization, carbon dioxide, cellulose carbonate, alkyl dihalides, macromolecular networks.*

## Highlights

The linkage between dissolved cellulose chains can lead to the construction of macromolecular networks with different properties depending on the extent of the reaction and the crosslinking agent used.

## Resumo/Abstract

With the depletion of fossil resources, academia and industry perceive the need for more sustainable approaches, particularly concerning polymer science. In this context, cellulose, the most abundant naturally occurring macromolecule on the planet, has received substantial attention. Despite the number of products and processes developed from cellulose's physical and chemical modification in solid-state, its dissolution has always been a topic of great scientific interest, since it allows obtaining more homogeneous products. The DMSO/DBU/$CO_2$ system, a system in which a non-ionic liquid (an alcohol and an amine base) converts to an ionic liquid (a salt in liquid form) upon exposure to an atmosphere of carbon dioxide, was described in 2005 by Jessop for organic synthesis and separations and recently optimized for cellulose dissolution. In addition to producing homogeneous solutions, this system allows the chemical modification of cellulose under milder conditions. Recent studies have demonstrated the derivatization of cellulose from reagents with different functionalities. Nevertheless, these works describe only the modification of cellulose with monofunctional reagents in this solvent system. Based on this, the study consisted of the reaction of cellulose solutions with 1,4-dibromobutane. In this process, cellulose carbonate is formed during the dissolution step, which will act as a nucleophile in the $S_N2$ reaction by attacking the alkyl dihalide. Since there are two substitution possibilities, cellulose chains may crosslink. Figure 1 illustrates the steps of the process. The product is isolated by precipitation in water followed by washings with water and then methanol. The formed gel is dried under vacuum. Infrared spectroscopy and X-ray diffraction analyses confirm the success of the reaction by the appearance of the symmetrical stretching band C=O of a carbonate ester at 1740 $cm^{-1}$ and by the disappearance of the crystalline pattern of the cellulose. For the next steps of this study, we intend to investigate the carbon size chain influence of the bifunctional reagent.


Microcrystalline Cellulose

Cellulose solution

Product after reaction with **1,4-dibromobutane**

In solution

Dried precipitate

**Figure 1.** Visual aspects of the dissolution process and gel formation.

## Agradecimentos/Acknowledgments

Instituto de Química de São Carlos (IQSC-USP) and Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq).

**Área: ORG**

# CHEMOENZYMATIC SYNTHESES OF PROPAFENONE ANALOGS

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Keywords: *Propafenone, lipases, enzymatic kinetic resolution.*

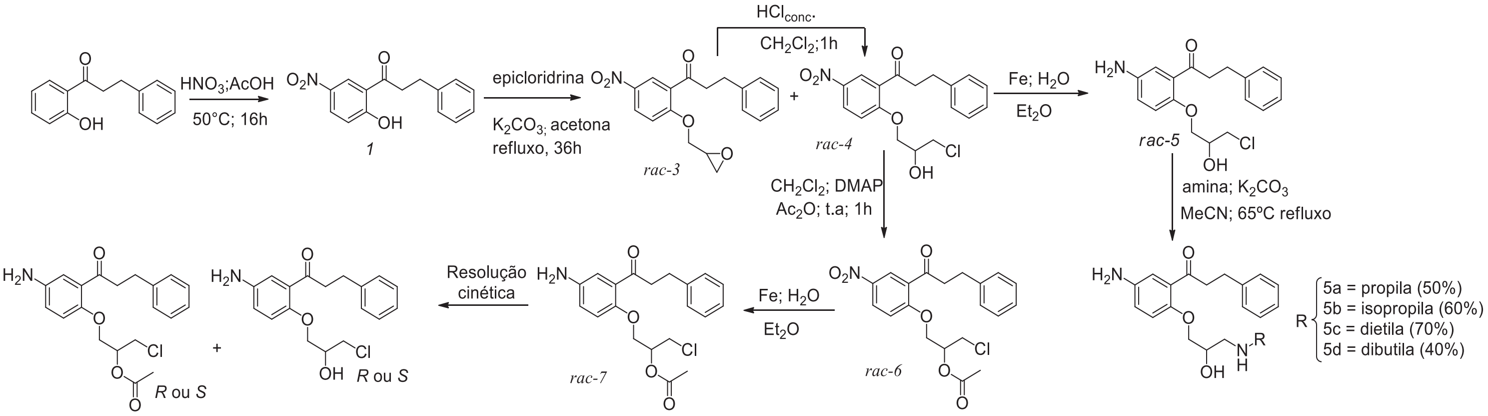
## Highlights

- Propafenone analogs were synthesized as a strategy to discover new biological activities.
- The key step in the syntheses of propafenone analogs was the kinetic resolution of rac-7 catalyzed by lipases.

## Abstract

Propafenone belongs to class 1c of antiarrhythmic drugs blocking sodium channels and is metabolized to two main metabolites, 5-hydroxypropaphenone and *N*-depropylpropaphenone. The impairment or increase in metabolism can be investigated to obtain drugs with more favorable pharmacological profiles. The modifications were carried out with the insertion of an amino group in the C-5 phenolic benzene ring and the introduction of alkylamines in the side chain, such as propylamine, isopropylamine, diethylamine and dibutylamine leading to the analogs rac-5a (50%), rac-5b (60%), rac-5c (70%) and rac-5d (40%), respectively.

**Figura 1.** *Chemoenzymatic synthesis of chiral intermediates of propafenone analogs*



In parallel, a protocol was developed for the enzymatic kinetic resolution of a key intermediate common to rac-5a-5d analogs, 1-[4-amino-2-(3-phenylpropanoyl)phenoxy]-3-chloropropan- 2-yl (rac-7), via hydrolysis reaction, catalyzed by lipases. After a detailed study of the reaction parameters, rac-7 can be resolved in a 0.1 M solution of 80% phosphate buffer (pH 7) and 20% toluene, at 40 °C for 30 h, with an enzyme/ substrate (m/m) of 1:1, in the presence of immobead-150 immobead-150 lipase from Thermomyces lanuginous (TLL), leading to chiral chlorohydrin (5) 1-(5-amino-2-(3-chloro-2- hydroxypropoxy)phenyl)-3-phenylpropan-1-one with >99% enantiomeric excess and the remaining chiral substrate (7) 1-[4-amino-2-(3-phenylpropanoyl)phenoxy]-3-chloropropan-2 acetate -ila with 98% enantiomeric excess, 50% conversion and E > 200.

### References

1. LOWES, D.J., *et al*. **Journal of Medicinal Chemistry**. v. 54, p. 7477–7485, 2011.
2. KROEMER, H. K., *et al*. **Circulation**, v. 89, p. 2396-2400, 1994.

## Acknowledgments

The authors are grateful to UFC and LABS for infrastructure and support, to FUNCAP, CNPq and CAPES for supporting a cooperation project and to for granting research fellowships.

**Área: ORG** **Nº de Inscrição: 654**

# Dereplication by (-)ESI-MS and screening for Antiproliferative Activities of *Eugenia aurata extracts*

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*[1]Department of Biological Sciences, Faculty of Sciences and Letters, University of São Paulo State (UNESP), [2]Biological Chemistry Laboratory, Institute of Chemistry, University of Campinas (UNICAMP) [3]Faculty of Pharmaceutical Sciences University of Campinas (UNICAMP)*

*Key words: flavonoids, phenolic compounds, (-) ESI-MS*

## Highlights

*Eugenia aurata* extracts showed a different antiproliferative activity due to their phenolic profiles.

## Abstract

The Myrtaceae is used in folk medicine for diabetes, hypertension and ulcers[1,2]. These activities are frequently attributed to their phenolics. Some these constituents were found in *Eugenia aurata*: ethyl acetate (AEA) and methanolic (MEP) leaves extracts**,** which it was identified from (-) ESI-MS (Thermo LTQ Orbitrap Velos). Extracts were provided from the dried leaves collection at Horto Florestal (Assis-SP) after maceration (1:10 plant/solvent ratio, 3x2h, r.t), filtration and evaporation in rotaevaporator. Both extracts showed ion of *m/z* 447, which was assigned to quercetin-3-O-$\beta$–deoxipentose. Its MS/MS data showed an aglycone fragment of *m/z* 301 loss a sugar of 146 Da and *m/z* 271 typical of flavon-3-*O*-monoglycoside. MEA was found gallic (*m/z* 169) and (*m/z* 191) quinic acids[2]. MEA showed ion of *m/z* 463 (myricitrin) and saponins. As the phenolic extracts' composition was different, they also showed a different antiproliferative activity, as expected. So, these extracts were tested for five different cancer lineages[1] (Table 1). MEA presented low activity for tested cells but it was selective for MCF-7 and 786-0 cell, while AEA showed a potential growth inhibition for MCF-7, assuming the criteria stablished by Fouche[3]. Moreover, all the tested extracts showed low toxicity for normal cells (HGF).

**Table 1. $GI_{50}$ (µg/mL)**

| | MCF7 | 786-0 | NCI-H460 | HT29 | HGF |
|---|---|---|---|---|---|
| **Doxorrubicin** | >0,015 | 0,027 | >0,015 | 0,15 | 0,017 |
| **AEA** | 30,0 | >150 | >150 | >150 | >150 |
| **MEA** | 96,0 | 75,5 | >150 | >150 | 141,5 |

Human tumor cell lines: MCF-7 (breast); 786-0 (kidney); NCI-H460 (lung, non-small cells); HT-29 (cólon). Normal human lineage: HGF (finite culture of gingival fibroblasts). $GI_{50}$: *Growth Inhibition 50*

[1]Costa et al. BMC Complementary and Alternative Medicine (2016) 16:403; [2]Santos et al. *Molecules* **2018**, *23*, 986; Fouche, G.; et al, J.; J. Ethnopharmacol. 2008, 119, 455

## /Acknowledgments

Fapesp (grant number 2017/15610-0)

**Área: ORG**

# Desenvolvimento de uma metodologia sintética one-pot para obtenção de derivados 4-oxoquinolinocarboxamídicos

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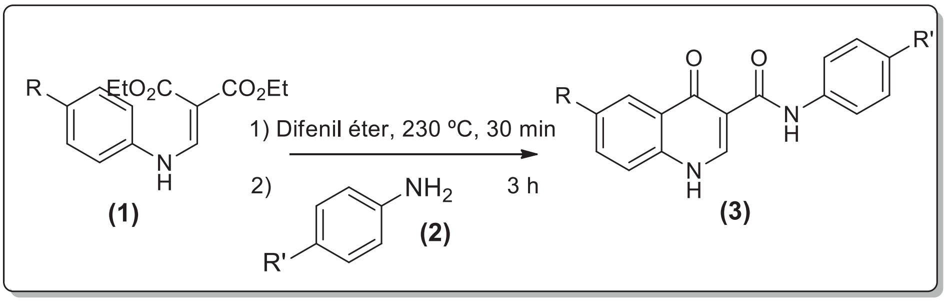
*Palavras Chave: One-pot; Síntese; Quinolona; Quinolonocarboxamidas*

## Highlights

Development of a one-pot synthetic methodology to obtain 4-oxoquinolinecarboxamide derivatives. A new synthetic route to obtain 4-oxoquinolinecarboxamide derivatives were designed and synthesized. They were obtained in 43-82% global yield and were fully characterized using spectroscopic analysis.

## Resumo/Abstract

As 4-oxoquinolinocarboxamidas são substâncias orgânicas, derivadas das 4-oxoquinolinas, muito utilizadas na química medicinal. O grupamento funcional carboxamida vem sendo amplamente estudado, estando presente na estrutura de 25% dos medicamentos produzidos[1], o que torna evidente a sua importância no desenvolvimento de novas substâncias com atividade biológica. A literatura descreve a obtenção das 4-oxoquinolinacarboxamidas em duas etapas, onde a primeira consiste na síntese da 4-oxoquinolinas via metodologia da Gould Jacobs, a partir de diferentes anilinoacrilatos, seguida da reação de substituição nucleofílica à carbonila destes derivados 4-oxoquinolínicos. Esta metodologia apresenta rendimentos globais que variam 37% a 83% e utilizando em média 20 ml de solvente para cada grama de carboxamida formada.[2] Mediante o exposto, este trabalho tem como objetivo o desenvolvimento de uma nova metodologia sintética para obtenção de derivados 3-carboxamida-4-oxoquinolínicos, em um único pote reacional, a partir de diferentes anilinoacrilatos. Logo, não há necessidade de isolar o intermediário 4-oxoquinoliníco obtido na primeira etapa do procedimento usual. A metodologia proposta está descrita no esquema 1.



**Esquema 1:** Metodologia one-pot para a síntese de 4-oxoquinolinacarboxamidas

Como resultado foram obtidos 15 derivados 4-oxoquinolinocarboxamídicos, diretamente a partir dos anilinoacrilatos, com rendimentos que variaram entre 43 a 75%. As substâncias obtidas foram caracterizadas por todos os métodos físicos de análise. Por fim, é possível confirmar que a metodologia utilizada se mostrou viável e reprodutiva, visto que possui rendimentos próximos aos rendimentos globais relatados, quando se faz as reações em suas etapas isoladas. Além disso, essa nova metodologia sintética representou uma redução de 50% do volume de solvente empregado, uma economia significativa, tornando esta metodologia ainda mais importante.

## Agradecimentos/Acknowledgments

CNPq, FAPERJ, CAPES (Código de Financiamento 001)

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

**Nº de Inscrição:** **000214**
*(Inserir o número de inscrição do autor que fez a submissão)*

# Development and Validation of a method for quantification of pellucidina a in the aerial parts of *Peperomia pellucida* (l.) H.B.K. by CCDAE-densitometry

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Palavras Chave: *Peperomia pellucida. Pellucidina A. Validação. Método. CCDAE.*

## Highlights

Development of the quantification method, the interest matrix (aerial parts, dried and crushed), via CCDAE-densitometry, for the quantification of pellucidin A, present in the acetonic extract of the aerial parts of *P. pellucida*.

## Resumo/Abstract

Peperomia pellucida is a plant of the Piperaceae family that occurs in the Amazon, where it is known by the popular name of jabi-herb. Reports in the literature indicate that this plant has potential as analgesic, anti-inflammatory, antibacterial and antifungal. Phytochemical studies performed by researchers from the Federal University of Pará led to the isolation and structural identification of a substance derived from 2,4,5-trimethoxystyrene, an ArC2 dimer called pellucidin A, obtained from the aerial parts of this species. Thus, even considering that the substance can be seen as a chemotaxonomic marker of the plant and because it presented antinociceptive effect in biological assays, the present work had as objective to develop and validate a method, via CCDAE-densitometry, for the quantification of pellucidin A, present in the acetonic extract of the aerial parts of P. pellucida. For the development of the quantification method, the interest matrix (aerial parts, dried and crushed) was subjected to ultrasonic extraction in acetone. The resulting extract was subjected to solid phase extraction (SPE). For the chromatographic development, a wide gradient elution system was used using hexane, dichloromethane, chloroform, acetone and methanol, consisting of 7 steps and with a maximum chromatographic path of 85 mm, the analyte of interest being monitored at λ of 292 nm. The method developed was valid according to the validation parameters recommended by ANVISA Resolution 899 (2003), and it was linear in the applied mass range (0,15-3,0 µg), selective (with good separation between the peaks close to the Rf of the marker), in addition, the validated method provided 95.08 to 116.76%. The limit of detection was 0.12 µg and the limit of quantification was 0.24 µg. The method was robust against small modifications.

## Agradecimentos/Acknowledgments

A Universidade Federal do Pará pelo apoio financeiro.

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

# Design and Synthesis of Potential SmTGR Inhibitors from Fragment-Based Screening hits

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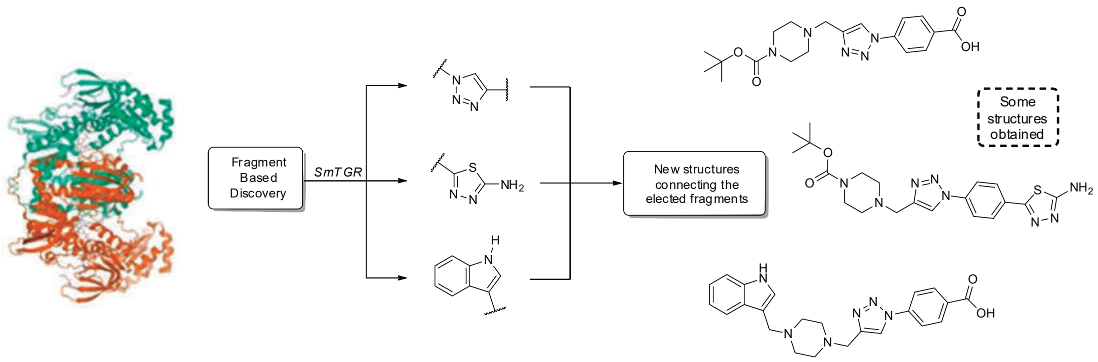
Keywords: *drug-discovery, fragment-based discovery, rational design, SmTGR.*

## Highlights

Planning and Synthesis of Potential SmTGR Inhibitors Following Fragment Based Design Approach. New structures exploring design and synthesis using the triazole, 2-aminothiadiazol and indol scaffold.

## Resumo/Abstract

The treatment of *S. mansoni* disease, which occurs at South American continent with prominence in Brazil, is made using praziquantel as a reference medicine. Last year, Park and coworkers demonstrated that PZQ activates a transient receptor potential melastatin ion channel ($\text{TRPM}_{\text{PZQ}}$) in schistosomes. However, the prolonged use of this drug can promote side-effects and promote resistance development. Experimental evidence reinforces general low toxicities with good activities against the SmTGR as a potential target to treat the disease. Computational study of tertiary structure of *S. mansoni* thioredoxin-glutathione-reductase (SmTGR) finding molecular fragments with interesting interactions on certains cavities elected as target, to build potential drugs to treat the disease. Three fragments shown excellent scores. The discovery of new drugs can explore several methods and approaches. This work presents the possibility of *fragment-based discovery* electing three scaffolds, which must be connected by rational design and synthesis.



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## Agradecimentos/Acknowledgments

CAPES, CNPq, FIOCRUZ, FAPERJ

**Área: ORG** **Nº de Inscrição: 00792**

# Design and synthesis of selenium-naphthoquinone derivatives as anti-tubercular leads against clinical multidrug resistant isolates of *M. tuberculosis*

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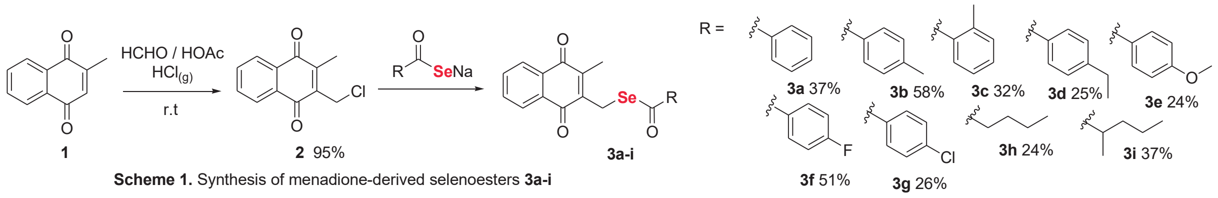
Keywords: Tuberculosis, Naphthoquinones, Organoselenium Compounds

## Highlights

A series of menadione-derived selenoesters was prepared with good yields and had their activity evaluated against *M. Tuberculosis* H37Rv and multidrug resistant clinical isolates (CDCT-16 and CDCT-27).

## Abstract

Tuberculosis is a fatal disease that infects millions of people around the world. One of the most recent scientific frontiers is the development of new drugs that can overcome the drug-resistant TB phenomenon.[1] In this context, naphthoquinones are a characteristic group of quinones which are widely distributed in nature, and several of their synthetic and natural products are very important in different areas of chemistry and biochemistry.[2] More specifically, studies have shown promising results in the use of naphthoquinones as active agents on MT drug-resistant strains.[3] As part of our endeavors at designing and developing new biologically active organoselenium compounds, herein we report the synthesis of a series of naphthoquinone derivatives via the selenofuncionalization of 2-(Chloromethyl)-3-methylnaphthalene-1,4-dione and their evaluation against *M. Tuberculosis* H37Rv and multidrug resistant clinical isolates (CDCT-16 and CDCT-27). Broadly, the designed scaffold bears two main fragments, one derived from menadione (naphthoquinone) and the other being the selenium moiety. The desired products were obtained in moderate to good yields (24-75%).



**Scheme 1.** Synthesis of menadione-derived selenoesters **3a-i**

All products were evaluated for their *in vitro* activity against *M. tuberculosis* H37Rv and excellent results were observed, especially for the compounds **3a**, **3c** and **3f** (MICs 2.1 μM, 8.0 μM and 8.1 μM, respectively). In addition, **3a**, **3c** and **3f** demonstrated potent *in vitro* activity against multidrug resistant clinical isolates (CDCT-16 and CDCT-27), with very promising MIC values (0.78 to 3.1 μM). In conclusion, we have developed a straightforward, fast and efficient method for the synthesis of a series of menadione-derived selenoesters. Furthermore, compounds **3a** and **3f** sustain a promise for further progress in the discovery of new antibiotics against drug-resistant tuberculosis.

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## Acknowledgments

CAPES, CNPq, FAPERJ and FIOCRUZ.

**Área: ORG**

# Enantioselective Synthesis of Spiro Dihydrobenzofurans by Intramolecular Heck-Matsuda Reaction Directly from Anilines

**Edson Leonardo Scarpa de Souza (PG),[1] João Marcos Batista Junior (PQ),[2] Carlos Roque Duarte Correia (PQ)*.[1]**

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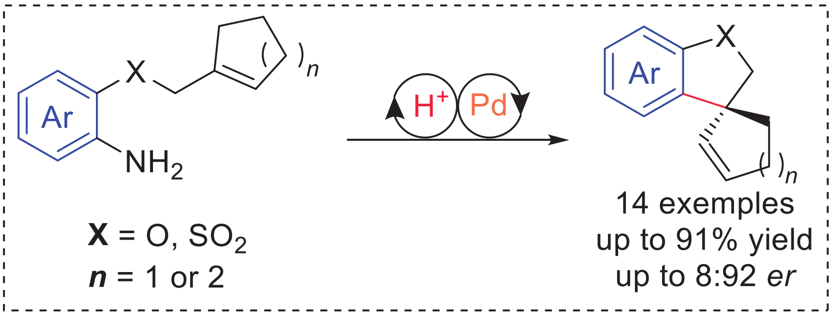
Palavras-Chave: *Catalysis, Enantioselectivity, Intramolecular, Heck-Matsuda Reaction, Spiro Compounds.*

## Highlights

Herein we present an unprecedented palladium-catalyzed enantioselective intramolecular Heck-Matsuda reaction aimed at the synthesis of chiral, non-racemic, spiro dihydrobenzofurans in a very straightforward fashion starting from anilines. The reaction proceeds with the *in situ* generation of the aryldiazonium salts coupled to the intramolecular Heck arylation. For comparative purposes, the Heck-Matsuda reactions were also carried out with preformed aryldiazonium salts, when possible. The enantioenriched dihydrobenzofuran spiro scaffolds were obtained in good to high yields in excellent enantiomeric ratios under mild conditions in an operationally simple manner.

## Resumo/Abstract

The palladium-catalyzed coupling of aryldiazonium salts to olefins carries an enormous synthetic potential due to its intrinsic reactivity, practicality, and broad scope. The first enantioselective intramolecular version of this reaction was reported recently in the research group of prof. Correia, and it opened up new opportunities for the synthesis of complex new compounds in an enantioselective manner. The synthesis of complex arenediazonium carrying functional groups is a very challenging procedure, with many of them being unstable, difficult to prepare, or prepared in low yields. Other critical aspects are related to safety and sustainability, as for many researchers arenediazonium salts can be dangerous to work with. Therefore, the challenge of synchronizing the diazotization and Heck reaction steps in a complex medium was successfully faced by us directly from the correspondent anilines in an efficient manner, opening up new prospects for the intramolecular Heck-Matsuda, adding more practicality, sustainability, saving experimentalist time, and the much welcome safety aspects to this synthetic method. The absolute stereochemistry of the new spiro compounds was determined using Vibrational Circular Dichroism (VCD). In summary, we reported herein an efficient way to synthesize several spiro dihydrobenzofuran compounds by a new enantioselective intramolecular Heck-Matsuda reaction with *in situ* generation of the arenediazonium salts in good to excellent yields and in good to high enantioselective ratios.



## Agradecimentos/Acknowledgments

We thank FAPESP (proc. 2019/25657-9 and 2014/25770-6), CNPq, CAPES, and UNICAMP for financial support.

**Área: ORG** **Nº de Inscrição: 00437**

# Enantioselective Total Synthesis of (*S*)-nuciferine

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*Instituto de Ciências Ambientais, Químicas e Farmacêuticas, Universidade Federal de São Paulo*

Key-words: *Benzyne chemistry, Enantioselective hydrogenation, (S)-Nuciferine*

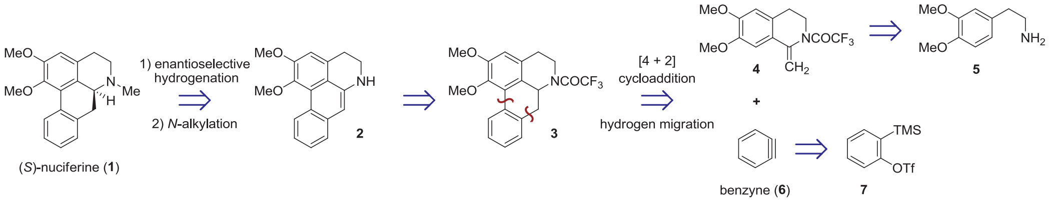
## Highlights

Benzyne chemistry and enantioselective hydrogenation were employed in the total synthesis of (*S*)-nuciferine, which presents potential affinity for the serotonin 5-HT$_{2A}$ receptor.

## Abstract

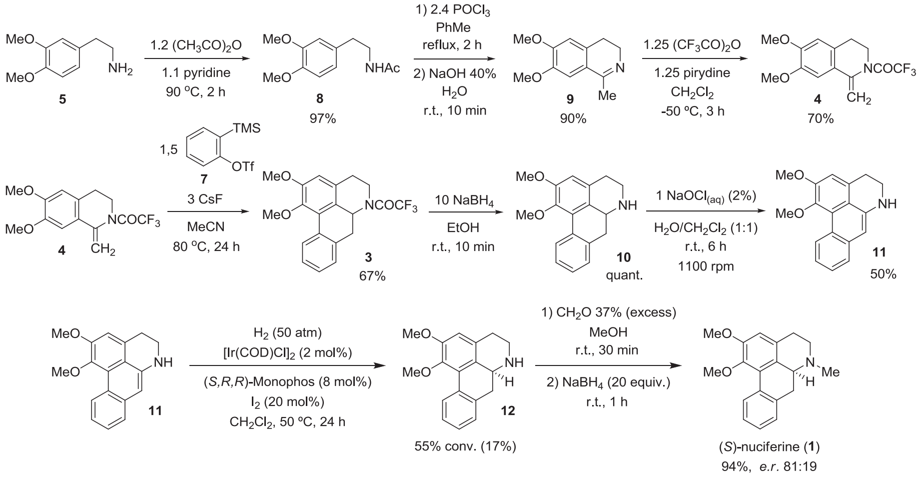
Aporphine compounds present potential affinity for the serotonin 5-HT$_{2A}$ receptor, which in therapeutic terms is related to several disorders, including schizophrenia, insomnia, and ischemic heart disease.[1] In this context, we propose an enantioselective total synthesis for the (*S*)-nuciferine (**1**) based on the retrosynthetic analysis outlined in **Scheme 1**.

**Scheme 1.** Retrosynthetic analysis for the (*S*)-nuciferine (**1**).



The synthesis of (*S*)-nuciferine (**1**) was initiated by production of intermediate **4**, which was obtained through 3 reaction steps in 61% overall yield. Compound **4** was subjected to reaction with benzyne precursor **7** in the presence of CsF, affording intermediate **3** in 67% yield. Compound **3** was deprotected to provide (±)-nornuciferine (**10**) in quantitative yield.[2] Compound **10** was oxidized using sodium hypochlorite promoting the formation of intermediate **11** in 50% yield.[3] Compound **11** was enantioselectively reduced using a chiral iridium (I) complex[4] and after a *N*-alkylation[2] (*S*)-nuciferine (**1**) was obtained with an enantiomeric ratio of 81:19 (**Scheme 2**).

**Scheme 2.** Enantioselective synthesis of (*S*)-nuciferine (**1**).



(*S*)-nuciferine (**1**) was obtained after 8 reaction steps in 3% overall yield, with an enantiomeric ratio of 81:19. Currently, we are optimizing the conditions for the enantioselective hydrogenation to convert compound **11** into **12**.

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## Acknowledgments

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**Área: ORG** **Nº de Inscrição: 00274**

# Exploring the Dimroth rearrangement on the synthesis of 1,2,3-triazoles: new promising molecular Nutlins analogues

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keywords: *1,2,3-triazole, Dimroth rearrangement, reactivation of p53, MDM2 inhibitor*

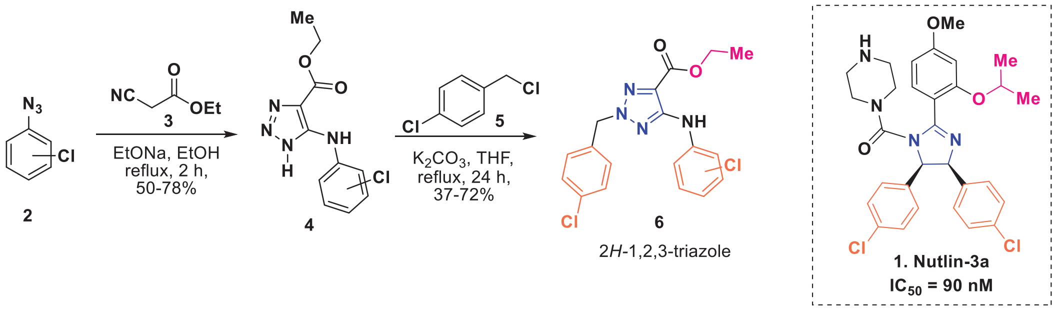
## Highlights

The p53 protein is often inactivated in various types of human cancer by abnormally high levels of the MDM2. In this work, we aimed to synthesize 1,2,3-triazole via Dimroth rearrangement as MDM2 inhibitor.

## Abstract

The p53 protein plays a critical role in the regulation of the cell cycle and apoptosis.[1] This protein is often inactivated in various types of human cancer by abnormally high levels of its negative regulator, the Minute Double Mourine 2 (MDM2).[1] As a result, the reactivation of p53 function by inhibiting the protein-protein p53-MDM2 interaction has been pointed as a promising strategy for cancer therapy. In 2004, 1,2,4,5-tetrasubstituted-4,5-*cis*-imidazolines, also known as Nutlins, were discovered through high throughput screening at Hoffman-La Roche as potent MDM2 inhibitors.[2] However, the stereogenic centers present in the structure of the Nutlins prevents the use of simple synthetic routes towards them, which promotes the search for new small molecule inhibitors of MDM2.

In this context, the 1,2,3-triazole system has been extensively studied and used in medicinal chemistry. Considering the vast experience of our group in this field,[3] the objective of this work was to synthesize 1,2,3-triazole compounds as new promising molecular analogues to the Nutlins family.



**Scheme 1.** Synthesis of new 1,2,3-triazole compounds

The synthesis of the new Nutlins analogues started with the cycloaddition reaction between different chloro-substituted arylazides **2** with ethyl acetoacetate **3** in the presence of sodium ethoxide under reflux. Then, the intermediates 5-amino-2*H*-1,2,3-triazoles **4**, obtained via Dimroth rearrangement, were subjected to reactions of *N*-alkylation, with classic conditions employed in these type of reaction. The desired products **6** were obtained in yields ranging from 37-72%. Their structures were confirmed using different physical methods of analysis such as 1D and 2D NMR, IR and HRMS. The study of the biological activity of the new 1,2,3-triazoles against MDM2 will be carried out in the future.

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## Acknowledgments

CAPES, CNPq, FAPERJ and FIOCRUZ.

**Área: ORG** **Nº de Inscrição: 00781**

# Extraction of paracetamol: chemical comparison between reference and generic medicines as an undergraduate experiment

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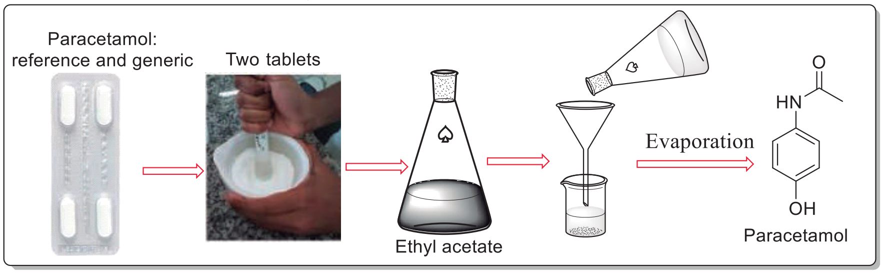
Keywords: Paracetamol, extraction of active ingredients, generic drugs

## Highlights

A new undergraduate experiment based on the extraction of reference and generic paracetamol tablets.

## Abstract

Medicines are employed in undergraduate courses as motivational strategy, and the development of new experiments performable in simple laboratory infrastructure deserve attention.[1] The experiment herein developed compares the extraction of paracetamol from reference and generic drugs. Paracetamol was chosen due to its general use by the population and ease access. Tablets were used from two commercial sources of reference (750 mg) and generic drugs (750 and 500 mg) purchased from local drugstores. For the average weight analysis 20 tablets were individually weighed by each group. Two tablets were pulverized and extracted in triplicate with ethyl acetate. After filtration and solvent evaporation, the active ingredient was obtained and identified by melting point and FTIR analyzes. The experiment was carried out by different groups of students and at different times, Table 1. Analysis of average weight of all groups had variation limit of less than 1.1%, in accordance with the limit of ±5% specified.[2] There was similar performance between the extractions of each group, which corroborates the analysis of pharmaceutical equivalence. Comparing different groups of students at different times, there was change in the mass of paracetamol extracted, which may be associated with changes in the excipient content of drugs over time. The procedure was efficient since there was similarity between the results obtained for generic and reference drugs. Therefore, it is consistent for use in the undergraduate classroom because allows discussion on pharmaceutical equivalence and interchangeability, involves simple laboratory infrastructure, execution and materials are easily obtained.



| TABLET | REFERENCE | | GENERIC | |
|---|---|---|---|---|
| **Student Group** | **2009/UFBA** | **2018/UNEB** | **2009/UFBA** | **2018/UNEB** |
| **Tablet mass (mg)** | 750 | 750 | 500 | 750 |
| **Extracted mass (mg)** | 856.2 | 482.6 | 893.7 | 443.1 |
| **Standart deviation** | 97.2 | 3.3 | 250.0 | 15.7 |
| **Mass recovery (%)** | 56.22 | 32.16 | 59.34 | 29.48 |

## Acknowkedgments

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**Área: _____ORG_____ Nº de Inscrição: __00499__**

# Fluorescência e Propriedades Líquido-cristalinas de Moléculas Derivadas de Núcleos Benzazólicos

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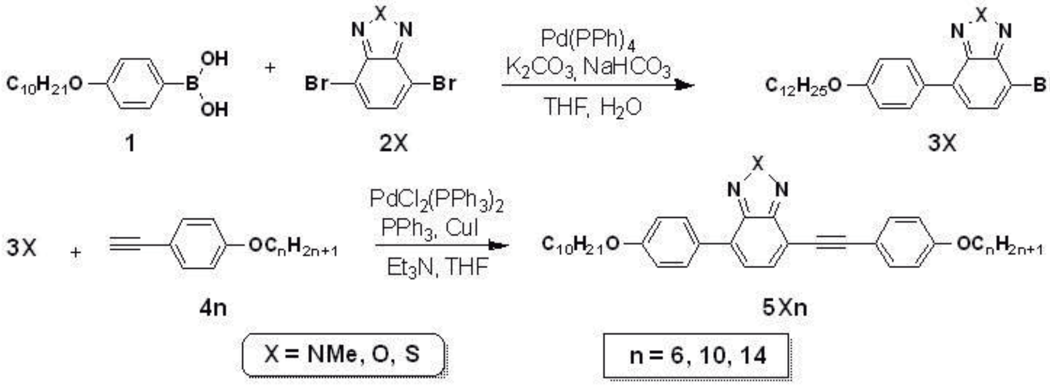
Palavras Chave: *Benzazóis, Cristais líquidos, Fluorescência.*

## Highlights

**Fluorescence and liquid-crystalline properties of molecules derived from benzazolic nuclei.** Here we present the synthesis and characterization of a series of benzazole-based compounds. The thermal and photophysical properties of the target were investigated.

## Resumo

As unidades benzazólicas (X = NMe, O ou S) são amplamente usadas como blocos de construção [1] por atuarem como porção aceptora de elétrons dentro de sistemas do tipo doador-aceptor [2]. Trabalhos recentes [3,4] mostraram a influência dos heteroátomos (X) nas propriedades térmicas e fotofísicas de moléculas π-conjugadas. Nesse trabalho os blocos de construção 4,7-dibromobenzazóis (benzotiadiazol, benzoxadiazol, metilbenzotriazol) foram submetidos a reações de Suzuki-Miyaura e posteriormente Sonogashira para realizar os acoplamentos das porções 4-(deciloxi)fenil e 4-(alcóxi)feniletinil, respectivamente (**Esquema 1**). O objetivo do trabalho é investigar como o padrão de disubstituição 4-fenil-7-feniletinil, nas unidades benzazólicas, pode afetar a relação estrutura-propriedades. Os rendimentos obtidos para os compostos finais variaram entre 43–87%. Todas as nove (09) moléculas da série **5Xn** foram caracterizadas por análises espectroscópicas de RMN $^1$H, $^{13}$C e IV. Os espectros de UV-Vis apresentaram banda de absorção com máximo em 365 nm no grupo **5NMen,** e próximo a 420 nm para **5On** e **5Sn**. O coeficiente de extinção molar foi determinado entre 1–4 x $10^4$ L $mol^{-1}$ $cm^{-1}$ em $CHCl_3$. As bandas de emissão estiveram a 80 nm deslocados para o vermelho no grupo **5NMen** e 120 nm nos demais grupos. Os rendimentos quânticos em $CHCl_3$ estiveram ao redor de 50% com relação ao padrão sulfato de quinina. O estudo de solvatocromismo mostrou que **5S6** possui uma notável dependência da fluorescência com a polaridade dos solventes. Análises de microscopia óptica de luz polarizada mostraram texturas típicas do tipo *schlieren* e *broken fan-shape* para as moléculas finais sugerindo a presença de fases líquido cristalinas do tipo esméctica A (SmA), esméctica C (SmC) e nemática (N). A calorimetria diferencial de varredura confirmou a existência das mesofases no intervalo de 98 e 138 ºC.



**Esquema 1.** Reações de Suzuky-Miyaura e Sonogashira utilizadas para obter os compostos-alvo.

[1] T. L. D. Tam e M. H. Chua. *Phys. Chem. Chem. Phys.* **19**, 15671 (2017). [2] P. Johari e S. P. Singh. *J. Phys. Chem. C* **119**, 27, 14890 (2015). [3] L. de O. Aguiar e A. A. Vieira. *Liq. Cryst.* **45**, 1, 49 (2018). [4] F. N. da Silva e A. A. Vieira. *Liq. Cryst.* **46**, 11, 1707 (2019).

## Agradecimentos

UFBA, UFSC, CNPq, CAPES e FAPESB.

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

# Fluorophores containing the 1,3,5-triazine core with BODIPY and organophosphorus substituents for application as molecular sensors

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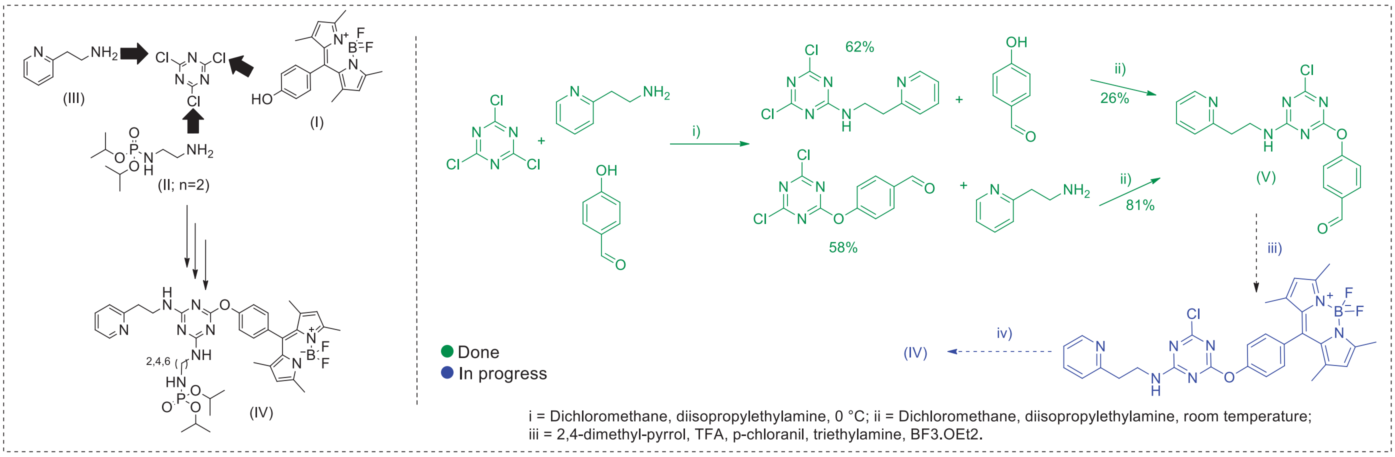
Palavras Chave: *BODIPY, Organophosphorus, Fluorescence, 1,3,5-triazine, Molecular sensors.*

## Highlights

Fluorophores containing the 1,3,5-triazine core with BODIPY and organophosphorus substituents for application as molecular sensors. To obtain novel fluorescent dyes for molecular sensing use, we planned the synthesis of compounds containing the BODIPY core and organophosphorus functions, conjugated through the 1,3,5-triazine nucleus.

## Resumo/Abstract

We have been working to develop a new class of molecular sensors (IV) that gathers, in the same molecule, one fluorescent BODIPY block (I), one phosphoramidate block (II) and one auxiliary 2-aminoethylpyridine block (III), all connected to the 1,3,5-triazine nucleus. (Figure 1) At this stage of our research we are searching the best stepwise substitutions of the three Cl atoms from the starting cyanuric chloride.



i = Dichloromethane, diisopropylethylamine, 0 °C; ii = Dichloromethane, diisopropylethylamine, room temperature; iii = 2,4-dimethyl-pyrrol, TFA, p-chloranil, triethylamine, BF3.OEt2.

Figure 1: Schematic pathway to fluorophores IV.

Among the nucleophiles I, II and III, 2-aminoethylpyridine showed the best result as the first substituent on cyanuric chloride. Attempts to react BODIPY (I) failed as the second substituent. Alternatively, we developed the new aldehyde intermediate (V) by two ways, in order to construct the BODIPY nucleus through the subsequent reaction with 2,4-dimethylpyrrole and $BF_3.Et_2O$. In addition, we are looking for the best conditions to introduce the phosphoramidate II (n=2), to complete the triad. (Figure 1)

## Agradecimentos/Acknowledgments

To Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPQ) and Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES)- Programa de Excelência Acadêmica (PROEX) - Brasil for Financial Support.

Área: ORG **Nº de Inscrição: 00048**

# Graphene oxide copper catalysts for azide–alkyne 1,3-cycloaddition

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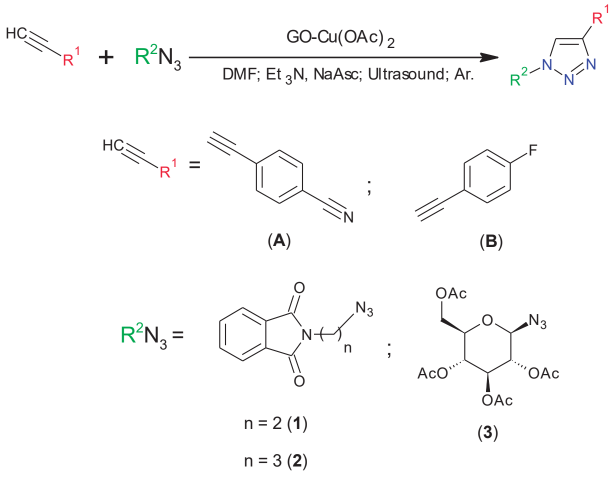
Keywords: Catalyst, Composite, Huisgen reaction, 1,2,3-Triazole.

## Highlights

Graphene oxide composite functionalized with copper acetate and reduced graphene oxide functionalized with copper oxide were prepared and used to promote azide-alkyne 1,3-dipolar cycloaddition reaction.

## Abstract

1,2,3-Triazole compounds have been shown inhibitory activities over some diseases, such as anti-inflammatory, anticancer, antimalaria and antimicrobial. [1] Therefore, the graphene oxide composites functionalized with copper acetate [(GO-Cu(OAc)$_2$] and the reduced graphene oxide functionalized with copper oxide (RGO-Cu$_2$O)$_2$ were prepared [2] and employed in 1,3-dipolar cycloaddition reaction. The synthesis of 4-phenil-1-[2-phthalimide-2-il)propil-1*H*-1,2,3-triazole, as a model reaction, was performed and the optimized condition afforded the product with 83% of yield (condition: GO-Cu(OAc)$_2$, DMF; Et$_3$N; sodium ascorbate-NaAsc; ultrasound; room temperature; 1,0 hour; Argon ). Having determined the optimal condition, the 1,2,3-triazole derivatives **1A**, **2A**, **2B**, **3A** and **3B** were synthesized in moderate-to-good yields of 53-79% (Scheme 1). In addition, the reuse of the catalyst showed good reaction yield (79-81%), even after four catalytic cycles. The compounds were characterized by NMR$^1$H and $^{13}$C. All compounds are being studied for leishmanicidal activity.



**Scheme 1:** Synthesis of 1,2,3-triazole derivatives **1-3(A,B)**

[1] BOZOROV, K. *et al*. 1,2,3-Triazole-containing hybrids as leads in medicinal chemistry: A recent overview. *Bioorganic & Medicinal Chemistry*. v. 27, p. 3511-3531, **2019**.

[2] WANG, A. *et al.* Preparation and characterizations of Cu$_2$O/reduced graphene oxide nanocomposites with high photo-catalytic performances. *Powder Technology*, v. 261 p. 42–48, **2014**.

## Acknowledgments

CAPES, CNPq, CENAPESQ.

**Área: ORG**

# Green synthesis of a series of chalcogenyl-2,3-dihydrobenzofurans with potential biological application

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*Keywords: Microwave Synthesis, Green Chemistry, Chalcogen, Heterocyclic, Chalcogenofunctionalization*

## Highlights

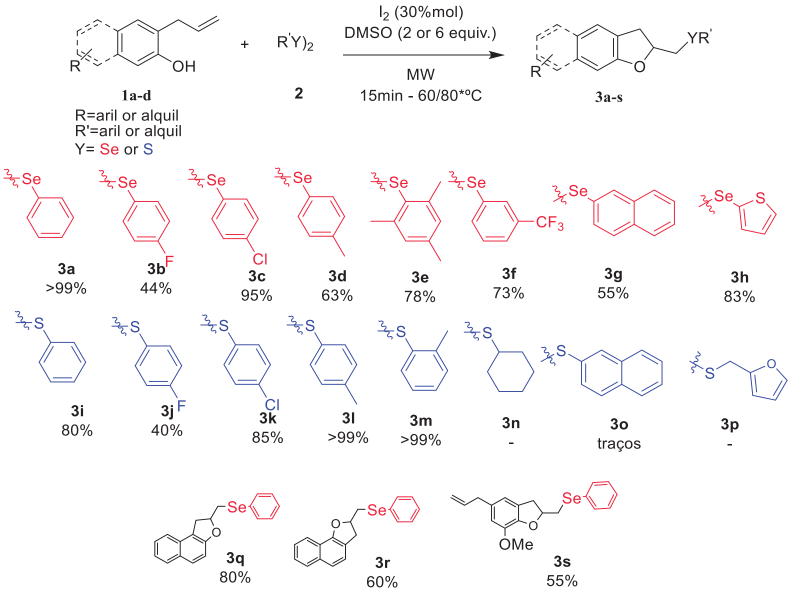
Chalcogenyl-2,3-dihydrobenzofurans synthesis based on the principles of Green Chemistry, using the $I_2$/DMSO catalytic system, metal and solvent freeunder microwave irradiation.

## Resumo/Abstract

Organochalcogens and the 2,3-dihydrobenzofuran scaffold have been the subject of great synthetic interest due to their pharmacological potential.[1,2] The sustainable synthesis of molecules formed by the junction of nuclei of biological interest, such as organochalcogens and dihydrobenzofurans, has become a target. Therefore, the objective of this work was the development of a sustainable methodology for the combination of organochalcogens and dihydrobenzofurans. The optimization of the reaction conditions are summarized in Table 1, where the best yield of >99% for the product **3a** was obtained under microwave irradiation, 15 minutes 1 equivalent of allylphenols/naphthols and 1.5 equivalents of diorganoyl dichalcogenides, without the use of solvents, with 30 mol% of molecular iodine and 2 DMSO equivalents (Scheme 1). Using the optimized condition, 9 selanyl-2,3-dihydrobenzofurans was obtained with yields that varied between 44% and >99%. For the synthesis of suphenyl-2,3-dihydrobenzofurans the conditions had to be modified in some parameters, since the yields were low. The variations were in temperature and DMSO equivalents, being re-optimized at 80°C and 6 equivalents. Thus, the yields obtained were between 40% and >99% (**Scheme 1**). Finally, compared to traditional methods, the methodology developed is a simple and practical tool free of solvents and metals, following the principles of green chemistry for the oxychalcogenation of 2-allyl-phenols/naphthols core derivatives, in addition to presenting probable biological potential.

| # | RSe)₂ | $I_2$ (%mol) | DMSO | T (°C) | Tempo (min) | R (%) |
|---|---|---|---|---|---|---|
| 1 | 1eq | 20 | 2eq | 60 | **15** | 70 |
| 2 | 1eq | 20 | 2eq | 60 | **20** | 68 |
| 3 | 1eq | 20 | 2eq | 60 | **10** | 60 |
| 4 | 1eq | **10** | 2eq | 60 | 15 | 70 |
| 5 | 1eq | **30** | 2eq | 60 | 15 | 80 |
| 6 | 1eq | **25** | 2eq | 60 | 15 | 55 |
| 7 | 1eq | 30 | 2eq | **75** | 15 | $55^b$ |
| 8 | 1eq | 30 | 2eq | **45** | 15 | 62 |
| 9 | **1.5eq** | 30 | 2eq | 60 | 15 | >99 |
| 10 | **1.2eq** | 30 | 2eq | 60 | 15 | 79 |
| 11 | 1.5eq | 30 | **1.5eq** | 60 | 15 | 78 |

**Table 1**: Optimization of reaction conditions



**Scheme 1**: Chalcogenyl-2,3 dihydrobenzofurans synthesis

## Agradecimentos/Acknowledgments

UFF, CNPq, CAPES, FAPERJ, PPGQ-UFF, LaReMN.

[1] Chem. Ver., **2004**, 104, 6255. [2] Org. Biomol. Chem., **2020**, 18, 4916.

**Área: ORG**

# Hantzsch Multicomponent Reaction: a detailed mechanism study by kinetics and transition state theory

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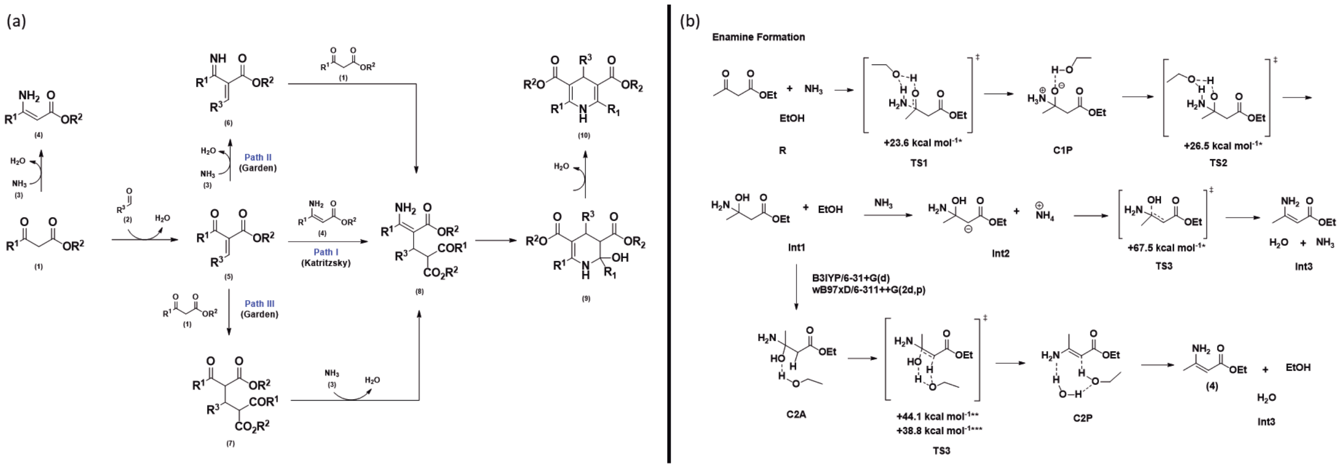
Palavras Chave: *Hantzsch Multicomponent Reaction, Density Functional Theory, Transition State Theory, Mechanism, Kinetics.*

## Highlights

The mechanistic study of the Hantzsch multicomponent reaction elucidates the limiting step and evaluates the three most discussed pathways present in the literature.

## Resumo/Abstract

Previous works by Katritzky and coworkers[1] pointed out that two intermediates are always present in the Hantzsch multicomponent reaction, the enamine (**4**) and the Knoevenagel adduct (**6**). Also, the formation of the Knoevenagel adduct was pointed as the limiting step of the reaction.[1] The use of the two intermediates as initial reactants and the formation of the Hantzsch adduct give evidence for the first studied path (Path I, **Scheme Ia**).



**Scheme I. (a)** Possible pathways for the Hantzsch dihydropyridine synthesis. **(b)** Example of pathway calculation for the enamine (**4**) formation (only transition state energies are given). *M06-2X/6-311++G(2d,p), **wB97xD/6-311++G(2d,p), ***B3LYP/6-31+G(d)

Also, recent works based on the identification of intermediates of reaction pointed to the possibility of two other pathways (Path II and III, **Scheme Ia**).[2] Therefore, based on these previous works, a detailed study of the mechanism of the reaction was done based both in *Ab initio* calculations and kinetic experiments. *Ab initio* calculations were performed for all pathways in **Scheme Ia** (**Scheme Ib** shows an example of results obtained for the enamine formation mechanism), analyzing the influence of the solvent in the studied mechanism and demonstrating the limiting step of the reaction as the formation of the Knoevenagel adduct. Kinetic experiments are yet in development, based on NMR $^1$H and infrared *in situ* techniques, enabling the identification of reaction key intermediates and determining the overall reaction order.

### References

1. Katritzky, A. R., Ostercamp, D. L. & Yousaf, T. I. The mechanism of the hantzsch pyridine synthesis: A study by 15N and 13C NMR spectroscopy. *Tetrahedron* **42**, 5729–5738 (1986).
2. Santos, V. G. *et al.* The multicomponent Hantzsch reaction: Comprehensive mass spectrometry monitoring using charge-tagged reagents. *Chem. - A Eur. J.* **20**, 12808–12816 (2014).

## Agradecimentos/Acknowledgments

FAPESP, CAPES, FAEPEX, UNICAMP

**Área: ORG**

# Intramolecular hydrogen bonding and $^{n}J_{FH}$ in fluorinated amino alcohols: an NMR and theoretical study

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Palavras Chave/Keywords: Fluorine, NMR, Conformational analysis.

## Highlights

This work aimed to evaluate the conformational preferences and occurrence of IntraHB on fluorinated amino alcohols. NMR experiments showed scalar coupling and spatial proximity between H(NH) and F.

## Resumo/Abstract

Fluorinated compounds are being widely applied in the pharmaceutical industry due to their ability to improve cell permeability, primarily due to the formation of intramolecular hydrogen bonding involving fluorine atoms[1]. To understand the behaviour at the molecular level that the incorporation of fluorine atoms may generate in the conformational preference, as well as the occurrence of intramolecular hydrogen bonding (LHIntra), it was studied three fluorinated amino alcohols: **(a)** *trans*-2-((2-fluorophenyl)amino)cyclohexan-1-ol, **(b)** *trans*-2-((3-fluoropyridin-4-yl)amino)cyclohexan-1-ol and **(c)** *trans*-2-((perfluoropyridin-4-yl)amino)cyclohexan-1-ol. Compounds were synthesized, adapting the procedure described in the literature[2,3]. The studied compounds were characterized by 1D and 2D NMR experiments. A conformational search was performed in the Spartan18 software, and then the minima of energy were optimized using M06-2X/aug-cc-pVDZ level of theory available in the Gaussian16. $^{1}$H-$^{19}$F COSY and $^{1}$H-$^{19}$F HOESY experiments show scalar coupling and spatial proximity between H(NH) and F (Fig. 1a-b). For compound **a** the $J_{FH}$ coupling was measured (-2.3 Hz) directly from $^{1}$H NMR spectrum in DMSO-$d_6$, while for compounds **b** and **c** the value of this coupling cannot be measured directly from $^{1}$H spectra for, probably due to $^{14}$N quadrupolar moment which affects the relaxation of hydrogens from NH groups broadening its signal, therefore it was performed a $^{1}$H-$^{15}$N CLIP-HSQC experiment, where it was observed $J_{FH}$ = 2.3 Hz for compound **(b)** (Fig. 1c). This coupling is observed even in polar solvents such as DMSO-$d_6$, and it was not observed in the fluorinated starting materials, which may indicate that the $J_{FH}$ coupling is transmitted through space (IntraHB) instead of through chemical bond. A similar IntraHB was observed in flattened amine moieties[4], suggesting that changes in the geometry of compound **(a)** and its starting material (2-fluoroaniline) may play an important role in the occurrence of a possible N-H---F interaction.

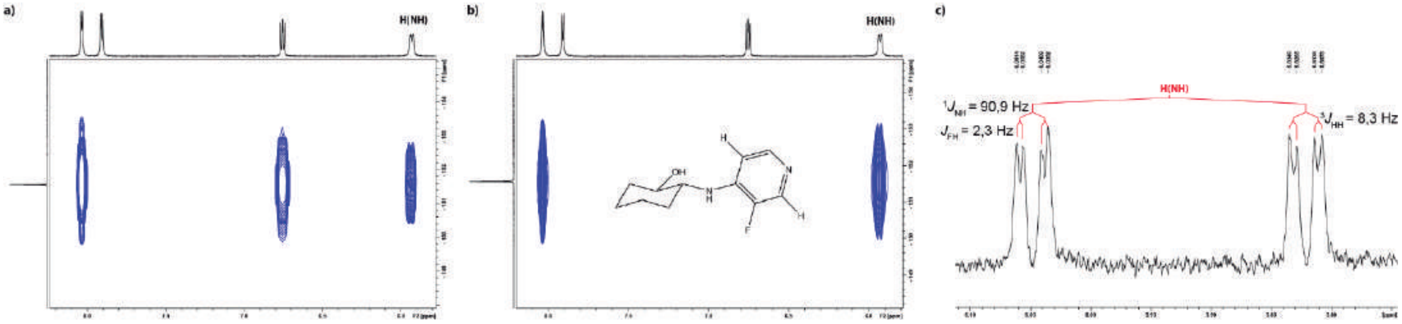

Figure 1. NMR experiments for *trans*-2-((3-fluoropyridin-4-yl)amino)cyclohexan-1-ol in DMSO-$d_6$: **a)** $^{1}$H-$^{19}$F COSY, **b)** $^{1}$H-$^{19}$F HOESY and **c)** 1D projection from $^{1}$H-$^{15}$N CLIP-HSQC.

References: 1) C. Davit, *et al.*, *J. Fluor. Chem.* **2017**, 202, 34; 2) M. Hosseini-Sarvari, *Can. J. Chem.* **2008**, 86, 65; 3) J. D. Osborne, *et al.*, *J. Med. Chem.* **2016**, 59, 5221; 4) L. M. Urner, *et al.*, *Chem. Eur. J.* **2022** (doi.org/10.1002/chem.202103135)

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Área: ORG                Nº de Inscrição: 00339

# Metal-Free Photoarylation of Diazines with Aryldiazonium Salts

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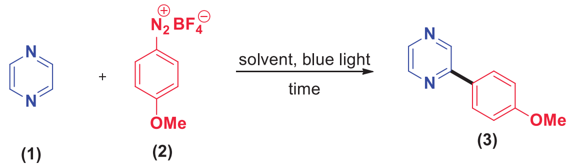
Keywords: *Photocatalysis, Arylation, Aryldiazonium Salts, N-Heteroarenes, Metal-free.*

## Highlights

The photoarylation of diazines with aryldiazonium salts in dimethylsulfoxide is described, using blue LED light.

## Resumo/Abstract

The direct functionalization of electron-deficient *N*-heteroarenes by radical addition is a straightforward method for synthesizing arylated diazines.[1] Herein, we have studied the photoarylation of diazines with aryldiazonium salts under blue light irradiation (455 nm, LED - 120 W) (Scheme 1). The screening of the reaction conditions was carried out using the pyrazine (**1**) and *p*-methoxybenzenediazonium tetrafluoroborate (**2**) (Scheme 1).



Scheme 1: arylation of **(1)** with **(2)** under blue light.

Initially, we observed that the use of photocatalysts (such as TPFPP, riboflavin, and Ru-complexes) did not afford a significant increase in yields (entries 1 and 2); thus, we decided to continue the studies without photocatalysts. In this situation, the initial screening of the reaction conditions showed us that the best result for this transformation could be water as solvent (entries 2-4), and using **1** in great excess (entries 4 and 5). Under these conditions, the aryl-pyrazine **3** was obtained in 43% yield. Therefore, we hypothesized that an electrophilic pyrazine, like its corresponding hydrochloride, could increase the susceptibility to aryl-radical attack, and could afford better results. However, using the corresponding pyrazine hydrochloride in water (entry 6) the product **3** was obtained in only 8% yield. To our delight, in DMSO, the aryl-pyrazine **3** was obtained in 83% yield (entry 7).

We proposed the occurrence of an electron donor-acceptor complex (EDA) which was identified by UV-Vis analysis (Figure 1).

Table 1: Screening of reaction conditions[a]

| Entry | (1) (mmol) | (2) (mmol) | Solvent | Photocatalyst | Yields[b] (%) |
|---|---|---|---|---|---|
| 1 | 1.50 | 0.10 | DMSO | TPFPP | 20 |
| 2 | 1.50 | 0.10 | DMSO | - | 15 |
| 3 | 1.50 | 0.10 | MeCN | - | 29 |
| 4 | 1.50 | 0.10 | $H_2O$ | - | 43 |
| 5 | 0.75 | 0.10 | $H_2O$ | - | 20 |
| 6[c] | 1.50 | 0.10 | $H_2O$ | - | 8 |
| 7[c] | 1.50 | 0.10 | DMSO | - | 83 |

[a]Reaction conditions: 0.10 mmol of **(2)**, in 0.3 mL of solvent, 14 h at room temperature and 455 nm LED irradiation (120 W). [b]Determined by $^1H$ NMR. [c]with pyrazine hydrochloride.

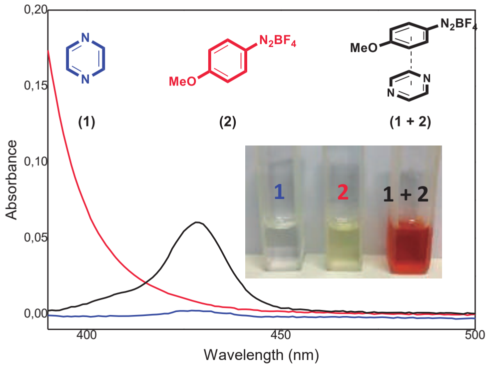


Figure 1: UV-Vis spectrum of **1**, **2** and the mixture (**1**+**2**).

Thus, metal-free photocatalyzed arylation of the pyrazine (**1**) with *p*-methoxybenzenediazonium tetrafluoroborate (**2**) is presented. Studies on the scope, mechanism and limitations of this methodology are ongoing.

## Agradecimentos/Acknowledgments

FAPESP (2018/00106-7 and 2018/00879-6) CNPQ and CAPES.

[1]Baran, *et al. JACS*, **2010**, *132*, 13194 – 13196.

**Field: ORG**

# Ni(0)-Catalyzed Alkene Isomerization Under Kinetic Control

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

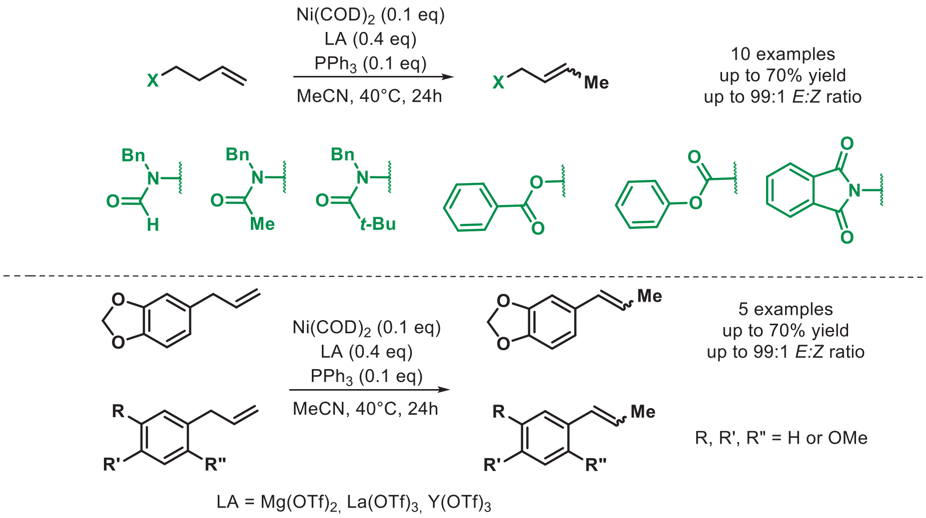
Keywords: *Catalysis, Olefin Isomerization, Nickel, Lewis Acid.*

## Highlights

The combination of Ni(0) and a Lewis acid allowed the stereoselective isomerization of terminal alkenes under kinetic control.[1]

## Abstract

The use of Ni(0) complex, a Lewis Acid (LA) and triphenylphosphine successfully allowed the isomerization of terminal double bonds. Interestingly, only one migration was observed, even when a further migration would lead to a more stable isomer.[1] Furthermore, allyl benzene derivatives underwent isomerizations, under the same reaction conditions, to provide stilbenes with *E*:*Z* ratio in up to 99:1.[2]



**Scheme 1.** Ni(0)-catalyzed alkene isomerization.

References:

1. Liu, X.; Zhang, W.; Wang, Y.; Zhang, Z.-X.; Jiao, L.; Liu, Q. *J. Am. Chem. Soc.* **2018**, *140*, 6873−6882.
2. Kapat, P. A.; Sperger, T.; Guven, S.; Schoenebeck, F. *Science*, **2019**, *363*, 391-396.

## Acknowledgments

**Área: ORG**

# Nova metodologia para síntese de chalconas via acilação de derivados fenólicos

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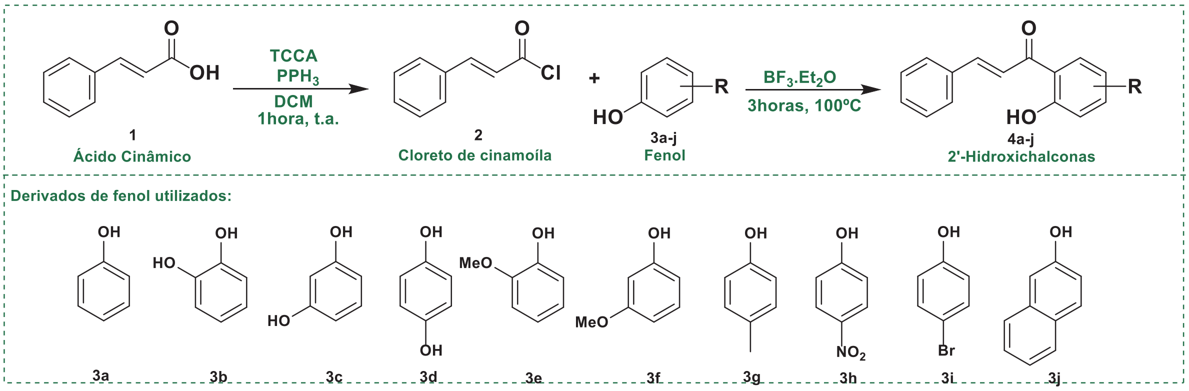
Palavras-Chave: *Chalconas, Flavonoides, Síntese Orgânica, Química Verde.*

## Highlights

**New methodology for chalcone synthesis by acylation of phenolic derivatives.** A new greener methodology of synthesis of differently substituted chalcones were carried out by acylation using cinnamic acid and phenolic derivatives. The results indicated this novel proposed reaction is rapid, and chalcones are achieved with good yields.

## Resumo

Chalconas são metabólitos secundários presentes em diversas famílias vegetais, dentre as quais pode-se citar Leguminosae, Compositae e Moraceae. São conhecidas por apresentar grande potencial farmacológico e grande versatilidade química para atuarem como blocos de construção na formação de novos derivados de interesse. Chalconas são biossintetizadas a partir da convergência entre as rotas do acetato e do chiquimato, na qual o ácido cinâmico é um intermediário importante. A síntese de chalconas é comumente acessada por condensação de Claisen-Schimdt empregando derivados de benzaldeído e de benzofenona. O presente trabalho descreve uma nova metodologia de síntese de chalconas com diferentes padrões de substituição, que mimetiza com mais fidelidade o processo de biossíntese. A rota sintética proposta tem apenas duas etapas, sendo a primeira correspondente à formação de cloreto de cinamoíla a partir de ácido cinâmico, na presença de ácido tricloroisocianúrico (TCCA) e trifenilfosfina ($PPh_3$). O produto desta etapa é obtido após uma hora de reação com uma filtração simples, e diretamente adicionado ao sistema reacional contendo um derivado de fenol, sob atmosfera inerte. Em seguida, trifluoreto de boro eterato é lentamente adicionado, para completar a segunda etapa da metodologia, que ocorre a 100ºC durante 3 horas. Os derivados de 2'-hidroxichalcona foram obtidos com rendimentos que variaram entre 53 e 72%. Observou-se, como esperado, que em alguns casos as respectivas flavanonas, obtidas por ciclização das 2'-hidroxichalconas, foram subprodutos desta reação.



## Agradecimentos/Acknowledgments

**Área: ORG**

# Novel lipophilic 2,4-D analogues by Ugi Reaction: synthesis and kinetics insights

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Palavras Chave: *Ugi reaction, peptoids, agrochemistry, kinetics*

## Highlights

Ugi 4-Component Reaction was applied to synthesize analogs of the commercially available and widely used herbicide 2,4-D. The synthesized product's degradation kinetics was assessed by UV-Vis.

## Abstract

Brazil is one of the largest herbicide consumers, along with China and the United States. Since agriculture is an essential activity, research in new agrochemical alternatives from renewable resources considering environmental impact minimization can contribute towards sustainable development. Ugi four-component reaction (U-4CR) is a well-known multicomponent reaction (MCR) using carboxylic acids, amines, aldehydes, and isocyanides to afford peptide-like α-acyloxycarboxamides[1]. Molecular libraries can be achieved by the high flexibility for different reactants, and the structurally diverse products can be further modified to obtain complex molecules with many different biological activities, such as drugs, agrochemicals, or natural products[2,3]. Fatty chain reactants are abundant and are extracted from renewable resources. Furthermore, they can provide tunable-properties molecules with enhanced lipophilic character, which can be of interest for many biological applications[4,5]. Recent work in our group indicates that the modification of commercial herbicide molecules with the addition of a fatty chain results in potentially effective, yet more readily degradable herbicides[6]. Therefore, a new lipophilic analog of the commercially available herbicide 2,4-D (2,4-Dichlorophenoxyacetic acid) has been synthesized by U-4CR in 67% yield, using octadecyl isocyanide **4** obtained by greener methodologies. Degradation kinetics studies of the U-4CR product were performed by UV-Vis at 60 ºC in three different conditions: neutral, acidic, and alkaline, monitoring the hydrolysis product, with evidence of different hydrolysis mechanisms for acidic and alkaline conditions. The synthesis with other aldehydes, amines, and isocyanides, to increase the compounds' diversity and kinetics analysis are currently under investigation.

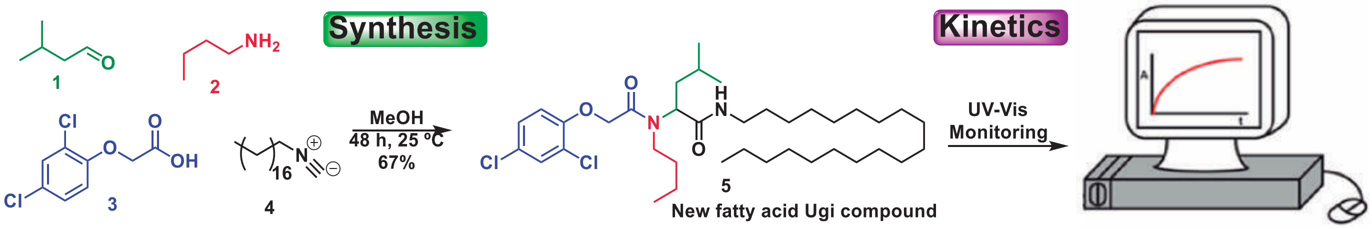

Figure 1. Methodological scheme of the U-4CR synthesis and kinetics studies by UV-Vis

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**Área: ORG**

# Obtenção de Cromonas a partir de reação multicomponente

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Palavras Chave: *Cromonas, Química Verde, Reação Em Água. RMCs, Sustentabilidade.*

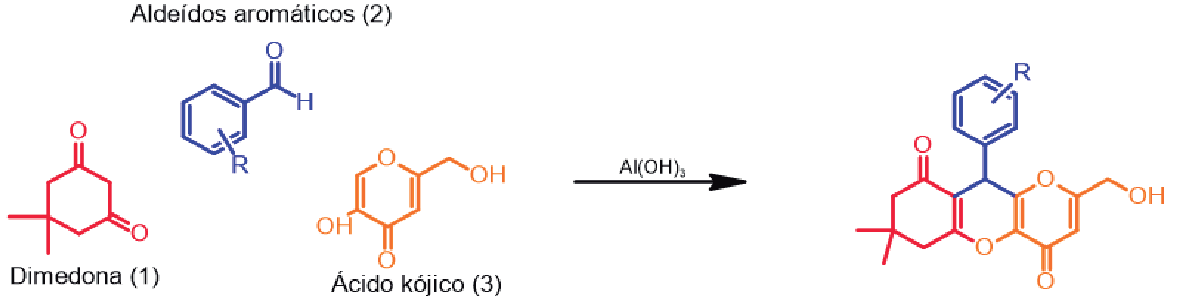
## Highlights

Obtaining Chromones from multicomponent reaction.

The synthesized compounds showed the absence of impurities and the methodology applied for the synthesis aimed to minimize the impacts generated to the environment.

## Resumo/Abstract

As Cromonas é uma classe de compostos heterocíclicos com inúmeras propriedades, tais como, anti-HIV, antioxidante, anti-inflamatório, antimicrobiano, antidiabético, anticonvulsionante, atividade inseticida entre outras. Reações Multicomponentes (RMCs) são caracterizadas como processos convergentes que partem de três ou mais reagentes, de modo a se obter um produto final que, de preferência, contenha todos ou a maior parte dos átomos de carbono envolvidos em sua formação. Neste sentido, o objetivo deste trabalho foi obter cromonas em única etapa a partir do ácido kójico. Para obtenção dos compostos utilizou-se 1mmol de aldeído aromático (1**a-i),** 1 mmol de ácido Kógico (**2**) e 1 mmol de dimedona (**3**), juntamente com hidróxido de alumínio hidratado (10%) como catalizador e água (5mL) como solvente à 80°C por 50 minutos de agitação magnética.



4a=R= H; ( 85,13%)*;
4b=R= 2F( 56,80%);
4c=R= 4Br (64,07%);
4d=R= 4OH; 3OMe (54,79%)
4e=R= 4OMe (48,33%);

4f= R= 4CN (56,99%);
4g=R= 4Cl (75,03%);
4h=R= 3NO3 (62,35%);
4i =R= 2OH; 5OH (57,01%).

*Posição, radical e rendimento.

Os compostos obtidos apresentaram-se no estado sólido de coloração clara, pode-se observar que a maioria dos intervalos de ponto de fusão foram estreito, indícios que pode retratar ausência de impurezas em relação a formação dos compostos. Desse modo a síntese dos compostos podem ser consideradas limpa e eficiente, pelo fato da reação ocorrer com um catalizador, como solvente a água e em única etapa. Dessa maneira diminuído os possíveis impactos que a reação poderia causar ao meio ambiente. Síntese de compostos com atividades biológicas e farmacológicas, como as cromonas, se torna necessária pois podem ter atividades ainda não comprovadas. Sugere-se para estudos futuros a aplicação desses compostos sintetizados afim de verificar alguma atividade inédita.

## Agradecimentos/Acknowledgments

Os autores agradecem ao PAPESQ/UNIFAP pelo suporte financeiro.

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

# Optimization of methodology for biotransformation of prochiral ketones by *Talaromyces Stollii* P7 with a view to enantiomeric enrichment.

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*Palavras Chave: Green Chemistry, bioreduction, chiral compounds, chemometry.*

## Highlights

The present work shows the high efficiency of whole cells of microorganisms as selective catalysts in chemical reactions, with a view to the reduction of steps using toxic chemical reagents.

## Resumo/Abstract

In comparison to traditional methods applied to the reduction of pro-chiral carbonyls, the use of biotransformation allows regio-, stereo- and chemoselectivity controls. The production of enantiomerically pure chiral alcohols is of great interest to the chemical, cosmetic and pharmaceutical industries.[1] The biotransformation reactions consume a small amount of organic solvents and avoid toxic reagents, and occur under mild temperatures and pressures, bring them to the principles of Green Chemistry.[2,3] The use of whole cells of microorganisms as biocatalysts facilitates the extraction of the reaction product, as well as contributes to the reduction of process costs.[4] *Talaromyces stolli* P7 showed conversion rates and enantiomeric excess equal to 99.7% and 78% to 85% endophytes, respectively, in the selective bioreduction of acetophenone into (*S*) -1-phenylethanol.

Seeking to enrich the enantiomeric excess of the cited reaction, it became interesting to use multivariate analysis in order to achieve, through adjustments and fluctuations in the values of each variable, the conditions that represents the optimal model system for this biotransformation. For the present work, a complete $2^4$ factorial design was generated, analyzing the independent variables (reaction time, agitation, amount of substrate and pH) with a view to increasing the enantiomeric excess as a response variable (dependent). The variables were treated in the Statistica® software version 7.0 (STATSOFT). After the analyses, the data were used to generate the response surfaces, demonstrating the behavior of each crossing of the data obtained.

After running, the experiments showed that pH and time significantly influenced the reaction, as well as the interaction of pH with the amount of substrate. In order to find an optimal predicted condition, the central rotational composite design (DCCR)[5] was generated in order $2^2$, in which it tends from $-\infty$ to $+\infty$, simulating extreme conditions of analysis. For this step of the study, the results are still awaited.

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**Área: ORG**

# Palladium-Catalyzed Enantioselective Intramolecular Heck-Matsuda Reactions of Unactivated Cyclopentenes Directly from Anilines: Efficient Synthesis of Enantioenriched methanobenzo[b]oxepine Scaffolds.

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Palavras Chave: Intramolecular Heck reaction, Enantioselective palladium catalysis, N,N-ligands, Open flask, in situ aryldiazonium salt generation.

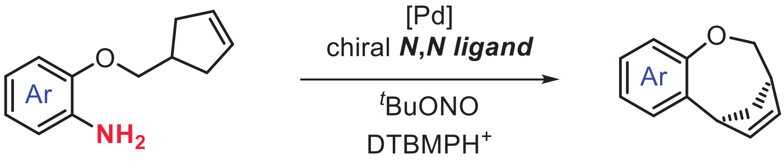
## Highlights

The first examples of enantioselective intramolecular Heck-Matsuda desymmetryzation of cyclopentenes with in situ generation of the aryldiazonium salts were achieved using Pd/N,N-ligand complexes. The enantioenriched methanobenzo[b]oxepine scaffolds were obtained in good to high yields with enantiomeric ratios of up to 97:3 under mild and operationally simple reaction conditions.

## Resumo/Abstract

The Heck reaction, an important palladium catalyzed coupling process, has emerged as a useful tool to construct C-C bonds. The Heck−Matsuda reaction is a very practical and efficient version of this reaction using aryldiazonium salts as arylating agents under open-flask and mild conditions to provide building blocks as attractive intermediates in organic synthesis. The interest in this reaction is demonstrated by the significant contributions made by our research group and others to extend the application of the Heck reactions to more complex olefins as well as to the construction of stereogenic centers. Aryldiazonium salts are useful tools for radical and ionic processes since their discovery in 1858 by Peter Griess. Despite the fact that these compounds are commonly employed in many transformations, they can be potentially hazardous and thermally unstable, especially at large scale.

To avoid the isolation of particularly unstable and/or hard-to-synthesize aryldiazonium salt, the *in-situ* generation of theses salts have emerged as a desirable, sustainable, and attractive synthetic strategy in organic synthesis. The work reported herein discloses unprecedented enantioselective intramolecular Heck-Matsuda desymmetrizations of cyclopentenes starting directly from anilines in a tandem-like process. The tricyclic Heck products were obtained in good to high yield and excellent enantiomeric ratios.



**12 exemples**
up to 83% yield
up to 97:3 *er*

- Construction of quaternary stereocenter
- Mild and open flask conditions
- High funcional group tolerance
- High enantiosselective

## Agradecimentos/Acknowledgments

We acknowledge FAPESP, CNPq, CAPES, and University of Campinas (UNICAMP). Financial support for this work was provided by FAPESP (processes 2018/16916-8 and 2014/25770-6).

**Área: ORG**

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# Physicochemical studies of fluorinated derivatives of mandelic acid: conformational analysis and stereo-electronic interactions

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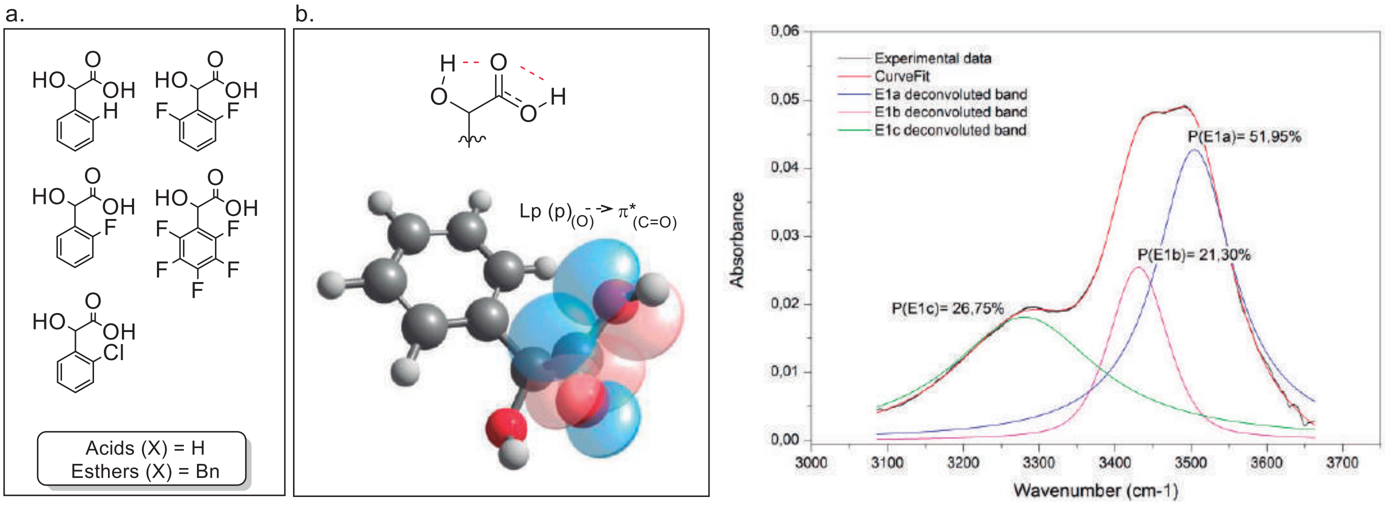
Keywords: *Organofluorinated compounds, DFT, Implicit solvation, Molecular Dynamics, Conformational Analysis*

## Highlights

- DFT studies of derivatives of Mandelic acid;
- Conformational analysis of organofluorinated compounds.

## Resumo/Abstract

The conformational behavior of mandelic acid and derivatives in nonpolar, polar and protic solutions was systematically studied in this work by theoretical calculations at the PBE0/aug-cc-pVTZ level and infrared spectroscopy. The molecules under study preferentially adopt a cis arrangement in the COOH acid group, being stabilized by electrostatic interaction between the α OH•••O=C, and mainly due to the conjugative effect of the order of 50 kcalmol$^{-1}$ between the π system of the carbonyl with the OH. Elucidation of the conformational preferences of mandelic acid and fluorinated derivatives was supported by the study of conformers using QTAIM, NBO and NCI. Furthermore, the infrared spectra, after curve fitting, showed that the theoretical populations of conformers agree with the experimental data.



**a.** Mandelic acid and derivatives, respectively A1, A2, A3, A4 and A5 when X=H. Esters E1, E2, E3, E4 and E5 when X=Bn. **b.** Syn arrangement, preferred in all conformers, with strong electrostatic and conjugative effect, represented by the orbital interaction $Lp(p)_{(O)} \rightarrow \pi^*_{(C=O)}$. Infrared spectrum of E1 at 0.01M in Dimethylsulfoxide. The theoretical populations of E1conformers at the PBE0/aug-cc-pVTZ level were, respectively, 54.1% (E1a), 24.2% (E1c), 21.8% (E1b), presenting values close to the experimental data.

## Agradecimentos/Acknowledgments

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**Área: ORG**

# Regiodivergent synthesis of 1*H*- and 2*H*-pyrazolo[3,4-*d*]pyridazinones by activation and regulated isomerization of the hydrazone intermediate

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Palavras Chave:*(Hydrazone, Regioselective Synthesis, Pyrazolo[3,4-d]pyridazinone).*

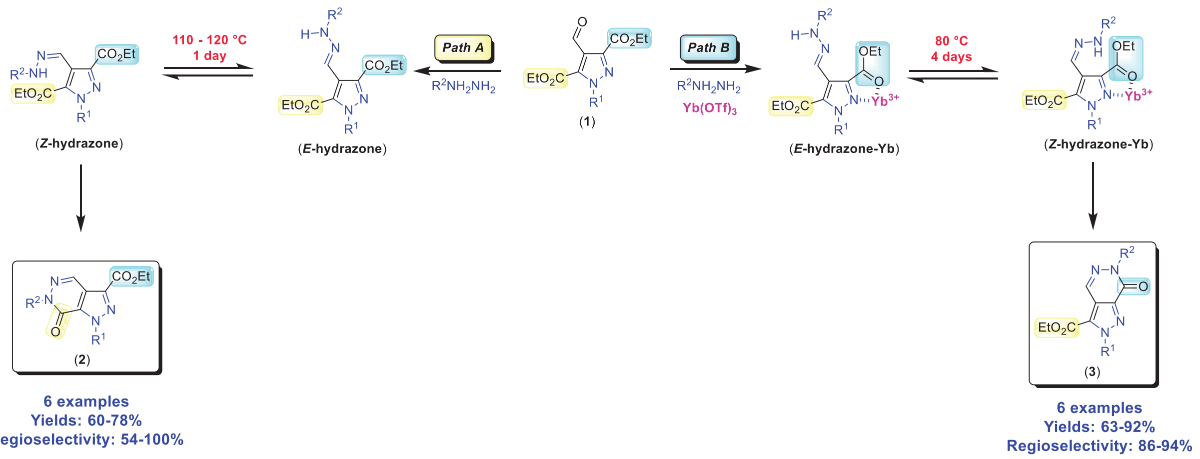
## Highlights

Regiochemical control of the annulation of 3,5-dicarboxyethyl 4-formyl pyrazoles with hydrazines.
Regioselectivity of the products seems to be regulated by the configuration of the hydrazone intermediate and the metal employed.

## Abstract

Nitrogen-containing heterocycles are of great importance because they are often found in many biologically active molecules.[1] Thus, efficient and highly regioselective methodologies for C-N bond-formation have been widely investigated. Cyclocondensation reaction is an attractive method, but it still requires further advances. Furthermore, it is worth mentioning that the regioselective synthesis of two or more possible regioisomeric products from the same precursor is hugely relevant for advancing in the development of powerful methods.[2] In light of this and with our continued efforts for the regioselective synthesis of aza-heterocycles, we envisioned an efficient strategy toward annulation of 3,5-dicarboxyethyl 4-formyl *N*-arylpyrazoles **1** with hydrazines for regiodivergent synthesis of 1*H*-pyrazolo[3,4-*d*]pyridazinone **2** and 2*H*-pyrazolo[3,4-*d*]pyridazinone **3** regioisomers. In general, the reaction was well controlled by temperature and the employment of $Yb(OTf)_3$. When the reactions were performed in toluene or solvent-free at 110-120 °C, 1*H*-pyrazolo[3,4-*d*]pyridazinones **2** were almost exclusively formed (Scheme 1, path A). Whereas the reaction promoted by $Yb(OTf)_3$ in MeCN at 80 °C provided the 2*H*-pyrazolo[3,4-*d*]pyridazinones **3** with good regioselectivities (Scheme1, path B).

**Scheme 1.** Synthesis of 1*H*-pyrazolo[3,4-*d*]pyridazinone **2** and 2*H*-pyrazolo[3,4-*d*]pyridazinone **3** regioisomers



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**Área: <u>ORG</u>** **Nº de Inscrição: 1277**

# Resolução cinética dinâmica da (±)-1-feniletilamina utilizando diferentes enzimas e líquidos iônicos dos tipos sais de amônio e de fosfônio

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Palavras Chave: *Resolução cinética dinâmica, catálise enzimática, aminas, líquidos iônicos, paládio.*

## Highlights

Dynamic kinetic resolution (DKR) of (±)-1-phenylethylamine using different enzymes and ionic liquids such as ammonium and phosphonium salts. In this work, we described different combinations of enzymes and ionic liquids for DKR mediated by the metal catalyst $Pd/BaSO_4$. Asymmetric acetamide was obtained in good yield and enantiomeric excess with the use of CaLB as an enzymatic catalyst.

## Resumo

Aminas enantiomericamente puras são importantes para a indústria, uma vez que estão presentes nas estruturas de uma série de compostos biologicamente ativos.[1] A resolução cinética dinâmica (RCD) constitui na combinação da resolução cinética com uma racemização, visando a produção de compostos assimétricos. Em nossos estudos, selecionamos 3 diferentes lipases para a resolução cinética: CaLB (Lipase from *Candida antarctica* B), Lipase from *R. oryzaes* e *Amano* Lipase PS. As reações com o uso da CaLB corresponderam àquelas que levaram aos melhores resultados. Já as reações de RCD com as demais lipases, cujos estudos são inéditos, não foi possível encontrar uma condição reacional que fosse capaz de promover a conversão da 1-feniletilamina à acetamida quiral. O catalisador escolhido para a etapa de racemização foi $Pd/BaSO_4$. Utilizamos líquidos iônicos para avaliar a melhoria na eficiência do catalisador metálico, uma vez que podem estabilizar as nanopartículas metálicas e prolongar seu efeito.[2] Selecionamos líquidos iônicos inéditos dos tipos sais de amônio ($N_{4444}.NTf_2$, $N_{8888}.NTf_2$) e de fosfônio ($P_{4444}.NTf_2$, $P_{8888}.NTf_2$). Entre todos os utilizados, o que demonstrou melhor eficiência foi o $N_{4444}.NTf_2$, uma vez que permitiu que a acetamida fosse obtida em rendimento e excesso enantiomérico superiores.

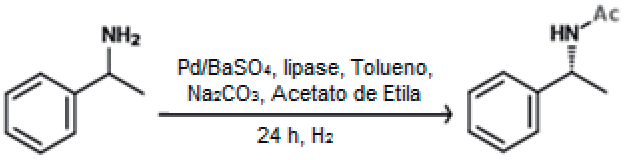
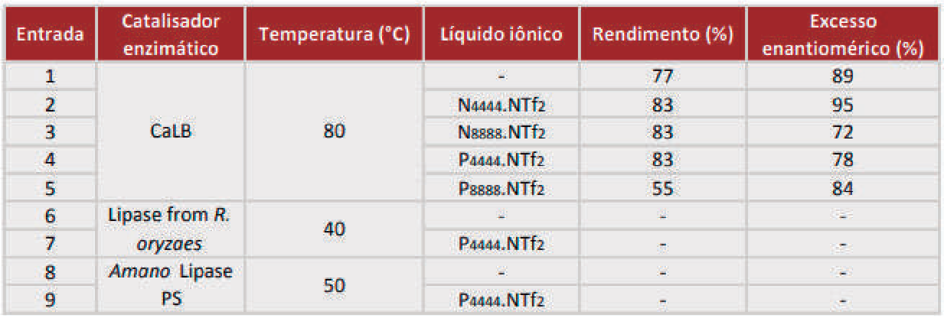


Tabela 1. Reações de RCD da (±)1-feniletilamina catalisada por lipases e $Pd/BaSO_4$.



| Entrada | Catalisador enzimático | Temperatura (°C) | Líquido iônico | Rendimento (%) | Excesso enantiomérico (%) |
|---|---|---|---|---|---|
| 1 | CaLB | 80 | - | 77 | 89 |
| 2 | | | $N_{4444}.NTf_2$ | 83 | 95 |
| 3 | | | $N_{8888}.NTf_2$ | 83 | 72 |
| 4 | | | $P_{4444}.NTf_2$ | 83 | 78 |
| 5 | | | $P_{8888}.NTf_2$ | 55 | 84 |
| 6 | Lipase from *R. oryzaes* | 40 | - | - | - |
| 7 | | | $P_{4444}.NTf_2$ | - | - |
| 8 | *Amano* Lipase PS | 50 | - | - | - |
| 9 | | | $P_{4444}.NTf_2$ | - | - |

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## Agradecimentos

Ao CNPQ e à FAPESP pelo apoio financeiro.

**Área: ORG**

# Ru$^{II}$-catalyzed asymmetric transfer hydrogenation of chalcones in water: straightforward access to 1,3-diarylpropan-1-ols

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Keywords: *Asymmetric catalysis, Ruthenium, Reduction, Total synthesis, Flavonoids.*

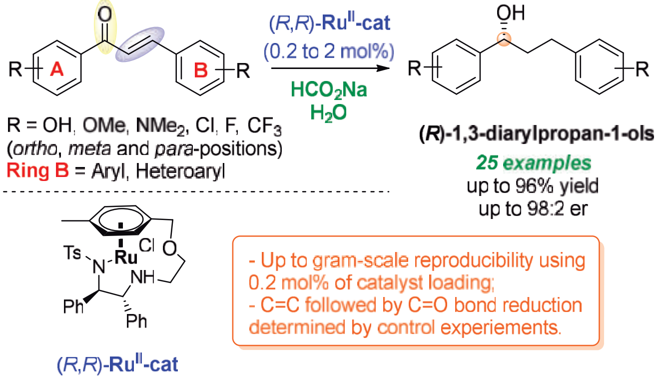
## Highlights

Twenty-five (*R*)-1,3-diarylpropan-1-ols were obtained selectively (up to 98:2 er) from one-pot C=C/C=O reduction of chalcones in water, allowing a convenient total synthesis of (*S*)-tephrowatsin E.

## Abstract

1,3-Diarylpropan-1-ols comprise a subclass of flavonoids endowed with interesting pharmacological properties. Besides, their basic skeleton is ubiquitous in numerous biologically active natural products such as the flavans.[1] However, little progress has been made towards the enantioselective synthesis of these compounds. In this context, asymmetric transfer hydrogenation (ATH) catalyzed by the Noyori–Ikariya type complexes has been highlighted as a green and robust methodology towards the enantioselective synthesis of flavonoids.[2] Hence, in this work, we report the one-pot C=C/C=O reduction of chalcones through a Ru$^{II}$-catalyzed ATH in water using $HCO_2Na$ as the hydrogen source (*Scheme 1*).

*Scheme 1. Ru$^{II}$-catalyzed ATH of chalcones in water*

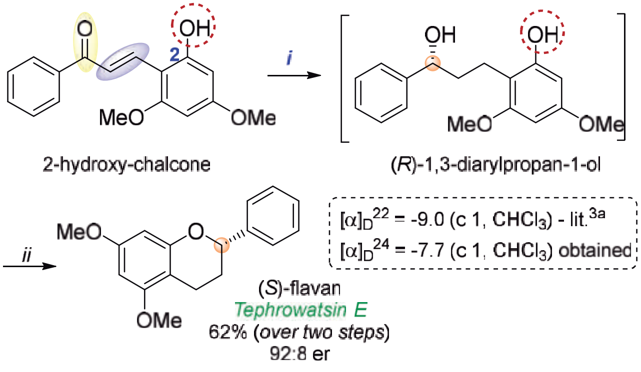


After reaction optimization, 2 mol% of Ikariya's *oxo*-tethered-Ru$^{II}$ precatalyst (*R*,*R*)-**Ru$^{II}$-cat** was found as the most suitable complex to obtain the (*R*)-1,3-diarylpropan-1-ols under mild reaction conditions, using $HCO_2Na$ as the hydrogen source in water at 60 °C for 5 h. A wide scope of enones was subjected to this condition (25 examples), bearing EDGs and EWGs at the *ortho*, *meta*, and *para* positions of both aromatic rings, allowing the evaluation of the stereoelectronic effects of the substituents over the reaction outcome.

The resulting saturated alcohols were obtained as major products in good to excellent yields (up to 96%) and enantioselectivities (up to 98:2 er). The OH group was evaluated at *ortho* position in both rings. At ring A, it increased the substrate reactivity, and the reaction was able to be carried out at rt. At both rings, it resulted in a higher level of 1,4-selectivity when compared with OMe and EWGs at *ortho* positions.

Finally, the one-pot ATH of a highly oxygenated 2-hydroxychalcone at ring B followed by a Mitsunobu cyclization allowed the total synthesis of the natural flavan (*S*)-tephrowatsin E in a straightforward manner when compared with the previously reported methods.[3]

*Scheme 2. Total synthesis of tephrowatsin E*



*i*: 2 mol% (*R,R*)-**H**, $HCO_2Na$, CTAB, MeOH:$H_2O$ (1:1), 60 °C, 5 h
*ii*: DIAD, $PPh_3$, THF, rt, 3 h.

## Acknowledgments

We gratefully acknowledge the financial support from CAPES, CNPq, FAPERJ and UFRJ.

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**Área: ORG**

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

# Ruthenium-catalyzed C–H activation as a powerful tool for annulation of nonsymmetric imidazoles: A new avenue towards trypanocidal compounds

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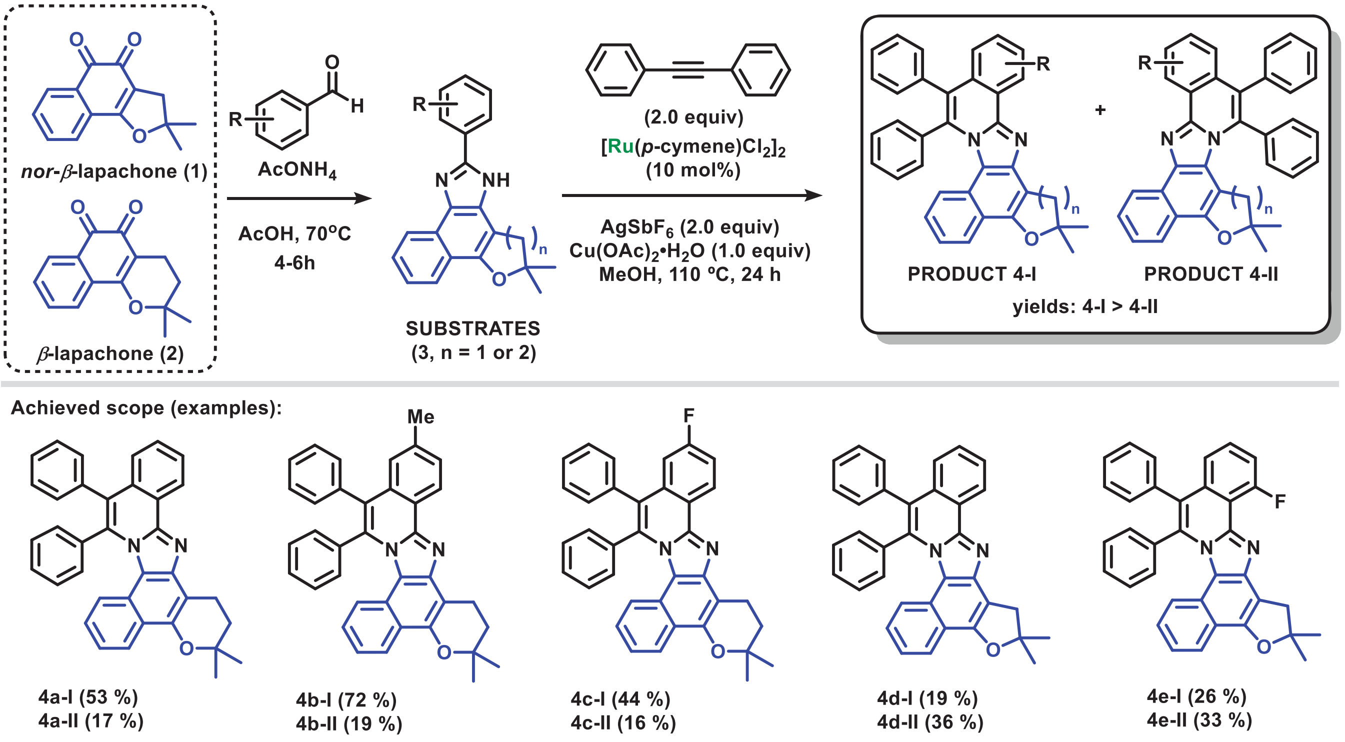
Key words: *Annulation, C–H Activation, Lapachones, Ruthenium Catalysis, Fluorescence.*

## Highlights

A ruthenium-catalyzed C–H annulation reaction leaded to the obtention of potentially trypanocidal molecules. Starting from *β*- and nor-*β*-lapachone, several polycyclic imidazoles were achieved.

## Abstract

Through C–H activation, it is possible to directly obtain a large variety of compounds with different substituents, valuable for the construction of important bioactive compounds. In this work, the synthesis of several modified polycyclic imidazoles **4** is described, *via* an elegant ruthenium-catalyzed C–H annulation reaction. Starting from *nor-β*-lapachone **1** and *β*-lapachone **2**, several arylated imidazoles **3** can be obtained, and subsequently used as substrates on the C–H activation process hereby described (Scheme 1). A certain regioselectivity was observed, due to steric effects originated from the structure of the substrate. The molecules obtained are under evaluation against *Trypanosoma cruzi* trypomastigote form, the parasite responsible for causing the neglected Chagas disease, from which valuable trypanocidal properties are expected to be observed.



**Scheme 1.** General overview of the developed ruthenium-catalyzed C–H annulation on imidazoles

## Acknowledgments

This research was funded by grants from CNPq, CAPES, FAPEMIG and INCT-Catálise.

**Área: ORG**

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

# Síntese de novas carboxamidas derivadas da 6-sulfonamida-4-oxoquinolina como potenciais inibidores colinesterásicos.

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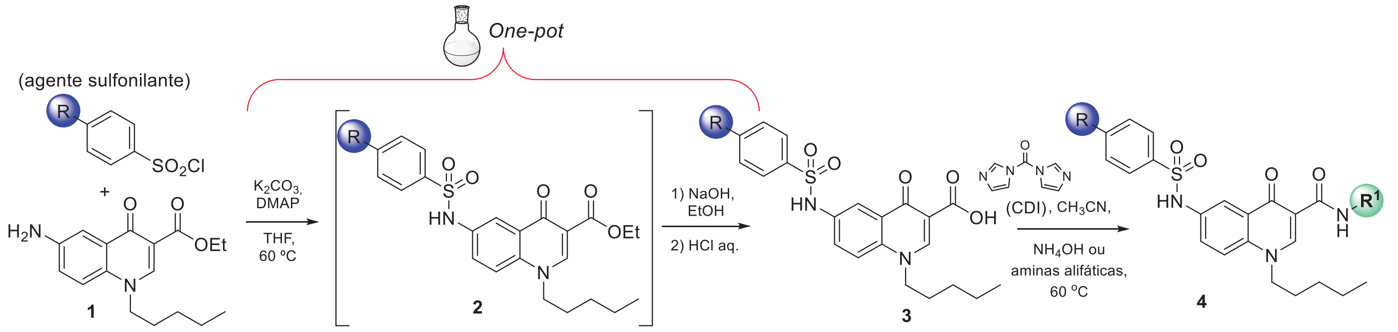
Palavras Chave: *quinolona; amida; sulfonamidas; intermediário sintético; heterociclos*

## Highlights

Synthesis of novel carboxamides derived from 6-sulfonamide-4-oxoquinoline as potential cholinesterase inhibitors. Mild conditions were applied for the synthesis of the products and their intermediates. New 4-oxoquinoline derivatives for the development of anti-Alzheimer agents.

## Resumo/Abstract

A Doença de Alzheimer (DA) é a sexta principal causa de mortes no mundo e afeta, na sua grande maioria, os idosos, sendo caracterizada por um processo neurodegenerativo progressivo que leva à deterioração cognitiva e da memória de curto prazo, e ao desenvolvimento de sintomas neuropsiquiátricos e de alterações comportamentais. Dentre os principais fatores responsáveis pelo surgimento da DA está a baixa concentração do neurotransmissor acetilcolina (ACh) presente no sistema nervoso central, no sistema nervoso periférico e nas junções neuromusculares. Os baixos níveis de ACh decorrem do aumento da atividade hidrolítica promovida pelas enzimas acetilcolinesterase (AChE) e butirilcolinesterase (BChE) para converter a ACh em colina e acetato. Diferentes grupos de pesquisa em todo o mundo têm despendido esforços para o planejamento e síntese de novas substâncias com ação inibitória frente a estas enzimas, visando o desenvolvimento de novos agentes anti-DA. Estudos indicam que o núcleo 4-oxoquinolínicos e os grupos funcionais carboxamida e sulfonamida estão presentes em diferentes substâncias capazes de regular o déficit colinérgico a partir da inibição colinesterásica. Dessa forma, neste trabalho é descrita a síntese de uma série de derivados 3-carboxamido-6-sulfonamido-4-oxoquinolínicos (**4**) com potencial atividade anti-AChE e anti-BChE. As substâncias propostas (**4**) foram sintetizadas partindo-se da 6-amino-4-oxoquinolina **1**, via uma reação *one-pot* envolvendo sulfonilação e hidrólise alcalina em sequência. Os ácidos carboxílicos intermediários (**3**) foram então reagidos com amônia ou aminas alifáticas, na presença de 1,1'-carbonildi-imidazol (CDI) como reagente de acoplamento, fornecendo as carboxamidas **4**, sem a necessidade de etapas de purificação posteriores. As substâncias do tipo **3** e **4** são inéditas na literatura científica, e tiveram suas estruturas confirmadas por métodos espectroscópicos de análise (IV, RMN de $^1$H e de $^{13}$C), e seus pontos de fusão foram determinados. Como perspectiva futura, espera-se expandir esta coleção de substâncias variando-se os substituintes destacados em R e R$^1$, e as substâncias sintetizadas serão avaliadas em ensaios de inibição enzimática em colaboração com o grupo da Profa. Marcela Cristina de Moraes, do Instituto de Química da UFF.



**4a:** R = $CH_3$, R$^1$ = H; **4b:** R = $CH_3$, R$^1$ = $CH_2CH_2OH$; **4c:** R = Cl, R$^1$ = H; **4d:** R = Cl, R$^1$ = $CH_2CH_2OH$

**Esquema 1** – Rota sintética para obtenção dos derivados **4**

## Agradecimentos/Acknowledgments

PPGQ-UFF, CAPES (Código de Financiamento 001), FAPERJ e CNPq

**Área: ORG**

# Síntese de novos derivados de marinoquinolinas indólicas com potencial atividade antimalárica

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Palavras Chave: Malária, Marinoquinolinas, Síntese.

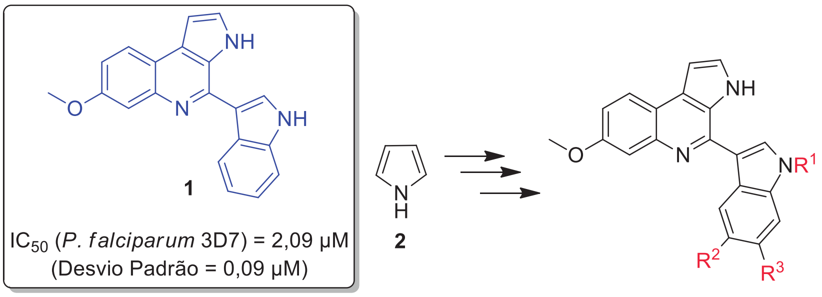
## Highlights

Synthesis of new indole marinoquinoline derivatives with potential antimalarial activity

New marinoquinoline derivatives containing an indole moiety were synthesized and their potential antimalarial activity was evaluated. From a synthetic route of 9 to 10 steps, 6 indole marinoquinolines (MQs) were obtained in good overall yields. These MQs were shown to be active against *Plasmodium falciparum* 3D7, with $IC_{50}$ ranging from 0.55 to 2.9 µM.

## Resumo/Abstract

A malária é uma enfermidade causada por espécies do parasita *Plasmodium* spp. De acordo com a Organização Mundial de Saúde (OMS), somente em 2020 a malária ocasionou a morte de 627 mil pessoas. Atualmente existem diversos fármacos disponíveis no mercado para o tratamento da malária, no entanto, os parasitas estão ganhando resistência a eles, tornando o tratamento ineficaz. Além disso, a única vacina disponível atualmente (RTS,S/AS01), não é eficaz contra todas as espécies do parasita. Portanto, é de extrema urgência o desenvolvimento de novos fármacos capazes de combater eficientemente essa doença. Neste contexto, a descoberta de novos fármacos torna-se relevante. Uma classe de compostos denominados marinoquinolinas (MQs) vêm ganhando destaque devido às suas atividades inibitórias apresentadas frente ao *Plasmodium*. A partir da estrutura da MQ **1**, sintetizada anteriormente pelo grupo do prof. Correia, decidiu-se realizar novas modificações na porção indólica dessa substância, visando realizar um estudo de relação estrutura-atividade (REA) para essa classe de substâncias. Até o presente momento foram sintetizadas 6 novas MQs (**3a-f**), obtidas a partir de uma rota sintética envolvendo 9/10 etapas. As MQs foram enviadas para os bioensaios de atividade antimalárica, em colaboração com o grupo de pesquisas do Prof. Dr. Rafael Victorio Carvalho Guido, do Instituto de Física de São Carlos da USP, que mostrou que as MQs foram ativas frente ao *P. falciparum* 3D7, com valores de $IC_{50}$ variando de 0,55 a 2,9 µM. Comparando esses resultados com a atividade antimalárica da MQ **1**, pode-se concluir que o NH do núcleo indólico é importante para a atividade biológica, e além disso, substituições em $R^2$ e $R^3$ resultaram em substâncias mais ativas.



**1**

$IC_{50}$ (*P. falciparum* 3D7) = 2,09 µM
(Desvio Padrão = 0,09 µM)

**2**

| | $IC_{50}$ (µM), *P. falciparum* (cepa 3D7) | Desvio Padrão (µM) |
|---|---|---|
| **3a)** $R^2$ = H, $R^3$ = H, $R^1$ = Me | 2,90 | 0,40 |
| **3b)** $R^1$ = H, $R^3$ = H, $R^2$ = OMe | 1,50 | 0,40 |
| **3c)** $R^1$ = H, $R^3$ = H, $R^2$ = COOMe | 1,49 | 0,07 |
| **3d)** $R^1$ = H, $R^3$ = H, $R^2$ = F | 1,00 | 0,10 |
| **3e)** $R^1$ = H, $R^3$ = H, $R^2$ = Br | 1,70 | 0,30 |
| **3f)** $R^1$ = H, $R^2$ = H, $R^3$ = Br | 0,55 | 0,08 |

## Agradecimentos/Acknowledgments

Ao CNPq pela concessão da bolsa de doutorado (Processo: 142488/2020-8).

**Área: ORG**

# Síntese de tricetonas assimétricas

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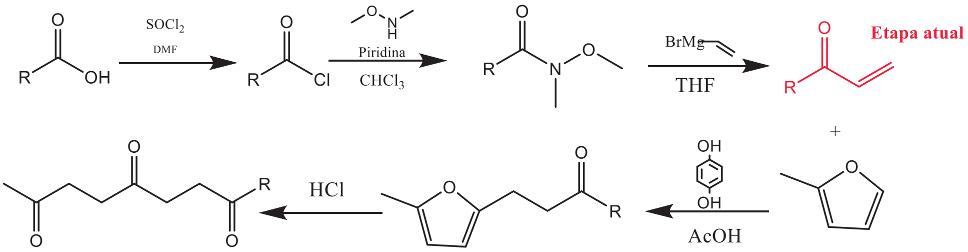
Palavras Chave:*(Tricetonas, Vinil Cetonas, Amida de Weinreb).*

## Highlights

Synthesis of asymmetric triketones: Reduce of metallic agents in the synthesis of triketones from carboxylic acids.

## Resumo

Os compostos carbonilados podem ser encontrados na natureza e apresentam importante atividade farmacológica, herbicida, antiviral e antibacteriana[1], a este grupo pertencem os compostos cetônicos, como por exemplo, as tricetonas que por sua vez, atuam como importantes blocos de construção na produção de compostos carbocíclicos substituídos[2]. Assim, este trabalho propõe a síntese de tricetonas que já estão consolidadas na literatura[3], entretanto, por meio de uma rota sintética que evita o uso de metais ao longo das etapas. Para isso o trabalho foi dividido nas etapas de: formação do cloreto de ácido carboxílico para obtenção das amidas de Weinreb, obtenção das vinil cetonas a partir das amidas[4], alquilação do metil furano com as vinil cetonas e por fim abertura do anel furano. O trabalho encontra-se na etapa da obtenção das vinil cetonas; partindo de ácidos carboxílicos comerciais reagindo com cloreto de tionila, ocorre a formação do correspondente cloreto de ácido carboxílico, esses foram utilizados na etapa seguinte da síntese, para a formação de amidas de Weinreb, que ao reagirem com brometo de vinil magnésio produziram vinil cetonas, que por sua vez, serão utilizadas para alquilar o metil-furano e por uma abertura do anel em meio ácido, produzirá as tricetonas de interesse o esquema 1 apresenta a rota sintética proposta para a obtenção dos produtos.



Esquema 1. Rota sintética proposta para obtenção das tricetonas.

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## Agradecimentos

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**Área: ORG**

# Síntese e caracterização de derivados aminoquinolínicos para investigação da atividade biológica

**Talia F. de Oliveira (IC),[1] Edriane T. da Silva (PG)[1], Geraldo J. da S. Neto (PG)[1], Dimas J. da P. Lima (PQ)[1], Mario R. Meneghetti (PQ)[1], fariastalia1@gmail.com; edriane@uol.com.br.**

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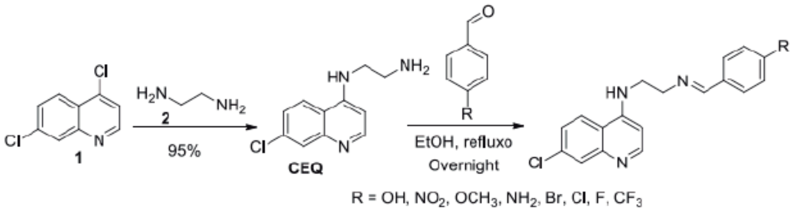
Palavras Chave:*Síntese, Iminas, Aminoquinolínas, Atividade biológica. .*

## Highlights

Synthesis and characterization of imines containing the aminoquinoline nucleus for investigation of biological activity. Imines containing quinolines. Condensation of a primary amine and an aromatic aldehyde. potential biological activity.

## Resumo/Abstract

Na química medicinal e sintética os derivados quinolínicos representam um importante papel na síntese de novos fármacos contendo heterocíclicos de reconhecida aplicação biológica. Iminas são o produto da condensação de uma amina primária com um aldeído ou cetona, que também tem apresentando conter diversas e interessantes propriedades biológicas, como atividade antibacteriana, anti-inflamatória, antimicrobiana, leishimanicida, antimalárica e antitumoral1 . Nesse contexto, o presente trabalho teve como propósito sintetizar uma série de compostos 4- aminoquinolinicos, contendo a função imina, e testá-los para possível atividade biológica, leishimanicida e antimalárica. Para a síntese desses derivados foi necessário preparar a N-(2-aminoetil) -7-cloroquinolin-4-amina (CEQ) a qual foi obtida, em 95% de rendimento, através da reação entre a 4,7-dicloroquinolina e etilenodiamina (Esquema 1). Posteriormente, a CEQ foi tratada com aldeídos aromáticos substituídos com grupos doadores e retiradores de elétrons na posição para fornecendo as iminas contendo o núcleo aminoquinolínico, em rendimentos que variaram entre 40 e 80%. Os compostos sintetizados foram caracterizados por IV, RMN de 1H e de 13C e serão encaminhadas para posterior investigação da citotoxidade e da atividade leishmanicida e antimalárica.



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## Agradecimentos/Acknowledgments

Agradecimentos: UFAL, IQB, PPGQB, CAPES, CNPq, FAPEAL e IFAL.

**Área:** ORG

# Síntese e caracterização de novos análogos de aciclonucleosídeos fosfonatos derivados de ácidos 4-quinolono-3-carboxílicos (ANPs).

**Alan G. de Souza (PG),[1]* Claudio S. Viana Junior (IC),[1] Thaís A. Tavares (IC),[1] Letícia V. Faro (PQ),[1] Marcos C. de Souza (PQ),[1] Fernanda C. S. Boechat (PQ),[1] Maria Cecília B. V. de Souza (PQ).[1]**

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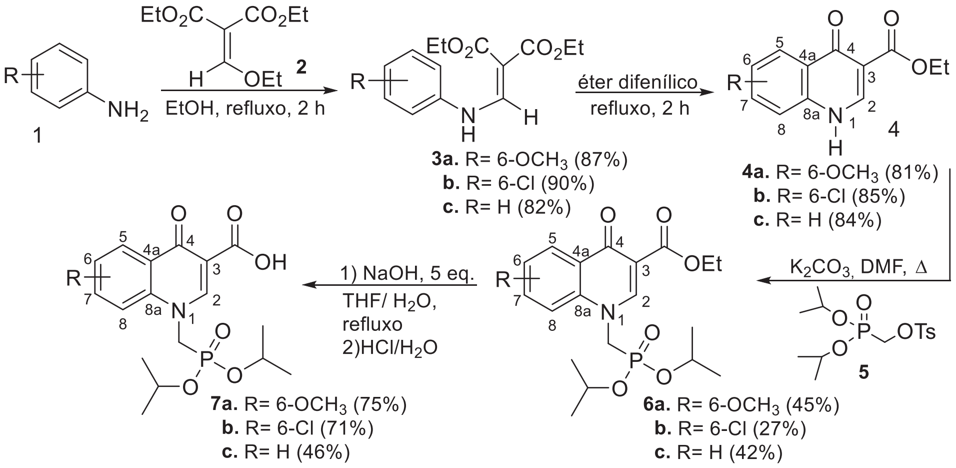
Palavras-Chave: *Aciclonucleosídeo, Quinolona, Fosfonato, COVID-19, Antiviral.*

## Highlights

Synthesis and characterization of new analogues of acyclonucleoside phosphonate 4-quinolone-3-carboxylic acids.
COVID-19 affected the world population causing a large number of deaths.
The lack of specific vaccines and drugs for the prevention and treatment of viruses makes the synthesis of new antiviral substances urgent and necessary.

## Resumo/Abstract

Com o cenário da pandemia atual causada pelo SARS-CoV-2, evidencia-se que o desenvolvimento de novas substâncias que possam atuar como fármacos de potencial ação antiviral frente a este vírus se faz urgente e necessário. Além do SARS-CoV-2, os arbovírus Zika (ZIKV) e Chikungunya (CHIKV) constituem-se em um grande problema de saúde pública. A inexistência de vacinas e fármacos específicos para prevenção e tratamento dessas infecções virais corroboram com a importância da busca por novas substâncias antivirais com foco nos vírus citados. Nesse sentido, foi preparada uma série de ANPs do tipo ácidos 4-quinolono-3-carboxílicos **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 em difenil éter produziram as 4-quinolonas **4**. Estas, submetidas à reação de *N*-alquilação com diisopropil(tosilmetoxi)fosfonato (**5**), levaram aos intermediários ANPs 4-quinolonônicos **6**, que foram convertidos, por fim, aos ANPs **7** por hidrólise básica, seguida de neutralização do meio reacional. Estes novos ANPs **7**, assim como os precursores **6**, tiveram suas estruturas confirmadas por RMN de $^{1}H$ e de $^{13}C$, por espectroscopia na região do IV, e se encontram sob investigação de sua atividade antiviral.



**Esquema 1.** Esquema reacional para obtenção dos derivados ANPs de ácidos 4-quinolono-3-carboxílicos (**7**)

## Agradecimentos/Acknowledgments

FAPERJ, CNPq e CAPES (Código de Financiamento 001).

**Área: ORG_______________**

# SÍNTESE E ESTUDOS BIOFÍSICOS DA ANGIOTENSINA I E II AMIDADA: INTERAÇÃO PEPTÍDEO MEMBRANA E AVALIAÇÃO BIOLÓGICA

**Amanda S. Félix (PG),[1*] Larissa S. Matsamura (IC),[1] Lucas F. Ferreira (PQ),[3] Daniel C. Villela (PQ),[2] Rodrigo M. Verly (PQ),[1]**

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Palavras Chave: Peptídeos bioativos, Angiotensina, Amidação, Hipotensão, Peptídeo interação-membrana.

## Highlights

SYNTHESIS AND BIOPHYSICAL STUDIES OF ANGIOTENSIN I AND II AMIDATED: PEPTIDE MEMBRANE INTERACTION AND BIOLOGICAL EVALUATION The effect of amidation of angiotensin I and II on peptide-membrane interaction was evaluated by impedance spectroscopy on phospholipid membranes. The influence on the organism was evaluated in vivo.

## Resumo/Abstract

O sistema Renina-Angiotensina-Aldosterona (SRAA) acontece devido às interações entre os três hormônios que agem de maneira contínua para que aconteçam reações orgânicas que proporcionam equilíbrio da pressão sanguínea e da quantidade de sódio e água do organismo. A desregulação desse sistema pode resultar na ocorrência de doenças renais, cardiovasculares e na hipertensão arterial (HTA). A cascata Renina-Angiotensina-Aldosterona é ativada pelo próprio organismo quando o equilíbrio é interrompido pela queda da pressão (hipotensão) ou quando há perda excessiva de líquidos. Assim, a renina secretada ficará presente no plasma sanguíneo atuando na clivagem da porção *N*-terminal do angiotensinogênio que gera um decapeptídeo inativo denominado de angiotensina I (DRVYIHPFHL), que por sua vez será convertida nos pulmões e rins no octapeptídeo angiotensina II (DRVYIHPF) por meio da enzina conversora de angiotensina (ECA). Não encontramos na literatura informações sobre a amidação natural da angiotensina I e de seus análogos no organismo vivo, porém sabe-se que muitos peptídeos usados pelos sistemas nervoso e endócrino para a comunicação célula-célula requerem um grupo amida no *C*-terminal para se tornarem totalmente ativos. Dessa maneira, o presente trabalho visou analisar a influência da amidação da angiotensina I e II no organismo e suas possíveis aplicações. Para isto, os peptídeos angiotensina I e angiotensina II nativos e amidados foram sintetizados pelo método de síntese de peptídeos em fase sólida via estratégia Fmoc (Chan & White, 200). A análise da síntese e purificação dos peptídeos foi realizada por cromatografia líquida de alta eficiência (CLAE) e caracterizados por espectrometria de massas (Electrospray - ESI), por meio da razão massa carga dos mesmos. A afinidade e interação dos peptídeos angiotensina I e II foram avaliadas por modelos de membranas fosfolipídicas de 1-palmitoil-2-oleoil-fosfatidilcolina (POPC) e palmitoil-2-oleoil-fosfatidilglicerol (POPG) por espectroscopia de impedância eletroquímica e para isso, o espaçador contendo três alaninas (AAA) foi inserido para que a mobilidade dos peptídeos não fossem prejudicadas e uma cisteína (C), nas regiões N- e C-terminal das cadeias peptídicas com o intuito de imobilizar os peptídeos na superfície de eletrodos impressos de ouro (DropSens 220AT) por meio da ligação do átomo de enxofre. Dessa maneira, os testes iniciais mostraram que a sequência CAAA–Angio I (CAAADRVYIHPFHL) promove maiores valores de resistência a transferência de carga quando comparada com a sequência Angio I–AAAC (DRVYIHPFHLAAAC), possivelmente devido a maior interação com as membranas fosfolipídicas de Angio I–AAAC quanto comparado com CAAA–Angio I. Ao interagir com as vesículas, a resistência a transferência de carga aumentou, sendo o efeito mais pronunciado em POPC, indicando maior interação dos peptídeos em meios zwitteriônicos. Tal observação condiz com a literatura, uma vez que os peptídeos possuem funções em células eucariontes. A sequência CAAA–Angio II (CAAADRVYIHPF) promove maior resistência a transferência de carga quando comparada com a sequência Angio II–AAAC (DRVYIHPFAAAC). Porém, essa alteração foi cerca de 8 vezes menos significativa quando comparada com a Angio I, fazendo com que não fosse possível visualizar de forma satisfatória a interação com as vesículas. Por fim, foram realizados testes de reatividade vascular e alterações cardiovasculares por infusão sistêmica em ratos Wistar, os quais mostraram que a Angiotensina I carboxi gera efeitos mais significativos do que a amidada, indicando que, caso essa amidação ocorra no organismo as funções equilíbrio da pressão sanguínea e da quantidade de sódio e água possam ser prejudicadas.

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## Agradecimentos/Acknowledgments

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**Área: ORG**

# Síntese *one pot* de híbridos triazólicos de aminonaftoquinona para o desenvolvimento de novos agentes anti-leishmania

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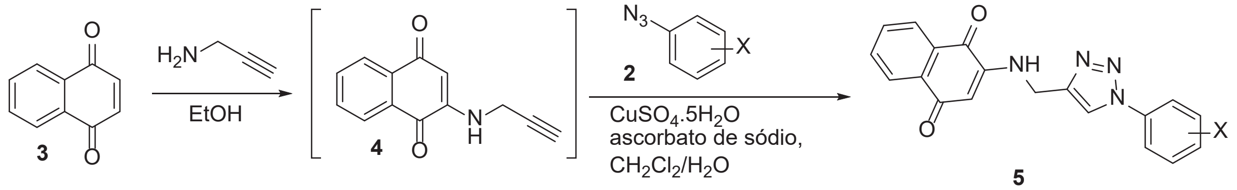
Palavras Chave: *1,2,3-triazol, aminonaftoquinona, inibidores enzimáticos, atividade antileishmania, enzima LdNH*

## Highlights

"One pot synthesis of aminonaphthoquinone triazole hybrids for the development of new anti-leishmania agents". New agents for the treatment of Leishmania. New potential *LdNH* enzyme inhibitors.

## Resumo/Abstract

Leishmanioses são doenças negligenciadas, oriundas de protozoários do gênero Leishmania que podem ser classificadas como visceral, monocutânea ou cutânea. Os tratamentos disponíveis destas doenças apresentam elevado custo e a ocorrência de resistência medicamentosa, motivando a busca por potenciais novos fármacos. Neste trabalho, uma biblioteca de doze triazóis aminonaftoquinônicos (**5**) foi preparada e avaliada frente a enzima nucleosídeo hidrolase da *Leishmania donovani* (*LdNH*), um alvo farmacológico associado à forma visceral da doença. Essas substâncias foram sintetizadas com rendimentos que variaram de 33 a 77%, a partir de uma adaptação do método descrito por da Silva Júnior e colaboradores em 2013, pela conversão da 1,4-naftoquinona (3) no intermediário 4 via tratamento com propargilamina, seguido da adição de azidas aromáticas (2), sob catálise de Cu(I), gerado *in situ*.



As substâncias **5** foram avaliadas quanto à inibição da *LdNH* através do monitoramento da atividade catalítica da enzima imobilizada em partículas magnéticas por cromatografia líquida de alta eficiência, quantificando-se diretamente o produto (hipoxantina) formado na catálise enzimática. Um ensaio de triagem inicial demonstrou que todos os compostos da biblioteca exibiram percentuais de inibição da *LdNH* entre 82 e 94%, a 100 μM, sendo os mais potentes aqueles que apresentam haletos como substituinte na posição *meta* do grupo 1-fenil-1,2,3-triazólico. As próximas etapas do trabalho envolvem a determinação dos valores de $IC_{50}$, do mecanismo e constante de inibição, além dos estudos de interação com a enzima por estudos *in silico* (docking molecular) e *in vitro* (RMN/STD).

## Agradecimentos/Acknowledgments

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

# Selective oxidation reactions in the synthesis of complex *ent*-beyeranes

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Palavras Chave: Diterpenes, synthesis, oxidation, catalysis, natural products

## Highlights

- Synthesis of two *ent-beyerane* metabolites for the first time;
- The first intermolecular metal-catalyzed remote C—H bond oxidation applied in a natural product synthesis in a non-activated position is reported.

## Abstract

Isosteviol methyl ester **1** was converted to the oxime **2** ($MeONH_3Cl$, NaOAc, $MeOH/H_2O$, 94%). Under Sanford conditions ($Pd(OAc)_2$, $PhI(OAc)_2$), **2** was acetoxylated to **3** in 52% yield and 26% rsm. Acidic hydrolysis of the oxime and the acetate afforded **4** (HCl, acetone, 84%). The acetylation of **4** delivered **5** in 95% yield. This compound was used as platform to the oxidation with Mn($CF_3$-PDP) under White conditions. The best condition (Entry 3) delivered alcohol **6** in 38% yield as the only isomer. The compound **6** was then submitted to basic hydrolysis conditions ($K_2CO_3$, THF, MeOH, 64%) and the ester was hydrolyzed (NaH, EtSH, DMF, 57%), resulting in the formation of the metabolite **8**. The metabolite **9** was also synthetized using this strategy, by hydrolysis of ester **4** to furnish compound **9** in 39% yield.

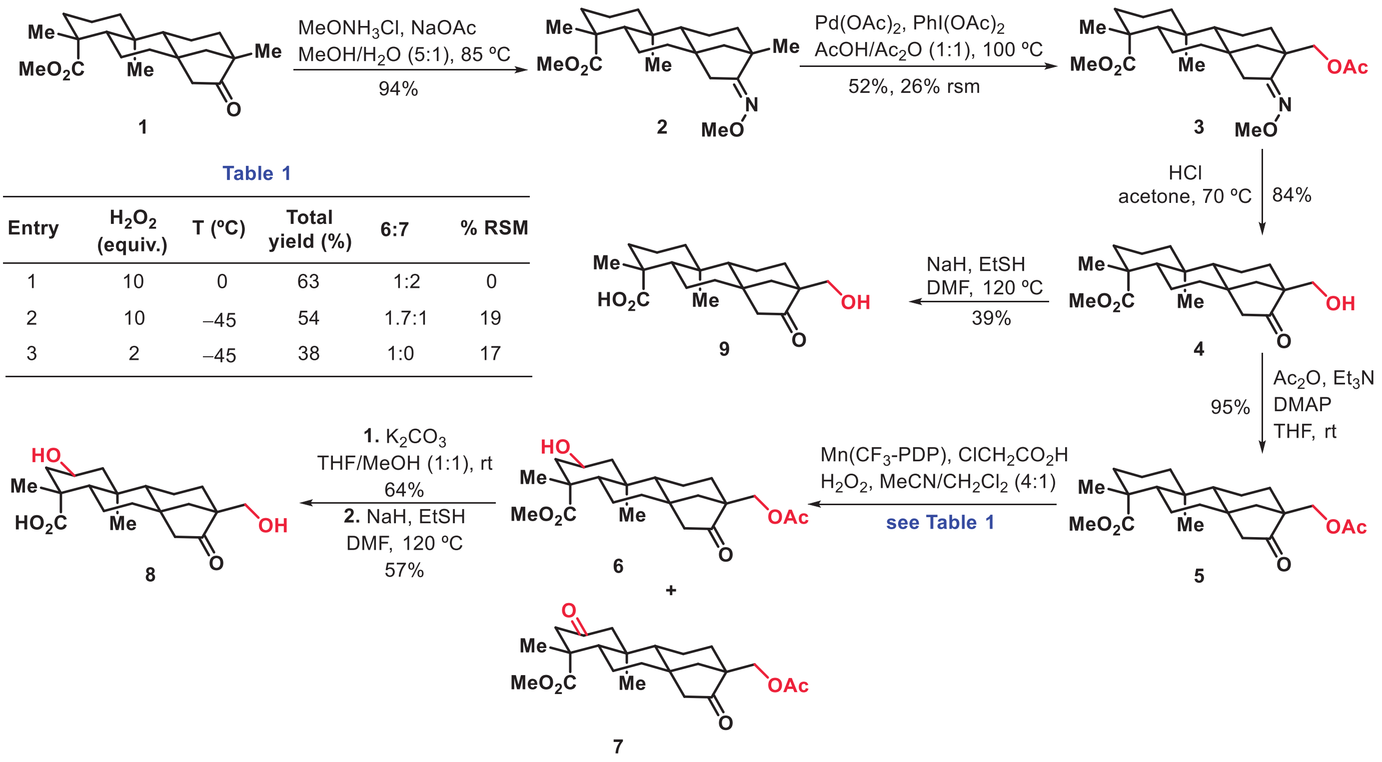

Table 1

| Entry | $H_2O_2$ (equiv.) | T (ºC) | Total yield (%) | 6:7 | % RSM |
|---|---|---|---|---|---|
| 1 | 10 | 0 | 63 | 1:2 | 0 |
| 2 | 10 | –45 | 54 | 1.7:1 | 19 |
| 3 | 2 | –45 | 38 | 1:0 | 17 |

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**Área: ORG** **Nº de Inscrição: 01039**

# Síntese de novos análogos triazólicos do fentanil

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Palavras Chave: *Opioides, atividade analgésica, anel triazólico, reação “click”.*

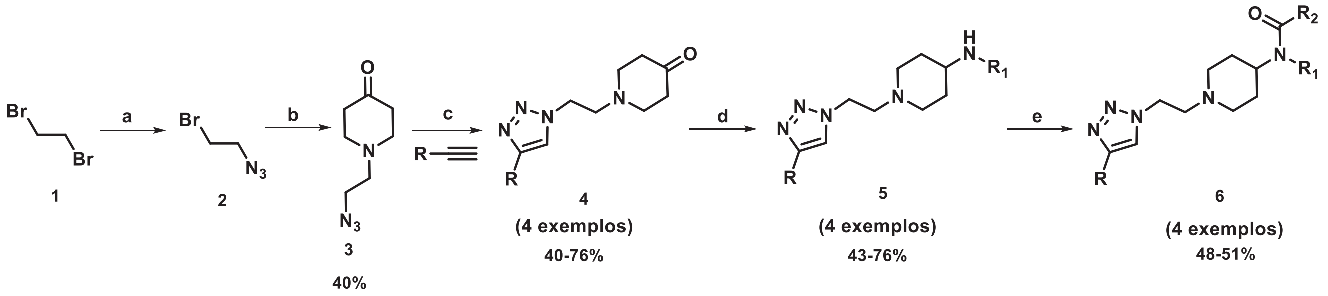
## Highlights

Synthesis of new triazole analogs of fentanyl. A series of novel analogs of fentanyl containing different organic groups on the 4-position of the triazole ring was synthesized and their biological activities will be evaluated.

## Resumo/Abstract

O fentanil é um opioide sintético utilizado principalmente como anestésico para controle da dor.[1] Entretanto, o fentanil apresenta graves efeitos colaterais como depressão respiratória, êmese, constipação e, principalmente, a dependência física. Diversos análogos do fentanil já foram sintetizados, com o intuito de modular suas propriedades farmacológicas, mas ainda existe a procura por um opioide ideal, que mantenha sua alta propriedade analgésica mas atenue seus efeitos colaterais.[2] O anel triazólico destaca-se como grupo funcional para a síntese de novos derivados do fentanil, pois esse heterociclo possui propriedades químicas de interesse que permitem interações do tipo ligação de hidrogênio, dipolo-dipolo e π *stacking* com diversos alvos biológicos.[3] Assim, o objetivo deste trabalho é a preparação de novos análogos triazólicos do fentanil do tipo **6** (Esquema 1) que serão testados como analgésicos. A rota de síntese consistiu na alquilação da 4-piperidona com o haleto **2** contendo um grupo azida, produzindo o intermediário **3** em uma metodologia *one pot*, a partir do dibrometo **1**. A reação de **3** com alcinos comerciais levou à formação de piperidonas triazólicas inéditas do tipo **4** (4 exemplos), via reação de cicloadição do tipo “click”. Estes intermediários foram submetidos à aminação redutiva usando aminas aromáticas e diversos agentes redutores foram testados para produzir os compostos do tipo **5.** A acilação dessas aminas secundárias gerou quatro novos derivados triazólicos do fentanil do tipo **6**, com rendimentos variando entre 48-51%.

**Esquema 1.** Rota sintética empregada para obtenção de novos derivados triazólicos do fentanil. Condições de reação: a) $NaN_3$, acetona, 24h, T.A.; b) 4-piperidona, $K_2CO_3$, acetona, 24h, refluxo; c) Alcinos comerciais, $CuSO_4$, NaAsc., $CH_2Cl_2/H_2O$, 24h, T.A.; d) $R_1$-$NH_2$, AcOH, $CH_2Cl_2$, agentes redutores, 48h, refluxo; e) $R_2$-COCl, $Et_3N$, $CH_2Cl_2$, 7h, T.A.



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## Agradecimentos/Acknowledgments

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**Área: ORG**

# Solvent-free 1,3-dipolar cycloaddition between enaminone and 4-aryl-azides for the synthesis of new 1,2,3-triazoles potentially bioactive

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Palavras Chave: *1,4-disubstituted-1,2,3-triazoles, 1,3-dipolar cycloaddition, solvente free*

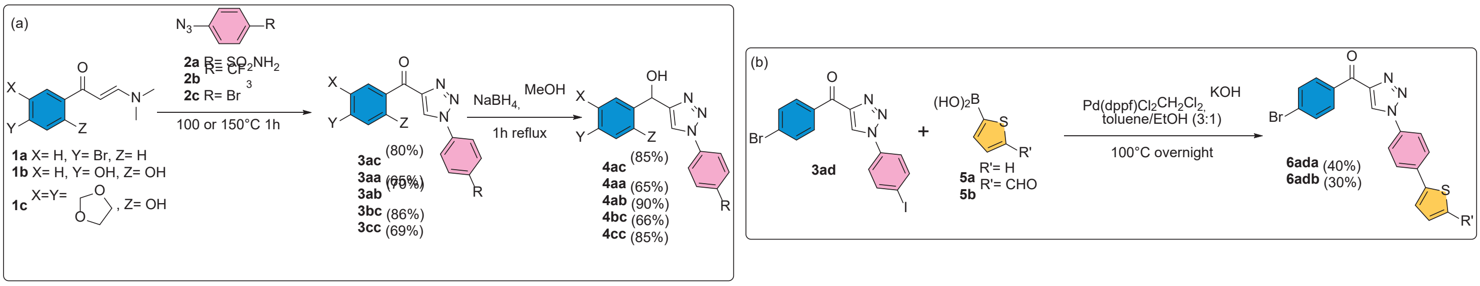
## Highlights

New hydroxy 1,4-substituted-1,2,3 triazoles were obtained by a solvent-free cycloaddition reaction as the key step

Hybrids 4-acyl-1,2,3-triazoles and thiophene were also obtained by Suzuki reaction

## Abstract

Functionalized 1,2,3-triazole heterocycles are an important scaffold due to their bioisosteric proprieties.[1] In 2021 our research group published the antileishmanial activity of 1,2,3-triazoles based compounds, highlighting compound **4ac** (Scheme 1a) that showed the best activity against both forms of the parasite.[2] Despite the well-established synthesis for these compounds, mainly by click chemistry,[3] new greener, simpler and scalable methodologies are increasingly needed. In this work, we report the synthesis of new hydroxy 1,2,3-triazoles with different substitution patterns counting 4-bromobenzene as pharmaceutical candidates against *Leishmania amazonensis*. 4-acyl-1,2,3-triazoles **3** were synthesized by a solvent-free 1,3-dipolar cycloaddition between enaminones **1**, previously synthesized from acetophenones using a DMA-DMF, and substituted aryl azides **2**. After reduction of carbonyl group using $NaBH_4$, the hydroxy 1,2,3-triazoles **4** were obtained in 66 to 90% yield (Scheme 1a). Compounds **6** were obtained by a Suzuki cross-coupling between **3ad** and the appropriate boronic acid **5** (Scheme 1b). All compounds were characterized by $H^1$ NMR, which a 1H singlet around 8 ppm confirms the 1,4-disubstituted-1,2,3-triazole formation and $C^{13}$ NMR.



**Scheme 1:** (a) Syntheses of hydroxy triazoles; (b) Suzuki Cross-Coupling between 4-acyl-1,2,3-triazoles and thiophene boronic acids

As result, a simpler, versatile and greener methodology to obtain different hydroxy 1,2,3-triazoles is presented, which demonstrates new synthetic possibilities. Cross-Coupling is also an alternative to vary substitution patterns, possibly more complex compounds. Also, the molecules will be tested for their anti-leishmanial activity expecting better results and less toxicity compared to **4ac**.

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**Área: ORG**

# Spiro compound green synthesis organocatalyzed by ionic liquid

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Keywords: *Spiro Compound, Organocatalyzed Synthesis, Ionic Liquid.*

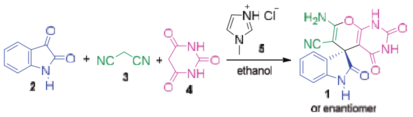
## Highlights

A new green multicomponent methodology was developed, using ethanol as solvent and ionic liquid as organocatalyst, to synthesize a spiro compound.

## Resumo/Abstract

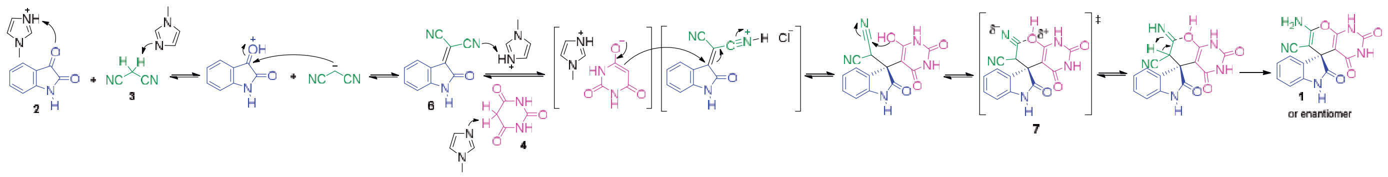
Multicomponent organocatalyzed methodologies have gained prominence in the spiro compounds synthesis. Furthermore, the use of ionic liquids as organocatalysts has emerged as an ecofriendly alternative to other catalysts. Therefore, a new green multicomponent methodology organocatalyzed by ionic liquid for the synthesis of a spiro compound was developed. Spiro compound **1** could be obtained by multicomponent domino Knoevenagel/Michael reaction from isatin **2** (1 mmol), malononitrile **3** (1 mmol) and barbituric acid **4** (1 mmol), using the ionic liquid **5** (0,3 mmol) as organocatalyst, in ethanol under reflux for 24 h (**Figure 1**).[1] Such reaction conditions were established from a methodological study varying solvent, temperature and amount of catalyst.

**Figure 1.** Synthesis of the spiro compound **1**.



A possible mechanism for the formation of **1** would result from the initial formation of the isatilidene-malononitrile intermediate **6** by the Knoevenagel condensation of **3** with **2**. Then, a Michael addition between **4** and **6**, followed by cyclization and tautomerization would provide **1** (**Figure 2**). The catalytic role of **5** can be based in stabilizing of the suggested polar transition state **7** and activating the species **6** and **4** toward the Michael addition.[2]

**Figure 2.** Plausible mechanism for the synthesis of **1**.



IR spectroscopy data showed bands at 3597, 3116, 2203 and 1685 $cm^{-1}$ relative to NH, aromatic CH, nitrile, C=O, respectively. In the $^{1}H$ NMR spectrum were observed singlets at 11.07 and 10.41 ppm referring to the NH of barbituric acid scaffold, a singlet at 7.32 ppm referring to the $NH_2$ and four signals in the 7.13, 7.09, 6.88 and 6.74 ppm referring to the aromatic hydrogens of the isatin scaffold. $^{13}C$ NMR spectrum showed an important signal at 47.1 ppm relative to the carbon spiro-atom. Finally, the mass spectrum confirmed the formation of **1** through the peak with mass/charge ratio 346.05469 m/z (error = -0,03 ppm) referring to the sodium compound $[C_{15}H_9N_5NaO_4]^+$.

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Capes, CNPq, Fapes, NCQP.

**Área:** **ORG**

# Statistical Modelling Offers Insights About Molybdenum Imido Alkylidene Catalysts for Olefin Metathesis

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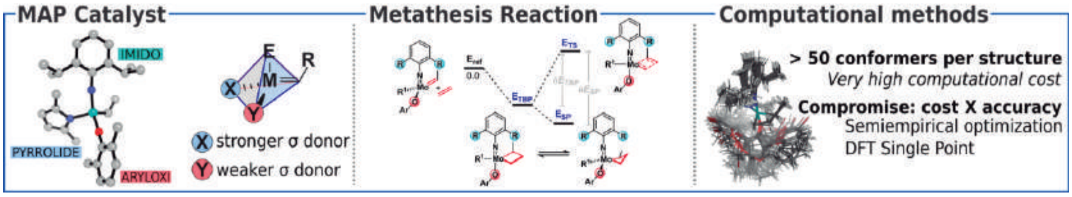
Palavras Chave: *Catalysis, Olefin Metathesis, Schrock Catalysts, Statistics, Multivariate Models.*

## Highlights

Prediction of *turnover frequency* for metathesis catalysts. Mo-based Schrock catalysts bearing aryloxi substituents have different reactivity based on non-covalent interactions. “High-throughput computational chemistry” using semiempirical model chemistries.

## Resumo/Abstract



Metathesis reactions are versatile transformations used to deploy a wide range of compounds – from carbocycles and heterocycles to E or Z olefins – by means of cross-metathesis, ring opening/closing and polymerizations from olefins[1]. From different catalysts that can be employed in these reactions, the Schrock-type Mo and W alkylidene complexes stand out for they excellent performances – as measured by TON and TOF – and also for they remarkable Z-selectivity, specially the monoaryloxi pyrrolide (MAP) complexes[2]. Several studies established a general mechanism consisting of four elementary steps for the metathesis reactions employing MAP catalysts[3]. These studies describe a Chauvin-like process, where the highly stable metallacycle with trigonal bipyramidal (TBP) geometry is obtained after olefin coordination and cycloaddition. An important issue with these reactions concerns the facile isomerization from TBP to a square bipyramidal (SP) intermediate, which is the entry channel to catalyst degradation pathways. This isomerization hampers the productive pathway, thus reducing the catalyst performance. To reduce the occurrence of isomerization events most works rely on highly substituted aryloxi substituents, whose steric effects are expected to destabilize the SP intermediate relative to the TBP. A more recent study, however, highlight the participation of non-covalent interactions (NCI) – both attractive and repulsive – on the reaction kinetics[4]. The nature of the observed NCI is dependent on the substitution pattern of the aryloxi substituent. Herein we report our ongoing efforts to rationalize how different interactions, mainly non-covalent and also steric and electronic, affects the main intermediates of the metathesis reaction and how the molecular structure of the catalysts can be correlated with their catalytic performance in a holistic manner. Our current results indicates that aryloxi ligands bearing ortho-aryl substituents are associated with less stable intermediates, which can be associated with higher catalytic activity. Overall, the cycloreversion barriers for a wide range of aryloxi substituents are close to 14 kcal/mol, thus suggesting that the catalytic parameters can be associated directly to the stability of the key intermediates. Thus, by means of the parameterization of intermediates both in terms of steric and electronic parameters and also using calculated kinetic and thermodynamic descriptors we expect to expand the scope of ligands used in these important reactions.

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| FAPESP | CAPES |
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| Process Number (2020/13563-7; 2020/01255-6) | Process Number (88887.597433/2021-00) |

**Área: ORG**

# Stereoselective Synthesis of a New Enuloside with Potential Antitumor Action

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**Keywords:** Cancer, Enuloside, CRM1, Carbohydrate, Glycosylation.

## Highlights

Enulosides are a promising class of antitumor agents.

## Abstract

Enulosides are carbohydrate derivatives that contain an α,β-unsaturated carbonyl unit and exhibit various biological activities. These compounds act as potential Michael acceptors, especially for nucleophilic amino acid residues present in natural receptors. Leptomycin B is one of the most relevant examples due to its ability to inhibit CRM1 protein, a target for cancer treatment. One of the great challenges for the development of new drugs based on carbohydrates has been their rapid degradation in the bloodstream by glycosidases before their therapeutic effect. This pharmacokinetic problem can be overcome by using modified carbohydrates that may not be recognized by the body's glycosidases.[1]

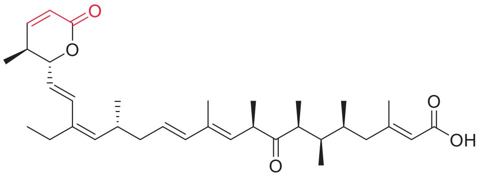
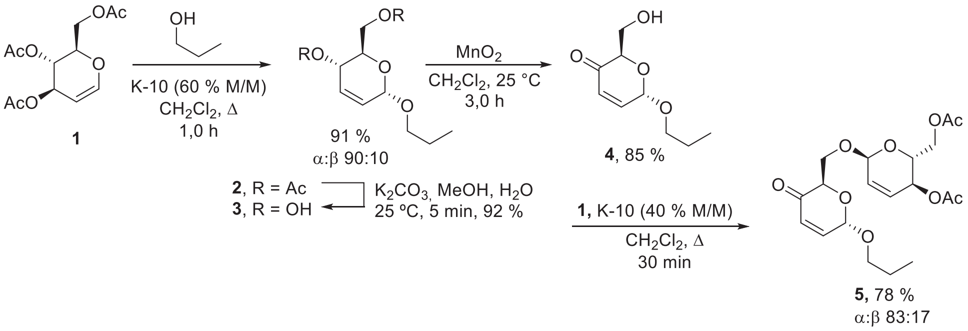


**Figure 1.** Structure of Leptomycin B.

The synthetic strategy for the synthesis of enuloside **5** was based on the use of glycal **1**, a commercially available D-glucose derivative, as a starting material. Initially, α-glycoside **2** was prepared from the glycosylation reaction with a yield of 91 % and a high stereoselectivity (α:β 90:10). Subsequently, α-glycoside **2** was subjected to a deprotection reaction (92%) followed by an oxidation reaction (85%) leading to compound **4**. The desired enuloside **5** was obtained through the glycosylation of compound **4** with a yield of 78 % and high α stereoselectivity (α:β 83:17). The synthesized compounds were characterized by the usual spectroscopic techniques and the data corroborate the structures. Therefore, we show that the adopted method is efficient to obtain enulosides with high yields and isomeric purity. The antitumoral evaluation of the synthesized compounds is currently in progress in our laboratory.



**Scheme 1.** Synthetic strategy for compound synthesis **5**.

1. Santos, J. A. M; Santos, C. S.; Almeida, C. L.; Silva, T. D. S.; Freitas, J. R.; Militão, G. C. G.; Silva, T.G.; Freitas, J. C. R. Menezes, P. H. *Eur. J. Med. Chem.* **2017**, *128*, 192-201.

## Agradecimentos/Acknowledgments

CAPES, CNPQ, FACEPE

**Área: ORG** **Nº de Inscrição: 540**

# Studies on the synthesis of Artepillin C

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Palavras Chave: *phenylpropanoids, prenylation, propolis*

## Highlights

Due to the great pharmacological potential of artepillin C, this work aims to optimize the reaction conditions for obtaining it via organic synthesis.

## Resumo/Abstract

Artepillin C (**Figure 1**) is one of the main prenylated phenolic found in green propolis (*Baccharis dracunculifolia*).[1] Because of the several biological activities assigned to artepillin C, especially the antimicrobial activity,[2] there has been a great interest in its obtaining via chemical synthesis. However, there are only two methodologies described in the literature so far, which require the use of expensive reagents or afford artepillin C in low yields.

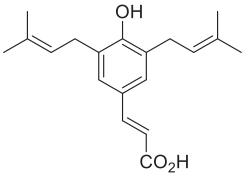
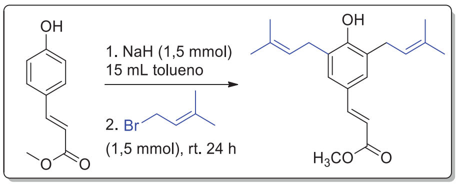
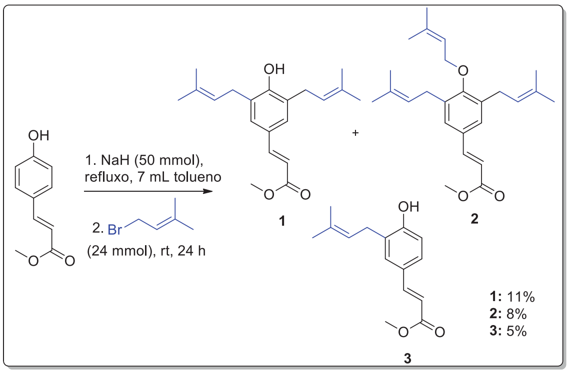


**Figura 1.** Artepillin C.

InitiallyThe studies for obtaining artepillin C via synthesis were initially carried out using the methodology described in the literature (**Scheme 1**), which was not reproducible.[3] In this way, some reaction conditions were changed, now employing the methodology described for phenol prenylation.[4] In this method, during the anion formation stage, the reaction remained at reflux for 30 minutes, which increased the prenylation rate. In addition, a stoichiometry different from that used in the literature was used (**Scheme 2**). Thus, in addition to mono and di-prenylated products, as described in the literature, a third tri-prenylated product was also obtained, which was not found in the literature. Therefore, due to the formation of this third product, the yield obtained for the product of interest, artepillin C, was extremely low.



**Scheme 1.** Synthesis of Artepillin C according to literature.



**Scheme 2.** Synthesis of Artepillin C according to the new methodology.

References
[1] Barth, O.M., Freitas, A.S., Matsuda, A.H., Muradian, L.B.A. *Grana*, **2013**, 52, 129-135.
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[4] Wang, TY, Wu, J., Xia, P. *Synthetic Communications*. **2006**, 36, 2685–2698.

## Agradecimentos/Acknowledgments

The authors acknowledge São Paulo Research Foundation (*FAPESP*) for research financial support (proc. 2019/11700-0 and 2017/04138-8), and thank National Science and Technological Development Council (CNPq) for the granting of scientific initiation scholarships.

**Área: ORG**

# Substrate- and PTSA-controlled regiodivergent synthesis of 3,4- and 4,5- *N*-methyl pyrazoles

**Julia Caroline Mansano Willig (PG),[1] Julia Poletto (PG),[1]* Karlos Eduardo Pianoski (PG),[1] Michael Jackson Vieira da Silva (PQ),[1] Fernanda Andreia Rosa (PQ).[1]**

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Palavras Chave: *β-enamino diketone, 4-acyl pyrrole-2,3-dione, N-methyl pyrazole*

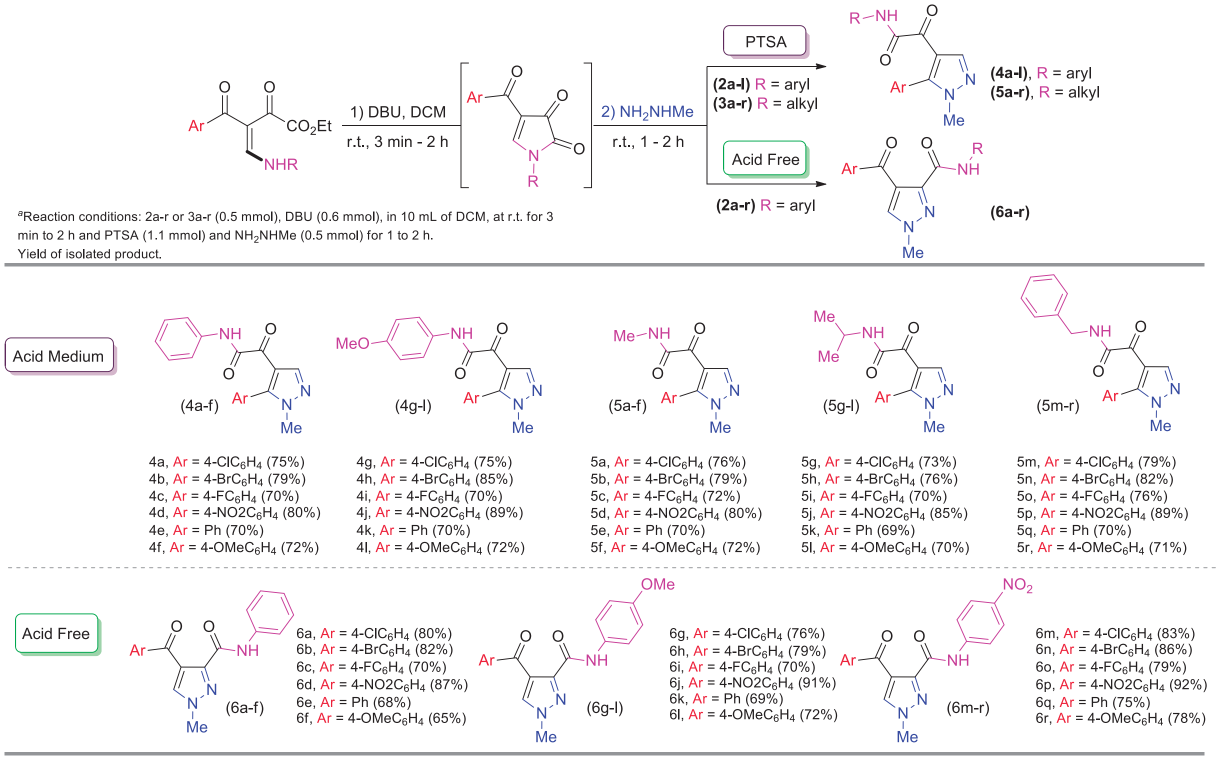
## Highlights

Simple and efficient methodologies were developed for the regiodivergent synthesis of 3,4- and 4,5-disubstituted *N*-methyl pyrazoles from 4-acyl pyrrole-2,3-diones and methylhydrazine.

## Resumo/Abstract

Considering the potential of the *N*-methyl pyrazole nucleus as a pharmacophoric subunit in bioactive molecules,[1] we synthesized in a highly regioselective way and good yields two series of 3,4- and 4,5-disubstituted *N*-methyl pyrazoles from *β*-enamino diketones and methylhydrazine. The regiochemistry of the reaction was controlled from the cyclic derivative 4-acyl pyrrole-2,3-dione structure, generated *in situ*, and the addition or absence of acid in the reaction medium.

**Scheme 1.** Synthesis of *N*-methyl pyrazoles from the reaction of 4-acyl pyrrole-2,3-diones and methylhydrazine[a]



[a]Reaction conditions: 2a-r or 3a-r (0.5 mmol), DBU (0.6 mmol), in 10 mL of DCM, at r.t. for 3 min to 2 h and PTSA (1.1 mmol) and $NH_2NHMe$ (0.5 mmol) for 1 to 2 h. Yield of isolated product.

(1) (a) Hanan, E. J., van Abbema, A.; Barrett, K.; Blair, W. S.; Blaney, J.; Eigenbrot, C.; Flynn, S.; Gibbons, P.; Hurley, C. A.; Kenny, J. R.; Kulagowski, J.; Lee, L.; Magnuson, S. R.; Morris, C.; Murray, J.; Pastor, R. M.; Rawson, T.; Siu, M.; Ultsch, M.; Zhou, A.; Sampath, D.; Lyssikatos, J. P. *J. Med. Chem.* **2012**, 55, 10090-10107. (b) Radi, S.; Tighadouini, S.; Feron, O.; Riant, O.; Bouakka, M.; Benabbes, R.; Mabkhot, Y. N. *Molecules* **2015**, 20, 20186-20194. (c) Wu, Z.; Hu, D.; Kuang, J.; Cai, H.; Wu, S.; Xue, W. *Molecules* **2012**, 17, 14205-14218.

## Agradecimentos/Acknowledgments

We thank the CNPq and CAPES for the financial support in the form of fellowships.

**Área: ORG**

# Synthesis and Biological Evaluated of New Coumarin-Benzothiazoles Hybrids as Multifunctional compounds against Alzheimer's Disease

**Adriane A. P. Amaral (PQ),[1] Bernardo F. Rezende (PG),[2] Fernanda P. Pauli (PQ),[1] Larissa A. P. Ferreira (PG),[3] Nathalia F. Nadur (PG),[3] Vitor F. Ferreira (PQ),[2] Arthur E. Kümmerle (PQ),[3] Fernando C. da Silva (PQ),[1] Luana S. M. Forezi (PQ).[1]***

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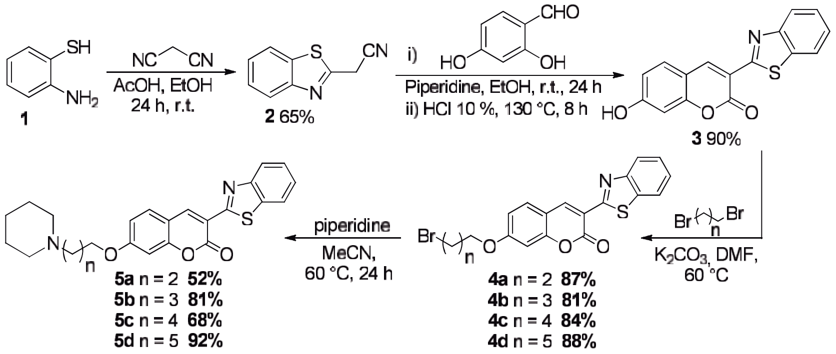
Keywords: *Biomarker, Theranostic, Acetylcholinesterase, Butyrylcholinesterase*

## Highlights

Nine coumarin-benzothiazole hybrids were obtained with satisfactory yields. These substances were biologically evaluated for their ability to inhibit enzymes involved in AD (AChE and BChE). One of the compounds was more active against the inhibition of AChE ($IC_{50}$ = 0.0073 μM) and another was the most active against BChE inhibition ($IC_{50}$ = 2.497 μM).

## Abstract

Neurodegenerative diseases are the major causes of dementia in the world, with Alzheimer's disease (AD) being considered the most common form of dementia.[1] The knowledge of AD disorders has led to the development of new drugs such as cholinesterase inhibitors and peptide aggregation inhibitors Aβ.[2] Another growing approach to AD is compounded capable of acting in the diagnosis and treatment of the disease (theranostic compounds), with the aim of optimizing therapeutic efficacy. In this context, coumarins have been described as an excellent prototype due to their interesting photophysical properties and their great applicability in studies against AD.[3] On the other hand, a coumarin-benzothiazole hybrid was used as fluorescent probes for the detection of Aβ aggregates, which are one of the biomarkers of AD.[4] Thus, the present work reports the synthesis of new coumarin-benzothiazole hybrids as multifunctional compounds against AD (Scheme 1).



**Scheme 1.** Synthesis of coumarin-benzothiazole hybrids **5a-d**.

In addition, molecular modeling studies were carried out in order to evaluate the mode of interaction of the compounds in the AChE enzyme. The results indicate that all **5a-d** substances interacted with the AChE catalytic site (PAS or CAS). Finally, all compounds obtained were evaluated for inhibition of the enzymatic activity of two enzymes involved in AD, acetylcholinesterase and butyrylcholinesterase. The results indicate **5a** ($IC_{50}$ = 0.0073 μM) as the most active against AChE inhibition and **5b** ($IC_{50}$ = 2.497 μM) as the most active against BChE inhibition.

In summary, nine substances were obtained, four of these unpublished, all with satisfactory yields. Based on the promising results, further studies will be carried out.

**References:** [1] MISHRA, P. *et al.*, Bioorganic & Medicinal Chemistry, **2019**, 27, 895-930 / [2] FALCO, A. *et al.*, Química Nova, **2016**, 39, 63-80 / [3] PEREIRA, T. M. *et al.*, Current Topics in Medicinal Chemistry, **2018**, 18, 124-148 / [4] RAJASEKHAR, K. et al., Scientific Reports, **2016**, 6,1-10.

## Acknowledgments

UFF, Labsoa, CAPES, CNPq, FAPERJ and FIOCRUZ.

**Área: ORG** **Nº de Inscrição: 935**

# Synthesis and Biological Prospection of Naphthoquinone Hybrids Containing 1,2,3-Triazolic Linked as Potential Anticancer Drugs

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acacio.farma@gmail.com

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keyword: Naphthoquinone, Menadione, 1,2,3-Triazole, Cancer.

## Highlights

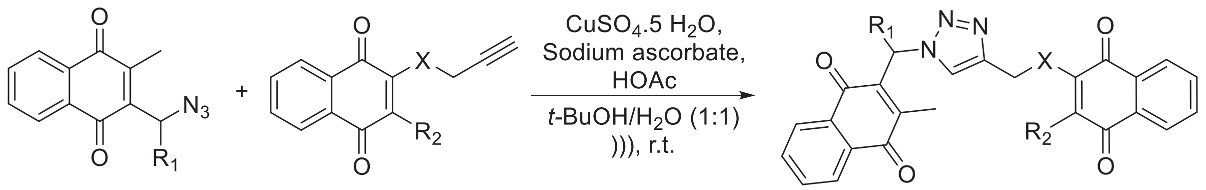
It is a search for new hybrids with a good relationship between structure and activity. Thus, it is intended to investigate how the junction of such systems may influence the anticancer activity.

## Abstract

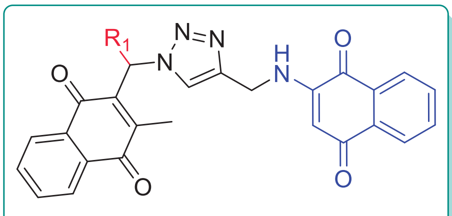
With approximately 9.6 million deaths in 2018, cancer is the second leading cause of death globally and in addition to the health impact, the economic impact of cancer is great, with an estimated cost of US$ 1.16 trillion in 2010.[1] The search for new drugs capable of reducing or eliminating the morbidity, mortality and suffering rates of patients affected by cancer has been one of the main focuses of organic synthesis. In this context, the literature has presented naphthoquinone and triazole derivatives, independently, as promising scaffolds for new antineoplastic drugs.[2,3]

Based on this, the objective of this work is to search for new naphthoquinone hybrids connected by a 1,2,3-triazole spacer, looking for a good relation between the structure and the activity, and possibly even acting as multitarget in biological systems. Thus, we intend to investigate how the combination of such systems - naphthoquinone and 1,2,3-triazole - may have an influence on the activity of these new molecules.

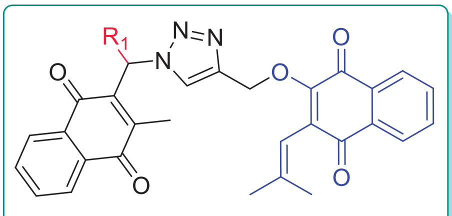
For the synthesis of the news naphthoquinone hybrids **3**, the azido-menadiones **1** were reacted with propargylated-naphthoquinones **2** in the presence of a catalytic amount of copper sulfate pentahydrate and sodium ascorbate under ultrasound irradiation.[4] The final products of type **3a-r** were obtained satisfactorily and with yields ranging from 52-63%. Their structures were confirmed using different physical methods of analysis such as 1D and 2D NMR, IV and HRMS. Currently, the obtained products are being evaluated for their antitumor activity. In parallel, the synthesis of new substances derived from *O*-propargyl-lawsone and *O*-propargyl-isolapachol is underway.



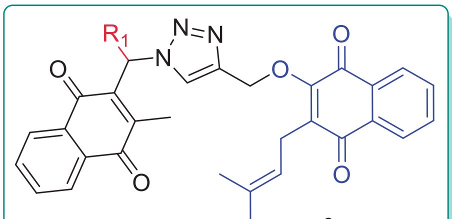
**1** **2** **3**



**3a-f**
**(43 - 62%)**



**3g-l**
**(52 - 70%)**



**3m-r**
**(44 - 67%)**

[1] Cancer; World Health Organization: Geneva, **2018**; https://www.who.int/news-room/fact-sheets/detail/cancer. Accessed in 30/01/2020.
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## Acknowledgments

CAPES, CNPq, FAPERJ and FIOCRUZ.

**Área: ORG**

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

# Synthesis, Biological Evaluation, and Molecular Modeling Studies of Novel 1,2,3-Triazole-linked Menadione-Furan Derivatives as Potent P2X7R Inhibitors

**Juliana P. S. dos Santos (PG),[1] Ruan Carlos B. Ribeiro (PQ),[2] Juliana V. Faria (PG),[3,4] Murilo L. Bello (PQ),[5] Carolina G. S. Lima (PQ),[2] Fernanda P. Pauli (PQ),[2] Amanda A. Borges (PG),[2] David R. Pinho (IC),[2] Matheus G. Moraes (PG),[2] Luana S. M. Forezi (PQ),[2] Vitor F. Ferreira (PQ),[2] Robson X. Faria (PQ),[3,4*] Fernando de C. da Silva,[2*]**

**cgslima@id.uff.br; fcsilva@id.uff.br; salvador@ioc.fiocruz.br**

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Palavras Chave: *P2X7R, furan, biomass, menadione, 1,2,3-triazole.*

## Highlights

- Lignocellulose-derived furfural was used in the synthesis of P2X7R inhibitors
- Docking studies revealed the occurrence of hydrophobic interactions and pi-stacking between different sites the molecules and the P2X7 receptor.

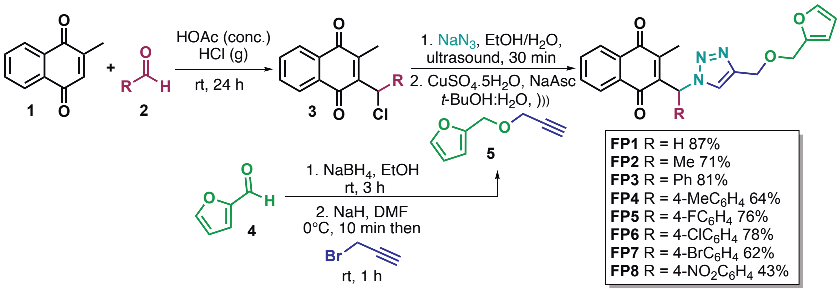
## Resumo/Abstract

The P2X7 receptor (P2X7R) is an ion channel that promotes the passage of ions through the membrane via brief stimulation activated by ATP, but in pathological processes such as inflammation, leads to cytokine release or even cell death.[1] In this sense, the search for new inhibitors for this receptor has been attracting a great deal of attention in recent years.[2] Considering the booming of biomass upgrading reactions in recent years and in continuance of our efforts on the synthesis of bioactive molecules containing the 1,2,3-triazole ring, in the present work we aimed to synthesize triazole-linked menadione-furan derivatives and investigate whether they present P2X7R inhibitory activity.[3] The synthesis of compounds FP1-8 was conducted via the reaction of menadione (**1**) with aldehydes (**2**) to furnish **3**, which underwent a one-pot reaction with sodium azide followed by CuAAC with alkyne **5**. Alkynes **5**, in turn, were obtained from the reduction of furfural (**4**) followed by alkylation with propargyl bromide. After initial tests, the most promising compounds had their inhibitory activity evaluated in mice peritoneal macrophage cells, and displayed $IC_{50}$ values lower than that of the P2X7R inhibitor BBG (Table 1). Molecular docking studies indicated that the active compounds bind to an allosteric site on P2X7R.

**Table 1.** Inhibitory activity of the FP series in mice peritoneal macrophage cells.

| Compound | $IC_{50}$ mice P2X7R (μM) |
|---|---|
| BBG* | 15.23 |
| A-740003* | 0.897 |
| FP1 | 10.94 |
| FP3 | 13.13 |
| FP6 | 5.52 |
| FP8 | 17.96 |

* Known P2X7R antagonists used as control.



**Scheme 1.** Synthetic route toward novel 1,2,3-triazole-linked menadione-furan derivatives.

[1] I.P. Chessell, J.P. Hatcher, C. Bountra, A.D. Michel, J.P. Hughes, P. Green, J. Egerton, M. Murfin, J. Richardson, W.L. Peck, *Pain* **2005**, 114, 386–396. [2] D.T.G. Gonzaga, L.B.G. Ferreira, T.E.M.C. Moreira, N.L. von Ranke, P.A.F. Pacheco, A.P.S. Simões, F. C. Silva. *Eur. J. Med. Chem.* **2017**, 139, 698–717. [3] L.S.M. Forezi, C.G.S. Lima, A.A.P. Amaral, P.G. Ferreira, M.C.B.V. Souza, A.C. Cunha, F.C. Silva, V.F. Ferreira, *Chem. Rec.* **2021**, 21, 2782-2807.

## Agradecimentos/Acknowledgments

UFF, FAPERJ, CAPES, CNPq.

**Área: ORG** **Nº de Inscrição: 00315**

# Synthesis, herbicidal activity and kinetic studies of new fatty acid derivatives

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[2] *Grupo de Catálise e Cinética, Departamento de Química, Universidade Federal do Paraná, Curitiba, PR, Brazil.*
[3] *Laboratório de RMN, Departamento de Química, Universidade Federal do Paraná, Curitiba, PR, Brazil.*
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Keywords: *Herbicides, 2,4-D, fatty acids.*

## Highlights

- Synthesis of new fatty acid amides and esters derivatives from renewable resources.
- Herbicide activity of all new compounds showed similar or superior efficacy to the reference's herbicides.
- Modulation of physicochemical properties as solubility, volatility and surface-active properties, from renewable resources as vegetable oils.

## Abstract

Increasing the production of food with environmental responsibility is a challenge for the research. Annually around 2.5 million tons of agrochemicals are used worldwide.[1] The herbicide 2,4-dichloro phenoxy acetic acid, or 2,4-D is the most commonly used herbicide in the world, but it exhibits high persistency in soils, and on the surface and groundwater effluents. The high hydro solubility of 2,4-D causes its mobility in the soil, polluting underground water resources through lixiviation.[2] The most significant contribution of fatty acid insertion on the structure of traditional herbicides in recent literature, is based on physicochemical properties modifications, mainly volatility, solubility and surface-active properties, which contribute to the increase of the contact surface between the leaves and active ingredient and contribute to enhancement of adsorption of the herbicide into the plant.[3] Besides, the production of bio-ionic liquids from triglycerides presents in vegetable oils pointed to the renewable source of chemicals to synthesis of actives and environmental-friendly compounds applied in agricultural practices.[4] In this work, the incorporation of fatty alkyl chain was explored by covalent bond construction in ester or amide linkage from fatty acid alcohols or amines, respectively. In addition, the herbicidal activity of the new compounds was evaluated towards growth inhibition of mono and dicotyledonous seeds. Moreover, the influence of these modifications in the reactivity/stability of the new target compounds were investigated by UV-Vis and $^1$H NMR experiments.

The synthesis of fatty acid esters derivatives was realized by esterification of carboxilic acid 2,4-D with palmitic (C16:0), stearic (C18:0) or oleic (C18:1) fatty acid alcohols, resulting in quantitative yields. The synthesis of fatty acid amides was realized from fatty acid amines analogues, in yields 72-89%. The pre-emergent herbicidal activities of compounds were evaluated against seeds of onion (*Allium cepa,* 'Anasac Jardin') and lettuce (*Lactuca sativa*,'Vilmorin Jardin') as mono and dicotyledonous models, respectively. All tested compounds had growth inhibition activity against *A. cepa* and *L. sativa* seeds. For dicotyledonous model, all new derivatives fatty esters and amides presented the same efficiency that 2,4-D. For monocotyledonous template, a lower response in germination inhibition was observed to the 2,4-D. In this case, the esters and amides derived from palmitic and stearic fatty alkyl chains shown superior activities to the original herbicide. The influence of fatty ester and amides in the chemical behavior of 2,4-D hydrolysis were investigated under acid or basic conditions by $^1$H NMR and UV-vis experiments. From these studies, it was possible to observe that the incorporation of fatty acid chains from ester or amide linkage doesn't result in significant changes in the chemical behavior related to hydrolysis and decomposition of the target compounds. Moreover, those compounds showed that could added properties to new fatty herbicides compounds, as solubility, volatility and surface-active properties, from renewable resources as vegetable oils, in substitution to mineral oils used in commercial formulations.

## Acknowledgments

CNPq, CAPES and Fundação Araucária, PhosAgro/UNESCO/IUPAC, L'Oréal-UNESCO-ABC, INCT em Nanomateriais de Carbono.

***References:*** [1]Ayoub, H. A. et al., *J. Agric. Food Chem.*,**2018**, *66*, 5491; [2]Liu, M. et. al., *J. Environ. Eng.* **2014**,*140*, 4014026; [3]Niemczak, M. et. al., *ChemPlusChem.*, **2018**, *83*, 529; [4] Pernak, J. et. al., *RSC Adv.*, **2018**, *8*, 28676.

## Area: ORG

# SYNTHESIS, NMR CHARACTERIZATION AND ANTIOXIDANTS EVALUATION DERIVED FROM FURANCHALCONES

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**eduardo.protachevicz@yahoo.com**

*[1]Chemistry Department UEPG; [2]Chemistry Department UEM.*

*Keywords: Organic synthesis, Furanchalcones, Antioxidant activity.*

## Highlights

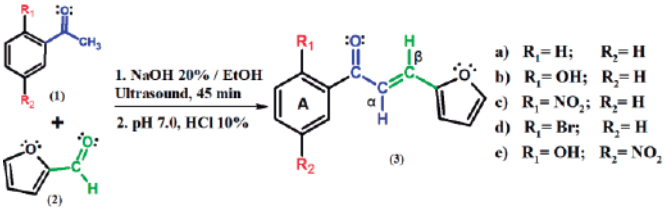
We report in this study the synthesis of five furanchalcones. Spectroscopic characterization by 1D/2D NMR. The evaluation of the antioxidant activity was carried out using two different methodologies.

## Abstract

The use of natural organic substances for disease treatments is common and of great importance from antiquity to the present day. A group of compounds analogous to chalcones and which is still little studied are furanchalcones, in which one of the aromatic rings is replaced by a furan group. The use of natural organic substances for disease treatments is common and of great importance from antiquity to the present day.

Furanchalcone (3), analogous to chalcone, has expanded its study in the face of biological activities. Furanchalcones (3a to 3e) were synthesized from a 2-Furaldehyde (1) and an Acetophenone with "R" substituents (2)[1]. Claisen Schmidt using with ultrasound assisted base is applied[2] (Figure 1).

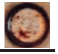
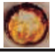
Figure 1 – General reactional conditions.



NMR spectra ($^1H$, $^{13}C$, DEPT-90, HMBC and HMQC) were acquired using deuterated chloroform ($CDCl_3$) as solvent.

The reactions occurred effectively with good yields (Table 01) and good purity and can be proven by NMR characterization[3], the spectra were evaluated and the attributions performed in a convincing way.

Table 1- Properties and yields of the products.

| | | | | |
|---|---|---|---|---|
| **3a** | 3-(2-Furano)-1-phenyl-prop-2-en-1-one, | mp<br>- | 83% |  |
| **3b** | 3-(2-furan)-1-(2-hydroxyphenyl)-2-propen-1-one | mp<br>104-105° C | 88% |  |
| **3c** | 3-(2-furan)-1-(2-nitrophenyl)-2-propen-1-one | mp<br>143-144° C | 81% |  |
| **3d** | 3-(2-furan)-1-(2-bromophenyl)-2-propen-1-one | mp<br>- | 74% |  |
| **3e** | 3-(2-furan)-1-(2-hydroxy-5-nitrophenyl)-2-propen-1-one | mp<br>132-134° C | 78% |  |

The antioxidant activity performed the DPPH and reduction of the phosphomolybdenum complex methods. The synthetic compounds were compared with the Quercetin pattern at different concentrations, obtaining $IC_{50}$ values.

Table 2 - Results $IC_{50}$ DPPH method.

| Sample | $IC_{50}$ ($mmol.L^{-1}$) |
|---|---|
| Quercetin | 3.31 |
| 3a | 35.44 |
| 3b | 28.85 |
| 3c | 20.48 |
| 3d | 32.21 |
| 3e | 16.06 |

Table 2 shows the results of the antioxidant evaluation by the DPPH methodology of the synthesis products compared with the Quercetin standard. The results show the compounds with promising $IC_{50}$ values, especially the compounds with hydroxyl and nitro substituent[4].

Table 3 - Results $IC_{50}$ reduction of the phosphomolybdenum complex method

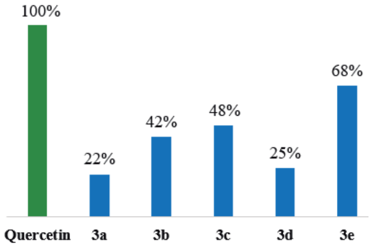


Table 3 shows the results of the antioxidant evaluation by the phosphomolbidnium complex reduction method, and the Quercetin pattern is considered 100% inhibition. It is evaluated that the closer the inhibition of Quercetin, the better the antioxidant power. The results show the compounds with hydroxyl and nitro substituents with promising antioxidant inhibition[4].

The reactions were effective and can be proven by NMR spectroscopy with good yields. In the evaluation of antioxidant power, compounds with hydroxyl and nitro substituents obtained better results compared to the Quercetin pattern, which may lead to a deepening of molecules with the substitutes mentioned in different biological evaluations.

## Acknowledgments

We thank the Prof. Dr. Adilson L. Chinelatto and Prof. Dr. André M. Brinatti for the technical facilities.

## References

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**Área: ORG**

# Synthesis of 1,2,3-triazole selenides with anti-*T. cruzi* activity

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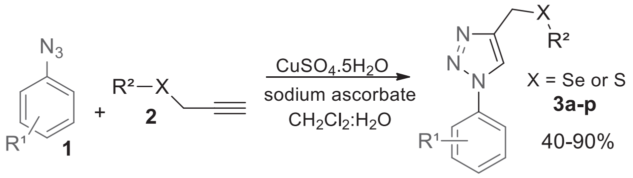
Key words: *antiprotozoan, chalcogen, heterocycle, organochalcogen.*

## Highlights

This work presents the synthesis of new 1,2,3-triazole selenides and their evaluation as a potential drug for Chagas disease.

## Abstract

Chagas disease (CD) is classified by the UN as a neglected tropical disease, caused by the protozoan *Trypanosoma cruzi* and causes more than 50,000 deaths a year. There are no major investments to improve the current treatment, which are only two medicaments available in the clinic since the 1940s.[1] Thus, research involving more efficient drugs for the treatment of CD is relevant to public health. In this work, we used a hybridization strategy combining organoselenium and 1,2,3-triazoles to design new 1,2,3-triazole selenides and evaluate their biological potential against T. cruzi. These two classes of compounds showed several biological activities such as antitumor, bactericidal, and antiprotozoal[2] and the combination of these two scaffolds appears as an alternative in the discovery of new drugs for the treatment of CD. The synthesis of the 1,2,3-triazole selenides (**3a-p**), was achieved by a 1,3-dipolar addition cycle with the copper and ascorbate catalytic system - as described in the scheme 1 - with aromatic azides **1** and terminal alkynes **2**, previously prepared. [2,3] A series of 16 new compounds were obtained with yields ranging from 40 to 90% and confirmed by $^1$H-NMR.



**Scheme 1.** Synthesis of new 1,2,3-triazole selenides

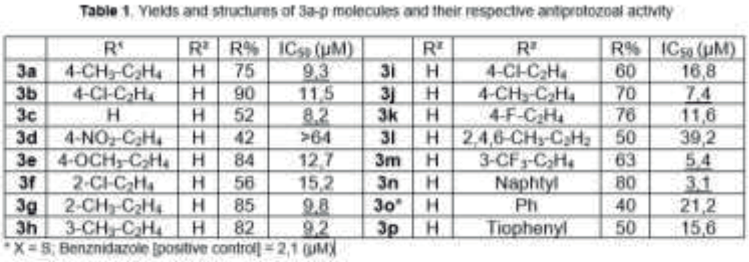


**Table 1.** Yields and structures of 3a-p molecules and their respective antiprotozoal activity

| | R¹ | R² | R% | $IC_{50}$ (μM) | | R² | R¹ | R% | $IC_{50}$ (μM) |
|---|---|---|---|---|---|---|---|---|---|
| **3a** | 4-$CH_3$-$C_2H_4$ | H | 75 | 9,3 | **3i** | H | 4-Cl-$C_2H_4$ | 60 | 16,8 |
| **3b** | 4-Cl-$C_2H_4$ | H | 90 | 11,5 | **3j** | H | 4-$CH_3$-$C_2H_4$ | 70 | 7,4 |
| **3c** | H | H | 52 | 8,2 | **3k** | H | 4-F-$C_2H_4$ | 76 | 11,6 |
| **3d** | 4-$NO_2$-$C_2H_4$ | H | 42 | >64 | **3l** | H | 2,4,6-$CH_3$-$C_2H_2$ | 50 | 39,2 |
| **3e** | 4-$OCH_3$-$C_2H_4$ | H | 84 | 12,7 | **3m** | H | 3-$CF_3$-$C_2H_4$ | 63 | 5,4 |
| **3f** | 2-Cl-$C_2H_4$ | H | 56 | 15,2 | **3n** | H | Naphtyl | 80 | 3,1 |
| **3g** | 2-$CH_3$-$C_2H_4$ | H | 85 | 9,8 | **3o*** | H | Ph | 40 | 21,2 |
| **3h** | 3-$CH_3$-$C_2H_4$ | H | 82 | 9,2 | **3p** | H | Tiophenyl | 50 | 15,6 |

* X = S; Benznidazole [positive control] = 2,1 (μM)

The ability of these compounds to kill the protozoan *T. cruzi* was demonstrated through $IC_{50}$ values described in Table 1. Seven of them were considered active, with derivatives **3m** and **3n** being the best in the series, considered potential candidates against CD. Since the effectiveness of a drug is related to its ability to penetrate biological barriers to reach the target site and induce its activity, the oral bioavailability of these compounds was predicted by Swissadme Web Tool and a moderate outcome was predicted for all compounds. In addition, other tests are being finalized, mainly to determine the mode of action of **3m-n**, and cytotoxicity results showed high selectivity of these hybrids. In conclusion, the series of new hybrid molecules with triazoles and chalcogen moieties fractions were synthesized and presented excellent results as possible new drugs against CD.

## Acknowledgments

CNPQ, CAPES, FAPERJ, FAPESP [1] LIDANI, Kárita In Public Health. 2019 [2] ZHAO, J. W.;Steroids, 2010, [3] JANA S. Org. Let., 2019 [4] CHENNA, Bala C.; JOC, 2020.

**Área:** QO

# Synthesis of amphetamine compounds through batch and continuous flow conditions for certified reference materials production

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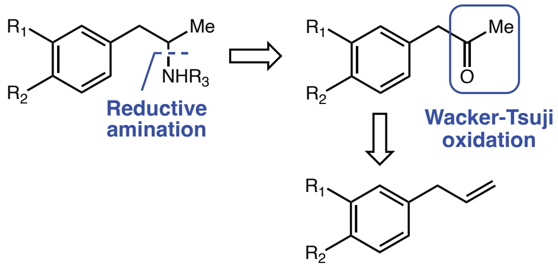
Keyword: *public security, organic synthesis, Wacker-Tsuji oxidation, reductive amination, amphetamine*

## Highlights

Identification of drugs in seized samples is performed by comparing chromatographic and MS analyzes with certified reference materials (CRM). Considering the importance of the availability of that for Public Safety and that ecstasy is one of the most consumed drugs in Brazil, herein we intend to develop an efficient synthetic strategy for amphetamine compounds aiming at the production of CRM.

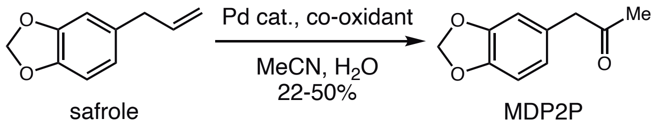
## Abstract

The synthetic strategy to obtain the target molecules consists of a reductive amination and a Wacker-Tsuji oxidation from the appropriate olefin (Scheme 1). We intend to study this route under batch and continuous flow conditions for large scale production.



**Scheme 1.** Synthetic strategy for the targets

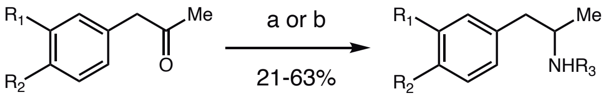
We started this work with the Wacker-Tsuji oxidation studies under batch conditions.[1,2] Safrole was submitted to the oxidation under different Pd catalysts, water and co-oxidant providing the corresponding ketone in 22-50% yield (Scheme 2).



**Scheme 2.** Wacker-Tsuji oxidation

The formation of the anti-Markovnikov product and the addition products of other nucleophiles were also observed. The optimization studies of this reaction in batch and continuous flow conditions are under investigation.

Simultaneously, the reductive amination of the MDP2P and 1-(4-methoxyphenyl)propan-2-one was also carried out.[3] Employing ammonium formate or methylamine and different reducing agents, such as $NaBH_4$ or $NaBH_3CN$ we could observe the formation of desired amines in 21-63% yields (Scheme 3).



a. $NH_4CO_2H$, $NaBH_4$ or $NaBH_3CN$, HOAc, MeOH, MS 4Å, rt, overnight; b. $CH_3NH_2$, $NaBH_3CN$, HOAc, MeOH, MS 4Å, rt, overnight.

**Scheme 3.** Reductive amination

During the studies of the reductive amination reactions, we observed as the main by-product the alcohols derived from the reduction of the starting ketones. Optimization studies of this reaction are ongoing, and our perspectives are the studies under continuous flow conditions.

## Acknowledgments

The authors would like to thank CAPES for financial support.

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**Área: ORG**

# Synthesis of Large Stokes Shift 2,6-Sulphur-Disubstituted BODIPYs

**Luana A. Machado (PG),[1*] Marcos C. de Souza (PQ),[2] Marcos M. Gouvêa (PQ),[3] Flávia F. C. Marques (PQ),[3] Eufrânio N. da Silva Júnior (PQ),[4] Leandro F. Pedrosa (PQ).[5]**

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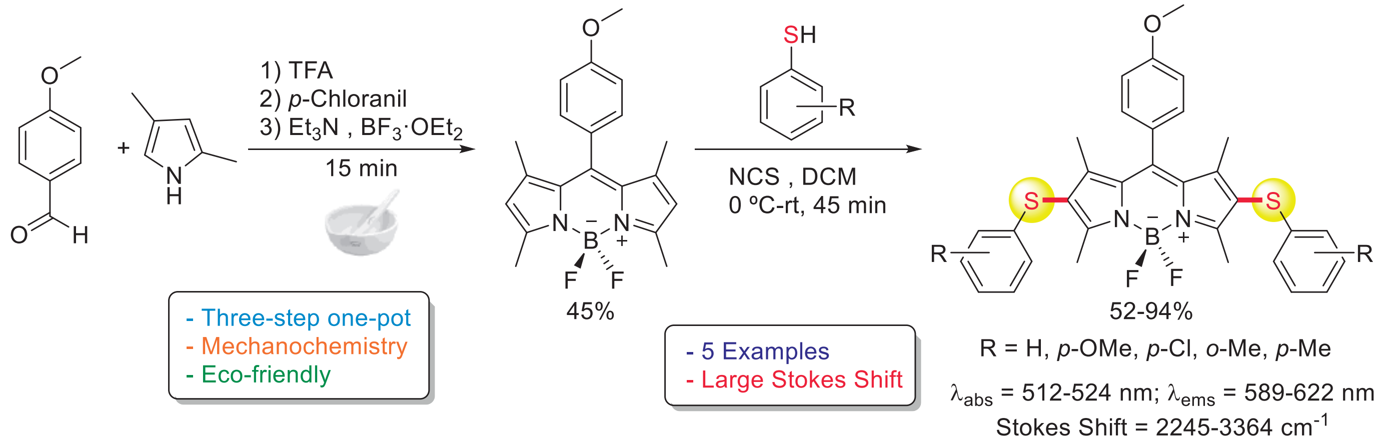
Palavras Chave: *BODIPY, Boron-dipyrromethene, Fluorophores, Thioarylation.*

## Highlights

2,6-thioaryl-BODIPY were synthesized via selective aromatic electrophilic substitution from thiophenols. Photophysical properties showed unusually large Stokes shifts for BODIPY fluorophores.

## Resumo/Abstract

Compounds containing chalcogen elements have wide applications in many areas of science. Importantly, they can act as redox centers and modulate the activity of biomolecules. In recent years, our research group have focused on the preparation of fluorescent compounds boron-dipyrromethene (BODIPY) derivatives. This family of compounds has been extensively employed in many research fields, including chemosensors, photosensitizers and OLEDs. The functionalization of BODIPYs with chalcogen groups has multiple motivations, such as the enhancement of their physicochemical properties. Synthetic methods for the insertion of sulphur atoms into the basic architecture of BODIPYs have been described, however, many of them require harsh reaction conditions. Therefore, we designed new 2,6-sulphur-disubstituted BODIPYs based on thiophenol derivatives (**Scheme 1**). The straightforward and selective functionalization of the BODIPY by thiophenol chloride prepared *in situ* from *N*-chlorosuccinimide and commercially available thiophenols allows for easy modification and addition of targeting moieties. Analysis of the photophysical properties shows that 2,6-thioaryl-BODIPY derivatives display large Stokes shifts, which can be advantageous for optical imaging.



**Scheme 1.** Synthesis of 2,6-thioaryl-BODIPY fluorophores.

## Agradecimentos/Acknowledgments

CAPES, CNPq, FAPERJ, FAPEMIG, UFF, UFMG.

**Área: ORG**

# Synthesis of Molecular Hybrids Containing Enuloside and Z-enyne with Potential Antitumoral Activity

**Arielly P. S. Silva (IC),[1] Cláudia L. A. A. Santos (PG),[2*] Evellyn T. V. Gomes (IC),[1] Wilson P. da Silva (PG),[2] Bárbara G. S. de Oliveira (PG),[2] Filipe M. C. Santos (PG),[2] Jonh A. M. Santos (PQ),[1] Paulo H. Menezes (PQ)[2]**

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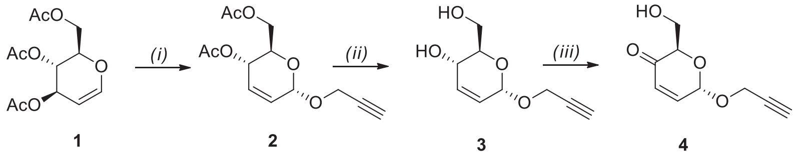
Palavras Chave: Carbohydrates, Enynes, Molecular hybrids.

## Highlights

An efficient approach for the synthesis of molecular hybrids containing *Z*-enynes and carbohydrate derivatives is described. The products were obtained in good to moderate yields in a stereoselective way.

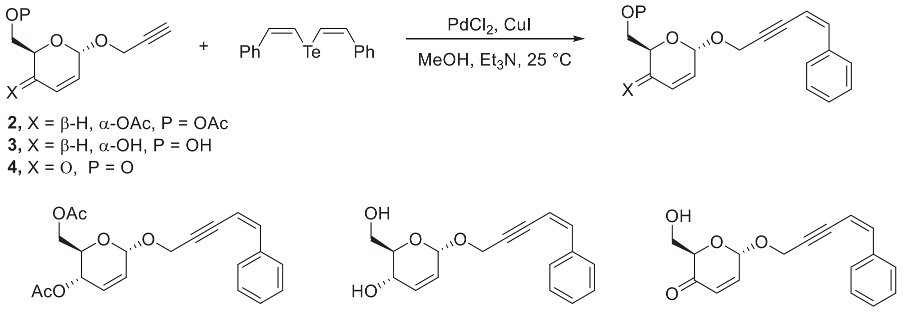
## Abstract

Molecular hybridization is a modern strategy employed in Medicinal Chemistry based on the combination of pharmacophoric fragments of different bioactive substances to produce a hybrid compound with improved affinity and/or efficacy when compared to the original drugs.[1] In this work, the combination of two pharmacophoric groups were envisioned in order to evaluate the antitumoral activity of the obtained hybrid. Thus, enulosides (enone-containing sugars)[2] and derivatives were prepared according to Scheme 1.



**Scheme 1:** *Reagents and conditions: (i) propargyl alcohol, TsOH (20 mol%), MeCN, 25 °C, 5 min (94%); (ii) $K_2CO_3$, MeOH:$H_2O$, 25°C, 5 min (98%); (iii) $MnO_2$, $CH_2Cl_2$, 25 °C, 2.5 h (89%).*

The required *Z*-bis-vinyl telluride was prepared following the literature procedure[3] and then coupled to compounds **2-4** to yield the desired hybrid compounds in good to moderate yields in a very stereoselective way (Scheme 2).



**2,** X = β-H, α-OAc, P = OAc
**3,** X = β-H, α-OH, P = OH
**4,** X = O, P = O

**Scheme 2:** Synthesis of hybrids.

In summary, we have shown an efficient method for the synthesis of hybrid compounds in a stereoselective way. The antitumoral evaluation of the synthesized compounds is currently in progress in our laboratory.

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## Acknowledgments

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**Área: ORG**

# Synthesis of new 2,5-bis(aryl(chalcogenophen-2-yl)methyl)thiophene derivatives with potencial fluorescent properties.

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Palavras Chave: *Chalcogenophenes, Synthesis, Photophysical*

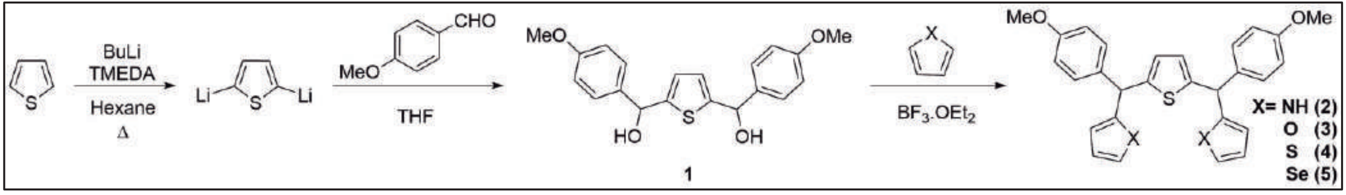
## Highlights

New class of 2,5-bis(aryl(chalcogenophen-2-yl)methyl)thiophene were synthesized.

## Resumo/Abstract

We report the synthesis of 2,5-bis(aryl(chalcogenophen-2-yl)methyl)thiophene, valuable building blocks used in the synthesis of 21,23-core-modified porphyrins.[1] The synthesis of the pyrrole substituted compounds (**2**, Figure 1) have been reported in the literature.[2] On the other hand, the chalcogen-heteroaryl substituted compounds (**3-5**, Figure 1) have scarce or no examples reported which could be assumed due the challenges associated with their synthesis. Herein, we report the synthesis and characterization of the chalcogen substituted thiophenes by a modified approach (Figure 1).

Figure 1: Synthesis of Compounds **1-5**.



The compounds were obtained by the lithiation of thiophene, followed by the reaction with the 4-methoxybenzaldehyde which resulted in the diol (**1**, Figure 1). The Lewis acid ($BF_3.OEt_2$) catalyzed reaction of the diol with the respective chalcogenophene results into compounds **3-5**. The formation of compounds was confirmed by High-Resolution Mass Spectrometry (HRMS) and characterized by 1D and 2D Nuclear Magnetic Resonance (NMR), IR and UV spectroscopies. HOMO/LUMO energies has been calculated by M062X/cc-pvdz method. Our preliminary studies showed that the compounds **2-5** have potential optical properties. The presented molecules showed fluorescence emission as depicted in figure 2 when excited in 365 nm. Selenodiol and thiophene were condensed with catalytic $BF_3OEt_2$ to give **6**. Thus, the photophysical investigation of the related compounds are being performed. Moreover, we will explore the chemistry of these compounds to understand their full potential for various applications, as coordination chemistry.

Figure 2: Samples **3**,**4**,**5** and **6** under UV light.

## Agradecimentos/Acknowledgments

CAPES, FAPEG and CNPQ

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**Área: ORG**

# Synthesis of new cyclic sulfoxonium ylides and their application in metal-carbene-mediated N-H insertion and C-H functionalization reactions.

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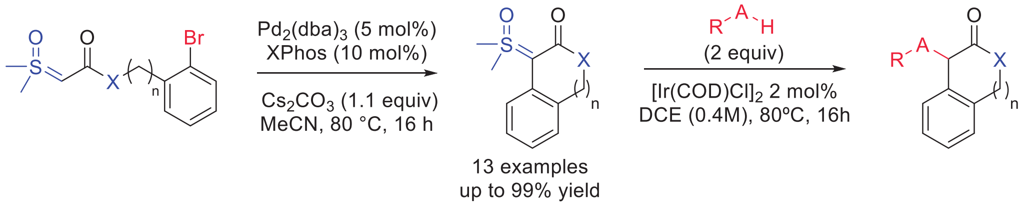
*Palavras Chave: Sulfoxonium ylides, Metal-carbene reactions, C-H functionalization, Indol functionalization*

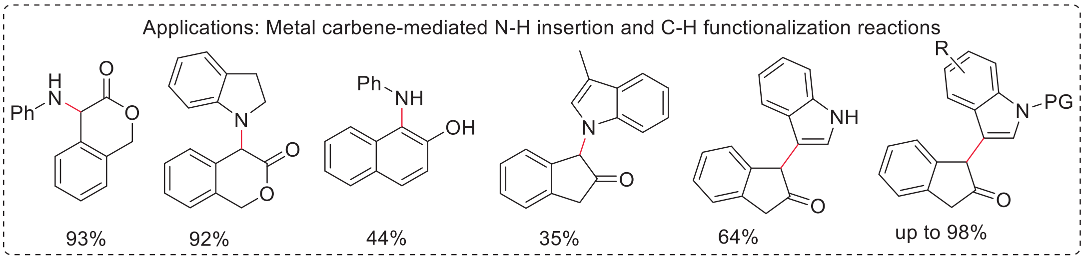
## Highlights

New examples of cyclic sulfoxonium ylides were synthesized by intramolecular Pd-catalyzed cross-coupling reactions and applied in C-H functionalization of indoles and N-H insertion reactions with anilines via metal-carbene complex formation in the presence of an iridium catalyst.

## Resumo/Abstract

In the last decade, sulfoxonium ylides have stablished as versatile α-carbonyl metal-carbene precursors in organic synthesis.[1] Owing to some of their inherent properties, such as the thermal stability, low toxicity and long shelf life, this class of compounds can be effectively applied in large scale reactions and has attracted the attention of many researchers, including those in the industry. The disclosure of efficient protocols to achieve new sulfoxonium ylides has also been a very active field and, as these new structures became accessible, some authentic new applications have emerged in the literature.[2] In this work, we present an intramolecular version of Pd-catalyzed cross-coupling reaction,[3] achieving 13 new examples of cyclic sulfoxonium ylides in good to excellent yields (up to 99% yield). The applicability of these compounds was demonstrated by metal-carbene mediated C-H functionalization of indoles and N-H insertion reactions with anilines in the presence of an iridium catalyst.





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## Agradecimentos/Acknowledgments

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Research Centre for
Greenhouse Gas Innovation

**Área: ORG**

# Synthesis of new Favipiravir-hydroxamic acid derivatives for biological activity investigation

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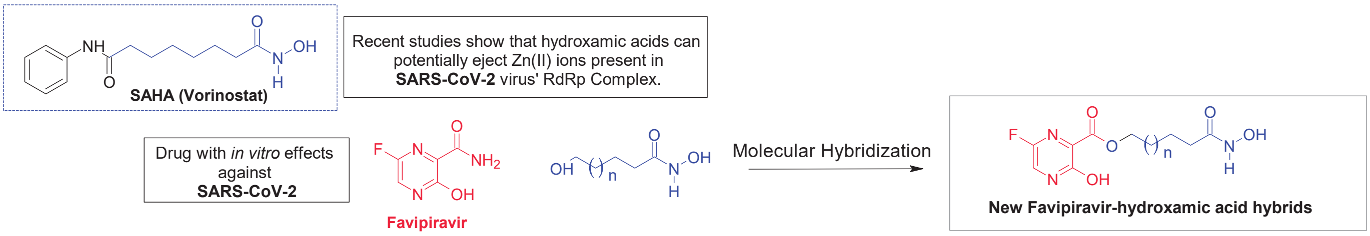
Keywords: *Favipiravir, COVID-19, Antiviral, Molecular Hybrids, Synthesis*

## Highlights

- New molecular hybrids Favipiravir-SAHA are being developed for SARS-CoV-2 treatment.
- The hybrid structure has great potential to inhibit viruses and other diseases, such as cancer.

## Abstract

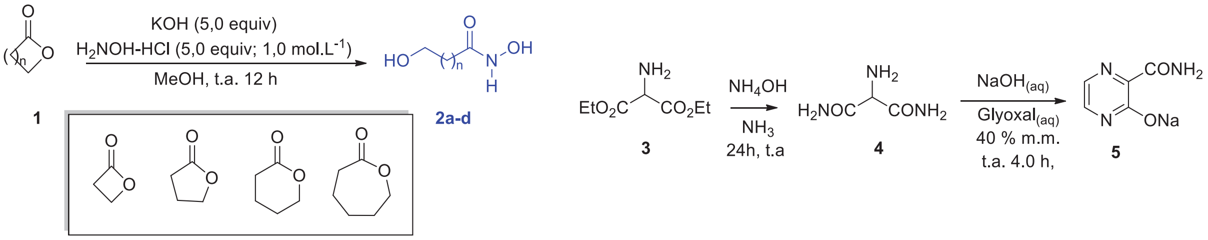
This work aims to synthesize new favipiravir-hydroxamic acid hybrid molecular compounds, still unpublished in the literature, with potential application in fighting COVID-19 and other similar diseases. The inclusion in the favipiravir moiety to the hydroxamic acid functional group, which has great affinity with Zn$^{2+}$ ions and proteases of the COVID-19 virus, could inhibit RdRp, a crucial viral RNA protein, potentially inhibiting the disease's symptoms.



Recent studies show that hydroxamic acids can potentially eject Zn(II) ions present in **SARS-CoV-2** virus' RdRp Complex.

Drug with *in vitro* effects against **SARS-CoV-2**

So far, a favipiravir precursor (3-hydroxypyrazine-2-carboxamide) has been synthesized from ethyl aminomalonate and four hydroxamic acids have been obtained from the respective lactones all in good yields. The work is currently underway to obtain favipiravir itself, as well as the new molecular hybrids, which in the future may be sent for biological antiviral tests.



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## Acknowledgments

Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – CAPES and Nuclear Magnetic Resonance Laboratory – LabRMN, UFPR.

**Área: ORG** **Nº de Inscrição: 01119**

# Synthesis of *N,N*-di-alkylnaphthoimidazoles derivatives of β-lapachone and evaluation of trypanocidal activity.

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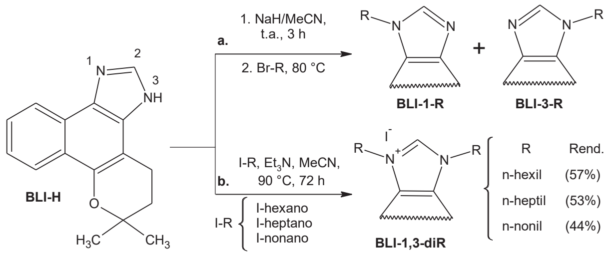
Palavras Chave: *Naphthoimidazoles, Beta-lapachone, Alkylation, Trypanosoma cruzi.*

## Highlights

In this work, we show a method for the di-alkylation of a naphthoimidazole derived from β-lapachone, and evaluate the potential of the di-alkylated products against the parasite *Trypanosoma cruzi*.

## Resumo/Abstract

Em estudos recentes, relatamos a síntese de uma série de naftoimidazóis derivados da β-lapachona, com grande potencial antichagásico, avaliado com base nos seus valores de concentração inibitória mínima ($CI_{50}$) contra a forma tripomastigota do *Tripanossoma cruzi*, parasita causador da doença de Chagas.[1] Dentre os compostos avaliados estão o BLI-H (Esquema 1) e alguns de seus derivados monoalquilados (BLI-1-R e BLI-3-R). Dos produtos alquilados, um deles, o BLI-3-hexil (R = n-$C_6H_{13}$) foi 2,8 vezes mais ativo do que o BLI-H e 3,4 vezes mais ativo do que o benznidazol (Tabela 1), fármaco indicado para o tratamento da doença de Chagas. Estudos apontam que os tratamentos disponíveis não são eficazes para todas as fases da doença, além de ocasionarem diversos efeitos colaterais. Neste trabalho mostramos a metodologia aplicada para a síntese de três derivados di-alquilados do BLI-H, além do resultado promissor de $CI_{50}$ de um deles, também avaliado contra a forma tripomastigota do parasita *Tripanossoma cruzi*.



**Esquema 1**: Síntese dos mono e dos di-alquilnaftoimidazóis.

| Composto | $CI_{50}$/ 24 h (μM) | Composto | $CI_{50}$/ 24 h (μM) |
|---|---|---|---|
| BLI-H | 89.5 (± 5.1) | BLI-1-dodecil | >500.0 |
| BLI-3-butil | 123.0 (± 2.2) | BLI-3-dodecil | 191.7 (± 10.4) |
| BLI-3-pentil | 123.7 (± 16.7) | BLI-3-AcOEtila | 375.5 (± 35.6) |
| BLI-1-hexil | 42.5 (± 7.3) | BLI-1-AcOipropila | 191.7 (± 14.6) |
| BLI-3-hexil | 31.5 (± 5.3) | BLI-3-AcOipropila | 329.4 (± 3.6) |
| BLI-1-octil | 376.1 (± 23.4) | **BLI-1,3-dihexil** | **7.9 (± 0.7)** |
| BLI-3-octil | 180.1 (± 3.2) | Benznidazol | 107.1 (±6.1) |

**Tabela 1**: Valores de concentração mínima inibitória.

Devido ao seu tautomerismo, em cada reação de alquilação do BLI-H se forma um par de isômeros *N*-alquilados.[1] Quando se usa um bromo-alcano (Br-R) como agente alquilante (a. Esquema 1), o par de isômeros é obtido (rendimentos acima de 80%). Já quando o alquilante é um iodo-alcano (I-R) (b. Esquema 1), além do par de isômeros, o produto di-alquilado (BLI-1,3-diR) é formado. No entanto, para que se possa ter rendimentos razoáveis na síntese do produto di-alquilado, são necessárias algumas adaptações nas condições, como o uso de uma base mais fraca para evitar a reação secundária de eliminação. Em nossa pesquisa, três di-alquil-naftoimidazóis derivados do BLI-H foram obtidos (b. Esquema 1). A determinação do $CI_{50}$ do BLI-1,3-dihexil ($CI_{50}$ = 7.9 ± 0.7) confirma o grande potencial antichagásico desse composto. Os produtos foram caracterizados com base nos seus espectros de massas de alta resolução e nos espectros uni e bidimensionais de RMN.

[1] Silva, A.M. et al. *Med Chem Commun.* **2017**, 8, 952-959.

## Agradecimentos/Acknowledgments

CAPES; CNPQ; IOC-FIOCRUZ

**Área:** *ORG*

# Synthesis of novel β-carboline-(piperazinyl)-1,3,5-triazines as potential anticholinesterase inhibitors

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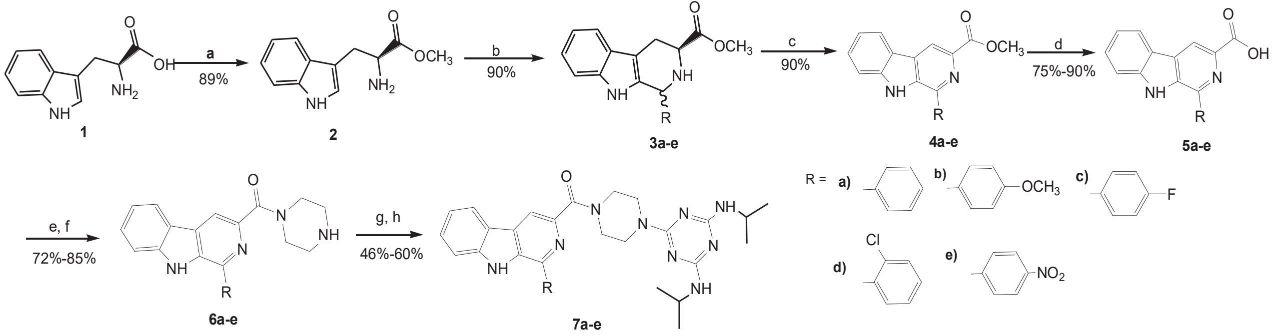
Keywords: *β-Carboline, Triazine, Alzheimer's disease, Anticholinesterase inhibitors.*

## Highlights

Novel *β*-carboline-(piperazinyl)-1,3,5-triazines were synthetized and assayed against AChE and BuChE. Compounds **7a** and **7b** showed 62.7% and 65.3% inhibition of AChE and BuChE, respectively.

## Resumo/Abstract

Alzheimer's disease (AD) is a multifactorial neurodegenerative disorder characterized by cognitive impairment and progressive loss of memory.[1] The AD treatment is commonly performed with inhibitors of acetylcholinesterase (AChE). Studies have shown that inhibiting also the butirycholinesterase (BuChE), cognitive improvements can be obtained. β-Carbolines and 1,3,5-triazines were reported as inhibitors for several targets involved in Alzheimer's disease, including AChE and BuChE.[2] In order to obtain novel cholinesterase inhibitors, in this work we proposed the synthesis of *β*-carboline-(piperazinyl)-1,3,5-triazine hybrids (**Scheme 1**). The β-carbolines **5a-e** were synthetized from the Pictet-Spengler condensation of *L*-tryptophan methyl ester (**2**) with aldehydes, oxidation of tetrahydro-β-carbolines **3a-e**, and hydrolysis of the carbomethoxy-β-carbolines **4a-e**, as previously reported for our group.[3] Reaction of **5a-e** with Boc-piperazine, in presence of 4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-methyllmorpholinium chloride (DMTMM), followed by deprotection with TFA, afforded the intermediates **6a-e**. *β*-Carboline-(piperazinyl)-1,3,5-triazine hybrids **7a-e** were obtained from the reaction of **6a-e** with cyanuric acid, in basic medium, at 0 $^0$C, followed by addition of isopropylamine and refluxing the reaction mixture. The structures of synthetized compounds were confirmed by $^1$H and $^{13}$C NMR data. The methodology employed was efficient for synthesis of proposed compounds, affording **6a-e** in good yields (72%-85%) from **5a-e**, and **7a-e** in moderated yields (46%-60%) from **6a-e**. Compounds **7a-e** were evaluated *in vitro* at concentrations of 10 μM and 100 μM against AChE and BuChE, according to the Ellman method, and their percentages of inhibition were determined. Compounds **7a** and **7b** inhibited AChE and BuChE at percentages of 62.7% and 65.3%, respectively, at 100 μM.



**Reagents and Conditions: a)** $CH_3OH$, $H_2SO_4$, reflux, 48h; **b)** RCHO, $CH_2Cl_2$, TFA, t.a, 48h, **c)** S, xylene, 48h; **d)** NaOH, MeOH, $H_2O$, reflux 24h **e)** DMTMM, Boc-piperazine, EtOH, reflux, 48h; **f)** $CHCl_3$, TFA; **g)** 2,4,6-trichloro-1,3,5-triazine, NaOH, THF, 1h, 0°C; **h)** isopropylamine, reflux, 48h.

**Scheme 1.** Synthetic route for *β*-carboline-(piperazinyl)-1,3,5-triazine hybrids.

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[3] Baréa, P.; Barbosa, V. A.; Bidóia, D. L.; Paula, J. C.; Stefanello, T. F.; Costa, W. F.;. Nakamura, C. V.; Sarragiotto, M. H. Synthesis, antileishmanial activity and mechanism of action studies of novel β-carboline-1,3,5-triazine hybrids. European Journal of Medicinal Chemistry, 2018, 150,579–590.

## Agradecimentos/Acknowledgments

CAPES, CNPq, FUNDAÇÃO ARAUCÁRIA, DEPARTAMENTO DE QUÍMICA-UEM.

**Área:ORG**

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

# Synthesis of paeonol derivatives and their potential antibacterial activity

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Palavras Chave: paeonol, triazole derivatives, ethers derivatives, antibacterial

## Highlights

Click chemistry, copper (I)-catalysed azide-alkyne cycloaddition (CuAAC), bimolecular nucleophilic substitution, paeonol 1,2,3-triazole and ethers derivatives, antibacterial activity.

## Resumo/Abstract

Multi-drug-resistant bacteria (MDR) are the cause of different infections and diseases that have affected humanity for a long time, and have been an emerging global health problem that has led to increased morbidity and mortality. The growing emergence of MDR bacteria has underline the need for development and discovery of new antibacterial compounds. In this context, a series of paeonol 1,2,3-triazole and ethers derivatives were synthesized using copper(I)-catalysed azide-alkyne cycloaddition (CuAAC) click chemistry reaction and nucleophilic substitution. Paeonol has been a natural product widely studied due to its several biological activities, as well as its derivatives. Three ether derivatives (two unpublished) and ten triazole derivatives (six unpublished) of paeonol were obtained, which were determined by NMR, FT-IR, FT-ICR MS and six of them by X-rays, being the first study of this type presented for these compounds. All the synthesized compounds were evaluated as antibacterial agents against *Sthaphylococcus aureus* and *Escherichia coli*, obtaining a minimum inhibitory concentration (CMI) above 100ug/ml. The results showed that click chemistry and nucleophilic substitution were very useful to obtain paeonol triazole derivatives and ethers. The advantages of these reactions (high yield in most compounds, reaction time, low impurities) performed show that it is advisable to use the method for the production of new derivatives and thus assist in the discovery of new potential bioactive compounds.

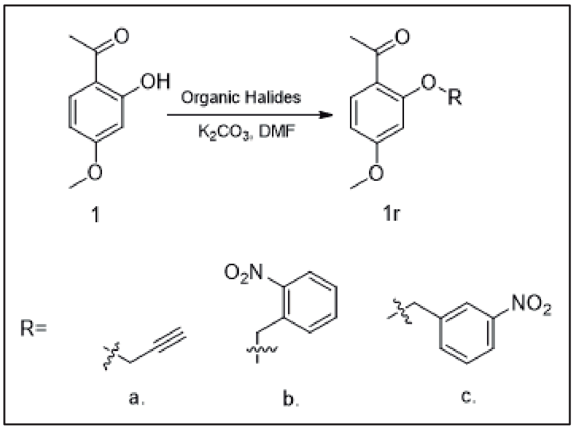

Figure 1. General synthesis of ether derivatives

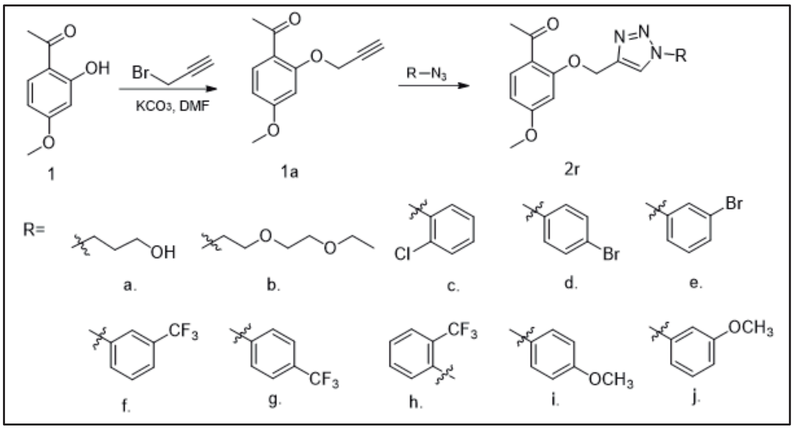

Figure 2. General synthesis of triazole derivatives

## Agradecimentos/Acknowledgments

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**Área: ORG**

# Synthesis of Pyrazolines via Pd-Catalyzed Heterocyclization/Carbonylation Reaction: Development and Parameterization Studies

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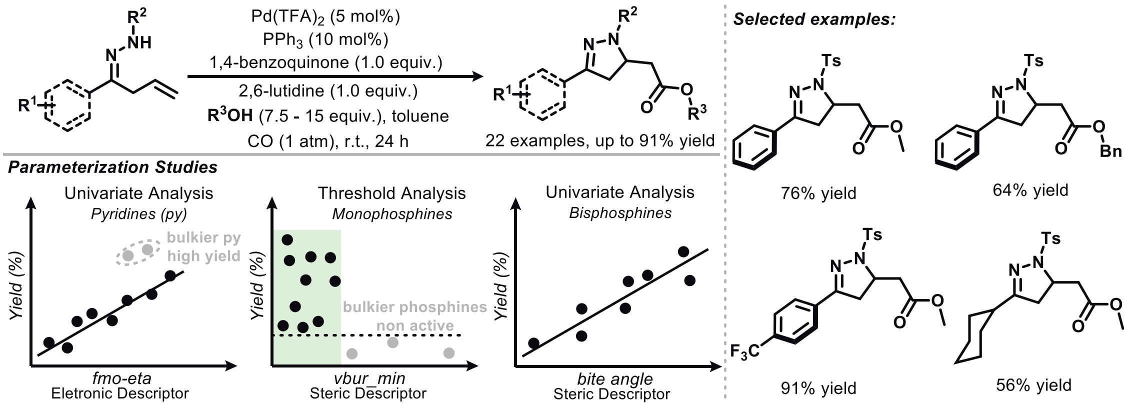
Palavras Chave: *Catalysis, Palladium, Carbonylation, Heterocycle, Statistics, Parameterization.*

## Highlights

Synthesis of pyrazoline-esters derivatives through palladium-catalyzed process. Parameterization studies to gain insights into mechanism and important aspects of the catalyst system.

## Resumo/Abstract

Development of effective methods for the synthesis of heterocyclic compounds has a long-standing history in the scientific community. Organometallic-catalyzed heterocyclization reaction via nucleophiles such as nitrogen, oxygen and sulfur are one of the most employed methodologies for heterocyclic synthesis. We are particularly interested in Wacker-type reactions employing carbonylation reactions of non-activated double bonds by CO capture in a palladium-catalyzed process. This approach has been shown to be effective to obtain functionalized heterocycles in a single step.[1] As a part of our ongoing interest towards the synthesis of heterocycles via Pd-catalyzed heterocyclization/carbonylation reaction,[2] herein, we present a new methodology to obtain pyrazoline-esters derivatives. The methodology described herein proved to be tolerant to different substitutions in strategic positions of the starting material. Moderate to good yields were obtained varying chains of hydrazone, protecting groups and alcohols. Additionally, we developed theoretical studies using statistical tools[3] to generate insights about important but non-intuitive relationships between the catalytic system and the reaction efficiency. These relationships are usually not seen by conventional systematic optimizations. We evaluated experimentally a data set of 25 phosphine ligands (14 monodentate and 11 bidentate) and 14 pyridines. With the aid of the statistical analysis was possible to rationalize the role of steric and electronic effects of the base and ligands in the reaction performance.



**[1]** (a) Beller, M., *et a*l, *Chem. Soc. Rev.* **2011**, *40*, 4986. (b) Beller, M., *et al*, *Chem. Rev.* **2013**, *113*, 1. **[2]** Ferreira, M. A. B., *et al*, *J. Org. Chem.* **2021**, *86*, 3923. **[3]** Sigman, M. S., *et al*, *Chem. Sci.*, **2018**, *9*, 6922. (b) Sigmam, M. S., *et al*, *Nature Chem.*, **2012**, *4*, 366.

## Agradecimentos/Acknowledgments

FAPESP
Process Number
(2020/13563-7; 2020/01255-6)

CAPES
Process Number (88887.597433/2021-00;
88887.342421/2019-00; 88887.569941/2020-00)

CNPq

**Área: ORG**

# Synthesis of pyrimidine nucleoside *1H*-1,2,3-triazole-linked carbohydrates

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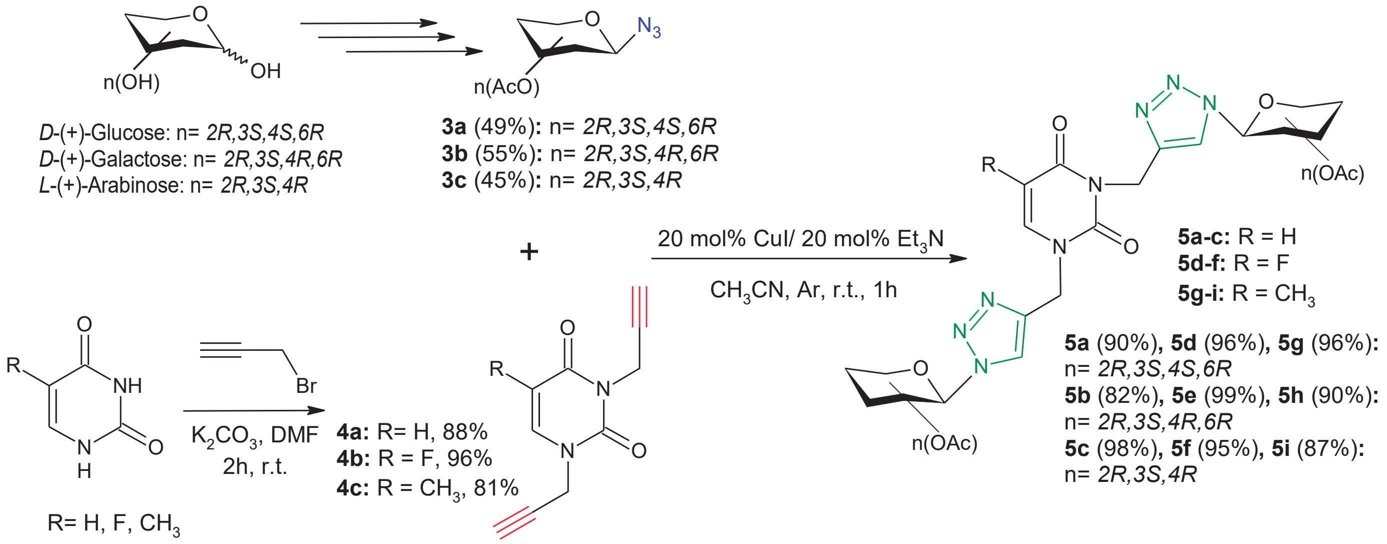
Palavras-Chave: *1,2,3-Triazole, Pyrimidine, Azido-glycopyranoside, 1,3-Dipolar Cycloaddition, Click Chemistry*

## Highlights

Nucleoside analogues containing the heterocycles 1,2,3-triazole and pyrimidine conjugated to glycopyranosides were prepared. The synthesis was carried out using CuAAC conditions to furnish bis-triazole-sugars **5a-i** in excellent yields (82-99%).

## Abstract

Nucleoside analogues are considered a viable therapeutic strategy in the treatment of cancers and viral infections;[1] these molecules can mimic the structure of natural nucleosides for recognition by cellular or viral enzymes.[2] Initially, *β*-azido-glycosides **3a-c** were synthesized from the corresponding sugars by acetylation, bromination, and azidation, using methodologies described in the literature.[3] *N¹*-,*N³*-Bis-alkylated pyrimidines **4a-c** were prepared by adapted method,[4] using propargyl bromide in excess to promote the bis-alkylation reaction. Then, *β*-azido-glycosides **3a-c** reacted with bis-alkylated pyrimidines **4a-c** via copper(I)-catalyzed alkyne-azide cycloaddition (CuAAC) to furnish bis-triazole-sugars **5a-i**. The literature[4] reports the synthesis of bis-triazole derivatives **5a,b** and **5g,h** using $CuSO_4 \cdot 5H_2O$ (10 mol%) and sodium ascorbate (20 mol%) in 6-8 h of reaction; however, attempts to prepare compound **5a** were unsuccessful. Therefore, the triazole derivatives **5a-i** were synthesized in excellent yields (82-99%) using CuI (20 mol%) and $Et_3N$ (20 mol%) after 1 hour. The compounds **5a-i** is being evaluated for leishmanicidal and antiviral activities.



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**Área: ORG** **Nº de Inscrição: 01130**

# Synthesis of Sulfur containing Enuloside Derivatives with Potential Antitumoral Activity

**Eduardo S. da Silva (PG),[1]* John A.M. Santos (PG),[2] João Bosco P. Silva,[1] Paulo H. Menezes (PQ).[1]**

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*Keywords: pseudoglycosides, S-enulosides, antitumoral.*

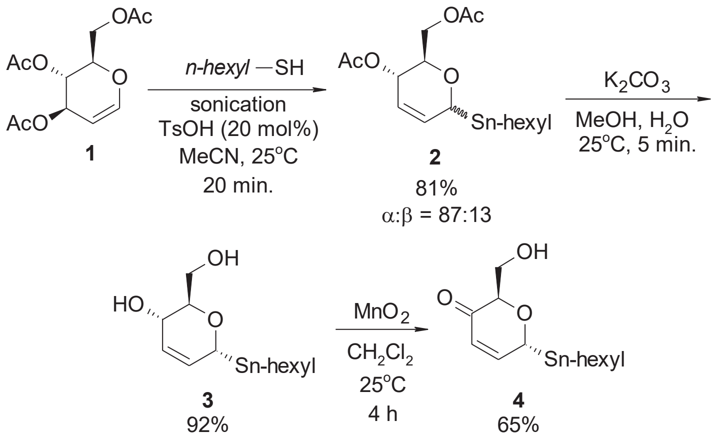
## Highlights

The synthesis of an *S*-enuloside analogue, simpler derivative of natural products containing an α,β-unsaturated unit is described. The desired compound was obtained in good yield and isomeric purity after three sequential steps.

## Resumo/Abstract

α,β-unsaturated δ-lactone is a structural motif present in several natural products known to exhibit various biological activities.[1] In this context, structurally simpler compounds that could act as a Michael-type acceptor for biological nucleophiles are of great interest. Naturally occurring enone-containing sugars – enulosides – are known to exhibited antibacterial and antifungal activity.[2]

Recently, we described the synthesis of enuloside derivatives with antitumoral activity in micromolar range.[3] These compounds open new possibilities to prepare an array of more active, site-specific or selective antitumor agents. Molecular calculations indicated that the substitution of oxygen atoms for sulfur atoms in these compounds could lead to an increase in their antitumor activity. Thus, commercially available 3,4,6-tri-*O*-acetyl-*D*-glucal, **1** was submitted to a glycosidation reaction using 1-hexanethiol catalyzed by TsOH under sonication gave the corresponding pseudoglycoside **2** in good yield and anomeric selectivity. Subsequent hydrolysis of acetyl groups of **2** using $K_2CO_3$ in MeOH gave **3**, which was then submitted to the oxidation reaction using $MnO_2$ to yield the desired *S*-enuloside **4** in good yield (Scheme 1).



**Scheme 1:** Synthesis of *S*-enuloside

In summary, we have shown an efficient method for the synthesis of *S*-enulosides in a very stereoselective way. The antitumoral evaluation of the synthesized compound is currently in progress in our laboratory.

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2. Xavier, N. M.; Rauter, A. P.; *Pure Appl. Chem.* **2012**, *84*, 803.
3. Santos, J. A. M.; Santos, C. S.; Almeida, C. L. A.; Silva, T. D. S.; Freitas Filho, J. R.; Militao, G. C. G.; da Silva, T. G.; da Cruz, C. H. B.; Freitas, J. C. R.; Menezes, P. H.; *Eur. J. Med. Chem.* **2017**, *128*, 192.

## Agradecimentos/Acknowledgments

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**Área: ORG**

# Synthesis, spectroscopic characterization and antioxidant activity of hydroxychalcones.

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Keywords: *Chalcones, Synthesis, Spectroscopic characterizations, Antioxidant activity.*

## Highlights

The method used for the synthesis of hydroxychalcones proved to be efficient, according to the spectroscopic data. The synthesized compounds with the hydroxyl group were shown to be good antioxidants.

## Abstract

Chalcones are a class of compounds that have different pharmacological properties, with different biological activities. This work presents the synthesis of five chalcones: CHAL, 2-CHALOH, 4-CHALOH, 2'-CHALOH and 2',2-CHALOH through Claisen-Schmidt's aldolic condensation methodology[1] (Figure 1), in addition to performing spectroscopic characterizations, by NMR and FT-IR techniques, and evaluation of antioxidant activity.[2]

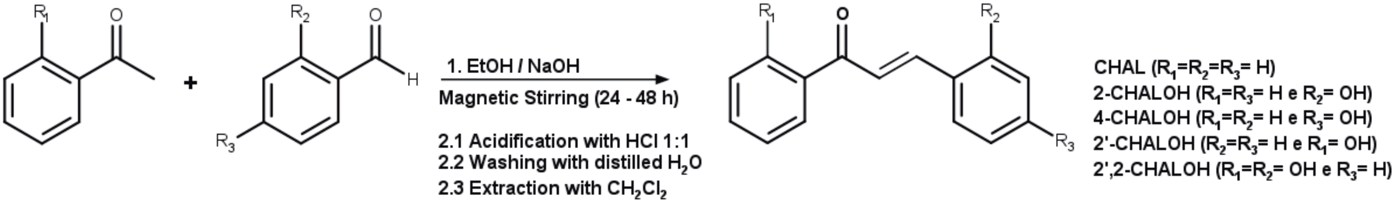

**Figure 1 -** Reaction scheme with all steps for the synthesis of hydroxychalcones.

Regarding spectroscopic characterizations, it is possible to observe the efficiency in obtaining the chalcones. With the presence of characteristic bands for these compounds in FT-IR. Mainly the bands referring to carbonyl (C=O) and the vinylic (C=C) bond. In the NMR, we observed the presence of signals that corroborate the formation of chalcones. The presence of two doublets referring to the formation of the vinylic bond (C=C), with coupling constant $^3J_{HH}$ between 14 and 18 Hz. About the evaluation of biological activities, the presence of the hydroxyl group in the synthesized compounds pleasantly increased the ability to inhibit the DPPH radical. The hydroxychalcones presenting themselves as good antioxidant compounds, with 4-CHALOH o presenting $IC_{50}$ (mM)= 240.89 against DPPH radical. Table 1 shows the results of the spectroscopic data, reaction yield, melting point and $IC_{50}$ (mM) against the DPPH radical of the synthetized hydroxychalcones.

**Table 1 -** Reaction yield, melting point, spectroscopic characterizations data and $IC_{50}$ (mM) against the DPPH radical.

| Compound | Spectroscopic Data | $IC_{50}$ (mM) |
|---|---|---|
| **CHAL** | **Yield:** 1.42 g (63.0 %), **m.p.**: 151.8-155.2 ℃. **NMR $\delta_H$ ($CDCl_3$)**: 7.79, 7.54 (2H, CH=CH), 8.50-7.00 (10H, phenyls). **NMR $\delta_C$ ($CDCl_3$)**: 190.52 (C=O), 144.89, 122.14 (C=C). **FT-IR $\nu_{max}$ (KBr) $cm^{-1}$**: 1660 (C=O), 1610 (C=C). | 3483.13 |
| **2-CHALOH** | **Yield:** 1.03 g (46.0 %), **m.p.**: 136.0-148.9 ℃. **NMR $\delta_H$ ($CDCl_3$)**: 8.19, 7.71 (2H, CH=CH), 8.20-7.50 (9H, phenyls), 6.78 (1H, OH). **NMR $\delta_C$ ($CDCl_3$)**: 190.08 (C=O), 155.89 (-OH), 141.11, 122.74 (C=C). **FT-IR $\nu_{max}$ (KBr) $cm^{-1}$**: 3360 (OH), 1652 (C=O), 1568 (C=C). | 307.49 |
| **4-CHALOH** | **Yield:** 1.14 g (51.0 %), **m.p.**: 176.8-186.3 ℃. **NMR $\delta_H$ ($CDCl_3$)**: 7.78, 7.41 (2H, CH=CH), 8.50-6.50 (9H, phenyls), 5.48 (1H, OH). **NMR $\delta_C$ ($CDCl_3$)**: 190.82 (C=O), 157.94 (-OH), 144.78, 119.86 (C=C). **FT-IR $\nu_{max}$ (KBr) $cm^{-1}$**: 3220 (OH), 1649 (C=O), 1599 (C=C). | 240.89 |
| **2'-CHALOH** | **Yield:** 0.65 g (29.0 %), **m.p.**: 85.4-87.6 ℃. **NMR $\delta_H$ ($CDCl_3$)**: 7.94, 7.67 (2H, CH=CH), 8.00-6.75 (9H, phenyls), 12.75 (OH). **NMR $\delta_C$ ($CDCl_3$)**: 193.78 (C=O), 163.62 (-OH), 145.41, 120.15 (C=C). **FT-IR $\nu_{max}$ (KBr) $cm^{-1}$**: 3030 (OH), 1639 (C=O), 1572 (C=C). | 593.32 |
| **2',2-CHALOH** | **Yield:** 0.46 g (19.0 %), **m.p.**: 158.4-162.3 ℃. **NMR $\delta_H$ (DMSO-$d_6$)**: 8.16, 7.96 (2H, CH=CH), 8.25-6.70 (8H, phenyls), 12.5, 10.8 (2H, OH). **NMR $\delta_C$ (DMSO-$d_6$)**: 194.31 (C=O), 162.32, 157.98 (-OH), 140.79, 120.76 (C=C). **FT-IR $\nu_{max}$ (KBr) $cm^{-1}$**: 3345 (OH), 1627 (C=O). | 377.54 |

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## Acknowledgments

**Área: ORG** **Nº de Inscrição: 00101**

# The First Total Synthesis of Bhutkesoside A: Polyacetylenic Glycoside With Potential Anticancer Activity Through Inhibition of UCK2

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**Keywords:** *Bhutkesoside A; Cadiot-Chodkiewicz coupling; Polyacetylenic glycosides; Antitumor.*

## Highlights

Total synthesis of naturally occurring polyacetylenic glycosides.

## Abstract

Polyacetylenic glycosides are derived from polyynes compounds, a class of natural products characterized by the presence of two or more conjugated triple bonds in their structure. These molecules are widely distributed in various medicinal plants.[1] In 2015, Adhikari and coworkers[2] reported the isolation of Bhutkesodide A from the roots of the *Ligusticopsis wallichiana* plant. Bhutkesodide A has shown promising antineoplasic activity. In addition, it is a potential inhibitor of uridine cytidine kinase 2 (UCK2), which is expressed in cancer cells, so this enzyme is an important biological target in cancer treatment. Thus, in this work we report the first total synthesis of Bhutkesodide A.

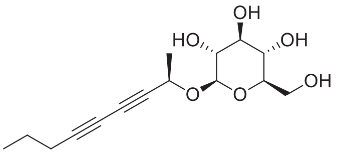

**Figure 1:** Structure of Bhutkesoside A

The disconnection of the target molecule led to synthetic intermediates **A** and **B**. Fragment **A** was prepared from acetylation of D-glucose followed by a glycosylation reaction. The β-glycoside was obtained with high stereoselectivity (β/α = 97/3) in a 69% overall yield after two steps. Fragment **B** was obtained from 1-petyne in moderate yield (55%). The Cadiot-Chodkiewicz cross coupling reaction between β-glycoside **A** and fragment **B** followed by hydroxyl deprotection led to Bhutkesoside A. A convergent synthesis of Bhutkesoside A was achieved after five reaction steps in 25% overall yield. The synthesized compounds were characterized by the usual spectroscopic techniques and the data corroborate the structures.

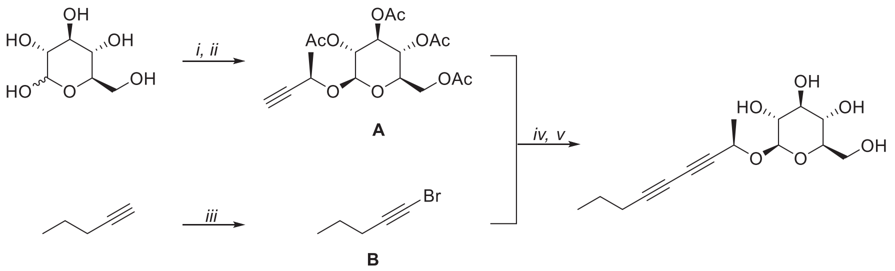

**Figure 2:** Reagents and conditions: (i) $Ac_2O$, NaOAc, 140 °C, 10 min, 98%; (ii) (*R*)-(+)-3-Butyn-2-ol, $BF_3{\bullet}OMe_2$, $CH_2Cl_2$, 0 °C, 15 h, 70%; (iii) NBS, $AgNO_3$, $CH_2Cl_2$, 0 °C, 2 h, 55 %; (iv) CuI, $PdCl_2(PPh_3)_2$, $Et_3N$, $CH_2Cl_2$, 25 °C, 1,5 h, 40 %; (v) $K_2CO_3$, MeOH, $H_2O$, 10 min, 92 %.

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## Acknowledgments

CAPES, CNPQ, FACEPE

**Área: ORG**

# The impact of severe COVID-19 on human metabolism: an NMR-based metabolomics study

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Keywords: COVID-19, SARS-COV-2, Metabolomics, Nuclear magnetic resonance.

## Highlights

The 1-Methylhistidine metabolite has been considered a biomarker of COVID-19.

The model OPLS-DA of patients diabetic and non-diabetics showed no separation, defining null hypothesis. These results suggested that infection by SARS-CoV-2 caused perturbations in the cell absorption of glucose in patients non-diabetics.

## Abstract

In December 2019, the new severe acute respiratory syndrome coronavirus 2 (SARS-CoV-2) emerged with a global public health threat. This virus is a positive-sense single-stranded RNA belonging to the Betacoronavirus genus. Its resultant disease, the Coronavirus Disease 2019 (COVID-19), causes a range of clinical profiles from either asymptomatic or mild disease to severe respiratory symptoms and multi-organs failure, leading to death. Currently, some biochemical parameters have been proposed as predictive for COVID-19 severity. Nevertheless, the screening of biomarkers is still critical because it can assist in the clinical management of the patients. A multidisciplinary study to understand COVID-19 effects and find biomarkers that can differentiate between healthy and non-healthy individuals is intuitively attractive for this complex disease. In this sense, the goal of this work was to provide new information about the metabolism and altered biological pathways of patients due to SARS-CoV-2 infection. For this purpose, an NMR-based metabolomics study was performed involving plasma samples of 54 patients with severe COVID-19 and 20 healthy control. As a result, some metabolites were potential biomarkers to distinguish between COVID-19 and healthy control. The score plot OPLS-DA (Figure 1A) revealed a high degree of separation between groups, showing excellent performance demonstrated by its cross-validations (Q2 0.78 and R2Y 0.83) permutation tests n = 2000, and statistical significance p-value < 0,0005. In addition, the OPLS-DA revealed key discriminatory metabolites of COVID-19 positive patients (Figure 1B). The Venn diagram (Figure 1C) highlights the metabolites significantly changed with SARS-CoV-2 infection associated with gender and age. Notably, the metabolite 1-Methyl-Histidine was considered a biomarker for COVID-19 positive. Some metabolites identified are mainly involved in the metabolism of the Krebs cycle, ketone bodies, glutamate, and histidine. Finally, we showed the impact of SARS-CoV-2 infection on human metabolism.

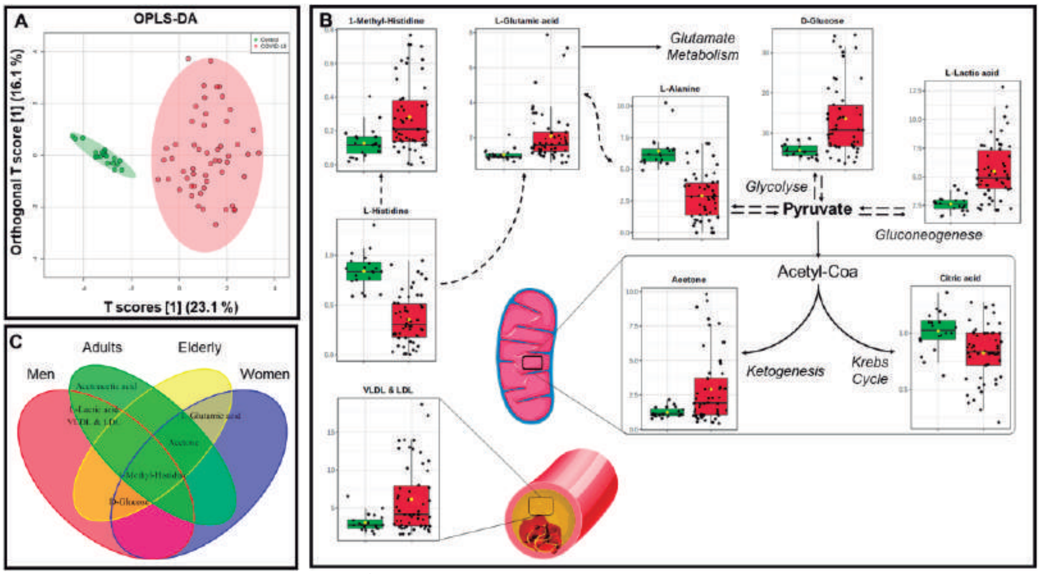

**Figure 1: (A)** OPLS-DA score plots of data obtained by $^{1}$H-NMR spectra. **(B)** Box-and-whisker plots of relative concentrations for biomarkers ($p < 0.01$). Y-axes are represented as relative units and medians are indicated by golden diamond within each box. **(C)** Venn diagram showing of metabolites significantly changed in subgroups COVID-19 associated with gender and age. Healthy controls (green) and COVID-19 (red).

## Acknowledgments

UFAL, FAPEAL, CAPES, CNPq

**Área: ORG**

# The Solvent Key Role in the Ugi-type Multicomponent Reaction: a Theoretical and Experimental Investigation

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Palavras Chave: *Multicomponent Reaction, Solvent Effect, DFT, α-acyl aminocarboxamides, α-amino amidines.*

## Highlights

A new mechanism for the Ugi-type reaction was proposed, pointing out the effect of methanol as solvent-reagent. The variation of few conditions could chemoselectively provide two classes of products.

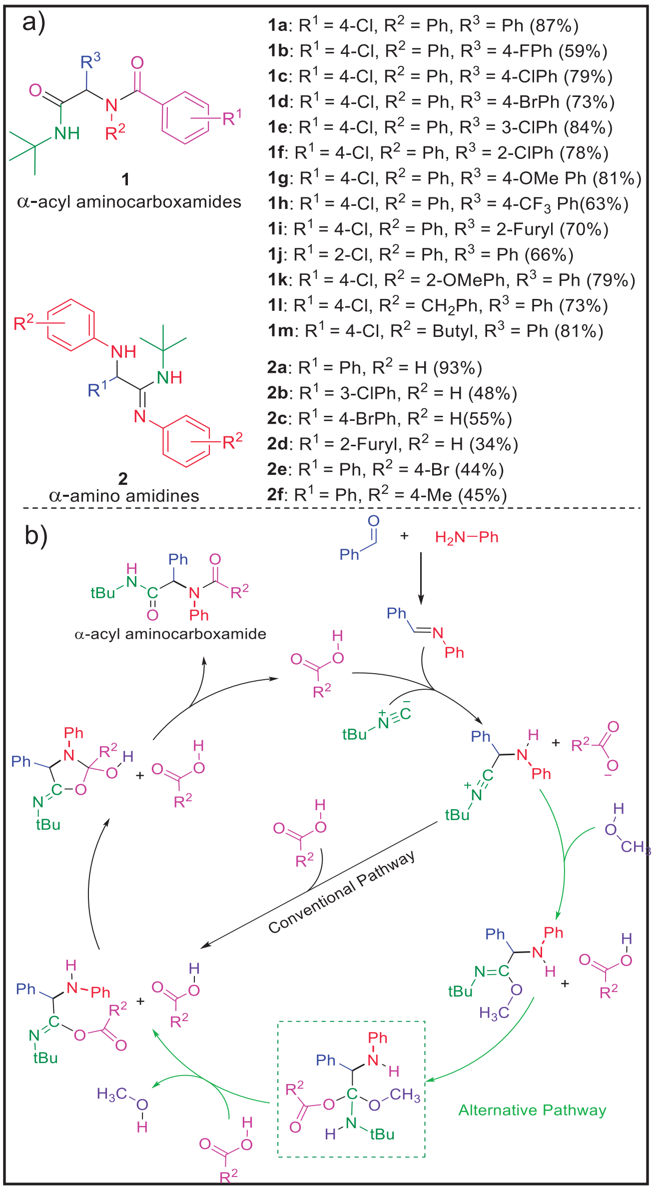
## Resumo/Abstract

One of the most classical multicomponent reactions (MCR) is the Ugi reaction, which involves a carboxylic acid, an aldehyde, an amine and an isonitrile, forming α-acyl aminocarboxamides. The use of computational calculations to better comprehend the mechanism of this reaction can provide an important tool for the prediction of reactivities and to confirm experimental data.

This work aims to access two classes of products through multicomponent reactions, with only subtle variations in the reaction conditions. Experimentally, it was observed that it was possible to obtain α-amino amidines and α-acyl aminocarboxamides from the conventional Ugi-type synthesis. Interestingly, it was seen that exclusively in methanol the reaction occurred with greater selectivity for the Ugi product, which was not observed for any other polar protic, aprotic or apolar solvents. Thus, there was a need to understand what was special about methanol in this transformation. A scope of both products was prepared (Scheme 1a), yielding α-acyl aminocarboxamides in moderate to good yields (59-87%), and α-amino amidines in low to excellent yields (34-93%).

To understand the effect of methanol acting as solvent in Ugi reaction, a computational study was carried out using the density functional theory (DFT). A mechanistic study of both products was conducted, analyzing possible reaction pathways: in the presence and absence of a Brønsted acid acting as a catalyst; hydrogen bonds in which methanol could stabilize the transition state; and proposals involving the formation of alternative intermediates with methanol. Thus, we found that the most plausible mechanism involves the formation of a tetrahedral intermediate with methanol (Scheme 1b), enabling the formation of an energetically favored reaction pathway, when compared to the classical proposal. This intermediate hinders the reaction center to sterically bulkier nucleophiles, as seen with aniline, preventing the formation of α-amino amidines. The tetrahedral intermediate containing methanol, considered the key step for this mechanistic proposal, was found through of High-Resolution Mass Spectrometry studies.

**Scheme 1.** Scope and proposal mechanism



**1a**: $R^1$ = 4-Cl, $R^2$ = Ph, $R^3$ = Ph (87%)
**1b**: $R^1$ = 4-Cl, $R^2$ = Ph, $R^3$ = 4-FPh (59%)
**1c**: $R^1$ = 4-Cl, $R^2$ = Ph, $R^3$ = 4-ClPh (79%)
**1d**: $R^1$ = 4-Cl, $R^2$ = Ph, $R^3$ = 4-BrPh (73%)
**1e**: $R^1$ = 4-Cl, $R^2$ = Ph, $R^3$ = 3-ClPh (84%)
**1f**: $R^1$ = 4-Cl, $R^2$ = Ph, $R^3$ = 2-ClPh (78%)
**1g**: $R^1$ = 4-Cl, $R^2$ = Ph, $R^3$ = 4-OMe Ph (81%)
**1h**: $R^1$ = 4-Cl, $R^2$ = Ph, $R^3$ = 4-$CF_3$ Ph(63%)
**1i**: $R^1$ = 4-Cl, $R^2$ = Ph, $R^3$ = 2-Furyl (70%)
**1j**: $R^1$ = 2-Cl, $R^2$ = Ph, $R^3$ = Ph (66%)
**1k**: $R^1$ = 4-Cl, $R^2$ = 2-OMePh, $R^3$ = Ph (79%)
**1l**: $R^1$ = 4-Cl, $R^2$ = $CH_2$Ph, $R^3$ = Ph (73%)
**1m**: $R^1$ = 4-Cl, $R^2$ = Butyl, $R^3$ = Ph (81%)

**2a**: $R^1$ = Ph, $R^2$ = H (93%)
**2b**: $R^1$ = 3-ClPh, $R^2$ = H (48%)
**2c**: $R^1$ = 4-BrPh, $R^2$ = H(55%)
**2d**: $R^1$ = 2-Furyl, $R^2$ = H (34%)
**2e**: $R^1$ = Ph, $R^2$ = 4-Br (44%)
**2f**: $R^1$ = Ph, $R^2$ = 4-Me (45%)

## Agradecimentos/Acknowledgments

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**Área: ORG** **Nº de Inscrição: 00211**

# The use of organocatalyst ionic liquid for synthesis of pyranochromene derivates and study of antioxidant and antibacterial activities

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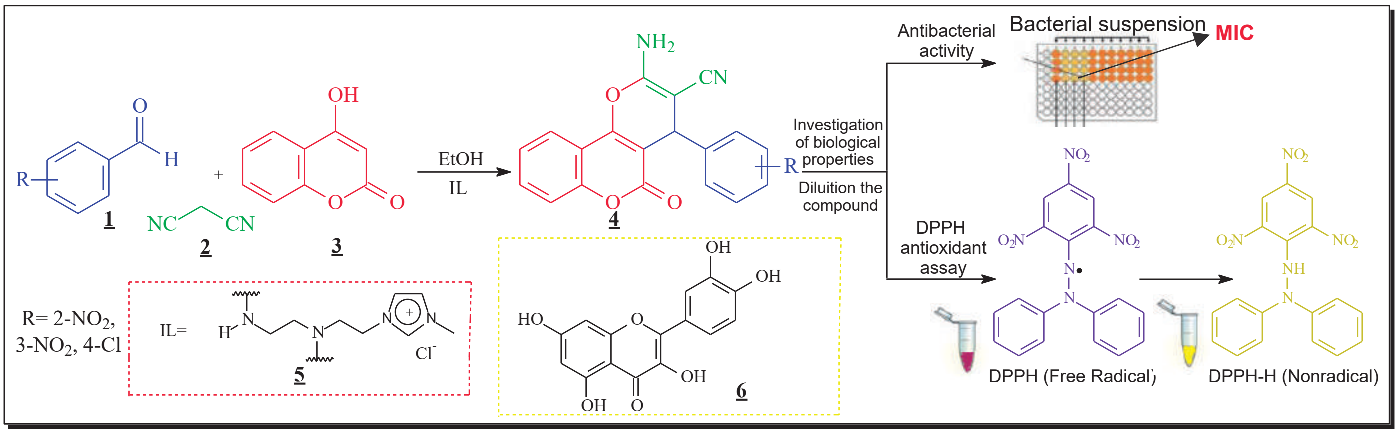
Palavras Chave: *Chromenes, Ionic Liquid, Multicomponent reaction*

## Highlights

The pyran[3,2-*c*]chromene compounds were obtained by multicomponent reaction using na ionically marked synthetic enzyme as catalyst. The compounds were sensitive to *Staphylococcus aureus* (ATCC 29213).

## Resumo/Abstract

Biolocial properties are related to pyranochromenes, such as antioxidant and cytotoxic activity[1]. The pyran[3,2-*c*]chromene compounds were synthesized by a multicomponent reaction using aromatic aldehyde **1** , malononitrile **2** and 4-hydroxycoumarin **3** was stirred under reflux in 1 mL ethanol and 100 mg of artificial synthetic enzyme (IL) **5**.
**Scheme 1.** Synthesis and study of the biological potentialities of pyran[3,2-c]chromene derivates.



As shown in Scheme 1 the ionic liquid (IL) **5**, was used as promoter of the catalytic reaction medium, was synthesized as reported in the literature[2], where polyethyleneimine was supported on chlorinated ionic liquid. The synthesized compounds having good yields between 72 – 94 %. The products under study were recrystallized and further characterized by IR, MS and $^1$H and $^{13}$C NMR and submitted to was evaluated for bactericidal potentials and radical testing for radical by DPPH. Broth microdiluiton assay results obtaining MICs between 125-1000 µg/mL against *Staphylococcus aureus* (ATCC 29213). Regarding antioxidant activity, the compounds have a percentage relevant antioxidant activity ranging from 63,2-91,5%, when compared to the quercetin **6** standard which presented 95%. In this context, exposed methodology contributed to obtain a series of bioactive compounds, with a method based on the green chemistry axes, employing lower energy expenditure and fewer steps to obtain the products of interest. And using alternative means of reuse, such as the catalyst IL.

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## Agradecimentos/Acknowledgments

CAPES, CNPq, FAPEG, UEG, IQ-UnB

**Area: ORG**

# Transaminase immobilization in Sodium Alginate Matrix

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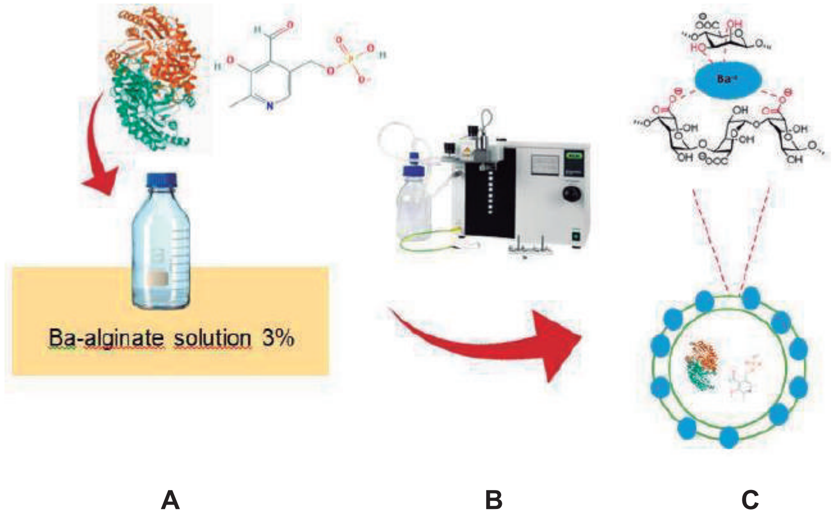
Key Words: *immobilization, transaminase, microcapsules*

## Highlights

Enzymatic immobilization of the heterologous expressed *S*-selective Transaminase *Vibrio fluvialis*. Application in biocatalysis in transamination mechanisms for chemical conversions of triketones into chiral pyrrolines.

## Abstract

Enzymes are known to be three-dimensional biological macromolecules of polypeptide composition, they play an important role in nature through their specific catalytic processes and substrate recognition. There are numerous advantages obtained in immobilization of enzymes for the biocatalytic processes, such as operations at low temperature and pressure conditions, high molecular selectivity and lower physiological toxicity. Transaminases (TA) are pyridoxal-5'-phosphate (PLP) dependent enzymes, in particular have extreme relevance in science, as they are closely associated with the biosynthetic pathways of nitrogenous compounds, which in general are of great importance to the pharmaceutical industry. In this sense, we proposed to immobilize TAs and PLP, by encapsulation with sodium alginate. The microcapsules were checked by microscopy in the OLYMPUS Q-Color3 equipment, at 500 micrometers, and by the Bradford assay that verified the existence of enzymes in the microcapsules.[1–4]



Scheme 1. Microencapsulation to enzyme immobilization.(**A**) Barium solution mixture with alginate for polymerization and immobilization. (**B**) BÜCHI Encapsulator B-390 equipment used in microencapsulation. (**C**) Formed microcapsules.

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## Acknowledgments

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**Área: ORG** **Nº de Inscrição: 01228**

# Zinc-Mediated Synthesis of β-Hydroxy-Ester by Ball Milling Method.

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Key words: β-Hydroxy-esters, Green method, Mechanochemistry, Reformatsky reaction.

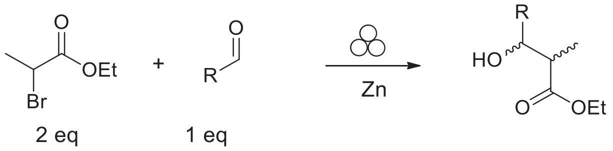
## Highlights

An efficient and solvent-free synthesis of β-hydroxy esters by ball milling (mechanochemistry) is developed for zinc-mediated reaction of aromatic and aliphatic aldehydes and ethyl 2-bromopropanoate.

## Resumo/Abstract

In the last decades, the development of green methods in synthesis has been highlighted in the literature. Mechanochemistry is becoming a widespread technique in organic synthesis because reactions can be performed in the absence of bulk solvents. Thus, this work aims at the synthesis of β-hydroxy esters via zinc-mediated Reformatsky reaction of aldehydes and 2-ethyl-bromopropianate by ball milling. The choice of a secondary ester as a starting material was based on the small number of examples described in the literature. Our preliminary mechanochemical studies indicated that the solvent-free reaction showed a better yield of **3a** (table 1) when compared to: liquid-assisted gridding reaction (50 $\mu$L $H_2O$); reaction with radical initiator (benzoyl peroxide), and radical inhibitor (BHT). These results suggested an organometallic pathway for this reaction. After optimization of the reaction parameters (e.g., weight of the ball milling, frequency, jar-type. LAG, etc.), the scope of this reaction with aromatic and aliphatic aldehydes and bromo-ester **1** was tested. The β-hydroxy esters were obtained in 80-98% yields for aromatic and aliphatic aldehydes, except for 4-formylbenzonitrile, whose yield was only 45%. In addition, no diastereoisomeric selectivity *syn:anti* was observed in the experiments performed.

Table 1: Zinc-mediated synthesis of β-hidroxy- esteres by ball milling.



**1** **2** **3**

| **Entry** | **2 a-h** | **3a-h** | % (***syn/anti***) |
|---|---|---|---|
| **1** | 4-methoxybenzaldehyde **(2a)** | 98%**(3a)** | 48/42 |
| **2** | benzaldehyde **(2b)** | 95%**(3b)** | 54/45 |
| **3** | 2- methylbenzaldehyde **(2c)** | 92%**(3c)** | 48/51 |
| **4** | 4-formylbenzonitrile (**2d**) | 45%**(3d)** | 46/54 |
| **5** | 4-fluorbenzaldehyde **(2e)** | 98%**(3e)** | 56/43 |
| **6** | 4-bromobenzaldehyde **(2f)** | 93%**(3f)** | 53/46 |
| **7** | 3-Phenylpropanal **(2g)** | 80%**(3g)** | 51/49 |
| **8** | Heptanal **(2h)** | 90%**(3h)** | 56/43 |

**Experimental conditions**: 0.5 mmol of aldehydes, 1.0 mmol of 2-ethylbromopropianate, 100 mg of zinc in polyethylene of 2 mL jar, 2 steel balls of 3 mm, vibrational frequency of 25 Hz, for 4 hours. The conversion yields by GC using internal standard. The *syn/anti* ratio determined by RMN $^1H$.

Therefore, an efficient and solvent-free method was successfully developed for a zinc-mediated Reformatsky reaction for aromatic and aliphatic aldehydes by ball milling. The reaction with ketones and other bromo-esters are being evaluated.

## Agradecimentos/Acknowledgments

FACEPE, CNPq, CAPES and UFPE

# QPN

# Produtos Naturais

**Área: QPN**

# Age-dependent variations of volatile profile and total phenolic compounds of *Piper alatipetiolatum* (Piperaceae) plants propagated by cuttings

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Key words: *vegetative propagation, sesquiterpenes, ishwarone, ishwarane, GC-MS, Plant development.*

## Highlights

The propagation in the greenhouse of *P. alatipetiolatum* plants was successful by cuttings.

The growth stage influenced the accumulation of oxygenated sesquiterpenoids and phenolics in the plants.

## Resumo/Abstract

*Piper alatipetiolatum* is a Brazilian native and endemic species occurring in the Amazon and Atlantic Forest, which present a high essential oil (EO) content with biological activities. This study aimed to develop a cultivation protocol and evaluate its secondary metabolites over the growth stages. For *P. alatipetiolatum* cultivation, cuttings containing two nodes were propagated in vermiculite expanded type B substrate with daily watering. After roots growth (30 days), the plants were moved to the commercial substrate. The leaves and roots were collected at 30, 60, 90, and 120 days after cultivation. The volatile compounds were extracted by the Likens-Nickerson method for two h and identified by Gas Chromatography-Mass spectrometer (GC-MS). In the leaves, Oxygenated sesquiterpenoids (Fig 1a) increased after 120 days. However, phenylpropanoids (Fig 1b) were higher only until 60 days of growth. The roots did not display variation in the volatile compound classes.

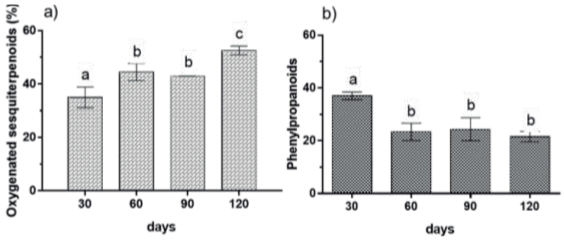

**Figure 1.** Oxygenated sesquiterpene (a) and phenylpropanoids (b) in leaves of *P. alatipetiolatum*. $^{a,b}$ represent statistically significant differences by Tukey test ($p<0.05$).

Regarding the main compounds in leaves, the content of ishwarone increased from the 60th day (Fig 2a). E-isoelemicin (Fig 2b) and in β-elemene (Fig 2c) decreased at 90 and 120 days, respectively. However, the contents of E-asarone and ishwarane did not display variation. Among the main compounds in the roots, only the monoterpene δ-3-carene showed a decrease at 60 days in the roots (Fig 2d). The major compounds ishwarone and ishwarane did not show a statistical difference. Chemically, the *P. alatipetiolatum* EO was similar to previous studies. Its major compounds can be widely exploited due to their larvicidal and pupicidal activity against Aedes aegypti[1].

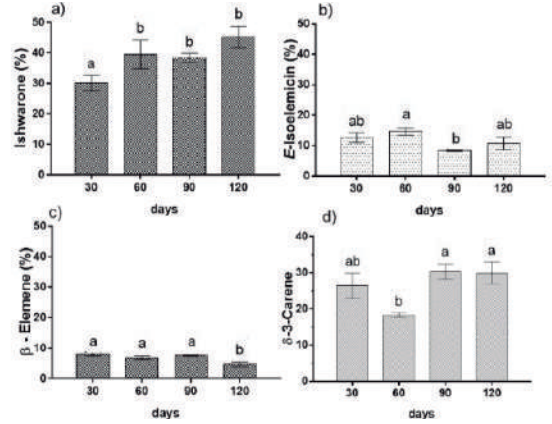

**Figure 2.** major compounds in *Piper alatipetiolatum* leaves: Ishwarone (a), *E*-isoelemicin (b), β-elemene (c); and roots: δ-3-carene (d). $^{a,b}$ represent statistically significant differences by Tukey test ($p<0.05$).

Total polyphenols content determined by the Folin-Ciocalteau method indicated an increase in leaves and roots from the 90th and 60th days of cultivation, respectively (Fig.3).

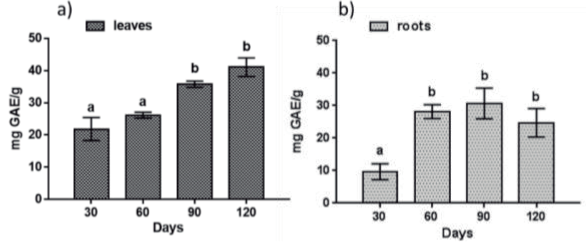

**Figure 3.** Total phenolics compounds in *P. alatipetiolatum*: leaves (a) and roots (b). $^{a,b}$ represent statistically significant differences, at the 5% probability level, by Tukey.

*P. alatipetiolatum* showed easy handling and a high success rate in the propagation by cuttings. Due to the dependence of secondary metabolites on the growth stage, the culture parameters need to be optimized for future exploitation of this species.

[1]Oliveira, et al. R. Br. de Farm., v. 30, p. 667-677. 2020.
[2]Wagay, et al. Springer, cap. 11, p. 241-276. 2020.

## Agradecimentos/Acknowledgments

We are grateful for CNPQ, CAPES for their financial support.

**Área: QPN**

# Amaryllidaceae species as source of anti-neurodegenerative agents: a review

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Keyword: *Amaryllidaceae, Alkaloids, Anti-neurodegenerative, Acetylcholinesterase.*

## Highlights

A review on Amaryllidaceae species that showed compounds with some anti-neurodegenerative effect, *in vitro* and/or *in silico*, especially the acetylcholinesterase (AChE) and butyrylcholinesterase (BuChE) inhibitory activity.

## Resumo/Abstract

Alzheimer's disease (AD) is the most commom degenerative neurological disease which is characterized by distubs in memory and cognitive function[1,2]. According to the Alzheimer's Association, there was a drastic increase in deaths from AD during the COVID-19 pandemic period[3]. *Amaryllidace*ae species are an important source for therapeutic agent in *AD*, since they content alkaloids with promising biological activity, such as anti-acetylcholinesterase (anti-AChE)[4,5]. Therefore, this study aims to carry out a literature review of plants belonging to Amaryllidaceae family with anti-neurodegenerative activity, like AChE inhibitory. Papers were accessed from *SciFinder®*, *ScienceDirect,* and others research platforms through *Portal de Periódicos CAPES* website. Seventeen articles were selected from January 2017 to April 2021 with the highlights "Amaryllidaceae alkaloids", "acetylcholinesterase" and "Alzheimer's disease". The research revealed twelve Amaryllidaceae genus (Figure 1), being *Crinum* and *Phaedranassa* the most investigated (37% and 20% respectively). Alkaloidal extracts and more then forty alkaloids, isolated or identified by gas chromatography, were tested *in vitro* and/or *in silico* for activities as AChE, BuChE inhibition and neuroprotection assays. Nevertheless, the Amaryllidaceae species proved to contain important anti-neurodegenerative actions.

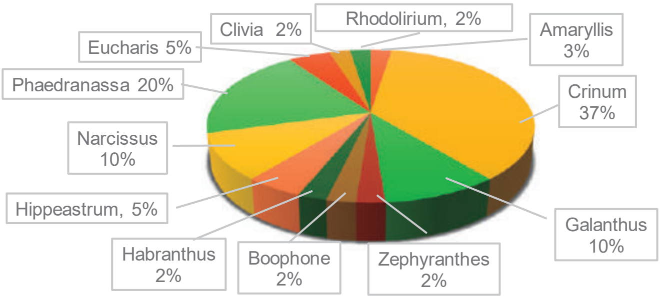

**Figure 1.** Statistical information on the Amaryllidaceae genus investigated.

[1]SINGH, M.; *et al. Eur. J. Med. Chem.*, **70**, p. 165–188, 2013; [2]KHAN, S., *et al. Cur. Neuropharmacol***.**, **18**, p. 1106–1125, 2020; [3]ALZHEIMERS DEMENT, **17**, p. 327-406, 2021; [4]CORTES, N., *et al. Life Sci.*, **122**, p. 42–50, 2015; [5]JIN, Z. *Nat. Prod. Rep.*, **33**, p. 1318–1343, 2016.

## Agradecimentos/Acknowledgments

This study is financed by Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq - Process: 140699/2020-1), Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – Brasil (CAPES) – Finance Code 001, and the Federal University of Espírito Santo.

**Área: QPN**

# Amides isolated from the roots of *Metternichia princeps* (Solanaceae)

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Keywords: *Phenolic amides, Phenylpropanoid amides, Ligananamides, Metternichia, Phytochemical.*

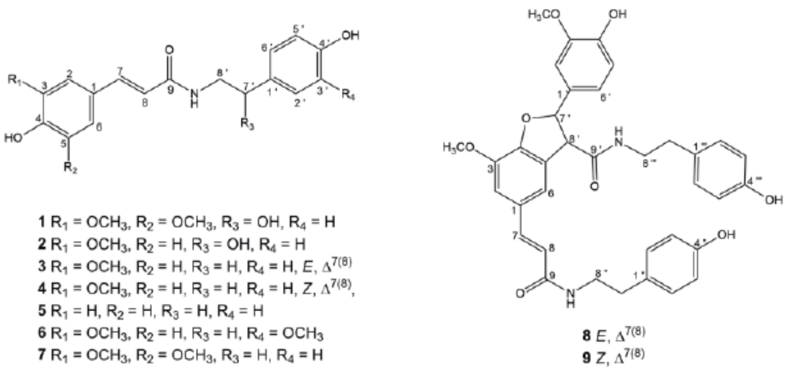
## Highlights

Phytochemical study of the roots of *Metternichia princeps* (Solanaceae). MPLC and HPLC-DAD applied to the isolation and purification of phenethylcinamide alkaloids (phenylpropanoid amides) and lignanamides. Structural characterization of amides by 1D and 2D NMR spectroscopy of $^1$H and $^{13}$C-APT, moreover, HRMS.

## Resumo/Abstract

*Metternichia princeps* is a species of monotypic genus belonging to the family Solanaceae. Endemic to the Atlantic Forest, its distribution ranges from the state of Bahia to Rio de Janeiro. Animal poisoning (goats, sheep and cattle) by accidental ingestion were related to the species[1,2]. In this work, the dried and pulverized roots of *M. princeps* were subjected to extraction by maceration in 95% ethanol. The EEB was partitioned using the solvents hexane, $CHCl_3$ and AcEOt, respectively. The chloroform phase was subjected to MPLC on silica gel and Hexane, AcEOt and MeOH pure or in mixtures, followed by HPLC on an analytical and preparative scale on an Ace $C_{18}$ column, MeOH and 0.1% formic acid: $H_2O$ v/v, resulting in the purification of 9 amides: *N-trans*-sinapoyloctopamine (**1**), *N-trans*-feruloyloctopamine (**2**), *N-trans*-feruloyltyramine (**3**), *N-cis*-feruloyltyramine (**4**), *N-trans*-coumaroyltyramine (**5**), the position isomers of *N-trans*-feruloyl-3-methoxytyramine (**6**) and *N-trans*-sinapoyltyramine (**7**), and the geometric isomers of *N-trans*-grossamide (**8**) and *N-cis*-grossamide (**9**). These were identified from the analysis of 1D and 2D NMR spectra of $^1$H, $^{13}$C-APT, HRMS and comparison with literature data, and are the first natural products identified in the genus *Metternichia*.

**Figure 1:** Chemical structures of the compounds 1-9.



**1** $R_1 = OCH_3$, $R_2 = OCH_3$, $R_3 = OH$, $R_4 = H$
**2** $R_1 = OCH_3$, $R_2 = H$, $R_3 = OH$, $R_4 = H$
**3** $R_1 = OCH_3$, $R_2 = H$, $R_3 = H$, $R_4 = H$, *E*, $\Delta^{7(8)}$
**4** $R_1 = OCH_3$, $R_2 = H$, $R_3 = H$, $R_4 = H$, *Z*, $\Delta^{7(8)}$,
**5** $R_1 = H$, $R_2 = H$, $R_3 = H$, $R_4 = H$
**6** $R_1 = OCH_3$, $R_2 = H$, $R_3 = H$, $R_4 = OCH_3$
**7** $R_1 = OCH_3$, $R_2 = OCH_3$, $R_3 = H$, $R_4 = H$

**8** *E*, $\Delta^{7(8)}$
**9** *Z*, $\Delta^{7(8)}$

[1] PEDROSO, P. M. O. et al. Intoxicação por *Metternichia princeps* (Solanaceae) em caprinos no Estado da Bahia. Pesquisa Veterinária Brasileira, v. 35, p. 448-450, 2015.
[2] ARAÚJO, P. A. M. SONKIN, L. C. Estrutura de *Metternichia princips* Mikan (Solanaceae). Rodriguésia, v. 36, n. 58 p. 85-88, 1984.

## Agradecimentos/Acknowledgments

We thank the Graduate Program in Natural and Synthetic Bioactive Products for their support. This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) - Finance Code 001. We are also thankful for collaborating with Norte-Nordeste de Fitoprodutos (INCT-RENNOFITO) and the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq).

**Área: QPN**

# ANALYSIS OF ANTIMICROBIAL ACTION OF ESSENTIAL OIL OF *SCHINUS TEREBINTHIFOLIUS* RADDI IN *STREPTOCOCCUS PYOGENES* STRAINS

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*Key words: Schinus terebinthifolius Raddi, Brazilian pepper, Streptococcus pyogenes, Essential oil, Antimicrobial action.*

## Highlights

Chemical characterization and evaluation of antimicrobial activity of *Schinus terebinthifolius* Raddi oil in bacterial strains. Methods of Disk Diffusion and Broth Dilution.

## Abstract

One of the major public health problems faced in contemporary times is the worsening of antimicrobial resistance in bacterial strains. In this context, numerous studies with therapeutic products from medicinal plants have been carried out in search of the maintenance of human health. *Schinus terebinthifolius* Raddi presents antibacterial activity on gram-positive bacteria and anti-inflammatory property by inhibition of phospholipase enzyme A2, and this action is of a specific inhibitory nature, being directly linked to the triterpenes present in the fruits (PIRES et al., 2004). Based on the pharmacological capacity of this plant, the objective of this study was to characterize the major chemical constituents and verify the antibacterial potential of essential oil on strains of *Streptococcus pyogenes*, *Streptococcus mutans*, *Staphylococcus aureus* and *Escherichia coli*. The ripe fruits of the plant presented levels of 22.3% moisture and 6.2% of oil in relation to dry matter. The oil was obtained by hydrodistillation by steam drag, for a period of 3h. For chemical characterization, the essential oil was submitted to analysis by Gas Chromatography coupled to Mass Spectrometry (GC-MS), where the identification of the compounds was performed by comparing the mass spectre obtained experimentally with the Wiey spectral bank and also by the relative retention index (ADAMS, 1995). Thirty-one peaks were recorded on the chromatogram, of which 23 were identified (totaling 92.78% of the oil), which can highlight: δ-3-fairing (29.22%); β-felandreno (18.08%); α-felandreno (13.04%); α-pineno (12.94%); α-pineno (5.02%); sabine (3.25%) and germacreno-D (3.09%), with a higher concentration of monoterpenes in the aforementioned sample. In order to perform the microbiological tests, antimicrobial susceptibility tests were performed in order to determined the minimum injunction concentration (MIC). The first stage for antibacterial evaluation of the oil was performed by diffusion disc test, where it was possible to observe the formation of halo, which varied according to the bacteria tested. *S. aureus* presented a mean halo of 12.2 mm, *S. mutans* average of 7.33mm, *S. pyogenes* mean of 4.33mm and *E. coli* did not present halo. This fact can be explained by the high viscosity of the oil, which can hinder its dispersion in the agar and, consequently, cause a small inhibition halo. In the microdilution test, the minimum inhibition concentration (MIC) was 0.5 µL of the essential oil for all bacteria tested. At the minimum bactericidal concentration (MBC), there was bacterial growth of *E. coli* at concentrations 2; 4 and 8, with its MBC of 16 µL. *S. pyogenes*, *S. mutans* and *S. aureus* did not present bacterial growth, and their MBC was 0.5 µL. From the results presented, it was concluded that Brazilian Rose Pepper oil has antibacterial power against *Streptococcus pyogenes*, *Streptococcus mutans*, *Staphylococcus aureus* and *Escherichia coli*. In this respect, the fruit oil of *Schinus Terebinthifolius Raddi* is an excellent alternative of antibacterial product, being economical and ecological, because it is a native species, found with abundance and in much of the Brazilian territory.

## Acknowledgments

We thank the Federal Institute of Education, Science and Technology of Goiás - IFG for the opportunity, the Institute of Tropical Pathology and Public Health - IPTSP/UFG for the partnership in the execution of microbiological assays and the National Council for Scientific and Technological Development for the PIBIC-EM grant.

**Área: QPN**

# Anthelmintic neolignans from *Saururus cernuus L.* (Saururaceae)

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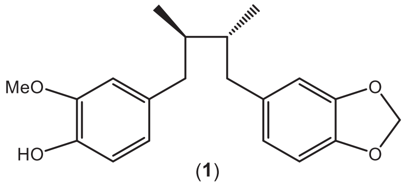
Palavras Chave: Saururus cernuus*, Neolignans, Anthelmintic activity.*

## Highlights

Activity-guided fractionation of EtOH extract from leaves of *S. cernuus* afforded *threo*-austrobailignan-6 (**1**) and verrucosin (**2**). Compounds **1** and **2** caused 100% of death in *S. mansoni* adult pairs after incubation period of 48h at 50 μM. Compound **1** showed $EC_{50}$ of 31.9 μM whereas compound **2** displayed $EC_{50} < 20$ μM, both with reduced toxicity ($CC_{50} > 200$ μM).

## Abstract

*Saururus cernuus* L. (Saururaceae) is an aquatic macrophyte found in North America and introduced in Brazil as an exotic species[1].Previous studies with *S. cernuus* describe the occurrence of neolignans with anti-*Trypanosoma cruzi* and anti-*Leishmania amazonensis* potential[2,3]. In continuation with our studies, the hexane phase from EtOH extract from leaves of *S. cernuus* were tested *in vitro* against the parasitic trematodes (flatworm) *Schistosoma mansoni,* a causative agent of schistosomiasis and displayed activity. Bioactivity-guided fractionation of this extract afforded two neolignans: *threo*-austrobailignan-6 (**1**) and verrucosin (**2**) (Figure 1), which were characterized by analysis of NMR and MS data. Both compounds caused 100% of death in *S. mansoni* adult pairs after the total incubation period of 48h at 50 μM. Compounds **1** and **2** were further tested at a range of concentrations for their effective concentration 50% ($EC_{50}$) determination. Compound **2** displayed high antischistosomal properties ($EC_{50} < 20$ μM), whereas **1** showed moderate anthelmintic activity ($EC_{50}$ of 31.9 μM), with both compounds exceeding the criteria established by the World Health Organization (WHO) for potential compounds as anthelmintic agents ($EC_{50}$ < 40-50 μM)[4]. Interestingly, compounds **1** and **2** showed a low potential of cytotoxicity, with cytotoxic concentrations 50% ($CC_{50}$) values > 200 μM for a monkey cell line (Vero) and a human cell line (SH-SY5Y), demonstrating the highly selective antiparasitic effect of these natural products. Collectively, the antischistosomal activity of compounds **1** and **2** surpasses criteria established by the WHO for anthelmintic hits, leads, and drug candidates.



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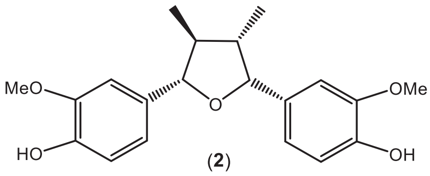

(**2**)

**References:** [1]Kubanek, J. et al. Phytochemistry, **2000**, 54, 281-287; [2]Brito, J. R. et al. *Fitoterapia*, **2019**, 137, 104251; [3]Brito, J. R. *J. Pharm. Pharmacol*. **2019**, 71, 12, 1871-1878. [4]Morais, C. S. et al. *Sci. Rep*. **2021**, 11, 23437.

## Acknowledgments

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**Área: ___QPN____**

# Antidiabetic, antiglycation, and antioxidant activities of ethanolic seed extract of Passiflora edulis and piceatannol *in vitro*

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*[1]Institute of Chemistry and Biotechnology, UFAL; [2]Dalhousie University Agricultural Campus, Truro, NS, Canada. [3] LAQV, REQUIMTE, Laboratory of Applied Chemistry, Department of Chemical Sciences, Faculty of Pharmacy, University of Porto, 4050-313 Porto, Portugal.*

Keywords: *Passion fruit, Piceatannol, Agro-industrial residues, Type 2 diabetes, Cytotoxicity, Seeds.*

## Highlights

Valorization of passion fruit seed residues for health. Piceatannol and PESE have potential for use in diabetes management. Were found to be capable of protecting cultured human cells from the oxidative stress.

## Abstract

Advanced glycation (AGEs) products are a diverse group of molecules formed through amino-carbonyl interactions and are associated with the development of several chronic-degenerative diseases, including diabetes type 2. Natural products offer a promising opportunity as a means of complementary interventions that can minimize the damage caused by the reactive products of glycation. Thus, the aim of this work was to investigate antidiabetic, antiglycation, and antioxidant potential of ethanolic extract of seeds of Brazilian *Passiflora edulis* fruits (PESE), a major by-product of the juice industry, and piceatannol (PIC), a major phytochemical of PESE. Antidiabetic activity was evaluated by the inhibitory potential of alpha-amylase, alpha-glucosidase and DDP-4 enzymes. The antiglycation potential was evaluated in the initial and intermediate stages of glycation. PESE, PIC, and acarbose (ACB) exhibited, $IC_{50}$ for alpha-amylase, 32.0 ± 2.7, 85.4 ± 0.7, and 0.40 ± 0.05 µg/mL, respectively and $IC_{50}$ for alpha-glucosidase, 76.2 ± 1.9, 20.4 ± 7.6, and 251.6 ± 4.5 µg/mL, respectively. The $IC_{50}$ of PESE, PIC, and sitagliptin (STG) for dipeptidyl-peptidase-4 (DPP-4) were 71.1 ± 2.6, 1138 ± 120, and 0.005 ± 0.001 µg/mL, respectively. PESE and PIC inhibited the formation of advanced glycation end-products (AGE) with $IC_{50}$ of 366 ± 1.9 and 360 ± 9.1 µg/mL for the initial stage and 51.5 ± 5.0 and 67.4 ± 4.6 µg/mL for the intermediate stage of glycation, respectively. Additionally, PESE and PIC inhibited the formation of β-amyloid fibrils up to 100%. $IC_{50}$ values for $DPPH^{\bullet}$ radical scavenging activity of PESE and PIC were 20.4 ± 2.1, and 1.7 ± 0.3, respectively. $IC_{50}$ values for scavenging HOCl were similar in PESE, PIC and quercetin (QCT) with values of 1.7 ± 0.3, 1.2 ± 0.5, and 1.9 ± 0.3 µg/mL, respectively. $IC_{50}$ values for scavenging $O_2^{\bullet-}$ for the PESE, PIC and quercetin were 38.2 ± 0.5, 7.3 ± 0.0 and 8.8 ± 0.3 µg/mL, respectively. PESE had no cytotoxicity on the human normal bronchial epithelium (BEAS-2B) cells up to 100 µg/mL, respectively. PESE and PIC were found to be capable of protecting cultured human cells from the oxidative stress caused by the carcinogen NNKOAc at 100 µM (Fig.1). The *in vitro* evidences of the inhibition of alpha-amylase, alpha-glucosidase, and DPP-4 enzymes as well as antioxidant and antiglycation activities, suggest further investigation on antidiabetic potential of *P. edulis* seeds and PIC.

## Agradecimentos/Acknowledgments

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**Area: ORG**

# Anti-inflammatory withajardins from the leaves of *Athenaea velutina*

**Késya Amanda Dantas Rocha (PG),[1] Tércio de Freitas Paulo (PQ),[1] Alejandro Pedro Ayala (PQ),[2] Valéria da Silva Sampaio (PQ)[3], Paulo Iury Gomes Nunes (PG)[4], Flávia Almeida Santos (PQ)[4], Kirley Marques Canuto (PQ)[5], Edilberto Rocha Silveira (PQ),[1] Otília Deusdenia Loiola Pessoa (PQ).[1*]**

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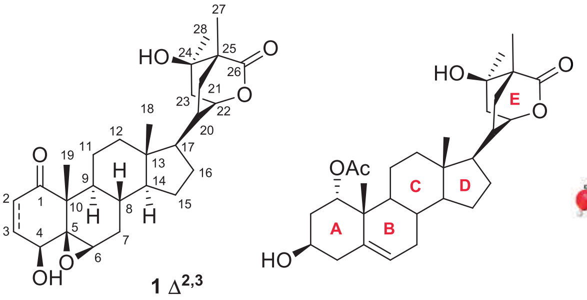
*Keywords*: *Athenaea velutina, Solanaceae, Withanolides, Withajardins, Anti-inflammatory activity.*

## Highlights

- Three withajardins were isolated from the leaves of *Athenaea velutina.*
- Their absolute configuration was determined by x-ray diffraction and circular dichroism analyses.
- The withajardins showed attenuated LPS-induced release of NO and decreased pro-inflammatory cytokines TNF-α and IL-6 in RAW264.7 cells.

## Abstract

Withajardins, uncommon modified withanolide-type steroids, have been isolated exclusively from plants of the Solanaceae family so far. Undescribed withajardins (**1** – **2**) and the known tuboanosigenin (**3**) were isolated from the hexane/EtOAc 1:1 extract from *Athenaea velutina* leaves. Their structures were established by an extensive analysis of 1D- and 2D-NMR and HRMS data. The absolute configuration was determined by x-ray diffraction (**1** and **3**) and circular dichroism (CD) analyses (**2**).



**1** $\Delta^{2,3}$

**2**

**3**

**Fig. 1.** Structures of withajardins **1 – 3**.

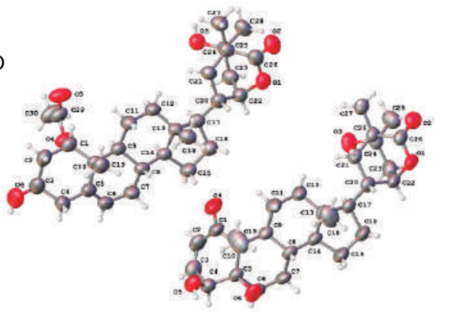


**Fig.2.** X-ray ORTEP drawing of withajardin L (**1**) and tuboanosigenin (**3**).

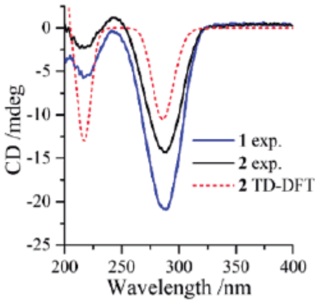


**Fig. 3.** Experimental CD spectra of **1** and **2** (in $CH_3OH$) and calculated CD spectrum of **2**.

The anti-inflammatory activity of **1** – **3** was evaluated through the inhibition of the lipopolysaccharide (LPS)-induced nitric oxide (NO), TNF-*α*, and IL-6 release in RAW264.7 cells. The cell viability effects to RAW 264.7 cells showed IC50 values of 74.43 to 354.40 μM. Compounds **1** – **3** attenuated LPS-induced release of NO and decreased pro-inflammatory cytokines TNF-*α* and IL-6 in RAW264.7 cells.

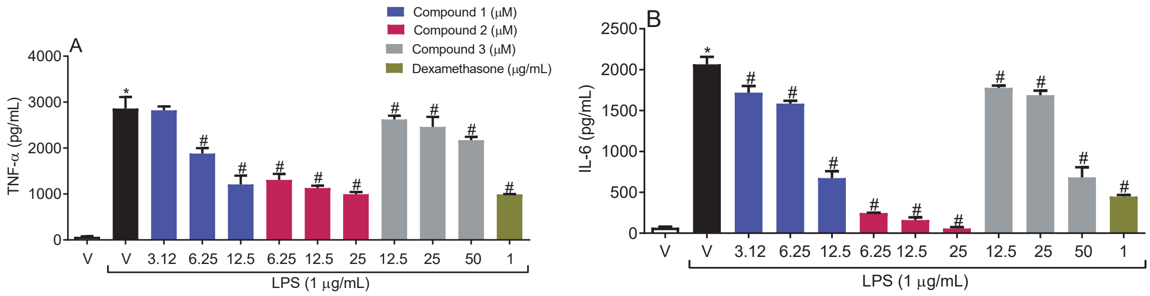


**Fig. 4.** Inhibitory effects of compounds **1** − **3** on the secretion of TNF-*α* (A) and IL-6 (B) in RAW264.7 cells stimulated with LPS (1 μg/mL). Dexamethasone (1 μg/mL) was used as the positive control. DMSO was used as a solvent for both the test compounds and dexamethasone was added to the control vehicle (V) and non-stimulated cells (C). The results are expressed as mean ± S.D. for three independent experiments, measured in triplicate. $^*p < 0.05$ compared to non-stimulated cells (C); # $p < 0.05$ compared to control vehicle (V).

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## Acknowledgments

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**Área: QPN**

# Antileishmanial activity of *triterpenes* from *Clusia studartiana*.

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Palavras Chave: *Clusia studardiana*, *leishmaniasis*, *antipromastigota activity, antileshimanial activity*

## Highlights

-Leishmaniasis is a group of endemic and neglected diseases caused by protozoa of the genus *Leishmania*.
-Currently there are more than 1 billion of people living in endemic areas for leishmaniasis with risk of infection.
-Drugs used to treat this illness have many toxic effects and cause several adverse reactions.
-Pentacyclic triterpene isolated from aerial parts of *Clusia studartiana* had shown a promising antileishmanial activity.

## Resumo/Abstract

Leishmaniasis is a group of endemic and neglected diseases caused by protozoa, belonging to the genus *Leishmania* and transmission occurs through the bites of female sandflies, and the reservoirs of the parasites are humans, wild rodents and domestic dogs. These parasites have two forms: the promastigote (flagellated form found in the vector's digestive tract) and the amastigote (intracellular spherical non-flagellated form lodged in macrophages)[1]. Currently, there are more than 1 billion of people living in endemic areas for leishmaniasis which risk of infection. Annually, it was estimated the occurrence of 30,000 new cases of visceral and more than 1 million of new cases of cutaneous leishmaniasis[2]. Drugs used to treat this illness have many toxic effects and cause several adverse reactions. In this way, it is relevant to research alternative medicines, especially those of natural origin. The aim of this study was to evaluate the leishmanicidal activity of partitions of the ethanolic extract of *C. studartiana* C. M. Vieira & Gomes da Silva (aerial parts) of and its pentacyclic triterpenes isolated. For this purpose, *L. amazonensis* promastigotes were incubated in Schneider's medium at 26° C for 72 h with partitions in chloroform (CS-C) or ethyl acetate (CS-Ac) or with pure four pentacyclic triterpenes (CS-3, CS-4, CS-5 and CS-15) at the concentrations 3.12-200 µM. The parasite viability was evaluated by adding of Alamar Blue (resazurin) and incubated for 3 h, using pentamidine (0.39 -25 µM) as positive control and DMSO (solvent) as negative control. This colorimetric assay is based on the reduction of non-fluorescent resazurin to resorufin that fluoresces red. Viable cells perform this conversion, generating a quantitative measure of viability that was measured by fluorimetry. After time of incubation, fluorescence was quantified by fluorimetry with excitation at 560nm and emission at 590nm. These experiments were performed in triplicate. The $IC_{50}$ calculation was determined by non-linear logarithmic regression in the GraphPad Prism 5.0 program. The chloroformic partition (CS-C) showed $IC_{50}$=19.97 ± 1,48 µg/mL, while the partition in ethyl acetate (CS-Ac) was higher than 100 µg/mL. Among these four isolated triterpenes evaluated, only CS-3 was a relevant anti-promastigote activity, with $IC_{50}$=12.5 ± 0.23 µM. In the next step, this triterpene will be evaluated in intracellular amastigotes, to continue studying its promising antileshimanial activity.

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## Agradecimentos/Acknowledgments

Farmanguinhos, FIOCRUZ

**Área: _QPN_______________**

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

# Antimycobacterial activity of biflavonoids from *Kielmeyera membranacea* by zebrafish larvae model

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*Keywords: Natural products, Biflavones, Podocarpusflavona A, Mycobacterium tuberculosis.*

## Highlights

The isolated biflavonoid, podocarpusflavona A, inhibition greater than 85% of growth of *Mycobacterium* strains *in vitro* and inhibited more than 80% of infection in zebrafish larvae. In addition, it was possible to observe the modulation of cytokines and no significant toxic effect.

## Resumo/Abstract

Tuberculosis (TB) is still a threat in many regions of the world. In 2019, it was estimated the world average of 10.0 million cases, with 1.4 million deaths. The increased incidence rates of multi- and extensively drug resistant strains, also makes it difficult to TB control. In this context, it is important to identify new anti-TB agents. Natural products are part of an important strategy for developing drugs for treatment of TB. The use of plants as a therapeutic resource or as a complementary therapy has been going on for centuries. Compounds of plant origin, belonging to different chemical classes, have been investigated and showed antimycobacterial activity. Therefore, the Jurubatiba Restinga National Park, which has a rich diversity of plants, is a promising source in the search for bioactive compounds. *Kielmeyera* species have been described with medicinal popular use for infections. However, little has been reported about *Kielmeyera membranacea* Casar. (Calophyllaceae). This study aims to evaluate the antimycobacterial activity *in vitro* and *in vivo* and the possible immunomodulatory action of *K. membranacea*. From leaves of *K. membranacea* the crude ethanolic extract was prepared and later its fractions by liquid/liquid partition with solvent of increasing polarity. The fraction in dichloromethane showed promising activity and was guided to the fractionation process in column with Sephadex LH-20. This process yielded 6 subfractions and isolated compound (podocarpusflavone A - PCFA). The samples were assayed against *Mycobacterium bovis* BCG, *M. tuberculosis* H37Rv e M299 e *M. marinum* 927 e Mcherry E11 strains. The fraction in dichloromethane was the most active, inhibited to the following strains BCG, H37Rv, M299, Mcherry E11 ($MIC_{50}$ de 0.95, 4.38, 21.16, 18.20 µg/mL, respectively). The subfractions showed different sensitivity for each of the strains. The PCFA, one of the most active, showed *in vitro* inhibition greater than 85% and continued to the next stage of evaluation *in vivo* by zebrafish larvae model. After analysing the data, it was possible to observe 18.07±8.75 relative fluorescence units (URF) compared to 100 URF in the infected control, suggesting an inhibition greater than 80% at the concentration of 32 µM. The subfraction 6, containing 2 biflavonoids, showed 23.70±2.10 relative fluorescence units (URF) compared to 100 URF in the infected control suggesting an inhibition greater than 75% at the concentration of 32 µM. No statistical differences were observed between PCFA and subfraction 6 when compared with antibiotic rifampicin at the same concentration (positive control). These results suggest that *K. membranacea* samples are promising against mycobacterial growth. Although further studies are needed to confirm its effectiveness and the action mechanism, the PCFA was active *in vivo*, inhibiting mycobacterial growth, modulating cytokines and showed no significant toxic effect. In addition, it was possible to demonstrate that *in vitro* screening may be an efficient strategy for selecting bioactive samples.

## Agradecimentos/Acknowledgments

CAPES, FAPERJ, UFRJ, IBL-Leiden

**Área:** QPN **Inscrição: 00479**

# Antinociceptive and Anti-inflammatory Activity of Biomass and Aqueous Extract of *Arthrospira platensis* Cultivated *Indoor*

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Palavras Chave: *Arthrospira platensis*, Microalga, *Antinociceptive activity, inflammation, Aqueous fraction, Biomass*

## Highlights

This work evaluated the antinociceptive and anti-inflammatory activity of biomass and aqueous fraction of the microalga *A. platensis* which is reported to have a broad spectrum of pharmacological activity.

## Resumo/Abstract

**Introduction:** *Arthrospira platensis* is a microalga with great pharmacological and alimentary value due to rapid growth and high productivity of several compounds as proteins, carbohydrates, carotenoids and the pigment phycocyanin. This pigment found in this biomass and aqueous extract is reported to produce a broad spectrum of biological activities, such as antiparasitic and anti-inflammatory activity.[1] This work investigated comparatively the antinociceptive and anti-inflammatory effects of the biomass and the aqueous fraction which was not previously described. **Objective:** To evaluate the antinociceptive and anti-inflammatory effects of biomass and its aqueous fraction of *A. platensis*, as well quantify the main compounds present in biomass and aqueous fraction in order to identify which compounds are responsible for these activities*.* **Methodology:** *A. platensis,* was cultivated in erlenmeyers (500 mL) containing Zarrouk medium modified by George, under LED white light, T=25±2ºC and constant stirring. After cultivation, biomass was recovered and lyophilized.[1] The aqueous extract was obtained by freezing / thawing method, which was also used to quantify the phycobiliproteins, according to Bennett and Bogorad (1973)[2] followed by lyophilization. Carotenoids and chlorophyll were extracted from the biomass according to the method described by Strickland & Parsons (1972) [3] and quantified according to Lichtenthaler (1987)[4] and lipids were extracted and quantified according to Bligh & Dyer (1959)[5]. Formalin (2.5%) was used to evaluate the antinociceptive and anti-inflammatory activity which was i.p. injected into the right hind paw of male Swiss mice (25–35 g, n=6) 1 hour after oral administration of either biomass or aqueous extract (1 mg/kg) or acetyl salicylic acid (300 mg/kg). The total time spent by each animal licking the injected paw was measured in the 2 phases of the test: neurogenic (5 min) and inflammatory (15 min).[6] **Results and discussion:** Formalin-induced reactivity was reduced from 101±0,4 to 48±0,3 and to 45±0,7 during the neurogenic phase after administration of biomass and aqueous extract, respectively. The reduction was more effective than with AAS (77±1,3). Similar results were observed with the biomass and AAS in the inflammatory phase, because the reactivity was reduced from 253±3,0 to 81±2,0 and 70±1,0, respectively. High amount of total lipids (207 mg/g) and a satisfactory amount of carotenoids (4,8 mg/g) were detected in the composition of the biomass which were not present in the aqueous extract, suggesting their involvement in the activity at the inflammation phase. Since both biomass and aqueous extract produced reduction of reactivity at the neurogenic phase, phycobiliproteins, in special phycocyanin (125 mg/g) could be responsible for this activity. This is the first report of about the difference between antinociceptive and anti-inflammatory action of the phycobiliproteins present in *A.platensis*, which are always reported as responsible for both activities, showing other compounds (carotenoids and lipids) as responsible for the anti-inflammatory activity. **References:** [1]Cavalcanti *et al.*, *Ed. Atena*, cap. 6, **2018** [2]Bennett & Bogorad. *J Cell Bio* 58(2), 419-435, **1973**; [3] Strickland & Parsons. A practical handbook of seawater analysis, Issue 167, **1972.** [4]Lichtenthaler, H. K. *Methods in Enzymology*, v. 148, p. 350-382, **1987**. [5]Bligh EG, Dyer WJ, *Canadian J of Biochem and Physio* 37(8): 911–917, **1959**. [6]Montes *et al. Molecules* 22 (800)**:** 1-14, **2017**.

## Agradecimentos/Acknowledgments

CNPq.

**Área: QPN**

# Antioxidant activity and neuroprotective effect hydroalcoholic extract of *Bougainvillea glabra* Choisy bracts

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Palavras Chave: *Antioxidant activity, Bougainvillea glabra* Choisy *bracts, Phenolic compounds, neuroprotective effect, Drosophila melanogaster*

## Highlights

Antioxidant activities and neuroprotective effect of Bougainvillea glabra Choisy (EBBGC) bracts were evaluated.
The antioxidant activity and neuroprotective effect were observed in EBBGC bracts.

## Resumo/Abstract

Antioxidant activity and neuroprotective effect of the hydroalcoholic extract of Bougainvillea glabra Choisy (BGC) Bracts were studied. Crude Extract (EBBGC) of fresh BGC Bracts were used (hydroalcoholic solution (1EtOH: 3H2O) extraction, shaken (150 rpm, 35 °C, 24h stirring), filtered, concentrated on a rotary evaporator and submitted to Freeze-Drying process). In vitro antioxidant activity of EBBGC against scavenging capacity was evaluated using ABTS (% INIB), DPPH (IC50) and FRAP assays. Total phenolic compounds were performed using the Folin-ciocalteu. Results were shown in Table 1. Mitochondrial activity (MTT) and ROS formation (DCF-DA) assays (Fig 1) were available. *In vivo* studies were performed using *Drosophila melanogaster* flies model through survival (Fig.2) and locomotor (negative geotaxis (Fig.3A) and locomotor behavior (Fig 3B)) assays[1].

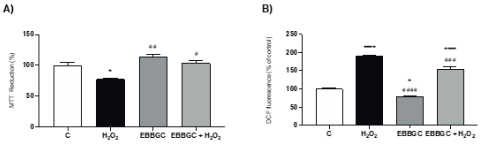

Fig. 1. In vitro antioxidant activity of EBBGC. A) effects of EBBGC on mitochondrial activity (MTT) and B) ROS production. Cell-rich fractions were incubated with H2O2 and EBBGC for 1 h. results are expressed as a control percentage. Data are mean ± SEM; ** $p < 0.01$, * $p < 0.05$ compared to control; # # # $p < 0.001$, # # $p < 0.01$, # $p < 0.05$ when compared to the $H_2O_2$ group.

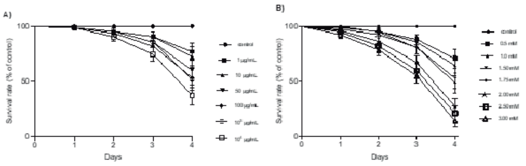

Fig. 2. Survival rate of flies exposed to different concentrations of A) EBBGC and B) Paraquat. Data collection was performed every 24 h for each group for 4 days. Data are presented as mean ± S.E. The total number of flies (80 per group) represents the sum of four independent experiments (n=4).

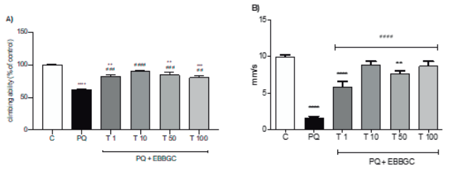

Fig. 3. Effect of PQ and EBBGC on behavior. A) climbing ability activity and B) Balance test co-exposed to PQ at a concentration of 1.75mM + EBBGC in different concentrations 1, 10, 50 and 100 µg/mL (T1, T10, T50 and T100, respectively for 4 days. The total number of flies represents the sum of 3-4 independent experiments. Data are expressed as mean ± SEM, followed by Tukey's Test. *$p \leq 0.05$, **$p \leq 0.01$, ***$p \leq 0.001$ and ****$p \leq 0.0001$ indicate differences considered significant in relation to the control group (C) and ($^{\#}p \leq 0.05$, $^{\#\#}p \leq 0.01$, $^{\#\#\#}p \leq 0.001$ and $^{\#\#\#\#}p \leq 0.0001$) indicate differences considered significant in relation to the PQ group.

Table1: Antioxidant activity of EBBGC.

| | ABTS (% INIB) | DPPH ($IC_{50}$) | FRAP (µM de $FeSO_4.mL^{-1}$) | FOLIN-CIOCALTEU (µg Eq Chlorogenic acid. $mL^{-1}$) |
|---|---|---|---|---|
| **EBBGC** | 86.42 ± 0.52 | 0.34 ± 0.04 | 3047.30 ± 86.92 | 2594.25 ± 1.63 |

Data are expressed as mean ± SD (n=3).

Results present in Table 1 indicate that EBBGC bracts present antioxidant activity. Similar results were observed in relation to MTT and ROS results (Figs. 1A and 1B) and *In vivo* results (Fig.2A and 2B; Fig.3A and Fig. 3B). We conclude that EBBGC has a high antioxidant capacity as well as showed a significant neuroprotective effect against paraquat stressor agent in *Drosophila melanogaster*.

**Reference:**

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DOI: https://doi.org/10.1016/j.biopha.2017.08.073

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**Área: QPN**

# Antiparasitic activity evaluation of a new pseudo-disesquiterpenoid and related eudesmanes from *Nectandra barbellata* (Lauraceae)

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*Keywords:* Nectandra barbellata*, ionic liquid, sesquiterpenes, pseudo-disesquiterpenoid,* Trypanosoma cruzi.

## Highlights

This work reports the use of ionic liquid in the microwave assisted extraction (MAE) of a new pseudo-disesquiterpenoid and related eudesmanes from *Nectandra barbellata* (Lauraceae) leaves with antiparasitic activity.

## Abstract

In this work, the leaves of *Nectandra barbellata* (Lauraceae) were extracted using the ionic liquid 1-butyl-3-methylimidazolium bromide (BMImBr) in $H_2O$, assisted by microwave (MAE).[1] This aqueous extract was partitioned with EtOAc and the organic phase was subjected to successive chromatographic steps on silica gel and/or Sephadex LH-20 to provide the isolation of four compounds (**1** – **4**): two eudesmane-type sesquiterpenes (**1** and **2**), an iphionane-type rearranged sesquiterpene (**3**) and one new pseudo-disesquiterpene (**4**). Structures of the isolated compounds (Figure 1) were elucidated using MS and NMR analysis, as well as comparison of the data obtained with those described in the literature.[2,3] In addition, compounds were evaluated for anti-*Trypanosoma cruzi* activity *in vitro* and cytotoxicity was evaluated on NCTC cells. The results obtained are shown in Table 1.

**Figure 1.** **S**esquiterpenes from *Nectandra barbellata* (Lauraceae).

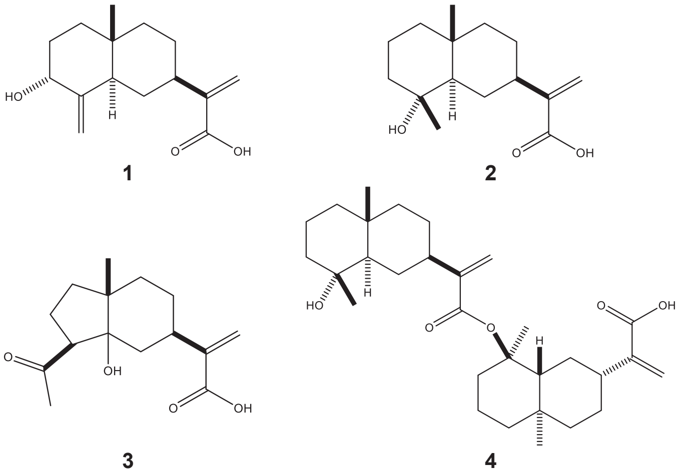

**Table 1.** Effects of compounds **1** – **4** against extracellular forms of *Trypanosoma cruzi* and NCTC cells.

| Compounds | ***T. cruzi*** **$EC_{50}$ / µM (95% CI)** | **NCTC $CC_{50}$ / µM (95% CI)** | **SI** |
|---|---|---|---|
| | trypomastigote | | trypomastigote |
| **1** | > 100 | > 200 | - |
| **2** | > 100 | > 200 | - |
| **3** | > 100 | > 200 | - |
| **4** | 13.2 ± 5.0 | 93.9 ± 2.7 | 7.1 |
| Benznidazole* | 5.5 ± 2.2 | > 200 | > 36.4 |

$EC_{50}$: 50% Effective concentration; $CC_{50}$: 50% Cytotoxic concentration; 95% CI: 95% confidence interval; SI: Selectivity index; NA: not active. *Standard drug.

The results of the anti-*T. cruzi* activity revealed that compounds **1** – **3** did not present toxicity against NCTC cells ($CC_{50}$ > 200 µM) and shown to be inactive for *T. cruzi* trypomastigote forms. On the other hand, compound **4** was active for *T. cruzi* with an $EC_{50}$ value of 13.2 µM and SI of 7.1. In view of these results, this work contributes to obtaining new compounds with antiparasitic potential through an alternative procedure, using ionic liquids and MAE.

## Acknowledgments

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**Área: QPN**

# Atividade anti-Leishmania de isocumarinas isoladas de *Aspergillus* sp. Endofítico de *Aspidosperma exceulsum* (Apocynaceae).

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Palavras Chave: *5-hidroximetilmalleina, 5-metilmalleina, Aspergillus sp., antiLeshimania.*

## Highlights

Anti-*Leishmania* activity of isocoumarins isolated from *Aspergillus* sp. Endophytes of *Aspidosperma exceulsum* (Apocynaceae). Isocoumarins are secondary metabolites found in a wide variety of organisms. The present work evaluated the leishmanicidal activity of iscomurins isolated from the fungus *Aspergillus* sp.

## Resumo/Abstract

A natureza fornece uma enorme variedade de moléculas complexas. A alta diversidade química em produtos naturais está relacionada com a disponibilidade de precursores e reações biossintéticas, além de sua função no sistema biológico. Os fungos endofíticos são microrganismos que vivem no interior de tecidos ou órgãos dos vegetais realizando interações simbióticas mutualísticas ou neutras, não causando doenças aos seus hospedeiros. Os metabólitos secundários produzidos por fungos endofíticos possuem um amplo espectro de bioatividade, como antimicrobianos, antioxidantes, antitumorais, enzimáticos e surfactantes. Isocumarinas são metabólitos secundários encontrados em uma grande variedade de organismos, como bactérias, fungos, liquens, entre outros. Esta classe de substâncias apresenta diversas atividades biológicas como inibidora de proteases, antimicrobiana, reguladoras de crescimento, antialérgica, antimalárica. Segundo alguns trabalhos reportados na literatura os fungos endofíticos são capazes de biossintetizar compostos semelhantes as plantas hospedeiras. O gênero *Aspidosperma* pertence à família Apocynaceae e tem como carcteristica a presença de alcaloides indólicos, com extenso espectro de atividades biológicas como antitumoral, antimicrobiana, antibacteriana e leishmanicida. Assim, o presente trabalho, avaliou a atividade leishimanicida de iscomurinas isoladas do fungo *Aspergillus* sp., endofítico de *A. excelsum*. Os extratos foram inicialmente fracionados por cromatografia em coluna de sílica usando hexano, acetato de etila e metanol como fase móvel em gradiente crescente de polaridade. As frações foram analisada por TLC e as melhores frações foram submetidas a HPLC seme-prep Waters® coluna C18 5µm 4,6 X 250 mm Sunfire, com uma eluição em gradiente $H_2O$/MeOH (90:10 → 0:100) por 30 minutos. Foram isoladas duas substâncias, que após analisadas por RMN de $^1H$ e $^{13}C$ e comparadas com a literatura pode-se constatar que se tratava das isocumarinas: 5-hidroximetilmalleina (1), 5-metilmalleina (2). As substâncias 1 e 2 foram avaliadas em ensaio antiparasitário. A avaliação da capacidade de inibição 100% das formas promastigotas de *L. amazonenses* foram realizadas após 24, 48 e 72 horas de tratamento. Os resultados evidenciaram um $IC_{100}$ maior que 1000 µg/mL em 24 horas, 100 µg/mL em 48 horas e 500 µg/mL em 72 horas para a substância 1. Já para a substância 2, foi observado $IC_{100}$ maior que 250 µg/mL nos três tempos de tratamento. Os resultados nos ensaios anti-leishmania são moderados, mas as substâncias serão modificadas estruturalmente a fim de se obter derivados mais ativos.

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**Área: QPN** **Nº de Inscrição: 753**

# Avaliação da síntese de ozonídeos na reação de ozonização do óleo de girassol (*Hellianthus annuus*) empregando a técnica de Infravermelho

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Palavras Chave: *Ozonídeos, Hellianthus annuus, Índice de peróxidos, Infravermelho*

## Highlights

Evaluation of ozonide synthesis in the ozonation reaction of sunflower oil (Hellianthus annuus) using the Infrared technique

- Ozonized sunflower oils in 8 concentrations were prepared via the ozonation reaction.
- The analysis of the ozonide content of the oil samples was carried out using the peroxide and infrared index methods.

## Resumo/Abstract

A utilização de óleos ozonizados no tratamento de patologias que acometem a pele, principalmente as feridas crônicas é crescente, visto que os tratamentos convencionais oferecidos para estas condições como o pé diabético, úlcera varicosa, úlcera por pressão, cirurgias, entre outras, muitas vezes não alcançam uma cicatrização completa e nos últimos tempos não tem trazido nenhum tipo de inovação para estes pacientes. A propriedade de oxigenação sobre os tecidos, promovendo a aceleração nos processos de cicatrização é o mecanismo de ação dos ozonídeos, substância ativa dos óleos ozonizados. Também atuam reduzindo drasticamente os processos de infecção devido à sua atividade antimicrobiana. A metodologia empregada na obtenção do óleo ozonizado foi a reação de ozonização com gerador de ozônio de potência 10g/h da marca WIER, através da técnica de borbulhamento do gás na matriz do óleo vegetal poliinsaturado da semente do girassol (*Hellianthus annus*), acrescido de 10% de água deionizada. A reação do ozônio com olefinas já foi revisada algumas vezes e o mecanismo aceito para esta reação é o proposto por Criegee.[1] Para avaliarmos o grau de ozonização das amostras foi aplicado o teste de índice de peróxidos. Os valores obtidos foram: 4,5 (amostra não ozonizada), 150, 280, 350, 500, 750, 1000, 1400 mEq. Uma metodologia alternativa para análise dos óleos ozonizados e que dispensa o uso de reagentes químicos é o emprego do infravermelho. Com esta técnica foi possível verificar a intensificação de sinais de forma crescente, à medida que as concentrações da amostra aumentavam, na região de 1740 $cm^{-1}$, referente à ligação C – O característica nos ozonídeos. Ao mesmo passo os sinais que indicam presença de olefinas, em torno de 1640 $cm^{-1}$ vão desparecendo à medida que o grau de ozonização aumenta. Portanto o acompanhamento da reação de ozonização pela técnica de infravermelho é uma forma prática, rápida, segura e de baixo custo para garantia da qualidade dos óleos ozonizados.

1.Criegee, R. Angew. Chem. Internat. Ed. 1975. Vol 14 (745-752)

## Agradecimentos/Acknowledgments

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Laboratório de Pesquisas em Substâncias Bioativas - LAPESB

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

# Bioguided Study of Bioactive Metabolites from Plant Species to Leishmaniasis Disease.

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Key words: *Natural Products, Phytochemistry, Leishmania amazonensis, Antipromastigote*

## Highlights

- Leishmaniasis is a neglected disease and still lacks effective alternative treatments.

- Tegumentary leishmaniasis is not lethal, but the visceral ones commonly affects children and can lead to death.

- Extracts, fractions and isolated substances from different species of plants had shown promissing antileishmanial activity

## Resumo/Abstract

Leishmaniasis is a neglected infectious but non-contagious disease that affects millions of people worldwide. It is caused by protozoa of the genus *Leishmania* and transmitted by mosquitoes commonly found in forest regions. Tegumentary leishmaniasis is not lethal, but the visceral is a systemic disease that commonly affects children up to ten years and can lead to death. The parasitological diagnosis is by direct examination or cultivation of materials of infected tissue. Immunological methods by indirect immunofluorescence, enzyme-linked immunosorbent assay (ELISA) and molecular methods (PCR) are also used. The drugs recommended for human use are expensive, but the SUS (Brazilian public healthcare system) offers treatment for this disease. Nevertheless, because it is long-lasting and causes relevant side effects, they end up leading to the discontinuity of treatment by the patient, leading to the development of parasite resistance to the drugs used. Consequently, there is an urgent need to search for effective alternative treatments. Natural Products have been used by humanity since the beginning of their existence, moreover Brazil occupies a prominent position in the biodiversity of the planet. Much of it still has an unknown phytochemical and pharmacological profile. Plants have been described as an excellent source of bioactive substances, and are therefore strong candidates for the development of new medicines. This study aimed to investigate extracts, partitions and substances isolated from different species of plants with potential antileishmanial activity. The families studied were Anacardiaceae, Bignoniaceae, Clusiaceae, Chrysobalanaceae, Lauraceae, Malpighiaceae, Marcgraviaceae, Piperaceae and Solanaceae. To realize this experiment, *Leishmania amazonensis* promastigotes were incubated in Schneider's medium at 26 °C for 72 h with increasing concentrations of extracts, fractions and isolated substances, diluted in DMSO. The parasite growth was evaluated using resazurin by fluorimetry 560/590 nm. The $IC_{50}$ (concentration that inhibits 50% of growth) was determined in relation to the control by logarithmic nonlinear regression analysis in GraphPad Prism 5.0. Among the samples studied, promising antipromastigote activities for *L. amazonensis* were shown for the butanol fraction of the partition of ethanol extract of leaves of *Schwartzia brasiliensis* (SBFE3Bu), hexane, dichloromethane, ethyl acetate and butanol fractions of the partition of leaf extract of *Aureliana fasciculata* (AFfPH, AFfPD, AFfPAc, AFfPBu) and precipitate of the ethanol extract of fruits of *Licania tomentosa* (LTPEW-pp), with $IC_{50}$ values of 55.30 ± 6.14 µg/ml, 26.62 ± 0.06 µg/ml, 1.85 ± 0.69 µg/ml, 11.37 ± 0.08 µg/ml, 12.98 ± 0.06 µg/ml and 27.19 ± 2.65 µg/mL, respectively. For the tested isolated substances, significant results were found for the phenolic acid derivative of *Schinus terebinthifolius* (GM), the *Piper tectoniifolium* lignan (PN1) and the *Ocotea odorifera* kavalactone (PN2), which exhibited the respective $IC_{50}$ values of 44.33 ± 7.88 µM, 36.33 ± 6.56 µM and 44.08 ± 3.37 µM. All the other samples tested were non-active up to 100 µg/ml. The next step will be to confirm the antileishmanial activity in intracellular amastigotes. This bioguided approach highlights the importance of natural products as a promising source of pharmacologically active substances in the discovery of new drugs.

## Agradecimentos/Acknowledgments

CNPq; FAPERJ; CAPES; FIOCRUZ

**Área: QPN**

# Can the trypanocidal activity of new derivatives from dehydrodieugenol B and its methyl ether, isolated from *Nectandra leucantha*, be improved by addition of methylformate group via olefin cross-metathesis reaction?

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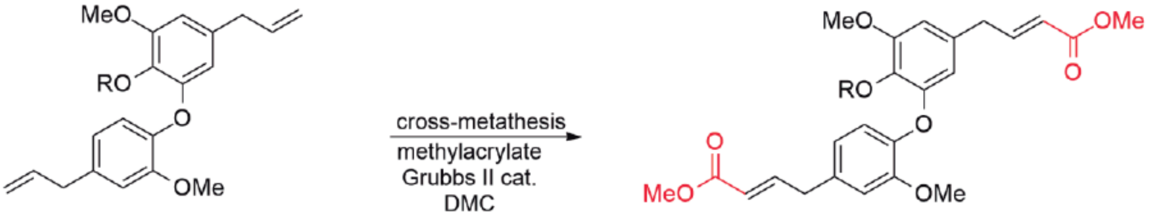
Key words: *olefin metathesis,* Trypanossoma cruzi*, dehyidrodieugenol B.*

## Highlights

This work presents the preparation and anti-*Trypanosoma cruzi* activity of two methylformyl derivatives from dehydrodieugenol B and methyldehydrodieugenol B, isolated from *Nectandra leucantha*, via olefin cross-metathesis reaction. Additionally, mechanism of action from these new derivatives on parasite were investigated.

## Abstract

Chagas disease is a tropical disease caused by *T. cruzi*.[1] It was estimated that at least one million people are infected in Brazil. Therapy is restricted to two drugs: benznidazole and nifurtimox, with severe side effects.[1] In this work, it was described the preparation of methylformyl-dehydrodieugenol B (**1a**) and methylformyl-methyldehydrodieugenol B (**2a**) using dehydrodieugenol B (**1**) and methyldehidrodieugenol B (**2**), isolated from *Nectandra leucantha* twigs[2], by cross-metathesis reaction using methyl acrylate catalyzed by the second generation Hoveyda catalyst (2 mol%) at 80°C in the environmentally friendly dimethyl carbonate solvent. Natural products **1** and **2** as well as derivatives **1a** and **2a** were tested against trypomastigote and amastigote forms of *T. cruzi*.



**1** R = H
**2** R = Me

**1a** R = H
**2a** R = Me

| | $IC_{50}$ (uM) trypomastigote | $IC_{50}$ (uM) amastigote | $CC_{50}$ (uM) NCTC |
|---|---|---|---|
| **1** | 38.6 ± 13.6 | 86.5 ± 10.4 | >200 |
| **2** | NA | NA | >200 |
| **BNZ** | 5.5 ± 0.9 | 18.7 ± 4.1 | >200 |

| | $IC_{50}$ (uM) trypomastigote | $IC_{50}$ (uM) amastigote | $CC_{50}$ (uM) NCTC |
|---|---|---|---|
| **1a** | 13.5 ± 11.0 | 10.2 ± 2.8 | 139.8 |
| **2a** | 23.0 ± 2.1 | 6.1 ± 0.7 | >200 |
| **BNZ** | 5.5 ± 0.9 | 18.7 ± 4.1 | >200 |

**Fig.1.** Preparation of compounds **1a** and **2a** via olefin cross metathesis reaction from **1** and **2** and $IC_{50}$ and $CC_{50}$ values against trypomastigote and amastigote forms of *T.cruzi*

As observed, the addition of methylformyl group at allyl side chain in starting material caused enhancement of antiparasitic activity, mainly against amastigote forms since compounds **1a** and **2a** displayed $IC_{50}$ values of 10.2 ±2.8 and 6.1 ±0.7 μM, respectively, superior than started materials **1** and **2** and standard drug benznidazole ($IC_{50}$ 18.7 ±4.1 μM). However, **1a** showed slightly toxicity ($CC_{50}$ = 139.8 μM) while **2a** was non-toxic ($CC_{50}$ > 200 μM) against NCTC cells. Based on these results, possible phenotypical mechanisms of action of **1a** and **2a** were evaluated. Initially, a depolarization of the plasma membrane electric potential of the parasite was observed for both derivatives as they were capable to depolarize the mitochondria membrane until two hours of incubation. Considering the potential of compound **2a** and its easily obtention from the natural product **2**, it could be considered a new hit compound for future drug design studies in Chagas disease.

[1]Secretaria de Vigilância em Saúde, Ministério da Saúde, Epidemiological Report – Chagas disease **2021**
[2]Grecco, S.S., S, F. F., et al. J. *Venom.Anim.Toxins Incl. Trop. Dis*, **2018**, 24 (5), 122.

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**Área: QPN**

# Carvacrol as larvicide for the control of *Aedes aegypti*: in vitro and in silico toxicity evaluation for humans as non-target organism

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Palavras Chave: *Carvacrol, Aedes aegypti, Larvicide, Toxicity, In vitro, In silico*

## Highlights

Carvacrol toxicity were evaluated using in vitro and in silico models. The data suggest that the proposed use as a sanitizing agent does not lead to side effects for the populations living around.

## Resumo/Abstract

The essential oils of oregano and fennel, rich in carvacrol, are natural products that have shown promising results as an alternative to conventional controls of *Aedes aegypti*, the main vector of dengue, Zika and Chikungunya viruses. The toxicological risk to humans exposed as non-target organism was assessed subjecting carvacrol to a series of in vitro biomimetic reactions using metalloporphyrins (oxidants iodosylbenzene, *m*-CPBA, $H_2O_2$ / ironporphyrin:substrate: oxidant ratio 1:20:30, 2 mL, 24 h) and human liver microsomes (0.5 or 1 mg/mL, 37 °C, 30 or 60 min). Analysis by GC-MS confirmed the non-reactivity of carvacrol by CYP450 enzymes and only a common artifact for natural products containing phenolic hydroxyl was formed by oxidative dimerization reaction of Fenton (Fig 1). Therefore, potential toxic effects could come from its basic structure and not from potential metabolites.

In silico analyzes were performed using SwissADME and ADMETLab 2.0 (Fig 2). Both tools suggested carvacrol as a probable CYP1A2 inhibitor, but with high $LC_{50}$ values in *Pimephales promelas* and *Daphnia magna* (4.2 mg/L) and in *Tetrahymena pyriformis* (3.8 mg/L).

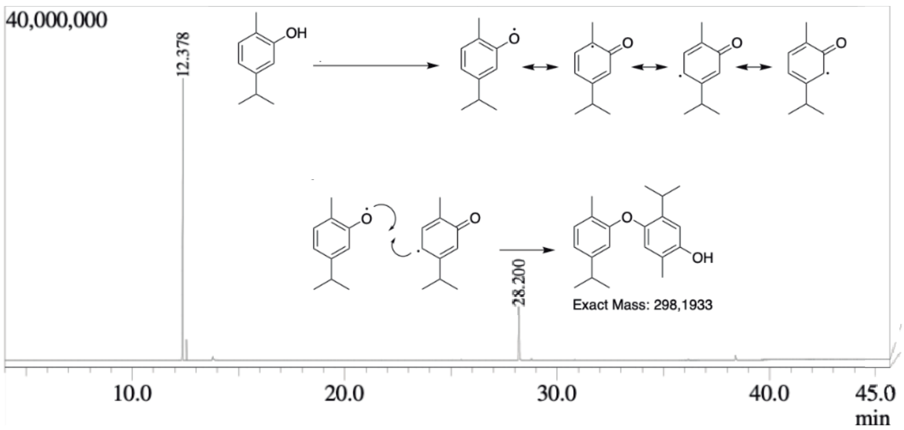

Fig. 1 Chromatogram indicating carvacrol dimerization and formation mechanism.

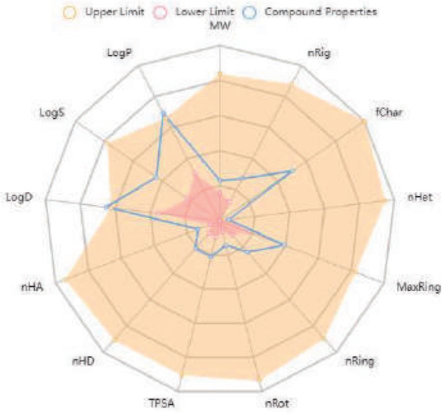

Fig.2 Diagram of general properties of carvacrol according to ADMET Lab 2.0.

The meta-analysis data suggest that the proposed use of essential oil as a larvicide, consisting mostly of carvacrol, can be used as a sanitizer without major side effects for populations living around the applied sites. These results provide the necessary support for the continuity of the development of a larvicidal product for the control of *Aedes aegypti* to the Ministry of Health of Brazil (ArboControl project).

## Agradecimentos/Acknowledgments

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**Área: QPN** **Nº de Inscrição: 232**

# Cellulose acetate-based membranes from the banana pseudostem containing extracts the fruit of *Butia catarinensis*.

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Keywords: *Banana pseudostem, Butia catarinensis, Cellulose extraction, Homogeneous acetylation, Soxhlet extraction*.

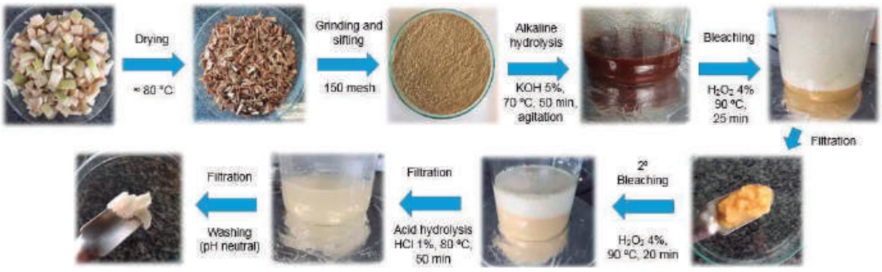
## Highlights

The cellulose of the banana pseudostem was isolated by alkaline/acid treatment and bleaching, and acetylated. Extracts from the fruit of *Butia catarinensis* were obtained using a Soxhlet extractor and incorporated into the membranes. The insertion of the extracts in the membranes did not change the thermal stability and improved the mechanical resistance of the membranes. The fatty acids of the coconut and pulp were determined by chromatography.

## Resumo

The cellulose was isolated (Fig. 1) and determining the content of cellulose and lignin of the bran in natura and treated (Van Soest, 1991). Thus, the bran in natura presented ≈38.19% of cellulose and ≈15.58% of lignin in dry mass, whereas the treaty had ≈92.2% of cellulose and ≈3.03% of lignin. FTIR (Fig. 2) also showed a reduction in lignin in the tract, with a decrease in peaks in the bands 1628 $cm^{-1}$ (stretch C=C) and 780 $cm^{-1}$ (CH stretch of aromatic H) and an increase of 896 $cm^{-1}$ (CH angular deformation of cellulose). The cellulose was acetylated via homogeneous acetylation and the degree of substitution was determined, obtaining 2.88 (triacetate).

**Fig. 1**. Steps for obtaining cellulose from banana pseudostem.



Extracts of coconut bran and "pulp+rind" from the fruit of *Butia catarinensis* were obtained by extraction with hexane in Soxhlet. The extracts were characterized via gas chromatography (Fig. 3). Cellulose acetate membranes with (5% by mass) and without extracts were prepared using the phase inversion method, using dichloromethane as solvent. TGA/DrTGA and mechanical resistance analyzes were carried out, and the incorporation of extracts did not alter the thermal instability (Fig. 4) and improved tensile strength performance (Fig. 5).

**Fig. 2.** FTIR of pseudostem bran and treated bran.

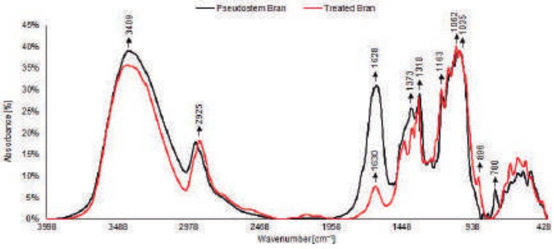


**Fig. 3**. Mass (g) of the main fatty acids in 100g of sample

| Fatty Acid | Pulp+Rind | Coconut |
|---|---|---|
| Caprylic Acid | 1,01 | 10,08 |
| Caproic Acid | 4,19 | 0,67 |
| Capric Acid | 0,11 | 10,42 |
| Stearic Acid | 2,03 | 2,97 |
| Lauric Acid | 0,15 | 39,56 |
| Linoleic Acid | 2,90 | - |
| Myristic Acid | 0,38 | 8,66 |
| Oleic Acid | 32,17 | 11,34 |
| Palmitic Acid | 41,04 | 7,45 |

**Fig. 4.** TGA and DrTGA of membranes.

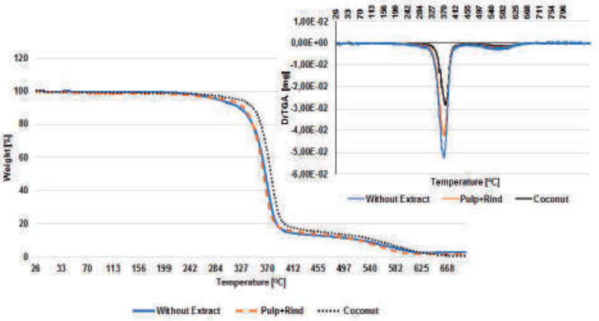
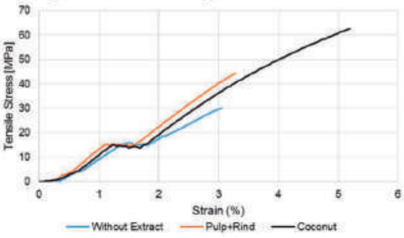


**Fig. 5.** Tensile strength of membranes.



**Acknowledgmen**

CAPES FAPESC

**Reference:** Van Soest. P.V.. Robertson. J.. Lewis. B. (1991)74. 3583–3597.

**Área: PN**
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# Chemical analysis by UPLC-DAD-qTOF-MS/MS of the honeys of stingless bee *Melipona mandacaia* (Mandaçaia)

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Palavras Chave: Honey, Native bee, Phenolics, Flavonoids.

## Highlights

Chemical composition of honey of stingless bee *Melipona mandacaia* (jandaira)

Presence of 53 phenolics were detected by UPLC-DAD-qTOF-MS/MS

Flavone and flavonol aglycones in *Melipona mandacaia* honeys

## Resumo/Abstract

The stingless bee *Melipona mandacaia* popularly known as mandacaia is endemic to the Caatinga biome, being found in the region of Vale do São Francisco. It is a very important bee for meliponiculture in the municipalities of Petrolina (PE) and Juazeiro (BA), where they are used for honey production. Due to its importance and endemism, the mandaçaia has been the subject of research, mainly due to the fact that there is little information about the species, together with the great demand for the rational creation and commercialization of its products. Profile of compounds by Ultra-Performance Liquid Chromatography coupled with a Diode Array Detector and quadrupole Time of Flight Mass Spectrometry (UPLC-DAD-qTOF-MS/MS) of sixteen *Melipona mandacaia* honeys from semiarid region of the Northeast of Brazil are presented. The melissopalynological analysis showed one principal pollen types of *Mimosa tenuiflora* (jurema preta). Mandaçaia monofloral honeys have similar characteristic profile of phenolic compounds. Fifty-three compounds were identified, mainly phenolic derivatives. Forty aglycone flavonoids: 26 flavones/flavonols and 14 flavanones/flavanonols.

## Agradecimentos/Acknowledgments

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**Área: QPN**

# Chemical characterization and evaluation of the anti-neuroinflammatory potential of a hydroethanolic extract of *Cecropia pachystachya* Trécul

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Keywords: *Cecropia pachystachya, Microglia, Neuroprotection, Nitric oxide, Rutin.*

## Highlights

LPS-induced neuroinflammation in the microglial murine BV-2 cell line was used to evaluate anti-neuroinflammatory potential by *Cecropia pachystachya* Trécul hydroethanolic extract.

## Abstract

*Cecropia pachystachya* Trécul (Urticaceae), popularly known as embaúba, is a plant native to Brazil and is also found in other countries of South America [1]. In traditional medicine, it is used to treat respiratory, cardiovascular, and gastrointestinal disorders [2]. Phytochemical investigations demonstrated the predominance of phenolic compounds, such as phenolic acids and flavonoids [3]. Studies with embaúba leaves have shown its antioxidant, antidepressant, anti-inflammatory, and neuroprotective potential [4,5]. Due to the increased prevalence of neurodegenerative diseases, such as Alzheimer's and Parkinson's, it is necessary to search for new therapeutic strategies related to regulating the production of inflammatory cytokines and nitric oxide (NO) by neuronal microglial cells [6]. In this context, this study aimed to evaluate the phytochemical profile and anti-neuroinflammatory potential of embaúba leaves. In the present study, hydroethanolic extract (HE) was obtained by a decoction of the leaves of *C. pachystachya* (1:10 m/v) in ethanol and water (75:25 v/v) at 60 °C for 30 minutes. The phytochemical profile was evaluated by ultra-performance liquid chromatography coupled with electrospray ionization/quadrupole-time-of-flight mass spectrometry (UPLC-ESI-Q-TOF-MS) and high-performance liquid chromatography with diode array ultraviolet detection (HPLC-DAD-UV). The anti-neuroinflammatory effects of HE were investigated in the microglial murine BV-2 cell line stimulated by lipopolysaccharide (LPS). A total of 14 substances were identified by UPLC-ESI-Q-TOF-MS, among which stands out the presence of quinic acid (*m/z* 191), chlorogenic acid (*m/z* 353), proanthocyanidin dimers type B (*m/z* 577) and C (*m/z* 865), orientin/isoorientin (*m/z* 447), vitexin/isovitexin (*m/z* 431) and rutin (*m/z* 609). In HPLC-DAD-UV analyses, the HE presented a rutin content of 6.40 ± 0.01 µg/mg. In the *in vitro* evaluation of anti-neuroinflammatory activity, the murine BV-2 microglial cell line remained viable (103.47 ± 24.44 %) after treatment and induction with HE at 25 µg/mL. In addition, HE was able to reduce significantly (*p-Value* < 0.0001) the production of LPS-induced NO (78.00 ± 11.04 %) in relation to induction control (105.07 ± 11.88 %). Activated microglial cells produce high levels of NO that contribute to oxidative stress and neuronal damage, directly associated with the emergence of neurodegenerative diseases. It was found that HE exhibited a neuroprotective effect by reducing the production of NO in BV-2 cells. These findings may be correlated with antioxidant and antiglycation effects already reported in previous studies with HE [7]. In addition, the predominance of phenolic compounds and flavonoids in embaúba leaves was confirmed, especially rutin. This glycosylated flavonoid is a potent antioxidant and anti-inflammatory agent, consisting of aromatic nuclei with reactive phenolic hydroxyls in its structure. These structural characteristics are probably related to the neuroprotective potential found in this study by favoring the neutralization of NO radical by HE [8]. Taken together, the present study demonstrated that HE has anti-neuroinflammatory potential and can be helpful as a therapeutic agent for the treatment of neurodegenerative diseases.

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## Acknowledgments

The authors are grateful to CNPq, CAPES, FAPEMIG, UFJF, UMinho, and FIOCRUZ.

**Área: QPN**

# Chemical characterization by gas chromatography coupled to mass spectrometry (GC-MS) of the essential oils from *Piper fuligineum* and *Piper macedoi*

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Palavras Chave: *Piper; CG-EM; Essential oil, Phenylpropanoid.*

## Highlights

The Fuligineum complex has high genetic similarities among its members. The chemical composition of the extracts does not reflect this similarity. Comparison of the composition of essential oils.

## Resumo/Abstract

*Piper fuligineum* and *Piper macedoi* are both members of the Fuligineum complex and present many morphological and genetic similarities that make it difficult to differentiate one from the other. This study compares for the first time the chemical composition by CG-MS of the essential oil of these two species. The results show that the species have the same composition of monoterpenes as alpha-Pinene, beta-Pinene, trans-beta-Ocimene, and beta-Ocimene, except D-limonene which appears only in *P. macedoi*. Regarding sesquiterpenes, it is possible to highlight the common presence only of the beta-Elemene, Caryophyllene, beta-Copaene, and Humulene. An important feature of *P. fuligineum* is the presence of the phenylpropanoid Safrole, Myristicin, and Apiol, which are absent in *P. macedoi*. Thus, the study of the chemical composition of the essential oil made possible the differentiation of the Piper species.

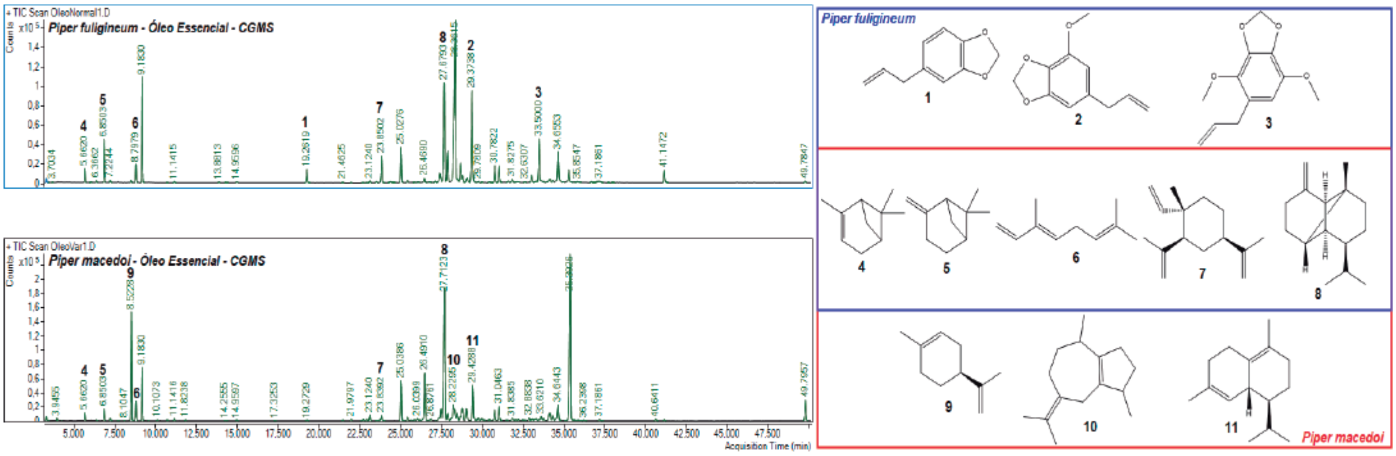

*Figure 1: Chromatograms and identified compounds found in Piper fuligineum e Piper macedoi. 1: Safrole, 2: Myristicin, 3: Apiol, 4: alpha-Pinene, 5: beta-Pinene, 6: trans-beta-Ocimene, 7: beta-Elemene, 8: beta-Copaene, 9: D-Limonene, 10: beta-Guaiene, 11: delta-Amorphene.*

## Agradecimentos/Acknowledgments

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**Área: QPN** **Nº de Inscrição: 00647**

# Chemical composition and antiglycation activity of the *Cocos nucifera* L. (Palmae) husk fiber ethanolic extract of the yellow dwarf variety.

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Palavras Chave*: Cocos nucifera, Phenolic Compouds, Antiglycation*

## Highlights

Chemical characterization of the ethanolic extract of coconut husk fiber of the yellow dwarf variety was performed by HPLC and five constituents were identified. The extract inhibited the formation of advanced glycation agents.

## Resumo/Abstract

The coconut tree is widely grown in tropical regions, especially in South Asia, Africa, South America, Australia, and other tropical countries[1]. The presence of phenolic compounds in coconut husk fiber may slow down the progression of various diseases such as cardiovascular diseases, cancers, neurodegenerative diseases and inflammatory diseases, caused by advanced glycation products (AGEs) generated by glycation reaction[2]. These compounds are capable of inhibiting protein glycation. Thus, the objective of this work was to evaluate the chemical characterization and antiglycation activity of the ethanolic extract of coconut husk fiber of the yellow dwarf variety. The extract was analyzed by HPLC and five constituents were identified (vanillic acid, caffeic acid, epicatechin, quercetin and catechin), as shown in Figure 1. Antiglycation activity of the extract and standards was performed by the BSA-Glucose/Fructose assay. The inhibition of AGEs formation by the extract was comparable to aminoguanidine, being around 70%, while vanillic acid was the best evaluated with values around 60%, as shown in Figure 2. In the extract chromatogram was observed that quercetin and catechin obtained greater intensity than other compounds, but the vanillic acid had a higher contribution to inhibition. This shows that the inhibition of AGEs performed by the extract is not related to the intensity of compound in the sample, but also due to its contribution during the reaction of formation of AGEs products. The extract of coconut husk fiber showed good antiglycation activity, suggesting that this natural product has potential against aging and diseases associated with oxidative stress.

**Figure 1**. Chromatogram of ethanolic extract yellow dwarf (EEYD) (4 mg $mL^{-1}$). Peaks: 1 – Quercetin, 2 – Catechin, 3 – Vanillic acid, 4 – Caffeic acid e 5 – Epicatechin, detected at 254 nm.

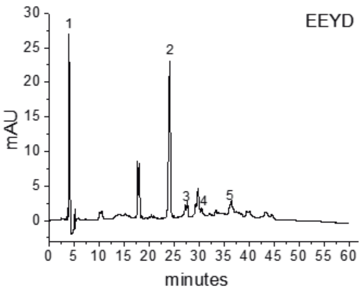
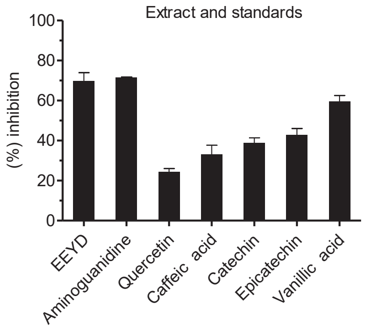


**Figure 2**. Inhibition percentage of the ethanolic extract yellow dwarf (EEYD) and standards. Concentration of 30 µg $mL^{-1}$.



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**Área: QPN** **Nº de Inscrição: 1314**

# CHEMICAL COMPOSITION AND ANTIMICROBIAL ACTIVITY OF THE FIXED OILS OBTAINED FROM LEAVES OF *Pachira aquatica* Aubl.

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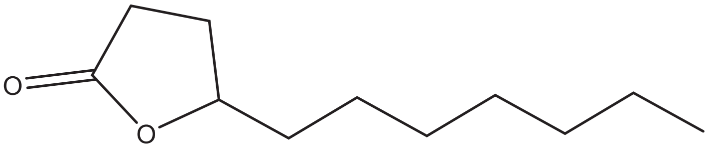
Keywords: *Pachira aquatica*, *GC-MS*, *antimicrobial activity, persicol.*

## Highlights

In this work, the antimicrobial activity and chemical composition of the fixed oil obtained from the crude methanolic extract of *Pachira aquatica* (MALVACEAE) leaves were investigated.

## Abstract

Dried and crushed leaves (600 g) of *Pachira aquatica* Aublet (MALVACEAE), popularly known as monguba, mamorana, munguba, chestnut from Maranhão, wild cocoa, fake cocoa or chestnut,[1] were extracted with methanol providing 20 g of crude methanolic extract (EBM). EBM (19 g) was subjected to fractionation in a classic column (CC) with 20% hexane / EtOAc (fraction 1; 0.7 g), 50% hexane / EtOAc (fraction 2; 7.0 g), 100% EtOAc (fraction 3; 1.24 g), 50% AcOEt / MeOH (fraction 4; 1.9 g) and 100% MeOH (fraction 5; 6.9 g). Fraction 3 was subjected to CC in hexane and ethyl acetate in an increasing order of polarity providing 17 subfractions. Subfractions 3-5, as they are rich in fatty acids, were esterified with methanol by adapted method[2] and analyzed by CG/MS (SHIMADZU QP-2010). Subfraction 3 presented Lupenyl Acetate (Lup-20(29)-en-3-ol, acetate) as its main components in 40%, palmitic (21%) and stearic (13%) acids, in the form of its methyl esters. Subfraction 4 presented as main components palmitic (27%), elaidic (11%) and stearic (11%) acids in the form of its methyl esters, in addition to ɣ-undecalactone 2(3H)-furanone-5-heptyldihydro known as Persicol (18%). The main constituents of subfraction 5 were palmitic acids (53%), stearic acids (14%) and cis-10-Nonadecenoic acids (13%), in the form of their methyl esters. The antimicrobial activities were evaluated by the BHI broth microdilution method based on the CLSI methodology (2003)[3] with some adaptations using Ciprofloxacin Hydrochloride as positive control. Subfractions 3, 4 and 5 were subjected to antimicrobial tests using certified strains of the following bacteria: *Escherichia coli* (ATCC 8739), *Salmonella* spp. (ATCC 4029), *Staphylococcus aureus* (ATCC 25923), *Klebsiella pneumoniae* (ATCC 70063) and *Proteus* spp (LACEN 8/7). Only *Salmonella spp* showed moderate sensitivity to subfractions. The subfractions 3 and 4 showed bactericidal activity with a minimum inhibitory concentration (MIC) of 1250 µg/mL and bacteriostatic activity with a MIC of 625 µg/mL



**Persicol**

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**Área: QPN**

# Chemical composition and cytotoxic activity of essential oil of *Piper tuberculatum* from Itacoatiara, Amazonas.

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Key-words: *Volatile compounds, Tumoral cells lineage, Piperaceae.*

## Highlights

This research aimed to analyze the chemical composition and the cytotoxic activity of essential oil of *P. tuberculatum*. Altogether 48 compounds (95.75%) were identified in this plant species' essential oil, being: α-pinene (9.6%), (*E*)-caryophyllene (9.5%), germacrene (8.8%), α-selinene (8.7%), (*Z*)-*β*-ocimene (5.6%) and D-germacrene (5.0%), its major compounds. The essential oil of *P. tuberculatum* showed inhibition of 88 to 92% against the tested cells lineages.

## Resumo/Abstract

Genus *Piper* belongs to the family Piperaceae has about 2000 species found in different regions in Brazil. *Piper tuberculatum* is used to treat snakebites and as a sedative. Its essential oils present antifungal and antiparasitic activity. The performance of the cytotoxic assay allows the preliminary indications of synthetic compounds or natural products with anticancer potential. This study is important because the cancer, a disease caused by the disordered proliferation of cells, is responsible for the death of approximately 8.2 million people each year. This study aimed to evaluate the chemical composition and cytotoxic activity of the essential oil extracted from the leaves of *P. tuberculatum*, collected in region of Itacoatiara, 264 km away from the capital Manaus in Amazonas-Brazil. In the process of extraction of essential oil, the leaves were collected, processed, and submitted to hydrodistillation in a Clevenger apparatus. After, the sample was analyzed by Gas Chromatography Coupled to Mass Spectrometry (GC-MS), and the elucidation of compounds was performed by calculating the arithmetic index and by comparison by literature data. The cytotoxic activity assay was performed using the MTT method, which is based on the colorimetric analysis of the conversion of 3-(4,5-dimethyl-2-thiazole)-2,5 -diphenyl-2-H-bromide tetrazolium salt (MTT) in formazan blue. The tumoral cells lineages were used at following concentrations: $0.7 \times 10^5$ cells/mL to HCT-116 (Colon Carcinoma), $0.1 \times 10^6$ cells/mL to SNB-19 (Astrocytoma) and PC3 (Prostate Carcinoma). The test was carried out in triplicate, and 1% of the essential oil was applied to cells described above, presenting 90%, 80%, and 92% inhibition for PC3, SNB-19 and HCT-116 lineages, in this order. The results showed 30.8% of monoterpenes, 64.7% of sesquiterpenes and 4.4% of phenylpropanoids. Majority compounds were α-pinene (9.6%), (*E*)-caryophyllene (9.5%), germacrene (8.8%), α-selinene (8.7%), (*Z*)-*β*-ocimene (5.6%) and D-germacrene (5.0%). Except for α-selinene and (*Z*)-*β*-ocimene, all the other compounds are described in the literature, presenting cytotoxic activity. The presence of one or two majority compounds may be related to the cytotoxic activity displayed.

## Agradecimentos/Acknowledgments

The authors thank Sociedade Brasileira de Química for the opportunity. Also are greatfull to Fundação Cearense de Apoio ao Desenvolvimento Científico e Tecnológico, to Universidade Federal do Amazonas, Universidade Federal do Ceará and Fundação de Amparo à Pesquisa do Estado do Amazonas for encouragement and financial support.

**Área: QPN**

# Chemical composition and hypoglycaemic effect of the dry extract of *Eugenia biflora* L. (DC.) leaves

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Palavras-Chave:*(Pedra-ume-caá, Dry extract, catechin, enzyme inhibition, hypoglycemic).*

## Highlights

Eight phenolics compounds by HRMS and NMR from *E. biflora* leaves; Dry extract inhibited the α-glucosidase *in vitro*; Dry extract showed a hypoglycemic effect and mortality in induced diabetic mice.

## Resumo/Abstract

Diabetes mellitus (DM) is a metabolic disease characterized by hyperglycemia. DM treatment includes oral antidiabetic agents that cause side effects. Therefore, alternatives to synthetic drugs are been explored. Considering the antidiabetic potential of certain plant species of Myrtaceae, popularly "pedra-ume-caá", this work aimed at the chemical and pharmacological study of *Eugenia biflora* (L.) DC. Its leaves are commercialized in popular markets and traditionally used by Amazonian peoples in the form of tea to control diabetes. The leaves of this species were collected in the Algodoal/Maiandeua Environmental Protection Area (Maracanã, Pará). The dry extract (EbAPA) was obtained by infusion (2.0% w/v) and analyzed by LC-HRMS and NMR. Catechin was quantified by $^1$H NMR (PULCON method). The antidiabetic effect of EbAPA was evaluated, *in vitro*, by inhibition of α-amylase and α -glucosidase, as well as by oral maltose tolerance and chronic multiple-dose (28 days) tests in diabetic mice induced by streptozotocin (STZ). In the multiple-dose trial, the hypoglycemic effect, and toxicity of EbAPA were evaluated. In addition, the levels of thiobarbituric acid reactive substances (TBARS) in the liver as well as histopathological aspects of the kidneys and liver were investigated. In total, 9 chemical constituents were identified in EbAPA, being quinic acid and 8 phenolic compounds [procyanidin dimer (B-type), catechin, procyanidin dimer monogallate (B-type), myricitrin, guaijaverin, quercitrin, isorhamnetin-3-*O*-glucoside and 3'-*O*-methyl-4-*O*-(rhamnopyranosyl) ellagic acid]. Catechin is one of the main compounds present in this extract (15.5 ± 1.73 mg $g^{-1}$). EbAPA [200 mg/kg body weight (bw)] inhibited the elevation of glycemic levels in healthy mice with maltose overload (90 min). This result corroborated the *in vitro* enzyme inhibition study against α-glucosidase ($IC_{50}$ = 22.2 ± 1.2 μg $mL^{-1}$) compared to the acarbose standard ($IC_{50}$ = 62.2 ± 1.2 μg $mL^{-1}$). In the multiple-dose study, on D15, administration of EbAPA (50 mg/kg bw) reduced glucose levels of diabetic mice by 60.6% compared to D1. These levels compared to the healthy control group showed no significant difference until D21. On D28, there was an increase of 54.9% in the glucose level, but it was not statistically different to the positive control group. However, diabetic mice treated with doses of 100 mg/kg and 200 mg/kg bw of EbAPA showed diarrhea, lethargy and decreased food intake, causing premature mortality of 100% (200 mg/kg bw) and 50% (100 mg/kg bw) within 22 days. These results suggest that the mechanism of toxicity of this extract may be related to the worsening of oxidative stress in the liver by prolonged use. This hypothesis can be supported by the TBARS indices in the groups of animals treated with EbAPA (50 and 100 mg/kg bw) that were not significantly different compared to diabetic control. Histopathological analysis indicated that chronic administration of this extract did not reduce the progression of STZ-induced diabetes toxicity. Therefore, this study demonstrated catechin as a possible marker as well as the hypoglycemic potential of this *E. biflora* extract. However, the prolonged use of this tea can be harmful to its users due to its considerable toxicity.

## Agradecimentos/Acknowledgments

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**Área: QPN**

# Chemical compounds from the leaves of *Pseudoxandra leiophylla* (Annonaceae) and investigation of their cytotoxic properties

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Palavras Chave: *Pseudoxandra leiophylla, Aporphinoid alkaloids, Triterpenes, Sesquiterpene lactone, Lignan, Cytotoxic activity.*

## Highlights

**1.** Seven compounds were isolated from the leaves of *Pseudoxandra leiophylla*. **2.** The isolated compounds belong to the class of aporphinoid alkaloids, triterpenes, sesquiterpene lactones and lignoids. **3.** All compounds are described for the first time in *P. leiophylla*. **4.** Crude extracts and fractions showed cytotoxic activities against tumor cell lines. **5.** Mixture of breine and maniladiol was active against B16-F10 tumor cells lines with an $IC_{50}$ of 8.32 μg.mL$^{-1}$.

## Resumo/Abstract

*Pseudoxandra leiophylla* (Diels) R.E. Fries is a species of Annonaceae family popularly known as 'envira-preta' and 'envira-roxa' native to the Amazon region, occurring in Brazil, Colombia and Venezuela. Its synonymy is *Pseudoxandra coriacea* R.E. Fries. According to the literature, there are no records of phytochemical and pharmacological studies. In this work, the phytochemical study and the investigation of the *in vitro* cytotoxicity of crude extracts, fractions (neutral and alkaloidal), and isolated compounds from *P. leiophylla* leaves were carried out against tumor cell lines using the Alamar Blue assay. The phytochemical study of the alkaloidal fraction resulted in the isolation of seven compounds belonging to the class of alkaloids, terpenes (sesquiterpene lactones and triterpenes), and lignoids (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. The alkaloids belong to the class of aporphines and oxoaporphines and were identified as liriodenine (**1**) and asimilobine (**2**), respectively. The terpenes are the triterpenes heinic acid (**3**), and the mixture of breine (**4**) and maniladiol (**5**), and the sesquiterpene lactone loliolide (**6**). In addition, the lignan grandisin was also isolated in good amounts (**7**). These compounds are described for the first time in the species. The results of the cytotoxicity assay of extracts and fractions showed potential cytotoxic activity against tumor cell lines with $IC_{50}$ values below 43 μg.mL$^{-1}$. Among the evaluated extracts, the hexane extract was the most active with $IC_{50}$ of 28.50 and 13.12 μg.mL$^{-1}$ against human colon carcinoma (HCT116) and human hepatocellular carcinoma (HepG2) cells, respectively. The methanolic extract was active only against HepG2 with $IC_{50}$ of 12.85 μg.mL$^{-1}$. On the other hand, the neutral and alkaloidal fractions presented results very close with $IC_{50}$ of 42.47 and 8.32 μg.mL$^{-1}$, and 31.86 and 9.85 μg.mL$^{-1}$ against HCT116 and HepG2, respectively, improving the methanolic extract activity with acid-base treatment. For the isolated compounds, the mixture of breine and maniladiol showed significant cytotoxic activity with $IC_{50}$ of 8.32 μg.mL$^{-1}$ against mouse melanoma tumor cells lines (B16-F10). The results contributed to the chemical and pharmacological knowledge of the species of Annonaceae from the Amazonas.

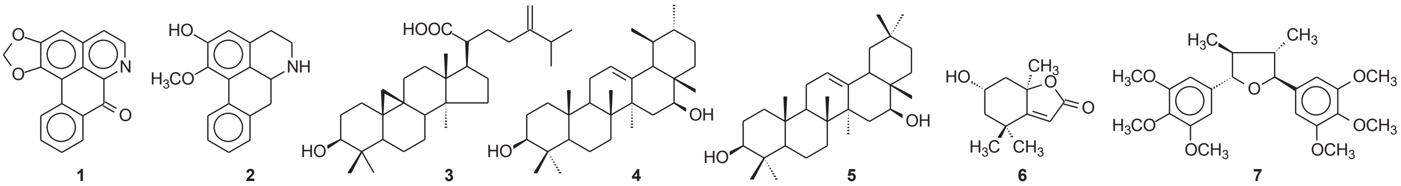

**Figure 1**. Chemical compounds isolated from the leaves of *Pseudoxandra leiophylla*.

## Agradecimentos/Acknowledgments

The authors are grateful to CAPES, CNPq, FAPEAM, IGM/FIOCRUZ-BA, and UFAM for financial support and CA/CAM/UFAM for NMR and MS analysis.

**Área: QPN**

# Chemical profile evaluation of the metabolic changes by cationic metals of the biomass produced by endophytic fungus *Aspergillus sp*. isolated from *Dizygostemom riparius* (Plantaginaceae) by UPLC – Ultra Performance Liquid Chromatography

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Key-words: *Aspergillus sp.; Metabolism induction; UPLC, Endophytic fungus.*

## Highlights

Metabolism induction by changes in the culture medium; endophytic fungus isolated from a new species of plant; chromatographic profile analysis by UPLC; OSMAC (One Strain Many Compounds)

## Resumo/Abstract

Recent discoveries of new molecules with active ingredients from a group of microorganisms considered endophytic, such as bacteria, cyanobacteria, and mainly fungi have been motivating researchers to investigate its mutualistic association with plants (SONG et al., 2019). Modern genomic-type studies involving OSMAC (One Strain Many Compounds) approaches are related to changes in the microorganisms growth medium such as temperature, pH, and composition of the medium, thus completely affecting the metabolite profile of many fungi, which can be a tool of great importance to explore the chemical diversity offered by endophytic fungi (LI et al., 2019). In the present paper, the metabolic induction of the ethyl acetate phase of the biomass produced by the endophytic fungus *Aspergillius sp.* was analyzed. The fungus was subjected to cultivation in Czapeck medium and two other culture media using Czapeck medium with the addition of the salts $CoCl_2$ and $MnCl_2$. The metabolic induction was analyzed by UPLC (Ultra Performance Liquid Chromatography) which was performed in gradient mode using a reversed-phase column with solid core (AcQUITY UPLC CSR C-18 column 1.7 µm 100 mm x 2.1 mm,) with the injection of 0.5 µL and a binary mobile phase of $H_2O$ and $CH_3CN$.

## Agradecimentos/Acknowledgments

**Área: QPN**

# Chemical profile of Black pepper plants during the control of *Fusarium* infection by foliar incorporation of *Piper divaricatum* in the soil.

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Keywords: *Piper nigrum, Lipoxygenase, Phenylpropanoids, Foliar incorporation, Piper divaricatum, α-muurolol.*

## Highlights

Incorporation of tolerant *Piper divaricatum* leaves in soil induced alterations in the metabolism of *Piper nigrum* and protected seedlings from *Fusarium solani* infection.

## Abstract

The incidence of fusariosis disease (*Fusarium solani* f. sp. *piperis*) (FS) in black pepper (*Piper nigrum* L.) (PN) has been causing a reduction in the production rates of the spice in Brazil since there are no forms of satisfactory control. In the present study, the foliar residues of *Piper divaricatum* (PD), a species tolerant to FS and rich in eugenol and methyl-eugenol, were incorporated into the soil, and its influence on secondary metabolites and resistance was evaluated. *P. nigrum* seedlings were inoculated with FS by the roots and transferred to sterilized soil with or without PD leaves residue at two concentrations: 10 g (PNI10F) and 50 g (PNI50F) of PD for each kg of the substrate (control: PN seedlings in soil without incorporation). The experiment was monitored at 30 and 40 days. Development parameters such as fresh biomass and plant height were observed. Volatile compounds were extracted from the leaves by Likens-Nickerson apparatus, and the identification was performed by Gas Chromatography-Mass spectrometry (GC-MS). The enzymatic activities of lipoxygenase (LOX) and phenylalanine ammonia-lyase (PAL) and the total phenolic content (TPC) were determined by spectrophotometric methods.

Foliar incorporation in soil resulted in deceleration of PN plants development compared to the control group: reduction in plant height and leaves weight specially in the treatment PNI50F at 30 DAI (days after inoculation); reduction of leaves and roots weight for PNI10F at 40 DAI. Also, foliar incorporation with PD at a concentration of 50g/kg reduced the symptoms in plants, such as yellowing leaves even after 40 DAI.

The predominant chemical classes in PN leaves were not affected by treatment: oxygenated sesquiterpenes (39.43-55.98%) and sesquiterpene hydrocarbons (19.09-40.83%). The major compounds were α-muurolol (16.41-26.75%), cubebol (7.85-11.18%), and bicyclogermacrene (4.51-7.11%). Plants incorporated with 10 g/kg of PD foliar residue were influenced by treatment time, increasing the α-muurolol content at 40 DAI compared to 30 DAI (*Figure 1.A*).

LOX activity was increased in all treatments at 40 DAI compared to the same groups at 30 DAI (Figure 1.B). For PAL enzyme, there were no changes after treatments. TPC decreased at 40 DAI in PNI50F compared to control. The results demonstrate that foliar incorporation with PD at a concentration of 50g/kg induced alterations in secondary metabolism and promoted the tolerance of PN to FS, but the mechanisms were not completely elucidated. Studies must be carried out to understand the defense mechanism of PN in a substrate incorporated with PD and inoculated with the phytopathogen FS.

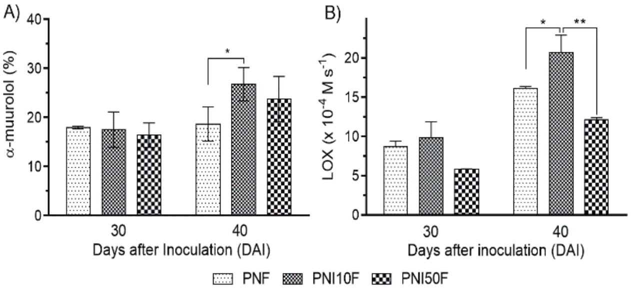

**Figure 1**. A) % of α-muurolol on the total volatile concentrate after 30 and 40 DAI; B) LOX activity after 30 and 40 DAI. Statistical difference according to Tukey test: p=0,332, **: p=0,0021.

## Acknowledgments

To the Conselho Nacional de Desenvolvimento Científico and Fundação Amazônia de Amparo a Estudos e Pesquisas for providing the necessary financial suppot to carry out this work.

**Área: QPN** **Nº de Inscrição: 714**

# Chemical study of *Fusarium solani,* an endophyte fungal strain isolated from the red marine alga *Dichotomaria marginata*

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keywords: *Fusarium solani, Dichotomaria marginata, endophytic fungi, chemodiversity.*

## Highlights

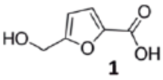
Isolation of endophytic fungus *Fusarium solani* from the marine red alga *Dichotomaria marginata*; identification of low molecular weight phenolic acids by GC-MS; bioassays evidenced antileishmania and cytotoxic potential of the crude extract.

## Abstract

*Fusarium* genus endophytic fungi are known as phytopathogens associated to several agriculture diseases as soybean and cassava root rot and darkening and flavor alteration in papaya, banana and grapes.[1] They are also human pathogens, associated to mycosis and cornea inflammation.[2] *Fusarium solani* is usually found in terrestrial plants along with other *Fusarium* species, but in this work a *F solani* strain has been isolated from the marine red alga *Dichotomaria marginata.*[3] Recent studies have disclosed marked chemodiversity and bioactivities of marine derived endophytic fungi, including promising compounds for the development of novel therapeutic agents.[4] After isolation and cultivation in Petri dishes using PDA medium, this *F. solani* strain was grown in malt extract liquid medium, and the supernatant was partitioned with EtOAc. The crude extract was then analyzed by GC-MS which led to the identification of low molecular weight phenolic acids (Table 1). In addition, the extract was bioassayed and disclosed promising antileishmania and cytotoxic activities. These results confirm the high chemodiversity of marine biome derived endophytic fungi as well as their relevance for bioprospection.

Table 1: Phenolic acids from *Fusarium solani* extract identified by GC-MS.

| | Compound | Rt | Theoret. RI | RI | Similarity |
|---|---|---|---|---|---|
| 1 | 5-Hydroxymethyl-2-furoic acid | 8,86 | 1560 | 1556 | 87 |
| 2 | 3-Phenyllactic acid | 9,88 | 1600 | 1597 | 93 |
| 3 | 4-Hydroxybenzoic acid | 10,92 | 1629 | 4634 | 92 |
| 4 | 4-Hydroxybenzeneacetic acid | 11,28 | 1648 | 1646 | 95 |
| 5 | 3, 4-Dihydroxyphenylacetic | 17,28 | 1832 | 1846 | 87 |
| 6 | 5-Hydroxyindoleacetic acid | 28,16 | 2199 | 2201 | 84 |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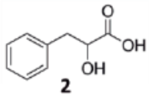
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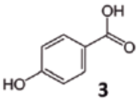
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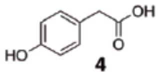
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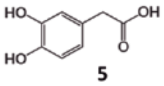
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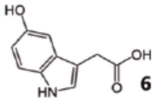
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## Acknowledgments

CAPES, CNPq (INCT/BioNat), FINEP and FAPESP (Cepid/CibFar and INCT/BioNat) for research financial support and fellowships.

**Área:** QPN **Nº de Inscrição:** ________

# Chemical study of *Penicillium* sp. (AcR02), endophyte of *Rhizophora mangle*

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Palavras Chave: *Penicillium, Chemical study, Endophyte, Rhizophora mangle.*

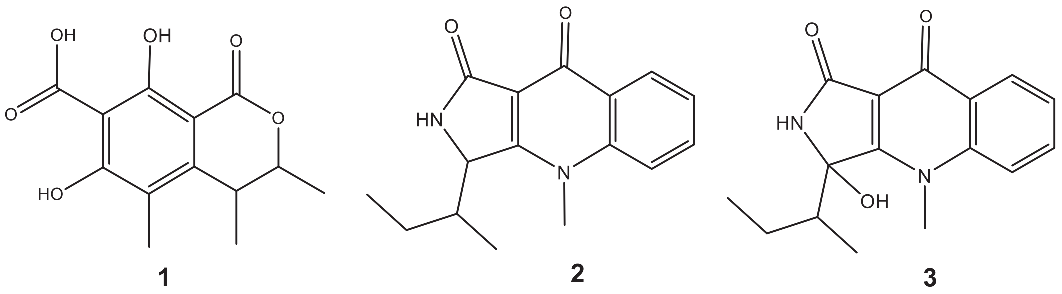
## Highlights

The present work reports six substances produced by the fungus *Penicillium sp.* (AcR02), endophyte of *Rhizophora mangle*, from Village of the Acarajó, Bragança-PA.

## Abstract

The chemical study of microorganisms marine has increased in last decades, research shows that fungi associated with mangrove plants are important sources of metabolites with various biological activities[1,2]. The present work reports the preliminary chemical study of substances produced by the fungus *Penicillium* sp. (AcR02), endophyte of *Rhizophora mangle*, from Village of the Acarajó, Bragança-PA. The microorganism was grown in solid rice medium (2 kg) for 25 days, and after extracting the biomass with EtOH (92.8º INPM, Santa Cruz®), the material was concentrated and the partitioned with hexane and EtOAc and the concentrated organic solutions. The excreted liquid was partitioned with EtOAc and the organic phase was concentrated. The EtOAc phases were fractionated in column chromatography (adsorption and molecular exclusion). The fractions were monitored by TLC, and those that were shown to be pure were analyzed by NMR. With this, it was possible to identify six substances (Figure 1): ergosterol, ergosterol peroxide, mevalactone, dihydrocitrinone (**1**)[3], quinolactacins A (**2**) and C (**3**)[4]. These results confirm the importance of studies marine endophyte as an attractive and alternative source in the search for secondary metabolites.

**Figure 1:** Substances produced by the fungus *Penicillium* sp. (AcR02).



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## Acknowledgments

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**Área: QPN**

# Circular miniproteins from *Pombalia atropurpurea*

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Keywords:*Cyclotides, cyclic peptides, Pombalia atropurpurea, Violaceae.*

## Highlights

Nine putative cyclotides have been annoted from leaves and stem of *Pombalia atropurpurea*.

## Resumo/Abstract

Cyclotides are disulfide-rich mini proteins found in some plant families: Violaceae, Rubiaceae, Fabaceae, Solanaceae, and Poaceae.[1,2] They have a unique circular backbone with 28-37 amino acid residues, a head-to-tail cyclization, and a knotted arrangement of three conserved disulfide bonds named CCK (cyclic cystine knot). Currently, have been discovered around 720 cyclotides, according to cybase: a database of cyclic protein sequence and structures.[3] These stable structures are resistant to proteolytic degradation[1,2,4,5] and are involved in plant defense. A wide range of biological activities and/or therapeutic applications have been reported for these peptides, including insecticidal, nematocidal, molluscicidal, antimicrobial, anti-HIV, and antitumor activities.[6] Aiming to contribute even more in the area of cyclotides, our research group is dedicated to studying this class of natural products present in plants. Thus, the present work describes the extraction and identification of putative cyclic peptides present in *Pombalia atropurpurea* (*synonymia *Hybanthus atropurpureus* and *Ioidium atropurpureum*), Violaceae family. This native plant is a shrub, found in a vast tropical savanna ecoregion of Brazil, named Cerrado. [7] Their dried and pulverized stems and leaves were extracted with MeOH/$H_2O$ (60:40, v/v) and partitioned with $CH_2Cl_2$:MeOH:$H_2O$, under room temperature. The aqueous phases were concentrated and eluted through solid-phase extraction (SPE) cartridge, with the mixture 20% and 80% buffer B (90% acetonitrile, 0.08% trifluoroacetic acid) in A (0.1% aqueous trifluoroacetic acid). The fractions eluted in 80% buffer B (leaves and stem) were considered the peptide-rich fractions. These fractions were submitted to MALDI-TOF-MS and LC-MS analyses. It was observed the presence of many mass signals in the 2500-4000 Da range, indicating a presence of a variety of putative cyclotides. Thereby, through this study was able to identify nine putative cyclotides that were compared to available data in cybase. Further studies for isolation and sequencing is needed to propose the sequences.

**Table.** Putative cyclotides identified by LC-MS in leaves and stems $C_{18}$_80% fractions from *Palicourea atropurpurea.*

| Leaves | | Stem | |
|---|---|---|---|
| Rt | MM (Da) | Rt | MM (Da) |
| 15,9 min. | 3420,6 | 16 min. | 3422,6 |
| 16,2 min. | 3395,4 | 17,2 min. | 2961,24 |
| 17,6 min. | 3110,13 | 18,6 min. | 3156,45 |
| 18,3 min. | 2533,74 | 19,2 min. | 3149,46 |
| 19,5 min | 3001,26 | 19,6 min. | 3000,21 |
| 20,4 min. | 2984,25 | 20,7 min. | 2984,25 |

## Agradecimentos/Acknowledgments

CAPES, CNPq (INCT/BioNat), and FAPESP (Cepid/CibFar and INCT/BioNat) for research financial support.

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**Área:** ______________
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**Nº de Inscrição:**________
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# Coffee $^{\beta}$*N*-alkanoyl-5-hydroxytryptamides–synthesis and antinociceptive evaluation

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*Keywords:Synthesis,Serotonin amide, Antinociceptive, Coffee.*

## Highlights

- The synthesis of different *N*-acylated serotonins using 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) and dimethylaminopyridine (DMAP) as coupling reagents is a simple and effective route.
- The C-5HTs investigated here showed significant effect in thermal and chemical models of nociception.

## Abstract

$^{\beta}$*N*-alkanoyl-5-hydroxytryptamides (C-5HTs) are an interesting class of metabolites present in raw coffee bean wax.These compounds have demonstrated to be neuroprotectant in Parkinson[1] and Alzheimer´s[2] disease models and to have antinociceptive properties, recently described by our research group.[3] Structurally, the C-5HTs from coffee are saturated *N*-acylated serotonins containing mostly 20 and 22 carbons derived from arachidic ($C_{20}$-5HT) and behenic ($C_{22}$-5HT) acids, as well as other minor derivatives such as stearoyl one ($C_{18}$-5HT).[4] Most strategies of C-5HT synthesis so far explored are extremely laborious, given the high number of consecutive steps which must occur under anhydrous conditions. In addition, the use of some toxic reagents as thionyl chloride and the low yields are other disadvantages of the route commonly used for the synthesis of these compounds. With this in mind, we proposed a simple and effective route for the synthesis of different *N*-acylated serotonins ($C_n$-5HT, n = 10, 12, 16, 18, 20 and 22) using 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) and dimethylaminopyridine (DMAP) as coupling reagents, resulting in good yields ranging from 77 to 95%.

Antinociceptive activity was studied using Swiss Webster mice (25-30g, n=5, protocols 31 and 34/19) in thermal (hot plate) and chemical (capsaicin- or formalin-induced licking) models. In the hot plate model, C20 and C22 (3 and 10 mg/kg, v.o.) significantly increased the antinociceptive effect similarly to morphine. This effect was completely abolished by opioid and cholinergic receptor antagonists (naloxone and atropine, respectively) and partially reversed by serotoninergic receptor antagonist (ondansetron).

## Acknowledgments

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**Área: QPN**

# Cytototic Activity and Chemical Profile of Methanolic Extract Obtained from Avelós Stem (*Euphorbia tirucalli* L.) Euphorbiaceae

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*Keywords*: *Avelós. Chemical profile. Cytotoxic activity. Euphorbia tirucalli*.

## Highlights

The phytochemical study conducted with methanolic extract of *Euphorbia tirucalli* from the crude methanolic extract allowed the identification of phenolic compounds, flavonoids, and terpenes. Assays of cytotoxic potential showed that the methanolic extract of *E. tirucalli* has activity against the cell lines of breast adenocarcinoma (MCF-7) and human melanoma (SK-MEL-37).

## Abstract

Avelós (*Euphorbia tirucalli* Linnaeus), a plant selected for this study, has been popularly used in the fight against tumors, arousing the interest of researchers in this area so that it can be used safely in the auxiliary treatment of different types of cancer.**[1]** It belongs to the family Euphorbiaceae and to the genus *Euphorbia*, it is also the object of studies related to the treatment of a range of infectious and inflammatory diseases. Herbaceous much used by popular and traditional medicine, presents, a latex rich in molecules that confirm its high toxicity. The objective of this research was to verify the chemical profile of the methanolic extract obtained from the stem (modified leaves) of the plant in question and to determine the cytotoxicity of the crude extract by cytotoxic assay against the lineages of adenocarcinoma (MCF-7) and neoplastic cells of human melanoma (SK-MEL-37).**[2]** For this, the plant was collected, and after drying and milling the material was extracted with methanol. Subsequently, the present compounds were separated by the thin-layer chromatography technique and the classes of substances found in the extract were identified by the technique of Nuclear Magnetic Resonance of Hydrogen and Carbon-13 (NMR).**[3]** The combination of cyclohexane with Acetone and Hexane (5:3:2) provided a suitable polarity for the elution of the extract, which was revealed with ultraviolet detection and different reagents: sulfuric acid solutions; aluminum chloride; ferric chloride; 10% potassium hydroxide in ethanol; green bromocresol indicator solution; potassium permanganate, Dragendorff Reagent, vanillin and iodine vapors. The phytochemical study of the methanolic extract of *Euphorbia tirucalli* allowed to identify the presence of phenolic compounds, flavonoids and terpenes, a result confirmed by NMR spectra. The cytotoxic potential assays, although they are in low concentration thus altering the result, show that the methanolic extract of *Euphorbia tirucalli* shows activity against the tested cell lines. The observed activity may be related, according to information available in the literature, with the classes identified in the samples studied.

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## Agradecimentos/Acknowledgments

**Área:** ***QPN***

# CYTOTOXIC ACTIVITY EVALUATION OF *Stizophyllum perforatum* (CHAM.) MIERS (BIGNONIACEAE) AND ISOLATED COMPOUNDS.

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Palavras Chave: *Verbascoside, Ursolic acid, Quercetin-3,6,7,4'-tetramethyl ether, Stizophyllum perforatum, cytotoxic activity.*

## Highlights

*Stizophyllum perforatum* crude extracts, fractions, and isolated compounds were not cytotoxic to macrophages.

## Resumo/Abstract

Neglected Tropical Diseases (NTD) are infectious diseases that are spread and perpetuated in environments with precarious sanitary structures, housing, and food conditions. In addition to the population's difficulty in accessing the health system, and thus still represent a major public health problem.[1] Leishmaniasis is an infectious disease caused by protozoan parasites of the genus *Leishmania*, and is considered a NTD. The drug used as the first choice in the treatment of leishmaniasis is methylglucamine antimoniate, and amphotericin B is employed as a secondary treatment. The major problem with these drugs is toxicity, such as the nephrotoxicity of amphotericin-B.[2] Additionally, there are studies showing that some strains are already resistant to these compounds. Thus, there is a great need for new compounds against leishmaniasis.[3] The species *Stizophyllum perforatum* demonstrated antileishmanial potential.[4] Thus, the present study aimed to evaluate the *in vitro* cytotoxicity activity of the extract of *S. perforatum*, fractions, and isolated compounds against macrophages. We evaluated the cytotoxicity of these compounds *in vitro* on macrophages (J774A.1), using the MTT method. Briefly, in a 96 wells plate, 200 µL of cell suspension were plated at a concentration of $1x10^6$ cell/mL in RPMI culture medium and incubated at 5% $CO_2$ at 37°C for 24 and 48 h. After cell adhesion, the wells were exposed to *S. perforatum* extracts, fractions, and isolated compounds at different concentrations ranging from 100 to 3.12 µg/mL. The supernatant was removed and 100 µL of a 1 mg/mL MTT solution (Sigma-Aldrich) in an incomplete RPMI medium was added and incubated for 4 h. The supernatant was removed and isopropyl alcohol (100 µL) were added to solubilize the formed formazan crystals. The absorbance was measured in an ELISA reader at 570 nm. Cell viability was calculated as a percentage, considering the negative control as 100%. Our results demonstrated that the samples tested, in both periods, allowed the growth of cells. The 50% cytotoxic concentration (CC50) obtained for extract, and fractions were > 100 µg/mL and for the compounds were > 100 µM. Thus, *S. perforatum* crude extracts, fractions and ursolic acid, verbascoside, and quercetin-3,6,7,4'-tetramethyl ether do not have cytotoxicity under these conditions. Further *in vitro* studies are in progress to evaluate the samples in amastigote models of *L. amazonenses*.

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## Agradecimentos/Acknowledgments

The authors are grateful to CAPES, CNPq, and FAPESP (# 2016/10313-4 and 2017/24860-0).

**Área: QPN**

# Cytotoxic compounds of sediment-associated marine actinomycetes from Brazilian oceanic islands

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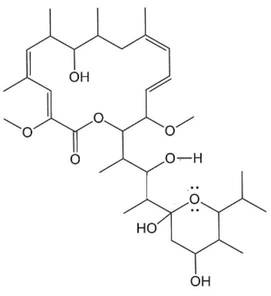
*Palavras Chave: Actinomycetes, Bafilomycins, Marine bacteria, GNPS.*

## Highlights

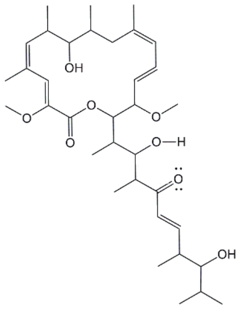
- Marine bacteria were cultivated using *OSMAC* approach and evaluated through GNPS and cytotoxicity assay
- The bioactive extract from strain BRB389 was fractionated and fractions were again analyzed
- GNPS annotated bafilomycins and cytotoxic evaluation revealed unknown bioactive compounds

## Resumo/Abstract

A total of 42 marine bacterial strains from the Trindade and Martim Vaz, Rocas Atoll and Alcatrazes oceanic islands, unique and underexplored environments, were submitted to *OSMAC* approach in order to elicit silent BGCs for the production of secondary metabolites. After bacterial cultivation in five different media, extracts were analyzed through molecular networking and submitted to cytotoxicity assay. The combined approach allowed the identification of strain BRB389 as producer of the bioactive macrolides bafilomycins. In order to confirm the bioactive compounds and further investigate the metabolite production, BRB389 extract was fractionated and fractions were evaluated through LC-MS/MS, GNPS and cytotoxicity assay. The active fractions were analyzed by HPLC-MS/MS and the mass spectra obtained showed that the isolated compounds really belong to the bafilomycin class. Bafilomycins A1 and D were annotated by searching the GNPS spectral library and confirmed by the ion-extracted chromatogram and by analyzing the fragmentation pattern observed in the mass spectrum. Ions of *m/z* 645.4006 $[M+Na]^+$ and *m/z* 627.3896 $[M+Na]^+$ were observed, which presented very similar $MS^2$ fragmentation spectrum. Both fragmentations generated the ion of *m/z* 443.24, which is described in the literature as a product of bafilomycin fragmentation. Molecular networking analysis of the fractions revealed a cluster containing several other analogs of the detected bafilomycins. Such compounds, due to their low abundance, were not initially observed in the HPLC-DAD analyses and their presence was only detected due to the high sensitivity of the LC-MS/MS. The cytotoxicity assay of the fractions indicated two active fractions with compounds not related to bafilomycins that were not annotated by the GNPS spectral library search, indicating that not only the initial annotated compounds were responsible for the observed activity.



bafilomicina A1
*m/z* 645.3973 [M+Na]+
$C_{35}H_{58}O_9$



bafilomicina D
*m/z* 627.3867 [M+Na]+
$C_{35}H_{56}O_8$

## Agradecimentos/Acknowledgments

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**Área: *QPN***

# Dereplication of steroidal alkaloids from herbarium samples of *Solanum jabrense* Agra and M. Nee using HPLC-ESI-MS/MS and support of GNPS

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Palavras Chave: *Solanaceae, Clado Lepstostemonum, Voucher samples, Natural Products, Molecular Network, Glycoalkaloids*.

## Highlights

- It is possible to identify secondary metabolites in fragments of herbarium samples using HPLC-ESI-MS
- Sixteen steroidal alkaloids were identified from herbarium specimens of *Solanum jabrense* collected in different years
- Herbarium samples are useful for the natural products chemistry studies and for chemophenetic studies

## Resumo/Abstract

*Solanum jabrense* belonging to *Solanum* subg. *Leptostemonum* (Solanaceae), is an endemic species from Brazil, distributed in the phytogeographic domains of the Caatinga and Atlantic Forest, in the states of Northeast. *Solanum* L. species are popularly known as "jurubebas", and have great economic importance not only because they are used in human food, but also because they present several secondary metabolites, especially glycosylated steroidal alkaloids and flavonoids, giving them medicinal properties. Recently, dry herbarium specimens have been used to identify metabolites of interest preserved even after years of storage, using a simple and fast method of extraction and analysis by liquid chromatography coupled to mass spectrometry. Dereplication techniques aided by *Global Natural Products Social Molecular Networking* (GNPS) were used to analyze the chemical composition of methanolic extracts from samples of *S. jabrense* herbarium specimens, and to identify chemical markers and bioactive molecules with potential medicinal use. From the LC-MS/MS dataset of the crude extracts, a standard (solasodine) and mobile phase injections as a blank, a molecular network was generated that resulted in the dereplication of 16 spirosolane-type alkamines. Our results suggest that dereplication using fragments of dried *Solanum* specimens is a quick tool to identify potential conserved metabolites, being useful not only for the discovery of new molecules in natural products but also for chemotaxonomy.

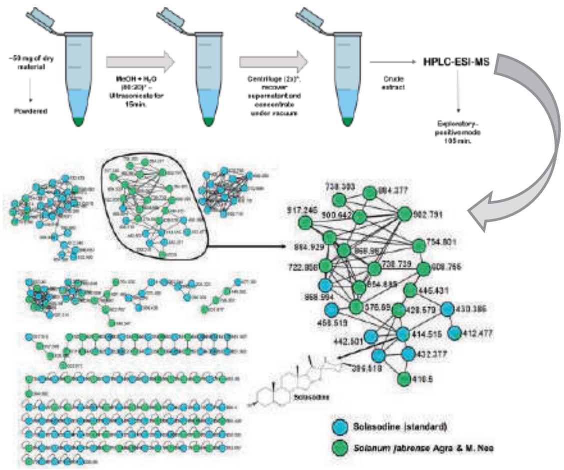

**Table 01.** Glycoalkaloids identified in extracts of *Solanum jabrense* by HPLC-ESI-MS$^n$.

| No. | R.T (min.) | $[M+H]^+$ | Molecular Formula | Error (ppm) | MS$^n$ *m/z* | Idetification |
|---|---|---|---|---|---|---|
| **1** | 18.8 | 608.3793 | $C_{33}H_{53}NO_9$ | -3.5 | MS$^2$ [608]: 590;<br>MS$^3$ [590→ 572]: 410, 285 | Solasodina-2OH-hex ou isômero |
| **2** | 19.0 | 902.5108 | $C_{45}H_{75}NO_{17}$ | -3.1 | MS$^2$ [902]: 884, 394;<br>MS$^3$[884→ 738]: 592, 430, 412 | Não identificado |
| **3** | 20.3 | 916.4900 | $C_{45}H_{73}NO_{18}$ | 0.7 | MS$^2$ [916]:898<br>MS$^3$[898→752]: 736, 606, 590, 444, 428, 410 | Não identificado |
| **4** | 20.7 | 900.4951 | $C_{45}H_{73}NO_{17}$ | 1.6 | MS$^2$ [900]: 882;<br>MS$^3$[882→ 736]: 590, 428, 410 | Solasodina-2OH-rha-hex-rha ou isômero<br>ou Solasodina-OH-rha-hex-hex ou isomero |
| **5** | 21.0 | 738.4423 | $C_{39}H_{63}NO_{12}$ | -1.4 | MS$^2$ [738]:720; 702<br>MS$^3$ [720→ 574]: 412, 396 | Solanigroside P ou isômero |
| **6** | 21.1 | 884.5002 | $C_{45}H_{73}NO_{16}$ | -0.4 | MS$^2$ [884]:866, 848;<br>MS$^3$[866→ 720]: 702, 574, 412, 394, 378 | Solasonina ou isômero |
| **7** | 21.7 | 414.3367 | $C_{27}H_{43}NO_2$ | -0.8 | MS$^2$ [414]: 396, 271, 253, 156 | Solasodina |
| **8** | 21.7 | 754.4372 | $C_{39}H_{63}NO_{13}$ | 0.5 | MS$^2$ [754]: 736, 608;<br>MS$^3$ [608 → 446]: 428, 410, 285 | Solasodina-2OH-hex-rha ou isômero |
| **9** | 21.9 | 884.5002 | $C_{45}H_{73}NO_{16}$ | 1.9 | MS$^2$ [884]:866;<br>MS$^3$[866→ 720]: 704, 558, 396, 378 | Solasonina ou isômero |
| **10** | 22.3 | 868.5053 | $C_{45}H_{73}NO_{15}$ | 2.7 | MS$^2$ [868]: 850;<br>MS$^3$ [850→ 704]: 558, 396 | Solamargina ou isômero |
| **11** | 23.9 | 854.4896 | $C_{44}H_{71}NO_{15}$ | -1.2 | MS$^2$ [854]: 836, 704, 558, 396 | Anguivine, Isoanguivine ou isômero |
| **12** | 24.2 | 576.3908 | $C_{33}H_{53}NO_7$ | 0.1 | MS$^2$ [576]: 558, 396, 253 | γ-solamargina ou isômero |
| **13** | 24.8 | 722.4469 | $C_{39}H_{63}NO_{11}$ | -1.1 | MS$^2$ [722]:704, 558, 396, 271 | β$_1$-solasonina ou β$_2$- solamargina |
| **14** | 24.9 | 446.3265 | $C_{27}H_{43}NO_4$ | -2.8 | MS$^2$ [446]: 428, 410, 285, 267, 239, 175 | (3β,12β,25R)- 3,12-dihydroxy-siprosol-5-en- 27-oic-alcohol ou isômero |
| **15** | 24.9 | 428.3159 | $C_{27}H_{41}NO_3$ | -0.4 | MS$^2$ [428]: 410, 285 | 22α,23α-Epoxysolasodina ou isômero |
| **16** | 29.4 | 410.3054 | $C_{27}H_{39}NO_2$ | -0.7 | MS$^2$ [410]: 392, 267, 239, 173 | 22α, 23α- Epoxy-solanida-4-en-3-one ou isômero |
| **17** | 30.5 | 412.3210 | $C_{27}H_{41}NO_2$ | -0.6 | MS$^2$ [412]: 394, 269, 173 | (25*S*) -22*βN*-espirosol-4-en-3-ona |

## Agradecimentos/Acknowledgments

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**Área: QPN** **Nº de Inscrição: 00143**

# Derivation of bergenin isolated from stem bark of *Endopleura uchi* (Huber) Cuatrec

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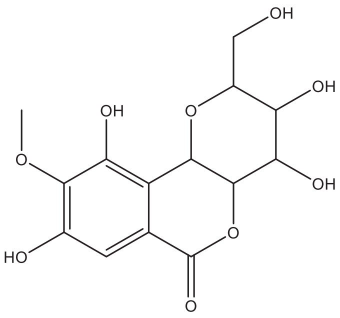
Keywords: *Bergenin, Endopleura uchi, Esterification reaction, Derivatives.*

## Highlights

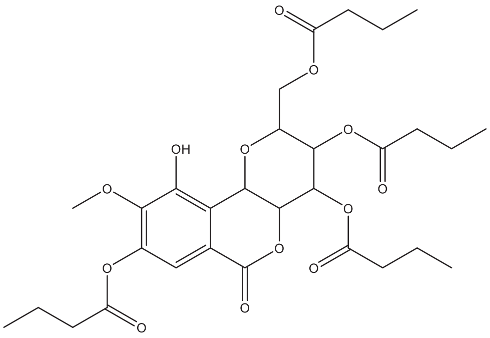
Isocoumarin bergenin was isolated from the methanolic extract of stem bark of *Endopleura uchi*. Bergenin derivatives was obtained by esterification reaction. The substances were identified by Nuclear Magnetic Resonance spectroscopy.

## Abstract

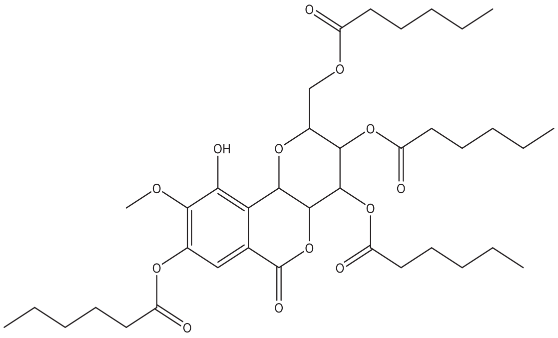
Isocoumarin bergenin is a C-glycoside of 4-O-methylgallic acid which occurs naturally in various plant genera such as *Endopleura uchi* (Huber) Cuatrec (stem bark), a native tree from Amazon. Bergenin is the major component of stem bark and is responsible for several biological activities such as antiasthma, antitussive, anti-inflammatory, antifungal (Prithiviraj et al., 1997), anti-HIV (Piacente et al., 1996) hepatotoxic (Kim et al.,2000), among others. This work aimed the derivation of bergenin through esterification reactions with acid chlorides to obtain derivatives with an improved bioactive potential. Bergenin was obtained from the methanolic extract of the stem bark of *E. uchi*. The derivations of bergenin by esterification reactions were performed following the methodology of Singh et al., (2017) with some modifications, using the butyryl and hexanoyl acid chlorides, obtaining **D1** (50%) and **D2** (60%). The reactions were carried out under reflux for 24h without heating and extracted with AcOEt. The reaction products were purified by CC and evaluated by CCDC and HPLC. The substances (bergenin, **D1** and **D2**) were identified by uni and bidimensional $^1$H and C$^{13}$ Nuclear Magnetic Resonance spectroscopy.



**Bergenin**



**D1**



**D2**

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## Acknowledgments

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**Área: QPN**

# Desreplicação molecular de misturas de acetogeninas acetilênicas com ação anti-*Leishmania infantum* das sementes de *Porcelia macrocarpa*

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Palavras Chave: Porcelia macrocarpa*, Annonaceae, acetogeninas acetilênicas.*

## Highlights

This work reports the molecular dereplication of a bioactive fraction obtained from seeds extracts of *Porcelia macrocarpa*, leading to the characterization of six chemically related acetylenic acetogenins.

## Resumo

As plantas são importantes fontes de moléculas a serem exploradas para o desenvolvimento de protótipos e potenciais fármacos frente ao tratamento de diversas doenças, principalmente aquelas consideradas negligenciadas. Neste contexto, tendo em vista a Leishmaniose que consiste em umas das principais doenças parasitárias que aflige a população brasileira[1], o presente trabalho teve como objetivo realizar o estudo fitoquímico do extrato em $CH_2Cl_2$ das sementes de *Porcelia macrocarpa* (Warm.) R. E. Fries (Annonaceae). Em um estudo prospectivo inicial, foi observado que o extrato bruto mostrou atividade expressiva para as formas amastigotas do parasita (100% de morte a 200 µg/mL) induzindo a realização de processos de isolamento dos compostos ativos. Assim, o extrato bruto foi submetido a cromatografia em coluna de sílica, processo que resultou em quatro frações (A - D) sendo que destas, o grupo C foi o que apresentou maior potencial. O espectro de RMN de $^1$H deste grupo, registrado a 600 MHz, mostrou sinais característicos de acetogeninas acetilênicas em $\delta$ 2,55 (dd, $J$ = 9,9 e 4,9 Hz, H-2), $\delta$ 4,24 (dd, $J$ = 4,8 e 3,1 Hz, H-3), $\delta$ 4,43 (dq, $J$ = 6,5 e 3,0 Hz, H-4) e em $\delta$ 1,41 (d, $J$ = 6,5 Hz, H-5). Esse espectro apresentou ainda um simpleto intenso em $\delta$ 1,26 referente aos hidrogênios da cadeia metilênica longa e um tripleto em $\delta$ 2,11 ($J$ = 6,8 Hz, H-10' e H-13') compatível aos hidrogênios ligados a carbonos adjacentes a ligação tripla. Além desses, foram observados dois sinais característicos de uma ligação dupla terminal em $\delta$ 5,79 (ddt, $J$ = 16,9; 10,2 e 6,7 Hz, H-19'), em $\delta$ 4,94 (m, H-20') e em $\delta$ 0,86 (t, $J$ = 6,8 Hz, H-20'), sendo esse último referente a presença de uma metila terminal. Assim, visando a caracterização estrutural de tais compostos, a mistura foi submetida a analise via CLAE/EM-EM, o que permitiu inferir a presença de seis compostos (**1** – **6** - Figura 1) com formulas moleculares definidas como $C_{18}H_{38}O_3$ ($[M+H]^+$ em *m/z* 363,2890, composto **1**), $C_{25}H_{42}O_3$ ($[M+H]^+$ em *m/z* 391,3140, composto **2**), $C_{23}H_{40}O_3$ ($[M+H]^+$ em *m/z* 365,3041, composto **3**), $C_{25}H_{44}O_3$ ($[M+H]^+$ em *m/z* 393,3400, composto **4**), $C_{27}H_{48}O_3$ ($[M+H]^+$ em *m/z* 421,3679 composto **5**) e $C_{29}H_{52}O_3$ ($[M+H]^+$ em *m/z* 449,3992, composto **6**). Além disso, o estudo da fragmentação observada para cada composto nos espectros EM-EM permitiu inferir a posição da ligação tripla na posição C-11', sendo a variação entre os compostos referente a extensão da cadeia metilênica entre a ligação tripla e a terminação. Dentre esses compostos, apenas **2** e **3** foram descritos anteriormente na espécie[2] sendo os demais, portanto, inéditos. Na próxima etapa do trabalho, pretende-se isolar cada um desses derivados e avaliar a atividade frente a formas amastigotas de *L. infantum*, visando, assim, o estabelecimento de relações estrutura química/atividade biológica.

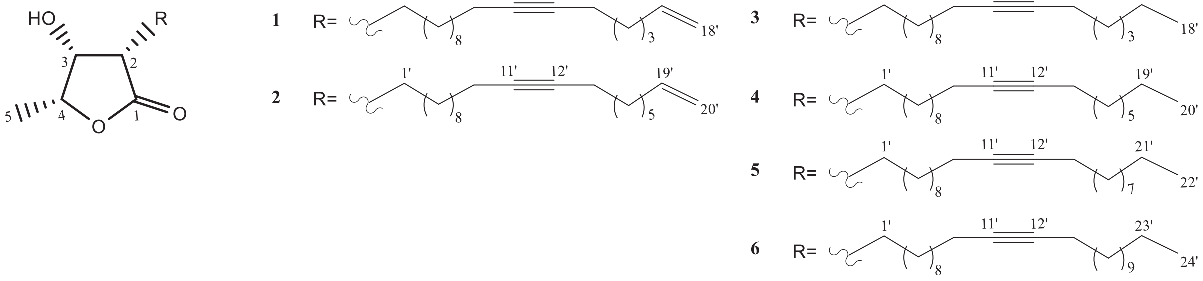

**Figura 1**. Estruturas químicas das acetogeninas **1** - **6**.

## Agradecimentos

**Agradecimentos**: FAPESP, CNPq e a UFABC.

**Referências**: [1] DNDI, **2018**. [2] Chaves, M. H.; Roque, N. F. *Phytochemistry*, 44, 523-528, **1997**.

**Área: QPN**

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

# Determinação da composição química de óleos essenciais das folhas de *Schinus terebinthifolius* e *Siparuna guianensis*

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Palavras Chave: *Óleos essenciais, Monoterpenos, Atividade Antioxidante, Aroeira, Negramina.*

## Highlights

Determination of the chemical composition of essential oils from the leaves of *Schinus terebinthifolius* and *Siparuna guianensis*
β-myrcene was identified as major compound in the essential oil of Negramina.
D-limonene was identified as major compound in the essential oil of Aroeira.
The essential oils showed antioxidant activity.

## Resumo/Abstract

Essential oils are mostly characterized by their biological actions, such as analgesics, anti-inflammatory, fungicides, antimicrobials, insecticides and antioxidants. They are extracted from aromatic plants through the branches, seeds, fruits, roots, buds, flowers, leaves, stems, wood, bark where their chemical constituents are deposited. The present work aimed to evaluate the chemical composition of the essential oils of two species found in the Cerrado of Tocantins State. The essential oil of *Schinus terebinthifolius* (aroeira) and *Siparuna guianensis* (negramina) were obtained from the leaves by hydrodistillation, using Clevenger apparatus, with a yield of 0.16% and 0.20% respectively. Sixteen constituents were identified by gas-chromatography coupled to mass spectrometry (GC-MS) in the essential oil from *S. terebinthifolius* and 20 constituents in the essential oil from *S. guianensis*, the most of them being monoterpenes in both essential oils. The main volatile constituent of *S. terebinthifolius* essential oil was identified as D-Limonene with 12.09%, while for *S. guianensis* species β-Myrcene with 79.47% was identified as the major constituent (Figure 1). The antioxidant activity was determinate using qualitative DPPH method and both essential oils were active. However, the allelopathy activity, using lettuce seeds, was not evidenced for the two essential oils.

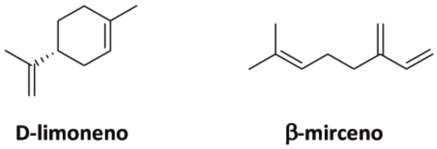

**Figura 1**. Chemical structures of the major constituents of essential oils from the leaves of the species.

## Agradecimentos/Acknowledgments

A UFT e ao Conselho de Desenvolvimento Científico e Tecnológico (CNPq) pela bolsa de Iniciação Científica.

**Área: QPN** **Nº de Inscrição: 965**

# Determination of phenolic compounds in aqueous phase from pyrolysis of guava seeds using LC-DAD and biological evaluation.

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*Keywords*: *Biomass, Pyrolysis, Aqueous phase, LC-DAD, Phenols, Biological evaluation.*

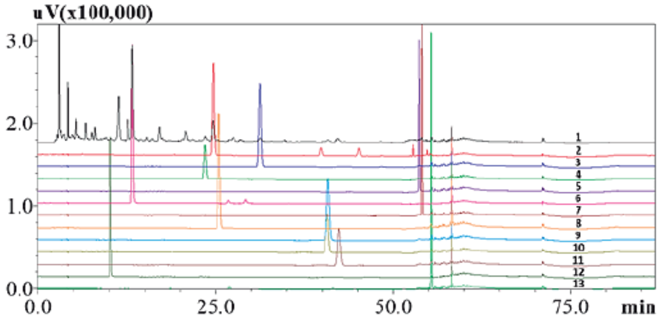
## Highlights

Four phenolic derivatives were identified in the aqueous phase produced from pyrolisis of guava seeds. Catechol was the major compound. The aqueous phase showed potent antioxidant activity.

## Abstract

Pyrolysis is a decomposition of materials by using a thermochemical process involving an irreversible change. The three products obtained from pyrolysis of biomass include biochar, bio-oil and gases. The bio-oil consists of two phases, one aqueous and the other organic. In this aqueous phase, a high concentration of phenolic compounds is present [1]. Thus, the aim of this study is the qualitative and quantitative determination of phenolic compounds present in the aqueous phase of guava seeds, collected at "Pomar do Brasil Indústria e Comércio de Alimentos®", in Aracaju, Sergipe state, using Liquid Chromatography-Diode Array Detection (LC-DAD). Antioxidant (DPPH test) and antifungal tests (microdilution method) [2] were performed with the aim of providing another use for residues generated by biomass pyrolysis. The chemical profiles were obtained by LC-DAD using gradient elution at reverse phase elution mode. Chromatographic analyses were performed on the analytical phenyl-hexyl column (Phenomenex Luna®, 5 µm, 250 x 4,6 mm) following the conditions: mobile phase consisting of 0.5% aqueous formic acid solution (v/v, A) and acetonitrile (B). The gradient elution was: 5-20% (B) in 47 min, 20-100% (B) in 10 min, 100% isocratic (B) for 10 min. The system was then restored to initial conditions in 10 min, and each run was followed by equilibration time of 10 min before the next injection. The solvent flow rate was 1 mL/min and the column temperature was maintained at 40°C. The DAD detector was set at 280 nm and injection volume was 25 µL of a 1.0 % (v/v) solution sample [3]. Of the twelve standard phenolics injected, only four were identified in the sample: 4-methylcatechol, catechol (majority, 6223.6201 ppm), phenol and *para*-cresol (Figure 1). The aqueous phase showed an inhibition of 68% against *Candida albicans* and DPPH inhibition of 80%.

**Figure 1**: Chromatograms of the aqueous phase and the twelve standard phenolic compounds.



**1**: Aqueous phase; **2**: 4-methylcatechol; **3**: Guaiacol; **4**: Phenol; **5**: 3,5-dimethylphenol; **6**: Catechol; **7**: 4-ethylphenol; **8**: 4-methoxyphenol; **9**: *para*-cresol; **10**: *meta*-cresol; **11**: *orto*-cresol; **12**: Resorcinol and **13**: Eugenol.

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**Área:** QPN **Nº de Inscrição: 00908**

# *Diaporthe phaseolorum* molecular family analysis using GNPS platform

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*Keywords: endophytic fungus, special metabolites, chemical classification, molecular families, GNPS, MolNetEnhacer.*

## Highlights

Through MolNetEnhacer, 11 chemical classes were identified in the *D. phaseolorum* ***(Dp)*** ethyl acetate extract, indicating that this endophytic fungus has a chemical structure diversity.

## Resumo/Abstract

Natural products are an important source of bioactive compounds discovery. These compounds played a relevant role on biotechnology development, as medicine prototypes, in the fungi and bacteria control and used as allelochemicals to plant growth inhibition.[1,2] Due to the importance of natural products, new computational approaches to chemical interpretation of large data sets have been develop, such as molecular networks, which is a molecular mining tool to find molecular families and substructures in mass spectrometry fragmentation data.[3,4] Despite these advances, interpreting large-scale, non-targeted metabolomic dataset is still a challenge when reference spectra are not available or when chemical structures need to be assigned.[4] Thus, in order to improve chemical structural information in a molecular network, the MolNetEnhacer tool (https://ccms-ucsd.github.io/GNPSDocumentation/molnetenhancer/) was implemented on the GNPS platform (Global Natural Products Social Molecular Networking), which accelerates the chemical structural annotation in complex mixtures through the combined use of networks spectral molecular masses, fragmentation patterns and *in silico* annotations, providing a more comprehensive chemical overview of spectral data.[4] This tool is based on the molecular structure similarity (analogs) which generate fragmentation spectra that can be grouped according to the chemical classes present in the biological sample.[4] The chemical classes knowledge of secondary metabolites present in an extract increases the ability to supply mechanistic explanations for the biological behavior of the matrix (structure / activity relationship), in addition to enabling a prior analysis of whether the matrix will answer the proposed research hypotsis.[3,4] Therefore, in this work, the MolNetEnhacer tool was employed to track and identify the chemical classes contained in *Diaporthe phaseolorum* (***Dp***) ethyl acetate extract, which has biological potential already described in the literature as bioherbicide, antioxidant, antimicrobial, antifungal, antibactericide, antitumor and larvicide[1,5,6], using LC/Q-TOF-MS/MS and the GNPS platform (http://gnps.ucsd.edu). There were identified 109 compounds of 11 chemical classes in the network using MolNetEnhancer, where molecular families are mainly described as carboxylic acids and derivatives, fatty acids, flavonoids, homoisoflavonoids, indoles and derivatives, organooxygen compounds, piperidines, prenol lipids, nucleosides of purine, azoles, steroids and derivatives. Based on these results, we conclude that MolNetEnhancer is an useful tool that greatly helps the researcher allowing prior knowledge of the chemical characteristics of the matrix of interest.

References

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## Agradecimentos/Acknowledgments

FAPEMAT, CAPES e CNPq for financial support.

**Área: QPN**

# Dimeric flavonoids from *Fridericia prancei* (Bignoniaceae)

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Palavras Chave: *Fridericia*, Bignoniaceae, Flavonoids

## Highlights

Phytochemical studies on *Fridericia* (Bignoniaceae) have been furnished new compounds

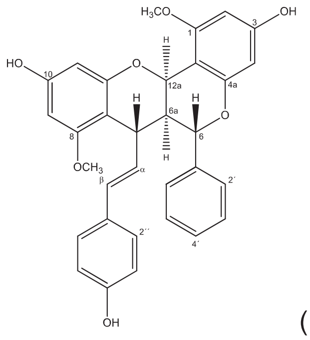
Some species were described as anti-inflammatory, anticarcinogenic and wound healing proprieties

Two unusual dimeric flavonoids were reported here

First ever investigation of chemical components from *Fridericia prancei*

## Resumo/Abstract

*Fridericia* Mart (Bignoniaceae) comprises 60 species, mainly lianas, although some are treelets and scrubs. These species are distributed from Mexico through Argentina, in wet and drought forests[1]. Several phytochemical studies have reported new compounds in this genus, such as unusual dimeric flavonoids, anthocyanidins and xanthones. Also, isolated compounds, as well as extracts and fractions, have shown anti-inflammatory, anticarcinogenic and wound healing activities[2-5]. Thus, the aim of this work is to describe the chemical composition of *Fridericia prancei* (A.H. Gentry) L.G. Lohmann. Leaves of *F. prancei* were collected at Adolfo Ducke Forest Reserve (Manaus, AM), air- dried, grinded, and extracted until exhaustion with hexane and, subsequently, with methanol. After removal of solvent, MeOH extract was re-suspended in MeOH:$H_2O$ (8:2) and partitioned affording hexane, DCM, EtOAc, BuOH and hydroalcoholic (HA) extracts. DCM fraction was fractionated using a Sephadex column eluted with MeOH furnishing 9 fractions. Fraction-6 was purified through semi preparative HPLC, yielding two isolated compounds. These compounds were analyzed by HRMS and NMR (1H, 13C, HSQC and HMBC) and their structures were elucidated as Brachydin A (1) and Brachydin C (2). These unusual dimeric flavonoids were previously reported in *Fridericia platyhphylla* and showed cytotoxic, anti-inflammatory, and analgesic properties.



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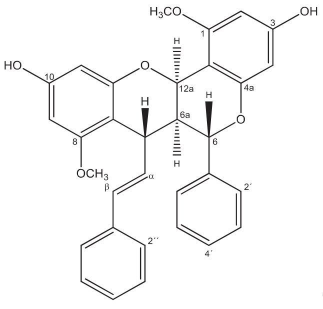

(2)

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# Diterpenes isolated from *Croton lanjouwensis.*

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*Keywords: Clerodane; labdane; NMR; terpenoids.*

## Highlights

- Three compounds were isolated from *Croton lanjouwensis.*
- Report of differents diterpenes in *Croton lanjouwensis*.
- Isolation performed in reversed-phase chromatography by HPLC-DAD.

## Resumo/Abstract

*Croton lanjouwensis* (Jabl) is a species popularly known as "sangra d'água", "orelha de donkey", "maravuvuia" used in folk medicine as a depurative and in the treatment of infections, fractures and colds. This species has synonymy with *Croton matarensis* (Aubl.), the few chemical investigation studies carried out with this species have focused on volatile constituents. Thus, this study aimed to investigate the chemical composition of *Croton lanjouwensis*. To this end, the botanical material, trunk bark, was collected on a privately owned farm in Manaus - AM, in July 2018. An exsiccate was deposited in the INPA Herbarium (Instituto Nacional de Pesquisas da Amazônia) under code JBN-492. This study was registered in SISGEN with registration number A812037. The material was dried in a circulating air oven (45°C) for 5 days and pulverized in a mechanical mill. It was then subjected to extraction by maceration with n-hexane (400:1, g/L), every 72 hours the extractive solution was collected, this procedure under the same extracted material was repeated 5 times. The extractive solution was concentrated under reduced pressure using a rotary evaporator, resulting in the hexane extract (42.8 g). An aliquot of 10 g of this extract was subjected to column chromatography (CC) using silica gel 60 (70-230 mash) as the stationary phase and the solvents n-hexane, chloroform and ethyl acetate, pure or in binary mixtures, as the mobile phase. From this CC, 14 fractions were obtained. Fraction 10 (700 mg) of this CC, after monitoring by CCDA, was subjected to analysis by analytical HPLC-DAD, having C-18 as stationary phase and water and acetonitrile mobile phase, both in a degree of purity suitable for the technique, which after method development, chromatographic peaks were obtained with adequate resolution to carry out their transposition to the preparative scale, which resulted in obtaining 3 peaks with a purity index above 0.99. These peaks were identified in ascending order of retention time as peak: **1** (202.0 mg, $R_T$ = 61.0 min), **2** (39.0 mg, $R_T$ = 66.0 min) and **3** (2.2 mg , $R_T$ = 74.0 min). From the $^1H$ and $^{13}C$ NMR spectroscopic analysis, it was possible to characterize the isolated chromatographic peaks as hardwickiic acid (**1**), 8(17),12*E*,14-labdatriene-18-oic acid (**2**) and communol (**3**). All identified compounds are reported for the first time in the species. In view of the results obtained, this chemical bioprospecting study corroborated with the species *C. lanjouwensis* bioproducer of diterpenes, an important class of secondary metabolites, which are not restricted only to the physiological importance in the plant, but also to its ecological importance and the biological activities that these compounds have antibacterial, antifungal, antimalarial, antibacterial, anthelmintic, antineoplastic, antiviral activity, among others. This fact contributes to the expansion of chemical knowledge of the genus *Croton* and corroborates the chemophenetics of Euphorbiaceae.

## Agradecimentos/Acknowledgments

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**Área: QPN** **Nº de Inscrição:**

# Effects of *C. guianensis* Dichloromethane and Acetone crude Flower Extracts against antiproliferative activity on human tumor cell lines

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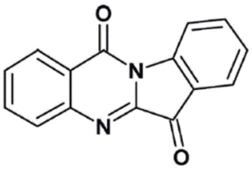
Key words: *Couroupita guianensis* Aubl., alkaloids, Anticancer activity.

## Highlights

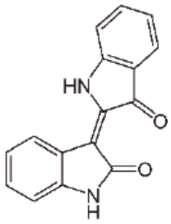
Effects of *C. guianensis* flowers dichloromethane and acetone crude extracts tested *in vitro* on human tumor cell lines demonstrated best results for the acetone extract with selectivity for U251 (TGI=10.8 µg/mL) and PC-3 (TGI=10.1 µg/mL).

## Abstract

Flowers of *C. guianensis* contain a variety of secondary metabolites, among them alkaloids, Tryptanthrin and Indurubin that are reported to be involved with many different pharmacological activities, nevertheless no mention was found for the cytotoxic effect on human cancer cell lines U251 (glioma), MCF-7 (breast); 786-0 (kidney); PC-3 (prostate); and a non-cancer cell line HaCaT (keratinocytes) that prompted this study. The *in vitro* antiproliferative activity test on the above-mentioned human cancer cell lines were performed according to protocol described by Monks et. al (1991). Stock cultures were grown in 5 mL of RPMI 1640 supplemented with 5% fetal bovine serum. Doxorubicin chloridrate used as positive control to determine the sensitivity of cell lines. Cells in 96-well plates (100 µL cells/well) were exposed to sample concentrations in DMSO/RPMI for 48 h at 37 °C and 5% of $CO_2$. Cell proliferation was determined by spectrophotometric quantification of cellular protein content at 540 nm (Molecular Devices®, model VersaMax) using sulforhodamine B (SRB). The total growth inhibition (TGI) was calculated by non-linear regression (sigmoidal fit) using Origin 7.5®. Both dichloromethane and acetone crude extracts were prepared with the fresh plant. The acetone extract had a 10fold better outcome for U251 with TGI acetone extract 10.8 µg/mL against TGI dichloromethane 101.7 µg/mL; for 786-0 TGI acetone 37.0 µg/mL against TGI dichloromethane above 150 µg/mL and for PC-3 TGI acetone 10.1 against TGI dichloromethane 61.1 µg/mL.



**Tryptanthrin**
M.W. 248.1



**Indirubin**
M.W.262.32

This work was supported by the Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) (grant numbers 2018/20252-8).

**Área: QPN**

# Enediyne γ-lactones from *Porcelia ponderosa* (Annonaceae)

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Palavras-chave: Porcelia ponderosa*, enediyne system, γ-lactones.*

## Highlights

Bioactive $CH_2Cl_2$ extract from seeds *Porcelia ponderosa* seeds was subjected for dereplication procedures using NMR and UPLC/MS$^2$ and allowed the identification of two new enediyne γ-lactones.

## Abstract

Antiparasitic acetylene γ-lactones from seeds of *Porcelia macrocarpa* (Annonaceae) were previously described[1,2]. In continuation of these studies, in the present work, the seeds of *Porcelia ponderosa* were sequentially extracted using $CH_2Cl_2$. Obtained extract were tested against trypomastigote forms of *Trypanosoma cruzi*, promastigote forms of *Leishmania infantum* and against the flatworm *Schistosoma mansoni*. As result, the $CH_2Cl_2$ extract exhibited 100% of activity to all tested parasites at 200 μg/mL, suggesting the presence of bioactive compounds. In order to perform the dereplication of this bioactive extract, it was initially analyzed by UPLC – obtained results indicated the predominance of compounds **1** and **2**. In the $^{13}$C NMR spectrum of crude extract were observed signals at δ 172.3 (C-1), 162.3 (C-3), 149.8 (C-4), 105.3 (C-2), and 92.5 (C-5) assigned for the conjugated γ-lactone ring unit.[1] Other signals were observed at δ 85.1 (C-12'), 78.5 (C-14'), 71.8 (C-13'), and 65.1 (C-15'), which, in association with those observed at δ 146.5 (C-16') and 108.6 (C-17'), indicated the presence of an enediyne system.[3] Furthermore, several signals was also observed in the region between δ 28 – 30, indicative of an aliphatic side chain. Finally, it was observed two signals at δ 137.5 (C-23') and 115.1 (C-24'), referring to the terminal double bond carbons, as well as one signal of methyl group at δ 14.0 (C-24'), suggesting the presence of a mixture of unsaturated (**1**) and saturated (**2**) terminal side chain.[1] UPLC/ESI-HRMS$^2$ analysis was performed and displayed $[M - H]^-$ ion peaks at *m/z* 435.2921 and 437.3072, compatible for the molecular formulas $C_{29}H_{40}O_3$ (**1**) and $C_{29}H_{42}O_3$ (**2**). The presence of the γ-lactone ring was confirmed by observation of fragments at *m/z* 137.0255 (**1**) and 137.0245 (**2**). Finally, positioning of enediyne system in the side chain at C-12' was proposed by analysis of fragmentation peaks at *m/z* 263.1665 and 263.1639 for compounds **1** and **2**, respectively, similar of related compounds isolated from *P. macrocarpa*.[2] Therefore, structures of two new acetogenins from *P. ponderosa* were determined as presented in Figure 1. In continuation of this study, both compounds will be isolated using HPLC and individual antiparasitic effects will be evaluated *in vitro*.

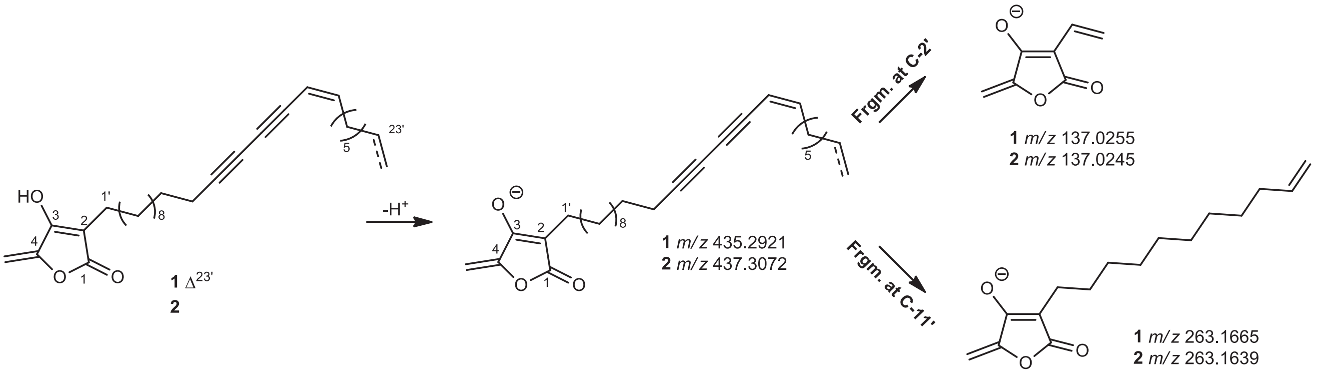

**Figure 1** – Structures of new acetogenins **1** and **2** and their fragmentation pattern observed in the ESI-HRMS$^2$ spectra.

**References** [1]Oliveira, E. A. et al. *J. Nat. Prod*. **2019**, *82*, 1177-1182. [2]Brito, I. A. et al. *J. Braz. Chem. Soc.* **2021**, *32*, 447-453.[3]Bousseroue, H. et al. *Phytochem. Lett.* **2012**, *5*, 29–32.

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**Área: QPN**

# Estudo de secagem por nebulização em mini Spray Dryer MSDi 1.0 LabMaq

**Regina S. Acácio (PG),[1] Vanderson B. Bernardo (PQ),[2] Henrique F. Goulart (PQ),[1] Johnnatan D. Freitas (PQ),[3] Antônio Euzébio Goulart Santana (PQ) [1]***

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Palavras Chave: *spray-drying, maltodextrina, goma arábica.*

## Highlights

Spray Drying Study in Mini Spray Dryer MSDi 1.0 LabMaq.
Spray-drying technique for microencapsulation.
Subsidize the experimental design on the Mini Spray Dryer MSDi 1.0 LabMaq equipment.

## Resumo/Abstract

Os secadores por nebulização, mais conhecidos por "spray dryers", têm como princípio básico a maximização da área de troca de calor e massa durante a secagem, reduzindo o tempo de exposição à alta temperatura, o que permite que materiais de outra forma termolábeis possam ser microencapsulados. Esta técnica pode ser aplicada a qualquer material em meio líquido, seja como emulsões, pastas ou soluções, e gera partículas em tamanho micro em forma de pó. Este trabalho teve como objetivo avaliar a influência do volume usado para microencapsular uma suspensão pela técnica *spray-drying* no equipamento mini spray-dryer MSDi 1.0 da LabMaq (Brasil), de forma a averiguar a variação o de rendimento obtido durante o processo, e portanto, possibilitar a otimização do preparo de suspensões/soluções para o uso do equipamento. Neste trabalho foram microencapsuladas soluções contendo maltodextrina, goma arábica e dióxido de silício coloidal dissolvidas em etanol: água 20%, nos volumes 10, 50, 100, 500 e 1000 mL, a fim de verificar a variação de rendimento destas soluções. Uma vez que esta formulação é base para o preparo de emulsões com óleos de interesse comercial. Os rendimentos foram calculados pela fórmula: R = $\frac{massa\ obtida}{massa\ dos\ sólidos\ totais}\ x\ 100$. Os resultados estão expressos no gráfico 1, e indicam que há aumento no rendimento obtido, à medida que foi aumentado o quanto maior é o volume utilizado durante a secagem. As micrografias obtidas por Microscopia Eletrônica de Varredura (MEV) indicam que as micropartículas formadas são esféricas e uniformes com tamanho médio de 5 µm. Os resultados obtidos subsidiam o planejamento experimental, com base nos rendimentos obtidos, para estudos futuros usando óleos essenciais incorporados à formulação.

Gráfico 1: Rendimento obtido nos respectivos volumes de solução testados.

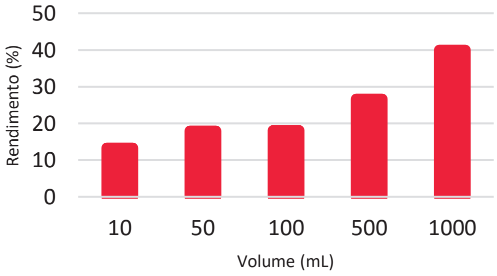
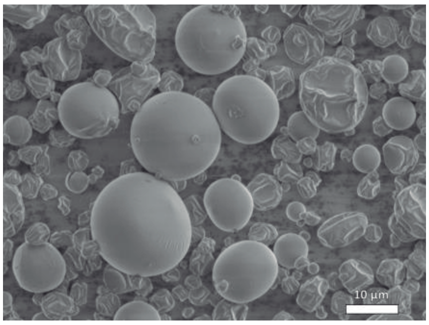


Figura 1: Micrografia das micropartículas.



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**Área: QPN** **Nº de Inscrição: 1032**

# Estudo químico e atividade antibacteriana de fungos endofíticos de *Phanera splendens.*

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Palavras Chave: *Fungos endofíticos, Phanera splendens, Phomoxantona A, Ensaio antimicrobiano.*

## Highlights

Chemical study and antibacterial activity of endophytic fungi of *Phanera splendens*. In this work, it was verified the chemical and biological potential of endophytic fungi of *Phanera splendens*.

## Resumo/Abstract

Fungos endofíticos têm motivado interesse em diversos estudos e vêm representando uma fonte promissora na bioprospecção de novas moléculas com potencial de aplicação tanto na área de fármacos quanto de defensivos agrícolas.[1] *Phanera splendens* (família Leguminosae), popularmente conhecida como escada de jabuti, é uma espécie medicinal que entre seus usos tem a casca do caule empregada pela população indígena para o tratamento de asma e diarréia.[2] Diante disto, este trabalho teve como objetivo o estudo químico e a avaliação da atividade antibacteriana de extratos de fungos endofíticos de *P. splendens.* Foram selecionados 3 fungos endofíticos de *P. splendens* com base nas características morfológicas, *codificados como EJC 14, EJF 04 e EJCP 06,* que estavam depositados na micoteca do Laboratório de Bioensaio e Química de Micro-organismos (LaBQuiM) e cultivados em meio sólido de arroz por 25 dias. Após este período, os extratos foram obtidos a partir da maceração estática com metanol por 3 dias e concentração em evaporador rotativo. Foi avaliada a atividade dos extratos frente às bactérias *Bacillus subtilis, Escherichia coli*, *Pseudomonas aeruginosa e Xanthomonas axonopodis* pv. *passiflorae.* Os extratos foram fracionados por métodos cromatográficos e os compostos isolados identificados por RMN e EM. Apenas o extrato EJC 14 apresentou resultado positivo no ensaio antibacteriano, demonstrando atividade bacteriostática sobre *B. subtilis* e *E. coli* nas concentrações de 125 e 7,8 µg/mL, respectivamente. O extrato EJC 14 foi fracionado em coluna cromatográfica de sílica gel, utilizando hexano, acetato de etila e metanol como fase móvel em gradiente crescente de polaridade. Após análise por CCD, as frações de 164 a 166 foram reunidas, resultando no isolamento do composto (1); um sólido de coloração amarela e solúvel em diclorometano. No espectro de RMN $^1$H de (1), foram observados sinais para hidroxilas queladas em $\delta_H$ 11,50 e $\delta_H$ 14,08, para hidrogênios aromáticos em $\delta_H$ 6,57 e $\delta_H$ 7,39, hidrogênio de carbono ligado a oxigênio em $\delta_H$ 5,39 e $\delta_H$ 4,25/4,18, sinal de hidrogênio metínico em $\delta_H$ 2,34 e sinais de hidrogênios de metilas ligadas ao grupo acetato em $\delta_H$ 1,88, $\delta_H$ 2,05, $\delta_H$ 2,34 e $\delta_H$ 1,01. No espectro de RMN $^{13}$C foram observados 19 sinais, sendo 6 sinais de carbonos aromáticos, 2 sinais de carbonos de duplas ligações e carbono ligado à hidroxila, 3 sinais de carbonos de metilas, 3 sinais de carbonos ligados a heteroátomo, 1 sinal de carbono carbonílico, 2 sinais de carbonos carbinólicos, 1 sinal de carbono metilênico e 1 sinal de carbono metínico. No espectro de massas ESI(+) foram observados os íons de *m/z* 751,55 $[M+H]^+$ e *m/z* 773,41 $[M+Na]^+$, que indicaram massa molecular de 750 Da. No entanto, a presença de apenas 19 carbonos no espectro de RMN $^{13}$C revelou estrutura homodímero simétrica para este composto. Junto com as correlações dos experimentos de COSY e HMBC, e comparação com dados da literatura, a substância isolada foi determinada como sendo a phomoxantona A. Na avaliação da phomoxantona (1) frente a bactéria *B. subtilis* apresentou atividade bactericida até a concentração 39,0 µg/mL, contra *E. coli* revelou atividade bacteriostática na concentração 125 µg/mL. O composto (1) ainda foi avaliado frente a *X. axonopodis* pv. *passiflorae* e apresentou atividade bacteriostática na concentração de 1.000 ppm. A phomoxantona A foi avaliada quanto sua toxidade frente à *Artemia salina* e não apresentou toxidade. Assim, o presente trabalho verificou a capacidade de fungos endofíticos de *P. splendens* em produzir metabólitos com potencial biológico, e levou ao isolamento de phomoxantona A como composto bioativo.

## Agradecimentos/Acknowledgments

À CNPq, Pibic-UFPA

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**Área: QPN** **Nº de Inscrição: 00486**

# EUGENILLA ACETATE PRODUCTION FROM *Syzygium aromaticum* ESSENTIAL OIL BIOCATALIZED BY THE ENDOPHYTIC FUNGUS *Sordaria* sp.

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*Keywords: Essential oil, esterification, endophytic fungus, biocatalysis*

## Highlights

*Stephylium lycopercisi* was immobilized in polyurethane foam and applied in the esterification of clove (*Syzygium aromaticum*) essential oil affording eugenyl acetate as main product.

## Resumo/Abstract

Essential oils are mixtures of volatile, lipophilic substances, usually odorous and liquid, composed of more than 300 different chemical components, including terpenes and phenylpropanoids, making them a product of industrial importance. There are basically three methods for obtaining aroma substances: direct extraction from nature, chemical transformations or transformations by biotechnological route. In addition, to being less aggressive to the environment, biotechnological processes produce aromas considered natural. The solvent-free system, in addition to the use of immobilized biocatalyst, facilitates purification processes, promotes cost savings and enables the use of high concentrations of substrates. The objective of this work was to verify the production of eugenyl acetate from the essential oil of cloves - OECI (*Syzygium aromaticum*) in a system free of organic solvent, using as a biocatalyst the crude enzymatic extract immobilized in polyurethane of the fungus *Sordaria* sp. (TB1). The OECI GC-MS analysis showed eugenol (NIST 05 library) as the major constituent, with a relative area of 63.3% and a retention time of 19.32 min. The determination of the percentage of conversion to eugenyl acetate was carried out by monitoring by CG-EM, the reduction of the integrated area of the signal referring to the limiting agent (eugenol) in the OECI, in comparison to the esterified OECI. In 5 h it was possible to observe 55.9% of esterification, while at the end of the reaction time it was possible to verify 72.55% of eugenol esterification, affording eugenyl acetate as main product. Eugenyl acetate is industrially used in perfumes to emphasize floral odor in clove and in food as flavoring additive. Vanian (2014) described the esterification of eugenol in the OECI of 99.87% under the same conditions used in this work, however, with the commercial enzyme Novozym 435; which makes our data even more promising, considering that we focus on the use of an immobilized enzymatic crude extract. Further studies need to be carried out in order to determine the reaction kinetics and the applicability of the crude enzyme extract in other reactions of esterification of aroma products, as well as the recycling of the biocatalyst in successful reactions.

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## Agradecimentos/Acknowledgments

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**Área: QPN**

# Evaluation of *in vitro*, *in silico* activity and dereplication of alkaloids in *Fusaea longifolia*

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*Keywords: Fusaea longifolia, Alkaloids, LC-MS/MS, Molecular Networking and Molecular Docking.*

## Highlights

*Fusaea longifolia* is a source of bioactive substances that have antiprotozoal activity against *Plasmodium falciparum*, moderate cytotoxic activity, and antioxidant activity. Furthermore, through *in silico* simulation of molecular docking, the stepholidine alkaloid is able to bind strongly to the molecular target, so it is suggested that stepholidine can be used as a prototype for the planning and development of new drugs to combat malaria, capable of inhibiting *P. falciparum* enzymes.

## Abstract

The species *Fusaea longifolia* (Aubl.) Saff, popularly known as “envira” is a species of the Annonaceae family distributed in South America, particularly in the Amazon region. *F. longifolia*, from the chemical and pharmacological point of view, presents few studies so far. Annonaceae species are characterized by the presence of an important class of secondary metabolites, mainly alkaloids with isoquinoline skeletons, to which several biological activities are attributed [2]. Considering the importance of the Amazon rainforest and the continuous discovery of new drugs, rapid characterization of known constituents is required, therefore, dereplication studies in complex matrices by LC-MS/MS and molecular networking (MN) constitute a powerful approach. For this, the bark and leaves of *F. longifolia* were extracted and their respective alkaloid-rich fractions were analyzed by tandem and MN mass spectrometry. A total of 13 isoquinoline alkaloids were de-replicated from *F. longifolia*, through manual MS/MS interpretation, of which eight are reported in the literature and five are unpublished. The alkaloids found: *N*-methylcoclaurine, coclaurine, reticulin *N*-oxide, reticulin, stepholidine, isocoripalmine, oxoxylopine and berberine. In addition, the fractions studied showed high antiprotozoal activity against chloroquine-resistant *Plasmodium falciparum* ($IC_{50}$ =1.6 µg/mL), as well as moderate cytotoxic activity for HCT116 ($IC_{50}$=24.63 µg/mL) and moderate antioxidant activity ($IC_{50}$ =47.63 µg/mL). Considering that the stepholidine alkaloid has already been described as bioactive in the literature [3], in the present study, this alkaloid was submitted to pharmacological analysis in silico by means of molecular anchoring, against the enzyme dihydrofolate reductase-thymidylate synthase from Plasmodium falciparum (PfDHRF- TS). As a result, the alkaloid stepholidine interacted positively with the enzyme PfDHRF-TS (-8.8 kcal/mol), which could be used as a prototype for the development of new drugs to combat malaria, capable of inhibiting *Plasmodium falciparum* enzymes. The results obtained contribute to the knowledge of natural products of the Annonaceae family, as well as point to *Fusae* as a source of bioactive substances.

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**Área: PN** **Nº de Inscrição: 00880**

# Exploration of *Trichoderma spirale* chemical classes employing GNPS

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Keywords: *Trichoderma spirale, special metabolites, chemical class, MolNetEnhacer.GNPS*

## Highlights

Through MolNetEnhacer, 14 chemical classes were identified in the *spirale* ***(Ts)*** ethyl acetate extract, indicating that this endophytic fungus has a chemical structure diversity.

## Resumo/Abstract

Mass spectrometry is a technique used to identify compounds in undirected metabolomics experiments. [1] Due to the reference spectra absence, most molecules cannot be identified and many spectra cannot be used.[1] In this context, the *MolNetEnhacer* (https://ccms-ucsd.github.io/GNPSDocumentation/molnetenhancer/), a method that was implemented on the GNPS platform (http://gnps.ucsd.edu), to accelerate the chemical structural annotation in complex matrix combining mass spectral molecular networks, fragmentation patterns and *in silico* annotations, providing a more comprehensive chemical overview of spectral data.[2] This tool allows analysing the chemical classes and subclasses in the molecular networking. Based on the predominant chemical classes present in a plant extract, significantly increases the ability to provide explanations for the matrix biological behaviour, as well as assessing whether molecular families are of particular interest for the research objective.[2] Therefore, in this work, the MolNetEnhacer tool was employed to track and identify the chemical classes contained in *Trichoderma spirale* ***(Ts)*** ethyl acetate extract, which has biological potential already described in the literature as bioherbicide, antioxidant, antimicrobial, antifungal, antibactericide, antitumor and larvicide[1,5,6], using LC/Q-TOF-MS/MS and the GNPS platform (http://gnps.ucsd.edu). There were identified 111 compounds of 14 chemical classes in the network using MolNetEnhancer, where molecular families are mainly described as azoles, benzene and derivatives, carboxylic acids and derivatives, cinnamic acids and derivatives, diazines, fatty acids, flavonoids, oxanes, pirans, phenolic ethers, prenol lipids, pyrimidine nucleosides, organooxygen compounds, steroids and derivatives.

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## Agradecimentos/Acknowledgments

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**Área: QPN**

# Fenilpropenos raros identificados no óleo essencial de *Croton grewioides* Baill. (Euphorbiaceae) coletado em Sergipe, Brasil

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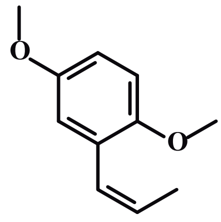
Palavras Chave: *Croton grewioides, Óleo essencial, Fenilpropenos.*

## Highlights

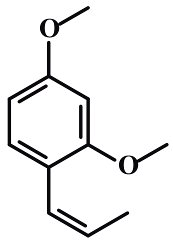
Identification of rare phenylpropenes in the essential oil of *Croton grewioides* Baill. (Euphorbiaceae) collected in Sergipe, Brazil. Rare phenylpropenes were found as the major compounds in the essential oil of *C. grewioides* growing in Poço Verde-SE. This species is a promising natural source of this compounds.

## Resumo

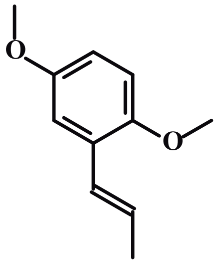
*Croton grewioides* Baill. é uma espécie pertencente à família Euphorbiaceae, endêmica do nordeste brasileiro e que possui alto teor de óleo essencial comparado a outras espécies do mesmo gênero. No presente estudo, realizamos a prospecção química dos óleos essenciais de *C. grewioides* oriundo de Poço Redondo-SE (OECGPR) e de Poço Verde-SE (OECGPV) através da caracterização dos constituintes dos óleos essenciais utilizando GC-MS/FID, nos quais fenilpropenos foram os compostos majoritários. Os conhecidos fenilpropropenos eugenol e metileugenol foram os principais compostos identificados no OECGPR. Já o OECGPV foi submetido a separação por cromatografia em coluna usando sílica-gel e eluição com hexano:$CH_2Cl_2$ em gradiente crescente de polaridade. Treze frações foram obtidas e, após análise por CCDA seguido por GC-MS/FID, duas frações que continham os compostos majoritários foram analisadas também por ressonância magnética nuclear (RMN 1D e 2D). Estas análises permitiram identificar que os fenilpropenos majoritários do óleo essencial de *C. grewioides* oriundo de Poço Verde (OECGPV) são os isômeros (*E*)- e (*Z*)-isoosmorhizol [2,4-dimetoxi-1-(1-propenil)benzeno], os quais são produtos naturais raros [1,2] e inéditos no gênero *Croton*, e (*E*)- e (*Z*)-pseudometilisoeugenol [1,4-dimetoxi-2-(1-propenil)benzeno], os quais estão sendo relatados pela primeira vez como produtos naturais.



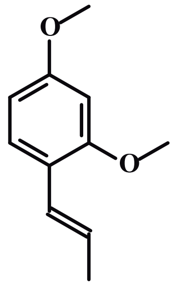
**(*Z*)-pseudometilisoeugenol**



**(*Z*)-isoosmorhizol**



**(*E*)-pseudometilisoeugenol**



**(*E*)-isoosmorhizol**

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**Área: QPN**

# Flavonoid Brachydin A shows selective cytotoxicity and antitumoral activity in human metastatic prostate (DU145) cancer cells

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Palavras Chave: *Apoptosis, Fridericia platyphylla, Chemoprevention, Cytotoxicity, Phytochemical*

## Highlights

Treatments with Brachydin A did it was observed increased cell death by necrosis in metastatic prostate DU145 cells. Brachydin A did not induce cell death non-tumor prostate cells (PNT2).

## Resumo/Abstract

In prostate cancer, flavonoids possess a wide variety of anticancer effects, focused on the antioxidant/ pro-oxidant activity, inactivation of the androgen receptor, cell cycle arrest, apoptosis induction, metastasis inhibition, among others. This current research investigated the antitumoral in vitro activity of Brachydin A (BrA), a dimeric flavonoid (Fig. 1) isolated from *Fridericia platyphylla*, in human castration-resistant prostate cancer DU145. It was compared BrA selective effects in tumor prostate DU145 cells with non-tumor prostate epithelial PNT2 cells. Cell viability experiments (resazurin, neutral red, MTT, and LDH release assays) showed that BrA was sevenfold more cytotoxic to tumor cells than non-tumor prostate cells, with $IC_{50}$ values of 77.7 μM and 10.7 μM for PNT2 and DU145 cells, respectively (Fig. 2). Furthermore, BrA induced necrosis and apoptosis (triple fluorescence staining assay) without interfering with oxidative stress (CM-H2DCFDA) in DU145 cells. Also, BrA (15.36 μM) reduced cell proliferation on clonogenic assay (DU145 cells) but no change in cell number and protein content was observed when cell growth curve assay was used. Wound healing and transwell assays were used for checking the effects of BrA on cell migration and invasion, and BrA impaired these processes in PNT2 (wound healing) and DU145 cells (transwell). Our results inspire further studies to test BrA as a novel chemotherapeutic drug and to evaluate its effects on drug-resistant metastatic cancer cells.

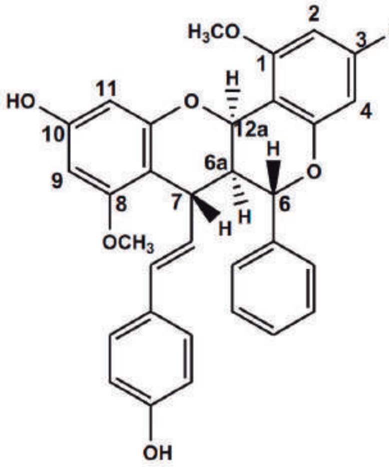

**Fig. 1:** Chemical structure of Brachydin A

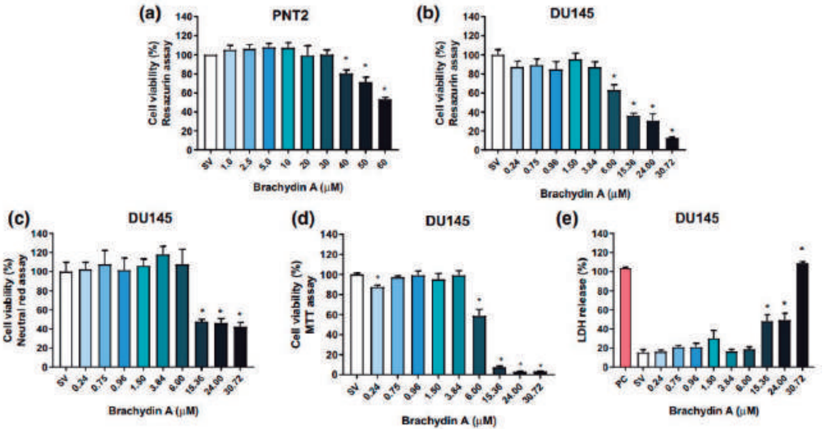

**Fig. 2:** The resazurin assay has assessed cell viability (%) in **a** PNT2 and **b** DU145 cells treated with different concentrations of Brachydin A (BrA) for 24 h. Additional cell viability assays in DU145 cells treated with BrA for 24 h were assessed by **c** NR, **d** MTT, and **e** LDH release.

## Agradecimentos/Acknowledgments

This work was supported by FAPEMA (Proc.: 145775/2021), CNPq (Proc.: 409680/2021-4, 426246/2018-7, and 401516/2016-4), and CAPES - [Finnance Code 01].

# Flavonoids and benzoic acid derivative isolated in the EtOAc fraction from *Paepalanthus acanthophyllus* (Eriocaulaceae)

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Keyword: *Eriocaulaceae, Paepalanthus acanthophyllus, Flavonoids, Benzoic acid derivative.*

## Highlights

Three novel and one known compounds were isolated in the ethyl acetate fraction from *Paepalanthus acanthophyllus* (Eriocaulaceae) by classical e modern chromatography techniques.

## Abstract

*Paepalanthus* genus belongs to the Eriocaulaceae family. Studies on the chemical constituents of *Paepalanthus* species identified, mainly, the presence of flavonoids and naphthopyranones. In *P. acanthophyllus*, a single phytochemical study has been found so far, performed with the methanolic extract, in which three glycosylated derivatives of 6-methoxykaempferol, paepalantine and one of its glycosylated derivatives were isolated. To continue and contribute to thespecies' phytochemical study, this work aims to isolate chemical compounds from the EtOAc fraction from *P. acanthophyllus* capitula. The capitula were collected in Goiás State, dried, milling, weighed, and extracted with methanol. The methanol extract was partitioned with the hexane, $CH_2Cl_2$, EtOAc and MeOH. The EtOAc fraction was submitted to classical and modern chromatography techniques, obtaining the compounds **PaAc-01**, **PaAc-02**, **PaAc-03**, and **PaAc-04**. Compounds were elucidated by nuclear magnetic resonance (NMR) (Figure 1) and it was determined the presence of 6-methoxykaempferol (**PaAc-01**), *p*-hydroxybenzoic acid (**PaAc-02**), 6-methoxykaempferol-3-*O*-β-D-6''-(*p*-cumaroyl)-glycopyranoside (**PaAc-03**), and 6-methoxykaempferol-3-*O*-β-D-glycopyranoside (**PaAc-04**). It is important to emphasize that only **PaAc-04** was previously isolated in the species.

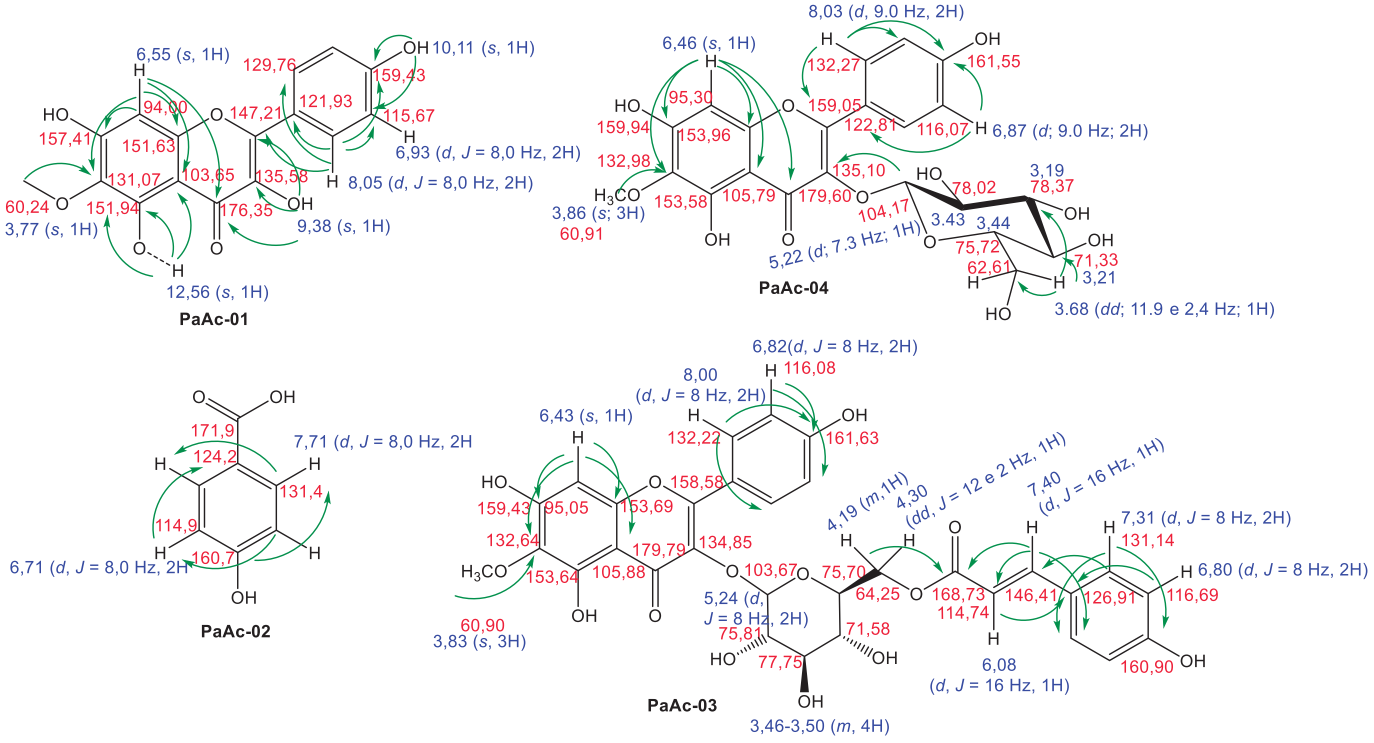

**Figure 1.** Compounds isolated in the EtOAc fraction from *P. acanthophyllus* capitula.

## Acknowledgments

This study was financed by the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq - Process: 140164/2020-0), Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – Brasil (CAPES) – Finance Code 001, and the Federal University of Espírito Santo.

**Área: QPN** **Nº de Inscrição: 00778**

# Glycosylated pyrone derivative from fungi basidiomycete *Neonothopanus gardineri* and evaluation of its cytotoxic potential

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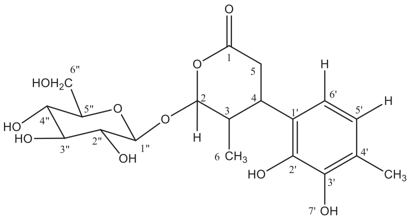
**Keywords: mushroom, fungi, pyrones, *Neonothopanus gardineri.***

## Highlights

In this work one substance was isolated from the bioluminescent mushroom *Neonothopanus gardineri*. According to the literature, this substance is not identified from this specie up until the present. In terms of the cytotoxic potential of *N. gardineri*, its methanolic extract showed to be cytotoxic against anaplastic thyroid cancer cells (KTC-2), reducing cell viability.

## Abstract

*Neonothopanus* is a bioluminescent fungi basidiomycete genus belonging to Marasmiaceae, with only two species described in the literature: *N. nambi* and *N. gardineri.* Both of them occur mainly in Australia, Malaysia and in Brazil [1]. *N. gardineri* is known for its bioluminescence, capable of emitting green light, which metabolism is not well known up until the present [2]. In terms of the metabolites produced by this specie, only a few of them are described, being most of them terpenes, such as sesterpene, sesquiterpenes and triterpenes [3]. Therefore, this work aims to evaluate its cytotoxic potential of the methanolic extract obtained from *N.* gardineri against anaplastic thyroid cancer cells (KTC-2), as well as identify its metabolites. According to the results obtained, it was possible to see that the methanolic extract from *N. gardineri* is cytotoxic against KTC-2 at 60 μg/mL after 72 h of treatment, resulting in reduction of cell viability. O the other hand, chromatographic fractionation the methanolic extract afforded the isolation of a glycosylated substance: glycosylated calopin analogue **(1)**. The substance was characterized with of the bases of spectroscopic and spectrometric techniques. To the best of our knowledge, this substance was not isolated from this specie until nowadays.



**(1)**

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## Acknowledgments

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**Área: QPN** **Nº de Inscrição: 01231**

# Identificação de compostos químicos por FT-TR e atividade antioxidante do extrato hexânico de cascas de jambo-vermelho (*syzygium jambos*).

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Palavras Chave: *Jambo, Antocianinas, Infravermelho por Espectroscopia*

## Highlights

Identification of chemical compounds by IF-TR and antioxidant activity of the hexanium extract of red jambo (syzygium jambos) barks. The jambo extract showed good antioxidant activity due to the presence of antigens detected by the phytochemical testicles and by the IF-TR.

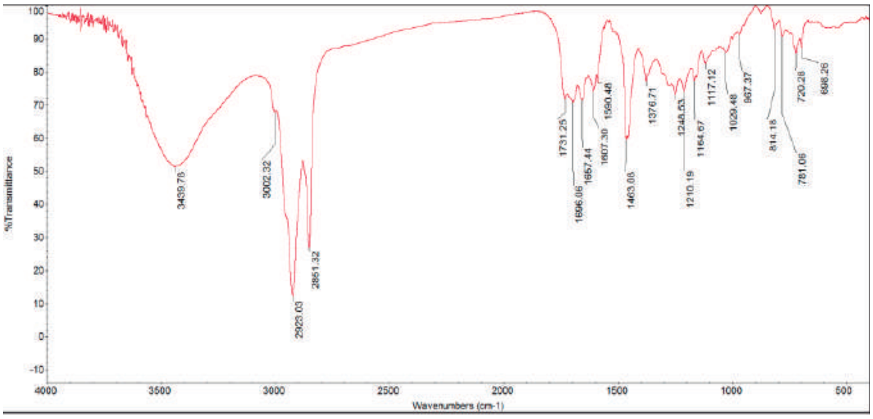
## Resumo/Abstract

A espectroscopia no infravermelho se baseia no fato de que as ligações químicas das substâncias possuem frequências de vibração específicas, as quais correspondem a níveis de energia da molécula (chamados nesse caso de níveis vibracionais). A Espectroscopia no infravermelho por transformada de Fourier (FT-IR) é uma técnica de análise para colher o espectro infravermelho mais rapidamente. Em vez de se coletar os dados variando-se a frequência da radiação infravermelha, a radiação IV (com todos os comprimentos de onda da faixa usada) é guiada através de um interferômetro. Neste trabalho foi utilizado o extrato hexânico de cascas de jambo-vermelho (*Syzygium jambos*) para avaliação fitoquímica, antioxidante e determinação das moléculas de substâncias ativas presentes em suas cascas. O extrato hexânico foi realizado por meio de extração a quente em Soxhlet durante 4 horas. Os espectros de infravermelho foram obtidos utilizando um espectrofotômetro modelo Nicolet iS5 da Thermo Scientific. As amostras foram preparadas na forma de pastilhas de KBr na proporção 1:100 (m/m) (amostra:KBr) e os espectros registrados no intervalo de 4000 a 400 $cm^{-1}$, empregando-se 32 scans e resolução de 4 $cm^{-1}$. Na avaliação fitoquímica de acordo com Matos (1994), o teste fitoquímico deu positivo para antocianinas, fato esse semelhante a outras espécies de frutos de coloração vermelha, como acerola e morango (Figura 01). Essas substâncias presentes nessas frutas trazem benefícios para saúde tendo boa antioxidante, pois são moléculas doadoras de elétrons, impedindo a formação dos radicais livres. A determinação da atividade antioxidante foi realizada utilizando o radical DPPH, apresentando um potencial de varredura de aproximadamente 10000 ppm. A presença de antocianinas no extrato das cascas de jambo-vermelho foi confirmada pela o espectro obtido pelo FI-TR (Figura 02), de acordo coma presença dos grupos hidroxilas, IDH igual a 5 é compatível com a presença de um anel aromático. As absorções entre 1300 e 1100 $cm^{-1}$ (nC-O) e a presença de banda de absorção a 3312 $cm^{-1}$ (nO-H) permitem assinalar que a substância tem função mista - éster e fenol. Através dos resultados obtidos concluímos que as cascas de frutas ricas em fibras e substâncias como antocianinas possuem um potencial alimentar, muitas vezes descartados para ingestão alimentar.

**Figura 01**

| Compostos fitoquímicos | Ext. hexânico |
|---|---|
| Flavonas, Flavonóis, Flavonóides | Traços p flavonóides |
| Fenóis | traços |
| Esteróis | ausente |
| Antocianinas, antocianidinas | presente |
| Saponinas | ausente |
| Taninos | presente |

**Figura 02**



## Agradecimentos/Acknowledgments

Ao LQPN – UECE pela análise da mostra pelo FI-TR.

**Área: QPN** **Nº de Inscrição: 00604**

# Identification of bisresorcinol derivatives in wood residues from *Roupala montana* (Aubl) and activity against *Cryptococcus*

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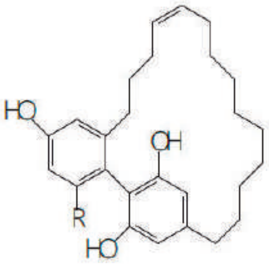
Palavras Chave: Louro-faia, kermadecin, *Cryptococcus neoformans*, *Cryptococcus gattii*

## Highlights

The chromatographic fractionation of the methanolic extract from wood residues of *Roupala montana* led to the isolation of bisresocinol derivatives with activity against the fungi *Cryptococcus neoformans* and *Cryptococcus gattii.*

## Resumo/Abstract

*Roupala montana* (Aubl), belonging to the Proteaceae family, has a geographic distribution in northern Brazil, where it is known as “louro-faia”. There are few reports in the species related to its secondary metabolites, only three flavonoids glycosyled in aerial parts[1] and one resorcinol derivative from wood residues resorcinol.[2] In this studies with wood residues of the species the methanolic extract was subjected to chromatographic fractionations in successive columns using silica gel (230-400 mesh), sephadex and cellulose resulting in purification of **1** (17 mg) and **2** (10 mg) (Figure 1). The antifungal test with compound 1 was performed based on the microdilution technique in syrup using strains of fungi *Cryptococcus neoformans* and *C.* gattii. The compounds were identified based on the $^{1}$H and $^{13}$C NMR spectra, HSQC and HMBC. The $^{1}$H NMR of **1** showed signs of 4 aromatic hydrogens (δ 6,42 - 6,29), olefinic hydrogens (δ 5.34), methylene groups (δ 2.56-1.29) and methoxy (δ 3.61). The $^{13}$C NMR spectrum shows displacements of the olefinic pair in δ 129.73 and 129.51, in which in HSQC it showed correlations with hydrogens in δ 5.34. The HMBC experiment helped in the positioning of hydroxyls and methoxyl. The spectral data of **2** were similar to that of **1** with the absence of methoxyl. Thus, the compounds were identified as methoxy kermadecin H and kermadecin H, respectively. The 20-membered macrocycle with methyl in ring B is being reported for the first time and showed excellent antifungal activity to *C. neoformans* and *C. gattii.*



| CIM (µg/mL) de 1 | |
|---|---|
| *Cryptococcus neoformans* | *Cryptococcus gattii* |
| 5 | 10 |

1) R = OMe
2) R= OH

**Fig 1.** Compounds identified from *Roupala montana* and antifungal activity

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## Agradecimentos/Acknowledgments

**Área: QPN** **Nº de Inscrição: 01192**

# Identification of compounds present in two different Caatinga medicinal plants obtained in free markets in Senhor do Bonfim – BA

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Palavras Chave: *Medicinal plants, Caatinga, Sene, Senna alexandrina, Umburana, Commiphora leptophloeo*

## Highlights

We identified compounds present in several samples of two medicinal plants. Compounds had a high variation between samples, which can mean adulteration, misidentification or storage error.

## Resumo/Abstract

Medicinal plants of Brazilian native flora are consumed with little or no proof of its pharmacological properties, based only on users' or traders' reports. Although they are natural and, therefore, popularly considered free of side effects, medicinal plants' toxicity is a serious public health concern, either because of the plant's own compounds, either by adulterations or interaction with other medicines.[1] Since these medicinal plants are usually sold in markets and free fairs by people without formal education, there may be labeling or manipulation problems, resulting in the absence of the desired effects or presence of adverse effects.[1] These plants should have stricter control regarding the plant origin, time since it was harvested, way of collection, storage, drying and packing, and contamination presence.[2] In this work we identified compounds present in different medicinal plants samples found in Senhor do Bonfim free market (BA): six samples of Sene (*Senna alexandrina*; Fabaceae) and six samples of Umburana (*Commiphora leptophloeo*; Burseraceae). For the extraction of the compounds in sene, we used hydrodestilation, and for umburana we extracted the compounds using maceration with hexane. All extracts were analyzed by GC-MS. The main compounds present in sene extracts were n-hexadecanoic acid (49,79-84,64%), (Z,Z,Z)-9,12,15-octadecatrienoic acid (1,97-13,2%), tetradecanoic acid (2,15-4,57%), and two unidentified compounds in 1,89-11,95% and 1,45-8,49%. For umburana, the compounds present were octadec-9-enoic acid (34,56-63,14%), cumarin (5,57-48,27%), n-hexadecanoic acid (4,93-8,32%), octadecanoic acid (2,11-3,79%) and two unidentified compounds in 3,38-7,35% and 3,48-8,97%. As we can see, compounds in both plants had a high variation between samples, which can mean either that some of the medicinal plants sold in free markets belong to a species different from the announced one or, at least, that compounds found in the sample had degraded between harvest and sale. Further analysis in molecular level will define if all samples are from the same species. Genotoxicity and cytotoxicity tests will be done with all samples in the future in order to confront chemical and toxicity data.

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## Agradecimentos/Acknowledgments

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**Área: QPN** **Nº de Inscrição: 00602**

# Influence of circadian rhythm on chemical composition of *Ruellia paniculata* essential oils from Northern Ceara state (Brazil).

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Palavras Chave: *Circadian Rhythm, R. paniculata, Terpenics.*

## Highlights

- Influence of circadian rhythm
- Chemical composition of *Ruellia paniculata* essential oils.

## Resumo/Abstract

The genus *Ruellia* L. comprises about 300 species, which are broadly distributed in tropical and subtropical regions of the planet. Among the species that comprise the genus, *Ruellia paniculata* (Figure1), known popularly as "Melosa" and "Melosa-purple". Phytochemical research about species belonging to the genus *Ruellia* are scarce, however the literature reveals that some of these species are widely used in folk medicine. *Ruellia paniculata*, is a hairy, sticky shrub, with opposite leaves, rough and square stem. It is found naturally in soils affected by salts, which occur in shallows, more favored by moisture. The fruits have a curious way of releasing the seeds, which, in the form of a disk, are thrown away in a manner similar to a catapult. The purple flower with a funnel-shaped corolla is visited by different species of bees, being important for composing its diet in the dry period of the year. Therefore, the objective of this work was to evaluate the time of harvest (6 am, 12 pm and 17 pm) in the volatile composition of the aerial parts of *R. paniculata*. The essential oils were extracted by hydrodistillation for 2 h from the aerial parts of the vegetable and analyzed by gas chromatography coupled to a mass spectrometer (GC-MS). The results showed that the essential oil from *R. paniculata* is composed predominantly of sesquiterpene compounds, being variable according to the time of harvest. A low percentage of monoterpenes was observed only at 6 am (0.62%) and 17 pm (0.71%). Regarding the major componentes, α-cadinol (**1**), germacrene D (**2**) and β-caryophyllene (**3**) (Figure 2) stood out with the highest percentage in all harvest times evaluated, although germacrene D (17.33%) was identified only at 6 am. The α-cadinol sesquiterpene varied by 14.44%; 20.95% and 28.56% for the hours of 6 am, 12 pm and 17 pm, respectively. The β-caryophyllene (23.83%) presented a higher percentage in 6am of harvest, with a reduction to 9.39% (12 pm) and 10.08% (17 pm). Finally, considering the results obtained from the present study, the chemical composition of the essential oil from *R. paniculata* present in the Northern region of Ceará is dependent on the time of harvest, and future studies of this variation in the biological properties of this species are pertinent.

**Figure 1**. *R. paniculata*

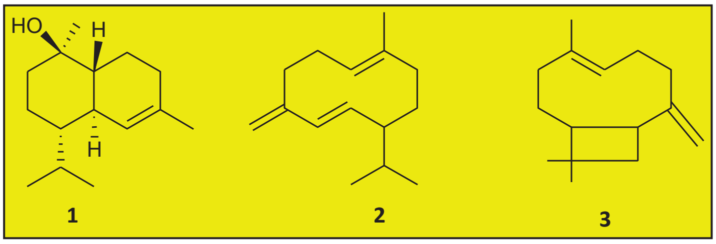

**Figure 2**. Major componentes of the essential oils from *R. paniculata*

## Agradecimentos/Acknowledgments

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**Área: QPN** **Nº de Inscrição: 00923**

# Insecticidal activity of essential oils of *Pelargonium graveolens* l'Herit and *Lippia alba* (Mill) N. E. Brown against *Spodoptera frugiperda* (J. E. Smith)

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Palavras Chave: *Lippia alba; Pelargonium graveolens; Spodoptera frugiperda.*

## Highlights

Essential oils of *L. alba*, *P. graveolens* and its insecticidal activities against *Spodoptera frugiperda*. Bioinsecticide, Azamax®, cause lower mortality geraniol, linalol, carvona and citral.

## Abstract

*Lippia alba* (Mill) N. E. Brown and *Pelargonium graveolens* L'Herit are major producers of essential oils (E.O) and have several applications, mainly in the perfumery, cosmetics and pharmaceutical industries. *L. alba* is an aromatic medicinal plant that occurs in almost all regions of Brazil. Several volatile compounds are present in the E. O of this plant, among which stand out: citral (geranial + neral), linalool, limonene, carvone, camphor and 1,8-cineole. *P. graveolens* is known as fragrant mallow or geranium and was introduced in India in the early 20th century. Citronellol, geraniol, linalool and citronellate formate are the main components present in oil essential of this species. In this work, insecticidal activity of E. O of *Pelargonium graveolens*, *Lippia alba* and compounds geraniol, linalool, 1,8-cineole, limonene, carvone, citral and Azamax® were evaluated against *Spodoptera frugiperda*. Topical application assay showed E. O of *P. graveolens* has acute toxicity against *Spodoptera frugiperda* larvae (third instar) with LD50 1.13 µg/mg per insect and LD90 2.56 µg/mg per insect. Three E. O of *L. alba* also exhibited insecticidal activity with LD50 ranging from 1.20 to 1.56 µg/mg per insect and LD90 from 2.60 to 3.75 µg/mg per insect (Table 1). Geraniol, linalool, carvone and citral caused significant mortality of 30, 90, 84 and 64% respectively, compared to negative control. The bioinsecticide, Azamax®, caused lower mortality than the compounds of the E. O.

**Table 1**. Estimates of $DL_{50}$ e $DL_{90}$ (in µg/mg insect) and confidence interval of essential oils for third instar *Spodopetra frugiperda* caterpillar, after 24 hours topical application. Temp.: 25 ± 1°C; U.R.: 70 ± 5%; photophase: 12 hours.

| **Essential oils** | **Angular coefficient (± EP)** | **$DL_{50}$ (IC)[a]** | **$DL_{90}$ (IC)[a]** | **$\chi^{2\,(b)}$** | **g.l.[c]** |
|---|---|---|---|---|---|
| *P. graveolens* (PEL-001) | 3,61±1,04 | 1,13 (0,83 - 1,45) | 2,56 (1,83 - 7,23) | 1,09 | 2 |
| *Lippia alba* (LA-10) | 3,98±0,95 | 1,24 (0,89 - 1,52 ) | 2,60 (2,04 - 4,45) | 0,85 | 2 |
| *Lippia alba* (LA-22) | 3,37±0,69 | 1,56 (1,18 - 2,02) | 3,75 (2,75 - 6,99) | 1,21 | 2 |
| *Lippia alba* (LA-57) | 3,13±0,74 | 1,20 (0,90 - 1,57) | 3,08 (2,15 - 7,18) | 1,12 | 2 |

[a] IC: confidence interval to 95% of error probability. (b) $\chi^2$: calculated chi-square value.c[c] g.l.: degrees of freedom.

## Acknowledgments

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**Área: QPN** **Nº de Inscrição: 00593**

# Integrated Analytical Tools for Discovering Anti-Leukemia Metabolites from *Urena lobata* L. (Malvaceae)

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Key words: *dereplication, leukemia assays, Urena lobata.*

## Highlights

Crude extracts obtained from *Urena lobata* L. were submitted to anti-leukemia assays. Among them, dichloromethane extract from the aerial parts was selected to start our chemical approach. Based on this, the study is being performed using two rapid dereplication strategies: *Target Analysis* (Bruker Daltonics®) MS data analysis combined with MS/MS data obtained from GNPS platform. Preliminary data showed the presence of different classes of Natural Products in the cytotoxic extracts.

## Abstract

The combination of hyphenated techniques may increase the efficiency and speed of analysis, being useful tools to access unrevealed natural products (**NPs**), which include molecular dereplication [1,2]. In this sense, our goal is the employing of integrated analytical techniques to accelerate the discovery of metabolites (*unknown or not*) from *Urena lobata* L., guided by anti-leukemia assays. For this, different human leukemia cells were employed in an initial screening: Raji (Lymphocyte B), CCRF-CEM (Acute Lymphoblastic Leukemia) and Kasumi-1 (Acute Myeloid Leukemia). The cytotoxic assays (during 24 hours at 100 µg/mL) allowed us to select the dichloromethane extract from the aerial parts of *U. lobata* L. (**ULD**). After a chromatographic column (on silica flash), ten subfractions from **ULD** (2,0 g) were obtained; all of them were submitted to the cytotoxic evaluation again. Most of them practically inhibited at least 85% of the leukemia cells proliferation (figure 1A). Our UHPLC-MS analyzes revealed the presence of more than 100 ions present in the subfractions. Through the integrated tools we were able to find some compounds related and also unrelated in the literature for the species, for example (figure 1B), urenalobaside A (**1**), glycosilated urenoside (**2**) and hydroquinidine (**3**) which reveals, therefore, good perspectives for discovering anti-leukemia and/or unrelated **NPs** from *U. lobata* L.

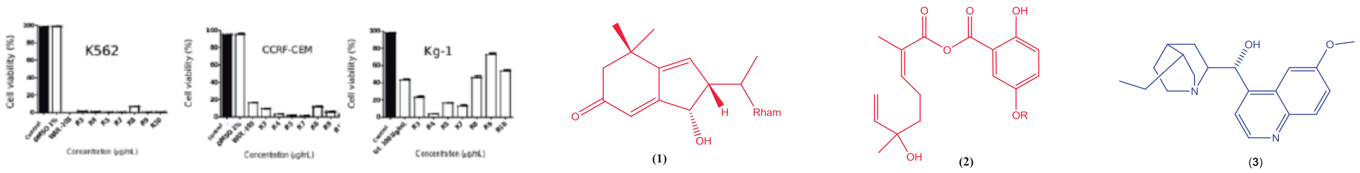

Figure 1. (**A**) Effects of the subfractions obtained from dichloromethane extract from the aerial parts of *U. lobata* L. (**ULD**). (**B**) Detected natural products in the **ULD** through integrated analytical tools, *Target Analysis* (Bruker Daltonics®) MS (highlighted in red) combined with MS/MS data from GNPS platform (highlighted in blue).

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**Área: QPN** **Nº de Inscrição: 538**

# Effects of different batches of *Schinus terebinthifolius* Raddi fruits Essential Oil against antiproliferative activity on human tumor cell lines

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Palavras Chave: *Essential oil, Schinus terebinthifolius Raddi, Anticancer activity.*

## Highlights

Effects of *Schinus terebinthifolius* Raddi fruits Essential Oil batches tested in vitro on human tumor cell lines demonstrated best results for batch A with selectivity for multidrug-resistant ovarian/NCI-ADR/RES (TGI=0.02 µg/mL).

## Abstract

*Schinus terebinthifolius* Raddi fruits are a promising source of bioactive compounds; nevertheless, few studies have investigated the anticancer activity of the plant's essential oil (EO). Herein the effects of different batches of *S. terebinthifolius* fruits tested *in vitro* antiproliferative activity in human tumor cell lines is reported. Ripe fruits were collected from native trees in Aracruz (Espírito Santo, Brazil) in 2014 (batch A) and 2015 (batch B). A voucher specimen (number 188116) was deposited at the Herbarium of the Institute of Biology/UNICAMP. Extraction of EO was accomplished by hydrodistillation in a Clevenger apparatus. EO samples were analyzed by gas chromatography (Agilent Technologies, HP-6890, USA) equipped with a mass detector (Agilent Technologies, HP5975, USA) operating in electron impact mode (70 eV) and a quadrupole mass analyzer. The *in vitro* antiproliferative activity experiments on human tumor cells were performed according to protocol described by Monks *et.al*. Stock cultures were grown in 5 mL of RPMI 1640 supplemented with 5% fetal bovine serum and penicillin-streptomycin 1000 UI/mL:1000 µg/mL. Doxorubicin chloridrate was used as positive control to determine the sensitivity of cell lines. Cells in 96-well plates (100 µL cells/well) were exposed to sample concentrations in DMSO/RPMI for 48 h at 37 °C and 5% of $CO_2$. Cell proliferation was determined by spectrophotometric quantification of cellular protein content at 540 nm (Molecular Devices®, model VersaMax) using sulforhodamine B (SRB). The total growth inhibition (TGI) was calculated by non-linear regression (sigmoidal fit) using Origin 7.5®. The results showed that the chemical composition and anticancer activity of *S. terebinthifolius* fruits EO depend on the quality of raw material. Batch A extraction yield (6.71%) was greater than Batch B extraction yield (5.56%). Gas chromatography-mass spectrometry analysis enabled detection of 27 compounds in *S. terebinthifolius* fruits' EO; 21 compounds were identified, representing, approximately 98% of the chemical composition of the EO. The main compounds identified in batches A and B were: $\delta$-3-carene (34.07% in batch A and 19.14% in batch B), $\alpha$-phellandrene (16.26% in A and 20.46% in B), limonene (15.22% in A and 18.28% in B), $\alpha$-pinene (7.03% in A and 5.36% in B), $\beta$-myrcene (3.06% in A and 12.75% in B), germacrene D (6.92% in A and 6.25% in B), and caryophyllene (3.32% in A and 3.73% in B). These variations in the chemical composition of the EO resulted in different antiproliferative activities. The results revealed a better antiproliferative activity for batch A. Batch B showed potent activity against prostate cancer/PC-3 (TGI=5.64 µg/mL), nonetheless activity than observed for batch A (TGI=0.08 µg/mL). EO from batch B showed moderate activity against human breast cancer/MCF7 (TGI=13.58 µg/mL), leukemia/K562 (TGI=10.21 µg/mL), lung/NCI-H460 (TGI=13.32 µg/mL), and glioma/U251 (TGI=8.86 µg/mL). The most promising results of batch A EO were found for kidney/786-0 (TGI=0.04 µg/mL), multidrug-resistant ovarian/NCI-ADR/RES (TGI=0.02 µg/mL), and prostate/PC-3 (TGI=0.08 µg/mL) cancer cells, and leukemia/K562 (TGI=0.08 µg/mL). Therefore, these results showed the importance of standardizing raw material input to obtain a high quality product from a plant species.

## Acknowledgments

This work was supported by the Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) (grant numbers 2018/20252-8 and 2015/08600-2).

**Área: QPN**

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

# *In vitro* antitrypanosomal activity of dicentrine and its quaternized derivatives

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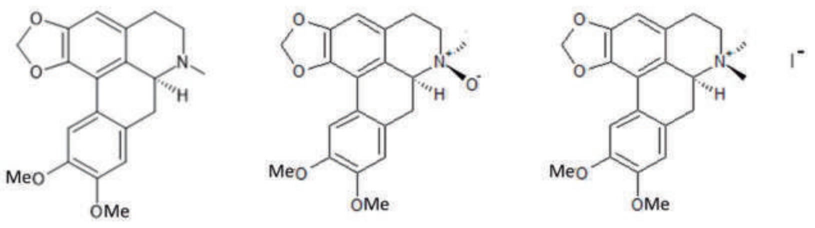
Palavras Chave: *aporphine alkaloids,* Trypanossoma cruzi*, dicentrine, quaternization.*

## Highlights

A comparative study of natural alkaloid dicentrine and two chemically related quaternized derivatives was performed, aiming to evaluate the effects of these compounds against *T. cruzi*.

## Abstract

Chagas disease (CD), also known as American trypanosomiasis, is a Neglected Tropical Disease endemic in Latin America, caused by the protozoan *Trypanosoma cruzi*. It is a great public health concern in Brazil, for example, once the country has only one approved drug for CD treatment – benznidazole – and it has several side effects associated and controversial efficacy for treating the chronic disease stage. It is estimated that 8 to 10 million people are infected worldwide.[1] Therefore the prospection of new substances against *T. cruzi* is a relevant demand, with natural products chemistry being a protagonist in bringing to light candidate molecules. As part of the effort to identify new compounds and deepen the understanding on their preliminary structure-activity relationship, this work reports the comparison among the antitrypanosomal activity of the aporphine alkaloid dicentrine (**1**) and two quaternized derivatives – dicentrine-β-*N*-oxide (**2**) and dicentrine methiode (**3**), which were evaluated *in vitro* against trypomastigote forms of *T. cruzi*. Dicentrine (**1**) was isolated from leaves of *Ocotea puberula* (Lauraceae) by different chromatographic procedures[2], and compounds **2** and **3** were prepared, respectively, by reacting **1** with *m*CPBA or MeI in $CHCl_3$ or acetonitrile.[3,4,5]. After work-up, these compounds were characterized by $^1H$ and $^{13}C$ NMR spectroscopy. Comparatively to dicentrine (**1**), with $EC_{50}$ of 76.8 μM, $CC_{50}$ of 37.8 μM and SI < 1.0, compound **2** exhibited a higher potential with $EC_{50}$ value of 18.2 μM, reduced toxicity ($CC_{50}$ > 200 μM) and SI > 11.0, similar to positive control benznidazole ($EC_{50}$ of 17.7 μM and SI = 10.7). Compound **3** had no activity against *T. cruzi* trypomastigote and $CC_{50}$ > 200 μM. The higher antiprotozoal potential exhibited by dicentrine-β-N-oxide (**2**) and the reduced toxicity against mammalian cells suggest that the presence of the N-oxide group plays an important role in the antitrypanosomal activity, being this type of quaternization decisive for the increment of activity since derivative **3** was inactive. Further studies, including effects against intracellular amastigote and determination of the mechanism of action, must be performed in order to comprehend the effectiveness of these compounds.



1 2 3

**Figure 1**: Natural dicentrine (**1**), isolated from *O. puberula* and quaternized alkaloids (**2** and **3**) derivatives.

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## Acknowledgments

FAPESP, CAPES and CNPq.

**Área: QPN**

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

# Ishwarane, ishwarone and ishwarol: rare sesquiterpenes in *Piper alatipetiolatum* essential oil with anticholinesterase activity

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Keywords: *Piperaceae, essential oil, sesquiterpenes, Acetylcholinesterase*

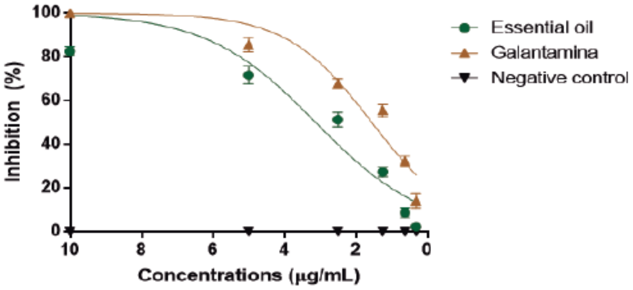
## Highlights

Three rare sesquiterpenes ishwarane (2.36%), ishwarol-B (8.2%) and ishwarone (78.58%) were identified in the essential oil of *Piper alatipetiolatum* by GC-FID, GC-MS and NMR. The essential oil also inhibited the enzyme acetylcholineserase.

## Resumo/Abstract

Popularly known as "canela de velho", *Piper alatipetiolatum* (Piperaceae) is widely found in northern of Brazil. However, studies describing the chemical constituents of its essential oil, as well as its biological activity against insect vectors are scarce in the scientific literature. Previous studies in our research group confirmed the activity of *P. alatipetiolatum* essential oil against *Aedes aegypti* larvae. The chemical composition of the essential oil was analyzed by GC-MS, GC-FID and $^{13}$C NMR. The hydrodistillation of leaves of *P. alatipetiolatum* yielded a colorless oil with 7.6 ± 0.1% yielding, a pH of 4.5 ± 0.8, a refractive index of 1.57 ± 0.40, density of 0.92 ± 0.10 g/cm$^3$. The chemical constituents were identified as being selin-11-en-4α-ol (2.88%), β-elemene (6.87%), ishwarane (2.36%), ishwarol-B (8.2%) and ishwarone (78.58%). The ishwarane type sesquiterpenes are rare and contain an unusual tetracyclic structure that was first described by Ganguly and coworkers (1936) in *Aristolochia indica* (Aristolochiaceae). First a two-column identification by GC-FID was performed and a non-resolved peak in apolar column resulted in a RI of 1,680 that was consistent with IR value in literature for ishwarone. On the other hand, the separation obtained in polar column, resulted in a good separation and two compounds were resolved, but no IR in polar columns were found for them. Besides, the match analysis of the mass spectrum data in commercial libraries (NIST and Adams) could not confirm neither ishwarol nor ishwarone. Earlier Andrade and coworkers (2009) had already studied the essential oil o *P. alatipetiolatum* and had identified ishwarone and ishwarol, but no data, including RI were published. Hence, we carried out a quantitative broad band decoupled $^{13}$C NMR experiment. It clearly indicated two sets of signals corresponding to two components that are in agreement with the literature for ishwarone (major compound) and ishwarol-B (Cavalli et al., 2005). The acetylcholinesterase inhibitory activity for the essential oil was also evaluated that showed a significant inhibitory activity (Figure 1), with inhibition percentages 2.3 ± 1.5 to 82.7 ± 2% (LC$_{50}$ of 2.14 µg/mL, $r^2 = 0.9118$) compared to galantamine (positive control), which inhibited 14.1 ± 3.5 to 100 ± 0% (LC$_{50}$ of 1.55 µg/mL, $r^2 = 0.9899$) ($p < 0.05$).

**Figure 1.** Inhibition of acetylcholinesterase treated with essential oil.



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## Agradecimentos/Acknowledgments

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**Área: QPN** **Nº de Inscrição: 01050**

# Isolation of bioactive compounds from copaiba oil by Dry Column Chromatography

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Keywords: *Copaiba oil, Copaifera spp, Dry column chromatography*

## Highlights

Copaiba oil is a source of bioactive compounds. Dry column chromatography as a pre-purification methodology.

## Resumo/Abstract

Copaiba oil is obtained from the Copaiba tree (*Copaifera* spp.), a species of the Leguminosae family widely found in Brazil mainly in the Amazon region and in the Brazilian Cerrado. The balm, popularly known as oil or oleoresin, is extracted from the tree trunk through holes and collected with the aid of tubes or channels. It is widely used in folk medicine for its anti-inflammatory and healing activities. The chemical composition is distinct, presenting mainly sesquiterpene hydrocarbons and diterpene acids. The objective of this work was isolating bioactive compounds present in copaiba oil using the Dry Column Chromatography (DCC). DCC is a “non-elution” method of column chromatography, meaning, the separated substances remain in the column at the end of the chromatographic process[1]. Dry column fractionation was carried out from 0.7 g of copaiba oil, which was placed on top of the cellulose acetate column (support), containing about 70 g of silica gel 60 (0.063 to 0.2 mm) as stationary phase. Three different mobile phases with different polar indices were evaluated: dichloromethane and methanol (95:5, polar indice 3.56), dichloromethane (polar indice 3.40), and hexane and ethyl acetate (80:20, polar indice 0.91). After elution, each column was divided into 8 fractions of 5 cm and numbered from 1 to 8 (Fr 1 to Fr 8). After filtration and concentration, the fractions were analyzed by Thin Layer Chromatography (TLC) and Gas Chromatography coupled with a Spectrometer Mass Detector (GCMS). The TLC analysis showed that the mobile phase with the best resolution was the least polar, mixture of hexane and ethyl acetate (80:20). This column presented yields of 6.37, 20.43 and 23.45% for fractions 1 to 3, respectively, and yields below 20% for the other fractions. The chemical composition of the fractions 1 to 3 showed an enrichment in sesquiterpene hydrocarbons and in the fractions 4 to 8 an enrichment in diterpene acids. Among the major volatile compounds of the fractions 1 to 3 were identified by GCMS, the sesquiterpenes α-cubebene, α-bergamotene and β-bisabolene with relative percentages above 20%, however the best result was noted in the fraction 3 that contained β-bisabolene above 60% (about 35% in crude oil, Table 1).

**Table 1.** Relative percentages of major volatile compounds identified by GCMS

| $t_R$ (min) | Compound | MM (g.mol$^{-1}$) | Copaiba oil (crude oil) | Fr 1 | Fr 2 | Fr 3 |
|---|---|---|---|---|---|---|
| 5.06 | α-cubebene | 204 | 4.37 | 33.19 | ND | ND |
| 6.23 | α-bergamotene | 204 | 17.92 | 20.78 | 35.07 | ND |
| 8.21 | β-bisabolene | 204 | 34.58 | ND | ND | 60.60 |

*Subtitle: $t_R$- Retention time; MM- Molecular mass; Fr 1 to 3- fractions obtained with the mobile phase hexane and ethyl acetate (80:20); ND- Not detected*

Thus, we conclude that under the conditions employed, the dry column chromatography technique presented moderate resolution and allowed separating sesquiterpene hydrocarbons from diterpene acids present in a complex mixture in a single step, demonstrating to be a simple, fast, low cost tool with great potential when applied in the phytochemical study of copaiba oil.

## Agradecimentos/Acknowledgments

Pro-Rectory of Research at UNICAMP for funding through the CAF 2020 project (FAEPEX 519292).

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**Área: QPN**

# Isolation of limonoids from *Carapa guianensis* Aublet seeds and their antipromastigote activity on *Leishmania amazonensis*

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Palavras Chave: *Limonoids, Carapa guianensis, Countercurrent chromatography, Leishmania amazonensis, Promastigote.*

## Highlights

Limonoids extracted from seeds of *Carapa guianensis* (Meliaceae), isolated by countercurrent chromatography, showed promising antipromastigote activity against *Leishmania amazonensis*.

## Resumo/Abstract

Leishmaniasis is caused by more than 20 species of *Leishmania*, belonging to the Trypanosomatidae family. Chemotherapy treatments are unsatisfactory because of their limited efficacy, long-term treatment, high cost, and severe side effects. Thus, the development of safer and more effective drugs for the treatment of leishmaniasis is a priority [1]. The plant species *Carapa guianensis* Aublet (andiroba, Meliaceae) is used as a medicine by the indigenous peoples of Brazil [2]. Limonoids are tetranortriterpenoids, widely found in the Meliaceae family, of considerable interest due to their structural variety and biological activities, such as insecticidal, antibacterial, antifungal, antimalarial, anticancer and antiviral [3]. The present work aims to isolate limonoids from a complex extract of *C. guianensis* seeds by countercurrent chromatography (CCC) and to evaluate their activity against the promastigote form of *L. amazonensis*. Hexanic extract from squeezed seeds of *C. guianensis* was prepared by Soxhlet extraction and precipitation after cooling. Of this extract, 800 mg were subjected to CCC, using the solvent system hexane:ethyl acetate:methanol:water 1/2/1.5/1. In this procedure, 165 fractions were collected. The substances methyl angolensate (1), 7-deacetoxy-7-oxogedunin (2), deacetylgedunin (3), 6α-acetoxygedunin (4), gedunin (5) and andirobin (6) were isolated. Limonoids 1, 2, 4 and 5 showed promising results in the antipromastigote activity assays of *L. amazonenses*, becoming an interesting therapeutic alternative in the treatment of leishmaniasis. The use of CCC was an alternative to classical chromatographic methods for exploring small variations in the partition coefficient between substances, for solvent savings and reduced time in the isolation process.

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**Área: QPN**

# LC-MS/MS-Based Molecular Networking of *Mimosa gracilis* Benth extracts associated with inhibition of toxicity of Bothropic and Crotalic venoms.

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Keywords: *Bothrops, Crotalus, Envenomation, Extract, M. gracilis.*

## Highlights

Snake bites are considered a public health problem that affects millions of people around the world. The extracts were incubated with the venoms (1:20 venom:extract), and two of them inhibited 90% of the hemolytic activity on red cell decreasing the hemolysis halo formed by the venom from 10 to 1 mm, besides increasing plasma clotting time from 60 to over 500 seconds. Also, 19 compounds were annotated from which were highlighted the followings: apigenin (*m/z* 269), luteolin (*m/z* 286), myricitrin (*m/z* 463), quercitrin (*m/z* 492), and ellagic acid (*m/z* 301).

## Abstract

Snake bites are considered a public health problem that affects millions of people around the world. The WHO has classified them as a neglected tropical disease due to the high cost of antivenoms production (antivenom serum) and the lack of adequate assistance in the first hours after the accident. Therefore, it is necessary the search for accessible, safe, and low-cost therapy. In this research, it was evaluated the antiophidic potential *in vitro* of nine ethanolic extracts from three varieties of *Mimosa gracilis* Benth. (1. *M. gracilis* subsp. *capillipes* var. *capillipes*; 2. *M. gracilis* subsp. *gracilis* var. *capillipes*; and 3. *M. gracilis* subsp. *gracilis* var. *invisiformes*) collected in the state of Goiás – Brazil, on the proteolytic, hemolytic, and coagulant activities from *Bothrops alternatus*, *B. diporus*, *B. moojeni*, *B. pauloensis*, and *Crotalus durissus collilineatus* venoms. In addition, it was performed the LC-MS/MS-based molecular networking of the three varieties as a dereplication strategy. The extracts were incubated with the venoms (1:20 venom:extract), and two of them (roots of 1, and leaves of 2) inhibited 90% of the hemolytic activity decreasing the hemolysis halo formed by the venom from 10 to 1 mm, besides increasing plasma clotting time from 60 to over 500 s, i.e. 100% inhibition, they also maintained the integrity of the casein bands, demonstrating strong antiproteolytic activity. Subsequently, in the molecular networking-based dereplication, it was observed 86 ions common to the three varieties (Figure 1). Moreover, 14 ions were found in the roots of *M. gracilis* subsp. *capillipes* var. *capillipes*, and 22 in the leaves of *M. gracilis* subsp. *gracilis* var. *capillipes*. Also, 19 compounds were annotated from which were highlighted the followings: apigenin (*m/z* 269), luteolin (*m/z* 286), myricitrin (*m/z* 463), quercitrin (*m/z* 492), and ellagic acid (*m/z* 301). In conclusion, extracts from *M. gracilis* Benth. may inhibit the action *in vitro* of the main classes of active proteins of bothropic and crotalic venoms. These findings help the development of new products for the treatment of snake envenomation.

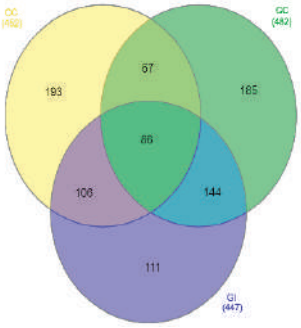

Figure 1. Venn plot of the number of ions in the molecular network.

## Acknowledgments

**Área: QPN**

# Lignanas com ação antiparasitária isoladas dos galhos de *Piper truncatum*

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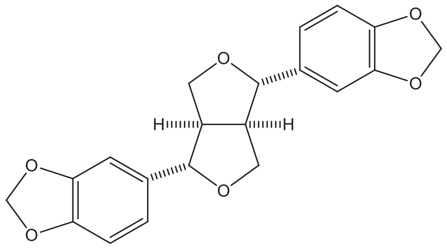
Palavras Chave: *Piper truncatum Vell., lignanas, doença de Chagas.*

## Highlights

Como parte de nosso estudo visando a prospecção de produtos naturais com ação antiparasitária, nesse trabalho descrevemos o isolamento de três lignanas bioativas dos galhos de *Piper truncatum*.

## Resumo

A Doença de Chagas, causada pelo protozoário *Trypanosoma cruzi*, apresenta reduzido arsenal terapêutico – benznidazol e nifurtimox – ambos com ação reduzida na fase crônica da doença e causadores de diversos efeitos colaterais.[1] Desta forma, a busca por novas entidades moleculares que possam ser consideradas novos hits bioativos, é crucial. Nesse contexto, o estudo sistemático de produtos naturais é indispensável para essa descoberta. Assim, o extrato hexânico dos galhos de *Piper truncatum* foi preparado e o mesmo apresentou atividade frente as formas tripomastigostas de *T. cruzi* (100% de morte a 300 µg/mL). Frente a esse resultado, o extrato bruto foi submetido a fracionamento em gel de sílica o que forneceu oito grupos (A – H) sendo que esses apenas H se mostrou inativo. Visando o isolamento de compostos ativos, o grupo E foi submetido a fracionamento em gel de Sephadex LH-20, fornecendo oito grupos (E1 – E8). Após avaliação da atividade, os grupos E3, E7 e E8 mostraram ação anti-tripomastigota. Após analise por RMN de $^{1}H$ foi possível inferir a presença de lignanas nos três grupos. A purificação via CLAE permitiu o isolamento de três compostos: sesamina (**1**), kobusina (**2**) e hinokinina (**3**). As estruturas dos compostos **1 – 3** foram confirmadas via analise por RMN e EM seguido de comparação com dados descritos na literatura[2,3,4].



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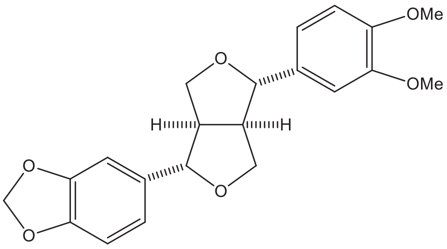

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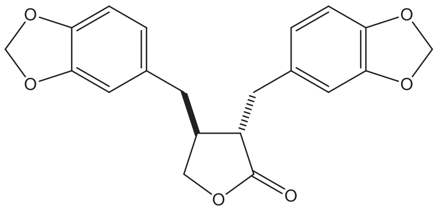

**3**

Trabalhos anteriores[5] descrevem apenas a ocorrência de eudemina em *P. truncatum*, sendo, portanto, a primeira descrição de **1 – 3** na espécie em estudo. Quando avaliadas individualmente, os compostos **1** e **2** mostraram reduzida toxicidade frente a células NCTC ($CC_{50}$ > 200 µM). No entanto quando avaliados frente a tripomastigotas de *T. cruzi,* o potencial de **1** ($IC_{50}$ de 36,6 µM) se mostrou superior ao de **2** ($IC_{50}$ de 109,3 µM). Tal resultado permite sugerir que o grupo metilenodioxilico ligado ao anel aromático exerce um papel importante na atividade visto que a presença do sistema *orto*-dimetoxilico causa redução no potencial. Por outro lado, a lignana **3** se mostrou ativa com $IC_{50}$ de 17,0 µM e reduzida toxicidade ($CC_{50}$ > 200 µM). Conforme evidenciado por RMN, os demais grupos bioativos se mostraram também compostos por lignanas relacionadas estruturalmente – desta forma, esses grupos serão também estudados posteriormente visando o isolamento dos compostos ativos para estabelecimento de relações estrutura/atividade.

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## Agradecimentos

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**Área: QPN**

# *Cinnamomum verum* chemotypes based on its Essential oil composition and DNA barcode of cultivated and commercial samples from the Amazon.

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Keywords: *benzenoids*, *phenylpropanoids, genetic variability*, *psbA-trnH*.

## Highlights

*C. verum* essential oils showed three chemotypes rich in benzenoids and phenylpropanoids; DNA barcodes were developed based on chloroplastic regions; The *psbA-trnH* provided greater discrimination.

## Abstract

*Cinnamomum verum* (Lauraceae), also known as "true cinnamon" or "ceylon cinnamon" is widely used in traditional folk medicine and culinary for a long time[1]. In literature, its essential oils are reported as antioxidant, antimicrobial, anti-inflammatory, anticancer, and antidepressant[2]. However, its botanical identification presents some difficulties due to genetic variation and morphological similarity among other *Cinnamomum* species[3]. For this reason, the present work aimed to find chemical and molecular markers of *C. verum* samples from Amazon (Brazil). Essential oils (EO) and the genetic material (DNA) were extracted from cultivated (Cve1, Cve2, Cve3, Cve4 and Cve5) and commercial samples (Cve6-c, Cve7-c, Cve8-c and Cve9-c). The EOs were analyzed by Gas Chromatography coupled to mass spectrometry (GC-MS). To discriminate the chemotypes, the compounds (>3%) were submitted to Hierarchical Cluster Analysis (HCA), using the software Minitab 19 (Minitab Inc., State College, PA, USA). The HCA was performed by Complete linkage method and the Euclidean distance, and grouped the samples into three main clusters. The Cluster I presented similarity of 24.28% and grouped the oils Cve1, Cve2, Cve7-c and Cve8-c, rich in benzyl benzoate (15.83-76.51%), (*E*)-cinnamyl acetate (4.43-32.1%), and (*E*)-cinnamaldehyde (3.76-19.74%). Group II was represented only by Cve3, which displayed a mixture of benzyl benzoate (44.11%), (*E*)-cinnamyl acetate (14.94%), and caryophyllene oxide (7.54%) and a similarity of 5.39% with Group I. Group III included the Cve4, Cve5, CVe6 and Cve9-c samples rich in eugenol (54.51-91%), with a similarity of 45.87%. DNA barcodes were developed for phylogenetic analysis using chloroplastic regions of the *matK*, *psbA-trnH* and *rbcL* genes. Maximum Likelihood (ML) and Bayesian Inference (IB) analyzes were applied with the markers separately and combined. The *psbA-trnH* sequences provided greater discrimination among the samples and confirm the identity of *C. verum*. The phylogenic analysis of the three regions (*rbcL*+*matK*+*psbA-trnH*) resulted in the formation of clades moderately supported by IB (PP: 0.89) and ML (BS: 87%). The combination of DNA barcode and volatile profile showed to be an important tool for discrimination of *C. verum* varieties and to examine the authenticity of herbal industries (Fig. 1).

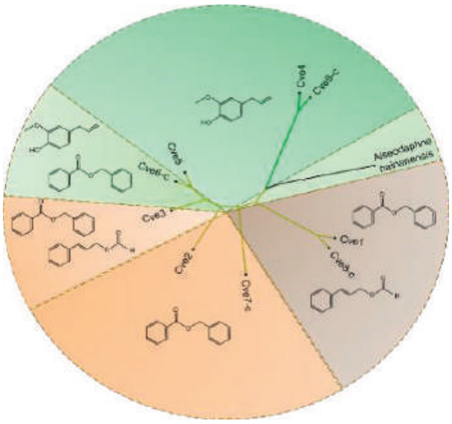

Figure 1. Chemical and phylogenetic profile of species in the *C. verum*, based on their volatile constituents. Cultivated (Cve1-Cve5) and commercial samples (Cv6-c-Cve9-c).

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Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES-Coordination for the Improvement of Higher Education Personnel) for granting the scholarship and Aromatic Plant Research Center (APRC, UT, EUA) for their financial support for the execution of this project.

**Área: QPN**

# Mass spectrometry-based untargeted metabolomics reveals unusual larvicidal aliphatic nitro esters from *Heteropterys umbellata* (Malpighiaceae)

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Palavras Chave: *neglected diseases; Aedes aegypti larvae; metabolomics; multivariate analysis; nitro compounds.*

## Highlights

394 Malpighiaceae extracts were tested for larvicidal activity against *Aedes aegypti*. A metabolomic-based approach led to the isolation of unusual nitro compounds from *Heteropterys umbellata*.

## Resumo/Abstract

The *Aedes aegypti* (Diptera: Culicidae) mosquito is the vector of several arboviruses such as dengue, Zika, and chikungunya [1]. Arboviruses are considered a concern in several tropical and subtropical countries around the globe, and so far, the most effective way to control these diseases is to combat the vector. Synthetic pesticides are still the most widely used for this purpose, but the search for natural products as an alternative is increasing significantly [1]. Therefore, the main objective of this study was to search for bioactive natural products from the Malpighiaceae botanical family, toxic to *Ae. aegypti* larvae. For this, 197 Malpighiaceae samples (39 genera, 137 species) were initially subjected to microextraction using EtOH–$H_2O$ (4:1) or EtOAc, leading to 394 extracts. A larvicidal screening was performed to determine the most promising species for a metabolomic-guided investigation. This initial step revealed that *Heteropterys umbellata* caused a 100% mortality rate after only 24 h. Due to the lack of any deeper chemical investigation of *H. umbellata*, it was selected for an in-depth study. Thus, larger amounts of plant material were collected for two different plant organs (leaves and stems) in two different States of Brazil (São Paulo and Minas Gerais), totalizing 14 samples for metabolomic investigation. These extracts were analyzed by LC-MS/MS in an untargeted method, and the data was processed in MZmine2. The outputs were subjected to analysis in the MetaboAnalyst [2] (for multivariate analysis: PCA and PLS-DA) and GNPS [3] (for molecular networking and comparison with spectral libraries) platforms. The multivariate analyses revealed that the chemical profiles obtained for the leaves' extracts differed significantly from the stem ones. Furthermore, the State of collection also significantly impacted the metabolic profile when only leaf or stem extracts were considered. Through the PLS-DA analysis, it was also possible to retrieve a list of features that most significantly impact the differentiation of the described groups, being valuable to guide the study. The molecular networks in GNPS showed three main molecular families with library matches: *O*-glycosylated flavonoids, *C*-glycosylated flavonoids, and caffeoylquinic acid derivatives. These last two classes comprised relevant features recovered in the PLS-DA analysis to differentiate plant organs and collection sites. In addition, two other abundant features did not show any correspondence with the libraries, being recovered as important in differentiating the collection points – both for leaves and for stems. A guided isolation and further characterization by NMR and HRMS revealed unusual nitropropanoyl glycosides, in addition to isochlorogenic acid A. These compounds were used to validate the analytical method (MRM mode) and for quantification in all extracts, which corroborated the PLS-DA results. When tested pure, the nitro compounds showed moderate larvicidal activity, but the activity was potentiated when tested in fractions containing other isomers with the same fragmentation pattern, suggesting a possible synergistic effect on the activity.

**References:** [1] Silvério, M.R.S. et al. *Molecules*, **2020**, 25, 3484; [2] Pang, Z. et al. *Nucleic Acids Research*, **2021**, 49, W388–W396; [3] Wang, M. et al. *Nature Biotechnology*, **2016**, *34*, 828.

## Agradecimentos/Acknowledgments

The authors acknowledge CNPq, the Fulbright Commission, the Arbocontrol Project, and FAPESP for the financial support.

**Área: QPN**

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

# Mastruz essential oil inhibits Capim annoni development

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Keywords: *Bioherbicide, Biological inputs, Invasive plants.*

## Highlights

New alternative in bioinputs.
Mastruz essential oil was efficient for the control of capim annoni germination.
Efficient and sustainable bioherbicide.

## Resumo/Abstract

The annoni grass (*Eragrostis plana* Nees) is an exotic species with aggressive dispersion and difficult eradication, being among the invasive species with the greatest impact in the Pampa biome. Control management of this species is restricted to chemical inputs. In this sense, essential oils (EOs) emerge as an efficient and environmentally viable alternative to this problem. The EO of dried leaves of mastruz (*Chenopodium ambrosioides* L.) was obtained by Hydrodistillation technique, characterized by CG-MS and tested at concentrations of 0.005; 0.01; 0.05; 0.1; 0.1; 0.5; (v/v) on the germination of annoni grass. Mastruz leaves yielded 1.06% of essential oil and the characterization study showed the majority presence of the monoterpene compounds, Ascaridole glycol (10%), Linalool acetate (11%) and dihydro citronellol acetate (19%). In bioassays, the germination was completely inhibited from the concentration of 0.5% of mastruz EO, and from the lowest concentration tested a reduction of more than 40% in this variable was observed. The mortality results followed those of germination and the germination speed was significantly reduced from the concentration of 0.05% of matruz EO. The initial growth of annoni grass was significantly impaired by low concentrations of mastruz EO so that height, tillering and biomass data can be considered unfeasible when exposed to concentrations greater than 0.05% of EO. The results indicate that the mastruz EO was efficient, at low concentrations, for the control the germination and initial growth of this grass under controlled conditions.

## Agradecimentos/Acknowledgments

Special thanks to PPGQ/Unifesspa and Secretaria da Agricultura, Pecuária e Desenvolvimento Rural do Rio Grande do Sul.

**Área: QPN**

# Megastigmanes and loliolide from *Palicourea tomentosa* (Rubiaceae)

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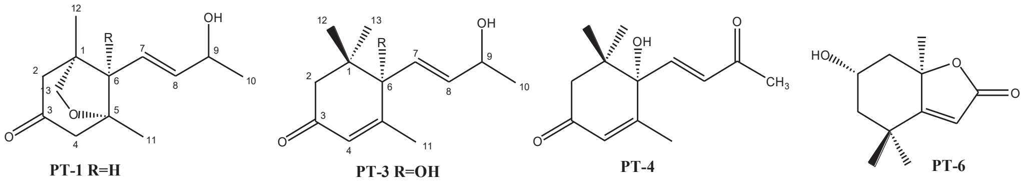
Palavras Chave: *Palicourea tomentosa, Rubiaceae, Megastigmanes, Loliolide*

## Highlights

Chemical study of *Palicourea tomentosa* resulted in isolation of five megastigmanes (**PT-1** to **PT-5**) and loliolide (**PT-6**). This is the first report of compounds **PT-1** and **PT-5** in *Palicourea* genus.

## Resumo/Abstract

*Palicourea tomentosa* (synonym *Psychotria poeppigiana* Mull. Arg.) belongs to the Rubiaceae family and is used in folk medicine for pain and inflammation related symptoms. Studies of this plant, with the synonym *Psychotria poeppigiana*, describes its vasorelaxant effects and angiotensin II receptor inhibitory activity.[1] In our previous work on *P. tomentosa* we demonstrated that the methanol extracts inhibited acetylcholinesterase (AChE), and reduce the inflammation and hyperalgesia in mice.[2] UHPLC-HRMS/MS analysis showed the presence of calycanthine, hodgkinsine, asperuloside, scopoletin, vomifoliol and loliolide in the methanol extract. In continuity to our study on *P. tomentosa*, in the present work we investigated the dichloromethane fraction, aiming to isolate their specialized metabolites. The aerial parts (315 g) were collected in April 2021, in Dourados/MS. An exsiccate was deposited in the herbarium of UFGD (0006), and the research registered at SisGen A51F665. The crude methanol extract (23.0 g) was suspended in MeOH:$H_2O$ (1:1) and partitioned into *n*-hexane, dichloromethane and ethyl acetate. The dichloromethane fraction was successively fractionated on CC (silica gel), using hexane and hexane/ethyl acetate as eluent, to afford the compounds **PT-1** (3 mg), **PT-2** (2 mg), **PT-3** (5 mg), a mixture of **PT-4** and **PT-5** (7 mg), and **PT-6** (2 mg). The structures of isolated compounds (**Figure 1**) were elucidated by analysis of their uni- and bidimensional NMR data. The $^{1}H$ NMR data of **PT-1** displayed signals of a megastigmane skeleton, in which one of the geminal methyl groups at C-1 is oxygenated and connected to C-5 by the oxygen atom. The $^{13}C$ NMR and HMBC spectra confirmed the identification of **PT-1** as 5,13-epoxy-9-hydroxy-7-megastigmen-3-one. This compound was previously isolated from *Centaura salmantica*; however only its $^{1}H$ NMR data was reported.[3] Compound **PT-2** exhibited similar data of that **PT-1**, which were consistent with the literature for drummondol. The NMR data of compounds **PT-3**, **PT-4** and **PT-5** also showed signals characteristic of megastigmanes. Comparison of the NMR data with those of literature allowed the identification of these compounds as vomifoliol (**PT-3**), dehydrovomifoliol (**PT-4**) and 3-oxo-α-ionol (**PT-5**). Compound **PT-6** was identified as loliolide. Compounds **PT-2**, **PT-3**, **PT-4** and **PT-6** were previously related in *Palicourea* species This is the first report of compounds **PT-1** and **PT-5** in the *Palicourea* genus. Megastigmane derivatives have been reported to present anti-inflammatory effects, which can corroborate our previous studies on *P. tomentosa*.



**PT-1** R=H
**PT-2** R=OH

**PT-3** R=OH
**PT-5** R=H

**PT-4**

**PT-6**

**Figure 1.** Compounds isolated from the dichloromethane fraction of *Palicourea tomentosa*

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**Área: QPN**

# Metabolomics of plants from Melastomataceae family found in different fragments of Atlantic Forest

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Palavras Chave: *Atlantic Forest, Melastomataceae, GNPS, Mass Spectrometry, Metabolomics, PCA.*

## Highlights

Metabolomics of plants from Melastomataceae family collected in five fragments of Atlantic Forest suggests influences of environments on biosynthesis of metabolites.

## Resumo/Abstract

Atlantic Forest is the most diverse biome of Brazilian territory. The deforestation of biome after five centuries of human occupation led to the drastic reduction of landscape into fragments. Fragmentation exposes plants to different ecosystem conditions, as well to emergence of secondary forest, which may influence the biosynthesis of secondary metabolites. Melastomataceae family comprises more than four thousand species, most of which in tropical and subtropical regions of the Earth. In Brazil, Melastomataceae is one of the five most diverse families, with more than 1300 species, and 894 endemics. Moreover, 582 species of Melastomataceae are found in Atlantic Forest, which is the seventh family with the largest number of species in biome. Thus, we performed the metabolomics of Melastomataceae specimens (genera *Miconia* and *Tibouchina*) from five Atlantic Forest fragments located in State of São Paulo, Brazil, aiming to observe the chemical composition of this family in different environments. Leaves of 22 specimens were collected by botanists of the ECOFOR/FAPESP project. Plant extracts were analyzed by HPLC-HRESI-MS/MS with both positive and negative ionization modes. MS/MS data were preprocessed in MZmine software and then processed in FBMN workflow (GNPS platform) to perform the Molecular Networking (MN). Further, molecular annotations were based on matches with spectral libraries of GNPS, *in silico* predictions of analogues with NAP tool, and manual dereplication based on literature data. Unsupervised statistical analysis (PCA) was also performed using MS/MS data from the sample set. The PCA score plot showed a clustering tendency of specimens in three of five fragments. Furthermore, it was verified the dissimilarity tendency of samples from two *Miconia* species according to their fragments. These findings suggest the influence of environments on chemical composition of Melastomataceae plants. The MN showed annotations of polyphenolics, such as flavonoids and tannins. Flavonoid-*O*-glycosides occurs in specimens of *Miconia* and *Tibouchina* from all fragments, while hydrolysable tannins, such as galloyl, HHDP-*O*-hexose derivatives, were found only in two fragments. Flavonoid aglycones were found only in *Miconia* specimens from fragments numbered as 3 and 9, while dimeric proanthocyanidins (condensed tannins) are distributed only in specimens of *Miconia* from fragments 5 and 14. Flavonoid-*C*-glycosides were annotated exclusively in *Tibouchina* specimens from fragment 4. Variations in the biosynthesis of metabolites might be explained since the fragments are in an anthropogenic disturbance gradient, as well in regions with distinct levels of altitude. Flavonoids play a key role in protecting plant tissues against UV radiation. The different levels of altitude of fragments may influence the production of phenolic derivatives, such as flavonoids, as plants in environments with higher altitudes are more susceptible to UV radiation. Therefore, the results suggest effects of environments on secondary metabolism of Melastoamataceae. Additionally, these data contribute with the chemosystematics of Melastomataceae family and the micromolecular compilation of Atlantic Forest.

## Agradecimentos/Acknowledgments

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Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP).

**Área: QPN** **Nº de Inscrição: 00398**

# Microwave and ultrasound extraction of antioxidant compounds from *Croton grewioides*: optimization using response surface method.

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*[1]Department of Chemistry, UFS; [2]Department of Agronomic Engineering, UFS.*

*Keywords: Croton grewioides, Experimental Design, Ultrasound- Assisted Extraction, Microwave-Assisted Extraction.*

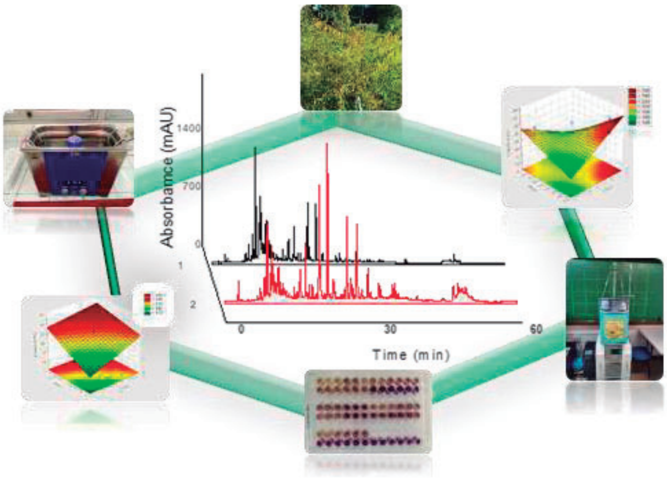
## Highlights

Optimization of the extraction processes of the phenolic compounds of the species *C. grewioides*, using ultrasound and microwaves to determine the antioxidant capacity of the species.

## Abstract

The complexity of compounds present in plants allows them to be used for different diseases, which is due to the presence of bioactive compounds known as secondary metabolites [1]. The aim of this study was to optimize the extraction processes by ultrasound (UAE) and microwave (MAE) [2] for five accessions from *C. grewioides* species (SisGen nº A8CCB3B), varying parameters such as: time (5 and 10 minutes), solvent composition (20 and 50% ethanol in water) and potency (30 and 90% for EAU; 300 and 600 watts for EAM), in order to maximize the extraction of phenolic compounds and evaluate their antioxidant activities. The Total Phenolics Content (TPC) was used as an answer to determine best extraction condition of the methodologies. For this purpose, an experimental design was carried out, and its results were processed using statistical treatments (ANOVA, Pareto chart and response surface). After statistical treatment, extractions were performed under the best conditions of each technique. Thus, for UAE: time 10 minutes; solvent composition 20% and potency 90%; for MAE: 10 minutes; 50% ethanol and 600 watts, fixing the matrix/solvent ratio (1g/15 mL) of five accessions from *C. grewioides* leaves. All extracts were assessed for their antioxidant activities and analyzed by Liquid Chromatography- Diode Array Detection (LC-DAD) in order to obtain their chemical profiles. The antioxidant tests showed DPPH inhibition ≥50% for accessions 106, 112 and 120, obtained by UAE. For the extracts obtained by MAE technique, the accessions that displayed DPPH inhibition ≥50% were: 104, 106, 112 and 120. Among them, the extracts from accession 120, obtained from the two applied methodologies, showed the highest antioxidant potential with inhibition values of 63.72 and 73.35%, for UAE and EAM, respectively.

**Global representation of the optimization process, analysis by LC-DAD and antioxidant activity of the *C. grewioides* species by using UAE and MAE as extraction methodologies for antioxidant compounds.**



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**Área:** IC

# Nanoformulations from essential oil of Aroeira *(Schinus terebinthifolius* RADDI)

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Key Words: *Low contribution, Colloidal system, Dynamic light scattering*, *Emulsifiers.*

## Highlights

- The DLS analysis, nanometer-sized particles were observed in the concentrations of 15% and 20% of emulsifier with HLB 15
- Diluted samples obtained greater stability than undiluted samples in naked eyes
- The nanoformulations stability were analyzed at intervals of zero hour, three days, and seven days.
- Refractive index, pH, turbidity were used to measure the nanoemulsion stability in different temperature and centrifugation processes.

## Resumo/Abstract

Several plant species have medicinal properties beneficial to health and the essential oil of *Schinus terebinthifolius* has antimicrobial and antioxidant activities. Nanoemulsions are systems with a dispersed phase and a continuous phase, which the size of their particles are between 50 nm and 1000 nm. In this work, nanoformulations were prepared using essential oil from aroeira (pink pepper). Nanostructured colloidal systems (NCS) were produced with essential oil and the emulsifiers: polysorbate 20, polysorbate 80, sorbitan monooleate and sorbitan trioleate, these are called oily phase, while water is the aqueous phase. For this, NCS were obtained with LHB values of 10, 11, 13 and 15, as well as the concentrations of the mixtures of the emulsifiers of 5%, 10%, 15% and 20%, always keeping the essential oil at the concentration of 5%. The method used to obtain the NCS was by low energy supply using a vortex. Of all the NCS produced, LHB 15, using the mixture of polysorbate 20 and trioleate of sorbitan at concentrations of 15% and 20%, 5% of essential oil and aqueous phase to 100% of the system, showed, visually, greater stability after 24h of production, as well as slightly bluish and translucent staining. The most stable samples were diluted 1:10 (v/v) to 1 mL, 2 mL, 3 mL and 4 mL and subjected to stability tests by analysis of 1 - dynamic light scattering (DLS), 2 - centrifugation; 3 - refractive index; 4 - pH; 5 - turbidity and 6 - temperature at 8ºC, 25ºC and 40ºC. The DLS test was performed with both diluted and undiluted samples. Samples were prepared and analyzed at the same time and then at three-day and seven-days time intervals. Thus, the results showed that the diluted samples form smaller and more stable droplets. While in the undiluted 20% colloidal system, the diameter of 382 nm was obtained, the diluted one had an average of 46.1 nm at zero hour. After one week, values were obtained without dilution of approximately 225.5 nm, while with dilution they remained around 41.1 nm. For the other stability analyses, the samples remained stable in the analyzed period. After about four months the samples submitted to 8ºC and 40ºC lost stability, becoming more turbid. The obtained nanoformulations can be of great collaboration for the potentiation of antioxidant and antimicrobial activities of medicinal and cosmetic products in general.

## Agradecimentos/Acknowledgments

The Federal Institute of Espírito Santo (IFES) for the scientific initiation grant from the Rectory 02/2021 - Pibic and to the Aracruz campus, on behalf of Prof. André Romero, for the DLS analyses.

**Área: QPN**

# Naturally occurring Michael adducts of withanolides from leaves of cultivated *Iochroma arborescens* (*Acnistus arborescens*)

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Palavras Chave: *Iochroma arborescens, Acnistus arborescens, Solanaceae, withanolides.*

## Highlights

-*Iochroma arborescens*, under agronomic reproduction, was investigated;
-Fifteen withanolides, including six new, ones were isolated;
-Six of the new derivatives are Michael naturally occurring adducts.

## Resumo/Abstract

Currently, *Iochroma arborescens* (L.) J. M. H. Shaw is the accepted designation of *Acnistus arborescens* (L.) Schltdl, a medicinal plant with antitumor properties, belonging to the Solanaceae.[1,2] In Brazil, it occurs at the South, Southeast and Northeast regions, where it is popularly known as “fruta-de-sabiá”.[1] In previous phytochemical investigations, ca. 30 withanolide-type compounds ($C_{28}$ ergostane-type steroidal lactones), have been reported, their including withacnistins and withaphysalins.[3] These secondary metabolites have attracted particular attention due to pharmacological properties, such as cytotoxic, anti-inflammatory and immunosuppressive.[3,4] Recognizing the pharmacological potential of *I. arborescens* and considering the possibility of using this plant as a crude drug for a possible phytotherapic medicine, it was cultivated in order to better understand its chemical behavior under agronomic reproduction. In this work, the isolation of new withanolides is reported from the leaf acetone extract of cultivated specimens. The dried and crushed leaves (1.25 kg) of *I. arborescen,* cultivated at the Núcleo de Estudos e Pesquisa em Agricultura Urbana (NEPAU-UFC), were extracted under maceration with n-hexane (3.7 g) followed by acetone (8.0 g). The acetone extract was solubilized in a $MeOH/H_2O$ 6:4 mixture and subjected to a liquid-liquid partition with $CH_2Cl_2$ (4.1 g) and EtOAc (3.2 g). Chromatographic procedures of the EtOAc fraction using SPE, silica gel, and HPLC resulted in the isolation of 15 withanolides, six of which are new entities. Their structures were elucidated by HRMS and $^1H$ and $^{13}C$ NMR, including 2D experiments. Contrary to our expectations, the isolated compounds are withanolides, whereas the main compounds isolated from wild specimens are withaphysalins.

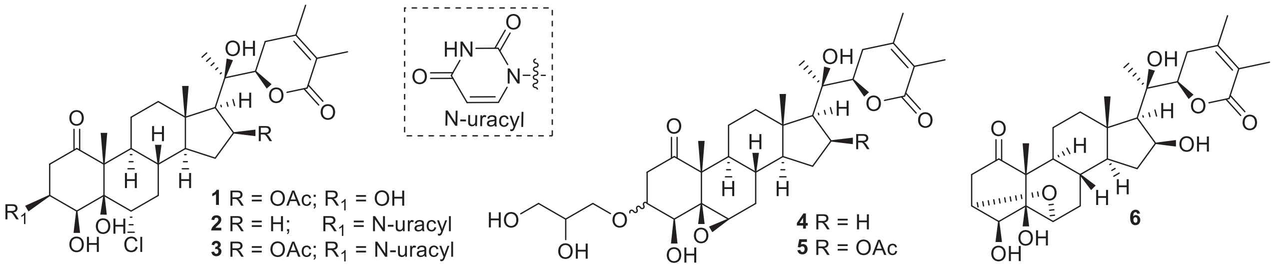

**Figure 1 –** Structures of the new *withanolides* **1** - **6**.

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## Agradecimentos/Acknowledgments

The authors are grateful to CNPq, CAPES, and INCT-BIONAT with for the fellowships and financial support

**Área:** **QPN**

# New acetogenins from *Annona squamosa* L. and their biological activities

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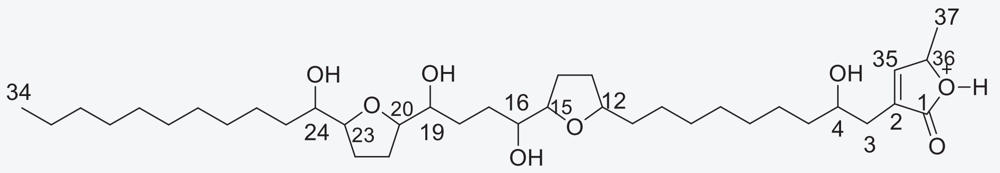
Palavras Chave: *Annonaceous acetogenins*, *Bullatanocin*, *Annonaceae*, *Antitumor agent*.

## Highlights

Acetogenins were isolated of leaves. Structures were established by QTOF-MS/MS and NMR. Antitumor activity was tested against two cancer cell lines. The acetogenins showed antitumor activities.

## 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 exclusively in plants of the Annonaceae (Gonçalves et al., 2017), called Annonaceae acetogenins (ACGs). ACGs presented a broad range of biological activity, such as antiparasitic, insecticide, antimicrobial, antifungal and antitumor, giving an important impetus to the biochemical and pharmacological investigations of these molecules. In the work, three acetogenins were isolated of leaves from *A. squamosa* using the HPLC-Shimadzu-DAD equipment with a wavelength of 210 nm. The acetogenins were analyzed by "Ultra Performance Liquid Chromatography on a Quadrupole Time-of-Flight Mass Spectrometry (UPLC-QTOF-MS/MS)" in positive ionization mode. The results demonstrated 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. Subsequently, 1D and 2D NMR analysis were performed, which confirmed the presence of three acetogenins, being isomers respectively. They are isomers of bullatanocin, containing a minor carbon chain between the lactone and the first tetrahydrofuran ring (**1**) (Liu et al., 1998). Isomers differentiate by the position and stereochemistry of their hydroxyl groups. The cytotoxicity of the acetogenins was determined using MTT (3-(4,5-dimethyl-thiazol-2-yl)-2,5-diphenyltetrazolium bromide), which recommends that cell viability is proportional to the formation of crystals (MTT reduction product), being tested in A549-Lung cancer, MCF-Human breast adenocarcinoma and in MRC-5 human cell lines. The results demonstrated a high anticancer potential in the biological assays performed and a low toxicity in human cells. The insecticidal activity against *Spodoptera frugiperda* are in development.



**1**

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## Agradecimentos/Acknowledgments

This work was supported by grants from FAPESP (2020/03390-8) and CAPES

**Área: QPN**

# New cadinanolide from *Vernonanthura cuneifolia* (Asteraceae) and evaluation of antileishmanial activity

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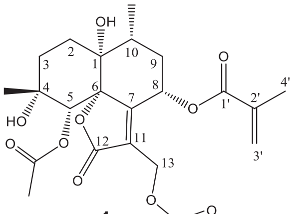
Keywords: *Asteraceae, Sesquiterpene lactones, Leishmania amazonensis, Antiprotozoal activity, Cytotoxicity*.

## Highlights

This is the first phytochemical study of *Vernonanthura cuneifolia*. A new sesquiterpene lactone was isolated. Dichloromethane fraction exhibited promising antileishmanial activity against *L. amazonensis*.

## Abstract

Sesquiterpene lactones are an important class of specialized metabolites, frequently isolated from the Asteraceae, that present a variety of biological activities[1]. *Vernonanthura cuneifolia* (Gardner) H. Rob. is a subshrub, native to Brazil, occurring in the Midwest, Southeast, and South regions[2]. There are no reports of chemical and biological studies with this species. This work aimed to evaluate the antiprotozoal activity of *V. cuneifolia*, and to isolate compounds from the active fraction. The aerial parts of *V. cuneifolia* were collected in the Campos Gerais region, in Ponta Grossa, Paraná State. The crude ethanolic extract was produced by exhaustive maceration (35.4 g) and then partitioned into hexane, $CH_2Cl_2$, and EtOAc. The crude extract and fractions were submitted to antiprotozoal activity assay against *Leishmania amazonensis* (IFLA/BR/1967/PH8) by cell viability method by XTT reduction[3]. The cytotoxicity assay was determined by the MTT reduction method[4] in J774A.1 macrophages. Crude extract and hexane fraction exhibited moderate activity against *L. amazonensis* ($IC_{50}$ ± SD (μg/mL) 76.54 ± 3.46 and 68.67 ± 3.41, respectively). The dichloromethane fraction showed promising potential against the protozoan with $IC_{50}$ 9.80 ± 1.10. This fraction exhibited moderate cytotoxicity $CC_{50}$ ± SD (μg/mL) 94.45 ± 9.59 with a selectivity index of 9.64. Part of the dichloromethane fraction (3.0 g) was subjected to successive chromatographic columns over silica gel, Sephadex LH-20, and semi-preparative HPLC, which provided two sesquiterpene lactones. The isolated compounds were identified by comparison of their spectroscopic data (NMR and HR-MS/MS) as an undescribed cadinanolide derivative denominated 8α-methacryloxycadinan-7(11)-en-6,12-olide (**1**) (7.0 mg) and a known compound 8α-(2′-methyl)acryloyloxy-13-ethoxyvernojalcanolide (**2**) (3.5 mg)[5]. Compound 1 was obtained as a colorless oil, and the molecular formula was established as $C_{23}H_{30}O_{10}$ on the basis of ion peaks at *m/z* 467.1912 $[M+H]^+$ (calcd. *m/z* 467.1904 $[M+H]^+$) in the UHPLC-HR-MS/MS. In the NMR spectrum, it showed characteristic signs of the skeleton of the cadinanolide-type[5,6]. Furthermore, an examination of the 2D-NMR (HSQC, HMBC and NOESY) spectra of **1** indicated that it was similar to sesquiterpene lactone previously isolated from *Vernonanthura nudiflora*[6], but differed at C-8 methacryloxy substituent group. This study shows the antiprotozoal potential of *V. cuneifolia* against *L. amazonensis*, as well as a potential source of new molecules.



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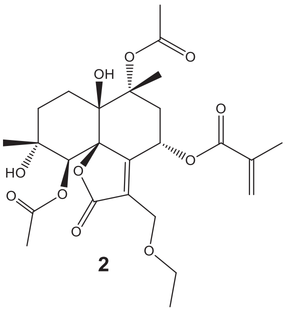

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## Acknowledgments

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**Área: QPN** **Nº de Inscrição:01189**

# New flavonoids from bark of *Brosimum parinarioides* Ducke (Moraceae) and their anti-inflammatory activities

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Palavras Chave*:* (Anti-inflammator, *Brosimum parinarioides*, Chalcone, Flavane)

## Highlights

1. Four flavonoids were isolated from the bark of *B. parinarioides*
2. The structures of two previously undescribed flavonoids were established based on spectroscopic data
3. It is the first report of these compounds in the *Brosimum* genus
4. This is the first phytochemical study with *B. parinarioides*

## Abstract

The biodiversity of the Amazon rainforest is one of the richest in the world, being the habitat for thousands plant species. Although the knowledge regarding the natural products has been extensively explored, several genera still unexplored (eg. *Brosimum*). The genus *Brosimum* belongs to Moraceae family *and* is widely represented in the Amazon rainforest (13 species). These Amazonian species are applied in traditional medicine due their activities, such as anti-inflammatory, anti-tumor, anti-weaknesses agent; remedies against respiratory and skin diseases, and osteoporosis. The species *B. parinarioides* Ducke is a tree native to Northern Region of Brazil, growing up to 40 meters. In the Amazon Region, it is known as "amapá-doce" or “amapá”. The chemical composition of this specie has never been studied. In this study, we investigated the chemical constituents of the bark of *B. parinarioides* and obtained two new flavonoid: 4’,6-dihydroxy-5’-prenyl-flavan (**1:** *m/z 309.1486* $[M-H]^-$*,* $C_{20}H_{22}O_3$) and 2,4,4’-trihydroxy-5’-(2”-hydroxy-3”-methyl-3-butenyl) chalcone (**2:** *m/z 339.1247* $[M-H]^-$*,* $C_{20}H_{20}O_5$), named parinarioidins *A-B*, as well as licograchalcone A (**3:** *m/z- 323.1289* $[M-H]^-$*,* $C_{20}H_{20}O_4$), and Kanzonol B (**4:** *m/z 321* [M-H], $C_{20}H_{18}O_4$). The flavonoids were isolated by classical chromatography techniques such as column chromatography (CC) and preparative thin layer chromatography (TLC). The structural elucidation was based on spectroscopic and spectrometric analyses, such as 1D and 2D NMR and HR-APCI-MS. The compounds **1-4** and the methanolic extract exhibited significant anti-inflammatory potential (39.77% - 54.68%) by inhibiting the lipoxygenase enzyme (LOX), when compared to a NDGA standard (58.66%). These results represent the first report on the chemical constituents of *B. parinarioides,* which possess a promising anti-inflammatory potential.

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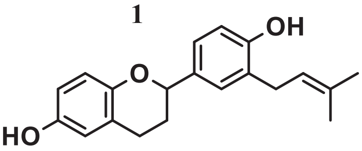

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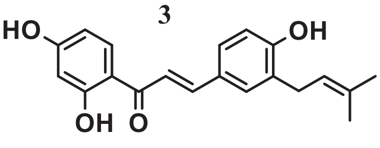

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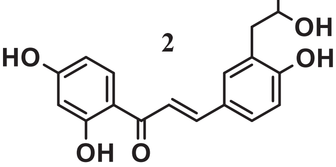

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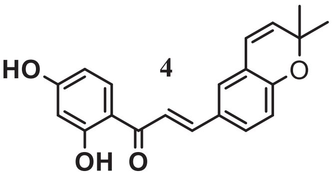

## Acknowledgments

The authors are grateful to Analytical Center(UFAM) for analysis, and CAPES, CNPq/MCT (CT-Amazônia Ed. No. 77/2013, proc. No. 408172/2013-4), FINEP, and FAPEAM for financial support.

**Área: QPN**

# New *seco*- and abietane lactone from *Medusantha martiusii* (Lamiaceae)

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*Keywords: oxygenated diterpenoids, seco-abietane, abietane lactone, Lamiaceae, Caatinga.*

## Highlights

New aromatic abietanes were isolated from the species *Medusantha martiusii* present in the Caatinga biome.
The isolated compounds presented functionalization in an unusual position in abietanes (C-2).

## Abstract

*Mesudanta martiusii* (Benth.) Harley & J.F.B.Pastore is known as cidreira-do-mato or cidreira-do-campo and popularly used for the treatment of ovarian inflammation and gastric disorders.[1] According to literature data, its phytochemistry is related to the presence of aromatic abietane diterpenoids.[2,3] The aerial parts of *M. martiusii* were collected in July 2019 in the municipality of Maturéia, a Caatinga region of Paraíba. The aerial part was dried, ground, and then extracted first with hexane and then with ethanol. The hexane extract was submitted to Vacuum Liquid Chromatography (Silica gel, hex:$CHCl_3$ 80:20, 60:40, 50:50, 40:60, 20:80, AcOEt). The acetate fraction was subjected to different chromatographic procedures such as analytical HPLC-DAD (C18, ACN-$H_2O$ 70:30-75:25, gradient with 0.1% FA) and preparative HPLC-DAD (C18, ACN-$H_2O$ 50:50 - 70:30, gradient with 0.1% FA) to give two abietane diterpenes described for the first time in the literature (Figure 1). Structural elucidation of the compounds was based on 1D and 2D NMR spectroscopy, IR and HRMS data analyses. In this study, two types of abietanes (*seco*- and abietane lactone) are reported and their bioactivities will be further evaluated. These results reinforce that Caatinga endemic species have a high chemical diversity and encourage the preservation and appropriate use of the biodiversity of this uniquely Brazilian biome.

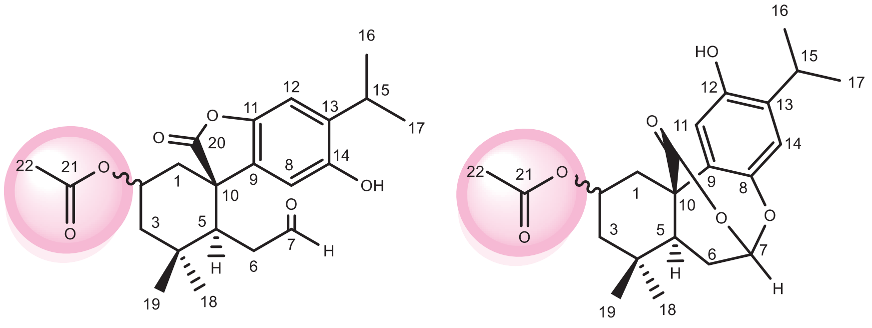

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Figure 1. Chemical structure of the compounds isolated from *M. martiusii*

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## Acknowledgments

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**Área: QPN**

# New Macrocyclic Humulene-Type Sesquiterpenoids from *Anaxagorea dolichocarpa* and Structure Review of Nordine

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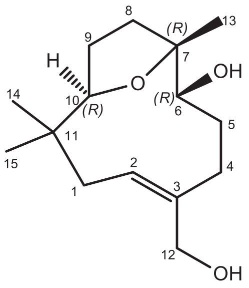
Keywords: *Anaxagorea*, Annonaceae, Sesquiterpenoid, Nordine.

## Highlights

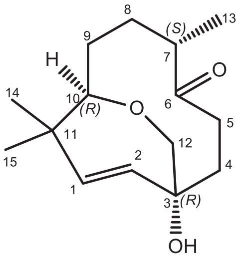
Five macrocyclic humulene-type sesquiterpenoids were isolated from the roots of *Anaxagorea dolichocarpa*. Four are undescribed in the literature, dolichocarpol G-J and nordine that had previously been isolated from *Anaxagorea javanica*. However, in this work we present a review of its structure.

## Resumo/Abstract

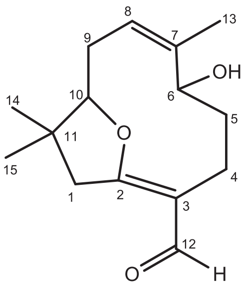
The Annonaceae family is the largest within the order of Magnoliales with about 107 genera and 2400 species of pantropical occurrence with predominance in tropical forests.[1] Among its species, *Anaxagorea dolichocarpa*, popularly known as “envira” or “paixinho” is a plant widely distributed in South America, being found in Brazil mainly in the North and Northeast regions.[2] Previous studies have reported the presence of alkaloids and sesquiterpenes showing the species as promising in the search for new bioactive compounds.[3,4,5] Thus, a phytochemical study of the roots from *Anaxagorea dolichocarpa* was carried out. The plant material of *A. dolichocarpa* was collected on April 2018 in Cruz do Espírito Santo-PB and subjected to processes of extraction, purification and analysis of its chemical constituents. These procedures were carried out by classical laboratory methods as well modern techniques of HPLC, 1D and 2D NMR, IR, HRMS and Circular Dichroism. From the chloroformic fraction, it was possible to isolate and characterize the chemical structures of five macrocyclic humulene-type sesquiterpenoids, four of them being related for the first time in the literature, dolichocarpol G-J (1-4) and nordine (5) previously isolated from *A. javanica*.[4] However, the chemical structure of nordine was incorrectly proposed, as we can verify that the ether fusion is between C-10 and C-7 and not between C-10 and C-6 as the authors proposed. These findings, contributes to the chemotaxonomic knowledge of the Annonaceae family and the *Anaxagorea* genus.



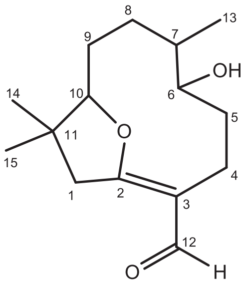
**Dolichocarpol G**



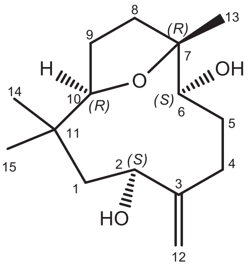
**Dolichocarpol H**



**Dolichocarpol I**



**Dolichocarpol J**



**Nordine**

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## Agradecimentos/Acknowledgments

CNPq / CAPES / UFPB / LMCA / IPeFarM / INCT

**Área: QPN**

# New polyketide derived metabolites produced by *Peroneutypa* sp. M16

**Marcelo Rodrigues de Amorim (PQ),[1]* Tiago Antunes Paz (PQ),[2] Antonio G. Ferreira (PQ),[3] Camila de Souza Barbosa (PG),[4] Rafael Victorio Carvalho Guido (PQ),[4] Roberto Gomes de Souza Berlinck (PQ).[1]**

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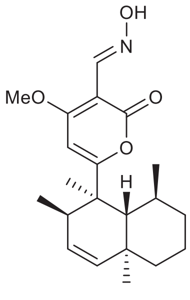
Palavras Chave: *Natural products*, *Antiplasmodial*, *Marine fungi.*

## Highlights

First chemical study of the extract produced by *Peroneutypa* sp. Undescribed polyketides were isolated and characterized. Absolute configurations were determined by electronic circular dichroism.

## Abstract

The World Health Organization (WHO) has reported that in 2019, 229 million new cases and 409,000 deaths of malaria, even though these numbers indicated a reduction of approximately 41% of cases between 2000-2015 and 67% of mortality [1]. The discovery of new bioactive natural products is an important approach to identify novel antimalarial agents [2]. In the present investigation we assessed the biological and chemical profile of the organic extract and fractions obtained from culture of a marine-derived fungus *Peroneutypa* sp. M16, isolated from a sea cucumber, which were collected in Espírito Santo – ES, Brazil. The fungi strain was grown with nutrients and artificial sea water. After the growth, the organic extract was obtained [3]. The crude extract was fractionated by gel permeation chromatography and grouped by HPLC-MS to yield eleven final fractions, which were evaluated for antiplasmodial activity against *Plasmodium falciparum* 3D7 strain [4]. Antiplasmodial activities (Inhibition > 80% at 50 µg/mL) were observed for five fractions (F2, F3, F4, F5 and F11). Separation of fraction F4 by semipreparative HPLC-UV led to the isolation of new compounds **1** and **2** along with the known compounds **3** and **4**, which structures were established by NMR analysis. Absolute configurations of compounds were determined by the comparison of their experimental ECD spectra with calculated ECD data. The isolated compounds are under evaluation in antiplasmodial assays.



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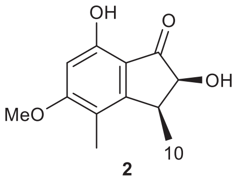

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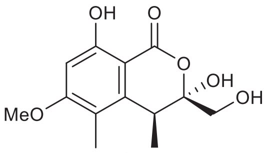

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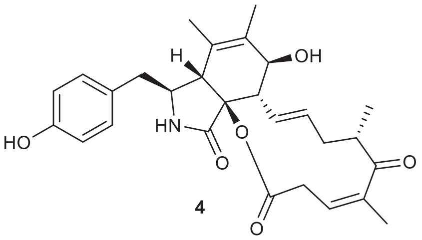

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## Acknowledgments

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**Área: QPN**

# New withaphysalin-F derivatives isolated from leaves of wild *Iochroma arborescens* (*Acnistus arborescens*)

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Palavras Chave: *Iochroma arborescens, Acnistus arborescens, withaphysalin, cytotoxic activity, antileishmanial activity, antimicrobial activity.*

## Highlights

- ✓ Nine new withaphysalin-type withanolides along with three know were isolated.
- ✓ The cytotoxic, antileishmanial, and antimicrobial effects of two epimeric withaphysalins were evaluated.

## Resumo/Abstract

Withanolides ($C_{28}$ ergostane-type steroidal lactones) are a family of secondary metabolites well known for their large spectrum of biological and pharmacological activities, such as cytotoxic, antitumor, immunosuppressive, antimicrobial, antifeedant, and anti-inflammatory.[1,2] *Acnistus arborescens,* currently renamed as *Iochroma arborescens*,[3] is a medicinal plant known for its antitumor properties.[4] It has been the subject of several phytochemical and biological studies, inclusive in our research group. Several withanolide-types, either with normal or modified skeletons, have been reported from this species.[1,2,4] In a continuing effort to isolate active compounds from this species, the acetone extract (64.2 g) from leaves of wild specimens collected at Pico Alto (Guaramiranga Mountain, Ceará State, Brazil) were investigated using silica gel and Sephadex CC, and HPLC. As a results, twelve withaphysalin-type withanolides were isolated, nine of which (**1** - **9**) are new compounds. The structures of all compounds **1** - **12** (Figure 1) were elucidated by HRMS and NMR experiments. The new compounds **1** and **2** exhibited cytotoxicity on HCT-116 and MCF-7 cancer cell lines showing $IC_{50}$ ranging of 0.30 - 1.34 μM. **1** and **2** also showed activity on *Leishmania amazonensis* with $IC_{50}$ values of 4.21 *μ*M and 2.38 *μ*M, respectively, and antimicrobial activity on *Staphylococcus aureus* at concentrations of 62.50 and 31.25 *u*g/mL, respectively. In conclusion, the withaphysalins are the main withanolides produced by the wild plants and, based on the test results, have great biological potential.

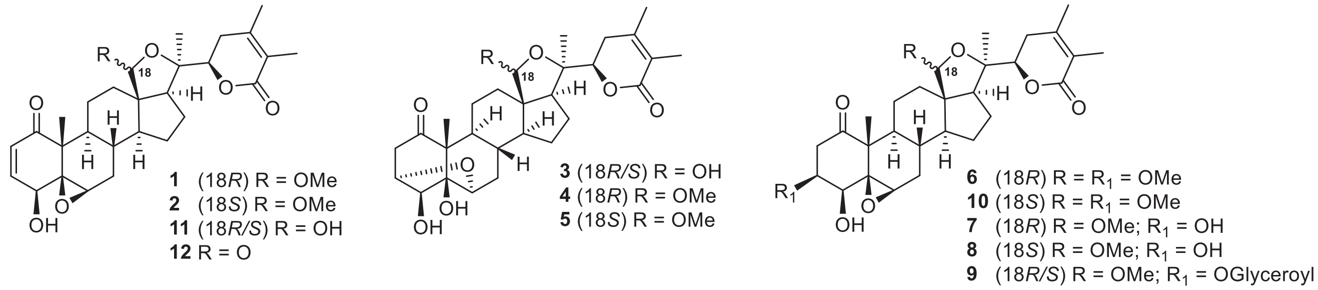

**Figure 1 -** Structures of the withaphysalins **1** – **12**.

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## Agradecimentos/Acknowledgments

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**Área: QPN**

# Optimization of extraction conditions for improving gallic acid and quercetin content in *Pouteria macrophylla* fruits: a promising cosmetic ingredient

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Key words: *Experimental design, Process optimization, Phenolic compounds, Antioxidant activity.*

## Highlights

The experimental design improved gallic acid and quercetin content in *P. macrophylla* fruit extract, showing a great industrial process for future cosmetic applications.

## Resumo/Abstract

*Pouteria macrophylla* (Sapotaceae) is distributed from the Andean slopes of Peru to the western Amazon. The pulp fruit extract present high concentrations of gallic acid, quercetin and other phenolic acids, which showed inhibition of free radicals, tyrosinase and melanogenesis genes[1] justifying its promisor use in cosmetology. Therefore, the optimization of extraction conditions by an experimental design is important to enhance economic potential of *P. macrophylla*. A statistical analysis was designed according to a Central Composite Design (CCD) model for three factors, totaling 11 experiments with 3 central points (Table 1). The CCD model was interpreted based on analysis of variance (ANOVA), as well as the polynomial model generated by this type of planning. All statistical analyzes were performed considering a confidence level of 90% ($p<0.1$). Lyophilized fruits (0.5g) were pulverized and dissolved for the extraction in three different proportions of ethanol/ water (C) in three different times (t) in ultrasound using three different solvent-fruit ratios (SFR). After the extraction, the samples were diluted 150x, and the content of gallic acid (GAC) and quercetin (QC) were carried out by measuring the absorbance in a UV-visible spectrophotometer at 260nm and 362nm, respectively. The standard curves of gallic acid ($y=0.0786x$; $R^2 = 0.9957$) and quercetin ($y=0.0658x$; $R^2=0.9995$) were applied to express the samples results in mg per liter of extract. The polynomial model for gallic acid and quercetin content were generated by the responses tested in the proposed model, where $X_1$, $X_2$ and $X_3$ can be related to the real variables (SFR, C and T, respectively). Antioxidant activity and total phenolic compounds were evaluated by DPPH and Folin-Ciocalteu methods, ranging from 88.65 to 20.54% of inhibition and 4293.7 to 897.04 mgEAG/L, but neither were significant nor predictive. Based on ANOVA results, the models were identified as significant and predictive for gallic acid and quercetin content, although the only influential statistical variable was the solvent-fruit ratio for gallic acid content ($p< 0.006$). High values of GAC ($X_2 = -1$; SFR= 1:5) were observed in low levels of SFR. On the other hand, the only non-influential variable for quercetin amounts was the time in ultrasound ($p<0.361$). QC was positive and directly proportional influenced by SFR and C, where a higher water concentration and high solvent-fruit ratio led to high quercetin content. Previous studies described that low concentrations of ethanol could also favor the extraction of phenolic compounds[2] and a high proportion of solvent-fruit ratio[3]. A predictive and significant model for these answers shows great prospects in terms of industrial processes and an efficient economic and cosmetic application.

Table 1. CCD experiments matrix

| Central Composite Design | | | | | | | |
|---|---|---|---|---|---|---|---|
| | Level of independent variables | | | | Level of independent variables | | |
| Experiment | % $H_2O$ (v/v) | Solvent-fruit ratio (m/v) | time (min) | Experiment | % $H_2O$ (v/v) | Solvente-fruit ratio (m/v) | time (min) |
| 1 | 25 (-1) | 5 (-1) | 10 (-1) | 6 | 75 (+1) | 5 (-1) | 30 (+1) |
| 2 | 75 (+1) | 5 (-1) | 10 (-1) | 7 | 25 (-1) | 15 (+1) | 30 (+1) |
| 3 | 25 (-1) | 15 (+1) | 10 (-1) | 8 | 75 (+1) | 15 (+1) | 30 (+1) |
| 4 | 75 (+1) | 15 (+1) | 10 (-1) | 9 (PC) | 50 (0) | 10 (0) | 20 (0) |
| 5 | 25 (-1) | 5 (-1) | 30 (+1) | 10 (PC) | 50 (0) | 10 (0) | 20 (0) |
| | | | | 11 (PC) | 50 (0) | 10 (0) | 20 (0) |

[1] GRATIERI, T. et al; Composição contendo extrato do fruto do Cutite (Pouteria macrophylla) (Lam.) Eyma em nanoemulsão e seu uso tópico despigmentante para tratamento de hipercromias. Titular: Fundação Universidade de Brasília. Br n BR 10 2021 008059 0. Depósito: 27 abr 2021

[2] CHEN, S. et al; Simultaneous optimization of the ultrasound-assisted extraction for phenolic compounds content and antioxidant activity of Lycium ruthenicum Murr. Fruit using response surface methodology; 2018.

[3] CHUYEN, H. V. et al; Optimization of extraction conditions for recovering carotenoids and antioxidant capacity from Gac peel using response surface methodology; 2017

## Agradecimentos/Acknowledgments

CAPES for the financial support

**Área: QPN** **Nº de Inscrição: 01152**

# Optimization of extraction methods and chromatographic analysis of bee extracts for pesticide analysis.

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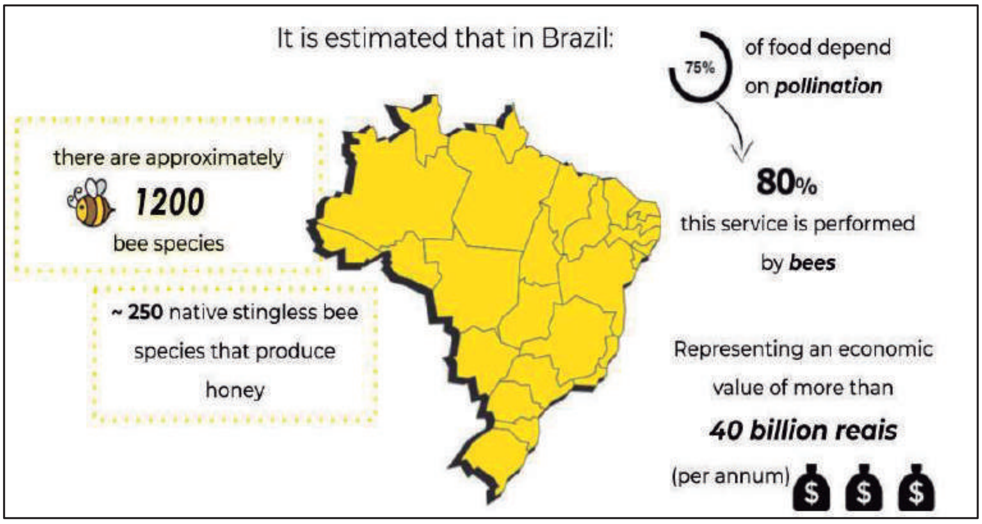
Keywords: *Pollination, Chromatography, Hymenoptera, Biodiversity.*

## Highlights

Drop in the bee population may be related to the indiscriminate use of pesticides.

Search for pesticide residues in bee extracts.

## Resumo/Abstract



Bees are pollinating agents that find nectar and pollen as their source of food and energy. They belong to the order Hymenoptera, of extreme importance for the conservation of plant and animal species, since they house the largest number of pollinators. Pollination is one of the most important mechanisms for maintaining biodiversity, and in this scenario, according to the United Nations Food and Agriculture Organization (FAO), it is estimated that of the 100 species of crops responsible for providing 90% of the food in the world, 71 are pollinated by bees. In addition, bees are responsible for the production of honey and other supplies, such as wax and propolis, which contribute to human well-being. Since the 80's and 90's there has been a gradual reduction in the number of bees, but in a small magnitude. Currently, these insects are at high risk of extinction, and it is believed that a combination of several factors causes this population decline, such as deforestation, climatic variations, pathogens (viruses, bacteria, mites) and use of pesticides. Contamination of bees by pesticides can result from the negligent use of farmers, for example, by striking them for imagining that they harm the crop. Pesticide residues can be absorbed by bees during the collection of nectar and/or pollen and water. This project aims to seek the correlation between bee mortality and the use of pesticides, through modern chromatography techniques coupled with mass spectrometry, which will support the attainment of metabolic profiles subsidizing the search for pesticide residues in these bees. This because it is extremely important to assess the reach of pesticides in the environment and understand what impact they cause on bees and other pollinators. To achieve this proposed objective, several methods of extraction and analysis were tested in order to obtain the best methodology.

## Agradecimentos/Acknowledgments

We thank CAPES (process 88887.473938/2020-00) and CNPQ for funding this Project.

# Optimization of extraction of phenolic compounds from of *Lippia alba* (Mill.) N. E. Brown leaves by ultrasound-assisted extraction

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*Keywords*: *Lippia alba, Ultrasound-assisted extraction, Polar extracts, Phenolic compounds.*

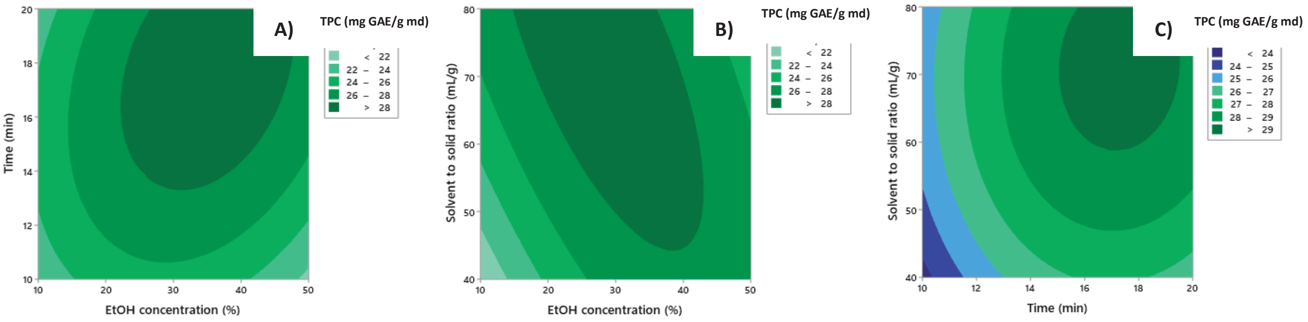
## Highlights

The extract of *Lippia alba* leaves obtained using the optimized conditions by ultrasound-assisted extraction showed a higher total phenolic content compared to the extract obtained by maceration.

## Resumo/Abstract

Medicinal plants are rich in phenolic compounds, which are responsible for several biological activities such as antioxidant activity. Several studies carried out with extracts of the species *L. alba* have shown promising results regarding its ability to act against oxidative stress due to the presence of a wide variety of phenolic compounds in its composition. However, since the chemical composition of the extracts obtained from these plants depends, among other factors, on the extraction process, it is necessary to choose the most efficient extraction method and at the same time evaluate the main variables that may affect the extraction process, aiming to find the most suitable conditions for obtaining preparations with high yields and high biological activities. In this sense, the objective of this study was to optimize the extraction process, by ultrasound-assisted extraction (UAE) using a Box-Behnken design (BBD), evaluating the effect of ethanol concentration (from 10 to 50%) as solvent, extraction time (from 10 to 20 min) and solvent to solid ratio (from 40:1 to 80:1 mL/g) on the total phenolic content (TPC) of the *L. alba* leaves extracts (SisGen nº A8CCB3B). Thus, 0.5 g of crushed leaves were extracted with appropriate volume of solvent according to the BBD using an ultrasound bath at a frequency of 37 kHz and at constant temperature (30 ± 1 °C). After that, all extracts were filtered and the organic solvent was removed by evaporation under reduced pressure and lyophilized. The total phenolic content was evaluated using the Folin-Ciocalteu method. The result was expressed as a milligram of gallic acid equivalent per gram of dry material (mg GAE/g dm) using a gallic acid calibration curve (0–200 mg/L). The highest TPC was obtained by the extract prepared using the following optimized extraction conditions: ethanol concentration of 29%, extraction time of 17.8 min and solvent to solid ratio of 71:1 mL/g (Figure 1). The results showed that the extract obtained by UAE from the of *L. alba* leaves under optimized conditions had a higher TPC (29.48 ± 0.32 mg GAE/g dm) compared to the extract obtained by maceration (24.18 ± 0.49 mg GAE/g dm) under similar extraction conditions (ethanol concentration of 29%; extraction time of 17.8 min and solvent to solid ratio of 71:1 mL/g).

**Figure 1**: Contour plots (A, B and C) considering the influence of ethanol concentration, extraction time and solvent to solid ratio on the total phenolic content in extracts obtained by UAE from of *L. alba* leaves.



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## Agradecimentos/Acknowledgments

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**Área: QPN**

# Oxidative potential of two Brazilian endophytic fungi towards progesterone

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Keywords: *Endophytic fungi, Steroids, Biotransformation, Selective hydroxylation.*

## Highlights

- Endophytic fungi carried out uncommon and stereoselective oxidation at the C-17 position of the progesterone;
- Five derivatives of the progesterone were detected in the endophytic fungi cultures.

## Resumo/Abstract

Biotransformation has been successfully employed to conduct uncommon reactions that would hardly be carried out by chemical synthesis. Microbial transformations require mild reaction conditions, such as room temperature (25-30°C), atmospheric pressure, and pH close to neutral, avoiding problems such as isomerization, racemization, epimerization, and rearrangement of reactants or products[1]. A wide diversity of compounds may be metabolized by fungi, leading to chemical derivatives through selective reactions that work under ecofriendly conditions[2]. Endophytic fungi live inside vegetal tissues without causing damage to the host plant and they make available unique enzymes for interesting chemical derivatization[3]. Steroids display various biological activities, and their derivatization is in the interest of chemical and pharmaceutical industries. Biotransformation of steroids by endophytic fungi may provide new derivatives as these microorganisms came from uncommon and underexplored habitat[4]. In this study, endophytic strains isolated from *Handroanthus impetiginosus* leaves were assayed for biotransformation of progesterone, and its derivatives were identified through GC-EI-MS analysis with NIST library match. Unequivocal structures identification was provided on the basis of the proposition of fragmentation mechanisms, along with the determination of the ion structures seen at spectra. The endophytic fungus *Talaromyces purpurogenus* H4 was capable of selectively transforming the steroidal nucleus into four derivatives (androstane-3,17-dione, androst-4-ene-3,17-dione, 17α-hydroxy-androst-4-ene-3-one, and 5α-pregnane-3,20-dione) through selective C4-C5 ene-reduction and C-17 oxidation. For estimating the efficiency of biotransformation by the selected endophytic strains as well as its selectivity, we provided a detailed analysis of all peak areas in GC chromatograms. The best conversion rate of progesterone (> 90%) was reached with *Penicilium citrinum* H7 which converted the substrate exclusively into 17α-methyltestosterone. The results obtained highlight the importance of the use of endophytic fungi to produce new and interesting steroidal derivatizations. This work comes up with new approaches for the achievement of a variety of bioactive steroids building blocks, which can be a good starting point for the synthesis of new compounds combining biotransformation and other chemical approaches.

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**Área: QPN**

# Pest ant nests – interactions between their members, their controls with natural products and new methodologies

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Key-words*: Plague ant, Bioinsecticids, Natural products, Nanoencapsulation, Fungus, Biosensors*

## Highlights

Complex interactions between insects, mutualistic fungi, microparasites, actinobacteria and black pathogenic yeasts occur in the ant´s nest. Nest control can be done applying new methods using natural products, nanoencapsulation, disposable electrochemical sensor and statistical tool. Co-culture of the organisms contribute to control the nests

## Abstract

Brazil is prominent in the world supply of agricultural products, and pest ants are one of the main problems for Brazilian agriculture, causing enormous losses to agribusiness. News chemicals and biologicals techniques are under development specially to reduce costs and the amount of insecticides applied. The ants of the Attini tribe, especially the genus *Atta* (saúvas) and *Acromyrmex* (quenquéns), are characterized by cultivating a single fungal species, *Leucoagaricus gongylophorus*, a mutualistic fungus that is essential for their survival. There is a very complex organization in leaf-cutting ant nests, formed by interactions between insects, mutualistic fungi (*L. gongylophorus*), microparasites (*Escovopsis* sp), actinobacteria (*Pseudonocardia* sp) and black pathogenic yeasts (*Exophiala* sp).

Disposable electrochemical sensor (DES) using acetylcholinesterase enzyme (AChE) can be used to understand the interaction in the nest. The DES modified with AChE (DES-AChE) was applied in inhibition studies using the Square Wave Voltammetry (SWV).

Technique of co-culture of nests members is important to understand their interactions. In the AChE of fish assays, the percentage of inhibition of extract of *Exphiala* sp was I=75.04 (± 0.099) and for *Atta sexdens* mortality was I= 46.42 (± 0.005). Toxicity to environment is relevant and it is done using assay with *Danio rerio.*

Nanoencapsulations using new biopolymers in the presence of extracts, pure compounds, essential oils and complex of natural products with metal are new methodologies that can optimize the efficiency and durability of natural products with insecticidal, fungicidal and bactericidal power, reducing the damage in the agricultural sector caused by pest ants in a more sustainable and less harmful to other species.

Statistical tools, among them, PCA (Principal Component Analysis) were applied to methodology of co-cultures; PLS (Partial Least Squares), which performs supervised data analysis and HCA (hierarchical cluster analysis) are exploratory methodologies that show similarities or differences between samples in each data set which, in these cases, become perfectly applicable. The HeatMap method (heat map) is also used, which is a map generated by automatic tools that uses colors to facilitate the understanding the information. This analysis is interesting to observe the reproducibility of samples analyzed by LC/MS. Molecular networks are used – GNPS Platform (Global Natural Products Social) of the co-cultivation that was most expressed in number of metabolites. The results showed that co-cultures of nest components were differentiated from monocultures through principal component analysis (PCA) and several metabolites were annotated by the platform.

Compounds from different classes were obtained from plants and co-culture, and flavonoids, coumarins, terpenes, chalcones, anthraquinones and chromone were the most actives as insecticidal, fungicidal, and bactericidal.

## Acknowledgments

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CNPq, 403210/2016-

**Área: QPN**

# Physicochemical determination of bioactive compounds from lyophilized cambuí fruit (*Mircyaria tenella O. Berg*)

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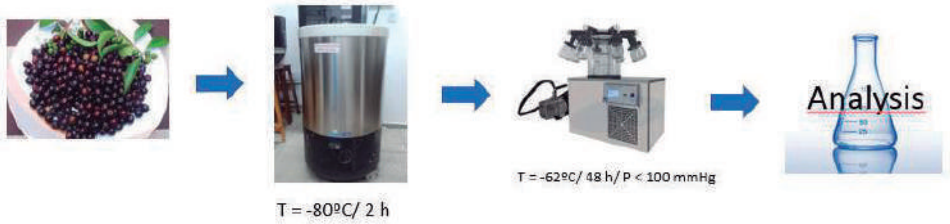
Keywords: *Antioxidants, Lyophilized Cambuí, Total Flavonoids, Total Phenolic Compounds.*

## Highlights

Investigation of the mineral composition and nutritional potential of the cambuí fruit (*Myrciaria tenella O. Berg*).

## Abstract

This project aims to generate scientific knowledge about the biochemical properties of cambuí (*Myrciaria tenella O. Berg*), as scientific production is scarce. The fruit was harvested in Povoado Barreira, in the municipality of Morro de Chapéu - BA, in May 2021. The methodology applied is described below.



Analyzes of bioactive compounds in different extracts were performed, in addition to physical-chemical analyzes, according to the results presented in the tables below:

Table 01. Determination of bioactive compounds in different extracts of cambuí fruit

| Bioactive Compounds | Methanol extract 20% | Methanol extract 40% | Methanol extract 60% | Ethanol extract 20% | Ethanol extract 40% | Ethanol extract 60% |
|---|---|---|---|---|---|---|
| Total phenolics (ug/g) | 1392,74±0,08 | 2400,38±0,04 | 2535,03±0,02 | 1761,84±0,04 | 1826,42±0,03 | 2221,60±0,05 |
| Total flavonoids (ug/g) | 1261,40±0,05 | 1930,07±0,01 | 2400,07±0,14 | 1247,07±0,26 | 1767,40±0,07 | 2221,40±0,09 |
| Antioxidant activity (%DPPH) | 75,69±0,02 | 60,58±0,02 | 45,98±0,03 | 87,10±0,09 | 68,03±0,08 | 7-,99±0,05 |

Table 2: Physicochemical determination of cambuí fruit

| Lipides (%) | pH | Titratable acidity (%) | Moisture (%) |
|---|---|---|---|
| 81,31±3,22 | 3,94±0,22 | 2,76±0,46 | 17,09±0,37 |

The results indicate that the *fruit Myrciaria tenella O. Berg*, popularly known as Cambuí, has its nutritional potential.

Reference

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## Acknowledgments

IFS, CNPQ

**Área: QPN**

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

# Phytochemical investigation of hexane and dichloromethane fractions from the leaves of *Lantana caatingensis* Moldenke (Verbenaceae)

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Palavras Chave: *Lantana, Nonpolar compounds, Fatty acids, Terpenes.*

## Highlights

This work presents the identification of compounds of the hexane and dichloromethane fractions from *Lantana caatingensis* by GC-MS. Identified compounds: fatty acids, hydrocarbons, phenolic compounds.

## Resumo/Abstract

*Lantana caatingensis* Moldenke is an endemic bush from the mountainous regions of the Brazilian Northeast, occurring in the states of Pernambuco, Piauí and Bahia. The literature reports the modulatory and antibacterial effect of the essential oil from the leaves of *L. caatingensis*. The aim of this study was identify the metabolites present in the hexane (FHexLC) and dichloromethane (FDCMLC) fractions of *L. caatingensis* leaves by Gas Chromatography with mass spectrometry (GC-MS). The leaves were collected in the town of Simões-PI (voucher number 27183, SISGEN A587160), dried at room temperature, ground and submitted to extraction with 70% ethanol. The fractionation of the extract was carried out on a silica gel column, under vacuum, using a gradient of increasing solvent polarity, obtaining the hexane fractions (31.9 mg), dichloromethane (5.1 g), ethyl acetate (16.8 g) and methanol (21.9 g). For analysis by GC-MS, the FHexLC and FDCMLC fractions were silylated using BSTFA (N,O-bistrifluoroacetamide - Sigma Aldrich®) and analyzed in a Shimadzu® model GCMS-QP2010SE gas chromatograph with an AOC-5000 autoinjector (Shimadzu® ), the analysis conditions were: initial temperature of 70 °C, maintained for 2 minutes (min), with heating rate of 6 °C min$^{-1}$, until the final temperature of 310 °C, maintained for 10 minutes. The samples were injected in split mode (10:1) and the mass spectrometer operating in electron ionization mode at 70 eV with a mass range of 47-650 Da. Identification was performed by spectral comparison with data in the literature and also with the WILEY® and NIST® library. By analyzing GC-MS, it was possible to identify 68 compounds distributed in fatty acid (14.67%), hydrocarbons (61.64%), phenolic compounds (>0.07%), among others. It was observed that FHexLC is mainly composed of unsaturated hydrocarbons (48.7%) and saturated (43.1%), isoprene compounds such as caryophyllene oxide (0.12%), geranyl acetate (0.16%) and squalene (47.84%), the most abundant compound of FHexLC fraction. In FDCMLC, fatty acids, methylated and ethylated derivates, steroids and triterpernoids and phenolic derivatives were found at trace levels. Phytol (16.4%) was the major compound of the FDCMLC fraction, the steroids identified were campesterol (0.72%), stigmasterol (2.24%), sitosterol (12.38%), stigmastanol (0.44%) and sitostenone (0.91%) and the triterpenoides identified were $\alpha$- and $\beta$-amyrenone (0.86% e 1.49%, respectively), germanicol (0.30%) e $\beta$-amyrin (7.52%).

## Agradecimentos/Acknowledgments

This study was supported of the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) - Código de Financiamento 001. Programa de Pós-Graduação em Química, UFPI and Laboratório de Geoquímica Orgânica (LAGO), UFPI.

**Área: QPN**

# Phytochemical Investigation of Hexanic Extract of the Species *Melaleuca Leucadendra* (L) L. Myrtaceae

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Palavras Chave: *Myrtaceae, Melaleuca leucadendra, Leaves,Hexanic extract, GC-MS.*

## Highlights

Identification of compounds from the hexanic extract of *Melaleuca leucadendra* leaves by GC-MS.

## Resumo/Abstract

The Myrtaceae family has 145 genera and approximately 3,500 species, widely distributed in tropical regions. Among the genera of this family, the *Melaleucadeno* have hardly been investigated from a phytochemical point of view, and usually found only ethnobotanical reports. The aim of this study was the phytochemical characterization of hexanic extracts from the leaves of *Melaleuca leucadendra* (L) L. using analysis by GC-MS. Thirty-seven secondary metabolites were identified in hexanic extracts of the leaves. There was evidence of: Nerolidol B (Cis or Trans), Heneicosane, Vitamin E, 2-Hexadecen-1-ol, 3,7,11,15-Tetramethyl-, [R-[R*,R*-(E)]]-, Gamma-sitosterol, Cyclopropanemethanol, Squalene, (-)-Caryophyllene oxide, Neophytadiene, in the hexanic extracts of this species. Due to the importance and the various biological activities described in the literature on compounds identified in this study *Melaleuca leucadendra* (L) L. can be considered an alternative source of bioactive secondary metabolites for pharmaceutical therapy.

## Agradecimentos/Acknowledgments

Thanks to everyone who participated in the preparation of this work and Coordenação de Aperfeiçoamento de Pessoal de Nível superior - CAPES, for financial support to Péricles Tavares Austragésilo Filho. To UNIFACOL for the support to the other authors.

**Área: QPN**

# Phytochemical investigation of *Evolvulus frankenioides* Moric (Convolvulaceae)

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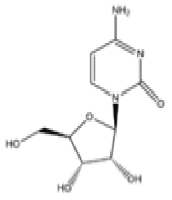
Palavras Chave *Convolvulaceae; Evolvulus frankenioides; Caatinga; Flavonoids*

## Highlights

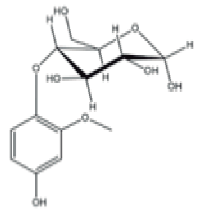
The present study reports the tentatively identification by HPLC-ESI-MS$^n$ and isolation of compounds from *Evolvulus frankenoides* Moric . In summary, 28 substances were assigned and other 4 were isolated.

## Resumo/Abstract

The family Convolvulaceae Juss. has a cosmopolitan distribution and comprises about 1.880 species classified in 58 genera. Many of its members have traditional medicine applications, such as Ayurveda and Unani. Among these species, *Evolvulus numularios* (L.) L. and *Evolvulus alsinoides* (L.) L. are applied in India to reduce stress and improve memory. In Brazil, the genus Evolvulus occurs mainly in the phytogeographic domains of Caatinga and Cerrado, about 71 species are recognized today. However, chemical studies concerning these specimens are still limited. *Evolvulus frankenioides* Moric, is a native Brazilian shrub. No description about its compounds has been found in the literature. Therefore, this study aimed to identify and isolate potentially active secondary metabolites from *Evolvulus frankenioides* Moric. In order to achieve this main goal, the crude ethanol extract of whole plant was partitioned with hexane, $CH_2Cl_2$ and n-BuOH (3x each). After that, the n-BuOH soluble fraction was subjected to dereplication by High Pressure Liquid Chromatography coupled to Mass Spectrometry (HPLC-MS) in negative mode. Afterwards, it was chromatographed in medium pressure liquid chromatography (MPLC), yielding twelve fractions. Fraction 1 was separated by HPLC and led to the isolation of 4 compounds, identified by $^1$H and $^{13}$C NMR. Mass spectrometry analysis allowed the tentatively assignment of 28 compounds, including 14 C and O-glycoside flavonoids and 13 phenolic and quinic acids derivatives. These classes were also reported for *E. numularios* (L.) L. and *E. alsinoides* (L.) L., indicating Evolvulus species as conspicuous producers of phenolic compounds. Regarding to the isolation, cytidine (**1**), tachioside (**2**), 3-caffeoylquinic (3) and 5-caffeoylquinic (4) acids were identified.



**1**



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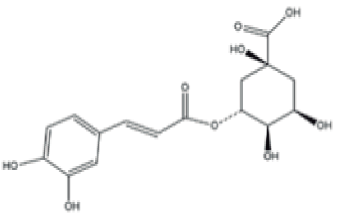
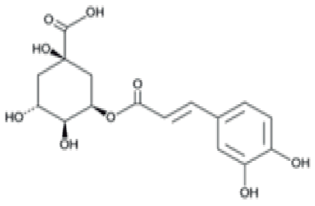


**3**



**4**

## Agradecimentos/Acknowledgments

The authors acknowledge CAPES and FINEP for financial support.

**Área: QPN** **Nº de Inscrição: ________**
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# Phytochemical prospecting of banana peel biomass

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Keywords: Extraction, Biomass, Banana peel, Mass spectrometry, Chromatography, Natural products classes

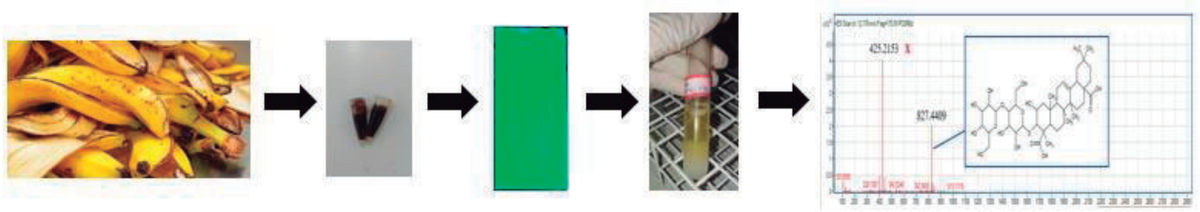
## Highlights

The objective of this work is to study the methods of extracting the banana peel. TLC, qualitative tests and HPLC-MS analyses were carried out to determine the chemical composition of major compounds.

## Resumo/Abstract

Biomass includes any organic matter, such as vegetables of all kinds, food crop residues, wood and even animal residues. The banana species used in this work includes the genus *Musa Paradisiac* of the family Musaceae. Banana is the fruit with occupies the main culture in Bahia state [1]. Hence, the peels constitute a biomass residue. According to the literature review [2-4], the main classes of natural products related to banana peels include tannins, flavonoids, steroids and saponins. Herein, different extraction methods were studied, such as maceration, friction maceration (mechanical procedure), Soxhlet and decoction. To extract preparation, hexane, ethanol and hydroalcoholic solution were chose as solvents. Qualitative tests were carried with prepared extract in order to identify the major classes of natural products present and TLC was run in an attempt to separate the main constituents in extracts. The polar solvent system exhibited higher yields when compared with hexane. HPLC-MS were carried out and a good correlation amongst qualitative assays and TLC was achieved being possible to determine the correct chemical composition of found substances. Figure 1 shows the route followed in this work, from the separation of banana peels to the instrumental analysis for the extracts obtained by maceration and friction maceration using hydroalcoholic solvent system. For both extracts, TLC plate showed intense spots as well as they gave positive test for saponins (Figure 1) which was confirmed by HPLC-MS.

*Figure 1- Analysis made from banana peel extracts*



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## Agradecimentos/Acknowledgments

Authors would like to thank UFRB and the Herbário do Recôncavo da Bahia (HURB/UFRB) for identifying the banana species studied herein and also the Laboratory of Nanobiotechnology of the Institute of Biotechnology - Research Center on Bioactive Compounds (NPCBio)/UFU for HPLC-MS analysis.

**Área: QPN** **Nº de Inscrição:00932**

# Phytochemical prospection of *Eugenia* species (MYRTACEAE) leaves extracts

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Palavras Chave: *Eugenia*, *Ácidos triterpênicos, Fitoquímica.*

## Highlight

Results obtained from phytochemical prospection showed that Eugenia species may have different chemical classes. First report of the presence of barbinervic acid from species of *E.florida*.

## Resumo/Abstract

Entre os gêneros da família Myrtaceae, o gênero *Eugenia sp.* apresenta espécies com uma ampla gama de atividades biológicas tais como: anti-inflamatória, antibacteriana, antioxidante, antitumoral e antiviral [1]. A *Eugenia brasiliensis*, a *Eugenia florida* e a *Eugenia punicifolia* apresentam em comum ácidos triterpênicos, como os ácidos betulínico, ursólico e oleanólico. O objetivo deste trabalho é avaliar de forma geral o perfil químico dos extratos preparados a partir das folhas dessas espécies de *Eugenia,* em diferentes estações do ano, assim como identificar os principais ácidos triterpênicos presentes. A coleta do material botânico, folhas de *E. brasiliensis* e *E. florida*, foi realizada durante as quatro estações do ano, em espécies localizadas no Jardim Botânico do Rio de Janeiro, já as folhas de *E. punicifolia* na Universidade Federal da Amazônia. Após coleta, as folhas foram secas em estufa a 40°C, em seguida trituradas em moinho de facas e submetidas a extração por maceração em frasco vedado em etanol P.A por 7 dias. A prospecção fitoquímica foi realizada nos extratos brutos (**Tabela 1**), sendo utilizadas placas Kieselgel GF254 (20 × 20 cm, 1 mm de espessura)[2]. A quantificação dos ácidos triterpênicos foi realizada por HPLC-DAD. As análises foram realizadas em sistema LC 20ADXR com amostrador automático e detector SPD-M20A. Foi utilizada coluna Supelcosil LC-18 (250 mm x 4,6 mm; 5 µm), fase móvel acetonitrila e solução aquosa de ácido fosfórico (0,05% v/v), fluxo de 1 mL/min e detecção 205 nm. Os resultados preliminares mostraram uma composição variável dos ácidos triterpênicos( betulínico, ursólico e oleanólico) entre as espécies e estações do ano. Além disso,o ácido barbinérvico foi encontrado em quantidades significativas na espécie de *E. florida,* sendo o primeiro relato para esta espécie, pois não há dados publicados sobre a presença deste ácido.

**Tabela 1 -** Resultados *Eugenia brasiliensis* (EB), *Eugenia florida(*EF*)*, *Eugenia punicifolia*(EP).

| Classe química | EBO | EBI | EBP | EBV | EFO | EFI | EFP | EFV | EPV | EPI |
|---|---|---|---|---|---|---|---|---|---|---|
| Ácidos triterpênicos | + | + | + | + | + | + | + | + | + | + |
| Taninos | + | + | + | + | + | + | + | + | - | - |
| Flavonoides | - | - | - | - | - | - | - | - | - | - |
| Ácidos fenólicos | - | - | - | - | + | + | + | + | + | + |

*As letras O, I, P, V referem-se às estações outono, inverno, primavera e verão respectivamente.

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## Agradecimentos/Acknowledgments

Farmanguinhos, FIOCRUZ. Jardim Botânico do Rio de Janeiro. Universidade Federal da Amazônia

*Sociedade Brasileira de Química (SBQ)*

# Phytochemical study and evaluation of the biological activity of extracts from seeds of the species Spondias purpurea L. (Anacardiaceae)

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[2] *Departamento de Química Orgânica, UFBA*

Palavras Chave: *Biological activity, phytochemical, Quantification of total flavonoids, Seeds, Spondias purpurea, Industrial residual study.*

## Highlights

-The total flavonoid content was performed by colorimetric assay using aluminum chloride as chromophoric agent, following the methodology described by Santos et al. (1998), with modifications.

- The total flavonoid content was expressed as mg of EQ (quercetin equivalent) per g of extract.

## Resumo/Abstract

The semi-arid region of Bahia has a unique biodiversity, little known, and of high pharmacological potential. The medicinal properties of the species of the Anacardiaceae family, the edible fruits are widely used by the industries for the manufacture of juices, sweets and pulps. It is worth mentioning that these food industries produce waste that can have a much more beneficial purpose to man and the environment, from the use of seeds that are discarded. These seeds are considered good sources of oil that can be used in the food industry, such as edible oil, biodiesel, and mainly can be used in the cosmetics and pharmaceutical industries. In this context, the objective of the project is to take advantage of the pharmacological properties of the species of the Anacardiaceae family. The study involved obtaining the ethanolic extract of the seeds of the species under study, by maceration with 70% ethanolic solution. This work presents the study of the total flavonoid content, carried out following the methodology described by Santos et al. (1998), with modifications, and analysis of the total phenolic content described by Rufino et al. (2007). The presence of flavonoids was evidenced, being proven through the quantification of total flavonoids. The antioxidant activity was measured using the DPPH free radical scavenging method, which indicated high antioxidant potential in some fractions of the species. The presence of phenolic substances was evidenced and infrared studies that corroborated this result through the presence of characteristic signs of these substances, which are known to have antioxidant action, in the extract and fractions of the seriguela.

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Laboratório do Centro de Estudo e Análises Cromatográficas - CEACROM

Laboratório de Pesquisas em Substâncias Bioativas - LAPESB

**Área: QPN**

# PHYTOCHEMICAL STUDY OF THE SPECIES *Anaxagorea dolichocarpa* Sprague & Sandwith

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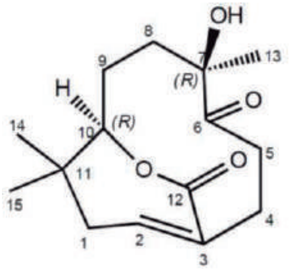
Keywords: *Annonaceae, Anaxagorea, Sesquiterpene.*

## Highlights

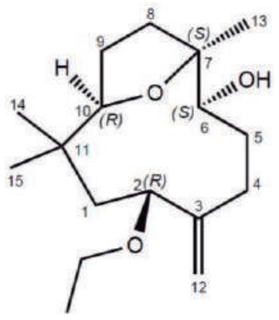
In this work, three humulene-type macrocyclic sesquiterpenes were isolated from the hexane phase of the gross ethanol extract of the species *Anaxagoreae dolichocarpa.*

## Resumo/Abstract

The species *Anaxagorea dolichocarpa*, popularly known as “paixinho” is a species of Annonacae with a wide neotropical distribution, occurring in Colombia, Venezuela, Costa Rica, the Guianas and Brazil. In the latter, it is mentioned for the North, Northeast, Center-West and Southeast regions, inhabiting humid and low-altitude forests.[1,2] Regarding the phytochemical studies of this species, the isolation of aporphine-type alkaloids and azaphenanthrenes and macrocyclic humulene-type sesquiterpenes.[3] In this work, the roots of *A. dolichocarpa* were dried and pulverized, then it was extracted by maceration with 95% EtOH, filtered and concentrated. A part of the GEE was partitioned using the solvents Hex, $CHCl_3$, EtOAc and n-BuOH. The Hexanic phase was subjected to column chromatography using hex, DCM, EtOAc and MeOH, obtaining 24 fractions, which after analysis by Thin Layer Chromatography (TLC) were pooled. Fractions 7 to 12 were subjected to Medium Pressure Liquid Chromatography (MPLC), yielding 29 fractions that were grouped by TLC. Fractions 7 to 10 were submitted to preparative High Performance Liquid Chromatography (HPLC) at C-18, obtaining the substances Ad-1, Ad-2 and Ad-3. After analysis of $^{1}H$, $^{13}C$, one and two-dimensional Nuclear Magnetic Resonance, Mass Spectrometry and Electronic Circular Dichroism the substances were identified as Dolichocarpol K (Ad-1), Dolichocarpol L (Ad-2), Dolichocarpol M (Ad-3). From the phytochemical study of the Hexanic phase of *A. dolichocarpa*, it was possible to identify and isolate three humulene-type macrocyclic sesquiterpenes. Thus, it contributes to the chemotaxonomic knowledge of the Annonaceae family and the *Anaxagorea* genus.



Ad-1



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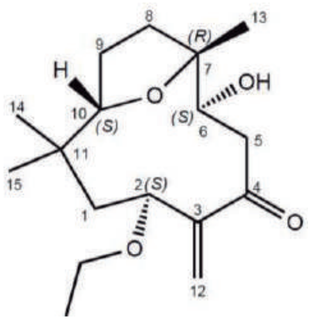

Ad-3

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## Agradecimentos/Acknowledgments

CNPq / CAPES / UFPB / LMCA / IPeFarM / INCT

**Área: __QPN_______ Nº de Inscrição: _00638___**

# Polyphenolic compositon (LC-MS) and antifungal properties (*Candidas*) of green propolis ethanolic and hydroalcoolic extracts from Caatinga biome at dry season.

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Palavras Chave: *Anacardic Acids, C. albicans*, *C. tropicalis, Flavonoids, Green propolis.*

## Highlights

- Polyphenolic composition (LC-MS) of Caatinga green propolis extracts (ethanolic and hydroalcoholic) from the Northern Ceara dry season.
- Antifungal properties investigation against *Candidas*.

## Resumo/Abstract

Propolis is a bee product produced by the collection of exudates from various parts of the plants. Many biological activities are attributed for propolis, including antimicrobial, anti-tumor, anti-inflammatory, antioxidant, hepatoprotective among others. In some regions of Brazil, propolis is produced throughout the year, and seasonal variations may influence its composition. The state of Ceara has two seasons, rainy season in the first half of the year and dry season in the second semester. It is known that the propolis chemical profile is dependent on the flora and environmental conditions of the region where it is produced, and these factors can influence not only its composition but also its biological properties. In this sense, the aims of this work were to study the chemical composition of ethanolic and hydroalcoholic extracts of Caatinga green propolis obtained at dry season (Northern Ceara) and its antifungal properties agaist *Candidas* (*C. albicans* and *C. tropicalis*). The polyphenolic composition was determined by high-resolution LC-MS chromatography system and antifungal properties against *C. albicans* (LABMIC 0105 and LABMIC 0102) and *C. tropicalis* (LABMIC 0109 and LABMIC 0111) strains. According to the results, the green propolis hydroalcoholic extract had predominantly flavonoids in its composition such as isorhamnetin, apigenin, kaempferide e 3,7-dimethylquercetin isomer II. On the other hand, in ethanolic extrac were identified three different types of anacardic acids (15:3, 15:2 and 15:1). The antifungal potential study of green propolis hydroalcoholic and ethanolic extracts revealed that the majority of the yeasts tested were inhibited by both propolis extracts, ranging from 0.078 mg/mL to a 1.25 mg/mL (MIC) for hydroalcoholic extract and 0.313 mg/mL to 1.25 mg/mL (MIC) for ethanolic extract. It should be noted that only the yeast *C. albicans* LABMIC 0105 was not inhibited by the ethanolic extract. The positive control (amphotericin B) resulted in an MIC of 4 μg/mL. The results obtained in this work allowed the determination of chemical composition and antifungal potential of Caatinga green propolis produced at dry season period. Therefore, results obtained in this work create possibilities for further studies of Caatinga green propolis therapeutic potential and add-value to a local product at Northern Ceara market.

## Agradecimentos/Acknowledgments

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**Área: QPN** **Nº de Inscrição: 00409**

# Polyphenolic profile changes of *Lycopersicon esculentum* (tomato) leaves caused by fluorescent lamps residue

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Keywords: *Lycopersicon esculentum, Tomato, Phenolic profile, Fluorescent lamp.*

## Highlights

Changes in the polyphenolic profile of *Lycopersicon esculentum* Miller (tomato) leaves from contamination with fluorescent lamp powder; analysis of flavonoids and antioxidant activity by TLC with PN-PEG and DPPH reagents.

## Abstract

The present study investigates the cultivation of *Lycopersicon esculentum* Miller (tomato) under fluorescent lamps (FL) powder contamination stress that were stated in 10 and 20 g of FL powder by 300 g of soil, during 60, 90 and 120 days, in triplicate and using control samples (specimens cultivated without FL powder contamination - Blank). The FL residues contain Hg in their compositions that lead it to the "class **I**" classifying (Dangerous)[1]. Beyond Hg, there are others Potentially Toxic Elements (PTE), such as Cu, Pb, Cd, Mn, Ni and Zn. In Brazil, it is estimated that 100 million FL per year are consumed and only 6% of them are recycled[2]. The main parameters adopted to evaluate the influence of soil contamination in plants development were the anatomical characteristics and the changes in the phenolic substances production of the cultivated specimens. The plants were collected and cleaned, then separated into roots, stems and leaves, followed by the drying process at 40°C. In general, the masses of roots, stems and leaves, from contaminated plants were heavier than those of the control. Then, the leaves (5 mg) were extracted with methanol (MeOH)/$H_2O$ 3:1 (v/v) (1 mL) and partitioned with hexane (3 × 1 mL). The dried defatted extracts were solubilized in 100 µL of MeOH and analyzed by thin layer chromatography (TLC) under polyphenolic substances monitoring conditions (flavonoids, phenolic acids, among others)[3]. The TLC chromatographic profiles suggested the selective production of at least one flavonoid from specimens grown under the conditions of FL powder contamination at the two levels studied and in the 90 and 120 days of culture. Moreover, the supposed flavonoids and others substances showed prominent potential antioxidant activity through the DPPH reaction. The determination of these substances is still under study using HPLC-MS.

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## Acknowledgments

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**Área: QPN**

# Potencial antioxidante e fotoprotetor do extrato etanólico de *Genipa americana*

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Palavras Chave: Jenipapo, Ácido hipocloroso, Radical ânion Superóxido, Estresse oxidativo.

## Highlights

Antioxidant and photoprotective potential of the ethanolic extract of *Genipa Americana*.
The extract showed ability to capture reactive species of biological importance. The SPF at the concentration of 2.0 mg mL$^{-1}$ was similar to the standard benzophenone.

## Resumo/Abstract

O sol é a fonte primária de radiação ultravioleta e a exposição a ele leva ao envelhecimento da pele e o surgimento de doenças, como o câncer de pele.[1] Além disso, o desequilíbrio entre a produção das espécies reativas de oxigênio (EROs) e sua neutralização pelas defesas antioxidantes é definido como estresse oxidativo, o aumento da concentração dessas EROs pode levar ao surgimento de diversas doenças humanas.[2] A espécie *Genipa americana* apresenta diversos compostos que atribuem propriedades antioxidantes e ação fotoprotetora. Assim, o objetivo deste trabalho foi avaliar a capacidade antioxidante do extrato etanólicos de *Genipa americana* (EEGA) através dos ensaios de CTF, FRAP, HOCl, e $O_2^{\bullet-}$ e o potencial fotoprotetor (FPS) pelo método de Mansur. O EEGA apresentou um teor de fenóis totais de 761,60 mg equivalentes de ácido gálico (EAG) g$^{-1}$ de extrato seco, FRAP foi de 141,61 µmol de equivalentes de Trolox (ET) g$^{-1}$ de extrato seco, 77,3 % de inibição do HOCl e 30,6 % de inibição do $O_2^{\bullet-}$ revelando seu potencial antioxidante em especial na captura de espécies reativas de importância biológica. A avaliação da atividade fotoprotetora revelou valores de FPS para o extrato que variaram de 1,56 a 17,20 nas concentrações de 0,25 mg mL$^{-1}$ a 2 mg mL$^{-1}$. O extrato e os padrões apresentaram FPS≥6 (Tabela 1), que é o limite mínimo estabelecido para ser considerado um protetor solar. A Figura 1 apresenta os espectros de absorção obtidos para o extrato, e os padrões benzofenona-3 e quercetina, caracterizados pela absorção espectrofotométrica na região UV-vis.

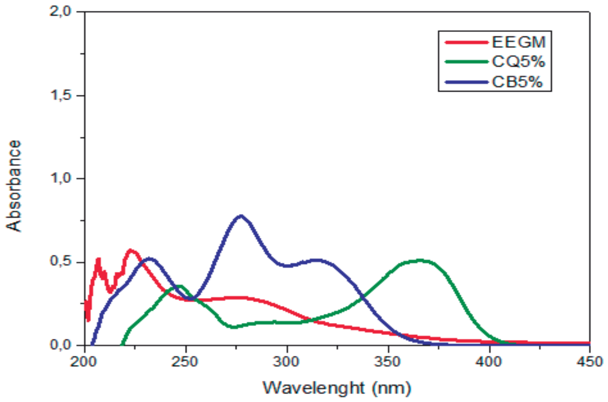

**Figura 1.** Espectro de absorção UV Vis do EEGA (0.2 mg mL$^{-1}$), creme + 5% benzophenone-3 (CB5) (0.2 mg mL$^{-1}$) and creme + 5% quercetin (CQ5) (0.2 mg mL$^{-1}$).

**Tabela 1.** Fator de proteção solar (FPS) do extrato etanólico de *Genipa americana* (EEGA) e suas formulações padrão.

| | **Concentração (mg mL$^{-1}$)** | |
|---|---|---|
| **Samples** | **0.25** | **2.0** |
| **EEGA** | 1.56 ± 0.46 | 17,20 ± 0.10 |
| **CB5** | 4.89 ± 0.62 | 16.54 ± 1.34 |
| **CQ5** | 1.44 ± 0.06 | 10.78 ± 0.96 |

EEGA = Extrato etanólico de *Genipa americana*,
CB5 = creme + 5% benzophenone-3 (m/m) e
CQ = creme + 5 % quercetin (m/m).
Resultados expressos como média + desvio padrão.

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## Agradecimentos/Acknowledgments

CAPES, CNPQ and FAPEAL

**Área: QPN**

# Preliminary insights into the influence of lead nitrate on the metabolism of the fungal strain I1CXS1C1 isolated from a mining environment: a chemometric approach.

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Keywords: *Metabolic Induction, Metallophilic Fungi, Heavy Metals, ANOVA-PCA*.

## Highlights

Metabolic induction, a potential strategy to promote metabolic variability. PbNO3 affects the metabolism of the fungus I1CXS1C1. PCA data show inhibition of metabolic expression.

## Resumo/Abstract

Fungi have been drawing the attention of the scientific community due to their high ability to adapt and grow in extreme conditions, above all, the ability to resist the stress caused by toxic metals, a condition that can result in the production of new substances. In this context, the fungal strain I1CXS1C1, isolated from copper mining tailings in the state of Pará, was submitted to metabolic induction experiments using lead nitrate (PbNO3). To evaluate the effects of the fungus/heavy metal interaction on the metabolic profile, small-scale cultures were developed, obtaining organic extracts (AcOEt), and chromatographic profile of the extracts via high performance liquid chromatography (HPLC) using diode array as detector. These experiments were developed from an experimental design $2^4$ with a central point, and the variables studied were: lead nitrate salt concentration (100, 550 and 1000 ppm), cultivation time (7, 11 and 15 days), temperature (30, 35 and 40 ºC) and type of cultivation (static and dynamic - 130 rmp) all in duplicates. Each experiment was carried out in the presence of a biotic control (culture without the addition of PbNO3). The chromatograms obtained were explored via ANOVA-PCA, using packages developed in R language. The analysis of the data set (graph of scores and loadings) allowed us to observe that lead affects the metabolic profile of the strain under study, promoting an inhibition of the variability of compounds. contribution to the observed effects. The results of the design of experiments indicate that the decrease in metabolic variability will be more evident in the condition in which the PbNO3 concentration is 550 ppm, temperature of 30 °C and static culture. An interesting finding is that even under conditions of greater stress there are no substances produced different from those present in the biotic controls, which indicates that stress causes an inhibition in the formation of the constituents already observed in the absence of lead. The results obtained stimulate the accomplishment of in-depth studies to characterize the metabolic profile of the strain using mass spectrometry.

## Acknowledgment /Agradecimentos

Special thanks to PPGQ/ Unifesspa and to Universidade Federal do Sul e Sudeste do Pará.

**Área: QPN**

# PREPARATION OF PISOTEROL DERIVATIVES AND EVALUATION OF THEIR CYTOTOXIC ACTIVITY

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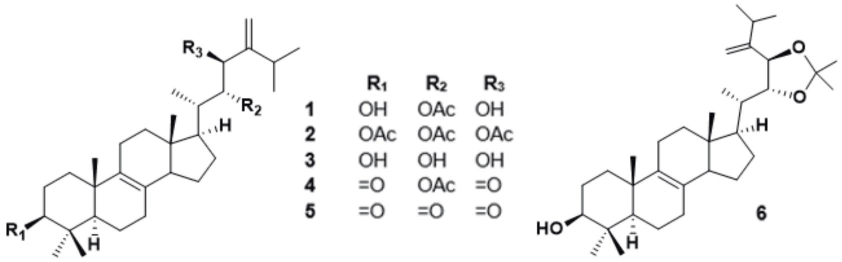
Keywords: *Pisosterol, Semisynthesis, Biological activity.*

## Highlights

Five derivatives of pisosterol were prepared through semisyntheses. Chemical reactions included acetylation, basic hydrolysis and oxidation of the natural product. Pisosterol and derivates were assayed against five tumor and one non-tumor cell lines.

## Resumo/Abstract

*Pisolithus tinctorius* is a basidiomycete that grows in association with plant species of *Eucalyptus* and *Pinus* genera. Among the secondary metabolites produced by this fungus, pisosterol (**1**) is highlighted as one of the major constituents[1]. This lanostane-type triterpene has shown the abilit to inhibit different tumor cells, especially leukemic and melanoma cell lines[2]. The semisynthesis of pisosterol derivatives was used as strategy to produce new cytotoxic compounds and to investigate the influence of structural changes on their activity. The natural product **1** was subjected to an acetylation reaction to obtain the tri-acetylated product (**2**) and a basic hydrolysis reaction of **1** led to the trihydroxylated product (**3**), which are already described in the literature[1]. The derivatives **4** and **5** were obtained through the oxidation of products **1** and **3**, respectively. The acetal derivative **6** was also prepared from **3**. All derivatives were characterized by spectroscopic techniques ($^1$H and $^{13}$C NMR). The *in vitro* cytotoxic activity of **1** and its derivatives was evaluated against the tumor cell lines HCT-116, PC-3, SNB-19, RAJI e HL-60 and the non-tumor cell line L929 in a single concentration of 10 µg/mL. The triterpene **1** and their derivatives **3**, **4** and **5** showed better results and had the IC50 evaluated against the same tumor cells. The derivates **3**, **4** and **5** showed better IC50 results in the leukemic tumor lines RAJI and HL-60, with emphasis on the derivate **4** gave an IC50 value in the range 1.31 and 3.45 µg/mL. The derivate **4** also presented higher selectivity than **1**, about six times more selective for RAJI and twice more selective for HL-60 than the non-tumor line (L929).



|  | R1 | R2 | R3 |
|---|---|---|---|
| **1** | OH | OAc | OH |
| **2** | OAc | OAc | OAc |
| **3** | OH | OH | OH |
| **4** | =O | OAc | =O |
| **5** | =O | =O | =O |

[1] GILL, M., *et al*. **Australian Journal of Chemistry**, 42, 995-1001, 1989.

[2] MONTENEGRO, R.C., *et al*. **Zeitschrift für Naturforschung**, 59, 519–522, 2004.

## Agradecimentos/Acknowledgments

**Área:** IC

# Production of nanoemulsion from commercial eugenol

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Key Words: *Nanoformulations, Nanostructured Colloidal Systems, Eugenol, Emulsifiers*

## Highlights

- Preparation of Nanostructured Colloidal Systems (NCS) from the commercial eugenol by mixing the emulsifiers polysorbate 20, polysorbate 80, sorbitan monooleate and sorbitan trioleate
- Stability analyses: pH, refractive index and transmittance measurements before and after centrifugation and temperature variation at 8ºC, 25ºC and 40ºC
- The NCS more stable (naked eyes) was HLB 13 with concentration of 20% of the emulsifiers polysorbate 80 and sorbitan monooleate, 5% of commercial eugenol

## Resumo/Abstract

Nanoemulsions are colloidal systems characterized by being dispersions obtained by two immiscible liquids, so that one of them is dispersed in the form of nanodroplets, that is, presenting drops with a diameter smaller than 1000nm. In this work nanoemulsions were prepared using commercial eugenol oil. For the production of NCS (Nanostructured Colloidal Systems), tests were carried out with the surfactants: polysorbate 20, polysorbate 80, sorbitan monooleate and sorbitan trioleate, varying the HLB (Hydrophilic Lipophilic Balance) at values of 10, 11, 13 and 15. Through the calculation, their concentrations are varied by 5%, 10%, 15% and 20%, keeping the oil concentration at 5% and adding water in proportion to complete 100%. The satisfactory result of these tests was at the concentration of 20% of the emulsifiers polysorbate 80 and sorbitan monooleate with HLB 13, which observed the Tindall effect with blue color in the system. Soon after, the samples were diluted in the proportion of 1:10 (v/v) and submitted to stability analyses. Thus, for stability analysis, several methods were applied, such as pH, refractive index and transmittance measurements before and after, centrifugation and temperature variation at 8ºC, 25ºC and 40ºC. Even after these analyses, the samples remained stable. Only with centrifugation there was a small cremation and increase in turbidity. In this way, it is possible to carry out analyzes with these samples, aiming at the elaboration of some product, such as cosmetics or herbicides.

## Agradecimentos/Acknowledgments

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**Area: QPN** **N° of Registration: 262**

# Pyrrolizidine alkaloids of two species of *Crotalaria* grown under conventional and *in vitro* conditions

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Keywords: *Crotalaria, In vitro culture, pyrrolizidine alkaloids, UPLC-QTOF-MSE*

## Highlights

Pyrrolizidine alkaloids are markers for *Crotalaria*.
*In vitro* culture was performed to obtain alkaloids and compare with conventional culture.
Alkaloids were identified by UPLC-QTOF-MSE.

## Abstract

The genus *Crotalaria* (Fabaceae) is well-known for its richness in pyrrolizidine alkaloids. They are bioactive compounds toxic to mammals. However, the use of these alkaloids to control soil nematodes has been described, as well as the use of *Crotalaria* species as green manure and soil erosion control. To increase the production of the content of these alkaloids, and *in vitro* culture was performed in comparison with the conventional one. Thus, a conventional cultivation was carried out under greenhouse conditions, whereas *in vitro* cultures were established in the tissue culture laboratory. For the *in vitro* test, the seeds were surface-sterilized and transferred individually to the test tubes (25x150 mm) containing MS-based culture medium and kept in the dark for 15 days. After that period, cultures were transferred to light environment (16 h photoperiod and 24 µmol $m^{-2}$ $s^{-1}$ irradiance), for 30 days. After 45 days, leaf and root explants (average 5 mm) derived from germinated seedlings were excised. The roots were transferred to conical flasks (250 mL) containing 50 mL of liquid culture medium under orbital shaker for 30 days. After this period, the material was subjected to methanol-based extraction. In conventional culture, *Crotalaria retusa* leaves were used for extraction with ethanol for a period of 72 h, under agitation. At the end of this period, the material was filtered and the ethanolic solution was concentrated on a rotary evaporator. Following, the ethanolic extract was submitted to acid-base extraction and treated with powdered zinc. The two extracts obtained were analyzed in UPLC-QTOF-MS. The data generated by UPLC-QTOF-MS were processed in MassLynx software version 4.1 and had all their possible molecular formulas deduced from the exact mass of each component. The chemical profiles of the extracts were established by analyzing the chromatograms together with the mass spectrum in the positive ionization mode (ESI+), based on reports of metabolites already described in the same family, genus and species (Chemotaxonomic approach). With this method, it was possible to tentatively identify 10 metabolites: 7 pyrrolizidine alkaloids, and 3 flavonoids. The results of the present study showed the efficiency of the UPLC-QTOF-MS technique for chemical identification of *Crotalaria retusa* extracts, supporting the performance of biological tests with the obtained extracts and isolated compounds. The results of the metabolites of *Crotalaria retusa* are being analyzed for comparison with the constituents from conventional cultivation.

## Acknowledgements

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**Área: QPN**

# Síntese de novos ésteres 4-metilcumarínicos com atividade antioxidante e inibidora da acetilcolinesterase

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Palavras-Chave: *Cumarinas antioxidantes, Ésteres cumarínicos, inibição AChE.*

## Highlights

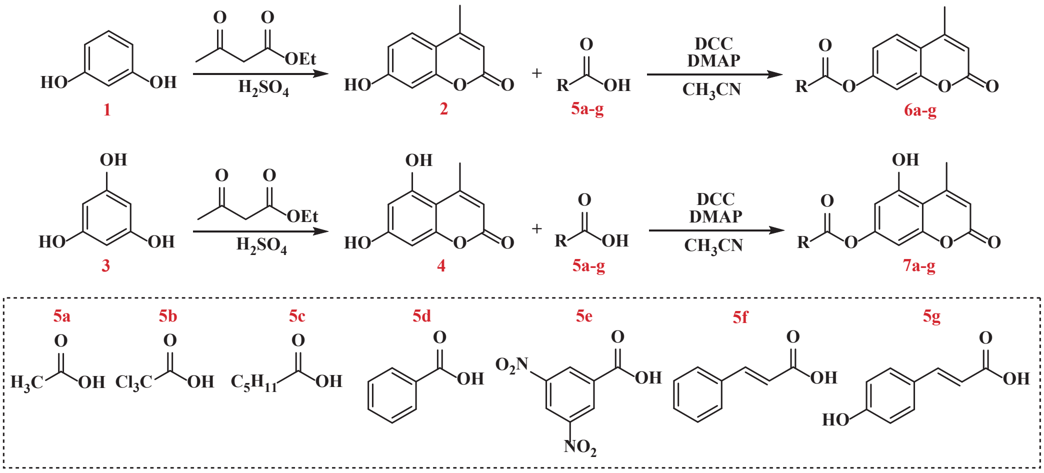
**Synthesis of novel 4-methylcoumarin esters with antioxidant and acetylcholinesterase inhibitors.** This work describes synthesis of coumarin esters employing Steglich esterification between 4-methylhydroxycoumarins and different carboxylic acids. Antioxidant and acetylcholinesterase inhibition activities of the products were also investigated.

## Resumo

Cumarinas compõem uma importante classe de produtos naturais abundantemente presente no reino vegetal, sendo encontradas em raízes, flores e frutos de diferentes espécies de plantas, além de serem também biossintetizadas por espécies de fungos e bactérias. Atividades biológicas tais como antioxidante, antibacteriana, antifúngica e anti-inflamatória, tornam as cumarinas e seus derivados de grande interesse para o desenvolvimento de meios de prevenção ou tratamento de doenças. Neste trabalho é apresentada a síntese de novos ésteres derivados de 4-metil hidroxicumarinas (**6a-g** e **7a-g**), bem como a avaliação de suas potenciais atividades biológicas (antioxidante e inibição da AChE) .

A síntese dos compostos-alvo foi realizada a partir das 4-metilhidroxicumarinas **2** e **4**, obtidas com excelente rendimento empregando-se a metodologia de Pechmann. Os novos derivados foram acessados por esterificação de Steglich, a partir de **2** e **4**, em acetonitrila, utilizando ácidos carboxílicos com diferentes cadeias carbônicas (**5a-g**). Os produtos das reações foram purificados com filtração do sistema reacional, seguido por cromatografia em coluna utilizando-se sílica gel e eluídos com diferentes sistemas de solventes. Os rendimentos obtidos variaram entre 16,4 % e 86,2%.

Os compostos finais (**6a-g** e **7a-g**) foram submetidos a avaliação da capacidade antioxidante frente ao radical DPPH. Comparado ao padrão ácido gálico, somente o composto **7a** apresentou capacidade de sequestro de radicais livres, com percentual modesto (14%). Os 14 ésteres cumarínicos obtidos também foram avaliados quanto a inibição da enzima acetilcolinesterase, e dentre eles os dados quantitativos de inibição mais promissores corresponderam aos compostos **7b** ($IC_{50}$ 383,09 $\mu g.mL^{-1}$) e **7g** ($IC_{50}$ 113,42 $\mu g.mL^{-1}$), comparados a fisiostigmina, inibidor padrão ($IC_{50}$ 163,11 $\mu g.mL^{-1}$).



## Agradecimentos

# Searching for anti-*Trypanosoma cruzi* compounds in natural products using random forest model

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Keywords: *Machine learning, American trypanosomiasis, Natural products.*

## Highlights

The present work proposes an extensive analysis of a natural products dataset through computational methods aiming to choose natural products or classes of natural products with activity against *Trypanosoma cruzi*.

## Abstract

Chagas disease (CD) is an illness induced by *Trypanosoma cruzi* protozoan[1]. In the last decades, the incidence of CD in non-endemic countries has increased in contrast with a decrease in endemic countries. An estimated $7.2 billion/year globally is spent on CD, including for treatment and disabilities[2]. In this context, Natural Products (NP) provides a large variety of molecular prototypes with unique structures which may have potential for treatment of this disease[3]. In this work, we propose the use of machine learning techniques to direct the search for new molecular prototypes, after which these compounds will be subjected to structural modification and evaluation against *T. cruzi* forms. **Dataset I** consists of 343 natural products, subdivided in active against epimastigotes, trypomastigotes and amastigotes and was built through a vast review of *in vitro* anti-trypanosomal natural products literature, covering the period between 2012-2021. Aiming to build a classification model, the continuous values of IC$_{50}$ against the protozoan amastigote forms were divided in two classes using 10 nM as the activity threshold. Then, circular molecular fingerprints of radius 2 were calculated, similar to the commonly used ECFP4[4,5]. Finally, these fingerprints were used to train a Random Forest model[6], through a validation scheme of 10 stratified iterations. The training set of each iteration was balanced using SMOTEN[7,8] and the results were externally validated using 20% of the total set, isolated part of the cross-validation process. This assessment showed terpenes as the major class, representing 54% of reported NPs with anti-trypanosomal activity followed by alkaloids with 23% and phenylpropanoids with 13%. The set for amastigote intracellular forms were the most homogeneous with 43% of active compounds and 57% of inactive compounds (**Figure 1**). The resulting model, trained in 138 molecules and externally validated in 35, showed a good sensibility identifying positive compounds with 87% of attempts, a true negative rate of 75% and 72% of accuracy.

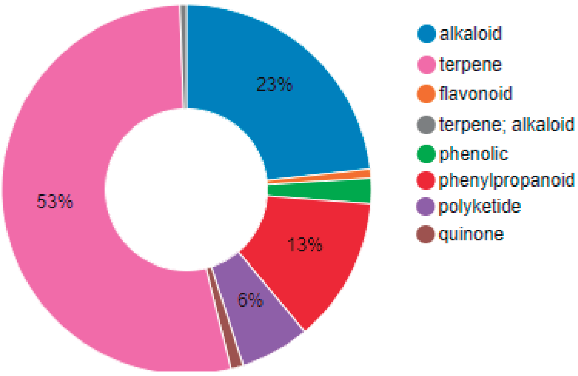

Figure 1 - Activity data for amastigote forms of *T. cruzi*

The next step of this work will be to use this model to search for potential hit compounds in a NP database such as the Naturally occurring Plant based Anti-cancerous Compound-Activity-Target DataBase (NPACT, **dataset II**). This database will direct the plant selection in the search for new molecular prototypes, which will be subjected to bioactivity-assay guided fractionation.

## Acknowledgments

UFABC, Unifesp, CAPES, FAPESP and CNPq.

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**Área:** **QPN**

# Seasonal variation of total flavonoid content and DPPH● free radical scavenging capacity in brown propolis from União dos Palmares

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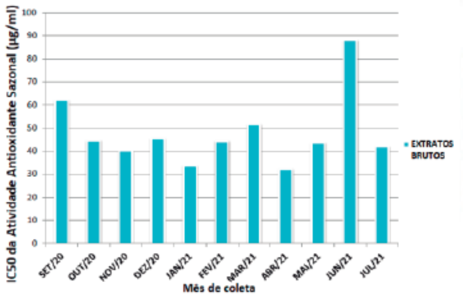
Palavras Chave: *Propolis, Antioxidant, Flavonoid, DPPH, Variation, Content.*

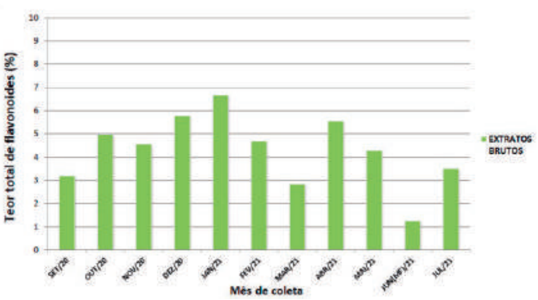
## Highlights

This study aimed to investigate the brown propolis from União dos Palmares. Total flavonoid contents ranged from 1.24% to 6.65%, and $IC_{50}$ from 62.11 µg/ml to 32.26 µg/ml, throughout 11 months.

## Resumo/Abstract

Propolis is a natural product made by bees through the collection of exudate from plants close to their hives. It has about 300 substances already identified, responsible for the antimicrobial, anti-inflammatory, antiproliferative and antioxidant effects. Since brown propolis has good antioxidant activity and high levels of flavonoids and phenolic acids, this study aimed to investigate its seasonal variation in the scavenging capacity of DPPH● radicals and total flavonoid contents throughout 11 months. BPUP samples were collected from September 2020 to July 2021. BPUP extraction was performed by macerating 15g of each sample with 50 mL of 92.8% hydroethanolic solution (m/m), in two cycles of 48h. The total flavonoid content of the BPUP extracts was determined through a calibration curve for the quercetin standard, which reacted with 100 µL of 5% (m/v) methanolic aluminum chloride solution; the same reaction occurred with the BPUP extracts at concentrations of 150 µg/ml, 175 µg/ml and 200 µg/ml. The DPPH● radical scavenging capacity of BPUP was evaluated by reacting BPUP extracts at 5 µg/ml, 10 µg/ml, 25 µg/ml, 40 µg/ml, 50 µg/ml, 75 µg/ml, and 100 µg/ml with 2 ml of 0.1 mM DPPH● stock solution. Total flavonoid contents in BPUP extracts ranged from 1.24% (June 2021) to 6.65% (January 2021). BPUP significantly exceeded the concentration of flavonoids in brown propolis from São Paulo (0.47%, FONSECA 2011). BPUP had better results than brown propolis from the states of Minas Gerais, Paraná, Santa Catarina and Rio Grande do Sul, (0.0%-2.6% (m/m), COELHO, 2017). The DPPH● radical scavenging capacity ranged from 62.11 µg/ml (September 2020) to 32.26 µg/ml (April 2021), showing a significantly lower performance of BPUP than the brown propolis of Mato Grosso do Sul, Paraná, and Minas Gerais (DEMBOGURSKI, 2018). Nevertheless, BPUP showed a good capacity to scavenge DPPH● radicals.





Pearson's correlation coefficient between the results of both assays represents a strong correlation (R2 0.7159). The used methodologies showed good sensitivity in this study, which highlights the therapeutic potential of PMUP and the need for conservation of Alagoas' genetic heritage.

## Agradecimentos/Acknowledgments

**Área: QPN** **Inscrição: 01434**

# Secondary metabolites from *Annona sylvatica*

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Palavras Chave: *Annona sylvatica, Metabolic profile, NMR, HPLC-ESI-MS/MS, Candida albicans, Citrobacter freundii.*

## Highlights

*A. sylvatica* leaf hydroalcoholic fraction was analysed by HPLC/DAD/MS and NMR. Glucose, trigonelline, ferulic acid, rutin, quercetin-3-*O*-*β*-L-arabinopyranoside and quercetin-3-*O*-*α*-L-rhamnopyranoside were identified. The fraction showed activity against *C. albicans* and *C. freundii.*

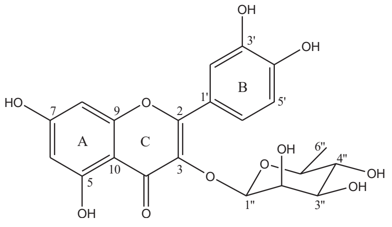
## Resumo/Abstract

Several methods have been proposed for the study of natural products and the quality control of herbal medicines. Spectrometric techniques coupled to chromatography permit a relatively quick analysis of an extract or fraction with a possible identification of known compounds. This methodology, described as dereplication, enables detection of a large number of metabolites and can be part of a metabolomic study. Here are reported the phytochemical research of the *Annona sylvatica* leaves through HPLC-DAD, HPLC-MS and $^1$H NMR dereplication-based techniques as well as the isolation of some compounds. The derepliction studies permitted identify α,β-glucose, sucrose, trigonelline, ferulic acid, rutin, alanine, proline, quercetin and quercetin-3-*O*-*α*-L-rhamnopyranoside. The phytochemical study of leaf hydroalcoholic fraction of the *A. sylvatica* led to the isolation and identification of rutin, quercetin-3-*O*-*α*-L-rhamnopyranoside, quercetin-3-*O*-*β*-L-arabinopyranoside and glucose. This is the first time that these metabolites are reported in *Annona sylvatica*. The leaf hydroalchoolic fraction and the flavonoids isolated showed activity against *Candida albicans* and *Citrobacter freundii.*

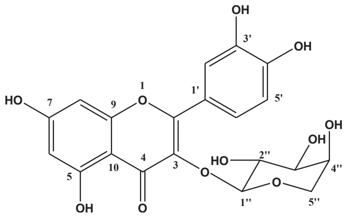
Table 1. Antimicrobial activity of the *A. sylvatica* leaf hydroalchoolic fraction and the flavonoids isolated

| *Samples* | $IC_{50}$ (µg/mL) | | |
|---|---|---|---|
| | *S. aureus* | *C. freundii* | *C. albicans* |
| Leaf hydroalcoholic fraction of the *A. sylvatica* | ND | 911.73 ± 2.65 | 209.30 ± 1.28 |
| rutin | 401.52 ± 1.59 | 725.02 ± 2.73 | 296.71 ± 0.96 |
| quercetin-3-*O*-*α*-L-rhamnopyranoside | 444.64 ± 3.42 | 748.34 ± 3.52 | 327.89 ± 1.17 |
| quercetin-3-*O*-*β*-L-arabinopyranoside | 608.25 ± 3.76 | 812.44 ± 1.75 | 292.90 ± 1.07 |
| Ampicilin[a] | 10.72 ± 1.38 | 10.74 ± 1.45 | NT |
| Nistatin[b] | NT | NT | 13.78 ± 1.74 |
| Miconazole[b] | NT | NT | 20.36 ± 1.42 |

[a]Positive control for bacteria; [b]positive control for yeast, NT: not tested, ND: Not detected



quercetin-3-*O*-*α*-L-rhamnopyranoside



quercetin-3-*O*-*β*-L-arabinopyranoside

Acknowledgments: FAPEMIG, UFMG, Center Renné Rachou, FIOCRUZ MINAS.

**Área: QPN**

# Secondary metabolites from the endophytic fungus *Hypomontagnella monticulosa* using factorial design and GNPS molecular networking

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Keywords: *Endophytic fungi, Macroalgae, Marine Natural Product, Molecular networking, Factorial design.*

## Highlights

Chemical study of the endophytic fungus *Hypomontagnella monticulosa* isolated from the red alga *Dichotomaria marginata*, using factorial design and molecular networks to maximize chemodiversity.

## Abstract

*Hypomontagnella monticulosa* is an endophytic ascomycete fungus belonging to the family Hypoxylaceae, occurring in both terrestrial and marine environments,[1] and isolated in this work from the red alga *Dichotomaria marginata*. For improved experimental conditions, the complete factorial design ($2^3$) was used, inserting three variables time, pH and temperature, during the growth of the fungus and considering the number of peaks in the chromatograms as a response variable. The endophyte was cultivated in liquid malt medium and after growth, the broth was extracted with EtOAc and evaporated, to yield the crude extract, which was analyzed by LC-MS. MS/MS data were compared using molecular networking through the GNPS platform and the results obtained were observed in Cytoscape and the Statistica program was used to better observe the influence of variables during growth. The results showed little influence of time of cultivation in the metabolism, whereas the interaction between pH and temperature (Figure 1A) was significant. Their influence was compared to the number of peaks in the LC-MS chromatograms of (Figure 1B), evidencing a significant number of peaks when growth was performed at higher pH values and temperatures. Molecular networks analysis (Figure 1C) as a function of pH, shows that certain metabolites were detected at both pH and temperature values used in the factorial design, while others were found only in a specific range of pH and temperatures, such as in the case of some terpenes and alkaloids. Such results evidenced that the metabolic production and consequently the chemodiversity of the endophytic fungus extract varied depending on external factors applied during its growth.

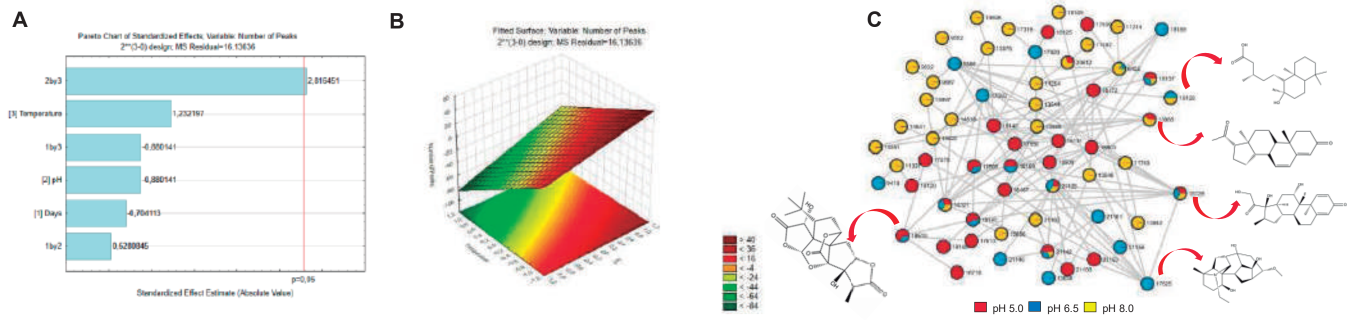

**Figure 1:** (A) pareto chart with effect between variables during factorial design, (B) interaction response between pH and temperature variables and (C) molecular networks generated in GNPS

## References

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## Acknowledgments

CAPES, FAPESP, CNPq and NuBBE for the support and funding of this work.

**Área: QPN**

# Selective cytotoxicity of *ent*-kaurene diterpenoids isolated from *Baccharis lateralis* and *Baccharis retusa* (Asteraceae)

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Palavras Chave: Baccharis retusa, Baccharis lateralis, *diterpenoids, breast cancer, cytotoxicity.*

## Highlights

Selective cytotoxicity of *ent*-kaurene diterpenoids isolated from *Baccharis lateralis* and *Baccharis retusa* (Asteraceae). *Ent*-kaurene diterpenoids derivatives were isolated and subject to bioassay screening. *Ent*-kaurenoic acid has been shown to be highly selective towards tumorigenic breast cancer cell lines.

## Resumo/Abstract

This work consists of cytotoxicity activity evaluation of natural diterpenes *ent*-kaurenoic acid (**1**) and 15β-hydroxy- (**2**), 15β-senecioyloxy- (**3**), and 15β-tiglinoyloxy- (**4**) derivatives (**Fig. 1**), isolated from Brazilian native plants *Baccharis lateralis* and *B. retusa* (Asteraceae). Dried aerial parts were grounded and exhaustively extracted with *n*-hexane. The obtained extract was subjected to column chromatography over silica gel and Sephadex LH-20 to afford compounds **1** – **4** which were chemically characterized by NMR, MS and optical methods. Using MTT colorimetric assay, it was observed that compound **1** displayed *in vitro* activity towards aggressive MDA-MB-231 adenocarcinoma cell line and reduced toxicity against MCF-10A non-tumorigenic epithelial cell whereas compounds **2** – **4** exhibited reduced toxicity and selectivity to tested cells (**Fig. 2**). Based on the chemical structures of compounds **1** – **4**, it was suggested that the presence of additional functional groups at C-15 position – a hydroxyl group in compound **2** and isoprenyl unities in compounds **3** and **4** – might be responsible for reduction in the potential/selectivity. In conclusion, *ent*-kaurenoic acid (**1**), a common diterpenoid isolated in high amounts from different plants belonging to *Baccharis* genus, has been shown to be a promising cytotoxic agent against aggressive adenocarcinoma cell line through its high selectivity when in comparison with non-tumorigenic cells. As such, compound **1** could be used as a scaffold in the development of molecular prototypes and alternative treatments for the treatment of breast cancer.

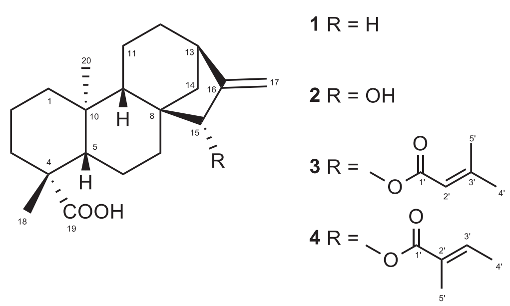

**Fig. 1.** Structures of compounds **1- 4**

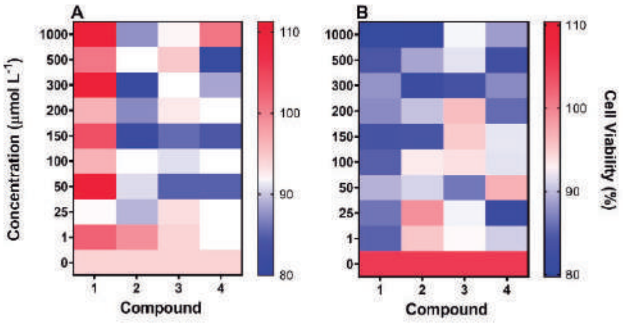

**Fig. 2.** Heat maps of tested compounds **1 - 4** against MDA-MB-231 (adenocarcinoma cell line - A) and MCF-10A (non-tumorigenic epithelial cell line – B)

## Agradecimentos/Acknowledgments

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**Área: QPN - INO**

# Selective extraction and screening of siderophores from marine sponges

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Key worlds: *Iron chelate, Marine sponges, Fluorescence probe, XAD, Kupchan.*

## Highlights

Resins and solvents were tested to obtain fractions from marine sponges with concentrated iron chelators. A selective fluorescence competition test with calcein was used for screening the fractions.

## Abstract

The marine hydrosphere is a known source of drugs. The selective search for specific bioactive compounds in marine organisms is a key challenge for researchers. Siderophores are iron chelating compounds possibly found in marine sponges and their symbionts, with remarkable activities against iron overload diseases and as antimicrobials. Here, we describe a systematic bioinorganic approach for the selective isolation of Fe(III) chelators from marine sponge extracts. Sponges were collected by diving between 3 - 8 m deep at two sampling points on the coast of São Sebastião (SP - Brazil). Each specimen was separated according to morphological characteristics, washed with seawater, drained, taxonomically identified and stored at -20 °C. Extracts were obtained by ultrasonic bath (3 min) with 7 mL of ethanol per gram of wet sponge, then concentrated by speedvac. The extract of each sponge was partitioned using the Kupchan's method [1] or XAD4 - XAD16 resins. Then, fractions and compounds were screened for iron chelation activity by a competitive equilibrium with ferric calcein (CA; $\beta \approx 10^{32}$) and subsequent fluorescence enhancement, both *in vitro* (HBS buffer) and *ex vivo* (HeLa cells). The positive controls were desferrioxamine (DFO) or salicylaldehyde isonicotinoyl hydrazone (SIH). The fractions with the highest iron chelating activity were obtained using the water-methanol mixture in Kupchan and in XAD16 resin. Figures 1 and 2 show the kinetics of fluorescence recovery of the calcein probe when exposed to one of the isolated compounds (2EAM1P2) from the sponge *Aplysina fulva*. In conclusion, it was possible to selectively obtain a compound with promising intracellular chelating activity, comparable with standard siderophores, in extracts from sponges found in the southeastern coast of Brazil.

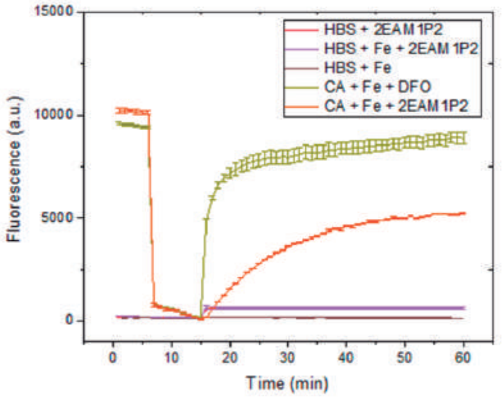

**Figure 1.** Chelating activity of *A. fulva* compound 2EAM1P2 followed by calcein (CA) fluorescence
Conditions per well: extracts in water (10 µL at 50 mg $mL^{-1}$); ferrous ammonium sulfate (10 µL at 38 µM); CA (180 µL at 2 µM); n=3.

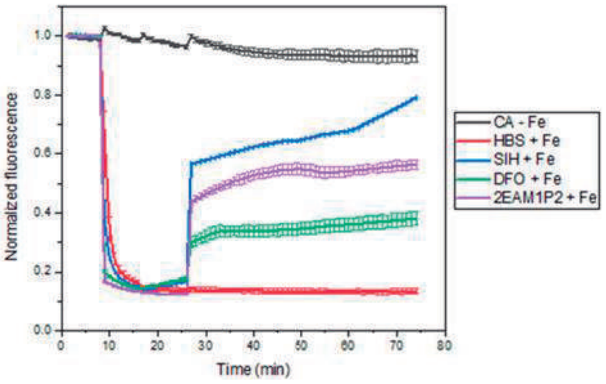

**Figure 2.** Intracellular chelating activity of *A. fulva* compound 2EAM1P2 in HeLa.
Conditions per well: CA-acetomethoxy (100 µL at 0.5 µM); iron hydroxyquinoline (2 µL at 125 µM); 2EAM1P2 (2 µL at 50 mg $mL^{-1}$); $5x10^3$ cells/well; SIH or DFO (2 µL at 1 mM); DTPA (1 µL at 25 mM); n=3

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CAPES; FAPESP; CEBIMAR; Prof. Dr. Márcio Reis Custódio (IBUSP)

**Área: _______QPN________**

# SEMISYNTHESIS OF BIOACTIVE COMPOUNDS FROM NATURAL PRODUCTS: OBTAINING STEMODIN DERIVATIVES

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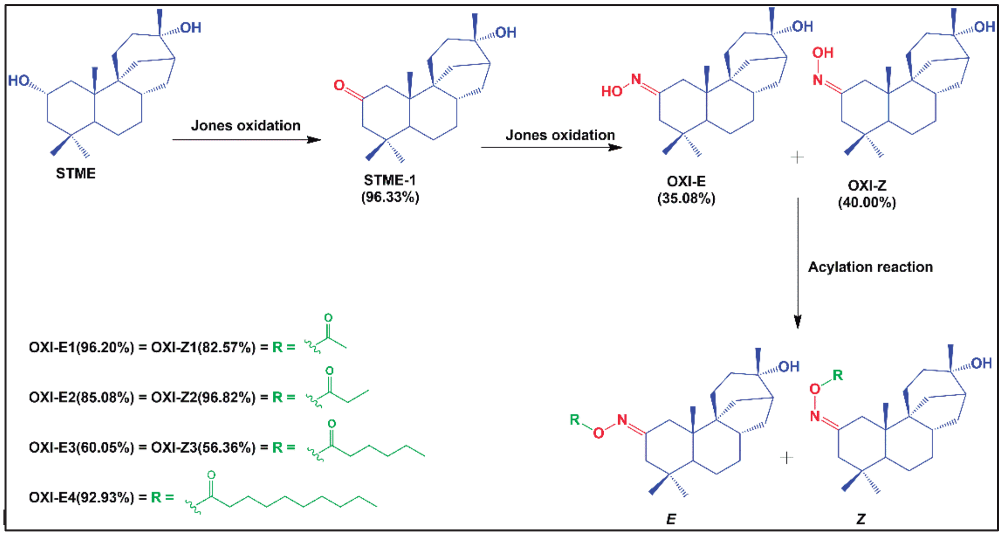
*Keywords*: *Stemodin, Semisynthesis, Bioactive derivatives.*

## Highlights

- Ten semisynthetic derivatives of diterpene stemodin were obtained.
- All derivatives were tested in the inhibition of human cancer cell lines (PC3, HCT-116, HL60, and SNB-19).
- The OXI-E3 compound has been detached as a possible anticancer agent.

## Resumo/Abstract

The structural modification of bioactive molecules, with the objective of optimizing physical-chemical and pharmacological properties has been a useful strategy in the discovery and development of new drugs[1]. Stemodin diterpene (STME, figure 1), isolated from *Stemodia maritima*, a cytotoxic and antiviral[2] natural product was submitted to structural changes from classical organic reactions, as shown in figure 1. As products of the chemical reactions, oximes and their respective acylated derivatives were obtained, which were characterized using physical (p.f.) and spectrometric data ($^{1}$H and $^{13}$C NMR, IR and Mass spectrometry). A total of ten semisynthetic derivatives were obtained, which nine of them are unpublished (STME-1, OXI-Z, OXI-Z1, OXI-Z2, OXI-Z3, OXI-E, OXI-E1, OXI-E2, OXI-E3, OXI-E4). The *in vitro* cytotoxic activity of stemodin, *E/Z* oximes and its acylated derivatives against human cancer cell lines (PC3, HCT-116, HL60 and SNB-19) were tested. The derivatives OX1-Z1, OXI-E1, OXI-E2 and OXI-E3 showed promising results with percentages of cell growth inhibition (≥75%) higher than stemodin and positive control (doxurrubicin) in at least one of the tested strains. In general, *E*-acylated and stereoisomers showed higher cytotoxic activities than *Z* stereoisomers. The OXI-Z3 compound was highlighted, which showed inhibition percentages for three significantly high strains PC3 (92.05%), SNB-19 (72.22 %) and HCT-116 (94.27 %). However, the determination of IC$_{50}$ and the evaluation of cytotoxicity in healthy cells of bioactive derivatives should be performed to validate the antitumor potential of these substances. In addition, computational theoretical studies such as molecular docking and molecular dynamics of these molecules may support the observed experimental activities.



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**Laboratório de Fitoquímica Aplicada**

**Laboratório de Biotecnologia e Síntese Orgânica**

**Área: QPN**

# Semisynthesis of bioactive compounds with anticancer and analgesic potential obtained from triterpene 3β,6β,16β-trihydroxylup-20(29)-ene isolated from *Combretum leprosum*

**Carlos José A. da S. Filho (PG),[1] José A. C. de Oliveira (PG),[1] André L. O. Capistrano (IC),[1] Francisco G. Barbosa (PQ),[1] Fátima C. E. Oliveira (PQ),[2] Cláudia do Ó Pessoa (PQ),[2] Manoel O. Moraes (PQ),[2] Jair Mafezoli (PQ).[1*]**

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Keywords: *Semisynthesis, bioactive compounds, 3β,6β,16β-trihydroxylup-20(29)-ene, Combretum leprosum, anticancer activity.*

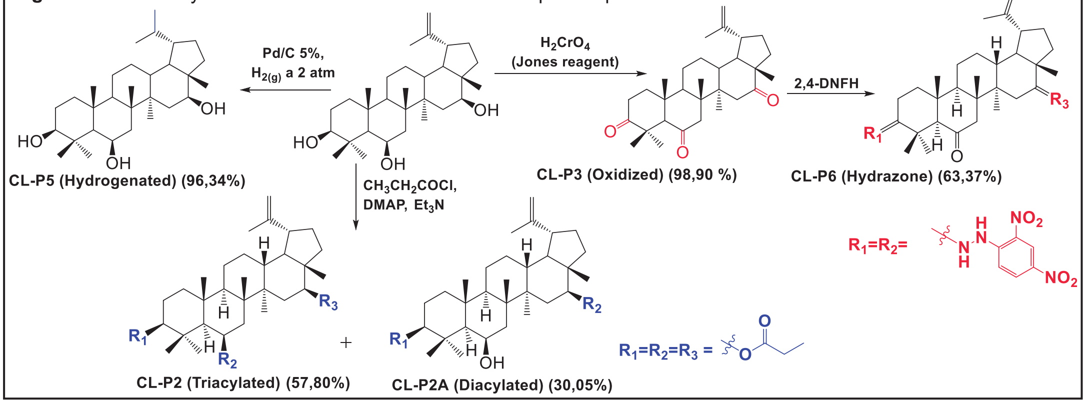
## Highlights

Six semisynthetic derivatives of the triterpene lupane were obtained (five unpublished); Evaluation of anticancer activities; The CL-P2 derivative presented strong analgesic activity.

## Resumo/Abstract

The species *Combretum leprosum* Mart. (Combretaceae) is a shrub dispersed in the Northeast region of Brazil, widely used in folk medicine as a sedative, antidiarrheal, expectorant, hemostatic and healing agent.[1] The triterpene 3β,6β,16β-trihydroxylup-20(29)-ene (**1**) is the main substance isolated from *C. leprosum*, which has several biological activities, such as anti-inflammatory, antimicrobial, leishmanicidal, healing, antinociceptive, anticancer and others.[2] Since chemical modifications of natural products are an important tool for obtaining compounds with better biological activities and fewer side effects,[3] this work describes the production of six semisynthetic derivatives (CL-P1, CL-P2, CL-P2A, CL-P3, CL-P5 and CL-P6), five of which are unpublished, as well as the evaluation of their cytotoxic and analgesic activities. All compounds were characterized by spectroscopic methods (MS, IR, one- and two-dimensional NMR). The cytotoxic activity of the derivatives, with the exception of the acylated ones, was tested against four human tumor cell lines (HL-60, HCT-116, PC-3 and SNB-19). Cell growth inhibition above 75% in all strains was evidenced for (**1**) and for the CL-P5 derivative, while the CL-P1 derivative was active only in the HCT-116 strain. The derivative CL-P2 was tested for its analgesic activity, showing excellent results at concentrations of 0.1, 1.0 and 10.0 μg/Kg in the model of zymosan-induced writhing in mice.

**Fig. 1:** Some semisynthetic derivatives obtained from triterpene lupane.



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LAFS
Laboratório de Farmacologia de Sobral

LABFITO
Laboratório de Fitoquímica Aplicada

NPDM
Núcleo de Pesquisa e Desenvolvimento de Medicamentos

LABS
Laboratório de Biotecnologia e Síntese Orgânica

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

**Nº de Inscrição: 00807.**
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# Sesqui and diterpene identified from the hexane phase of *Duguetia lanceolata* (Annonaceae) and evaluation of antileishmanial activity.

**Jackson Monteiro (PG),[1*] Luiz Felipe D. Passero (PQ),[2] João Henrique G. Lago (PQ),[3] PatriciaSartorelli (PQ)[1*]**

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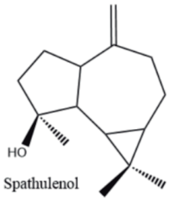
Key-words: *Duguetia lanceolata, Annonaceae, Sesquiterpene, antileismanial activity*

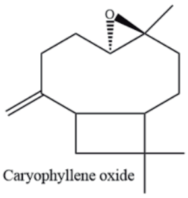
## Highlights

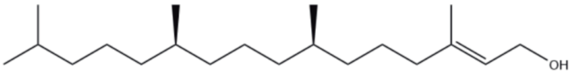
The chromatographic fractionation of the hexanic phase of the leaves of *D. lanceolata.* Bioguided fractionation by antileishmanial activity. Identification by spectroscopic analysis of $^1$H and $^{13}$C-NMR and by GC-MS.

## Resumo/Abstract

Annonaceae is composed by 135 genus, with an extensive diversity of species and a large diversity of chemical compounds. Although there are a large number of bioactive metabolites isolated, few studies have been conducted with *Duguetia lanceolata*. However, constituents of essential oils from plants of the genus *Duguetia* are mentioned in the literature.[1] The present work aimed to isolate and characterize special metabolites from *Duguetia lanceolata* apolar fraction and evaluate its potential against *L. amazonensis* promastigotes, since it is well known that treatment against leishmaniasis today uses highly toxic drugs, as well as intravenous application and high cost. The ethanolic extract was submitted to preliminary tests in order to evaluate antileishmanial activity. Thus, the hexane phase was subjected to CC on $SiO_2$ flash column with increasing polarity gradient, generating twenty fractions. The biomonitored fractionation of this extract leads us to the identification of active substances against promastigotes of *L. amazonensis*. Preliminary studies of the fraction DLH - 4 showed that this fraction has the most promising activity against *L. amazonensis* in extracellular promastigotes, with an $CI_{50}$ value of 43.02 µg $mL^{-1}$. Therefore, this fraction was submitted to CC on a sephadex column, and generated fraction DLH 4/4 with an $CI_{50}$ value of 28.1 µg $mL^{-1}$ which was submitted to CC on $SiO_2$ generated sub-fractions, DLH 4/4/1 and 4/4/2. Both of them were selected for characterization. Analyses of the NMR spectra and GC-MS data allowed the characterization of diterpene alcohol: Phytol (DLH 4/4/2) and two sesquiterpenes: Caryophyllene oxide (DLH 4/4/1) and Spathulenol (DLH 4/4/2). These compounds will be further subjected to evaluation of the cytotoxic potential against *L. (L.) amazonensis* promastigotes. The study of new metabolites obtained from non-polar fractions allows obtaining data that increase the possibilities of identifying new chemical constituents against neglected diseases.


Spathulenol


Caryophyllene oxide


Phytol

**References: 1.** Carollo et al., Biochemical Systematics and Ecology, 33, 647–649, 2005.

## Agradecimentos/Acknowledgments

FAPESP, CAPES and CNPq.

**Área: QPN** **Nº de Inscrição: ________**
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# Síntese, Caracterização e Aplicação de Novos Meios de Alinhamento para Medidas Anisotrópicas de RMN

**Cleyton Marcos de Melo Sousa (PQ)[1], Daiane de Souza Carvalho (PG),[2] Danilo Gleibson Bernardo da Silva (PG),[2] Gabriela de Paula Cavalcanti (PG),[2] Higor Diego Farias de Melo (PG),[2] José Adonias de França (PG),[2] Armando Navarro-Vásquez (PQ),[2] Fernando Hallwass (PQ).[2]***

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Palavras Chave: *RMN, gel, óxido de grafeno, cristais líquidos, estereoquímica*

## Highlights

Synthesis, Characterization and Application of New Alignment Media for Anisotropic NMR Measurements. New polymer gels, chromonic liquid crystals, and graphene-based mesophases, were prepared as weakly aligning media for the obtaining RDC and RCSA data in different solvents.

## Resumo/Abstract

O Brasil possui uma das maiores biodiversidades do mundo, sendo uma fonte de produção de substâncias com atividade biológica. Entretanto, muitas vezes, a determinação estrutural de novos produtos naturais é restringida pela quantidade de material extraído e/ou dificuldade de obtenção de cristais. Neste sentido, a espectroscopia de Ressonância Magnética Nuclear (RMN) tem se apresentado como uma ferramenta essencial para elucidação estrutural. Entretanto, algumas vezes os experimentos no meio isotrópico são insuficientes para a caracterização completa da estrutura química. Questões como a determinação da configuração relativa e/ou conformação permanecem em aberto. Para estas situações têm-se aplicado nos últimos anos as medidas de RMN em meio anisotrópico, a saber: Acoplamento Dipolar Residual (do inglês *Residual Dipolar Coupling* – RDC), Anisotropia do Deslocamento Químico Residual (do inglês *Residual Chemical Shift Anasotropy* – RCSA) e Acoplamento Quadrupolar Residual (do inglês *Residual Quadrupolar Coupling* – RQC). A questão chave para obtenção dos parâmetros anisotrópicos é a utilização de um meio eficiente para gerar um grau adequado de alinhamento molecular. Neste trabalho foi investigada a eficiência de novos sistemas, pertencentes a três classes de compostos, utilizados como meio de alinhamento: (i) Cristais líquidos cromônicos compatíveis com $D_2O$: foram estudados derivados de bisperilenimidas conjugados com aminoácidos e trifenileno (TP6EO2M). Para quantificar o grau de alinhamento gerado no sistema foi medido o desdobramento do sinal de RMN de $^2H$ do solvente Os derivados de bisperilenemida comportam-se como um meio de alinhamento fraco ($\Delta\nu_Q(D_2O)$=15 Hz a 23 ºC) e foi possível a observação simultânea das fases isotrópica e anisotrópica em um mesmo experimento.. No entanto a fase de TP6EO2M comportou-se como um meio com um grau de alinhamento médio ($\Delta\nu_Q(D_2O)$=~400 a 800 Hz) o que possibilitou a medida adequada de RCSAs. (ii) Géis indutores de alinhamento compatíveis com solventes de diversas polaridades: foram testados géis de poliacrilonitrila com compressão reversível compatíveis com DMSO. Além disso, foram preparados géis copoliméricos de *N*,*N*-dimetilacrilamida/acrilonitrila compatíveis com acetonitrila e géis de acrilonitrila/AMPS compatíveis com $D_2O$. (iii) Suspensão de óxido de grafeno (OG): grafeno comercial foi oxidado por via química. O composto obtido foi dissolvido em uma solução contendo 500 $\mu$L de $H_2O$ e 100 $\mu$L de DMSO-$d_6$, nas quantidades de 5 a 15 mg. O melhor resultado foi obtido nas soluções de 5 e 10 mg de OG, onde o desdobramento do sinal RMN de $^2H$ foi de 6Hz. Desta forma, conclui-se que todos os meios preparados podem ser utilizados como meio de alinhamento para obtenção dos parâmetros anisotrópicos de RMN.

## Agradecimentos/Acknowledgments

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**Área: QPN**

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

# Smartphone application for phenolic compounds determination in *Markhamia tomentosa* and *Bunchosia glandulifera* employing digital imaging

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Key words: *Digital image analysis, Fruit and flower analysis, Phenolic compound, PhotoMetrix®, Method validation*

## Highlights

*In situ* determination of phenolic compounds in fruit pulps and seeds in flowers using smartphone.

## Resumo/Abstract

A low-cost, simple method for *in situ* determination of total phenols in fresh and dry flower of *M. tomentosa* and in pulps and seeds of *B. glandulifera* through digital imaging was developed and validated. The determination of total phenolic was based on the chelation reaction between quercetin and ferric chloride forming a yellow complex. After optimization, an analytical curve was built to monitor the green color channel within the concentration range of 5 to 30 mg $L^{-1}$ (r = 0.9934). Quercetin recovery rate was 100.19 ± 0.09% (w/w). Limits of detection and quantification were 0.03 and 0.10 mg $L^{-1}$, respectively. The content of phenolic compounds found in the pulp (769.86 ± 0.02 mg 100 $g^{-1}$) was three times higher than in the seed of *B. glandulifera* (257.99 ± 0.51 mg 100 $g^{-1}$). Furthermore, the content of phenolic compounds found in the fresh flower (364.01 ± 0.60 mg 100 $g^{-1}$) of *M. tomentosa* was higher than that obtained in the dried flower (301.20 ± 0.54 mg 100 $g^{-1}$), indicating that drying may have degraded the bioactive compounds. Statistical tests have shown that the results obtained by developed method are similar to those obtained by Visible Ultraviolet Spectrophotometry (UV-Vis) technique. The proposed method affords simple manipulation, fast response and environmental safety.

## Agradecimentos/Acknowledgments

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# STUDY OF THE ANTIOXIDANT POTENTIAL OF BURITI (*Mauritia Flexuosa L.f.*) EXTRACTS IN VEGETABLE OILS

**Vanessa Albuquerque de Mescouto (PQ),[1*] Rayanne Danielle dos Reis Gonçalves (IC),[1] Maitê Thaís Barros Campos (IC),[1] Larissa Carla Pinheiro Gatti (IC),[1] Aiméé Souza da Silva (IC),[1] Samantha Siqueira Pantoja (PQ),[3] Luiza Helena de Oliveira Pires (FM)[2], Geraldo Narciso da Rocha Filho (PQ)[3], Luís Adriano Santos do Nascimento (PQ),[1,3]**

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Key words: *Antioxidantes naturais, Buriti, Estabilidade oxidativa.*

## Highlights

STUDY OF THE ANTIOXIDANT POTENTIAL OF BURITI (*Mauritia flexuosa L.f.*) EXTRACTS IN VEGETABLE OILS

Buriti pulp was investigated as a source of natural antioxidants. The effects of buriti pulp extracts in the Brazil nut and in the passion fruit oils were evaluated. The obtained hydroalcoholic extract had showed the highest antioxidant potential.

## Abstract

Vegetable extracts are extensively researched to act as effective and safe natural antioxidants. Thus, buriti (*Mauritia flexuosa Lf*) is an attractive alternative, as from the fruits of this palm a yellow oil is extracted, which is rich in oleic acid (C18: 1) and is very resistant to oxidation. Due to its composition in carotenoids and phenolic compounds, buriti oil is considered as a natural antioxidant.

In this work, antioxidant extracts - alcoholic and hydroalcoholic - of the buriti pulp were prepared. These extracts have been tested on Brazilian nut and passion fruit oils. The physical-chemical characterization of these oils was first carried out and the antioxidant potential of the extracts was analyzed using the DPPH methodology. The influence of extracts on the oxidative stability of vegetable oils was determined according to the AOCS Cd 12b-92 method.

In the DPPH tests, the obtained results for the alcoholic and hydroalcoholic extracts of buriti were, respectively, 55.2 (± 0.2) and 90.1 (± 0.03) in % inhibition. The greater antioxidant potential of the hydroalcoholic extract can be explained by the interaction of the constituents of the buriti pulp with the solvent of the extracting solution, which must have greater affinity with each other. In addition, ethanol allows partial solubilization of cell membranes, improving access to bound antioxidants (Bailón and Buelga 2003, *apud* Nogueira 2017).

The extracts were tested in the Brazilian nut and in the passion fruit oils in the concentrations of 1000 and 2000 ppm.

**ALCOHOLIC BURITI EXTRACT**

| OIL | 0 ppm | 1000 ppm | 2000 ppm |
|---|---|---|---|
| BRAZILIAN NUT | 6,18 h | 6,32 h | 6,59 h |
| PASSION FRUIT | 0,07 h | 0,21 h | 0,36 h |

For the tests with alcoholic extract there was no significant increase in the stability of the tested oils. Alcoholic extraction may have influenced the availability of extracted antioxidant compounds.

**HIDROALCOHOLIC BURITI EXTRACT**

| OIL | 0 ppm | 1000 ppm | 2000 ppm |
|---|---|---|---|
| BRAZILIAN NUT | 6,18h | 8,42h | 9,32h |
| PASSION FRUIT | 0,07h | 0,18h | 0,33h |

The hydroalcoholic extract, when tested in the Brazil nut oil, presented the longest induction period. It is possible to conclude, therefore, that there are antioxidant species in this extract capable of inhibiting oil degradation. The same extract when tested in passion fruit oil did not show such expressive results, which can be attributed to the degradation of this oil, since the results of peroxide and acidity index showed its high degree of oxidation. It is noteworthy that the incorporation of the antioxidant must be done at the beginning of the oxidation, because if the amount of peroxides is relatively high, its antioxidant action is canceled (Pereda *et al.*, 2005).

## Acknowledgments

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**Área: QPN**

# Synthesis from natural sources of N-3-Methylbutylacetamide, a component of the sex pheromone of the agricultural pest *Bactrocera carambolae*.

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Palavras Chave: *Síntese, Feromônio, Produtos Naturais, Pragas, B.carambolae, Agronegócio.*

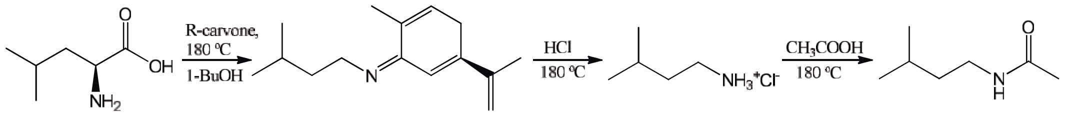
## Highlights

The work targets a main problem of fruit crops.
Good synthetic yield using inexpensive starting materials, reducing total production cost.
Pheromone was produced using plant primary and secondary metabolites.

## Resumo/Abstract

Insects from Tephritidae family, a complex containing approximately 50 genres, are commonly known as fruit flies. The most important ones are *Bactrocera, Ceratitis, Anastrepha, DirioxaeToxotrypana*, which present economic relevance to agribusiness, especially considering fresh fruit exports. We highlight in the present work the *Bactrocera* genre, a rapidly disseminating group of pest insects, exotic to Brazilian lands and native of Asian Southeast, that infests diverse fruit crops around the country, although it is most known as *carambola* (star fruit) fruit fly. The predominant control method currently used consists of large application of chemical pesticides, which are not only harmful to both men and the environment, but also inefficient against the insect larvae. Although they have already been identified, there are no pheromones commercially available for these flies. Pheromones are compounds released by living organisms and responsible for intraspecific communication, but they are produced by pest insect in the order of µg. Therefore, to use them as tools in Integrated Pest Management (IPM), these molecules must be synthesized through efficient routes to reach enough quantities to enable field tests. The present work aims to synthesize N-3-methylbutylacetamide, component of the pheromone blend of *B. carambolae*, through a low-cost synthetic pathway, using natural products as reactants, and then characterize the product by CG-MS and $^{1}H$ and $^{13}C$ NMR. The route we propose (Figure 1) substitute toxic reactants for greener and economically viable molecules, using primary (the amino acid L-leucine) and secondary (the terpenoid R-carvone) metabolites, to prepare the amide. The synthesis starts with a ketone (R-carvone) promoted decarboxylation of L-leucine under high temperature (180 ºC), which leads to an imine as the first intermediate. The next step is an acid catalysed hydrolysis of the imine to give the second intermediate, 3-methylbutyl-1-ammonium chloride. A liquid-liquid partition with an organic solvent – chloroform was chosen to avoid any side reaction in acidic medium – extracts the carvacrol formed and unreacted R-carvone, leaving only the water-soluble salt in the aqueous layer. After evaporating the solvent, the ammonium salt is obtained as a white solid. Acetic acid is then added and reacts, again under heat, to give N-3-methylbutylacetamide as the only product – no purification step is required – with a global yield of 45.66 %. Intermediates and final product structures were characterized by CG-MS and $^{1}H$ and $^{13}C$ NMR. Through this method, it was possible to synthesize a component of the pheromone blend of *B. carambolae*,important pest of fruit crops in Brazil, through an efficient and sustainable method. Future studies will be performed to optimize reaction yield and to attest the attractiveness of the product in the field.

**Figure 1.**Synthetic pathway to produce N-3-Methylbutylacetamide, component of the pheromone blend of *Bactrocera carambolae.*



[1]*Bactrocera carambolae.* Fichas de dados da EPPO sobre pragas recomendadas para regulamentação. **2022**. Disponível em: https://gd.eppo.int.
[2]Jackson, D. M.; Ashley, R. L.; Brownfield, C. B.; Morrison, D. R.; Morrison, R. W.*Synth. Commun.***2015**, 45, 23, 2691

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**Área: QPN**

# Synthesis of derivatives of 6-desoxyclitoriacetal isolated from *Clitoria fairchildiana* and the evaluation of AChE inhibition

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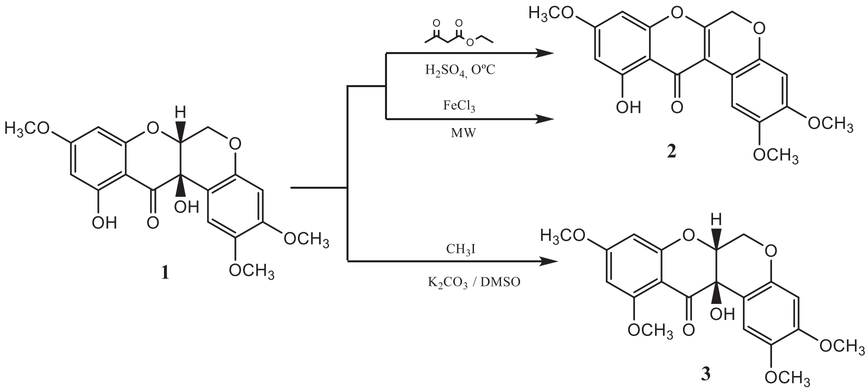
Key words: *Rotenoids, Clitoria fairchildiana, Peachmman reaction, anti-acetylcholinesterase.*

## Highlights

The 6-desoxyclitoriacetal besides other flavonoids were isolated from *C. fairchildiana* R.A. Howard root extract just in one-step. Chemical derivatives from this rotenoid were obtained and tested as AChE inhibitors.

## Resumo/Abstract

Natural rotenoids display a wide range of biological activities such as larvicidal, anti-inflammatory, antifungal, anticancer and antimicrobial activities. In Leguminosae, the rotenoids are commonly found in *Clitoria spp* especially in *C. fairchildiana* R. A. Howard (synonym *C. racemosa*). It is a tree largely distributed in Brazil and popularly known as “sombrero” and this plant is used in urban arborization. Clitioriacetal and 6-desoxyclitoriacetal **(1)** occur in good yields in roots and, they were previously isolated in seven steps chromatographic procedures. This work describes a methodology to isolate the 6-desoxyclitoriacetal **(1)** from root organic extracts of *C. fairchildiana* in just one-step procedure. In this same procedure it was obtained the prunetin and a mixture of prunetin and biochanin A. The 6-desoxyclitoriacetal was submitted to structural modification by the classical Pechmann reaction, to afford the coumaric derivative, but the acid condition promoted the elimination reaction, forming an unsaturated derivative **2**. Concomitantly the attempt to obtain the derivative with an acyl group into the ortho position with acetic acid in the presence of Lewis acids, $FeCl_3$, also provide the same product due to the acid condition. The rotenoid was also submitted to Williamson synthesis with methane iodine that permitted to obtain the methylated derivative **(3)**. All derivatives were submitted to inhibition of acetylcholinesterase employing the adapted Elman’s method to microplate. The structural modification showed interferences in the inhibitory activity of acetylcholinesterase, the compound **1** showed higher activity (202.7) compared to compound **2** (230.9) and **3** (298.3 µg.mL$^{-1}$) while the control serine, 44.6 µg.mL$^{-1}$.The isolates and the chemical derivative product were identified by spectroscopy analyses and literature data comparison.



## Agradecimentos/Acknowledgments

**Área: QPN**

# Terpenoids from the roots of *Jatropha ribifolia* (Pohl) Baill (Euphorbiaceae)

**Thalisson Amorim de Souza (PG),[1] Thiago Araújo de Medeiros Brito (PG),[1] Ana Carolina Ferreira de Albuquerque (PQ),[2] Roseana Araújo Ramos Meireles (PG),[1] Lydia Fumiko Yamaguchi (PQ),[3] Fernando Martins dos Santos Junior (PQ),[2] Lucas Silva Abreu (PQ),[1,2] Massuo Jorge Kato (PQ),[3] Josean Fechine Tavares (PQ),[1] Marcelo Sobral da Silva (PQ).[1*]**

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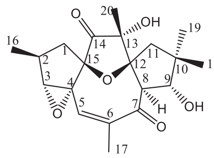
Key-words: Euphorbiaceae*; Jatropha ribifolia;* Caatinga; Terpenoids

## Highlights

The phytochemical investigation of *J. ribifolia* led to the isolation of eleven compounds. Among them four novel substances, three diterpenes and one sequiterpene-coumarin.

## Resumo/Abstract

*Jatropha ribifolia* (Pohl) Baill is a shrub ordinary known as "pinhão rasteiro", widely found in Brazilian semiarid region, ethnopharmacological studies related the antivenom activity of its latex. Concerning to the chemical composition, previous reports using classical chromatography describes the isolation of jatrophane type diterpenes, triterpenes, sesquiterpenes and coumarins. In view of the chemodiversity and pharmacological potential of *J. ribifolia*, the current work (SisGen A885D6F) carried out a new phytochemical investigation applying modern chromatographic techniques and fraction monitoring by $^1$H NMR. From the root barks hexanic extract 11 compounds were isolated. Based on uni and bidimensional NMR experiments, mass spectrometry and electronic circular dichroism was possible to identify six jatrophane type diterpenes, four sesquiterpenes and one sesquiterpene-coumarin. Among them, three diterpenes (compounds **1, 3** e **5**) and one sesquiterpene-coumarin (**11**) are not described in literature. Moreover, two diterpenes (**2,4,6**) e three other sesquiterpenes (**7,8,9**) were reported for the first time in this species.



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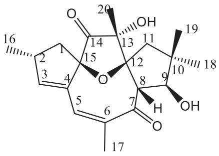

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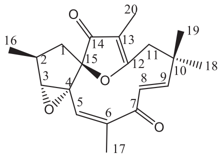

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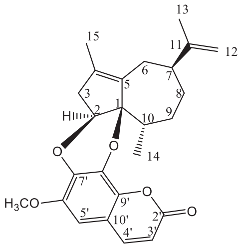

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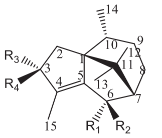
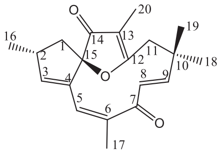


7 - $R_1$ = OH; $R_2$= H; $R_3$, $R_4$= H
8 - $R_1$, $R_2$ = O; $R_3$, $R_4$= H
9 - $R_1$ = OH; $R_2$= H; $R_3$, $R_4$= O



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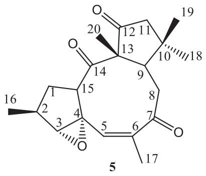

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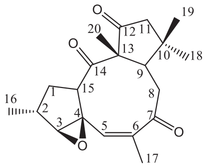

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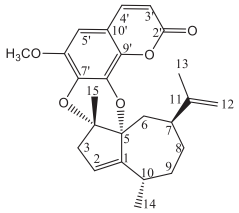

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## Agradecimentos/Acknowledgments

The authors acknowledge the Brazilian funding agencies; CAPES and FINEP for financial support.

# Terpenos com ação citotóxica isolados das folhas de *Schinus terebinthifolius* Raddi (Anacardiaceae)

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Palavras Chave:*Schinus terebinthifolius, sesquiterpenos, triterpenos, atividade citotóxica*

## Highlights

**Cytotoxic terpenes isolated from *Schinus terebinthifolius* Raddi (Anacardiaceae) leaves.** In present work, one new sesquiterpene – copaan-3α-ol – and three known terpenoids were isolated from leaves of *S. terebinthifolius*.

## Resumo

Como parte do nosso trabalho sistemático envolvendo a busca de metabolitos secundários de plantas com ação citotóxica[1], no presente trabalho, o extrato hexânico das folhas de *Schinus terebinthifolius* mostrou potencial. A análise do mesmo via RMN indicou a ocorrência reduzida de material graxo sugerindo também a presença de terpenos. O fracionamento cromatográfico biomonitorado usando gel de sílica e Sephadex LH-20 permitiu o isolamento do ácido (*Z*)-masticadienóico (**1**), schinol (**2**) e germacren-4α-ol (**3**) das frações ativas, os quais foram identificados via analise dos espectros de RMN e EM. Além desses compostos, outra fração ativa forneceu uma substância pura cujo espectro de massas de alta resolução, obtido via ESI, mostrou o íon $[M + Na]^+$ em *m/z* 245.1881, compatível com a formula molecular $C_{15}H_{26}O$, com três insaturações. O espectro de RMN de $^1H$ mostrou, dentre outros, um dupleto em δ 0,85 (*J* = 6,9 Hz, H-12 e H-13), dois simpletos em δ 1,25 (H-14) e 1,27 (H-15) além de multipletos em δ 1,48 (H-4), 1,97 (H-5) e 1,59 (H-10). Os espectros de RMN de $^{13}C$ e DEPT mostraram 15 sinais sendo quatro metílicos, quatro metilênicos, cinco metinicos e dois quaternários, sendo um deles carbinólico (δ 75,1). A ausência de sinais referentes a carbonos do tipo $sp^2$ indicou ser do tipo copaano o esqueleto sesquiterpênico, especialmente pelo sinal atribuído a C-4, observado em δ 61,2.[2] As correlações observadas nos mapas de contorno HSQC e HMBC confirmaram a estrutura sendo o grupo hidroxílico posicionado em C-3. Finalmente, a estereoquímica relativa de C-3, C-4, C-5, C-6, C-9 e C-10 foram definidas por meio das correlações espaciais observadas no espectro NOESY. Desta forma, a estrutura do composto isolado foi definida como copaan-3α-ol (**4** – figura 1), do qual não há registro na literatura. A atividade citotóxica dos compostos **1 – 4** foi avaliada frente as diversas linhagens tumorais (B16F10-Nex2, SKBR-3, HeLa, U87 e Skmel-28) além de uma linhagem não tumorigenica (melan-A), via ensaio colorimétrico baseado em MTT,[1] como visto na Tabela 1.

**Figura 1.** Estrutura molecular do composto **4**.

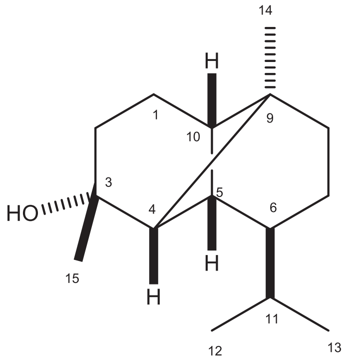

**Tabela 1**. Valores de $CI_{50}$ dos compostos **1 – 4**

| Linhagem Celular* | $CI_{50}$ / μg.mL$^{-1}$ | | | |
|---|---|---|---|---|
| | 1 | 2 | 3 | 4 |
| B16F10-Nex2 | 87.4 ± 6.6 | 43.3 ± 7.2 | 92.1 ± 5.6 | 24.0 ± 0.5 |
| SKBR-3 | 76.5 ± 9.1 | 52.3 ± 6.5 | 65.3 ± 2.5 | 25.2 ± 0.6 |
| HeLa | 99.5 ± 8.1 | 44.6 ± 1.3 | 55.4 ± 0.8 | 26.1 ± 1.1 |
| U87 | 93.5 ± 7.0 | 34.6 ± 6.6 | 67.4 ± 3.1 | 28.0 ± 1.1 |
| Skmel-28 | 77.2 ± 7.9 | 45.9 ± 9.1 | 81.3 ± 5.5 | 21.0 ± 0.3 |
| melan-A | 92.4 ± 5.6 | 88.3 ± 4.4 | 92.1 ± 2.9 | 47.7 ± 0.6 |

*B16F10 Nex2: melanoma murino; SKBR-3: câncer de mama humano; HeLa: câncer cervical humano; U87: gliobastoma humano; Skmel-28: melanoma humano; melan-A: melanócito normal humano

Como observado na Tabela 1, o composto **4** se mostrou promissor para todas as linhagens tumorigenicas mostrando seletividade se comparado a linhagem melan-A. Por outro lado, os compostos **1 – 3** apesar de serem isolados de frações ativas, mostraram reduzido potencial.

**Referências:** Sousa et al., *Bioorg. Med. Chem. Lett.* **2020**, 127349. Daniewsky et al., *Phytochemistry* **1996**, 43, 811.

## Agradecimentos

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**Área: QPN**

# The role of Countercurrent Chromatography to separate major volatile compounds from essential oil of *Manekia obtusa* L.

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Palavras Chave: *Piperaceae, HSCCC, phenylpropanoid, essential oils, green chemistry*

## Highlights

Safrole isolation from Piperaceae species

HSCCC separation of essential oils

Safrole separation of complex essential oil mixture by CCC

## Resumo/Abstract

Essential oils (EOs) are hydrophobic liquids, containing a number of volatile aromatic compounds. Safrole is considered one of the most used volatile compounds obtained from plants due to its commercial demand by the world industry. This fact has stimulated research on species with high yield safrole essential oils as well as the efficient separation processes. The preparative separation of pure volatile compounds from complex volatile mixtures is always a challenge due to their structural similarity, strongly hydrophobic properties and poor stability. The High-Speed Counter Current Chromatography (HSCCC), a support free liquid–liquid partition chromatographic technique, is considered a green chemistry chromatographic method that permits a fast-running time separation saving solvent process, especially with a very limited thermal and chemical stability. In this work, we present the successful separation process strategy of safrole from *Manekia obtusa* species in preparative scale using HSCCC. In this EO, safrole represents roughly 8-10 % among other 80 detected compounds. Four different solvent systems composed by *n*-hexane-methanol (1:1,v/v) and *n*-hexane-acetonitrile (1:1, v/v), petroleum ether/acetonitrile/acetone (4:3:1,v/v/v), *n*-hexane/acetonitrile/ethyl acetate (1:1:0.4,v/v/v) and *n*-hexane/acetonitrile/methanol (1:1:0.5, v/v/v) were tested. After the optimization, the solvent system composed by hexane/acetonitrile (1:1) was chosen. The plant leaves (300.0g) were submitted to hydrodistillation for two hours in a modified Clevenger apparatus. The leaf essential oil was analyzed by GC-FID and GC-MS. In the first run, (2.0g) of EO was subjected to CCC apparatus for the isolation of its major components. In first elution mode, the acetonitrile was used as stationary phase. Through this first HSCCC separation, it was obtained the fractions 19-20 (28mg of safrole 88.5% purity), fractions 20-22 (50mg of safrole 97.2% purity), and fractions 23-25 (52 mg of safrole in 94.5 % of purity), in 2h of running separation process. When *n*-hexane was used as stationary phase in the 2nd run, it was obtained the fractions 81-86 (45mg of safrole 96.2% purity), fractions 87-97 (52mg of safrole 92.7% purity), and fractions 101-111 (230 mg of $\delta$-3-carene in 65.3 % of purity), in 2h of running separation process. The obtained fractions were analyzed by thin-layer chromatography and by GC-FID and GC-MS. The isolated metabolites were analyzed by NMR. The HSCCC was useful for the isolation of volatile compounds from plant essential oils with high percentage of sample mass recovery, fast separation process (less than 30min) and with great economy of solvent volumes. Countercurrent chromatography technique showed to be a good choice for purification of safrole from complex essential oil mixtures.

## Agradecimentos/Acknowledgments

Agradecimento: Agradecemos à Farmanguinhos/FIOCRUZ.

**Área: QPN**

# Time dependency of chemodiversity of extracts from *Annulohypoxylon stigiun* endophytic fungi isolated from red alga *Asparagopsis taxiformis*

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Key Words: *Marine fungi, Time-scale metabolomics, GNPS, Untargeted metabolomics, Multivariate analysis.*

## Highlights

Metabolic profile of *A. stygium* depends on the cultivation time using PDB as culture medium. GNPS molecular networking and multivariate analysis tools provided identification of sterols in *A. stygium* extracts.

## Abstract

Metabolism of organisms is closely related to their developmental state, as their biochemical processes change over time responding to environmental fluctuations. These processes involve enzyme-catalyzed reactions, which are time dependent, as the biosynthetic enzymes have to be produced or modified, which leads to a dynamic metabolome expression variation according to the incubation time after inoculation[1]. So far, few studies have compared fungi metabolic profiles through time. In this work, we analyzed the variation of chemodiversity according to the time of cultivation of the fungus *Annulohypoxylon stygium*, an endophyte isolated from the red alga *Asparagopsis taxiformis*.

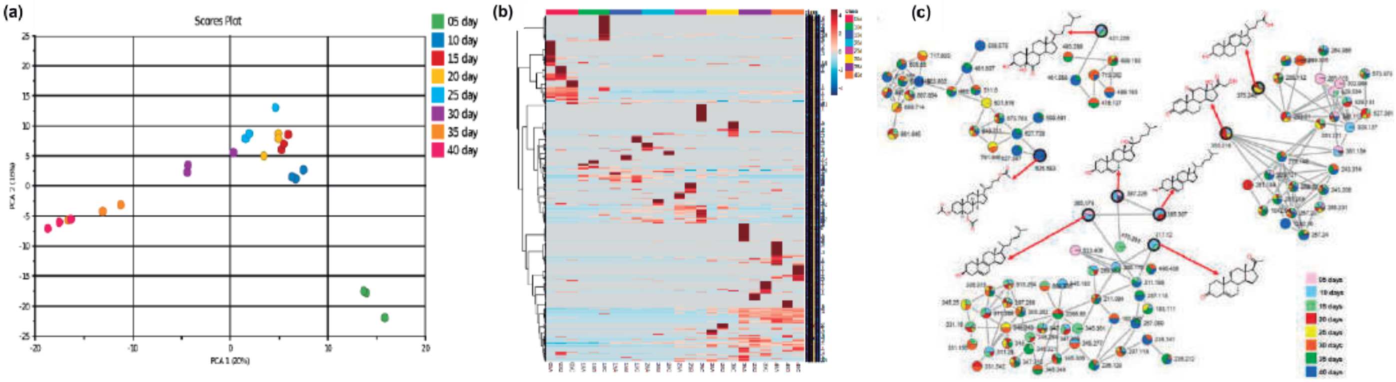

**Figure 1.** a) Score plot - Principal component analysis (PCA) obtained from LC-MS profiles corresponding to the extracts of fungi *A. stygium* from day 05 to day 40; b) heatmaps of the features with regards to the days of extraction c) Steroids molecular network generated by GNPS.

The fungus was cultivated in 24 Erlenmeyer flasks containing PDB (potato, dextrose broth) medium prepared with ultrapure water and incubated at 25 °C, in static mode. After incubation, the medium was separated from the mycelium by filtration and extracted with EtOAc, and this process was applied to 3 Erlenmeyer flasks every 5 days for 40 consecutive days. The samples were analyzed by LC-MS and MS/MS data were subjected to GNPS molecular networking (http://gnps.ucsd.edu), processed using the MZmine 2.53, and submitted to PCA using SIMCA 17, to generate heatmaps of the features related to each extraction date using MetaboAnalyst 5.0. PCA scores and heatmaps (Figure 1.a and 1.b) indicated a significant variation in the extracts chemical profile from day 05 to 40, highlighting the putative sequential compounds detection and disappearance in the extract over the cultivation period. The analyzes carried out through GNPS evidenced a series of clusters referring to the class of steroids, detected in different days of cultivation. The investigation of hits showed an increase in the number of oxidations in the chemical structures up to 25 days of culture, and a decrease after 25 days, possibly triggered by the consumption of these secondary metabolites by the fungus through time.

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## Acknowledgments

CAPES, CNPq (INCT/BioNat), FINEP and FAPESP (Cepid/CibFar and INCT/BioNat) for research financial support and fellowships.

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

# Triterpene profile of latex and stem of *Euphorbia tirucalli* by GC-MS

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Palavras Chave: *latex, triterpenes, euphol, GC-MS*

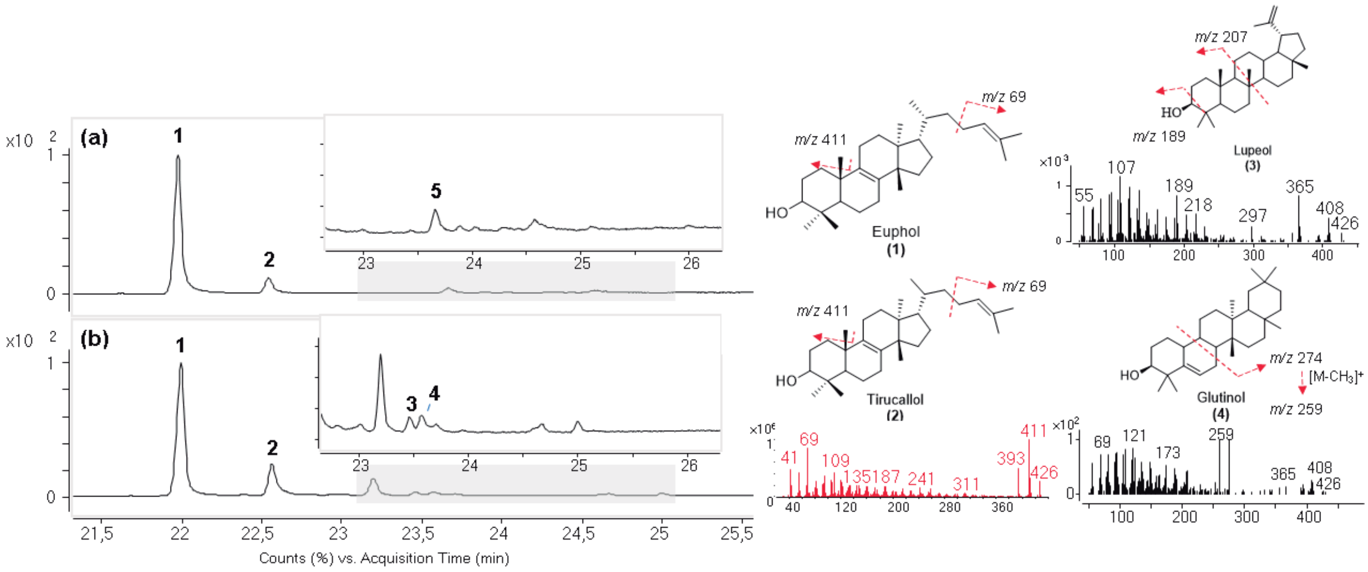
## Highlights

Triterpene compounds were identified in *Euphorbia tirucalli* latex and stem. GC-MS chromatography on DB-5 column separated compounds with the same molecular formula, which are abundant in the plant.

## Resumo/Abstract

About 80% of triterpenes constitute the latex of *Euphorbia tirucalli*.[1,2]. The presence of these compounds is also significant in the stem. This plant is used by folk medicine for different diseases, including cancer[3]. Therefore, these compounds may be associated with these effects. The hexane extracts of these two parts of the plant were obtained to compare their chemical profiles. They were prepared from liquid/liquid extraction of aqueous latex and stem ethanolic extract. The hexanic phases were rotaevaporated and solutions prepared (3 mg/mL) to be injected into the GC-MS. Lupeol and glutinol standards were injected under the same conditions. Several peaks were observed on the chromatograms and the major compounds were euphol and tirucallol in both parts. Euphol, the main triterpene of the plant, was the most abundant in the latex (81.4%).

Fig. 1: GC-MS chromatograms of the hexane fractions of *Euphorbia tirucalli* latex (a) and stem (b).



The triterpenes lupeol and glutinol were present in the stem and absent in the latex, indicating that, regardless of being collected from the same location, there is variability in the chemical composition of each part of the plant. A biosynthetic pathway may be preferred in each part of the plant. Thus, latex and stem may contribute to different cytotoxic effects.

## References

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## Agradecimentos/Acknowledgments

CNPq, CAPES, FAPES and Chromatography Laboratory/LabPetro.

**Área: QPN**
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**Nº de Inscrição:00616**
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# UMBELLIFERONE ESTERS WITH ANTIBACTERIAL ACTIVITY PRODUCED BY BIOCATALYTIC PATHWAYS

**Vitor Soares[1], Larissa Assis de Paula[1], Rafael Viana Calazans Maia[1], Maíra Barcellos Marini[1], Marcelo Mignoni[2], Camila Adão Malafaia[1] and Ivana Correa Ramos Leal[1]**
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Keywords:*Antibacterial activity*, *Biocatalysis, Endophytic fungi, Esterification, Lipases, Novozyme 435, Umbelliferone*

## Highlights

Esterification reaction of coumarin biocatalyzed by immobilized endophytic fungi and commercial lipases
Recycle reactions for process optimization
Esters of umbelliferone with antimicrobial activity against hospital bacteria

## Resumo/Abstract

Coumarins and their derivatives comprise an important class of secondary metabolites produced by a large range of plant sources. Literature reports different types of biological activities for these compounds and among them are the antimicrobial, anticoagulant, estrogenic, anti-inflammatory, anti-HIV, antioxidant, and other. As promising therapeutic agents, new and sustainable methodologies for those synthesis may gain even more prominence with a green and lower cost approach [1,2]. So, the derivatization of a coumarin skeleton can improve the activity as already observed in literature for other phenolic compound, such as flavonoids. The present report describes the enzymatic acylation of umbelliferone with different vinyl esters as acyl donors biocatalyzed by the commercial lipase Novozym® 435 and by an endophytic fungi immobilized in zeolite. It also aims the investigation for their antibacterial activity against ATCC and clinical strains isolated from hospital infection sites. The umbelliferone esters (**1—5**) were synthesized through the acylation reaction of 7-hydroxy-2H-chromen-2-one with different long chain vinyl esters catalyzed by the lipase Novozym 435. The reaction conditions were: 10 % Novozym 435; tetrahydrofuran:acetone (3(solvent):1(co-solvent)) for the reactions with acetate, propionate and butyrate vinyl esters, and (9(solvent):1(co-solvent)) for decanoate and laurate vinyl esters; acyl donor/umbelliferone molar ratio of 10:1 and 60 °C. Aliquots (20 µL) were withdrawn from 24 to 168 h and analyzed by GC-MS. All tumbelliferone esters were characterized by Nuclear Magnetic Resonance (NMR) and high resolution mass spectrometry (HRMS). The recycle of the reactions will be evaluated for both biocatalysts. The esters with short chain achieved 50—90 % conversion while with the long chain vinyl esters achieved 10 – 15 % conversion. The antibacterial activity of the products were tested in order to determine the minimum inhibitory concentration (MIC) against ATCC strains (*S. aureus* ATCC 33591 and ATCC 29213; *S. epidermidis* ATCC 12228; *S. hominis* ATCC 27844; *S. simulans* ATCC 27851; *S. saprophyticus* ATCC 15305; *Pseudomonas aeruginosa* ATCC 27853; *Klebsiella pneumoniae* ATCC 700603; *E. coli* ATCC 25922) and clinical strains (CS) (*S. aureus* CS 601, CS 664, CS527, CS 551, CS 517 CS 1025; *Acinetobacter spp.* CS OXA-51; *A. baumannii* CS 55a). The results displayed by 7-laurate and 7-decanoate-umbelliferone esters showed the highest antibacterial potential, with 1 mM inhibitory activity for ATCC 33591, a methicillin and oxacillin resistant *Staphylococcus aureus* strain. They were also able to inhibit gram-negative bacterial strains, such as *P. aeruginosa* (MIC: 0.5 mM) and *K. pneumoniae* (MIC:1 mM). In addition, 7-laurate- and 7-decanoate-umbelliferone esters were able to inhibit all clinical strains (MIC: 1mM; except 7-laurate-umbelliferone in which MIC: 0.5 mM against 55a). The reactions with the endophytic fungi immobilized in zeolite (rich in lipases) will be also conducted and the conversion rates established. This is the first study performing the biocatalysis of umbelliferone followed by the purification of the products and the antibacterial evaluation.

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## Agradecimentos/Acknowledgments

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**Área: QPN** **Nº de Inscrição: 00310**

# Using GNPS tools to accelerate the metabolites identification of complex marine bacterial extracts

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*Palavras Chave: Global Natural Products Social Molecular Networking (GNPS), Molecular Networking, Natural Products, Marine Bacteria, Metabolomics.*

## Highlights

GNPS tools annotated diverse marine bacterial metabolites, supporting a faster and more reliable dereplication process. The annotations included β-carbolines, lipopeptides, bile acids and carbazoles.

## Resumo/Abstract

Protection and rational use of biodiversity and natural resources depend on knowing biological richness' composition and distribution. Seeking this purpose and aiming for a better understanding of the chemical content of different extracts, new tools for the elucidation of natural products have been developed. The use of computational functionalities has reduced the cost and the time spent on manual analyzes, making dereplication a faster process, avoiding the re-isolation of known compounds and focusing the research according to the objective. Therefore, this study aimed to use new developed computational tools available at the Global Natural Products Social Molecular Networking (GNPS) platform to widely explore the secondary metabolites produced by marine bacteria under liquid cultures. The extracts were prepared by the inoculation of pure cultures in liquid media containing soluble starch, yeast extract and peptone. After 7 days under 28º C and agitation, the fermented broth was added to ethyl acetate for liquid-liquid partition, and dried under reduced pressure. Then, samples were solubilized in methanol (6 mg.mL-$^{1}$), and analyzed by UFLC-(ESI)-MS/MS (micrOTOF-QII), using an Ascentis® Express C18 column (15 cm x 4,6 mm, 2,7 µm particle size, Supelco™). The mobile phase was composed of (A) water and (B) acetonitrile, both containing 0.1% formic acid, at a flow rate of 0.7 mL.min$^{-1}$ and an exploratory gradient elution (5 to 100 % organic phase at 30 min). Data was acquired at positive ionization mode (from 50 to 1500 m/z). After that, data files were converted to mzXML format and uploaded to GNPS for further analyses. The Molecular Network is a computational approach that groups spectra from related molecules by similar fragmentation patterns. Considering that, consensus spectra were created with a parent mass tolerance of 0.06 Da and a MS/MS fragment ion tolerance of 0.02 Da. Edges were filtered to have a cosine score above 0.65 and more than 4 matched peaks. The spectra in the network were also searched against GNPS' spectral libraries. All matches kept between network spectra and library spectra were required to have a score above 0.7 and at least 5 matched peaks. The ideal parameters applied in data processing were optimized according to the equipments used for analyzes, the quantity of samples and their complexity. The resulting Molecular Network presented 20551 nodes and, among them, 237 consensus spectra were considered similar to the ones available in the libraries. The spectral library search annotated compounds from classes as diverse as β-carbolines, lipopeptides, bile acids and carbazol derivatives. Besides the Molecular Networking, another function used on the GNPS platform was the Insilico Peptidic Natural Products Dereplicator, which allows the annotation of known peptidic natural products from structural libraries using in silico fragmentation tree. With this tool, it was possible to successfully annotate another 10 peptides, most of them different from the hits indicated by the Classical Molecular Networking. Based on the annotations given by these computational functionalities, the dereplication process became more objective and reliable, once the platform visually organizes data in a manner that allows the correlation of similar compounds and gives access to high quality spectra and structure libraries. In general, the GNPS platform facilitates the investigation and further indication of possible structures for unknown substances.

## Agradecimentos/Acknowledgments

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**Área: QPN**

# Virtual Screening for selection of alkaloids with inhibitory activity against thioredoxin glutathione reductase from Schistosoma mansoni (SmTGR) - Part II

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Keywords: *Schistosoma mansoni, Schistosomiasis, SmTGR, QSAR, Alkaloids, Molecular Docking*.

## Highlights

In silico studies for the selection of alkaloids with inhibitory activity against SmTGR; Schistosomiasis is a neglected tropical disease caused by the parasite S. mansoni; Praziquantel (PZQ) is the only approved drug used to treat schistosomiasis highlighting the importance of the discovery of new drug candidates for the treatment of schistosomiasis; SmTGR is a validated biological target for the discovery of new drugs for the treatment of schistosomiasis; Alkaloids may be a chemical group of natural products promising to inhibit SmTGR.

## Resumo/Abstract

O *Schistosoma* mansoni é o parasito causador da esquistossomose hepática e intestinal registrada em 54 países, principalmente na África e Leste do Mediterrâneo, atinge as regiões do Delta do Nilo e países como Egito e Sudão. Atinge também a América do Sul, destacando a região do Caribe, Venezuela e Brasil. O Brasil apresenta o maior número de casos de *S. mansoni* entre os países da América Latina e o Caribe com cerca de 6 milhões de indivíduos infectados e 25 milhões em áreas de risco de infecção. O Prazinquantel (PZQ), fármaco utilizado para o tratamento desta doença, apresenta efeitos colaterais leves e transitórios e boas taxas de cura, mas é a ineficaz contra as formas imaturas dos vermes. Assim, o desenvolvimento de novos fármacos esquistossomicidas torna-se necessário. Nesse sentido, a SmTGR, responsável pelo metabolismo redox do parasito, foi validada como um alvo promissor para o desenvolvimento de fármacos. A partir dessa perspectiva, técnicas de triagem virtual baseadas em ligantes (LBVS) e baseadas em estrutura (SBVS) foram combinadas para seleção de alcaloides potencialmente ativos em inibir as atividades da SmTGR em um conjunto de dados com 844 alcaloides extraído de plantas medicinais. Um conjunto de compostos com atividade conhecida contra a SmTGR foi selecionado do banco de dados PubChem Bioassay (AID:485364) para criar quatros modelos Q/SAR de classificação com precisão superior a 89,5%. Os modelos RF e AdaboostM1 foram selecionados para a LBVS após validação (ROC = 0,96; 0,97 e kappa = 0,81; 0,84, respectivamente) e a análise de consenso selecionou 24 alcaloides potencialmente ativos com probabilidade de atividade variando de 56,4 a 89,2%. Posteriormente, foi realizado SBVS por meio de docking molecular na enzima (6FP4, código PDB). Finalmente, 14 alcaloides foram selecionados como promissores em inibir a SmTGR a partir da VS combinada com probabilidade de atividade variando de 63,4 a 79,2%. Os alcaloides Bucarbolines A, Epi-des-7-O-methylroraimine, Des-7-O-methylroraimine, Epiisopilosine, Episiopiloturine, Lindoldhamine e Variabiline foram os 7 melhores classificados. Dentre eles, a Epiisopilosine e a Epiisopiloturine, que podem ser isoladas das folhas de *Pilocarpus microphyllus* (jaborandi), apresentam atividade em estudos *in vitro* e *in vivo* contra *S. mansoni*. Assim, esta pesquisa aplicou com sucesso diferentes abordagens computacionais para acelerar a identificação de alcaloides com atividade esquistossomicida, que quando devidamente validados experimentalmente, poderão contribuir para o avanço na descoberta de candidatos a fármacos contra a esquistossomose.

## Agradecimentos/Acknowledgments

The authors thank Programa de Pós-Graduação em Química (PPGQ), Universidade Federal de Sergipe – UFS, Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES).

# QVE

# Química Verde

**Área: QVE**

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

# A greener method for determination of As, Cd, and Pb in soil and plant tissue by ICP-MS employing NADES in sample preparation

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Keywords: *Green analytical chemistry, sample preparation, toxic elements, microwave-assisted extraction (MAE).*

## Highlights

NADES were efficient in the extraction of As, Cd, and Pb from plant tissue and soil samples.
NADES combined with microwave-assisted extraction provided effective extraction of As, Cd, and Pb.

## Abstract

The principles of green analytical chemistry have been widely applied in the development of analytical procedures[1], with three main objectives: reduced use of reagents and toxic compounds; energy efficiency; and the development of safe compounds[2]. The scientific community has sought a balanced approach to adoption of the principles of green chemistry, considering performance parameters (precision, robustness, sensitivity, etc.) as well as the cost/benefit ratio[3] for the development of sustainable analytical methodologies. Natural deep eutectic solvents (NADES), which are considered to be green solvents, are composed of natural precursors whose interaction occurs when one is a hydrogen bond donor compound (HBD) and the other is a hydrogen bond acceptor compound (HBA)[4]. NADES have several attractive characteristics, including biodegradability, low toxicity, low cost, simple preparation and handling, minimal volatility, and, importantly, adjustable physicochemical properties (density, viscosity, and polarity)[5]. These solvents have been widely used in green sample preparation methods, with the aim of obtaining reliable and accurate results, while prioritizing the sustainability of the analytical process. In this work, NADES based on carbohydrates and carboxylic acids were synthesized, characterized, and evaluated in terms of their suitability for the determination of inorganic contaminants in soil and plant tissue samples. NADES based on citric acid/malic acid/water (CA-MA) and citric acid/xylitol/water (CA-Xyl) were synthesized under stirring and heating[6], followed by determination of the viscosity and density values. The NADES were employed in a microwave-assisted extraction (MAE) method that was optimized for the extraction of As, Cd, and Pb, according to a Doehlert-type experimental design. The analytes present in the soil and plant tissue extracts were determined by inductively coupled plasma mass spectrometry (ICP-MS), with the instrument operated in standard mode, as well as using a kinetic energy discrimination cell (KED) to avoid possible interferences. The density values for the CA-Xyl and CA-MA solvents were 1.2575 ± 0.0126 and 1.2631 ± 0.0034 g $mL^{-1}$, respectively, while the corresponding viscosity values were 7.54 ± 0.03 and 5.20 ± 0.01 mPa.s. The optimization of the extraction conditions considered the effects of the variables temperature, extraction time, and mass/volume ratio. Recoveries in the range from 80 to 110% were obtained for $^{111}$Cd and $^{208}$Pb, when the CA-MA and CA-Xyl NADES were used for the extraction of a soil certified reference material (CRM) (EMBRAPA, Agro E2002a), as well as for $^{75}$As and $^{208}$Pb, when the Ca-Xyl NADES was used to extract a forage grass CRM (*Brachiaria brizantha* cv. Marandu; EMBRAPA, FO-01/2012). The solvents proved to be highly promising as extractors for the samples evaluated. The use of experimental design assisted in optimization of the MAE process, obtaining an analytical method that was in accordance with the principles of green analytical chemistry.

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## Agradecimentos/Acknowledgments

The authors are grateful for financial support provided by Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES), FAPESP (grants #2015/08893-4, #2016/17304-0, #2017/18531-3, and #2019/22113-8), and Instituto Nacional de Tecnologias Alternativas para Detecção, Avaliação Toxicológica e Remoção de Micropoluentes e Radioativos (INCT-DATREM) (FAPESP grant #14/50945-4 and CNPq grant #465571/2014-0).

**Área: QVE**

# A new protocol for the synthesis of carbamates from $CO_2$

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Kay-Words: *Carbon dioxide, capture, carbamates, amines*

## Highlights

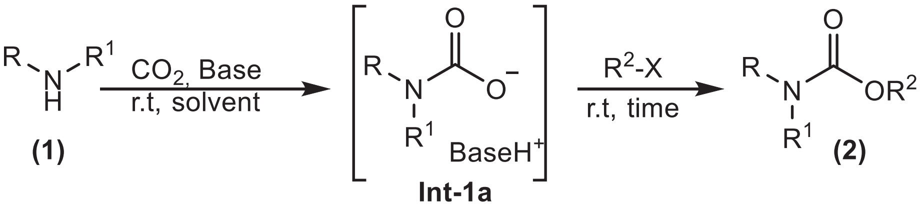
Activation of $CO_2$ by organic bases

Capture and transformation of $CO_2$ under mild rection conditions

Synthesis of several carbamates in good yields

## Abstract

Carbon dioxide ($CO_2$) has proven to be an important source of one-carbon (C1) building block in organic synthesis since it is a renewable raw material, economical, abundant and with low-toxicity. $CO_2$ is used in industry on large scales, *c.a.* 110 Mt of it is used as starting material in the production of urea, carbonates, methanol, and salicylic acid, demonstrating its industrial importance. Physiochemically, $CO_2$ is a thermodynamic and kinetic stable molecule with linear geometry, however, it can be transformed into value-added compounds using a suitable chemical environment.[1-3] The work presented herein showcases the synthesis of carbamates from $CO_2$ and amines (**1**) using mild reaction conditions. Carbamates are important amine protecting groups, as well as platforms in the synthesis of isocyanates. Initially, we evaluated different solvents, reaction times and bases (tertiary amines, guanidines and amidines) as catalysts for the capture and subsequent transformation of $CO_2$ into the corresponding carbamate (**2**). We found that in a one-pot, two sequence steps, the carbamic acid intermediate (**Int-1a**) formed between **1** and $CO_2$ can be transformed in **2** using alkyl halides as the alkylating agents at room temperature in good yields (up to 94%) (Scheme 1).



**Scheme 1**. Synthesis of carbamates from $CO_2$ and amines.

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Research Centre for Greenhouse Gas Innovation

**Área: QVE**

# Chemical characterization and thermic stability of biolubricant from babassu oil (Orbignya speciosa).

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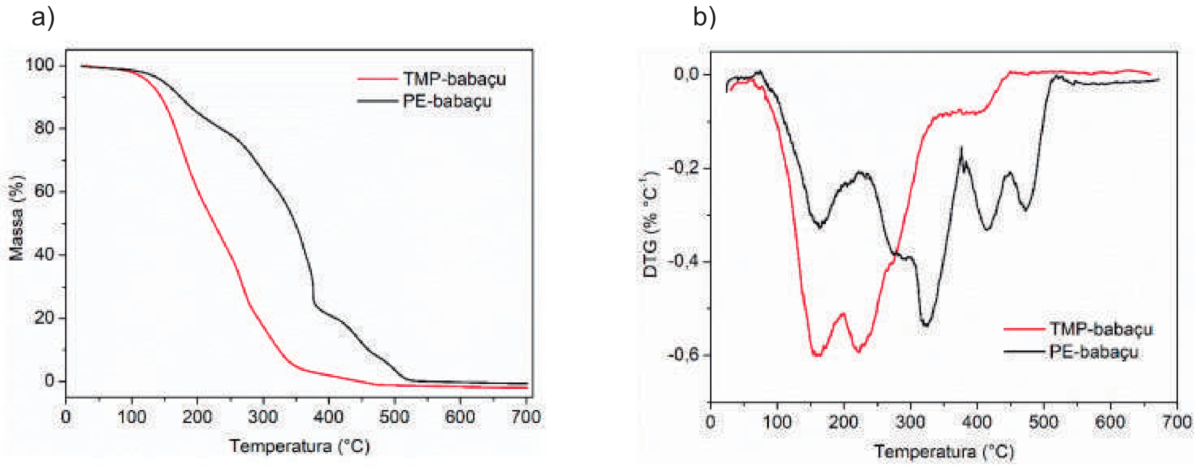
Keywords: *Babassu, Biolubricant, Thermic stability, Chemical Characterization.*

## Highlights

- Babassu oil was transesterified to produce biolubricants.
- Biolubricants were characterized using NMR and TG techniques.
- Biolubricant showed good thermic stability.

## Resumo/Abstract

Babassu is a typical fruit from Brazilian Cerrado. Due the potential of babassu fruits as source of oil, this work aimed the processing of babassu oil into biolubricant. The raw material was submitted to transesterification in two steps. The first transesterification was conducted using babassu oil in the presence of sodium hydroxide as catalyst and methyl alcohol. This way, methyl esters from babassu were obtained. Then, in the second step, methyl esters were submitted to transesterification using pentaerythritol (PE) and trimethylolpropane (TMP) using sodium methoxide as catalyst. The reaction time was 6 hours and temperature of 130 °C. The biolubricants were characterized using nuclear magnetic resonance of hydrogen (NMR $^{1}H$). The thermogravimetric analysis (TG/DTG) was responsible to the thermic evaluation. Thermic events observed in the thermogravimetric curves (Fig 1.) pointed the good thermic stability of the biolubricants. Babassu showed itself as potential resource for the substitution of non-renewable mineral lubricants.



(Figure 1 - TG (a) and DTG (b) curves to TMP-Babassu and PE-Babassu.)

## Agradecimentos/Acknowledgments

PPGER/ IFCE, CAPES, CNPQ.

**Área: QVE**

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

# Energy potential of brewers' spent grain from thermal analysis

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Palavras Chave: *BSG, Thermogravimetric analysis, High heating value, Waste.*

## Highlights

Brewers' spent grain (BSG) has a high biogas potential do trabalho de forma concisa e capturar rapidamente a Energy potential can be obtained from biomass characterization via immediate chemical analysis and high heating value; Thermogravimetric analysis (TGA) can be used as a simple tool in order to estimate the parameters required for a biofuel characterization.

## Resumo/Abstract

Considered a fuel of the future, green hydrogen is an indispensable element of a decarbonised energy system and could play a significant role in low-carbon future. There are many different sources of hydrogen and ways for producing it for use as a fuel. Today, most hydrogen used is extracted from natural gas in a process that requires a lot of energy and emits vast amounts of carbon dioxide. Commercial hydrogen producers and petroleum refineries use steam-methane reforming to separate hydrogen atoms from carbon atoms in methane (CH4). In this process high-temperature steam (1,300°F to 1,800°F) under 3–25 bar pressure (1 bar = 14.5 pounds per square inch) reacts with methane in the presence of a catalyst to produce hydrogen, carbon monoxide, and a relatively small amount of carbon dioxide (CO2). The methane-rich biogas can be reacted with steam to produce hydrogen, based on steam reforming in a circular economy perspective and the production of energy from renewable sources. Biogas can also be produced from lignocellulosic material by thermochemical conversions, co-digestion and dry fermentation of organic feedstock and waste. On the other hand, focusing on agro-industrial wastes, the scientists exploit new way to reuse. Brazil has widespread availability of organic feedstocks for the production of biogas, through inputs such as organic waste from the agro-industrial sector. Several researchers suggest that brewers' spent grain (BSG), a wet powder mostly composed of barley malt grain husks, has a high biogas potential. In this study, the thermogravimetric analysis (TGA) was used as a simple tool in order to estimate the parameters required for a biofuel characterization. The parameters required to reliably predict its behavior can be determined by the weight percentages (wt.%) of moisture, volatile matter (VM), fixed carbon (FC), chemical elements (carbon, hydrogen, nitrogen, oxygen and sulfur) and high heating value (HHV). The thermal behavior of the samples were evaluated by thermogravimetric (TG-DTG) analysis in atmosphere of synthetic air. For biomass characterization immediate chemical analysis and high calorific value were analized. The results showed that the samples of BSG displayed high calorific values and the immediate analysis showed that these residues displayed acceptable reactivities with a high volatile content (>76%). TGA analysis showed high biogas potential through HHV of BSG (13.54 MJ/kg). The contentes of hemicellulose, cellulose and lignina were determined using DTG curves deconvolution.

## Agradecimentos/Acknowledgments

Centro de Energias Alternativas e Renováveis (CEAR), Universidade Federal da Paraíba (UFPB), Fundação de Apoio à Pesquisa do Estado da Paraíba (Fapesq) e Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq).

**Área: QVE**

# On the Diels-Alder Reaction of Chitin-derived Dienes with several Dienophiles

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Keywords: *N-Acetylglucosamine, 3-acetamido-5-ethylfuran, maleimides*

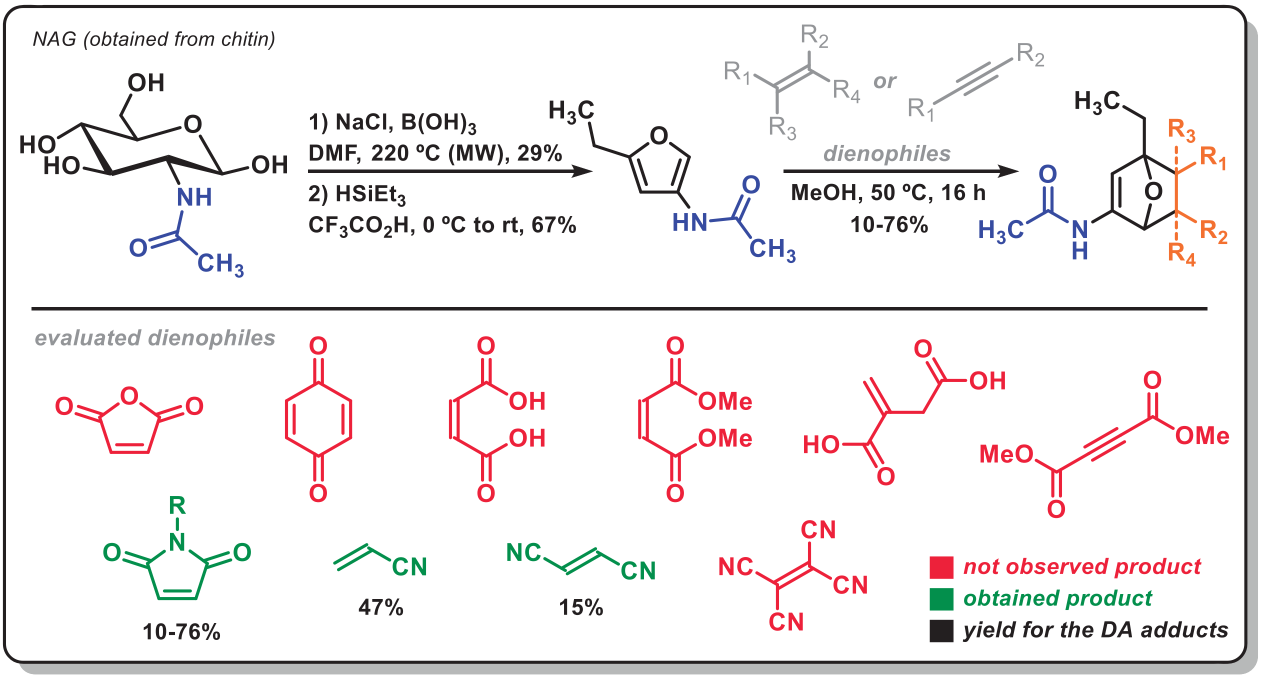
## Highlights

*N*-Acetylglucosamine (NAG) is a bio-based compound of economic importance in shell biorefinery.

Eight Diels-Alder adducts derived from renewable furans were synthesized and characterized.

## Abstract

Biomass refinery is considered to be a key technology in future due to the importance of the sustainable production of various bio-derived fuels and fine chemicals. Nitrogen-containing chemicals belong to some of the most important commodity and fine chemicals.[1] Shell biorefinery provides a sustainable access to a multiple nitrogen-containing chemicals, e.g. 3-acetamido-5-acetylfuran (3A5AF), which is obtained directly from *N*-acetylglucosamine dehydration.[2] 3-Acetamido-5-acetylfuran is an important platform chemical that can be transformed in others nitrogen-containing derivatives.[3] Our group is interested in Diels-Alder adducts containing furanic nitrogen-functionalized building blocks. Best results were obtained carrying out the reaction between maleimides and 3-acetamido-5-ethylfuran in MeOH at 50 ºC within 16 h to yield the adducts in 10–76% (sum of *endo*/*exo* isomers; *exo* is the major isomer).



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**Área: QVE**

# Síntese de biodiesel de óleo de algodão por rota etílica e adição de reagentes para favorecer a separação das fases

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Palavras Chave: *Óleo de algodão, Biodiesel, Etanol, Glicerina; Purificação.*

## Highlights

Biodiesel synthesis from cottonseed oil by ethyl route and reagents addition to improve phase separation. When ethanol is used in the reaction, greater amount of alcohol is required and there is greater dispersion of glycerin. The presence of water in the alcohol makes the reaction difficult.

## Resumo/Abstract

O biodiesel é um combustível produzido a partir da reação de transesterificação entre triglicerídeos e álcool (metanol ou etanol) na presença de catalisador (ácido, básico ou enzimático). Os produtos da reação são ésteres alquílicos (biodiesel) e glicerina. Quando se emprega etanol na reação é necessário maior quantidade de álcool e há uma maior dispersão da glicerina no biodiesel, dificultando a separação das fases. O objetivo desse trabalho foi verificar a influência do álcool utilizado na síntese do biodiesel de óleo de algodão por rota etílica, além de analisar a influência da adição de glicerina (P.A) e glicerina (P.A) + água na separação de fases. A fim de analisar a influência do etanol na síntese do biodiesel foram propostos diferentes procedimentos de purificação extra do etanol P.A: etanol seco com sulfato de magnésio, etanol destilado e etanol seco com sulfato de magnésio e destilado. As sínteses desses experimentos foram realizadas com dois ataques de 40% de etanol purificado, 1% de NaOH (catalisador) durante 1 hora a temperatura ambiente. O biodiesel obtido através da reação empregando etanol seco com sulfato de magnésio e destilado apresentou melhores resultados quando comparados aos outros tipos de purificação. Apresentou rendimento de 60,82% e viscosidade de 4,96 mm$^2$/s, para se obter resultados semelhantes utilizando etanol sem nenhum tipo de purificação extra foram necessários 60% de etanol e a reação teve que ocorrer a 60 °C por 1 h. Para avaliar a separação das fases foram realizados experimentos com a adição somente de glicerina (P.A) e adição de glicerina (P.A) + água destilada após o processo de transesterificação para auxiliar na separação do biodiesel e da glicerina. A síntese do biodiesel foi realizada em dois ataques com 60% de etanol, 1% de NaOH (catalisador) durante 1 hora a 60 ºC, sob refluxo. A taxa de conversão em ésteres etílicos determinada por Ressonância Magnética Nuclear de Hidrogênio foi de 98,7% mol/mol, para o biodiesel produzido a partir da purificação extra do etanol com sulfato de magnésio e destilado. A adição de água e glicerina ou apenas glicerina após a reação de transesterificação contribuiu para a separação das fases biodiesel-glicerina, mas o biodiesel apresentou índice de acidez elevado (Tabela 1).

**Tabela 1. Comparação dos resultados dos experimentos para auxiliar na separação de fases.**

| Parâmetro<br>Método | Rendimento (%) | Viscosidade ($mm^2$ $s^{-1}$) | Densidade (kg $m^{-3}$) | IA (mg KOH $g^{-1}$) | II (g $I_2$ 100 $g^{-1}$) | IS (mg KOH $g^{-1}$) | GL (%) |
|---|---|---|---|---|---|---|---|
| **Glicerina** | 60,02 | 5,05 | 874 | 0,595 | 114,50 | 236,77 | 0,013 |
| **Glicerina e água** | 65,05 | 4,45 | 868 | 1,342 | 97,38 | 193,35 | 0,011 |
| **ANP** | - | 3 - 6 | 850 - 900 | Máx. 0,5 | anotar | - | Máx. 0,02 |

IA = Índice de acidez; II = Índice de iodo; IS = Índice de saponificação; GL = Glicerina livre.

## Agradecimentos/Acknowledgments

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**Área: QVE**

# Synthesis and characterization of high surface area biocarbon derived from sugar and alcohol industry wastes.

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*Keywords: Activated biocarbon, High surface area, Biomass.*

## Highlights

Different granulometric fractions were found. Organic and inorganic matter were identified, with Si as main inorganic component. A surface area of 480 m$^2$/g was obtained.

## Abstract

Porous carbon derived from biomass is not just ecologically correct. It is also economical. The facility, together with the availability of the sugarcane bagasse as raw material, makes it a promising material with several domestic and industrial applications. This work aimed to characterize a high surface area biocarbon obtained from the sugar and alcohol industry waste. The biocarbon was characterized by granulometry, thermal analysis, X-ray fluorescence spectroscopy, and $N_2$ physisorption techniques. Granulometric analysis showed a total of eight granulometric fractions between 600 and 45 µm: >600µm (C1), 600µm>425 µm (C2), 425µm>300 µm (C3) e 300µm>212 µm (C4), representing 7%, 1%, 20% e 23% of the mass balance, respectively; the remaining 49% are associated to other fractions, not described in this work. TGA-DTA analysis showed 80%(C1), 54%(C2), 9%(C3), 2%(C4) in carbon, as well as 15%(C1), 9%(C2), 1%(C3) and 0.34%(C4) of humidity. From XRF analysis, the amount of Si was determined: 5,64%(C1), 16.80%(C2), 79.84%(C3), 85.16%(C4), being the second most abundant element in the analyzed samples. Ca, K and P were also found in lower concentrations. Physisorption analysis, figure 1, showed a surface area of 482 m$^2$/g, a pore diameter of 51 Å, and a cumulative pore volume of 0.067 cm$^3$/g for sample C1. Through the results obtained from the various analysis techniques, it can be said that the precursor material used has great potential.

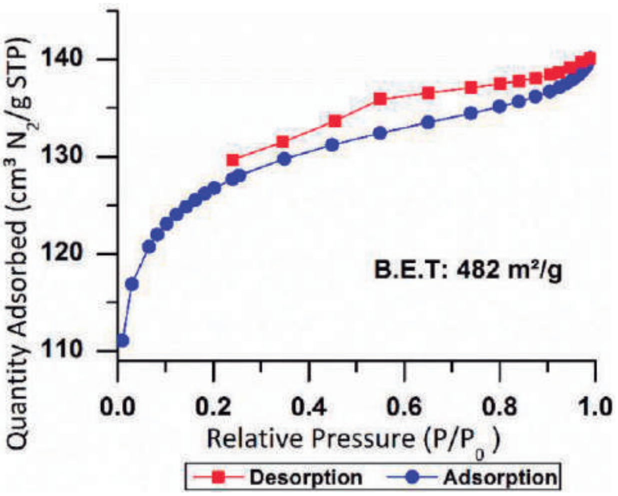

Figure 1 – C1 adsorption/desorption isotherms

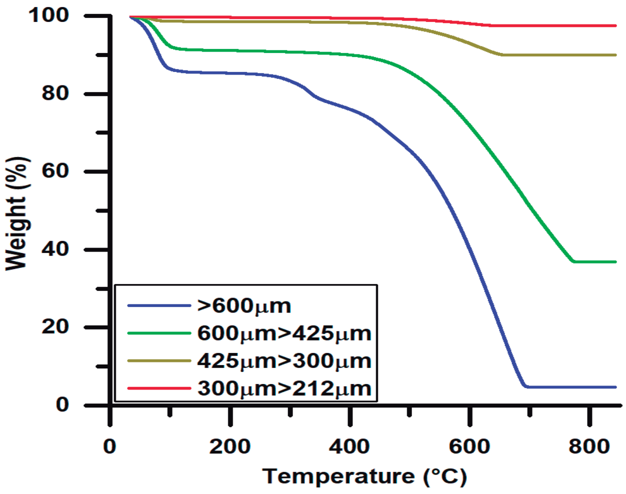

Figure 2 – TGA profiles: C1-C4

## Acknowledgments

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**Área: QVE**

# Uma proposta de índice de sustentabilidade de Departamentos de Química em Universidades baseado no *Greenmetrics*

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Palavras Chave: Sustentabilidade; Índice; *Greenmetrics*; Departamentos de Química

## Highlights

-Considerando a relevância da sustentabilidade, das ODS e do papel da Química é importante o levantamento dos parâmetros de criação de um ranking em sustentabilidade para os Departamentos de Química no Brasil;

-Adaptação do *Greenmetrics* para um índice que mede a sustentabilidade de Departamentos de Química;

-*Greenmetrics*: o índice mais importante mundialmente para avaliar a sustentabilidade de Universidades;

-Departamentos de Química preocupados com sustentabilidade são um importante exemplo para os químicos que estão sendo formados;

-A imagem negativa da química deve ser mudada por boas práticas que começam em nossos Departamentos.

## Resumo/Abstract

Neste trabalho, adaptou-se a metodologia *Greenmetrics*, que mede a sustentabilidade dentro de Universidades baseando-se em diversos parâmetros, para um índice focado em Departamentos ou Institutos de Química. Esse índice foi dividido em 6 categorias principais, a saber: Resíduos, Água, Energia e Mudanças Climáticas, Educação e Pesquisa, Infraestrutura e Transporte. Para cada uma dessas categorias foram definidos de 6-11 indicadores considerados relevantes para um Departamento de Química em uma Universidade. Esses indicadores foram descritos considerando as boas práticas em universidades e formas de mensurar foram sugeridas. A partir da análise desses indicadores foi possível mensurar sua relevância para o contexto da química. Entre os indicadores mais relevantes pode-se destacar os resíduos, água e educação e pesquisa.

Utilizando-se essas categorias e indicadores é possível mensurar a sustentabilidade de um departamento de química e a partir disso pode-se avaliar a sua evolução anualmente e mesmo criar um ranking nacional ou estadual referente à essa medida.

A definição de estratégias para estimular ações para que os departamentos de química sejam cada vez mais sustentáveis é de extrema importância e pode promover mudanças concretas e sistemáticas nesses ambientes. Além disso, essa prática pode, pelo exemplo, levar à formação de químicos mais conscientes e contribuir para a mudança da imagem da química na nossa sociedade.

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# TEC

# Química Tecnológica

**Área: TEC**
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**Nº de Inscrição: ________**
*(Inserir o número de inscrição do autor que fez a submissão)*

# Big Data in Chemical Science applied to penicillin's drugs

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Key words: Penicillin drug, Big data in chemistry, Knowledge management, Information science, Public Health.

## Highlights

Penicillin chemical drugs achieve 1600 patents in last years.
Challenges & opportunities in penicillin's drugs for Brazilian National Health System.
Knowledge management in Chemical Big Data Science.

## Abstract

Scientific and technological trends for antibiotics has increased significantly in the world. Analyzing the market, there is 100% of dependence in antibiotics' importation. In the last 20 years in official databases in Brazil note that there was a increase in imports of antibiotics. The amoxicillin is one of the most imported one. It ranks third among the ten pharmochemical imported in recent years - 53 tons of amoxicillin valued at approximately US$ 1.6 billion. There are 171 valid medicines registries in Brazil for these 06 groups of amoxicillin. Conclude that through almost 50 years, Brazil has lost its reasonable sovereignty in the production of antibiotics that it had in the 70's. In 2017, according Transparency Market Research (2018), the Active Pharmaceutical Ingredients market reached more than US$ 150 billion. In 2026 it is estimated that will exceed a value of US$ 219 billion. Investments in penicillin's drugs have already surpassed billions last decades. The pharmaceutical chemistry sector is one of the most competitive and profitable in the market. The health sector releases more than 1 million papers a year on scientific knowledge with advances 10%a.a. In knowledge technological has 110 million patents in European Patent Office (EPO). Thus, a case study using knowledge management in chemical Data Science drugs will provide a contribution for National Health System (SUS). According WHO (2013), 80% of the world's population does not have access to essential medicines. Its necessary new approach for R,D&I in health. The combination in chemical studies in the last 20 years for "penicillin" drugs match 1594 patents. Identified and processed (SciFinder®, EPO database) all patents with term in title and into abstract. Summary: areas whose production opportunities emerge are human needs, chemistry, textile, physics, new technologies etc. Figure shows opportunities. The main patent classification is for A61K (pharmaceutical preparations etc.). E.g. the last patent identified in October 2019 refers to Antibiotic therapy. Thus, knowledge management in penicillin's drugs could become a great allied to help decision-makers in the private and public sectors from R&D for innovation in chemicals.

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# Degradação de Polímeros: Prospecção Tecnológica de patentes com enfoque microbiológico

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Palavras Chave: *Prospecção de patentes; Biodegradação; Plásticos; Microbiologia.*

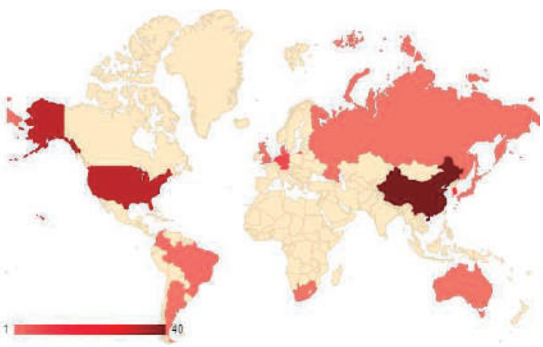
## Highlights

**Polymer Degradation: Technological Prospecting of Patents with a Microbiological Focus.** Technological prospecting of patents is an investigative study of world patents that envision the main technologies for the bioremediation of plastics by chemistry and microbiology due to the growing innovations in the market.

## Resumo/Abstract

Os plásticos possuem uma grande importância na sociedade contemporânea, pois são materiais de baixo custo e de ampla aplicação. Plásticos sintéticos convencionais derivados do petróleo são bastante resistentes à degradação natural, muitos deles exigem mais de 100 anos para degradar completamente[1]. A busca de metodologias para redução da dimensão desse dano ambiental tem reunido esforços há alguns anos. O mapeamento de patentes é um meio de revisão de informações tecnológicas que denomina-se prospecção tecnológica. Esse é um instrumento que contribui para tomadas de decisões, pois ajudam a detectar tecnologias relevantes, identificar nichos de mercado e etc.[2]. O presente trabalho demonstra o progresso patentário de metodologias para a degradação de polímeros, com foco microbiológico, tendo o propósito de contribuir com estudo para delinear inovações existentes e apontar perspectivas. O levantamento de dados foi realizado no portal *Espacenet* do Escritório Europeu de Patentes (EPO) e tratado em *software Excel*®. O código adotado foi o ***"C12R"*** que trata-se de patentes microbiológicas combinadas com as palavras-chave "*plásticos, biodegradação*", buscando identificar os depósitos de patentes referentes à biodegradação entre 1980 a 2020. Foi identificado 107 patentes relacionadas. Dentre esses, destaca-se a biodegradação de plásticos denominada por microbiologia orgânica com 27% das patentes depositadas. Dentre as instituições depositárias, o desenvolvimento ligado a centros acadêmicos e institutos de pesquisa correspondeu a 39% de depósitos. Ademais, os resultados demonstraram o uso crescente da bactéria *Pseudomonas aeruginosa* como agente microbiológico degradador de polímeros de polietileno através de técnicas de fermentação sólida. Outrossim, o desenvolvimento de fertilizantes químicos são fins comuns do plástico biodegradado. Dentre as áreas científicas que focam na busca de tecnologias relacionadas, a bioquímica ambiental apresentou aumento exponencial de 24% de contribuições patentárias no período de 2000 a 2020 perante ao desenvolvimento de tecnologias relacionadas. Dentre os principais países depositantes se destaca a China responsável por 37,3% de tecnologias, seguida dos Estados Unidos com 30,8% de patentes, o Brasil, por sua vez, responde a 1,86% da escala global, como expressa-se na figura 1. Das empresas aplicantes, foi possível identificar tecnologias progressivamente vindas de indústrias petroquímicas com 10% de patentes relacionadas. Portanto, o estudo prospectivo evidenciou, a partir da análise dos resultados encontrados, interesse econômico e científico no desenvolvimento tecnológico associado à biodegradação dos plásticos.

**Figura 1 -** Países Aplicantes de tecnologias relacionadas.



**Fonte:** Autoria (2021)

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**Área: TEC**

# Determinação de etanol em álcool sanitizante (líquido e gel) usando um instrumento portátil nariz eletrônico *lab-made*

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Palavras Chave: Nariz eletrônico, instrumento portátil, concentração de etanol, sanitizante.

## Highlights

Determination of ethanol in sanitizing alcohol (gel and liquid) using a lab-made portable electronic nose instrument

- Fast and low-cost determination of ethanol concentration in sanitizing
- Lab-made portable instrument using electronic nose and Arduino interface
- Quality control of sanitizing alcohol in field using a lab-made portable instrument

## Resumo

A pandemia gerou uma alta demanda comercial por álcool sanitizante para limpeza de mãos e superfícies no controle de contaminações. O potencial germicida do etanol ocorre na concentração de 60% a 80% para a inativação da maioria dos vírus lipofílicos e hidrofílicos. Assim, o produto adequado para ser usado como sanitizante para mãos, com ação biocida efetiva contra o Corona vírus, deve apresentar teor de etanol entre 60 e 70%. Análises de etanol em amostras de álcool gel são realizadas por técnicas como a cromatografia gasosa, que além de ser um equipamento de alto custo, requer reagentes e gases específicos, além de demandar muito tempo de análise.

Diante disso, este trabalho apresenta a construção de um instrumento portátil de baixo custo, usando nariz eletrônico (e-nose), visando a determinação rápida do teor de etanol em amostras de álcool sanitizante. Na construção, foram utilizados: um sensor de gás MQ3 (MOS-*metal oxide semiconductor*) produzido pela Hanwei Electronics (Zhengzhou, China), um microcontrolador ATmega328 em sistema Arduino Uno, microtubos tipo eppendorf como porta amostra, um botão do tipo táctil, um display alfanumérico 16 x 2, um cooler de 12 v, e uma patola confeccionada em impressora para acondicionar os componentes (Figura 1).

Figura 1. Nariz Eletrônico (e-nose) lab-made para determinação do teor de etanol em álcool sanitizante.

No instrumento, a corrente de ar gerada pelo ventilador (cooler) arrasta a parte da amostra que está em equilíbrio (volatilização do etanol) dentro do recipiente fechado, conduzindo-a em direção ao sensor de etanol MQ3. O sinal elétrico é então registrado pela interface do arduíno UNO durante 30 segundos. Para determinar a correlação do sinal obtido com a concentração de etanol presente na amostra, o equipamento foi calibrado a partir de uma curva analítica preparada com diferentes concentrações de etanol, variando de 50 a 75%.

Serão realizados testes com amostras adulteradas para avaliar possíveis interferentes, bem como, amostras analisadas pelo método convencional de cromatografia gasosa para comparação dos resultados e determinação da exatidão do método proposto.

O uso do nariz eletrônico lab-made mostrou-se uma alternativa rápida, portátil e de baixo custo para determinação do teor de etanol em amostras de álcool sanitizante, quando comparado aos métodos oficiais de referência.

## Agradecimentos

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**Área: TEC**

# Development of anti-SARS-CoV-2 packaging obtained from polypropylene composites

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Palavras Chave: *antimicrobial packaging, SARS-CoV-2, composites*

## Highlights

Design and development of new biocidal agents with a broad spectrum of antimicrobial activity.
Decreased proliferation of SARS-CoV-2 on polymeric surfaces.
Antimicrobial composite material for the manufacture of masks and packaging.

## Abstract

Many diseases can be spread to humans by fomite transmission, being them fungal, bacterial or viral. Thus, the factors that contribute to the survival of microbial on surfaces are of societal interest. One way to reduce the transmission of COVID-19 via surfaces is to design coatings based on functional nanoparticles that eliminate SARS-CoV-2 and apply them on common surfaces, such as packaging, continuously reducing the elimination period from weeks to minutes or hours. Additionally, polypropylene (PP) is currently one of the most consumed polymers for the manufacture of nonwoven surgical masks and aprons utilized in clinics and hospitals, besides being widely used as a packaging material. Despite the importance of this polymer in preventing and spreading the disease, a recent study indicated that the virus can be active for up to three days in different packing polymers. In this work, we present the synthesis of $\alpha$-$Ag_2WO_4$, $\beta$-$Ag_2MoO_4$ and $Ag_2CrO_4$ and their immobilization in PP in the amounts of 0.5, 1.0 and 3.0% wt, respectively. The antimicrobial activity of the composites was investigated against the Gram-negative bacterium *Escherichia coli*, the Gram-positive bacterium *Staphylococcus aureus* and the *fungus Candida albicans*. The best biocidal efficiency was achieved by the composite with $\alpha$-$Ag_2WO_4$, which completely eliminated the microorganisms in up to 4 hours of exposure. The composites were also tested for the inhibition of SARS-CoV-2 virus, showing virucidal efficiency higher than 98% in just 10 min. Additionally, we evaluated the maintenance of the antimicrobial activity, resulting in constant inhibition, even after material aging. The biocidal activity of the compounds was attributed to the production of reactive oxygen species, which can induce high local oxidative stress, causing the death of these microorganisms.

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**Área: TEC**

# Leaching of rare earth elements from phosphogypsum: optimization of experimental conditions and kinetic investigation

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Keywords: *Rare earth elements, Phosphogypsum, Leaching, Kinetics*

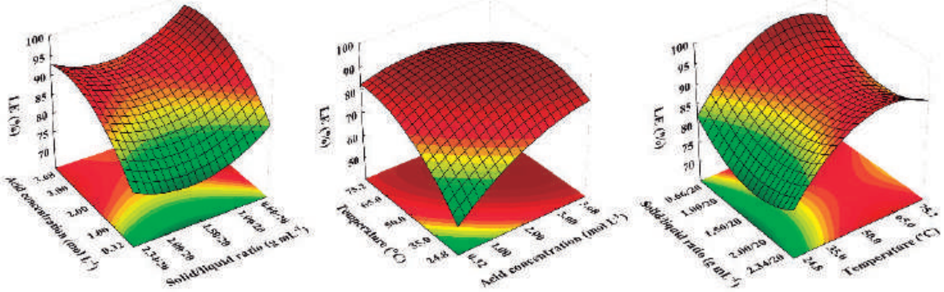
## Highlights

Optimization of leaching conditions was performed by CCRD;
Leaching efficiency value of 90% was obtained;
Leaching equilibrium was reached in around 20 min.

## Abstract

The high demand for rare earth elements (REE) has instigated the search for alternative solutions to obtain them.[1] Phosphogypsum (PG) is considered a promising secondary resource for these elements.[2] The recovery of REE from PG is usually performed through acid leaching. However, the reported leaching efficiencies are generally low and drastic leaching conditions are used.[3] Therefore, this work aimed to optimize the conditions of the leaching of REE from PG and to study the leaching kinetics. For caring out the experiments, sulfuric acid was used as the leaching agent. A predetermined amount of the PG sample was added in an Erlenmeyer flask with 20 mL of sulfuric acid at a predetermined concentration. The mixture was kept in a thermostatic bath at a constant temperature for 60 min, with a stirring rate of 400 rpm. The optimization of the leaching conditions was performed through central composite rotational design (CCRD) for three variables. The independent variables were: acid concentration, solid/liquid ratio, and temperature. Leaching kinetics experiments were carried out under the optimized conditions for different contact times (0–180 min). The concentration of REE in the leaching solution was determined by ICP–OES and the results were expressed as leaching efficiency of the sum of all REE present in the sample. The ANOVA results indicated that the statistical model obtained was predictive ($F_{calc} > F_{tab}$) and significant ($R^2 = 0.9467$) at the 95% significance level. The model indicated that the maximum leaching efficiency can be achieved with sulfuric acid concentration of 2.9 mol L$^{-1}$, solid/liquid ratio of 1.7/20 g mL$^{-1}$, and temperature of 55 °C. Under these conditions, the leaching efficiency was 90%. The response surfaces generated through the statistical model are shown in Figure 1. From the leaching kinetics study, it was observed that the equilibrium was reached in about 20 min. Therefore, the results found in this work indicated that a high leaching efficiency of REE from PG can be achieved under intermediate leaching conditions in a relatively short leaching time.

**Figure 1.** Response surfaces for the leaching of REE from PG.



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**Área: TEC**

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# Optimization of lipase enzyme production

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Palavras Chave: enzymes lipases; residual frying oil ; lipase activity

## Highlights

The production of the lipase enzyme can be performed using a fungus of the *Aspergillus niger* species and a residual frying oil (OFR) of soybean, with optimal results of lipase activity (U/mL).

## Resumo/Abstract

Lipases are enzymes that have an important role in the industry due to their wide use, arising great interest in their application in industrial bioprocesses due to their stability at high temperatures and wide pH ranges and, in the immobilized condition, can be applied using industrial conditions (FARIAS, 2013). In addition, they present ease of separation by filtration and centrifugation processes (ZENEVICZ, 2015). The production of this enzyme on an industrial scale uses the submerged bioprocess, which can be batch or fed-batch. In this process, many filamentous fungi of various genera are used for the production of lipases, among them, *Rhizopus, Aspergillus, Penicillium, Mucor, Geotrichum* and *Fusarium* (COLLA *et al.,* 2012; ZENEVICZ, 2015). These enzymes can be found in several sources in nature, such as animal, plant and microbial (BARBOSA, 2012; CENTURIÓN, 2017; LIMA *et al*., 2019). Also, they can be produced by microorganisms in the presence of an inducer oil, which can be substrate or hydrolyzed oil by-products, such as free fatty acids (FFAs) to stimulate production (ROVEDA *et al.,* 2010). Residual frying oil (OFR) is usually improperly disposed of in sanitary sewer systems and is a waste that accumulates and generates environmental damage (RASHID *et al*., 2014). This work consists of optimizing the production of lipases using a residual oil of soybean frying and a fungus of the species *Aspergillus niger*, and a submerged fermentation in batch mode. From the use of OFR as substrate, great results of lipases were obtained, because being a residue there is a reduction of costs in the production of enzymatic extracts, besides using an easily obtained microorganism. It was possible to obtain lipases with activity of 141.90 U/mL at pH 2 at ambient temperature for a period of 24 hours with residual frying oil concentration of 1,5 % (v/v), besides guaranteeing stability after 28 days.

## Agradecimentos/Acknowledgments

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# Performance de biodiesel de resíduo da gordura de frango em gerador MDGT-6500CLE

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Palavras Chave:*(Biodeiesel, resíduo de frango, gerador MDGT-6500CLE).*

## Highlights

Biodiesel performane of chicken fat residue in MDGT-6500CLE generator. The Brazilian biofuels sector has shown significant results in recent years and has been standing out in the development and use of renewable energy sources. Biodiesel can be obtained from several raw materials, such as vegetable oils and animal fats, with the possibility of using residues in its production. Given the above, this work evaluated the use of chicken fat residues in transesterification reactions for the production of biodiesel.The work also shows a comparative analysis of the consumption of the use of diesel and biodiesel in Engine for development and use of diesel energy model MDGT-6500CLE, from the Motomil 4T brand, electric start, powered by diesel fuel. The analyzes were carried out through practical tests, using fossil diesel and samples of biodiesel produced from chicken fat residues, using mixing rates of 5% (B5) and 10% (B10). In view of the analyzes carried out, it is possible to conclude that the studied samples presented results compatible with those obtained for the S500 diesel, considering the total time to consume 1L of fuel, obtaining the B10 type samples the closest results to commercial diesel.

## Resumo/Abstract

O setor de biocombustíveis brasileiro apresentou resultados expressivos nos últimos anos e vem se destacando no desenvolvimento e uso de fontes renováveis de energia. O biodiesel pode ser obtido a partir de diversas matérias-primas, como óleos vegetais e gorduras animais, com possibilidade da utilização de resíduos na sua produção. Diante do exposto, este trabalho avaliou o uso de resíduos gordurosos de frango em reações de transesterificação para produção de biodiesel.

O trabalho mostra também uma análise comparativa do consumo da utilização de diesel e biodiesel em Motor de desenvolvimento e uso energia a diesel de modelo MDGT-6500CLE, da marca Motomil 4T, partida elétrica, movido a combustível diesel. As análises foram realizadas por meio de ensaios práticos, fazendo uso de diesel fóssil e de amostras de biodiesel produzido a partir de resíduos gordurosos de frango, sendo utilizadas taxas de mistura de 5% (B5) e 10% (B10). Diante das análises realizadas, é possível concluir que as amostras estudas apresentaram resultados compatíveis com aqueles obtidos para o diesel S500, considerando-se tempo total para consumir 1L de combustível, obtendo as amostras do tipo B10 os resultados mais próximos do diesel comercial.

## Agradecimentos/Acknowledgments

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**Área: TEC** **Nº de Inscrição: 1099**

# Produção de biocombustíveis a partir da Syagrus flexuosa

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Palavras Chave: *Syagrus flexuosa; Biodiesel; Diesel renovável*

## Highlights

**Production of biofuels from *Syagrus flexuosa*.**
The extraction of fat from fruit of Syagrus flexuosa showed significant yield.
The production of biodiesel was carried out by homogeneous transesterification and the renewable diesel was produced by pressurized hydrocracking with 30 bar of $H_2$.
The biodiesel and renewable diesel showed physical-chemical proprieties within the requirements of ANP.

## Resumo/Abstract

A *Syagrus flexuosa* é uma palmeira do cerrado brasileiro, pertencente à família das Arecaceae. Ela representa uma fonte oleaginosa perene, extraído da amêndoa do seu fruto.

Nesse sentido, o trabalho tem como objetivo extrair a Gordura da *Syagrus flexuosa* (GSF) para produção de biodiesel e diesel renovável.

A extração da GSF apresentou cerca de 45 % de rendimento, em base seca. O ponto de fusão encontrado para a GSF foi de 27,23 °C, caracterizando como uma gordura.

A composição da GSF apresentou cerca de 39 % de ácido oléico, 26 % de ácido láurico, 13 % de ácido Mirístico e 12 % de ácido palmítico, determinado por Cromatografia Gasosa (CG-MS). Dessa forma, conclui-se que a GSF é formada, em sua maioria, por cadeias carbônicas saturadas

A produção do Biodiesel da Gordura (BDG) foi realizada por transesterficação homogênea com KOH, como catalisador. A conversão da GSF para BDG foi comprovada pela análise de RMN$^1$H, Figura 1. A partir dessa análise, verificou-se a ausência dos picos característicos dos hidrogênios da glicerina entre 4,4 e 4,1 ppm. Além disso, o pico característico dos hidrogênios da metila dos ésteres pode ser observado em 3,67 ppm.

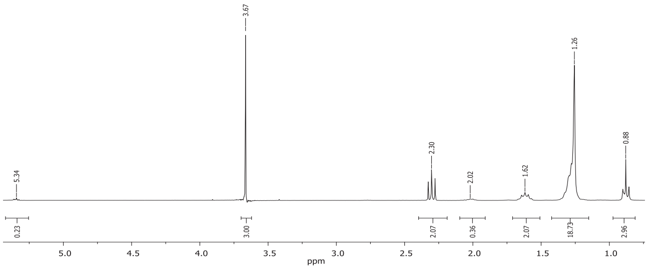

**Figura 1**. Espectro do RMN$^1$H do BDG.

O outro produto obtido, Diesel Renovável da Gordura (DRG), foi produzido por hidrocraqueamento pressurizado com 30 bar de $H_2$, catalisado por $NiMoS_2/Al_2O_3$. A conversão de GSF em DRG foi comprovada pela análise de FTIR, Figura 2, uma vez que houve o desaparecimento dos picos característicos dos ésteres dos ácidos graxos, picos 1740 e 1160 cm$^{-1}$.

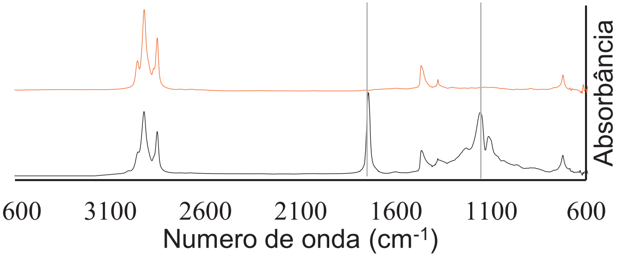

**Figura 2**. Espectro de FTIR do BDG (preto) e DRG (laranja).

Assim, os produtos obtidos e analisados, como GSF, BDG e DRG, apresentaram as propriedades físico-químicas dentro da especificação para o diesel, conforme Tabela 1. Assim assegurando a qualidade desses biocombustíveis como substituintes aos combustíveis fosseis.

**Tabela 1**. Propriedades físico-químicas dos produtos.

| **Propriedades físico-químicas** | **GSF** | **BDG** | **DRG** |
|---|---|---|---|
| **Densidade 40 °C (g.cm$^{-3}$)** | 0,8945 | 0,8550 | 0,7513 |
| **Índice de acidez (mg KOH/ g óleo)** | 3,81 | 0,23 | 0,9 |
| **Viscosidade Cinemática 40 °C (cST)** | 30,1 | 3,1 | 2,32 |

Dessa forma, a produção de BDG apresentou alta eficiência e propriedades físico-químicas dentro dos valores determinados pela Agência Nacional de Petróleo, Gás Natural e Biocombustíveis (ANP). O processo de hidrocraqueamento se mostrou eficaz, sendo o produto ser aplicado como diesel renovável, atendendo as exigências da ANP.

## Agradecimentos/Acknowledgments

CNPq, CAPES e FAPDF.

**Área: TEC**

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

# Rerrefino de óleos de aerogeradores a partir de combinação de processos físico-químicos com solventes/argila

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Palavras Chave:*(Rerrefino, Aerogeradores, Termocraqueamento, Argila).*

## Highlights

Re-refining of wind turbine oils from a combination of physical-chemical processes with solvents/clay. Re-refining is the name given to industrial processes aimed at removing contaminants, degradation products and additives from used or contaminated lubricating oils, giving them characteristics of base oils, according to specific legislation. Allied to the fact that the consumption of lubricants has been increasing substantially due to the increase in wind energy production in the country, especially in the Northeast, this study aimed to evaluate the process of recovery of oils obtained from wind turbines at a wind farm (located in Areia Branca/RN) through chemical treatments to reuse these oils. The material was subjected to solvent extraction [2-propanol (PPol) and di-methyl-ethyl-ketone (diMEC)], was clarified using natural clay and was physicochemically characterized together with samples of new and used lubricants, as well as new, used and recovered clays. The results allowed us to conclude that assays with diMEC resulted in a higher extraction yield (87%) compared to PPol (56%). IR assays made it possible to monitor oxidation products, additives and some impurities in the samples. The clarification process with natural clay, through columns by filtration, was satisfactory and minimized the formation of residues and also allowed the recovery of clays to be used again in the process.

## Resumo/Abstract

Rerrefino é a denominação dada aos processos industriais destinados à remoção de contaminantes, produtos de degradação e aditivos dos óleos lubrificantes usados ou contaminados, conferindo aos mesmos características de óleos básicos, conforme legislação específica. Aliado ao fato de que o consumo de lubrificantes vem aumentando substancialmente devido ao aumento da produção de energia eólica no país, especialmente no Nordeste, e com o intuito de minimizar impactos ambientais e financeiros, este estudo teve como objetivo avaliar processo de recuperação de óleos obtidos em aeroturbinas de parque eólico (localizado em Areia Branca/RN) através de tratamentos químicos para reutilização desses óleos. O material foi submetido a extração por solventes [2-propanol (PPol) e di-metil-etil-cetona (diMEC)], foi clarifificado utilizando argila natural e foi caracterizado físico-quimicamente juntamente com amostras de lubrificantes novos e usados, assim como argilas novas, usadas e recuperadas. Os resultados permitiram concluir que ensaios com diMEC resultaram em um rendimento mais elevado de extração (87%) frente ao PPol (56%). Ensaios de IV possibilitaram monitorar produtos de oxidação, aditivos e algumas impurezas nas amostras. O processo de clarificação com argila natural, através de colunas por filtração foi satisfatório e minimizou a formação de resíduos e possibilitou ainda a recuperação de argilas para serem novamente utilizadas no processo.

## Agradecimentos/Acknowledgments

Os autores agradecem ao Parque Eólico Mell II pelas amostras fornecidas e à UFRN pelas análises de IV realizadas.

**Área: TEC**

# Technological prospecting, assessment and scale-up of Macauba (*Acrocomia aculeata*)-based biosorption of metal ions from water

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Key words: Macauba, biosorption, metals, scale-up, Technological Prospecting

## Highlights

Macauba endocarp is a residual biomass of vegetable oil industry, which have a high capacity for metal biosorption and a potential scale-up into a separation process for water sanitation.

## Abstract

According to the World Health Organization, a person needs fifty liters of water a day to meet basic needs and keep public health risks low. In addition, due to the growth of the world population, an increase of 20-30% in the demand of this resource is estimated in the next 5 years. The importance of water in humanity contrasts with the oversights regarding the protection of this resource, where, in addition to contamination by anthropomorphic activities, environmental disasters such as those that occurred in Brazil (MG), Mariana (2015) and Brumadinho (2019), have polluted the water to levels that make their consumption unviable. This situation is a global concern, which is why the United Nations Organization, in the sixth Objective of Sustainable Development, proposes sanitation and access to clean water for all. The main objective of the present work is to evaluate the potential use of a biosorbent obtained from the residual biomass of the industrial vegetable oil extraction process from Macauba and its use in the design of adsorption systems with a high fluid dynamic regime, to contribute to technological innovation in the removal of metal ions in the water treatment and purification.

Chemical treatments of the macauba endocarp with NaOH, $H_2SO_4$, $H_2O_2$ and NaClO were evaluated, as well as physical treatment with ultrasound waves, to improve the biosorption capacity. The materials obtained were characterized by TGA, MEV-EDS, BET and Z potential. Adsorption tests were carried out, on a laboratory scale, with the metals $Al^{3+}$, $Mn^{2+}$ and $Fe^{3+}$ at different conditions of pH, temperature and contact time, and a comparison was made with the use of natural material. The best results were obtained with the material treated with NaOH, achieving removals above 40% for $Fe^{3+}$ and $Mn^{2+}$, and 25% for $Al^{3+}$.

Considering these results, the potential of this material for scale-up into a continuous separation operation is concluded, for which different strategies are being tested to obtain a prototype of a high fluid dynamic regime adsorption system as an innovative strategy (Figure 1). In addition, technology prospection and bibliometric studies were carried out using public and private database, such as Scopus and Questel-Orbit.

*Figure 1 Prototyping of the biosorption of metals endocarp of macauba*

## Acknowledgments

The authors would like to thank to the *Network for the study, development and application of technologies based on sustainable nanomaterials for the recovery of water from the Doce River basin* (N°06/2016), sponsored by the entities: FAPEMIG, CNPQ, CAPES, ANA, FAPES and development in Chemistry Department of UFMG.

**Área: TEC**

# The rational designing of redox-tagged peptide self-assembled monolayers for the diagnostic of dengue

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Palavras Chave*: Self-assembled monolayer; Biosensor; Ferrocene-tagged Peptide; Electroactive peptide; Capacitive biosensor; Point-of-care diagnostics*

## Highlights

Ferrocene-tagged peptides (Fc-Glu-X-X-Cys-$NH_2$, X = Ser, Phe, Gly) were evaluated as biosensing interface components to quantify NS1 protein. Fc-Glu-Gly-Gly-$NH_2$ showed the best analytical performance.

## Resumo/Abstract

Electrochemical capacitance methodologies based on a rational modification of interfaces are promising for biological recognition, offering advantages over traditional ELISA and RT-PCR methodologies by reducing time and cost[1] of the analysis. Peptides, due to their intrinsic biological characteristics and ability of forming self-assembling monolayers (SAMs) are promising for building sensitive and stable immunosensor interfaces. Our research group has previously studied the SAM Fc-Glu-Ala-Ala-Cys-$NH_2$ to detect C-reactive protein (CRP) antibodies[2] and NS1 protein[3]. The rational designing of peptide for this purpose includes one cysteine group to bind covalently to gold surface electrode, a N-terminus glutamic acid group that anchors a ferrocene (Fc) at an amine group and finally an antibody is bind to a δ-carboxyl group. In this work, we evaluate different redox-tagged peptides (Fc-Glu-X-X-Cys-$NH_2$, X = Serine, Phenylalanine or Glycine) for quantification of Dengue's NS1 protein. The Gly residue was selected due to its smallest side group, whilst, Ser and Phe were chosen for hydroxyl and aromatic groups, respectively. The peptides were synthesized by Solid-Phase Peptide Synthesis (SPPS) and the electrochemical properties were evaluated by cyclic voltammetry and impedance-derived electrochemical capacitance spectroscopy. The variations in the electrochemical capacitance response of the interface were able to be used as transducer signal to quantify NS1 protein in a linear range of 10 – 5,000 ng $mL^{-1}$, Gly-pep showed superior performance in terms of sensitivity of 5.6% per decade, a LOD of 1.4 ng $mL^{-1}$ and a LOQ of 2.6 ng $mL^{-1}$, followed by Phe-pep with a sensitivity of 1.2% per decade, a LOD of 1.5 ng $mL^{-1}$ and a LOQ of 3.1 ng $mL^{-1}$. The relative response of both Gly-Pep and Phe-pep for NS1 was successful compared to BSA (negative control) with values of 21% and 6%, respectively. Ser-pep exhibited no specific response for NS1 biomarker, not indicated as surface component for biosensing. The results indicate the selection of Gly-pep as a promising candidate for designing label-free redox-capacitive biosensing interfaces.

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**Área: TEC**

# Uso de visão computacional para a determinação da umidade relativa em ar

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Palavras Chave:*(imagem digital, sílica gel, umidade relativa, visão computacional).*

## Highlights

**Use of computer vision for the determination of relative humidity in air**

Silica gel blue as an active indicator to measure the amount of adsorbed water.

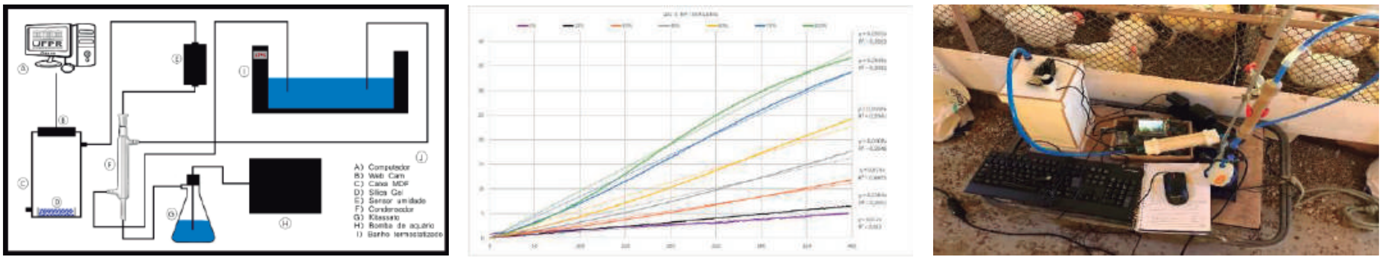
Chemical sensors aligned to computer vision.

Simple, green, and low-cost method to determine relative humidity.

## Resumo/Abstract

A utilização de imagens digitais vem sendo explorada no desenvolvimento de diferentes sensores químicos e dispositivos analíticos com aplicações que vão desde processos industriais a manutenção da qualidade de vida dos seres humanos[1]. Tais aplicações são baseadas nas mudanças de coloração resultantes da produção ou variação de grupos cromóforos e podem ser acompanhadas em tempo real por imagens digitais[2]. Neste trabalho submetemos porções de sílica gel azul seca com massa 10 g a uma atmosfera com umidade controlada[3], no qual a mudança de cor em tempo real foi acompanhada por uma webcam Logitech C920 HD Pro e um dispositivo *Raspberry* Pi 3 para armazenamento das imagens. O sistema de aquisição e calibração é representado na **Figura 1 -a.** Foram adquiridas imagens a cada 36 segundos por 14400 segundos (4 horas) totalizando 400 imagens para cada umidade relativa (U.R%). O método foi calibrado em 0, 12, 30, 45, 60, 75 e 100% de umidade relativa, tendo um sensor DHT22 como ferramenta auxiliar para verificação de temperatura e umidade. Foram traçados gráficos de mudança de cor para cada umidade. Um modelo linear foi construído em função Sinal de imagem(IMGs) e tempo (t), a derivada dessa função (dIMGs/dt) é proporcional a quantidade de água absorvida **Figura 1 -b**; $R^2$ mínimo de 0,9852. Após a calibração foram realizadas medidas de %U.R em uma estufa de plantas, um aviário experimental (**Figura 1-c**) para criação de frangos e um ambiente climatizado, tendo apresentado os seguintes resultados: 66,6, 76,9, 51,7% (com registro de chuva durante o experimento no aviário). O modelo mostrou-se robusto, de simples aplicação e permite medidas de campo, sendo que testes complementares de validação ainda devem ser realizados.

**Figura 1**. a) Diagrama do sistema de aquisição das imagens de sílica e padronização da umidade relativa b)Sinal da imagem IMGs x tempo c) Foto do equipamento em campo



(a) (b) (c)

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**Área: TEC**

# Zinc oxide Nanoparticles: Synthesis, physicochemical Characterization and Use to Remove Fe (III), Al (III) and Pb (II) From Contaminated Water

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Key words: *Zinc Nanoparticles, Adsorption, Metals, Bibliometrics.*

## Highlights

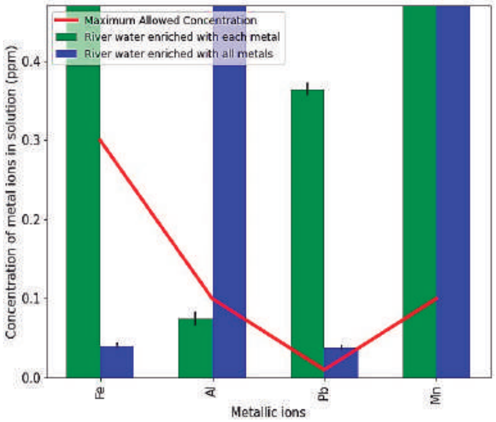
Preparation and characterization of promising zinc oxide nanoparticles that remove $Fe^{3+}$, $Al^{3+}$ and $Pb^{2+}$ from contaminated river water, bibliometric and technological prospecting studies using articles and patents databases.

## Abstract

According to UNESCO, about 2 million people die each year from drinking contaminated water of which 365.000 are children under 5 years of age. In Brazil, natural water resources have been contaminated by environmental disasters, related to poor management of waste from the mining industry, which has generated constant contamination by metal ions in solution. The main objective of the present work was to make systematic analysis of articles and patents in order to know the innovation opportunities of the area, as well as the preparation, characterization and statistical study of metallic ions removal from contaminated water using zinc oxide nanoparticles (ZnO-NPs) obtained by co-precipitation and hydrothermal methods.

The cluster analysis of the scientific production of the use of nanotechnology and ZnO nanoparticles for the removal of contaminants from water was carried out using the VosViewer (Van, E. et al) and CiteSpace (Chen, C. et al) software. The keyword occurrence map obtained (Fig. 1) from the searches shows defined and interrelated clusters that allowed determining the current position, relevance and opportunities of the use of ZnO-NPs in nanomaterials for the removal of metallic ions from contaminated water.

The physicochemical characterizations of the Zn-O NPs shown the presence of oxygen vacancy, smaller surface areas, reduced bandgap values, negative zeta potential values and particle size in the range of nanoscale. The adsorption experiments using the ZnO-NPs shown higher adsorption than 80% for $Fe^{3+}$, $Al^{3+}$ and $Pb^{2+}$, and no significant adsorption of $Mn^{2+}$. With this information, factorial experiments were carried out to determine the change and dependence of the control variables pH and contact time on the removal of metal ions in solution. A proof of concept using two different samples of contaminated river water (one of these enriched with known concentration of each metals in the study and the other enriched with the mixture of all metals). The results shown that the ZnO-NPs could adsorb $Al^{3+}$ ions below to the maximum permitted limits (MPL) by Brazilian regulations from the water enriched by the individual metal concentration. For water enriched with all metals, the ZnO-NPs remove $Fe^{3+}$ and $Pb^{2+}$ ions in solution to concentrations below the MPL (Fig. 2).



## Acknowledgments

The authors would like to thank to Network for the study, development and application of technologies based on sustainable nanomaterials for the recovery of water from the Doce River basin, sponsored by the entities: FAPEMIG, CNPQ, CAPES, ANA, FAPES and development in Chemistry Department of UFMG. To my advisor, friends, family, colleagues and teachers for the knowledge, service, patience, and attention in these difficult pandemic times.

# TEO

# Química Teórica

**Área: TEO**

# A numerical-variational solution of the Schrödinger equation for the hydrogen atom in parabolic coordinates

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Keywords: Hydrogen atom, Schrödinger equation, Numerical methods, Variational method, Parabolic coordinates.

## Highlights

A method was developed to solve the Schrödinger equation numerically. Results were obtained with high accuracy for the hydrogen atom in parabolic coordinates, but different from the usual orbitals were obtained.

## Abstract

A numerical method referred to as Fixed-Grid Variational (FGV) method was developed to solve the time independent Schrödinger equation [1]. The calculation initiates with a discrete arbitrary wave function represented by a mesh grid where each point is optimized to minimize the energy of the system. A Schrödinger equation was written using parabolic coordinates, $(u, v, \phi)$ and separation of variables: $\psi(u, v, \phi) = U(u)V(v)F(\phi)$. Coupled integral equations were obtained and optimized considering the variational principle.

Simulations were carried out in each coordinate with discrete wave functions using between 20 and 1000 points varying by ten. The best energy was obtained by extrapolation to an infinite number of points. Excited states were obtained by imposing the Gram-Schmidt orthogonalization condition, with respect to lower states. All states with quantum number $n = 1, 2$ and $3$ were calculated. The results yielded a mean absolute difference of $2 \cdot 10^{-6}$ a.u. with respect to results from the literature.

The shapes of the orbitals are not conventional. For the ground state, it is identical to that obtained using the polar spherical coordinates. For other states, the shapes are completely different. For example, **Figure 1** shows that the two orbitals obtained with $n = 2$ and $m = 0$, in the parabolic coordinate system, are different from the shapes of the $2s$ and $2p_z$ orbitals, which have the same quantum numbers in polar spherical coordinates.

From the point of view of quantum theory, there is no inconsistency with the results obtained, since in the case of degenerate states, any linear combination of the wave functions of these degenerate states is also an eigenfunction with the same eigenvalue.

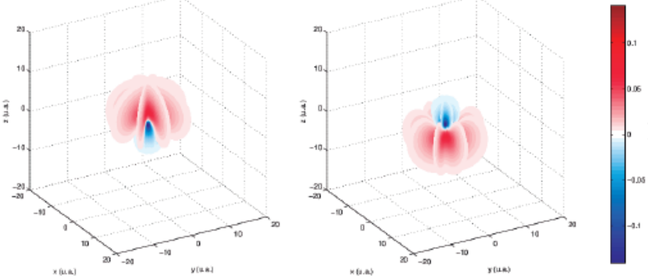

**Figure 1.** Orbitals obtained with $n = 2$ and $m = 0$ for hydrogen atom solved in the parabolic coordinate system.

The polar and parabolic spherical coordinates are borderline cases of the prolate spheroidal coordinate system. The authors are also applying the FGV method to solve the Schrödinger equation in the prolate spheroidal coordinate system showing the interconversion of the wavefunction some coordinate systems.

As shown in **Figure 1**, different shapes can be obtained changing the coordinate system and the GFV method is able to achieve accuracy of the order of microhartrees. These results suggest that the FGV method can be successfully applied to similar systems presenting the same level of numerical difficulty.

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## Acknowledgments

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**Área: TEO**

# Encapsulamento de ISRS/ISRN em Nanotubos de Carbono (CNT) por Docking Molecular.

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Palavras Chave: *Nanotubos de carbono, Docking molecular, Interações Moleculares, Encapsulamento.*

## Highlights

Encapsulation of SSRI/SNRI in Carbon Nanotubes by Molecular Docking: Based on the advent of nanotechnology, this work sought to analyze the molecular interactions in the encapsulation of SSRI and SNRI drugs in carbon nanotubes of different chiral configurations through molecular docking.

## Resumo/Abstract

Os nanomateriais[1] apresentam numerosas propriedades físico-químicas, que prometem ser chaves para a grandes questões, desde a otimização de circuitos eletrônicos até a criação de novas formas de terapêuticas biológicas direcionadas[2]. Nesse contexto, os nanotubos de carbono[3] tem sido um dos materiais mais estudados, devido suas propriedades, tais como semicondutores e potenciais adsorvente, esse último, muito visado para possíveis aplicações como no *drug delivery* [4]. Assim essa pesquisa objetivou analisar as interações moleculares no encapsulamento de fármacos em nanotubos de carbono. Para isso, utilizou-se como receptor nanotubos de carbono: CNT 7,7 e CNT 8,8, mantendo a quiralidade armchair; e como ligante, utilizaram-se dois fármacos: Atomoxetina (ISRN) e a Fluoxetina (ISRS), ambos atuantes na recaptação de neurotransmissores. O docking molecular foi realizado no software AutoDockTools 1.5.6, utilizando como algoritmo de busca o LGA, com 100 corridas em longa avaliação, com o grid abrangendo todo o espaço dos nanotubos (90x126x126 Å), com espaço de 0,375 Å. O tratamento as imagens, bem como as análises das interações foram realizadas pelos softwares Pymol e DiscoveryStudio 202. Ao fim das simulações, as conformações mais estáveis para os complexos (4 ao todo) ocorreram com os ligantes posicionados internamente a superfície dos nanotubos, e os melhores resultados para a energia de interação (EI) bem como o total de interações moleculares favoráveis, são mostrados na tabela 1.

Assim, percebeu-se que ocorreram números consideráveis de interações moleculares favoráveis para os 4 complexos, o que foi refletido diretamente nos valores de $\Delta G$, sendo as principais interações encontradas: interações de hidrogênio, interações hidrofóbicas e interações dipolo-$\pi$, sendo as mais favoráveis interações nos CNT 7,7, ou seja, uma influência direta da quiralidade do sistema. Percebeu-se que os nanotubos de carbono são capazes de formar interações moleculares favoráveis com outras moléculas no processo de encapsulamento, sendo tais interações influenciadas diretamente pela configuração quiral dos CNT's. Assim, do ponto de vista das interações moleculares e do $\Delta G$, os CNT's tem potencial para atuar como adsorventes, o que deve ser confirmado por estudos posteriores.

**Tabela 1**: Resultados do docking molecular.

| Complexo | Interações Moleculares | E.I. (Kcal/mol) |
|---|---|---|
| AX – CNT 7,7 | 61 | -22.20 |
| AX – CNT 8,8 | 56 | -20.01 |
| FX – CNT 7,7 | 62 | -23.29 |
| FX – CNT 8,8 | 59 | -20.12 |

## Agradecimentos/Acknowledgments

A Coordenação de Química, Instituto Federal do Pará – IFPA, Campus Belém e o Instituto Federal do Pará – IFPA, Campus Ananindeua.

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[2] TRINDADE, J. F. Egitania Sciencia. **Nanotubos de Carbono: Propriedades e Funcionalização**, p. 7–17, 2011.

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[4] SHAHABI, D.; TAVAKOL, H. Applied Surface Science. **DFT, NBO and molecular docking studies of the adsorption of fluoxetine into and on the surface of simple and sulfur-doped carbon nanotubes**, v. 420, p. 267–275, 2017.

**Área: TEO**

# Energetic Origins of Force Constants: Adding a new Dimension to the Hessian matrix via Interacting Quantum Atoms.

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Infrared frequencies, QTAIM, Force constants, Interacting quantum atoms, Energy decomposition

## Highlights

The IQA method partitions the energy of a molecule in atomic contributions, allowing the decomposition of force constants by adding a third dimension to the Hessian matrix and applying the Wilson's method.

## Resumo/Abstract

According to the Interacting Quantum Atoms (IQA) energy decomposition scheme, the total energy of a molecule can be partitioned into intra- and interatomic contributions. The former relates to the kinetic and potential energy of electrons inside one individual atomic basin, while the latter contains the Coulomb (cl) and exchange-correlation (xc) potential between electrons from two atomic basins.

When studying molecular vibrations, the force constants that determine the infrared frequencies can be obtained by the Wilson "**FG**" method, which involves careful manipulations of the Hessian matrix. Considering that the molecular energy is a sum of IQA contributions, the Hessian matrix can be written as a sum of "IQA Hessian" matrices, whose elements are second derivatives of IQA terms. Herein, we present a mathematical formalism for the IQA decomposition of force constants unveiling their energetic origins. The method consists of adding a new dimension to the Hessian matrix, which becomes 3Nx3NxN(N+1) with N being the number of atoms in the molecule and N(N+1) the number of IQA terms. Since there is no analytical method that produces the IQA quantities the second derivative, the 3D IQA Hessian is obtained numerically.

The calculated force constants agree with the experimental data with a small mean absolute error (Figure 1). An example is given for O-O bond in Table 1. Note that the smaller force constant in $O_3$ is caused by contributions of the third O atom, which makes de bond less rigid. For $H_2O_2$ the bond is weaken by the smaller Coulomb contribution between the oxygen atoms, as consequence of their atomic charges.

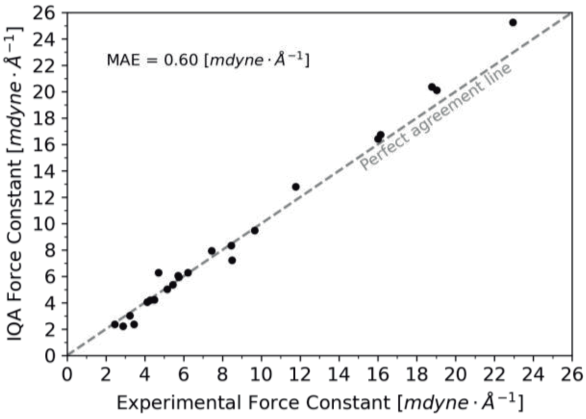

***Figure 1:*** *Experimental force constants versus IQA force constants.*

**Table 1:** IQA partitioning for O-O bond with different bond orders.

| Molecule | O-O bond order | Stretching force constant | IQA term contribution [mdyne·Å$^{-1}$] | | | | Σ others | Total |
|---|---|---|---|---|---|---|---|---|
| | | | $E_{intra}^{O1}$ | $E_{intra}^{O2}$ | $V_{cl}^{O1,O2}$ | $V_{xc}^{O1,O2}$ | [mdyne·Å$^{-1}$] | [mdyne·Å$^{-1}$] |
| $O_2$ | 2 | $f_{(O1,O2)}$ | 2.73 | 2.73 | 12.74 | -5.41 | 0.00 | 12.79 |
| $O_3$ | 1.5 | $f_{(O1,O2)}$ | 2.43 | 1.43 | 11.18 | -5.90 | -1.76 | 7.39 |
| $H_2O_2$ | 1 | $f_{(O1,O2)}$ | 2.27 | 2.24 | 2.76 | -3.41 | 1.07 | 4.93 |

## Agradecimentos/Acknowledgments

LJD thanks Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) for a Ph.D. fellowship (2017/22741-3). REB acknowledges FAPESP for funding research grant (2018/08861-9) and Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) for a research fellowship (302574/2019-0).

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

# Estudos Espectroscópicos de moléculas diatômicas $Br_2$, $I_2$ e BrI dentro do formalismo CASSCF(8,8)+PT2/CBS+PP

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Palavras Chave: Constantes Espectroscópicas, CASSCF(8,8)+PT2, CBS, Pseudopotencial

## Highlights

**Spectroscopic studies of diatomic molecules $Br_2$, $I_2$ and BrI using CASSCF(8,8)+PT2/CBS+PP methodology**

- Anharmonic potential constants;
- Diatomic molecules: $Br_2$, $I_2$ and BrI;
- Multi-Reference Perturbation Theory (MRPT2);
- Complete Basis Set (CBS) Extrapolation Scheme;
- Stuttgart–Dresden–Bonn SDB Relativistic Pseudopotentials

## Resumo/Abstract

A utilização de uma curva de energia potencial de moléculas diatômicas no estado fundamental permite a obtenção de constantes espectroscópicas dentro do formalismo anarmônico. Nesse trabalho foram obtidos além dos parâmetros espectroscópicos, informações energéticas e estruturais dos sistemas $Br_2$, $I_2$ e BrI. Para isso utilizou-se de cálculos de estrutura eletrônica no nível de teoria CASSCF(8,8) com adição de correlação eletrônica dinâmica no nível PT2. Os conjuntos de base foram adaptados com pseudopotencial relativístico de Stuttgart RLC ECP com funções primitivas do tipo aug-cc-pVnZ (n = 2, 3 e 4) através do Método da Coordenada Geradora na sua versão Discretização Integral Otimizada (MCG-DIO). A extrapolação para o Conjunto Completo de Base (CBS) foi feita considerando-se um ajuste de mínimos quadrados. E para a obtenção das constantes espectroscópicas empregou-se o método de Dunham, onde o potencial é expandido em uma série de Taylor. Os resultados obtidos são próximos dos valores experimentais e de outros cálculos mais rigorosos, porém a um custo computacional menor, graças ao uso do potencial efetivo de caroço. Todos os cálculos foram feitos com o programa de estrutura eletrônica GAMESS.

## Agradecimentos/Acknowledgments

Os autores agradecem ao Instituto de Química da UNICAMP pela infraestrutura computacional e a FAPESP e CNPq pelos recursos financeiros.

**Área: TEO**

# Growing Mechanism of Polysulfides and Elemental Sulfur Formation – Implications to Hindered Chalcopyrite Dissolution.

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Keywords: *Polysulfides, Elemental sulfur, DFT, MP2, Chalcopyrite.*

## Highlights

The pKa of the polysulfides have been estimated using a free energy relationship.
For larger polysulfides, pKas converge to 3.4 and 4.1.
The growing chain of the polysulfides by adding S2 is favored.

## Abstract

The metal-deficient polysulfides have been argued for a long time to be responsible for the low kinetics of chalcopyrite leaching to extract copper. It has been shown that chalcopyrite surfaces are the source of sulfur that is oxidized to form polysulfides and elemental sulfur (Figure 1). Electronic structure calculations were performed for $H_xS_n^{x-2}$ (x=0,1,2 and n=1..20) aiming to understand the effect of the pH on the growing chains and the formation of the elemental sulfur. The estimated pKa1 of the $H_2S_n$ polysulfides converges from 4.2 (n=3) to 3.4 (n>=8) and the estimated pKa2 converges from 7.6 (n=3) to 4.1 (n >=8). The initial steps of the formation of polysulfide chains are more favored for protonated species. The reaction energies at the gas phase follow the same tendency converging to an asymptotic value for larger chains. The inclusion of the solvent effects using the continuum method SMD is enough to make the two curves to converge to the same asymptotic value (Figure 2). The elemental sulfur formation due to the decomposition of polysulfides to form smaller chains is mostly favored for protonated species with n smaller than 12. For larger chains, the decomposition is thermodynamically favored for polysulfides with any degree of protonation. The consequences of these results to the understanding of the mechanism of chalcopyrite leaching process are discussed with the focus on the pH effect and the formation of elemental sulfur.

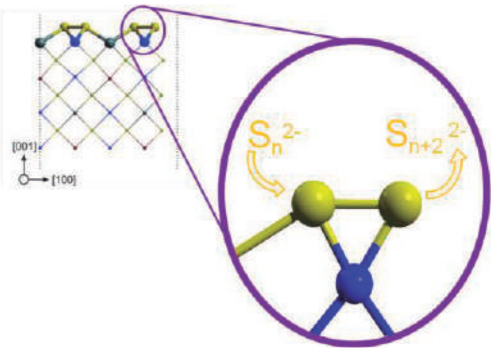

**Figure 1.** Formation of polysulfides from the chalcopyrite surface.

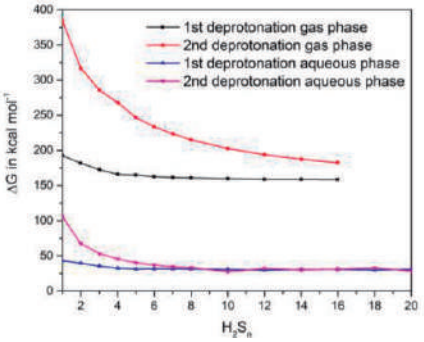

**Figure 2**. Estimated free energy for the first and second deprotonation of the polysulfides.

**Reference**: This work has been accepted for publication in the J. Phys. Chem. A (2022).

## Acknowledgments

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**Área: _________TEO_________**

# Interação de nanopartícula de Platina com folhas de Nitreto de Carbono Grafítico (g-$C_3N_4$) através de Dinâmica Molecular

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Palavras Chave: dinâmica molecular, fotocatálise, nitreto de carbono grafítico, nanopartícula metálica.

## Highlights

Interaction of Pt nanoparticles with Graphitic Carbon Nitride Sheets (g-C3N4) through Molecular Dynamics

- Lowest free-energy position for the nanoparticle is in the larger pore of the carbon nitride nanosheet.
- Spontaneous coating of the nanoparticle by the sacrificial molecule (triethanolamine).

## Resumo/Abstract

O nitreto de carbono grafítico (g-$C_3N_4$) é um polímero semicondutor repleto de anéis nitrogenados e que possui uma estrutura em camadas, sendo promissor para fotocatálise na região do UV-Vis e fabricação de sensores [1]. Em geral, os anéis nitrogenados podem ser de dois tipos: anéis de triazina (PTI) e anéis de heptazina (PHI). Contudo, a estrutura do nosso material possui tanto anéis de heptazina quanto uma cavidade maior, a qual confere carga negativa à estrutura, e por esta razão ela possui como contra-íons, os cátions $Na^+$ ou $Mg^{+2}$.

A aplicação deste material em fotocatálise envolve a presença de trietanolamina (TEOA) como molécula de sacrifício (em uma concentração de 10% v/v) e de uma nanopartícula de Platina (NP-Pt). Portanto, as simulações foram feitas em uma caixa de simulação de 8,0 nm de aresta contendo 14242 moléculas de água, 213 de trietanolamina, 3 camadas de PHI com uma NP-Pt (55 átomos) adsorvida em sua superfície. O modelo inicial da folha de PHI foi construído com 5,5 nm de aresta, contendo 6 cavidades maiores e 18 contra-íons de $Na^+$ (Na-PHI) ou 9 contra-íons de $Mg^{+2}$ (Mg-PHI). O *software* Themis [2] foi utilizado para encontrar a melhor posição, através da energia livre, para a NP-Pt interagir com o PHI, a qual está ilustrada na Figura 1 (a) para o Na-PHI e (b) para o Mg-PHI, onde se observa que a melhor posição corresponde à NP-Pt dentro de uma das cavidades maiores do PHI.

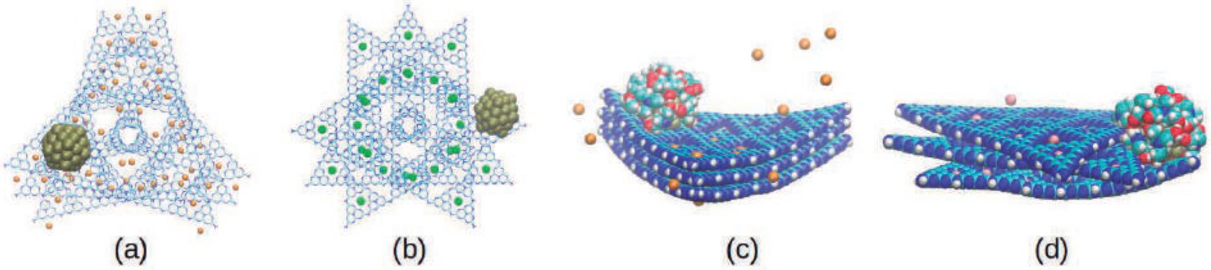

*Figura 1: Estrutura de menor energia livre para a NP-Pt com (a) Na-PHI e (b) Mg-PHI. Último passo da trajetória para (c) Na-PHI e (d) Mg-PHI interagindo com a NP-Pt.*

As dinâmicas moleculares foram realizadas no pacote computacional GROMACS [3], usando o campo de força CHARMM36 [4], sendo que incialmente foi feita uma minimização de energia, seguida de uma dinâmica NVT de 150 ps a 298,15 K, e por último, uma dinâmica NPT de 200 ns, à 298,15 K e 1 bar. A inspeção visual da trajetória mostra que a NP-Pt é estável na posição que o Themis encontrou e que a TEOA reveste a superfície da NP-Pt, como mostram as Figuras 1 (c) e (d). Isto se deve a tanto a TEOA quanto a NP-Pt serem mais hidrofóbicas do que o PHI. Assim, este resultado pode ser a base para desvendar o mecanismo pelo qual a fotocatálise ocorre. Contudo, cálculos quânticos de estados excitados serão realizados posteriormente para elucidar melhor tal fenômeno.

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[2]. COLOMBARI, F. et al. **ChemRxiv**. Cambridge: Cambridge Open Engage; 2020.
[3]. BERENDSEN, et al. **Comp. Phys. Comm.**, v. 91, p. 43-56, 1995.
[4]. BEST, R. B., ZHU, X., SHIM, J. et al, **J. Chem. Theory Comput**., v. 8, p. 3257, 2012.

## Agradecimentos/Acknowledgments

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**Área: TEO**

# Machine Learning Assisted Composite Method Based on a Classification Problem

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Keywords: Composite methods, Machine learning, Neural networks, Genetic algorithm.

## Highlights

A low-cost machine learning assisted composite method was developed for calculating heats of formation of small and medium-sized molecules.

## Abstract

The accurate calculation of thermochemical properties of atoms and molecules constitutes a great challenge in computation chemistry. Composite methods present a relatively inexpensive alternative for accurate electronic structure calculations. The goal behind composite methods is to reproduce accurate results by using a combination of energies computed using a lower, and therefore computationally cheaper, level of theory. Within this class of methods, those of the Gn family from Pople and Curtiss are the most popular formulations. One of them, the G3 method, is outlined as:

$$E[G3] = E(QCISD(T) + E(plus) + E(2df,p) + E(\Delta G3L) + E(SO) + E(HLC) + E(ZPE)$$

An adaptative composite method was developed by introducing a classification step in order to identify the best parameters to be used in each heat of formation computation of the G3/05 test set molecules (248 in total). The classification was performed through an Artificial Neural Network (ANN). The highest accuracy was achieved by considering 8 possible sets of parameters $[a, b, c, d]$ for the composite method below.

$$E_{total} = E(HF) + E[(a,b)(QCISD(T) - HF)] + E[(c,d)(MP2_{pvTz} - MP2_{pvDz})] + E[ZPE]$$

where HF, QCISDT, MP2 and ZPE correspond to the Hartree-Fock, Quadratic Configuration Interaction, Møller–Plesset, and Zero-point energies. All the single-point calculations were performed using molecular geometries optimized at the B3LYP/aug-cc-pvTz level of theory. Moreover, Stuttgart/Dresden's relativistic pseudopotential was also applied in order to evaluate the impact of the removal of the core electrons in the energy correction values given by the $[a, b, c, d]$ parameters.

The hyper-parameters (number of nodes, layers, activation functions, etc.) of the ANN used in the classification step were optimized using a genetic algorithm. In the optimized framework shown below, the black nodes refer to the input layer, the green nodes represent the hidden layers and finally, the red nodes correspond to the output layer.

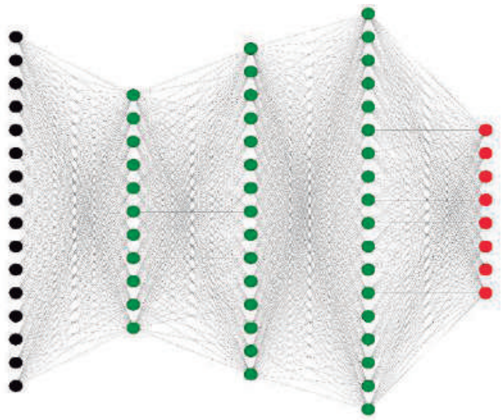

**Figure 1.** Framework of the ANN optimized by the genetic algorithm.

In the above ANN, each molecule has its chemical descriptors introduced in the input layer and processed throughout the hidden layers until one of the eight red nodes is fired defining the best set of parameters to be used in the composite method outlined before. The mean absolute error obtained for the heat of formation of the 248 molecules tested was of **1.06 kcal mol$^{-1}$**. This level of accuracy proves that the trade off between adding a classification step in the calculation and reducing both the computational cost and the average deviation is worth it.

[1]Pereira, G. C. (2020). *Desenvolvimento e avaliação de método composto adaptativo empregando redes neurais para o cálculo de propriedades termodinâmicas*. Campinas, SP. Retirado de https://hdl.handle.net/20.500.12733/1638865

## Acknowledgments

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**Área: TEO**

# Multistructural partition function truncation and their effects in the thermal rate constants

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Palavras Chave: *Combustion, Partition Function, Torsional Anharmonicity.*

## Highlights

1. Methyl Pentanoate (MP) can be a potential biodiesel surrogate.
2. Systematic convergence of MS-CVT/SCT rate coefficients as a function of transition states conformers.
3. Thermal rate constants, including all conformers, are in good agreement with the experimental findings.

## Abstract

A promising alternative to petroleum-derived fuels, biodiesel is mainly constituted by long-chain fatty acid esters. Due to the size of these molecules and their chemical variability, this fuel presents a complex combustion mechanism. Recently, smaller methyl esters have attracted interest because they present fewer elementary reactions in the combustion process. Besides, comprehensive knowledge of these kinetic parameters can be useful to understand the role of the ester functionality in the combustion of biodiesel. Methyl Pentanoate (MP) can be a potential surrogate of biodiesel or blended with conventional fossil fuels to reduce the emission of CO, NOx, and particulates from engine-like environments. To corroborate with the construction and validation of more accurate combustion mechanisms, we investigate the hydrogen abstraction (HA) reactions of methyl pentanoate by H atom, employing the multistructural variational transition state theory with small curvature tunneling (MS-CVT/SCT), as implemented in Pilgrim code. All conformers of MP and transition states, reached by internal rotations, were located using an algorithm that combined a systematic and stochastic search, performed at dual-level approach, available in TorsiFlex code. At MPWB1K/6-31+G(d,p) (high-level), we found 23, 46, 27, 43, 41, and 64 conformers (without the inclusion of enantiomers) for MP, TS1, TS2, TS3, TS4, and TS5, respectively. Torsional anharmonicity due to the hindered rotors was taken into account by calculating the rovibrational partition function using the multistructural method based on a coupled torsional potential (MS-T(C)), using the MsTor program. The influence of the multistructural and torsional anharmonicity effects was systematically included in the thermal rate constants through a truncation in the MS-T(C) rovibrational partition functions for methyl pentanoate and transition states. **Figure 1** shows the MS-CVT/SCT rate coefficients estimated as a function of numbers of conformers of transition states for the five HA possible sites in the methyl pentanoate.

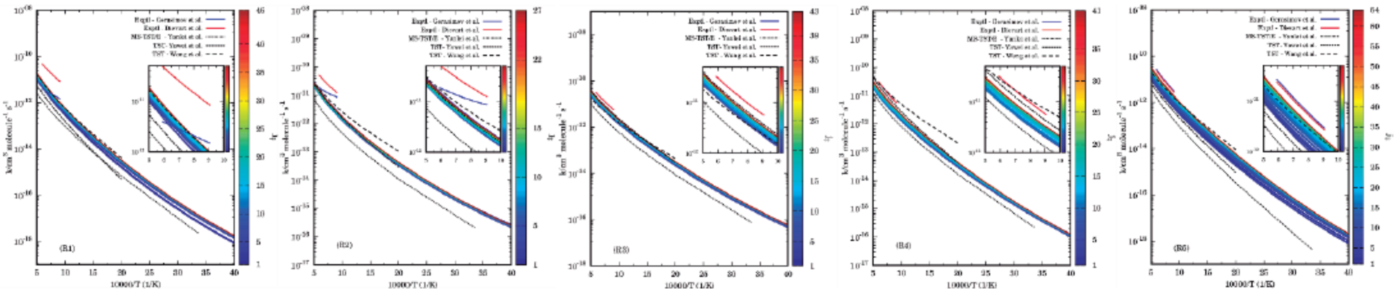

**Figure 1.** Arrhenius plot showing the convergence of the MS-CVT/SCT thermal rate constants as a function of numbers of conformers of transition states, for (R1)-(R5).

As we can see, the MS-CVT/SCT thermal rate constants show a strong dependence on the number of conformers includes in the rovibrational partition function. Our results agree with the experimental values of Gerasimov and collaborators [1].

**Reference:**

[1] Gerasimov, T. A et al., *Energy Fuels* **31**, 14129 (2017)

## Acknowledgments

J.L.N. acknowledges FAPESB for a graduate fellowship.

**Área: TEO**

# Non-equilibrium molecular dynamics of ionic liquids films under shear

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Keywords: *Ionic liquids, Molecular dynamics, Viscosity, Shear rate, Lubricants, Coarse grained model*

## Highlights

In an ionic liquid sheared between solid surfaces, the viscous heat produced is higher at the middle point which induces temperature, density and viscosity gradients inside the film.

## Resumo/Abstract

Ionic liquids (ILs) are defined as salts with melting point below 100ºC. Due to their good adhesion, great thermal stability, low vapor pressure and high viscosity index, there is great interest in the possible application of ILs as lubricants and as additives to traditional lubricants. In these applications, the liquid film between the solid surfaces can be of only a few nanometers thickness, which results in very high shear rates even at moderate operating speeds. Also, the confinement between two surfaces may affect the liquid structure and render physical properties different from the expected from the bulk. To study how confinement and the shear resulting from the movement of the solid surfaces affects the structure and the viscosity of ILs, molecular dynamics simulations were performed using a coarse-grained model for the IL 1-butyl-3-methyl-imidazolium tetrafluoroborate, [BMIM][BF4], based on the Martini 3.0 force field with adjustments to reproduce both the zero shear viscosity and the shear thinning behavior of the IL, as described in our recent work http://dx.doi.org/10.1039/D1CP05692A, confined between two solid surfaces perpendicular to z direction. After an initial relaxation, simulations were performed by inducing the movement of the two surfaces into opposite directions with different velocities, thus producing a shear stress over the IL. The thermal bath was applied only to the solid surfaces, allowing the liquid temperature to increase due to the viscous heating. The resulting shear rate was not homogenous, but higher in the middle point between the surfaces, which renders a higher temperature increase in the middle of the simulation box than close to the surfaces. This results in density and viscosity gradients along the direction perpendicular to the surface as shown in Figure 1 with a reduction of the viscosity due to the heating in addition to the shear thinning behavior of the IL.

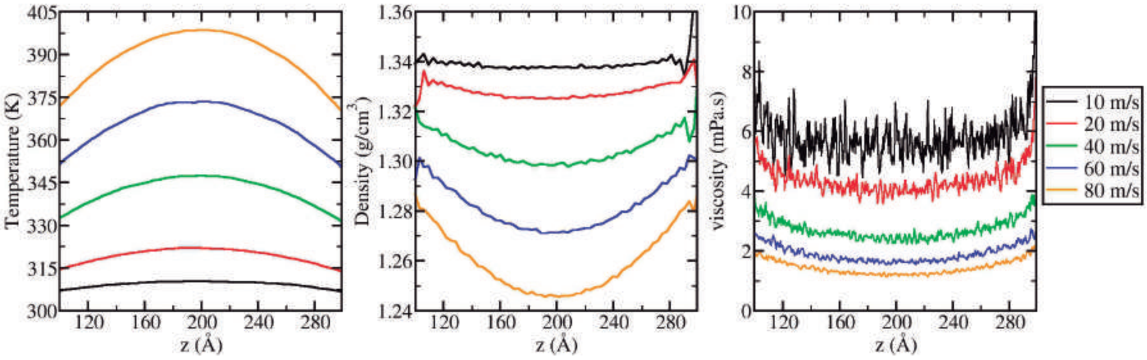

**Figure 1** - Variation of ionic liquid temperature, density and viscosity in the direction perpendicular to the surfaces at different surfaces movement speed.

## Agradecimentos/Acknowledgments

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**Área: ______TEO________**

# Structure and Solvation of CuF, $CuPF_6$, AgF and $AgPF_6$ in Acetonitrile Solvent: CPMD, QM/MM and Cluster-Continuum Study

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Palavras Chave: *Car-Parrinello Molecular Dynamics, single-ion solvation, copper catalysis, fluorination, quantum mechanics/molecular mechanics*

## Highlights

$CuPF_6$ and $AgPF_6$ exist as free ions, and both Cu(I) and Ag(I) ions have tetracoordinated acetonitriles.

CuF exist as an ion pair, tricoordinated $CuF(CH_3CN)_2$ species in acetonitrile.

AgF forms both $AgF(CH_3CN)$ and $AgF(CH_3CN)_2$ species.

## Abstract

Copper(I) has been investigated as a catalyst for fluorination of aryl halides using fluoride source such as AgF, CsF and KF. In special, copper(I) ions in acetonitrile are able to promote the catalysis with AgF. However, the mechanism has not been elucidated yet. The mechanistic possibilities involve the solvated $Cu^+$ ion and the CuF ion pair. In this work, the structure of these species and also of $Ag^+$ and AgF in acetonitrile solvent was investigated by Car-Parrinello Molecular Dynamics (CPMD), QM/MM (CuF only) and cluster-continuum approach. The CPMD and QM/MM methods point out that $Cu^+$ is tetracoordinated and CuF is tricoordinated, forming $CuF(CH_3CN)_2$. The $Ag^+$ ion is also tetracoordinated, and AgF exists as $AgF(CH_3CN)$ and $AgF(CH_3CN)_2$ species. The calculated solvation free energy of $Cu^+$ and $Ag^+$ by the cluster-continuum approach (Figure 1) are in agreement with experimental data, and also point out tetracoordinated species. On the other hand, CuF and AgF are predicted to be dominated by a single acetonitrile coordination, suggesting that the second acetonitrile is less bound to the central metal ions. Our calculations also point out that the process $Cu^+ + AgF \rightarrow CuF + Ag^+$ involving in solution species is viable, indicating that CuF could be the active species in copper catalyzed fluorination.

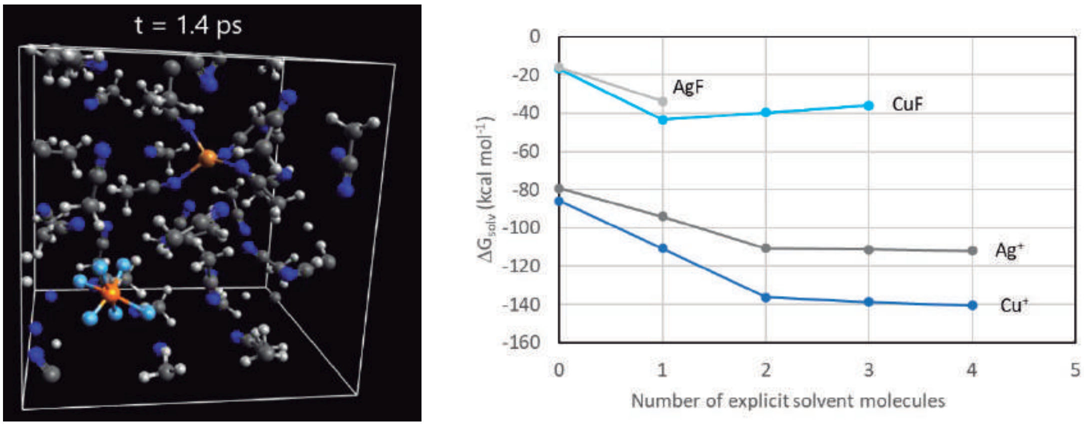

**Figure 1:** Snapshot of the $CuPF_6$ in solution and cluster-continuum calculation of the $\Delta G_{solv}$.

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# Theoretical Investigation of the Mechanism of Acid-catalyzed Dehydration of Pyrazol-4-ol in Methanol Solution

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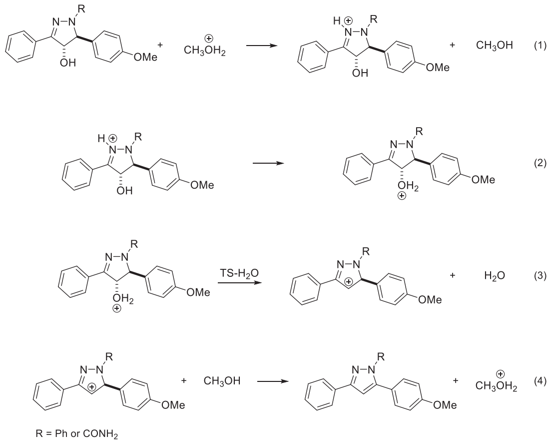
Keywords: *pyrazol-4-ol, acid catalysis, DFT, solvent effect.*

## Highlights

Theoretical calculations explain the reasons for carboxamide-pyrazol-4-ol to be unstable in acid medium.

## Abstract

Pyrazoles and their derivatives are an important class of heterocyclic compounds, which has raised in recent years in the development of new drugs.[1] In this work, the synthesis of several derivatives of pyrazol-4-ols conducted in acid methanol solution was effective except for carboxamide-pyrazol-4-ol, which has decomposed via a dehydration reaction, leading to pyrazole. In order to understand the origin of this instability, a theoretical investigation of the mechanism of the acid-catalyzed dehydration of carboxamide-pyrazol-4-ol and phenylpyrazol-4-ol was conducted using DFT methods and SMD solvation model. In our proposal, as shown in Scheme 1, the mechanism starts with protonation in the nitrogen atom of the ring, and the proton can migrate to the hydroxyl group, allowing this charged species to decompose via water elimination and formation of a carbocation. This carbocation quickly loses a proton to the solvent, forming the pyrazole. An analysis of the free energy profile allows a better understanding of the mechanism for each species. As presented in the free energy profile (Figure 1), the protonation of the nitrogen atom in the ring forms a much more stable species for phenylpyrazol-4-ol than for carboxamide-pyrazol-4-ol. As a consequence, there is an effective barrier of 16.7 kcal mol$^{-1}$ for carboxamide-pyrazol-4-ol and 20.4 kcal mol$^{-1}$ for phenylpyrazol-4-ol. Therefore, carboxamide-pyrazol-4-ol dehydration takes place in a higher reaction rate than for phenylpyrazol-4-ol, which justifies the experimental observations.[2]



**Scheme 1**: Steps of dehydration mechanism.

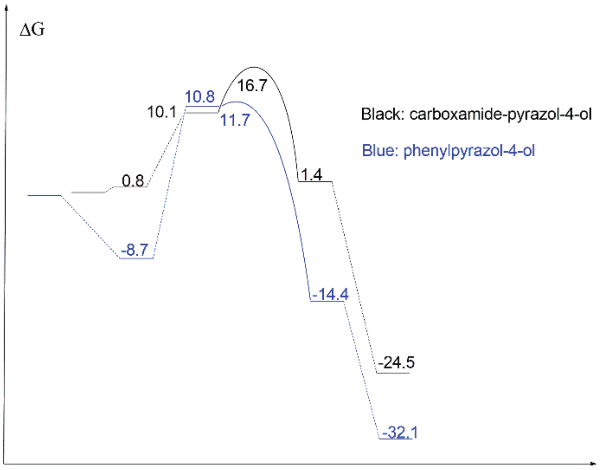


**Figure 1**: Free energy profile for pyrazol-4-ol dehydration.

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**Área: TEO**

# The Quantum-Size Effects on the First Dehydrogenation of $CH_4$ on 3d $TM_n$ (TM = Fe, Co, Ni, Cu where *n* = 4 - 15) Clusters: DFT Combined with Data Mining

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key-words: *Methane, Dehydrogenation, DFT, Data Mining, Quantum-Size effects.*

## Highlights

The quantum-size effect does not play a crucial role in the adsorption sites on the $TM_n$, but the QSE do play a crucial role for weakly adsorbed (physisorbed), particularly at a small size-scale (n < 6).

## Abstract

The goal of becoming a society not exclusively dependent on oil could be reached by the new processes for recycling natural gas. Those processes have been proved to be a potential alternative for this transition, since it has about 90% of methane ($CH_4$) in its composition. Besides that, the conversion of $CH_4$ into methanol could only be obtained using catalysts. Knowing that, various studies are exploring materials as catalysts. Analyzing those studies, the most viable material used is based on transition metal, specifically 3d metal, because of his low cost compared with the others, furthermore, it has been used industrially around the world in Fischer-Tropsch synthesis as $Ni/Al_2O_3$ and $Cu\text{-}ZnO/Al_2O_3$. However, it is hard to reach the knowledge of the atomistic structure of the catalysts, in particular, sub-nanoclusters. Therefore, in this work we investigated the dependence of the cluster size *n* in the first step of methane dehydrogenation on 3d $TM_n$ (TM = Fe, Co, Ni, and Cu where *n* = 4 - 15) through an *ab initio* DFT (PBE/vdW correction/*light-tier 2*) approach by using the FHI-aims package, combined with the unity bond index-quadratic exponential potential (UBI-QEP) approach and data mining (Spearman rank correlation, clustering). We found via clustering techniques that quantum-size effects (QSE) or the chemical species, TM, do not affect the adsorption modes (geometric orientation of the molecules) of $CH_4$, $CH_3$, $CH_3$+H, and H on the $TM_n$ clusters. Conversely, QSE plays a crucial role in modulating the magnitude of the adsorption energy, reaction energy, dissociation energy, and activation energy, in particular, for $Cu_n$ clusters due to the unpaired electron for clusters with odd number of electrons and weakly adsorbed (physisorbed), particularly at a small size-scale (*n* < 6). Through the UBI-QEP approach, we found small activation energy barriers for $Fe_n$ and larger for $Ni_n$ clusters, *i.e.*, QSE can be explored to tune energy barriers. Through the UBI-QEP and Spearman rank analysis, we could not identify a general trend due to the quantum-size effects that correlates activation energy with the adsorption and dissociation energies for the studied systems, but we found thermodynamic and kinetic parameters present strong dependence with the $TM_n$ size.

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**Área: TEO**

# Water hydrogen-bonding effects on the ground and low-lying excited states of dipyridyl isomers

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Palavras Chave: *Dipyridyl isomers, Interconversion, Photoabsorption, Solvation effects, Photoinduced degradation.*

## Highlights

All isomers presented excited electronic states that are both bright and energetically accessible when in solvation.
Photoabsorption is enhanced due to $H_2O$-dipyridyl hydrogen-bonding interactions.

## Resumo/Abstract

In this work, we examined the ground and low-lying excited states of six dipyridyl isomers (2,2′-dipyridyl, 2,3′-dipyridyl, 2,4′-dipyridyl, 3,3′-dipyridyl, 3,4′-dipyridyl, and 4,4′-dipyridyl), emphasizing the effects that solvation (water) molecules have on properties such as ground state equilibrium structures, relative energies in terms of conformations and transition states (regarding possible cis-trans interconversions), vertical excitation energies (VEs), generalized oscillator strengths (GOS), and excited state structures. Density functional theory (DFT) and its time-dependent formalism (TD-DFT) were used for determining all the ground state and excited state properties, respectively, both being employed with the CAM-B3LYP[1] exchange-correlation functional and the cc-pVTZ[2] basis set. In addition, effects caused by interactions with the solvent environment were probed by means of using two different approaches: i) the integral equation formalism polarizable continuum model (IEF-PCM)[3] and ii) a composite solvation model (CSM) through the incorporation of explicit water molecules in combination with the IEF-PCM. All computations were performed using the Gaussian 09[4] suite of software.

In general, a decrease in the relative energies regarding a given trans/cis counterpart is noticed when solvation is considered independently from the model used; all the dipyridyl cis/trans isomers became (practically) isoenergetical due to dipyridyl-$H_2O$ hydrogen-bonding interactions. Moreover, the interconversion barriers were also found to be lowered due to solvation effects. For instance, the energy barrier in terms of interconversion of the trans 2,2′-dipyridyl to the cis 2,2′-dipyridyl was determined as (approximately) 67% of the corresponding value obtained in the gas-phase. Although no major differences regarding the values of the VEs associated to a bright state are suggested from the comparison between the results obtained for a given isomer through the consideration of solvation and those corresponding determined in the gas-phase, the GOS are all increased when solvation is considered, suggesting an enhancement in the photoabsorption of all the isomers when in presence of solvent. In addition and in contrast to what was seen previously[5] in the case of the gas-phase, 4,4′-dipyridyl presented a bright state among the five lowest-lying excited singlets (accessible at the UVC energy region), which is located at 5.49 eV (with GOS = 0.4465) at the TD-DFT/CAM-B3LYP/cc-pVTZ level of theory in water (IEF-PCM) and at 5.47 eV (with GOS = 0.5331) at the same level of theory with the CSM. Given that no significant change was noticed in the optimized structures for the excited states, it is possible to infer that all the compounds will decompose through photo decomposition (chemical reaction occurring in the excited state) rather than direct photolysis when in solution.

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