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Determinação de elementos essenciais, não essenciais e potencialmente tóxicos em frutas da região amazônica por ICP OES

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Sara Teixeira [1]; Mariane Gama Nabiça [2]; Patrícia de Oliveira Nunes [3]; Kelly G. Fernandes Dantas [3]
[1] QUÍMICA / ICEN / Universidade Federal do Pará; [2] PPGQ / ICEN / Universidade Federal do Pará; [3] Instituto de Ciências Exatas e Naturais / Universidade Federal do Pará

A Amazônia brasileira apresenta uma diversidade de frutas comestíveis com cerca de 220 frutos. Nos últimos anos, o interesse por essas frutas nativas têm aumentado, principalmente devido à busca incessante por novos produtos e sabores exóticos. No entanto, devido à ampla biodiversidade amazônica, muitas frutas típicas são inexploradas e suas características químicas são indefinidas. Do ponto de vista nutricional e toxicológico, estudos que envolvem a composição química de alimentos são de extrema importância. Sendo assim, neste estudo a determinação de elementos essenciais (Ca, Na, Fe, K, Mg, Mn, Se e Zn), não essenciais (Al, Ba, Sr e Ti) e potencialmente tóxicos (As, Cd, Sb e Pb) em amostras de bacuri, biribá, cacau, muruci, tapereba e tucumã por espectrometria de emissão óptica com plasma acoplado indutivamente (ICP OES) foi proposto. As amostras 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-1. A exatidão do procedimento de preparo de amostra e das medidas por ICP OES foram avaliadas pelo método de adição e recuperação do analito e as recuperações obtidas variaram de 85 a 113%. Os limites de detecção (LDs) foram de 0,02 mg kg-1 (Cd) a 11, 27 kg-1 (K). Os resultados obtidos mostraram que nas amostras de frutas, o elemento que apresentou o teor mais elevado foi o K (5236,48 a 14568,04 mg kg-1), seguido por Ca (190,47 a 1952,37 mg kg-1), Mg (676,64 e 1637,92 mg kg-1), Na (5,17 a 236,53 mg kg-1), Fe (6,93 a 60,05 mg kg-1), Zn (3,79 a 25,83 mg kg-1), Mn (1,51 a 16,35 mg kg-1), Ba (5,17 a 236,53 mg kg-1), Sr (0,79 a 11,64 mg kg-1) e Cd (0,041 a 0,067 mg kg-1). Al, As, Pb, Sb, Se e Ti em todas as frutas estudadas estavam abaixo do limite de detecção. Além disso, os teores de Ca, Fe, Mg, Mn, K, Na, se e Zn não excederam os valores da ingestão alimentar recomendada (IOM, 2011; IOM, 2001) e a avaliação do percentual de contribuição nas frutas (0,1% a 95%) revelou que esses alimentos podem ser considerados como ricos ou fonte desses minerais para a dieta humana (ANVISA, 2019). Sendo assim, este estudo apresentou resultados que ampliam o conhecimento sobre a composição elementar das frutas da região amazônica e serão úteis e de interesse na área nutricional e toxicológica.

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Catálise - CAT

Cobalt and phosphine oxides: A successful partnership

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Fábio Godoy Delolo [1]; Ji Yang [2]; Johannes Fessler [2]; Helfried Neumann [2]; Kathrin Junge [2]; Christoph Kubis [2]; Eduardo Nicolau dos Santos [1]; Elena Vitalievna Goussevskaia [1]; Matthias Beller [2]
[1] Universidade Federal de Minas Gerais; [2] Leibniz-Institut für Katalyse e.V

In the presence of phosphine oxides, cobalt-based catalysts can act beneficially in hydroformylation reactions of olefins and epoxides, reductive etherification, expansion and opening of oxetane rings. These transformations take place under mild conditions compared to traditional processes. The presence of phosphine oxides dramatically improves the pre-activation of the cobalt precatalyst, saving time and energy. The developed system proved to be efficient in the synthesis of aldehydes, 1,3-diols, unsymmetrical ethers, oxetanes and alcohols. Particularly in the hydroformylation of olefins and epoxides, as well as the synthesis of unsymmetrical ethers, a wide range of products have been successfully prepared, including substrates containing diverse functional groups. Although in some cases one of the components in the synthesis gas (mixture of CO and H2) is not incorporated into the substrate, its role in the formation and stabilization of catalytically active species was evidenced by control experiments. In addition, anisole, a solvent with a high degree of sustainability, can be used to advantage in such processes matching efficiency and sustainability.

Cobalt Ferrites: structure and photoactivity.

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Fabiano Praxedes [1]; Maria Cecília Meneguette Ferreira [1]; Marcos Nobre [2]; Silvania Lanfredi [3]
[1] Instituto de Biociências, Letras e Ciências Exatas / Universidade Estadual Paulista "Júlio de Mesquita Filho"; [2] Física / Faculdade de Ciências e Tecnologia / Universidade Estadual Paulista "Júlio de Mesquita Filho"; [3] Química e Bioquímica / Faculdade de Ciências e Tecnologia / Unesp (Universidade Estadual Paulista)

Catalysts based on ferrite have shown promising for environmental remediation through photocatalysis [1]. The magnetic property of this class of materials allows easy recovery of the aqueous medium by the simple application of a magnetic field [2]. However, the structural relation and photoactivity of cobalt ferrite are still not clear, since cobalt ferrite can be stabilized in two distinct structures (normal or inverse spinel), remaining with the same stoichiometry [3]. Therefore, this work aims to investigate the photocatalytic property of cobalt ferrites and their correlation with the spinel structure. Cobalt ferrite powders were synthesized by the co-precipitation method, varying the cobalt concentration between 0.4 and 1.2 mol. The morphology of the nanoparticles was analyzed by Scanning Electron Microscopy, which indicated the presence of nanoparticle clusters. Structural characterization, carried out by X-ray diffraction, indicated the formation of single-phase cobalt ferrite powders in a spinel-like structure with cubic symmetry Fd-3m. The structural refinement showed an evolution of the inverse spinel structure to normal one with the increase in the concentration of Co2+. However, the concentration above 1 mol showed that cobalt starts to occupy both the octahedral and tetrahedral sites, favoring the normal spinel structure. The band gap energy, determined by Diffuse Reflectance Spectroscopy in the UV-Visible region, showed value of ca. 1.9 eV. The photoactivity of the powder (0.1 g) was evaluated by photodegradation of the dye rhodamine 6G (10.4 [illegible]mol L-1) under UV-Visible light. The photocatalytic degradation of the dye rhodamine 6G, with cobalt ferrite nanoparticles, followed the pseudo-first order reaction with a maximum apparent rate constant of 10.23x10-3 for $CoFe_2O_4$. The photoactivity of cobalt ferrites showed to be strongly influenced by the tetrahedral and octahedral sites of the spinel structure. The displacement of cobalt from the octahedral site to the tetrahedral site, with increasing cobalt concentration, favors the migration of photogenerated electrons. However, the concentration above 1 mol of cobalt, leads to the occupation of both octahedral and tetrahedral sites by cobalt, decreasing its photocatalytic activity.

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Hidroaminometilação para a síntese de aminas a partir de hidroxiolefinas

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Adelson de Oliveira Dias [1]; Jesus A. A. Villarreal [1]; Fábio Godoy Delolo [2]; Elena Vitalievna Goussevskaia [1]; Eduardo Nicolau dos Santos [1]

[1] Universidade Federal de Minas Gerais / Instituto de Ciências Exatas / Departamento de Química; [2] Universidade Federal de Minas Gerais

The hydroaminomethylation (HAM) is a tandem catalytic process involving four reagents: an alkene, an amine, carbon monoxide and hydrogen. The HAM process consists in three sequential reactions: first, the hydroformylation step in which an alkene reacts with carbon monoxide and hydrogen to give an aldehyde, then the condensation of the aldehyde with amine to give enamine or imine and, finally, the hydrogenation of the enamine resulting in a new amine. It is important to note that the HAM process perfectly aligns with the precepts of green chemistry. HAM allows to perform several chemical reactions in a single procedure in the same reactor with high selectivity to the product amines.
Amines represent a class of essential intermediates in the synthesis of drugs, agrochemicals, surfactants, and other fine chemistry products. Despite the various methods available, the direct synthesis of amines is difficult due to the large number of by-products formed and the need for protection and deprotection steps. In this work, using the HAM process, it was possible to synthesize several structurally complex amines with potential biological activity starting from biorenewable low-cost substrates. HAM reaction was applied to several hydroxyolefins (allylic and homoallylic alcohols), such as linalool, nerolidol, isopulegol and isoprenol. Several amines, such as 4-methylpiperidine, morpholine and 1,2,3,4-tetrahydroisoquinoline, were used as counterparts. $[Rh(COD)(OMe)]_2$ was used as a catalyst precursor and triphenylphosphine, tributylphosphine, tricyclohexylphosphine and tris(2,4-di-tert-butylphenyl) phosphite as auxiliary ligands. Reaction parameters (catalytic precursor/ligand ratio, temperature, ligand nature, catalyst concentration and CO/H_2 mixture pressure) were optimized to achieve high yields for the target products.
Several new amines were synthesized in a single one-pot procedure. In the absence of phosphorus ligands (unpromoted system) using high ratios of H_2 in the CO/H_2 mixture, the catalyst was effective in the hydrogenation of enamine, enabling to obtain linear amines as final products in good yields. As phosphorous ligands are known to stabilize the rhodium catalyst and facilitate its recycling, promoted catalytic systems were also developed to synthesize linear amines. In particular, in the systems with tricyclohexylphosphine, the hydrogenation of enamine becomes specially effective, enabling for the excellent yields of linear amines that can reach 99% depending on the substrate and initial amine nature.

On the other hand, we have found that certain phosphorus ligands inhibit the hydrogenation of the intermediate enamines, allowing to obtain in excellent yields cyclic amines as final products. The formation of these cyclic amines occurred through the intramolecular cyclisation of the enamines before their hydrogenation. Thus, the developed method offers a convenient access to two different groups of amines (linear and cyclic). It is important that the selectivity control can be performed by a simple change in the nature of the auxiliary phosphorus ligand.

Líquidos iônicos à base de triazol funcionalizados com OH como catalisadores eficientes de componente único, bifuncionais, sem metal e sem solvente para fixação de CO2

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Álvaro Farias Arruda da Mata [1]; Rafael Pavão das Chagas [1]; Jorge Luiz Sônego Milani [2]; Adilson David da Silva [2]; Pedro Henrique Fazza Stroppa [2]; Nicolas Glanzmann [2]
[1] Universidade Federal de Goiás; [2] Universidade Federal de Juiz de Fora

Carbon dioxide is the most abundant waste generated by anthropological processes. Its concentration in the atmosphere steadily increases, reaching 30 Gton.y-1; becoming a major environmental concern as it is primarily responsible for adverse global climate changes. In recent decades, the use of CO2 as a renewable feedstock has received attention from chemists to capture and transform it into high value products.

A series of HO-functionalized triazoles ionic liquids (1-10b) bearing different alkyl chains and counter-anions were evaluated as green, single component bifunctional catalysts for cycloaddition reaction of CO2 to epoxides. Ionic liquids 1-10b were all able to convert, selectively, PO into propylene cyclic carbonate (PCC), under the conditions described in Table 1.

These experiments motivated us to perform upscale reaction using 5b/PO (500 mmol) using 0.075 mol % of ionic liquid system which showed the highest TOF of this work (429 h-1) and 32 % of conversion at 1-hour reaction, increasing the reaction time to 10 hours, it was obtained 88 % of PC with TON = 1170 and TOF = 117 h-1, what shows that our cheap, easy to handle and easily synthesized catalyst is very active even in long periods and in very small catalytic loads compared to other organocatalysts. In optimal reactional conditions (25 mmol of epoxide, 140 °C, 30 bar of CO2, 1 hour), high conversions for a series of terminal epoxides were achieved using catalyst 5b. Moreover, the reaction using cyclohexene oxide achieved 85 % of conversion in only 6 hours.

In summary, HO-functionalized triazole-based ionic liquids are efficient single component, bifunctional, metal-free and solvent-free catalysts for CO2 fixation, presenting outstanding conversions, even in scale-up experiments

Metal-contaminated pyrolisis biochars as catalysts for furfuryl alcohol synthesis from furfural

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Thiago de Melo Lima [1]; Vinicius Gomes da Costa Madriaga [1]; Vinicius Rossa [2]; Joao Pedro Reys de Mattos [3]; Sancler Vasconcelos [4]; Eric T. Shimbakuro [1]; Luanne E. M. Ferreira [1]; Gilberto Alves Romeiro [1]; Ricardo Cassella [1]; Fabio Passos [1]

[1] Universidade Federal Fluminense; [2] Universidade Federal de Uberlândia; [3] Departamento de Engenharia Química e de Petróleo / Universidade Federal Fluminense; [4] Instituto de Química / Universidade Federal Fluminense

Two biochars were obtained from centrifuged sewage sludge (CLC) and non-centrifuged sludge (CLETE) by pyrolisis at 380°C (yield of 68% for both materials). The thermogravimetric characterizations showed ash contents of 58% and 65% due to the inorganic fraction in these materials.1 Atomic Emission Spectroscopy confirmed the presence of several metals in the biochars, highlighting Al and Fe that were found in higher concentrations (8.0% and 4.8% for CLETE and 4.3% and 4.5% for CLC, respectively). The samples also were evaluated by X-Ray Diffraction analysis, which indicated that these metals were mostly present as oxides. The organic portion was characterized by infrared spectroscopy and the characteristic bands for hydroxyl groups (3200 cm-1), Aromatic C=C stretch (1510 cm-1) and C-O stretch (1020 cm-1) were found, confirming the sludge pyrolysis. Scanning electron microscopy coupled with X-ray dispersive analysis (Figure 1) exhibited similar wrinkled and porous structures for both materials, however, the surface compositions were different, as expected. For the CLC sample, higher concentrations of aluminum (11%) and silicon (15%) were observed, while CLETE presented higher iron content (45%). Table 1 shows the acidity (by Pyridine-infrared and thermogravimetric analysis) and catalytic results (by Gas chromatography-Mass spectrometry). The CLETE biochar exhibited higher Brønsted and Lewis acidities and also presented higher furfural conversion. However, CLC presented a higher selectivity for furfuryl alcohol (FA) although its lower acidity. Other products, such as isopropyl furfuryl ether (PMF), furfuryl ether (DFE), and isopropyl furfuryl ester (IPF) were also formed, especially for CLETE, which explains the lower FA selectivity.2,3 Thus, these materials were suitable for furfural conversion to obtain not only furfuryl alcohol but also other valuable-added products.

Produção do bio-óleo a partir da pirólise de diferentes biomassas

https://proceedings.science/p/138791

Nehander Carlos Felisberto [1]; Luiz Eduardo Pizarro Borges [1]; Fabio Bellot Noronha [2]

[1] Instituto Militar de Engenharia; [2] Instituto Nacional de Tecnologia

Currently, the challenge of supplying energy needs efficiently and without causing irreparable damage to the environment has stimulated the search for alternative and renewable fuels. In this context, biomass is considered a material differentiated by being able to generate heat and energy directly by burning, as well as being used in the production of substitutes for petroleum products, as well as raw material for the chemical industry. In this work, the pyrolysis of açaí seed residues, eucalyptus and pine was studied in the production of different bio-oils, focusing on the yields and quality of the bio-oils generated. The pyrolysis technique aims to obtain products with higher energy density and better properties than the initial biomass. The yield and distribution of products during pyrolysis depends on parameters such as final temperature, heating rate, residence time, pressure used, biomass particle type and size, reactor type and process configuration [1]. To carry out the pyrolysis, the pine and eucalyptu were pyrolyzed with a particle size of approximately 5 x 5 x 2 mm and the açaí seeds was used as received. The residues of the three biomasses were pyrolyzed separately at a temperature of 450°C in

an autoclave reactor with a nitrogen flow of 20 ml/min and a heating rate of 10°C/min. The main products obtained during the pyrolysis of the three biomasses were bio-oil (liquid), coal (solid) and a gaseous fraction. The liquid fractions obtained from the three biomasses are similar and are composed of a complex mixture of hydrocarbons, with the presence of oxygenates and aromatics. The main signs in the FTIR (FIG. 1) were the elongation of the O–H group (3300–3390 cm−1), oxygenated functional groups such as aldehydes, ketones, carboxylic acids C=O (1630–1710 cm−1) and aromatic bonds of C=C (1500–1600 cm−1) [2]. In the operational conditions used, the eucalyptus biomass presented the highest yield in liquid, reaching 65%, while the biomasses of pine and Açai seed presented yields of 58% and 55% in liquid product weight, respectively. The results also indicated the formation of 25 to 33% by weight of solid coal and 9 to 12% by weight of non-condensable gases. These results are in agreement with what has been reported in the literature [1,2]. 1. BRIDGWATER, A. V. et al. Biomass and Bioenergy. v. 38, p. 68–94, 2012. 2. Li, H. et al. Energy Conversion and Management. v. 98, p. 81–88, 2015

Eletroquímica e Eletroanalítica - ELE

Changes in the catalytic activity of Pd nanoparticles induced by hybrid carbon-oxide supports

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Thayna Pereira de Araújo [1]; Hebe de las Mercedes Villullas [1]; Gabriel Martins de Alvarenga [1]

[1] Universidade Estadual Paulista "Júlio de Mesquita Filho" - Campus Araraquara

The catalytic activity of metal nanoparticles usually depends on properties, such as structure, shape and size, while for supported catalysts metal-support interactions can also have significant effects. In this work, a study of the effects of supports containing oxides on the activity of Pd nanoparticles for the methanol oxidation reaction (MOR) in alkaline medium was carried out. Hybrid carbon-oxide supports C-MOx were prepared using four different oxides (MOx = CeO2, SnO2 Co3O4 and Fe3O4) keeping the amount of oxide in 20 wt.%. In order to evaluate the influence of the support, it is important to ensure that the properties of the metal particles are the same. For that, Pd nanoparticles were prepared in a colloidal state in a liquid two-phase system containing oleic acid and oleylamine as protecting agents. Then, fractions of the same colloidal suspensions were supported on the hybrid C-MOx supports. For comparison purposes, a Pd/C catalyst was prepared by the method. The Pd load was 20 wt.% in all materials. The catalysts were used in the form of ultrathin layers, which were obtained by depositing an ink of the material suspension on a glassy carbon disk. The electrochemical behavior was initially characterized in acid medium and cyclic voltammetry experiments were performed for different high potential limits to determine the potential of completion of a PdO layer, which was, in turn, employed to evaluate the electrochemically active area of Pd. The MOR activity was evaluated by cyclic voltammetry and chronoamperometry in argon-saturated 0.5 M methanol in 0.1 M NaOH solution. It was observed that MOR activity of Pd nanoparticles is significantly affected by the oxides in the C-MOx hybrids, increasing in the sequence of C-SnO2 < C < C-CeO2 < C-Fe3O4 < C-Co3O4. These activity variations that result from metal-support interactions can be interpreted in terms of the formation of oxygenated species on the oxide surface that can facilitate the oxidation of reaction intermediates (bifunctional effect) or as associated to changes in the electronic properties of the metal, which could alter the strength of adsorptions on the Pd surface.

Development of high-performance SnO2 gas diffusion electrodes for CO2 reduction to formic acid in a flow cell

https://proceedings.science/p/138844

Osmando Ferreira Lopes [1]; Ilias Stamatelos [2]; Marcelo Carmo [2]; Meital Shviro [2]
[1] Universidade Federal de Uberlândia; [2] Low-temperature electrolysis / Electrochemical Process Engineering (IEK-14) / Forschungszentrum Jülich

CO2 electrochemical reduction reaction (CO2RR) to formic acid (HCOOH) is an attractive strategy to address both environmental and energy issues such as mitigate the CO2 emission and generates a key intermediate renewable chemical feedstock as well as a potential fuel for direct formic acid fuel cell. However, CO2 presents a high thermodynamic stability and low solubility in aqueous electrolyte, then the productivity is often limited by CO2 diffusion through a liquid electrolyte to the surface of the catalyst. Here, we developed a SnO2-based gas diffusion electrode by spray-coating to be applied in an alkaline flow-cell, where the CO2 can be fed directly through the electrode in the interface electrode/electrolyte to overcome the CO2 solubility issue. Carbon black and Sustainion® ionomer developed a key role in the GDE's conductivity and SnO2 particles distribution, respectively. The SnO2 loading and thickness presented a great impact in the materials performance. The increase at KOH concentration up to 1.0 M improved both current density and selectivity for HCOOH formation, however a further increase at KOH concentration to 2.0 M resulted in a worst selectivity for HCOOH. The optimized GDE and CO2RR conditions exhibited a current density higher than 160 mA.cm-2 and HCOOH selectivity higher than 93%, this performance is much better than when applied SnO2 as electrode in a classical H-cell. The GDE prepared in the commercial carbon paper presented a poor stability under CO2 electrolysis conditions. On the other hand, when the GDE was prepared using PTFE membrane as substrate a stable electrochemical cell performance for more than 24 h was experimentally demonstrated at a current density higher than 100 mA cm−2 at -1.2 V vs RHE.

Disposable electrochemical platform based on reduced graphene oxide, iron nanoparticles and molecularly imprinted poly(pyrrole) for determination of vanillic acid in banana peels

https://proceedings.science/p/138840

Edervaldo Buffon [1]; Nelson Ramos Stradiotto [1]
[1] Instituto de Química / Universidade Estadual Paulista "Júlio de Mesquita Filho"

The banana is one of the most consumed fruits in Brazil, so that 98% of the national production is directed to the domestic market. However, the processing of this fruit generates a large amount of waste. For each ton of banana produced, approximately 4 tons of waste are generated, including peels, leaves and pseudo-stems1. Banana peels have a rich composition of phenolic compounds, such as vanillic acid (VA). This phenolic acid is the precursor of vanillin biosynthesis, which, in turn, is responsible for the vanilla aroma of several products in the food and pharmaceutical industry2. Therefore, within a biorefinery concept, these industries could reuse the VA contained in banana peels for higher added-value products. In this context, effective analytical methodologies are necessary to characterize these substrates. Thus, the objective of this work was to develop a portable, simple, sensitive, selective and low-cost electrochemical platform for the determination of VA in banana peel. The proposed sensor was based on a screen-printed carbon electrode (SPCE) modified with reduced graphene oxide (rGO), iron nanoparticles (FeNPs) and a molecularly imprinted polymer (MIP) of poly(pyrrole). For this, using a 0.50 mg mL-1 graphene oxide aqueous suspension containing 0.10 mol L-1 Na2SO4, the SPCE was modified with rGO through the application of -1.40 V until the charge of 1.0 mC was reached. Then, using a solution of 0.10 mol L-1 KCl containing 5.0×10-3 mol L-1 FeCl3, the SPCE/rGO electrode was decorated with FeNPs by applying -1.30 V until the charge of 5.0 mC was reached. For MIP preparation, 50 µL of a solution containing 3.0×10-2 mol L-1 pyrrole and 7.0×10-3 mol L-1 VA (PBS; pH 7.0) were placed on the SPCE/rGO-FeNPs electrode and electropolymerization was performed by applying three consecutive voltammetric cycles in a potential range of 0.60 to 1.20 V at 50 mV s-1. After the electropolymerization process, the electrode was inserted in a solution of ethanol-acetic acid (9:1; v:v) for 60 seconds to remove the VA template from the polymer matrix and obtain the SPCE/rGO-FeNPs-MIP electrode. This electrode was characterized by cyclic voltammetry, electrochemical impedance spectroscopy, scanning electron microscopy and energy dispersive X-ray spectroscopy. For the rebinding experiments, 50 µL of VA solutions in different concentrations (PBS; pH 6.0) were placed on the electrode for 10 minutes. Under optimized conditions, the developed method exhibited two linear ranges from 1.0×10-9 to 1.5×10-7 mol L-1, with limit of detection and limit of quantification calculated to be 3.1×10-10 mol L-1 and 1.0×10-9 mol L-1 (n = 3), respectively. The proposed device presented excellent selectivity for the VA molecule and was successfully applied in banana peel extract sample. The quantification of VA was performed using the standard addition method and the results obtained were validated by recovery assays, where values between 98.6 and 106.7% were found.

Electrochemical sensor based on carbon nitride nanosheets for selective determination of hydroxychloroquine in synthetic urine and drugs samples

https://proceedings.science/p/138839

Jonatas de Oliveira Souza Silva [1]; Mércia Vieira da Silva Sant'Anna [1]; Ava Gevaerd [2]; Jéssica Brito dos Santos Lima [1]; Michael Douglas Santos Monteiro [1]; Sanny Wedja Melo Machado de Carvalho [1]; Eliana Sussuchi [3]

[1] Universidade Federal de Sergipe; [2] Hilab; [3] Centro de Ciências Exatas e Tecnologia / Universidade Federal de Sergipe

Hydroxychloroquine (HCQ) has attracted the interest of scientists in the last two years, as its use in combating SARS-CoV-2 was being considered. Literature reports side effects linked to the use of HCQ [1], making it necessary to develop analysis methods for its monitoring. In this context, the use of nanomaterials [2], such as carbon nitride nanosheets (CNNS) in the modification of electrochemical sensors, provides an increase in the surface area and ease of electron transfers due to their properties [3]. In this study, a modified electrode with CNNS (CNNS/E) was developed for the selective determination of HCQ. The CNNS/E showed a great analytical performance (Fig. 1) for detection of HCQ, with the values obtained for limits of detection (LOD) and quantification (LOQ) of 0.16 nmol l-1 and 0.52 nmol l-1, respectively, being the lowest reported for electrodes. The method was successfully applied in the determination of HCQ in drugs and synthetic urine samples, with recovery values between 99.6% and 102.0%, and there was no significant variation (<10%) in the current intensity of the HCQ, when evaluated in the presence of concomitant species, highlighting the analytical importance of the developed sensor.

Evidência de reestruturação de superficial em nanopartículas de Pt-Rh/C e Pt-Rh-Ni/C aplicadas à reação de eletrooxidação de metanol

https://proceedings.science/p/138845

Stefany Domingos dos Santos [1]; Vinicius del Colle [1]; Nelson Alexandre Galiote [2]; Germano Tremiliosi [3]; Giancarlo Richard Salazar Banda [4]; Larissa Melo [1]; Katlin Ivon Barrios Eguiluz [5]; Caio Vinicius da Silva Almeida [6]

[1] Universidade Federal de Alagoas; [2] USP - São Carlos; [3] Universidade de São Paulo - IQSC; [4] ITP/UNIT; [5] Universidade Tiradentes; [6] Laboratório de Eletroquímica e Nanotecnologia, Instituto de Tecnologia e Pesquisa / Universidade Tiradentes / Universidade Tiradentes

In this work, evidence of the surface reconstruction of the Pt-Rh/C and Pt-Rh-Ni/C catalysts during the methanol oxidation reaction is provided. Pt-Rh/C and Pt-Rh-Ni/C nanoparticles were synthesized by a chemical reduction method using sodium borohydride as a reducing agent. Characterization by X-ray diffraction revealed distortions in the parameters of the Pt network for the Pt-Rh and Pt-Rh-Ni catalysts, due to the different atomic radii of the Rh and Ni substituents of the Pt atom in the alloy structure. Transmission electron microscopy analyzes indicate that the nanoparticles were distributed in island shapes, in clusters of various nanoparticles, with spherical shapes and particle sizes of 2-6 nm. Furthermore, the reorganization of catalyst surfaces due to methanol oxidation was detected. It was found that a reconstruction of the catalyst surface in all studied materials occurs due to the adsorption/oxidation of methanol and by-products, such as CO,1 and that the catalytic activity and stability for methanol oxidation was improved.

Laser induced graphene electrodes for simultaneous determination of uric acid and sodium nitrite.

https://proceedings.science/p/138842

Waleska Renata Pereira Costa [1]; Rodrigo Muñoz [1]; Raquel Gomes da Rocha [1]; Tiago Araújo Matias [1]; Eduardo Mathias Richter [1]; Alessandro G. da Costa Dias [1]; Guilherme de Lima Fernandes [1]

[1] Universidade Federal de Uberlândia

The laser-scribed graphene (LSG) has already demonstrated as highly sensitive (bio)sensors. These flexible electrodes with large electrochemical areas were produced using direct-write laser process on polyimide sheets. The UV laser source was adapted into a Hypercube CoreXY 3D printer. In view of this, this work aims to produce and characterize LIG electrodes for simultaneous determination of uric acid (UA) and nitrite. First, the electrode was characterized by Raman spectroscopy, with three absorption bands being observed in 1349 (band D), 1585 (band G) and 2694 cm−1 (band 2D) confirming the formation of graphene. The X-ray diffractogram of the electrode exhibited a peak centered on 2□ = 25.1o indicating a high degree of graphitization of the material [1]. The scanning electron microscopy (SEM) images showed that the laser treatment converted the polyimide into a porous graphene film (Fig. 1A), as confirmed by Raman. Moreover, a peak-to-peak separation (ΔEp) of 90 mV for the voltammetric response for the [Fe(CN)6]3-/[Fe(CN)6]4- couple was achieved. Electrochemical impedance spectroscopy was used to evaluate the resistance to charge transfer (Rct) when compared to commercially screen-printed carbon electrodes (SPCE). The Nyquist plot showed that the electronic transfer on LSG surface electrodes was significantly greater than SPCE. As a proof-of-concept, the LSG electrode was applied for simultaneous detection of UA and sodium nitrite. Using differential-pulse voltammetry and Britton-Robinson buffer (pH=3) as the supporting electrolyte, a linear range from 10

to 100 µmol L-1 and 10 to 70 µmol L-1, and detection limit values of 0.074 and 0.27 µmol L-1 were achieved for UA and sodium nitrite, respectively.
Figure 1. (A) SEM image of laser induced graphene electrodes. (B) Baseline-corrected DPV response curves for uric acid and sodium nitrite at different concentrations. The corresponding calibration curve for (C) uric acid. (D) and nitrite.
In conclusion, it is possible to state that LIG electrodes are efficient for the determination of uric acid and nitrite. The electrode fabrication is easily reproduced, affordable and can be extended to large scale production.
[1] Nature Communications volume 5, Article number: 5714 (2014), Laser-induced porous graphene films from commercial polymers, DOI: 10.1038/ncomms6714.

Uma fotobatéria de Zn-ar usando Cu2O-CuO como fotoeletrodo bifuncional

https://proceedings.science/p/138843

Bárbara Antunes Cunha Sá [1]; Tatiana Santos Andrade [2]; Márcio César Pereira [1]
[1] Universidade Federal dos Vales do Jequitinhonha e Mucuri; [2] Universidade Federal de Minas Gerais

Photoelectrochemical batteries (PEBs) are emerging as promising devices to both convert and store solar energy in a single device. Essentialy, a PEB is a hybrid device that combines a metal-air battery, such as zinc, with a photoelectrochemical cell. The discharging process occurs through the metal oxidation followed by O2 reduction at the photoelectrode. Meanwhile, the charging process occurs through electron-hole pair generation after the photo-activation of the photoelectrode. Thus, the holes oxidize a fuel while electrons move through the external circuit to reduce the metal. A PEB configuration can offer some advantages compared to conventional metal-air rechargeable batteries: to act more efficiently on the charging oxidation reaction, to reduce the charging bias using sunlight and to increase the battery open circuit voltage. However, to find a bifunctional photoelectrode that are able to act in both processes limits the performance and application of such devices. In this study, we have constructed a novel PEB composed by a bifunctional Cu2O-CuO photoelectrode using sulfite as fuel and zinc as the metal. The constructed photobattery was able to improve both the charging and discharging performance using sunlight. In the discharging, the system achieved a short circuit current 45% higher and a gain of 0.3 V in the open circuit voltage (Fig. A) while for the charging, there was a 0.3 V reduction which is about 7% of energy saving (Fig B). These results bring new perspectives to the development of more advanced photoelectrochemical batteries.

Ensino de Química - EDU

Análise do livro de Projetos Integradores de CN do PNLD, uma atividade didática baseada na proposta do Novo Ensino Médio e da BNCC

https://proceedings.science/p/139162

Luciana do Nascimento Rodrigues [1]; Lília do Espírito Santo Azevedo [1]; Paulo Rogerio Garcez de Moura [1]; Mari Inez Tavares [1]; Sandra Aparecida Duarte Ferreira [1]
[1] Universidade Federal do Espírito Santo, Brazil

O presente estudo de caso trata de uma pesquisa qualitativa1, teórico empírica apoiada em observações, anotações, análise de artigos e livros da área de ciências e ensino de química. O estudo foi realizado com cerca de 20 estudantes do 7º e 8º períodos da Universidade Federal do Espirito Santo, na disciplina de Estágio Docência I e II do curso de Licenciatura Plena em Química que ocorreu concomitante e excepcionalmente no modelo remoto em consequência da pandemia do Covid 19. Devido a impossibilidade de o estágio acontecer presencialmente, as atividades da disciplina tinham o objetivo de suprir algumas demandas não vivenciadas pelos estudantes a partir do modelo de oficinas, visando a aprendizagem colaborativa. A menos de um ano de sua obrigatoriedade, a Base Nacional Comum Curricular (BNCC) e o Novo Ensino Médio (NEM) serão uma realidade em 2022. Pensando nessa organização, as escolhas dos livros de Projetos Integradores (PI) foram realizadas pelas escolas públicas do Estado do Espírito Santo no mês de março de 2021. O livro de PI deve incentivar a criatividade e se basear em projetos a serem desenvolvidos paralelamente ao livro didático. Produtos didático-pedagógicos, os livros são elaborados seguindo algum critério teórico-metodológico, o qual pressupõe um perfil epistemológico de seu autor ou autores para atender a uma determinada clientela2. Os projetos devem ser adequados à realidade de cada sistema ou rede de ensino e da instituição escolar, considerando o contexto e as características dos seus alunos3. A atividade consistiu em analisar as treze obras de Ciências da Natureza (CN) listadas no Plano Nacional do Livro Didático (PNLD), enfocando os critérios (quadro 1) que devem ser facilitadores do trabalho do professor. Os estudantes foram organizados em sete duplas/trios, a fim de pontuar os critérios estabelecidos. Vídeo tutorial, manual e material didático do professor foram pontuados com 0 (não possui) e 1 (possui). Os demais critérios com 0 (não atende), 1 (atende parcialmente), 2 (atende totalmente). Após soma, responderam a um formulário onde identificaram a obra de maior pontuação, onde quatro dos sete grupos, escolherem o mesmo livro. As justificativas das escolhas foram categorizadas a posteriori e os números de registros transformados em uma nuvem de palavras (figura 1).

Os livros trazem 6 PI com diferentes abordagens e a intencionalidade de articular as habilidades e competências da BNCC com os objetos de conhecimento de CN, em especial da disciplina de química. Conhecimento prévio e protagonismo a partir da elaboração de protótipos, foram critérios importantes durante a escolha. A ABP foi a metodologia mais citada, pautada em projetos atuais e interdisciplinares visando a sustentabilidade e o acompanhamento do desenvolvimento da aprendizagem do aluno. “Essa atividade foi muito significativa para nossa formação. Trabalhamos as propostas da BNCC, do NEM e os aspectos importantes na escolha do livro didático que é uma das bases para o andamento dos processos de ensino e aprendizagem”. Nesse cenário plural proposto pela nova Base, é necessária a articulação entre os diversos saberes, sem que se perca a identidade de cada componente curricular.

Aspects of the trajectory of the USP Graduate Program on Science Education

https://proceedings.science/p/138925

Caian Cremasco Receputi [1]; Daisy de Brito Rezende [2]

[1] Universidade de São Paulo; [2] Departamento de Química Fundamental / Instituto de Química / Universidade de São Paulo

Este trabalho apresenta quatro dos temas identificados (Quadro 1) em um estudo acerca da criação, em 1973, do PIEC-USP e sua trajetória em que se utilizou o referencial teórico-metodológico da História Oral (MEYHI, 2005), por privilegiar as narrativas dos colaboradores como aspecto central da investigação. Entrevistaram-se cinco docentes, orientadores do PIEC, vinculados ao Instituto de Física da USP (IF-USP), que participaram da trajetória inicial do Programa. Analisaram-se as transcriações (CAMPOS, 2013) das entrevistas gravadas na perspectiva da Análise Paradigmática dos Dados (MORIÑA, 2017) obtendo-se resultados que mostram que o PIEC foi criado em um contexto de mudança internacional de Políticas Educacionais, sob forte influência do Physical Science Study Committee (PSSC), ancorado em pressupostos cognitivistas. Estas características influenciaram tanto os primeiros trabalhos desenvolvidos no âmbito do programa como as relações engendradas. Houve resistência à criação do PIEC no IF-USP, como sugere a criação tardia, em 2009, do curso de doutorado.

BufferLator: Produção de ambiente virtual e cálculo de sistemas tamponantes

https://proceedings.science/p/139159

Rafaela Sant'Anna [1]; Francisco Bustamante [1]; Anderson Fortunato [1]; João Romano [1]; Juliana Godinho [1]; Pedro Nunes [1]; Matheus Lessa [1]

[1] Instituto Federal de Educação, Ciência e Tecnologia do Rio de Janeiro

Estudantes de diferentes níveis de ensino, normalmente possuem notável dificuldade de aprendizado quanto aos conceitos e contas que permeiam as disciplinas de química, biologia e matemática. Um exemplo de tema interdisciplinar que abrange as áreas mencionadas é o conceito de solução tampão. Em parte dos casos, ocorre um desamino oriundo da falta de compreensão do tema e os estudantes acabam apenas memorizando fórmulas e definições, sem absorver os conteúdos necessários para uma aprendizagem robusta, que consequentemente é mais eficiente.

A fim de minimizar alguma deficiência conceitual remanescente por parte dos discentes e do público que trabalha em indústrias e laboratórios, o projeto visa a criação de uma plataforma online e interativa, onde os usuários possam ter acesso à explicação dos conteúdos teóricos que permeiam o tema de solução tampão, além de interagir com uma calculadora online que através de informações inseridas pelos visitantes, irá gerar dados de preparos de soluções e mostrarão os efeitos da adição de um ácido ou uma base, força iônica e temperatura nos cálculos.

Os resultados serão apresentados com as devidas explicações, a fim que o usuário observe instantaneamente como os cálculos são realizados. A realização deste projeto mostra-se bastante relevante uma vez que os cálculos envolvidos na solução tampão, normalmente, são realizados de forma simplificada, sem correção dos erros agregados pela mudança de temperatura e força iônica do meio.

A proposta se baseia na disponibilização de um conteúdo gratuito e de qualidade a um grande número de pessoas externas à comunidade acadêmica, possibilitando ao IFRJ realizar uma divulgação científica eficaz, além de promover aos estudantes envolvidos na elaboração do projeto uma metodologia ativa de aprendizagem.

Como capturar gases do efeito estufa: da bancada para a sociedade.

https://proceedings.science/p/139163

Lucas Vieira de Souza [1]; Suzane de S. Oliveira [1]; Guilherme Rocha [1]; Hiasmin Christine Kurrle Pinheiro Sodre [1]; João Mario Brito Neto [1]; Rayane Souza Soares [1]; Stevan Matheus Maranha dos Santos [1]; Luiza C. de Moura [1]; Jussara Lopes de Miranda [1]
[1] Universidade Federal do Rio de Janeiro

O efeito estufa é um fenômeno natural, que tem por finalidade manter a temperatura global em equilíbrio. Nesse efeito, a luz solar que chega ao planeta tem parte absorvida e refletida para o espaço, mantendo a temperatura do planeta favorável para a vida como é conhecida hoje.1 As elevadas emissões de gases do efeito estufa (GEE) criam uma camada que impede a troca energética entre o planeta e o espaço, causando o aquecimento global. Como consequência, ocorre o acréscimo da temperatura do planeta, levando ao derretimento das calotas polares, o aumento dos períodos de seca, dentre outros.2 Devido aos problemas gerados, diversos conselhos incluem este tema em suas discussões, como o Protocolo de Quioto, em 1998, que determinou as tecnologias a serem utilizadas para capturar, armazenar e utilizar o carbono gerado e a COP21 que determinou manter o aumento da temperatura global abaixo de 2°C.3 O processo de captura de carbono pode ser realizado por meio de tecnologias como absorção e adsorção.4 Na técnica de adsorção de GEE, foco deste estudo, daremos destaque na captura com os hidróxidos duplos lamelares (HDL) e os híbridos metal-orgânico (MOF), tendo como objetivo apresentar esses materiais e seus atributos de forma acessível para o público geral. Os HDL são um grupo de compostos com estrutura derivada da hidrotalcita, feitos por camadas constituídas por uma mistura de cátions de M2+ e M3+ intercaladas por ânions e água.5 Diversas opções podem ser usadas para compor sua estrutura, o que influencia no desempenho de suas aplicações, por exemplo, na catálise e na captura de gases, graças a sua alta área superficial, estabilidade térmica e baixo custo de produção.6 Os MOFs são materiais constituídos por íons metálicos e ligantes orgânicos, criando estruturas tridimensionais que possuem diversas propriedades excepcionais, dentre elas, alta capacidade de adsorção e dessorção.7 O grupo já vem apresentando o tema à sociedade por meio de palestras, painéis temáticos e bate-papo virtual no Festival do Conhecimento da UFRJ (2020 e 2021), palestras em escolas e divulgações através de projetos de extensão como, por exemplo, a Arte no Lixo e a Química e o Coronavírus.

1HOF, A, et al. Environ. Sci. & Pol., 71, 2017; 2QIAO, H, et al. Sci. Total Environ., 671, 2019; 3MIKHAYLOV, A, et al. Entrepreneurship And Sustainability Issues, 7, 2020; 4OLAJIRE, A. A. Renew. Sustain. Energy Rev., 92, 2018; 5León, M; Diáz, E; Bennici; S. Ind. Eng. Chem, 49, 2010; 6LI, et al. New Carbon Mater., 36, 2021.

Criação de cursos de Licenciatura em Química e qualificação de professores do Ensino Médio: um olhar para as relações quantitativas

https://proceedings.science/p/138929

Nyuara Araújo da Silva Mesquita [1]; Larissa Queiroz Silva [2]; Gisele da Silva Gomes [2]; Márlon Herbert F. B. Soares [1]
[1] Instituto de Química / Universidade Federal de Goiás; [2] Universidade Federal de Goiás

Nos últimos anos houve avanços em termos da qualificação dos professores da educação básica e do

Ensino médio. Com o crescente aumento de cursos de Licenciatura em Química, principalmente por meio do Programa de Reestruturação e Expansão das Universidades Federais (REUNI) e pela expansão da Rede Federal por meio dos Institutos Federais, percebe-se que houve também um aumento no número de professores de química que têm formação específica atuando na educação básica. Essa pesquisa buscou relacionar a criação destes cursos com o aumento do número de professores licenciados em adequação à formação exigida para o exercício da docência em química na educação básica. Com relação ao levantamento de cursos de Licenciatura em Química ofertados pelas (IES), usamos como fonte de pesquisa a base de dados da plataforma e-Mec e foram analisados documentos em relação às informações que evidenciam o crescimento do quantitativo de professores com formação em licenciatura em química na educação básica. Os dados da plataforma e-Mec mostram que estão em atividade cerca de 352 cursos de Licenciatura em Química no Brasil, dos quais 96 são ofertados pelos Institutos Federais. A expansão deu-se de forma mais evidente a partir de 2008. Em relação aos Indicadores de formação docente no Ensino Médio por disciplina foi feito um levantamento de 2007 até 2020 e observou-se a variação de 13% de professores de química formados em licenciatura em química em 2007 para 65,6% em 2020. Assim, aumentar a oferta de cursos de qualidade, visando a realidade da sociedade é sim uma proposta muito importante, mas em conjunto, não se pode deixar de lado outros aspectos como questões salariais e estruturais da carreira. Mesmo com esse avanço não devemos esquecer que o interesse e a permanência de pessoas para cursarem licenciatura está atrelado a muitas questões que precisam ser revistas em termos de se priorizar a qualidade da educação no país. Melhorar a formação é o primeiro passo dessa caminhada em que se devem analisar todas as situações para que esse número de professores atuantes possa alcançar um quantitativo cada vez maior considerando a formação específica na área de atuação.

Divulgação Científica sobre as Laureadas com o Nobel de Química e a Educação para a Sustentabilidade

https://proceedings.science/p/138897

Camila Silveira [1]

[1] Universidade Federal do Paraná

O Prêmio Nobel é uma honraria importante e a análise de seus dados revela aspectos sobre a diversidade nas Ciências. De 1901 a 2020, o Nobel de Química agraciou apenas sete mulheres, o que representa menos de 4% do total das premiações. Tratar da representatividade feminina no Nobel pode ser uma estratégia de Divulgação Científica (DC) com potencialidade de atingir o grande público, evidenciando os feitos das ganhadoras e suas trajetórias, além de problematizar criticamente as questões de gênero, promovendo a Educação para a Sustentabilidade (EDS). Neste contexto, este trabalho investiga os materiais de DC produzidos pelo Projeto de Extensão “Meninas e Mulheres nas Ciências” (MMC), sobre as laureadas com o Nobel de Química, na perspectiva da EDS. A partir de uma análise documental, tomando como fontes de informação textos e atividades lúdicas do MMC, procedeu-se com a identificação dos temas abordados e dos objetivos de aprendizagem para o ODS 5 – Igualdade de Gênero -, a saber: a) cognitiva, b) socioemocional e c) comportamental. Compuseram o corpus, sete textos – um sobre cada ganhadora (Marie Curie, Irène Joliot-Curie, Dorothy Hodgkin, Ada Yonath, Frances Arnold, Emmanuelle Charpentier e Jennifer Doudna) e os respectivos quebra-cabeças online das laureadas. Da interpretação à luz da EDS depreende-se que as três categorias de aprendizagens foram contempladas, a exemplo da abordagem para a compreensão sobre as causas atuais e históricos da desigualdade de gênero na Química e do entendimento sobre processos de discriminação de mulheres cientistas da área, no campo cognitivo. No socioemocional, o reconhecimento sobre os papeis tradicionais de gênero de forma crítica foi estimulado. O comportamental foi notado na capacidade de avaliar a participação feminina no Nobel de Química e na identificação da discriminação de gênero. As relações entre gênero e educação, os reflexos da desigualdade na premiação, a interseccionalidade com outras categorias sociais e a dinâmica do ambiente acadêmico foram temas explorados com a linguagem lúdica e da DC presentes nos materiais, apontando a capacidade de alcançar o grande público e das aprendizagens relacionadas ao ODS 5.

Instagram Science-content creators profile

https://proceedings.science/p/138933

Kelly Ribeiro [1]; Daisy de Brito Rezende [2]

[1] Programa de Pós Graduação em Ensino de Ciências / Interunidades / Universidade de São Paulo; [2] Departamento de Química Fundamental / Instituto de Química / Universidade de São Paulo

Through exploratory research in which a questionnaire conveyed through Google Docs was applied, it was possible to identify different profiles of those content producers active in social media, specifically Instagram. A total of 360 questionnaires were sent to pre-selected subjects, according to some criteria: regularity and quantity of posts, number of followers and use of the Portuguese language. We gathered 66 responses which led to the results we report here concerning the analysis of their socioeconomic characterization.

The results show that 90% of these professionals got a degree in one of the areas of Nature Sciences (Biological Sciences, Physics and Chemistry). Of this percentage, most have a Master's or Doctorate in the field or are attending a graduation course stricto sensu. The channels are in charge of one member or a group, aged between 20 and 35 years, and the proportion of women to men is similar (49% and 51%, respectively). The followers of these Instagram profiles are high school or undergraduate students searching for curiosities and for deepening their scientific knowledge. Mostly, these content creators are from public school, entrants in undergraduate courses who needed to work, often as teachers, throughout their formative journey. When starting the scientific influencer project, their main intention is to gain visibility, creating a network of contacts to facilitate their entry into the formal labour market.

Lambe-sujos, Caboclinhos and Sugarcane Chemistry

https://proceedings.science/p/138958

Mariana Oliveira Fraga [1]; Elias Gerson da Silva Neto [1]; Isabelly Dhafny Soares Gomes [1]; Gabriel Barbosa Dória [1]; Carlos Fernando de Souza Santos [1]

[1] Universidade Federal de Sergipe

The work presents a relation between the Lambe-sujos and Caboclinhos historical context, the right to the expression of the culture and chemistry present in the sugarcane molasses production process.

QUÍMICA NA MÃO - CINÉTICA: Um aplicativo para o ensino de Cinética Química e Catalisadores no Ensino Médio

https://proceedings.science/p/139161

Silvana Wolke [1]; Mayara Antler [2]
[1] Instituto de Química / Universidade Federal do Rio Grande do Sul; [2] Universidade Federal do Rio Grande do Sul

A cinética química é uma parte da química muito abstrata e, por esse motivo, os estudantes apresentam dificuldades na compreensão dos conceitos. Essas dificuldades podem estar relacionadas à falta de conexão do tema com o cotidiano e à forma como esses conteúdos são explicados em aulas expositivas. Entre as estratégias para o ensino de Cinética Química, a mais utilizada é a da experimentação, pois consegue-se motivar o estudante através da contextualização dos conceitos com situações reais do cotidiano. Entretanto, nem todas as escolas dispõem de laboratórios ou de insumos, ainda que de baixo custo, para essa experimentação. Por outro lado, hoje em dia, tanto estudantes como professores utilizam smartphones e tablets, que são Tecnologias Móveis e Sem Fio (TMSF)), que podem contribuir para o ensino e aprendizagem no Ensino de Química, segundo as teorias do Mobile Learning e Bring your Device. O uso de aplicativos com caráter educacional viabiliza, por exemplo, a experimentação, sem que sejam necessários insumos ou laboratórios, além da possibilidade de acesso em qualquer lugar. Nesse contexto, com a finalidade de introduzir as TMSFs em nosso ambiente escolar, foi desenvolvido um produto educacional, na forma de aplicativo móvel, chamado QUÍMICA NA MÃO – CINÉTICA. O objetivo do aplicativo é proporcionar a construção de conhecimento em conceitos sobre Cinética Química e Catalisadores, em que o estudante possa assumir uma posição mais autônoma no seu processo de aprendizagem.
O QUÍMICA NA MÃO – CINÉTICA foi desenvolvido na plataforma MIT App Inventor e pode funcionar como uma apostila interativa, de uso intuitivo, sem a necessidade de internet. Os conteúdos são explanados através de textos, imagens, vídeos com experimentos e quizzes que testam os conhecimentos adquiridos. Um estudo preliminar sobre a utilização em sala de aula com 90 estudantes da terceira série do ensino médio, dentro de um roteiro de aulas mediadas pelo professor, mostrou que o aplicativo foi um facilitador no ensino e aprendizagem de Cinética Química. Para o professor, o ensino foi facilitado por que recursos como vídeos e gráficos de experimentos não estariam disponíveis sem o uso do aplicativo. Para os estudantes, a aprendizagem foi evidenciada durante as discussões e avaliações em sala de aula. Em seus relatos, os estudantes destacaram que a possibilidade de acessar os conteúdos antes das aulas e que as imagens e textos curtos facilitaram o aprendizado dos conteúdos abordados, motivando-os a utilizar o aplicativo como material de estudo.

Química no Enem: identificando tendências nos últimos dez anos.

https://proceedings.science/p/138957

Alessandra Stevanato [1]; Wilson Carvalho [2]; Alisson Sant' Ana Rodrigues [2]; Geovana Ribeiro Teixeira [2]; Geovana Rodrigues [2]; Bruna Borges Pinto [2]; João Caetano dos Santos [2]; Eduardo Candido Munhoz Lima [2]
[1] Campus Londrina / Universidade Tecnológica Federal do Paraná; [2] Universidade Tecnológica Federal do Paraná

Criado em 1998, o Exame Nacional do Ensino Médio (ENEM) a princípio pretendia avaliar o desempenho dos estudantes ao final da educação básica, com o objetivo de auxiliar na construção de políticas educacionais. Atualmente, muitas Instituições de Ensino Superior utilizam a nota do Enem para

classificação no ingresso de alunos em seus quadros, assim, precisam estar bem preparados para garantir uma vaga em uma instituição de ensino superior. Pensando nisso, os Licenciandos em Química da Universidade Tecnológica Federal do Paraná, campus Londrina, vinculados ao PIBID, elaboraram um levantamento com os assuntos mais recorrentes no ENEM com o intuito de nortear os estudos dos alunos do terceiro ano do ensino médio de um colégio público, localizado na periferia de londrina, em sua preparação para o exame. Posto isso, foram disponibilizadas as informações em um site desenvolvido pelos pibidianos. Essa pesquisa foi elaborada por meio de um levantamento dos componentes curriculares e objetos de conhecimentos no componente Química no Enem, com mais incidência entre os anos de 2010 a 2020, por intermédio da elaboração e interpretação de gráficos. Na edição de 2010 e 2013, o exame trouxe questões relacionadas à química orgânica, físico-química e química geral/inorgânica, sendo que esta apresentou maior ocorrência. A partir de 2016, o exame passou a apresentar em sua composição a química analítica e em 2020 a química ambiental. Em 2019 e 2020 as questões de físico-química apresentaram maior incidência com 38,46% e 40,00% da totalidade da prova de Química, respectivamente. No quadro geral das últimas 10 edições, esse componente foi o que mais se destacou com 33,33%, seguido pela química orgânica com 30,23%, química geral/inorgânica com 26,68%, química analítica com 6,20% e química ambiental com 1,55%. Em relação aos conhecimentos que mais se sobressaíram em físico-química temos: eletroquímica com 22,22% e termoquímica com 15,55%. Na química orgânica se destacam: as reações orgânicas com 30% e propriedades dos compostos orgânicos e isomeria com 10%. Desse modo, conclui-se que ao longo dos anos os assuntos relacionados a físico-química se destacaram, além disso ressalta-se que o Enem possui a tendência de interligar as áreas do conhecimento com os assuntos do cotidiano.

Teaching electrochemistry in high school through an experiment with an approach of simultaneous equilibria of oxidation-reduction and complexation

https://proceedings.science/p/139158

Nathália Júlio Silveira [1]; Valéria Almeida Alves [1]; Luís Antônio da Silva [1]; Júnia Fabricia Teixeira [1]; Jaqueline Freitas Sousa [1]
[1] Universidade Federal do Triângulo Mineiro

The literature points to the students' difficulty in learning various concepts of electrochemistry, related to galvanic, electrolytic and concentration cells, which may be the result of the teaching process itself and/or the textbooks1-4. There are authors who argue that, in order to understand chemical systems, it is important that students have the opportunity to make connections between the macroscopic, microscopic and symbolic representational levels5. Experimental activities allow students to observe chemical reactions at the macroscopic level5. The use of experimental kits aims to contribute to a more efficient teaching of electrochemistry, to overcome the difficulties and misunderstandings associated with the teaching-learning process of this topic6. Aiming to contribute to the teaching of electrochemistry and chemical equilibrium in basic education, this work proposes the assembly and use of an experimental kit, made with low-cost and easily accessible materials, which can be used as a didactic tool to enhance the teaching-learning process. The inspiration for making the experimental kit came from question number 6 from the 2019 entrance exam of the Military Institute of Engineering (IME), available in http://poliedroresolve.sistemapoliedro.com.br/#/resolucao/IME/2019/526, which involves concepts of electrochemistry and chemical equilibrium. The use of the kit, besides allowing the evidence of the complexation reaction due the strong blue related to the formation of the complex ion [Cu(NH3)4]2+ culminated in the determination of its formation constant, Kf, whose obtained value

(2,1x1013) was of the same order of magnitude of the value calculated by the IME question (4,0x1013) and also presents concordance with the value of the literature (2,1x1013)7. This work possibilities the contextualizing of chemical knowledge, making it socially relevant. The proposed experimental activity can contribute to overcoming alternative and misconceptions presented by high school students about various concepts of electrochemistry8. Given the students' difficulties, due to the importance of electrochemistry for scientific and technological development, it is relevant to seek alternative methods to facilitate their teaching and understanding, relating chemical phenomena to the student's daily life9. The experimental kit presented can enable basic education teachers to use a diversified, innovative didactic strategy, which is efficient in student learning, going beyond exclusively expository classes, which can also contribute to increasing their conceptual mastery of electrochemistry.

The diffusion of scientific poems as an interdisciplinary proposal to teach chemical concepts

https://proceedings.science/p/138927

Thiago Henrique Albino Rodrigues [1]; Nyuara A. S. Mesquita [1]; Márlon Herbert F. B. Soares [2]
[1] Universidade Federal de Goiás; [2] Instituto de Química / Universidade Federal de Goiás

A arte e a ciência são comumente retratadas de forma completamente divergentes, já que a arte tem um viés subjetivo e expressivo, valorizando saberes criativos, enquanto a ciência um viés objetivo e sistemático, valorizando métodos replicáveis. No entanto, há fatores que as duas apresentam em comum e até dialogam entre si, já que percebem e retratam um mesmo mundo, suas linguagens são diferentes, mas seus objetivos são os mesmos: as várias possibilidades de um desenvolvimento crítico e formação humana e integral.1 Como é um trabalho que se trata de poesia, nos valemos de uma visão defendida por Ferreira Gullar que critica a postura do movimento anterior, o concretista que abraçava uma perspectiva cientifica, porém positivista. O movimento neoconcretista relembra o caráter subjetivo que a poesia tem, porém sem deixar de lado a postura crítica e a liberdade de expressão, tanto na estrutura quanto na linguagem presente nos poemas. O neoconcretismo transcende o concretismo por permitir uma integração social e diálogo entre o artista, o público-alvo e a obra intermediadora.2 Dessa forma, esse trabalho tem como enfoque uma aplicação experimental de aulas sobre poemas como mediadores de conteúdos de química, sendo uma pesquisa de cunho lúdico e interdisciplinar, com uma análise qualitativa, buscando referencias da literatura poética para um embasamento teórico apropriado, de forma que a partir dessa aplicação seja possível disponibilizar recursos para possíveis planejamentos e aplicações de aulas diversificadas, tanto no ensino básico quanto em formação docente nos cursos de química. As aulas foram realizadas em uma oficina no Instituto Federal Goiano e em uma disciplina optativa aberta em nível nacional, com um total de 30 discentes em ambas. Foram produzidas poesias na forma de haikais, denominadas haiquímicos, mas também poesias concretas e neoconcretas. Os principais conteúdos foram sobre a conceituação da Química e da Ciência, além de ligações químicas e transformações físicas, como os haikais apresentados a seguir: Luto Me refletindo a um cátion Perdendo elétrons Da minha camada de valência. Estado Ao entrar em ebulição Líquidos em geral Aos seus olhos desaparecerão." É perceptível pelas leituras e várias interpretações das produções poéticas realizadas pelos inscritos, uma apropriação dos conceitos para aplicá-los em suas múltiplas possibilidades de sentidos, até mesmo, contextualizando-os. A leitura de poemas químicos permite ainda um olhar diferente para o conceito, instigando o estudante a compreender o conceito para também compreender o poema em constante ir e vir, entre o conceito e o poema, entre a ciência e a arte.

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The love chemistry of tacacá: an approach valuing traditional knowledge and non-formal spaces in Amazonia for teaching chemistry

https://proceedings.science/p/138937

Pamela Pereira Nunes [1]; Renato Henriques de Souza [1]; Maria Lenilda Glória Ferreira [1]; Welton Yudi Oda [1]

[1] Universidade Federal do Amazonas

A Caravana da Diversidade é uma rede de pesquisadorxs com ênfase na formação de professorxs sensíveis à diversidade cultural, respeito às diferenças e combate às desigualdades. Além disso, produz bionarrativas sociais digitais. A Caravana foi fundada em 2018, e nela realizamos duas edições remotas do evento homônimo, em 2020 e 2021. Nestes, apresentamos para cientistas, professores e estudantes uma atividade intitulada "A Química do Amor ao Tacacá". Nesta atividade, trabalhamos o tema do prato típico “tacacá”, além de relacionarmos os saberes etnológicos com o ensino da Química, valorizando o uso de espaços não formais amazônicos para o ensino e discussão da química.

Neste contexto, a região amazônica possui uma grande diversidade de ambientes para o ensino de Ciências. Estes espaços fora da sala de aula são conhecidos como espaços não formais e ocorrem em ambientes urbanos e rurais, e os encontramos tanto na capital como no interior do Estado. Para esta abordagem, apresentamos a origem, composição e importância econômica, bem como história, memória e legado das tacacazeiras de Parintins. Mulheres simpáticas, sorridentes e acolhedoras. As pioneiras subsistem na memória afetiva e no paladar da geração que vivenciou essa relação histórica com o tacacá na ilha do boi-bumbá. Essa iguaria é fruto de um processo histórico, dos nossos antepassados, dos povos indígenas, que foram passados por gerações, saberes etnológicos. Trazer o tema tacacá para a Caravana é reconhecer o valor social e gnosiológico da cultura local, base do saber local. Sua simbologia, identidade da culinária amazônica em Parintins, importância cultural e econômica. As bancas de tacacá não são apenas uma mesa de alimento, mas também um ambiente de aprendizagens, de troca de experiências e diversidade de saberes. Ademais, a riqueza de ingredientes e processos envolvidos permitiu discutirmos diversos aspectos relacionados à química.

Nas discussões, também exploramos os ambientes amazônicos, que são fontes de conteúdos para o ensino e, quando bem direcionados, podem trazer benefícios para a formação de alunos e professores, sendo utilizados como complemento em relação ao ensino formal. Desta forma é importante conhecermos os espaços e estudar as suas possibilidades didáticas. Portanto, com esta atividade, adotamos a temática regional para contextualizar conceitos químicos no ensino, além de enriquecermos conceitos da química da amazônia com o uso dos espaços não formais.

Use of furfural for the preparation of different molecules: Organic Synthesis in the context of Green Chemistry in an experimental undergraduate course

https://proceedings.science/p/138896

Aline Nakagawa do Nascimento [1]; Camila Oliveira [1]; Leonardo Carneiro [1]; Leonardo Barbosa [1]; Marco Filho [1]; Mirela Sairre [1]
[1] Universidade Federal do ABC

Traditional courses in experimental organic chemistry are held as a “cookbook”, in which students perform the experimental procedures determined by the teacher and verify the expected result. The development of practical courses with current and motivating themes using the problem-based learning (PBL) format allows a shift in educational focus from teacher-centred approach to a student-centred teaching and learning approach. In this way, students develop critical-thinking skills and experimental abilities.1 The chemical industry plays an important role in the global market, due to the different sectors in which it operates. In Brazil, the chemical industry has one of the largest contributions to the country's GDP (gross domestic product). However, a major challenge is to reduce the environmental impact caused. In this context, it is important to discuss the sustainable development in higher education courses, associating the principles of green chemistry with experimental courses. In recent years, there has been an increasing number of published studies on green chemistry practices and laboratory safety in experimental courses, mainly in analytical chemistry and organic chemistry.2 The experimental undergraduate course called Applied Organic Chemistry was taught to students of the Chemistry course at Federal University of ABC (UFABC) using the PBL method. The purpose of the course is developing projects for the preparation of potentially bioactive molecules using the furfural molecule, which has as its main advantage renewable sources and a versatile structural skeleton, which makes it possible to build a library variety of synthetic compounds. Students developed all stages of a research project in the area of organic synthesis: bibliographic search, planning and execution of the synthetic route, structural elucidation of the compounds obtained, discussion of results and conclusions. All projects developed were promising in terms of learning and real experience of developing a synthetic route in the laboratory. In addition, students needed to find alternatives for the difficulties encountered. Some projects have successfully provided the target molecules.At the end of the course, the students presented seminars, promoting important discussions about experimental procedures, structural elucidation, scientific research and organic chemistry. It was possible to develop the students' creative attitude and critical thinking, in addition to promoting constant questioning and their autonomy.

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2Mohan, R. S.; Mejia, M. P. Environmentally Friendly Organic Chemistry Laboratory Experiments for the Undergraduate Curriculum: A Literature Survey and Assessment. J. Chem. Educ. 2020, 97 (4), 943–959. https://doi.org/10.1021/acs.jchemed.9b00753.

Video-based simulations: a valuable resource for chemistry teaching and educational research

https://proceedings.science/p/138940

Guilherme Andrade Marson [1]; Yuri Barros de Araujo [2]; Camila Midori Peroni [2]; Heloisa Cristine Cruz [3]
[1] Universidade de São Paulo; [2] Departamento de Química Fundamental / Instituto de Química / Universidade de São Paulo; [3] Colégio Objetivo Sorocaba

The interface of a typical educational digital video is often limited to the play-pause and timeline console. In contrast, computer based simulators allow dynamic visualizing of hundreds of experimental outcomes. However, producing a digital video is increasingly simpler, cheaper and faster than making its simulator counterpart. Here we report a simple, yet effective, approach to make and use videos with simulation capabilities for both teaching and educational research purposes: on-screen data reading from a digital video, made by combining synchronous footage of the same experiment, taken with two cameras at different angles. Following this strategy, digital videos of acid-base titrations were recorded in an ordinary lab setup. These videos were embedded in three types of activities, presented in the following order: A1 a tutorial; A2, a classic simulator (with a spreadsheet); and A3, a decision-making scenario. A1 and A3 were annotated with an interactive layer over the video. A1 and A3 displayed the same representational repertory integrated by the video time-line: the titration curve, a bar chart of the chemical composition and the video itself. Also, A1 and A3 actively, but not explicitly, involved the reversible reaction concept in the video-embedded interactions. Although similar to A1, A3 was significantly more complex: it entailed interpreting different representations in decision making scenarios: "what reactant must be added to go from the current position on the titration curve to this system composition (displayed as bar chart)? HCl or NaOH?". At the end of both activities, users are prompted to chose, among three chemical reaction hypothesis, the one that best explained the simulated phenomena: stoichiometric only, static equilibrium and dynamic equilibrium. These resources were tested in a remote 8 h (2x 4 h) case based learning (Sá et al. 2007) teaching module for 265 undergraduate students from geology (32) and pharmacy (72) courses. Although considered laborious (79 %) and conceptually difficult (78 %), the module was regarded as useful (69 %) by the students. They also evaluated it as innovative (93 %) and were willing to have more activities alike (85 %). The conceptual profile (Solsona et al. 2003, Gonzáles, 2017) for the chemical equilibrium concept was also investigated in connection to the representational competence (Chang 2018). The analysis of students' answers suggest a close connection between the mobilization of the conceptual profile and the complexity of the representational task requested. Interestingly, in some cases, even when the reversibility hypothesis was indicated, it was not the actual working concept employed in the decision making activities. References: Chang, Sci. Edu. 2018, 102, p. 1129; Solsona et al. Int. J. Sci. Edu. 2003, 25, p.3.; González, EDUCERE 2017, 68, p. 113; Sá et al. Quím. Nova, 2007,30(3) p. 731. Committee for Research with Humans register number: 3.357.893.

[EduCátion(IFRJ)]+ Project

https://proceedings.science/p/138883

Letícia Fidelis Cunha [1]; Maria Fernanda Henriques Ferraz [1]; Natália Rosário da Silva [1]; Viviane Lírio Ferreira [1]; Rafaela Sant'Anna [1]; Eduardo Coelho Cerqueira [1]
[1] Instituto Federal de Educação, Ciência e Tecnologia do Rio de Janeiro

The internet has become the main source of information during the COVID-19 pandemic (1). However, it is crucial nowadays that the veracity of the content covered in social medias is checked to avoid fake news and unreliable information. In this context, to contribute in the scientific divulgation of free and reliable content in the area of chemistry, the [EduCátion(IFRJ)]+ Project was created. To achieve this, a YouTube channel (<https://www.youtube.com/channel/UCKoJ-jhtON2KFMu>) was created to host videos and an Instagram (@education.ifrj) was created to assist with divulgation by attracting the public with visual and direct content. The YouTube channel is divided in two sessions: Q-Conhecimento and Q-Prático. In Q-Conhecimento, the students will use the chemistry to explain how products of our daily lives work, such as glues, coffee, pigments and perfume. In Q-Prático, chemical experiments will be performed with easily accessible materials and the chemistry behind them will be explained. Special care was given to the visual aspects of all content published by creating color and font patterns as well as standardized recording methods, which helps create a reliable and pleasant environment. References for all information are also available on the videos descriptions, so that the public can confirm and deepen their comprehension. The social media management, the content production and the art/design are made by students from technician courses of IFRJ and advised by chemistry professors from the same institution. The project applies an active learning methodology, in which the students involved are their own knowledge promoters (2). Thus, by integrating education, research and extension, it is expected that [EduCátion(IFRJ)]+ Project not only promotes the formation of the students involved, but also disseminates the high quality scientifical education of IFRJ to the general public, allowing an educational transformation in the society. Currently, the YouTube channel has 85 subscribers, 4 videos and 526 views, while Instagram has 431 followers.

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Físico-Química - FIS

Cálculos de Espectros de IV em DMSO de Complexos de Losartana-Lantanídeos

https://proceedings.science/p/139200

Nelson Henrique Morgon [1]; Adriano Siqueira [2]; Aguinaldo Robinson de Souza [3]
[1] Universidade Estadual de Campinas; [2] Universidade Federal de Mato Grosso; [3] Departamento de Química / Faculdade de Ciências / Universidade Estadual Paulista “Júlio de Mesquita Filho”

Losartan (LOS) is a drug mainly used to treat high blood pressure. It is also used for diabetic kidney disease, heart failure, and left ventricular enlargement. In the present investigation, the quantum chemical approach employed to determine the molecular structures was the Becke three-parameter hybrid method using the Lee-Yang-Par correlation functional. The basis sets used for calculations were 6-311++G(3df,2p) or pseudopotential for lanthanide atoms. The IR spectra were obtained using harmonic vibrational frequencies. They were determined by the analytic evaluation of the second derivative of the energy with respect to nuclear displacemen. Solvent effects (DMSO) were described by SMD model and D3 version of Grimmes's dispersion with Becke-Johnson damping. The molecular calculations performed in this study were carried out using the Gaussian 16 program. The theoretical molecular geometries showed that the interaction of lanthanide ions (La, Ce, Pr, Nd, Sm, and Eu) with the 3 losartan ligands occurs through the tetrazole ring and the number of water molecules varies in the coordination sphere (6 or 7): [La(LOS)3(H2O)7], [Ce(LOS)3(H2O)6], [Pr(LOS)3(H2O)6], [Nd(LOS)3(H2O)6], [Sm(LOS)3(H2O)6], and Eu(LOS)3(H2O)6]. It is possible to observe a decrease in the wave number (displacement) of the bands referring to the vibrational modes of the tetrazole ring, ~1500 cm-1 (asymmetrical stretching), ~1300 cm-1 (angular deformation of the scissoring type) and ~800 cm- 1 (wagging-type angular deformation) in all molecular systems. These calculations are similar to those obtained for all synthesized metal compounds. Experimental data of FTIR of losartan compounds indicated vibrations stretching of NCN at 1492 cm-1 to [La(LOS)3(H2O)7] and 1491 cm-1 to others LOS compounds. The major variation of experimental data of LnLOS compounds, the angular deformation was observed at 1355 cm-1(LaLOS, NdLOS, SmLOS), 1354 cm-1(PrLOS, EuLOS), 1352 cm-1(CeLOS). So, our results can bring some light on the data performed by experimentalist groups.

Caracterização físico-química de óleo de pinhão-manso (Jatropha curcas L.) cultivado no semi-árido mineiro para a produção de biodiesel

https://proceedings.science/p/139202

Roberto Ananias Ribeiro [1]; Juliana Gomes Barbosa [1]; Jânio Almeida [1]
[1] Instituto Federal de Educação, Ciência e Tecnologia do Norte de Minas Gerais - Campus Salinas

O pinhão-manso é uma oleaginosa que tem grande potencial no semiárido mineiro em função da sua elevada resistência a condições edafoclimáticas muito variadas. É importante avaliar a qualidade do óleo vegetal destinado à produção de biodiesel e por isso, o objetivo do trabalho foi avaliar os índices de acidez (IA) e de peróxido (IP) de óleos de pinhão-manso, bruto e purificado por degomagens ácida e aquosa. O óleo purificado apresentou um IA (0,64 ± 0,13) menor do que o bruto (3,88 ± 0,01). Índices de acidez abaixo de 2 mg KOH/g de óleo são considerados apropriados para catálise alcalina na reação de transesterificação para produção de biodiese. Já para IP's, observou-se que o óleo purificado é que apresentou um valor maior (9,61 ± 0,55) em relação ao óleo bruto (3,32 ± 0,19). Maior ÍP na amostra indica a degradação do óleo devido à oxidação das duplas ligações. No processo de degomagens, a presença da água e o aquecimento final da amostra em estufa a 115oC por 2 h podem ter contribuído para as reações de oxidação, favorecendo a formação de peróxidos no óleo purificado. Na literatura, não se tem informação sobre a partir de que valor de IP, o óleo é considerado inadequado para a produção de biodiesel. Os valores encontrados de IP de óleos brutos estão de acordo com os valores obtidos para ambas as amostras no nosso estudo, indicando uma vantagem desse óleo oriundo de plantas cultivadas no semirárido mineiro. Para a produção de biodiesel a partir da catálise alcalina, o óleo purificado poderá apresentar um melhor rendimento na reação já que o catalisador não será consumido de forma significativa como no óleo bruto de acidez mais elevada. Estudos posteriores usando os óleos obtidos para a síntese de biodiesel deverão ser realizados. Assim, conclui-se sobre a importância da determinação dos índices de acidez e de peróxido para avaliar a qualidade do óleo destinado para a produção de biodiesel.

Determinação da concentração de urânio, rádio, tório e potássio em fertilizantes minerais fosfatados comercializados no Brasil

https://proceedings.science/p/138952

Camila Rodrigues e Silva [1]; Fabiana Monteiro de Oliveira [1]; Mariana Vezzone [2]; Roberto Meigikos dos Anjos [2]
[1] Instituto de Química / Universidade Federal Fluminense; [2] Departamento de Física / Universidade Federal Fluminense

Os fertilizantes minerais são uma das importantes fontes primárias antropogênicas de isótopos das séries de decaimento do urânio e tório ao meio ambiente, como a utilização desses insumos agrícolas tem crescido mundialmente, a fim de repor os nutrientes naturais, que estão sendo continuamente retirados do solo devido a atividades agrícolas e problemas de erosão, o estudo do acúmulo de isótopos devido ao seu uso tem se tornado cada mais relevante (Yamazaki; Geraldo, 2003; Bjørklund et al., 2017).
A contínua utilização de fertilizantes pode resultar no aumento da exposição humana a radiação ionizante, seja pela adsorção desses isótopos pelas plantas, pelo acúmulo contínuo deste nos solos, quando a taxa de lixiviação não for alta, ou pelo enriquecimento das águas subterrâneas quando há a mobilização desses elementos nos solos (Yamazaki e Geraldo, 2003; Solodukhin et al., 2015).
Em vista disso, o objetivo deste estudo foi determinar as concentrações de 238U, 232Th, 226Ra e 40K em três diferentes marcas de fertilizantes minerais fosfatados comercializados no Brasil com diferentes formulações NPK, por meio da técnica de espectrometria gama com o emprego de um detector de germânio de alta pureza (HPGe). As concentrações dos isótopos estudados nos fertilizantes NPK escolhidos variaram entre 72,2 e 2189,9 Bq kg-1, <LD e 2339,6 Bq kg-1, 28365,4 e 102689,2 Bq kg-1 e 44,0 e 3759,9 Bq kg-1 de Ra226, U238, K40 e Th232 respectivamente, sendo que, em geral os maiores teores de radioisótopos foram encontrados nos fertilizantes com formulação NPK 04-14-08. Tais resultados estão em conformidade com os obtidos na literatura.

Effect of chemical modification on cationic azo dye biosorption kinetics using Lagenaria as biosorbent

https://proceedings.science/p/138861

Jaqueline Nicolini [1]; Stephany Baumer Franceschini [1]; Keller Nicolini [1]
[1] Instituto Federal de Educação, Ciência e Tecnologia do Paraná - IFPR

The biosorbent (Lagenaria, LG) was ground, washed, dried (40-50 oC) and ground (<150 μm) (LG in natura (LG-in)). Part of LG-in was chemically modified by basic hydrolysis using 0.1 mol L-1 NaOH solution for 24 h, to delignify the biomass1 and increasing the pH (LG-b). The LG-b was again washed with distilled water, dried (40-50 oC) and ground (<150 μm). The pH was determined using 0.1500 g±0.0003 g of LG in 20 mL of distilled water for 30 min (LG-in pH=8.4; LG-b pH=11.4). Kinetic tests were carried out until equilibrium (t=30 min; T=25 oC; tartrazina cationic azo dye (CAD) concentration 7.5 x 10-5 mol L-1) using 0.1500 g of each biomass in 20 mL of aqueous CAD solution. Data did not fit for the pseudo-first-order model (physical adsorption). The kinetic parameters (Tab.1) demonstrate that the amount of CAD adsorbed calculated at equilibrium obtained from the pseudo-second-order kinetics (chemical adsorption) is equivalent to the maximum amount of CAD adsorbed in equilibrium at 25 oC (Tab.1). The highest correlation coefficient (R2,Tab.1) was obtained for the pseudo-second kinetics indicating that the sorption is determined by the rate of adsorption reactions, occurring at the solid/liquid interface.2 It is observed that the basic hydrolysis reduces the amount of CAD adsorbed in equilibrium (Tab.1). In intraparticle diffusion, the adsorbate molecules infiltrate the interior of the adsorbent particles.3 The data indicate that other interaction mechanisms may be acting simultaneously. There are two linearities (Tab.1): First (R2 dif,1) represents the instantaneous adsorption or on the external surface; Second (R2 dif,2), represents the stage of gradual adsorption by diffusion intraparticle.4 There is no kinetic adjustment to LG-b biomass using Elovich model (chemical adsorption).5

Table 1. Coefficients of Pseudo-second-order, Elovich and Intraparticle diffusion kinetic constants

Pseudo-second-order:6 qe (mg g-1): amount adsorbed in equilibrium; k2 (g mg-1 min-1): second-order adsorption constant. Intraparticle diffusion:4 C (mg g-1): constant related to diffusion resistance; Kp (dif,2) (mg g-1 min-1/2): intraparticle diffusion coefficient. Elovich:6 α (mg g-1 min-1): initial adsorption rate; β (g mg-1): desorption constant.

LACOPPI, IFPR, PIBIC/CNPQ, CNPq

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Estudo da descoloração e degradação do corante reativo Amarelo Sidercron VS-RNL através da reação de Fenton.

https://proceedings.science/p/138935

Jeferson Colzani [1]; Nicholas Johann Berner [1]; Paulo Cesar de Jesus [1]
[1] Fundação Universidade Regional de Blumenau (FURB)

A aplicação de métodos de descoloração e degradação de corantes vem sendo extensivamente pesquisada, devido ao impacto ambiental causado pelos mesmos.1,2 Neste trabalho foi estudado a degradação do corante reativo amarelo Sidercon VS-RNL (orange 107)3 (Figura 1a) aplicando a reação de Fenton. Foi preparado solução de corante na concentração de 0,02 gL-1 e solução de Fenton (H2O2/FeSO4) em diferentes concentrações de H2O2 (30%, 3%, 0,3% e 0,03%), ajustando o pH para 2 com H2SO4. Foram transferidas para uma cubeta de quartzo termostatizada, 3 mL da solução de corante e 0,2 mL da solução de Fenton (H2O2/Fe2+). Leituras da absorbância no comprimento de onda máximo do corante (ʎmax= 410 nm) foram realizadas de 2 em 2 minutos, nas temperaturas de 30°C, 40°C, 50°C e 60°C. A eficiência de descoloração e degradação da solução do corante foi determinada. A Figura 1b mostra o decaimento da absorbância vs tempo com H2O2 30% a 40°C e a Figura 1c mostra a eficiência de descoloração para a concentração de H2O2 30% nas diferentes temperaturas estudadas. Comportamento similar foi observado para as demais concentrações de H2O2. Pelos resultados obtidos, verifica-se que a degradação é favorecida pelo aumento da temperatura, onde a 50°C e 60°C e concentrações de H2O2 mais baixas (0,3% e 0,03%), se obtêm eficiências de descoloração e degradação acima de 90% em até 10 minutos de reação. As curvas cinéticas obedeceram ao modelo cinético de primeira ordem com kobs variando de 1,5x10-3min-1, 30oC com H2O2 30% a 5,2x10-1min-1, 60 oC com H2O2 3%. O método se mostrou viável na descoloração e degradação do corante reativo amarelo Sidercron VS-RNL.

Evaluating the Viscosity of Biolubricants via DOSY-NMR

https://proceedings.science/p/138948

Lucas Queiroz dos Santos [1]; Ivani Malvestiti [1]; Ricardo Oliveira da Silva [1]; Paulo Menezes [1]; Ricardo Luiz Longo [1]

[1] Universidade Federal de Pernambuco - UFPE

Viscosity(η) is one of the most important properties of (bio)lubricants along with its dependence with temperature and pressure. Many attempts are being made to modify and improve the viscosity of (bio)lubricants. However, standard procedures require a large amount of the sample that hinders the use of high-throughput approaches. Moreover, most common apparatus provides the kinematic viscosity(ν) which requires the mass density(ρ) to provide the viscosity: $\eta=\rho\nu$. Therefore, alternative procedures to determine the viscosity are quite relevant. In this context, the diffusion coefficient(D) of a species-i in a fluid is related to the viscosity of the medium, at a given temperature T, through the Stokes-Einstein equation: $D=aT/\eta$, with $a=k/(c\pi r)$, where r the hydrodynamic radius, k is the Boltzmann constant, and c is a factor(c~4-6) related mainly to its shape. Diffusion coefficient can be promptly measured by diffusion-ordered NMR spectroscopy(DOSY), which is simple to measure and requires small amounts of samples. So, we employed 1H-DOSY measurements at temperatures varying from 298 to 338K to provide estimates of the fluid viscosity. The diffusion of large species can be difficult to measure and a small amount of benzene (0.97:0.03mol lubricant/mol benzene) was added to the fluid, so the viscosity could be estimated from the diffusion of benzene. This approach was tested for methyl ricinoleate(MR), because its viscosity is available in a temperature range of 298-358K and can be promptly synthesized from known precursors. Viscosity can be expressed as $\eta(T)=A\cdot\exp[\Delta^{\ddagger}G/(RT)]$, where R is the molar gas constant and Δ‡G is the Gibbs free energy of activation. From the Stokes-Einstein equation, the diffusion coefficient of the (bio)lubricant becomes $D_{lub}(T)=A'\cdot T\cdot\exp[-\Delta^{\ddagger}G/(RT)]$. Therefore, plots of ln(η) and of ln(Dlub/T) versus 1/T should be linear and have slopes that yield the same values of Δ‡G. Indeed, from the available viscosity data and the diffusion coefficient of MR from DOSY measurements, these linear relationships were observed and provided 31.2±0.6 and 31.9±1.4kJ/mol for Δ‡G, respectively, with R2=0.996 and 0.989. The excellent agreement, within the uncertainty of the linear fits, indicates that the Stokes-Einstein equation is valid for this fluid. A value of 24.8±0.5kJ/mol for Δ‡G was obtained from ln(Dbenz/T) versus 1/T plot(R2=0.997). Besides, the better fit of benzene data compared to MR suggests that benzene can be an accurate probe for diffusion and viscosity of fluids. Estimates of the viscosity of the binary mixture 0.97:0.03(MR/benz) indicate that at this low mol fraction it does not affect the viscosity of the pure fluid. From the values of Dmr and Dbenz and η of MR, the geometric parameters (cr) were with the Stokes-Einstein equation and their average values over the temperature range of 298 to 328K were 18.35 and 4.26Å, respectively. MR was modified by performing its acetylation, MRA, and benzene diffusion coefficient was measured in the new fluid. Using the values of (cr)benz, the viscosity of MRA was estimated to be 16% smaller than MR at 298K, up to 40% smaller at 318K. This approach was simple and employed small amounts of the products, which can promptly screen suitable modifications.

High energy efficiency production of reactive nitrogen species in plasma activated water

https://proceedings.science/p/139201

Pericles Inacio Khalaf [1]; Érica Berlatto [1]

[1] Universidade Tecnológica Federal do Paraná

In this work, plasma activated water (PAW) containing a large amount of dissolved reactive nitrogen species (RNS) was produced. The cold plasma discharge was generated between a centered high voltage (HV) tungsten pin electrode and the water surface, which acted as the discharge electrode (grounded). A jacketed plasma reactor (200 mL) was filled with 100 mL of ultrapure water. AC high voltage of 60 Hz was applied to the plasma reactor through a HV transformer (NeonEna 17 kV). Ambient air at atmospheric pressure was employed as the plasma gas, and the gas exchange between the reactor and the atmosphere were free trough two cap openings. The waveforms of the voltage and current were measured using a real-time digital oscilloscope (Tektronix TDS 2012C) via a high voltage probe (Caltest CT4028) and a current monitor (Pearson 411). Temperature of the plasma rector jacket was kept constant at 5 oC through a thermostatic circulating bath (Microquimica MQBMP-01). The agitation of the plasma activated water was kept constant at 750 rpm by a magnetic stirrer (NovaInstruments NI 1111). RNS (HNO3 and HNO2) were determined spectrophotometrically (SHIMADZU UV-Vis Spectrophotometer, UV-1800) and their concentrations were calculated trough calibration curves. During the plasma activation time (180 min) samples of PAW were taken for analysis in predetermined time intervals. In the above conditions, the measured average power was 27.1 W, peak-to-peak voltage 7.0 kV and peak-to-peak current 81.3 mA. The energy density (ED, J L-1) was calculated based on the plasma power, treatment time and water volume in order to compare our results to the literature. It was found that the HNO3 concentration increased linearly with the increase of the ED, as HNO3 is a final stable nitrogen specie that accumulates in the medium. HNO2 concentration also increased with the increase of ED, however not linearly. This behavior is explained by the reactivity of HNO2 with reactive oxidant species (ROS) produced in PAW, which decreases HNO2 concentration quickly, especially in acid medium. Energy efficiency (EF) was calculated by the ratio of the observed RNS concentration and applied energy density. The maximum energy efficiency for production of HNO3, HNO2 and their sum (HNO3+HNO2) was 45.8, 34.1 and 62.6 nmol J-1, respectively. In comparison, another work found these values as 9.15, 22.7 and 29.9 nmol J-1, respectively for a RF plasma. In the aforementioned study the plasma discharge was also produced between a high voltage electrode and the water surface, which indicates that the energy efficiency found in the present work is 5.0, 1.5 and 2.1 times greater for HNO3, HNO2 and HNO3+HNO2, respectively for a similar plasma set up.

Interacting Quantum Atoms (IQA) Partitioning of Force Constants

https://proceedings.science/p/138857

Leonardo Duarte [1]; Roy Bruns [1]

[1] Instituto de Química / Universidade Estadual de Campinas

The total energy of a molecule can be decomposed 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 and exchange-correlation potential between electrons from two different atomic basins. When studying molecular vibrations, the force constants that determine the infrared

frequencies can be obtained following with the Wilson F and G matrices. Considering that the energy is a sum of IQA contributions, the Hessian matrix can be written as a sum of IQA Hessian matrices, which contains second derivatives of IQA terms.
A mathematical formalism for this analysis is being developed, consisting 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 cubic Hessian is obtained numerically. This method allows the determination of intra- and interatomic factors that correspond to the origin of the force constant values.

Observation of different pattern of bursts in the chlorate-nitrous acid-iodine-iodide oscillating reaction

https://proceedings.science/p/138886

Emily Vidal Monteiro [1]; Roberto de Barros Faria [1]
[1] Universidade Federal do Rio de Janeiro

The chlorate-nitrous acid-iodine-iodide oscillating reaction in a CTRS, presents three kinds of bursts at 0.45 M of acid concentration and flow rate equal to 0.005 s-1. One of these kinds of bursts was also observed interspersed with simple mode oscillations.

Point-charge models are incapable of reproducing IR intensities of out-of-plane vibrations

https://proceedings.science/p/138851

Wagner Richter [1]
[1] Engenharia Química / Campus Ponta Grossa / Universidade Tecnológica Federal do Paraná

Population analyses based on point charges are incapable of reproducing IR intensities of out-of-plane vibrations. The reason for that relies on the models obtained from point charges as they only allow the dipole moment derivative to be described by a C+CT sum for which C stands for the Charge term (equilibrium charges moving along the normal coordinate) and CT stands for Charge Transfer (the variations on these charges as the atoms are displaced from the equilibrium position). While for the great majority of vibrations these two terms are non zero, specifically in the case of planar molecules the out-of-plane bending shows a symmetry constraint first demonstrated by Dinur and Hagler in 1989 that obligates the CT term to vanish. As the dipole moment derivative is a C+CT sum and CT must be zero, only the Charge term remains and (as it is formed by static charges from the equilibrium position) it is incapable of accurately predict IR intensities for these out-of-plane vibrations (as these are composed by changes in the electronic density).

By using partition schemes featuring atomic dipoles, the dipole moment derivative is now described by a C+CT+DP sum, and even though the CT term also vanishes in this case, the fact that the DP term is not subject to the same constraint allows the total derivative to be described as a C+DP sum, which correctly assembles the electronic density changes and predicts the IR intensities of these modes very

accurately. The reason why CT vanishes whereas DP does not is due to the scalar nature of the atomic charges in contrast to the vector nature of the atomic dipoles. Atomic dipoles are then a much richer source of meaningful information for chemist than the charges themselves.

These findings hold regardless of the partition schemes or the planar molecules chosen. Numerical, algebraic and graphical results to be presented in full at the video presentation.

P.S. It is of my interest to present this e-poster (short video) as a selected presentation (longer video), if selected by RASBQ committee.

Quantitative analysis of intermolecular interactions in solid state of a family of pyrazole-based pro-ligands

https://proceedings.science/p/139196

Bruno Peixoto Rodrigues [1]; Guilherme Pereira Guedes [1]
[1] Universidade Federal Fluminense

In order to fully comprehend and describe chemical, physical or biological properties of new compounds, a proper understanding on how their molecules are involved in intermolecular interactions and how these contacts affect the stabilization of their agglomerates is necessary. Therefore, the crystal structures of a family of pyrazole pro-ligands were determined by single crystal X-ray diffraction and employed in the study of intermolecular interactions established by such compounds, in terms of packing and internuclear distances. More so, a deeper understading of these interactions was achieved by analyzing each intermolecular contact as a function of the electronic density mapped around each molecule, utilizing the Hirshfeld surface. These surfaces were generated by the Crystal Explorer Software using the pre-obtained structural information, and employed in the quantitative evaluation of existing contacts among the pyrazole-based system in the solid state. The quantitative evaluation afforded a common interactive pattern in the family, highlighting that closed-shell interactions and aromatic interactions were predominant in the stabilization of the crystal packing.

Study of tartrazine adsorption kinetic in oat residual biochar biomass

https://proceedings.science/p/139197

Keller Nicolini [1]; Janaina Pontes da Silva [1]; Jaqueline Nicolini [1]
[1] Instituto Federal de Educação, Ciência e Tecnologia do Paraná - IFPR

Char products, extending their potential applications, as pharmaceutical and cosmetic sectors. This work aim to determine kinetic parameters of the adsorption of tartrazine dye (TD) in oat biochar (BC). The residual biomass of oat, was pyrolyzed at 400 °C (± 5) for 30 min, generating BC, that was crushed (≤ 0.01 mm), washed with distilled water and dried at 60 °C (± 3). The adsorption of TD in BC, were done in becker cups containing 50 mL of TD 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.
The best fit was obtained for the pseudo-second-order kinetic model (R2: between 0.98 and 1.00). The highest adsorption capacity was shown for the temperature of 40 °C (qe (exp.): 5.27 and qe (teor): 5.40

mg/g). This suggests that this sorption system step may be involving valency forces through sharing or exchange of electrons between sorbent and sorbate. Pseudo-second order kinetic model suggests that chemical adsorption of TD by BC is the dominant mechanism, involving electrostatic attraction.

Temperature dependence of zeta potential on magnetic nanocolloids

https://proceedings.science/p/139198

Ruth Pinheiro Muniz [1]; Guilherme Siqueira Gomide [2]; Cynara Caroline Kern Barreto [1]; Alex Fabiano Cortez Campos [1]
[1] Universidade de Brasília - Laboratório de Nanociência Ambiental e Aplicada, Faculdade UnB Planaltina; Laboratório de Fluidos Complexos, Instituto de Física.; [2] Universidade de Brasília - Laboratório de Fluidos Complexos, Instituto de Física.

Magnetic nanocolloids are ultra-stable dispersions of magnetic nanoparticles (NPs). This class of materials have been gaining visibility in research and technology centers due to their broad application potential. In the case of a charged magnetic nanocolloids, the stability can be monitored by the zeta potential of NPs, which is strongly related to parameters such as NPs shape and size, viscosity and pH. Temperature is another important factor, since it affects the properties of the medium and the charge of NPs through the protonation and deprotonation of surface groups. This study aims to contribute to a better understanding of how temperature can modify the properties of a colloid, in addition to serving as a basis for possible technological applications in systems using thermodiffusion and thermoelectricity effects. In this context, this survey proposes a study of the effect of temperature on the zeta potential of a water-based magnetic nanocolloid sample with charged core-shell NPs based on cobalt ferrite (CoFe2O4@ɤ-Fe2O3) obtained via hydrothermal co-precipitation. The NPs and the colloid sample have been previously characterized using XRD, TEM, and SAXS. To investigate the effects of temperature, zeta potential measurements were performed in the temperature range of 25-60 °C, with different ionic strengths and using different co-ions. The zeta potential decreases with increasing temperature, which can be related to the decrease of the surface charge and the viscosity of the medium. The zeta potential also decreases with increasing ionic strength due to the screening effect of the counter-ions. Finally, the nature of the co-ions slightly changes the zeta potential due to its different intrinsic ionic mobilities.

Fotoquímica - FOT

Descarboxilação fotoeletroquímica do ácido caprílico usando fotoanodos W:BiVO4-V2O5

https://proceedings.science/p/138916

Rafael Rodrigues de Souza; José Domingos Fabris [1]; Márcio César Pereira [1]
[1] Universidade Federal dos Vales do Jequitinhonha e Mucuri

A conversão eletrocatalítica dos ácidos gordos derivados da biomassa é uma estratégia interessante,

embora a produção seletiva de hidrocarbonetos desoxigenados continue a ser um processo tecnológico desafiante para uma fonte de energia limpa. Em particular, a eletrólise de Kolbe baseada na eletro-oxidação de carboxilatos para olefinas tem excelentes perspectivas na produção de biocombustíveis líquidos energeticamente eficientes e aditivos para combustíveis. A reação eletroquímica da conversão de carboxilatos é normalmente realizada com elétrodos de Pt, que é um metal nobre e caro. A fim de permitir a eletrólise dos carboxilatos, é necessário aplicar um potencial superior a 2 V vs. RHE, o que resulta numa procura considerável da energia de entrada. Aqui, relatamos o desenvolvimento de um fotoanodo W:BiVO4-V2O5 que requer relativamente muito menos energia na descarboxilação do ácido octanóico, utilizando diretamente a radiação solar, que é bastante disponível na superfície da Terra. O fotoanodo foi preparado através de fundição por gota; as suas principais características estruturais foram avaliadas por difração de raios X, espectroscopia de reflexão difusa, e microscopia eletrônica de varredura. As partículas W:BiVO4 foram consideradas esféricas, enquanto que as do V2O5 tinham a forma de uma bastão. As energias de bandgap calculadas para W:BiVO4 e V2O5 foram de 2,4 e 2,3 eV, respectivamente, indicando que os filmes preparados podem de fato ser ativados com luz visível. Foram efetuados testes fotoeletroquímicos utilizando voltametria linear. As curvas J x V para o fotoanodo W:BiVO4-V2O5 sob iluminação mostraram que o potencial necessário para realizar a descarboxilação do ácido octanóico podia ser reduzido até 1,5 V, se comparado com o eletrodo convencional de Pt. Estes resultados demonstram que a descarboxilação do ácido octanóico pode ser economizadora de energia utilizando um fotoanodo contendo elementos químicos que são mais abundantes na crosta terrestre e mais baratos do que a Pt. Esperamos que estes avanços significativos possam ser uma alternativa inovadora para a desoxigenação fotoelétrica dos carboxilatos ou ácidos carboxílicos, que tem sido pouco explorada até agora.

Exploring the substituent effect on the fluorescence and chemiluminescence properties of polyphenylimidazoles

https://proceedings.science/p/138910

Fernando Bartoloni [1]; Alexander Pinto [1]; Andreia Boaro [1]; Diêgo Melo [1]; Leonardo Carneiro [1]; Roberta Reis [1]
[1] Universidade Federal do ABC

Lately, the fluorescent (FL) and chemiluminescent (CL) properties of polyphenylimidazoles have been of interest to our research group.1-4 Compounds such as 2,4,5-triphenyl-1H-imidazoles (TPI) and 1,2,4,5-tetraphenylimidazoles (TEPI) can be conveniently prepared using a single-flask multicomponent approach, by mixing the appropriate benzaldehyde with benzil and ammonia (or aniline) in glacial acetic acid. Recently,1 we have studied the CL decomposition of hydroperoxides and silylperoxides derived from TPI, upon the addition of base. The effect of the substituents in the 2-phenyl ring on the reaction rate constants and CL quantum yields was analyzed and evidence for the generation of a 1,2-dioxetane as a key intermediate was obtained from Hammett linear free energy relationships.1 On another study,5 we have observed that a Hammett relationship with the FL quantum yield of hydroxylated TEPI derivatives (i.e., TEPI-OH) can be used to rationalize the excited state intramolecular proton transfer (ESIPT) within this molecular framework. Moreover, TEPI and TEPI-OH can be used as activators of the CL transformation known as peroxyoxalate system, with emission efficiencies comparable to some polycyclic aromatic hydrocarbons and TPI derivatives.4 In conclusion, polyphenylimidazoles are valuable substrates for many FL and CL studies.

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Synthesis and photophysical study of new push-pull 1,4-naphthoquinone dyes

https://proceedings.science/p/138930

Juliana da Silva Goulart [1]; Nanci Lucas [1]; Simon Garden [1]
[1] Universidade Federal do Rio de Janeiro

Push-pull or acceptor-donor dyes are extensively studied for their versatile applications as dyes and sensors.(1) Naphthoquinones (NQ) can be found in many natural products and the rational design of new NQ with simple structural modifications can create colorful compounds. In this study, NQ was chosen as the acceptor and tetrahydroquinoline (THQ), diphenylamine (DPA), triphenylamine (TFA), carbazole (CBZ) and phenothiazine (PTZ) as the donor moieties. The synthesis of the molecules 1-5 occurs by an oxidative coupling(2) with triflic acid, as catalyst, in acetonitrile. The photophysical behavior of 1-5 was studied. The UV-visible absorption spectrum revealed an intramolecular charge transfer (ICT) band. In ACN, the λmax was 533, 494, 502, 458 and 531 nm for 1 to 5, respectively. However, only 1, 2 and 5 exhibited a significant solvatocromic effect. On changing the solvent from cyclohexane to t-butanol, a bathochromic shift was observed: 99, 70 and 80 nm, respectively for 1, 2 and 5. It was possible to distinguish up to 20% and 10% of ethanol in ethanol-hexane mixtures using 1 and 2, respectively, as colorimetric sensors. Compound 1 was observed to differ from the other derivatives in that its' solution was discolored by the addition of trifluoracetic acid due to protonation of the basic NH site, thus suppressing the ICT process. The protonation was reversed when triethylamine was added. Compounds 1 to 5 were weakly fluorescent in apolar solvents (0.002 ≤ Φf CyH ≤ 0.16), max for emission in cyclohexane for 1 to 5 was: 598, 565, 596, 525 and 695 nm. Polar solvents quenched the fluorescence for all structures. Finally, the insertion of donor groups increased significantly NQ absorption in the visible region and 1 and 2 are possible candidates as colorimetric sensors for alcohols in apolar media.

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Produtos Naturais - QPN

Amaryllidaceae species as source of anti-neurodegenerative agents: a review

https://proceedings.science/p/138939

Amanda Eiriz Feu [1]; Warley Borges [1]
[1] Universidade Federal do Espírito Santo

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]. Amaryllidaceae 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.

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Anti-Trypanosoma cruzi activity of aliphatic falcarinol-type poliacetylenes from Hydrocotyle bonariensis (Araliaceae)

https://proceedings.science/p/138879

Dalete Christine da Silva Souza [1]; Thais Costa-Silva [2]; André Gustavo Tempone [3]; João Henrique Ghilardi Lago [2]
[1] Institute of Environmental, Chemical and Pharmaceutical Sciences / Federal University of São Paulo; [2] Center of Natural and Human Sciences / Federal University of ABC; [3] Center for Parasitology and Mycology / Adolfo Lutz Institute

Aliphatic C17-poliacetylenes, also known as falcarinol-type poliacetylenes, displayed different biological activities described in the literature, such as antibacterial and antifungal. However, there is no previous information concerning he evaluation of antiparasitic activity of these compounds. In this context, the hexane extract from aerial parts of Hydrocotyle bonariensis (Araliaceae) was subjected to different chromatographic steps to afford a mixture of bioactive compounds which were characterized by NMR and HPLC/MS2. Analysis of 13C NMR spectrum indicated the presence of falacarinol poliacetylenes due to signals attributed to sp carbons at δ 64 – 80 (C-4 to C-7), sp2 carbons at δ 117 – 122 (C-1), δ 134 - 136 (C-2), 122 – 131 (C-9), and δ 133 – 134 (C-10) as well as signals to carbinolic carbons at δ 63 (C-3)/59 (C-8), including also signals of an acetyl group at δ 167.9 (C=O)/19.8 (CH3) as observed for compound 3. HRMS spectra shown fragmentation patterns characteristic of the cleavage of C-3/C-4 and C-6/C-7 bonds (m/z 187.1485 and 105.0338 for compound 1, m/z 203.1433 and

105.0344 for compound 2 and m/z 203.1433 and 147.0444 for compound 3), in addition of $[M – H]^-$ ions in m/z 243.1745, 259.1692 and 301.1804, confirming the molecular formulas in $C_{17}H_{23}O$, $C_{17}H_{24}O_2$ and $C_{19}H_{26}O_3$, and allowing the characterization of these compounds as falcarinol (1), falcarindiol (2), falcarindiol-3-acetate (3). The mixture of compounds 1-3 was evaluated against trypomastigote forms of Trypanosoma cruzi and shown an IC50 value of 8.2 ± 1.8 µg/mL, whereas the standard drug, benznidazole, exhibited IC50 value of 4.8 ± 1.1 µg/mL. In addition, the mixture was also tested on NCTC mammalian cells and displayed CC50 value of 82.2 µg/mL, and, thus, SI (Selectivity Index) value of 10, similar to that calculated for the standard drug. Therefore, these results had shown, at first time, the efficiency of this mixture of compounds against the T. cruzi parasite.

Antitrypanosomal activity and calcium storage alteration of enyne acetogenins from Porcelia macrocarpa (Annonaceae) fruit peels

https://proceedings.science/p/138860

Fernanda Thevenard dos Santos [1]; Thais Costa-Silva [2]; Guilherme Antar [3]; André Gustavo Tempone [4]; João Henrique Ghilardi Lago [5]

[1] Universidade Federal do ABC; [2] Center of Natural Sciences and Humanities / Universidade Federal do ABC; [3] Universidade de São Paulo; [4] Centro de Parasitologia e Micologia / Adolfo Lutz / Adolfo Lutz; [5] Centro de Ciências Naturais e Humanas / Universidade Federal do ABC

Chagas disease, caused by the protozoan Trypanosoma cruzi, afflicts millions in Latin America. Benznidazole is the only available drug in Brazil and very limited due to side effects.1,2 In this context, natural products offer a substantial variety of compounds that can be used for development of novel therapeutics3. Thus, looking to isolate further such compounds from Porcelia macrocarpa, bioactivity-guided fractionation against trypomastigotes of T. cruzi of the MeOH extract resulted in the characterization of a fraction containing two compounds. Antitrypanosomal activity of Fraction E was performed against cell-derived trypomastigotes and amastigotes. Cytotoxicity was evaluated against NCTC cells. In addiction the activity in the cell membrane permeability and calcium levels were evaluated. Part of this material (1 g) was subjected to column chromatography over Sephadex LH-20 and eight groups (A – H) were obtained. The 1H NMR spectrum of biologically active fraction D (18 mg) showed characteristic signals of a lactone ring as well as signals suggesting the presence of a triple bond similar to those previously isolated from seeds of P. macrocarpa4. However, additional peaks were indicative of an enyne conjugated system suggesting the presence of an internal double bond. Analysis of 13C and DEPT NMR spectra confirmed the proposal due to the observation of signals referring to the carbonyl carbon in the lactone ring, the internal double bond and the terminal double bond. Additionally, signals referring to two quaternary carbons were observed. Finally, by means of HPLC/ESI-HRMS it was possible to infer that bioactive fraction D is composed of a mixture of related compounds 1 and 2 (Figure 1), whose structures were determined for the first time in this work. Fraction E displayed EC50 of 4.9 µg/mL and 2.4 µg/mL against trypomastigote and amastigote forms of the parasite, respectively, with no cytotoxicity observed at the highest concentration tested (CC50 > 200 µg/mL). The selectivity index against amastigotes for this fraction (SI = 83.3) was higher than for the standard drug benznidazole (EC50 = 1.43 µg/mL and CC50 = 52.5 µg/mL, SI = 36.4). A SI higher than 10 is in agreement with hit criteria for Chagas disease treatment, established by the Drugs for Neglected Diseases iniciative (DNDi)2. Mechanism of action studies with trypomastigote forms showed that fraction E does not alter the parasite cell membrane but does affect intracellular calcium levels. Further studies will be done to determine if alterations are caused in T. cruzi mitochondria and/or acidocalsisomes (both organelles sources of calcium, important for cellular homeostasis in trypanosomatids), as well as analyses of the isolated compounds. While enyne γ-lactones have been isolated from other species of Annonaceae5, this is the first description of such conjugated compounds in P. macrocarpa.

Atividade antimicrobiana do ácido (E)-masticadienoico, isolado das folhas de Schinus terebinthifolius (Anacardiaceae), frente à Neisseria gonorrhoeae

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ERIC UMEHARA [1]; Maiara Romanelli [2]; Myron Christodoulides [3]; André Gustavo Tempone [4]; João Henrique Ghilardi Lago [5]

[1] Universidade Federal do ABC; [2] Instituto Adolfo Lutz; [3] Faculty of Medicine / University of Southampton; [4] Centro de Parasitologia e Micologia / Adolfo Lutz / Adolfo Lutz; [5] Centro de Ciências Naturais e Humanas / Universidade Federal do ABC

Neisseria gonorrhoeae, uma bactéria gram-negativa, é conhecida como o agente etiológico da gonorreia. A Organização Mundial da Saúde (OMS) estima cerca de 90 milhões de casos desta infecção, sendo esta, a terceira infecção sexualmente transmissível (IST) mais frequente no mundo. O aumento no número de infecções deve-se em parte, ao aumento da resistência a antibióticos devido a constante utilização desses medicamentos, como a ceftriaxona e a azitromicina que são utilizados para o tratamento eficaz desta infecção. Desta forma, com a possibilidade de surgimento de novas cepas resistentes aos antibióticos citados, diversos trabalhos tem sido direcionados à busca de novos agentes antimicrobianos. Nesse contexto, nosso grupo de pesquisa realizou um trabalho prospectivo com cerca de 100 diferentes extratos vegetais frente a N. gonorrhoeae. Dentre os extratos ativos, o hexânico das folhas de Schinus terebinthifolius (Anacardiaceae) apresentou atividade e foi submetido a diferentes procedimentos cromatográficos, fornecendo os ácidos (E)-masticadienoico (1) e (E)-schinol (2). A caracterização molecular desses triterpenos foi baseada na analise dos espectros de RMN e EMAR-IES seguido da comparação com dados descritos na literatura. Ambos os compostos isolados foram avaliados in vitro frente às cepas P9-17 de N. gonorrhoeae. Os resultados obtidos indicaram que o composto 1 se mostrou ativo com CIM50 de 12,5 μM e CIM90-100 de 3,125 – 6,26 μM ao passo que o composto 2 se mostrou totalmente inativo (CIM50 e CIM90-100 > 200 M). Além disso, ambos os compostos apresentaram baixa citotoxicidade, com CC50 de 96,5 μM frente às células de linhagem NCTC. Levando-se em consideração que a única diferença estrutural entre os dois tirucalanos está na presença de uma carbonila em C-3 em 1 a qual esta substituída por um grupo hidroxílico no composto 2, é possível inferir que a presença de tal grupo exerce um papel importante na ação biológica, de acordo com o observado para diferentes derivados triterpênicos, onde a carbonila na mesma posição exerce um fator crucial na atividade antimicrobiana3. Portanto, esse é o primeiro relato da atividade antimicrobiana do ácido (E)-masticadienoico (1) frente de N. gonorrhoeae, trazendo informações importantes para um promissor protótipo molecular antimicrobiano.

Avaliação da atividade anti-Trypanosoma cruzi de acetogeninas isoladas das sementes de Porcelia macrocarpa (Warm.) R. E. Fries (Annonaceae)

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Ivanildo Afonso de Brito [1]; Thais Costa-Silva [2]; André Gustavo Tempone [3]; Fernanda Thevenard dos Santos [1]; Joao Lago [1]

[1] Universidade Federal do ABC; [2] Center of Natural Sciences and Humanities / Universidade Federal do ABC; [3] Centro de Parasitologia e Micologia / Adolfo Lutz / Adolfo Lutz

A doença de Chagas, cujo agente etiológico é o protozoário Trypanosoma cruzi, encontra-se entre as principais doenças parasitárias que aflige a população brasileira, cujo tratamento é ainda incipiente e realizado com fármacos de baixa eficiência e alta toxicidade1. No Brasil, o benznidazol é o único medicamento disponível, sendo este muito limitado devido aos efeitos colaterais2. No presente trabalho, as sementes de Porcelia macrocarpa foram extraídas sucessivamente com hexano, CH2Cl2 e MeOH e cada um dos extratos obtidos foi submetido a avaliação da atividade anti-T. cruzi. Como resultado, o extrato em CH2Cl2 se mostrou o mais ativo (100% de morte das formas tripomastigotas a 200 µg/mL) e foi submetido a cromatografia em coluna de sílica, eluida com misturas de hexano-AcOEt em gradiente de polaridade, para fornecer quatro grupos (A – D). Tendo em vista que o grupo C se mostrou mais ativo que os demais no bioensaio, esse foi novamente submetido à cromatografia em gel de sílica, eluida com misturas de hexano-AcOEt em gradiente de polaridade, para fornecer oito grupos (C1 – C8). Dentre esses grupos, o C4 foi o único a apresentar atividade anti-T. cruzi e se mostrou composto, após analise via RMN, por uma mistura de acetogeninas acetilênicas, que foram separadas via CLAE. Após análise por RMN e EM, foi possível inferir as estruturas de 1 e 2.
Inicialmente, a mistura dos compostos 1 e 2 mostrou atividade frente as formas tripomastigotas de T. cruzi com CE50 de 7,8 ± 2,2 µM e toxicidade frente a células NCTC com valor de CC50 de 75,9 ± 9,6 µM. Após a purificação, os compostos 1 e 2 apresentaram valores de CE50 de 6,8 ± 1,2 e 52,1 ± 5,5 µM, respectivamente, sendo que ambos apresentaram reduzida toxicidade (CC50 > 200 µM). Comparativamente ao controle positivo benznidazol (CE50 e CC50 de 17,7 ± 2,4 e 190,6 ± 8,7 µM, respectivamente), a acetogenina 1 apresenta expressivo potencial. Considerando a diferença estrutural entre as acetogeninas 1 e 2, é possível inferir que a ligação dupla terminal exerce um papel fundamental na atividade, visto que o potencial anti-T. cruzi se mostrou inferior para o composto 2. Frente aos resultados obtidos, o efeito a ligação tripla na atividade foi também avaliado, submetendo-se a mistura de 1 e 2 a hidrogenação catalítica para gerar o composto 3, caracterizado por RMN e EM (Figura 1). Após avaliação desse derivado frente às formas tripomastigotas de T. cruzi, se observou que o mesmo é inativo (CC50 > 200 µm), o que indicou que a presença da ligação tripla nas acetogeninas é também crucial para a atividade. Frente ao exposto, este estudo contribui para o conhecimento da atividade antiprotozoária de acetogeninas acetilênicas de P. macrocarpa, o que pode contribuir para o desenvolvimento de novos protótipos moleculares para obtenção de fármacos para o tratamento da doença de Chagas.

Avaliação dos teores totais de fenóis e flavonoides e determinação por CLAE dos principais flavonoides em amostras comerciais de Miconia albicans

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Sarah N. do Nascimento [1]; Marcos Nakamura [2]; José L. Mazzei [2]; João Batista Freitas Tostes [2]; Antonio Siani [2]

[1] Programa de Pós-graduação Acadêmico em Pesquisa Translacional em Fármacos e Medicamentos, Fiocruz; [2] Departamento de Produtos Naturais / Instituto / FUNDAÇÃO OSWALDO CRUZ- FIOCRUZ

Folhas e galhos de Miconia albicans (Sw.) Triana (Melastomataceae), conhecida como canela-de-velho, são usados popularmente no tratamento de artrite e artrose, devido à ação analgésica e anti-inflamatória. Essas atividades têm sido relacionadas com a presença de flavonoides, ácidos triterpênicos e compostos fenólicos. O presente estudo teve como objetivo determinar a composição de fenóis totais e de flavonoides totais de 6 produtos de canela-de-velho, comercializados como partes aéreas secas e fragmentadas. Dois outros lotes de um mesmo fabricante foram incluídos. Folhas foram separadas, trituradas, extraídas com etanol e submetidas ao clean-up em resina XAD-4. O ensaio do teor de fenóis totais, pelo método Folin-Ciocalteu, foi realizado em placas de 96 poços com a adição de 25 µL de solução das amostras em metanol, mais 100 µL de reagente 0,2 N e 80 µL de Na2CO3 saturada. Após incubação por 2 h no escuro, as absorções foram medidas em 760 nm. O teor de flavonoides totais foi avaliado misturando 100 µL de solução das amostras em metanol e 100 µL de AlCl3 2%. Após 10 min, a absorbância foi lida em 415 nm. Diferentes concentrações de quercetina (controle positivo) e controles-branco foram paralelamente submetidos às mesmas condições de análise. Os teores totais de fenóis e flavonoides foram expressos em mg de quercetina/g de amostra (mg-EQ/g). A determinação qualitativa de flavonoides foi realizada por cromatografia líquida de alta eficiência (CLAE) em coluna LiChrospher 100 RP18 250 x 4 mm, com pré-coluna LiChrospher 100 RP18 4 x 4 mm. O detector por arranjo de diodos foi programado em 200-600 nm, monitorando a 350 nm. A fase móvel foi programada em gradiente de ácido fórmico a pH 3,0 (A) e acetonitrila (B) a 1,0 mL/min e 35 °C: 5-25% de B (0-30 min), 25-80% de B (30-50 min), 80-5% de B (50-60 min) e 5% de B (60-70 min). As amostras comerciais apresentaram teores de fenóis totais de 109-324 mg EQ/g e teores de flavonoides totais de 9,2-24,1 mg EQ/g. Os 3 principais flavonoides característicos da planta no rastreamento, identificados pelos tempos de retenção e espectros UV-VIS de padrões analíticos injetados separadamente, foram isoquercitrina, quercitrina e rutina (minoritária). Uma amostra da planta coletada in situ (SisGen AD104CA) apresentou quantidades similares (177 ± 30 mg-EQ/g e 11,9 ± 0,7 mg-EQ/g, respectivamente) e a presença dos 3 flavonoides selecionados (CLAE), sugerindo a seletividade da metodologia analítica voltada para o controle de qualidade da espécie M. albicans.

Bisflavonoides de Ouratea polygyna (Ochnaceae)

https://proceedings.science/p/138971

Mario Geraldo de Carvalho [1]; LIsieux de Santana Julião [2]; Tatiana Saldanha [2]; Mariana Rodrigues da Silva [2]; Alexandra Sawaya [3]

[1] Instituto de Ciencias Exatas / Universidade Federal Rural do Rio de Janeiro; [2] Universidade Federal Rural do Rio de Janeiro; [3] Universidade Estadual de Campinas

Ouratea polygyna is a endemic specie in Brazil. There are no reports phytochemical and biological studies of this specie. The plant material was collected in the Botanical Garden of Rio de Janeiro in September 2018, by the student M. R. da Silva, and Dr. Marcelo da Costa Souza, IB-UFRRJ. The plant

material was dried at room temperature and leaves separated from branches to be ground. The extract from the leaves was prepared by maceration with methanol to obtaining about 200 g of crude extract (OPFM). A yellow precipitate was formed in the bottom of the pot. It was separed and washed with dichloromethane to remove a darker coloration, 3 g of solid material was obtained (OPFMP). 1 g of OPFMP was submitted to Sephadex LH-20 Column using a mixture of dichloro-methanol (20:80), increasing the polarity with methanol. About 40 fractions were collected according to similarity by TLC. This procedure was repeated a few times so that material could accumulate. Similar fractions were later collected and analyzed with 1H and 13C NMR spectra to identify components even in mixture. From the fractions 12-13, 17, and 36-40 were identified robustaflavone, 2'-8'' biapigenin and amentoflavone, respectively. The structures of the biflavones were proposed by 1H and 13C NMR spectral data analysis including 1D and 2D experiments, and mass spectra analyses. The liquid part of the extract was submitted to partition with organic solvents and the fraction obtained with ethyl acetate (OPFA is being analyzed and some glucopyranoside derivative are being identified, witch structures are similar to those isolated from Ouratea semiserrata (Ochnaceae), DOI: 10.1002/pca.656.

Characterization of quercetin derivatives from butanol phase of aquatic macrophyte Hydrocotyle leucocephala by HPLC-DAD and HPLC-ESI-IT-MS2

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Gustavo Neves [1]; Joao Lago [2]; Paulete Romoff [3]; Oriana Fávero [4]; Fátima Otavina de Souza Buturi [5]; Edgard Antonio Ferreira [1]

[1] Universidade Presbiteriana Mackenzie / Escola de Engenharia; [2] Universidade Federal do ABC; [3] Faculdade São Bernardo; [4] Universidade Presbiteriana Mackenzie / Centro de Ciências Biológicas e da Saúde; [5] Universidade São Judas Tadeu / Faculdade de Ciências Biológicas e da Saúde

Hydrocotyle leucocephala Cham. & Schltdl. (Apiaceae), an aquatic macrophyte native from Brazil, popularly known pennyworth, is worldwide spread due its ornamental use.1 In the present work, leaves of H. leucocephala were submitted to extraction by maceration with MeOH, resuspended in a solution of MeOH:H2O (1:9) and subjected to a liquid-liquid extraction with hexane, EtOAc and n-BuOH, respectively. From HPLC-DAD analysis of n-BuOH phase, it was possible to infer the presence of flavonols based on its characteristic major absorption wavelength number in the UV region from 350 to 385 nm and 270 to 290 nm.2 The same chromatographic conditions were applied to HPLC-ESI-IT-MS2 analysis in the positive and negative mode. Due to observed ions at m/z 465, 597, 611 in the positive ionization mode spectra and fragmentation patterns that afforded ions Y1+ and Y0+, it was possible to affirm that all aglycones were attached to a sugar moiety. The cleavage at glycosidic O-linkages occurred with a concomitant H-rearrangement that resulted an elimination of monosaccharides residues, hexose (162 u), deoxyhexose (146 u) and pentose (132 u) resulting in a fragment with high intensity at m/z 303 and 301 in the positive and negative mode, respectively. In the negative ionization mode MS2 spectra, all quercetin derivatives displayed fragment ions at m/z 179, 255 and 271, which is formed by a specific fragmentation of quercetin aglycone which is in accordance with previous studies.2,3 In this way, it was possible to characterize three chemically related derivatives, quercetin-3-O-hexose-pentoside (1), quercetin-3-O-rutinoside (2), quercetin-3-O-hexoside (3). This is the first occurrence of compounds 1 and 2 in Hydrocotyle leucocephala.

Chemical composition and antitrypanosomal activity of essential oils from leaves, twigs and inflorescences of Nectandra barbellata (Lauraceae)

https://proceedings.science/p/138944

Vinicius Silva Londero [1]; Thais Costa-Silva [2]; André Gustavo Tempone [3]; Patricia Sartorelli [1]; Edgard Antonio Ferreira [4]; Guilherme Antar [5]; João Baitello [6]; João Henrique Ghilardi Lago [7]

[1] Universidade Federal de São Paulo; [2] Center of Natural Sciences and Humanities / Universidade Federal do ABC; [3] Centro de Parasitologia e Micologia / Adolfo Lutz / Adolfo Lutz; [4] Química / Escola de Engenharia / Universidade Presbiteriana Mackenzie; [5] Universidade de São Paulo; [6] Divisão de Dasonomia / Instituto Florestal / Secretaria de Infraestrutura e Meio Ambiente do Estado de São Paulo; [7] Centro de Ciências Naturais e Humanas / Universidade Federal do ABC

This study aimed to investigate the chemical composition, as well as antitrypanosomal activity of essential oils from leaves, twigs and inflorescences of N. barbellata. Fresh plant material was collected and individually submitted to hydrodistillation in a Clevenger apparatus. Crude oils were chemically analyzed by GC/FID and GC/MS, in combination with calculation of respective Kovats indices and it was possible to identify 82.6%, 84.0% and 88.5% of the compounds in the oils from leaves (NBL), twigs (NBT) and inflorescences (NBI), respectively. The main components were aristolochene (7.90%) and γ-gurjunene (7.86%) in NBL, costic acid (32.39%) and globulol (12.97%) in NBT, and α-pinene (13.57%) and α-gurjunene (12.29%) in NBI. The in vitro anti-T. cruzi potential against trypomastigote forms and the evaluation of cytotoxicity in mammalian cells (NCTC clone L929) of essential oils were evaluated (Table 1). Biological analysis revealed that NBL and NBI displayed higher antitrypanosomal potential with EC50 values of 12.1 and 14.9 μg mL-1, respectively, compared to NBT (EC50 of 20.2 μg mL-1). Regarding citotoxicity, NBT did not exhibit toxicity against NCTC cells (CC50 > 200 μg mL-1). Therefore, selectivity indexes of studied oils were calculated at 8.3 (NBL), > 9.9 (NBT), and 6.6 (NBI) being that calculated for NBT with similar value of positive control benznidazol (> 16.1). Thus, this work reports for the first time the chemical composition of essential oils from different tissues of N. barbellata, in addition to showing that this species can produce bioactive substances for the parasite T. cruzi.

Dereplication approaches for discovering anti-leukemia specialized metabolites from Myrsine guianensis (Aubl.) Kuntze. (Primulaceae)

https://proceedings.science/p/138887

Fernando Cassas [1]; Cauê Lima [1]; Heron Fernandes Vieira Torquato [1]; Edgar Paredes-Gamero [2]; Lívia Soman [1]; Thiago Veiga [1]

[1] Universidade Federal de São Paulo; [2] Universidade Federal de Mato Grosso do Sul

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 dereplication1. In this sense, our goal is the employing of integrated analytical techniques to accelerate the discovery of metabolites (unknown or not) from Myrsine guianensis (Aubl.) Kuntze. (MG), bioguided by anti-leukemia assays. For this purpose, an extensive literature survey was performed for the 131 species belonging to Myrsine genus for creating a in-house database to be used in Target Analysys (Figure 1A). Besides that, mass spectra obtained in our experiments were processed in the GNPS platform (Figure 1B). Target analysis suggestedd the presence of myrsinoic acids A, B, C, E and F in all extracts, being A the major constituent, along with 5-O-embelin and rapanone already described in Myrsine genus have been also detected. In addition of flavonoids and myrsinosides not associated to the species. Furthermore, through GNPS it was possible to group their spectra comprising the fragmentation

beyond the suggestion of the pheophorbide A. On the other hand, the cytotoxic assays (during 48 hours at 100 µg/mL) indicated that Kasumi-1 and Jurkat cell lines were sensitive to the fractions from M. guianensis (Figure 1C), revealing that is possible to establish integrated chemical and biological approaches for discovering unknown cytotoxic specialized metabolites.

Figure 1 - Base Peak Chromathogram (BPC's) of all extracts processed on Target Analisys software (1A); Clusters of mass spectra organized on the GNPS platform representing fragments and adducts of detected compounds (1B); Cell viability of 10 prepared extracts of M. guianensis under the cell lines Jukart and Kasumi-1 treated during 48h at 100µg/mL.

Ref. 1Carvalho, A.; Rodrigues, L.; Ribeiro, A.; Silva, M.; Medeiros, L.; Veiga, T. Integrated Analytical Tools for Accessing Acridones and Unrelated Phenylacrylamides from Swinglea glutinosa. Molecules 2020, 25, 153 2 Van Herwerden, Eric F.; Süssmuth, Roderich D. Sources for Leads: Natural products and libraries. In: New Approaches to Drug Discovery. Springer International Publishing, 2015. p. 91-12

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Digital image: an innovative tool for determining phenolic compounds in Markhamia tomentosa and Bunchosia glandulifera

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Daiane Einhardt Blank [1]; Antonio Demuner [2]; Luciana Santos [3]; Cristiane Isaac Cerceau [2]; Marcelo Henrique dos Santos [4]; Neusa Moura [5]
[1] Centro de Ciências Exatas e Tecnológicas / UFV / Universidade Federal de Viçosa - Campus VIÇOSA; [2] Universidade Federal de Viçosa; [3] Universidade Federal de Viçosa - Campus VIÇOSA; [4] Departamento de Química / CCE - Centro de Ciências Exatas / UFV - Universidade Federal de Viçosa - Campus Viçosa - MG; [5] EQA

This work use pixels of digital image as an innovative method for the determination phenolic compounds in Markhamia tomentosa and Bunchosia glandulifera with the PhotoMetrix® program application, using linear correlation techniques for univariate analysis, using systems of RGB colors (red, green and blue). To determine the total phenolics, the reaction with ferric chloride was used, using quercetin as the standard. For the acquisition of data or smartphone, the support made with low-cost materials was used, showing the possibility of using this analytical tool, the costs related to analytical instrumentation. The total phenolic content was also determined using a spectrophotometry technique in the visible ultraviolet (UV-Vis). The quantification of total phenolic compounds in all samples can be performed. However, the pulp of Bunchosia glandulifera showed the highest content of phenolic compounds. The content of phenolic compounds found in the seed of Bunchosia glandulifera was 259.54 mg 100 g-1 in relation to the results found in the analysis of total phenolics of Markhamia tomentosa can be observed in the flower in natura has a higher content of phenolic compounds. The dried flower had a 317 mg 100 g-1, the leaf having a concentration of 287.79 mg 100 g-1 and the peel with a concentration of 107.03 mg 100 g-1. Showing that drying may have degraded the bioactive compounds. With this easily accessible method it was possible to determine phenolic compounds in two plants from different families, totaling six concentration results using Photometrix and six results using the spectrophotometer to compare these results. Thus, we can have viable method for performing other tests with several samples. The method is reproducible and can be an efficient and economical alternative for determining these parameters in diversified foods.

Distribution of flavonoids and other phenolic derivatives in Brazilian Mikania species

https://proceedings.science/p/138884

Luís Guilherme Pereira Feitosa [1]; Marcelo Monge [2]; Norberto Peporine Lopes [1]; Dionéia Camilo Rodrigues de Oliveira [1]

[1] Faculdade de Ciências Farmacêuticas de Ribeirão Preto (FCFRP), Universidade de São Paulo (USP); [2] Universidade Federal de Uberlândia

The genus Mikania (Compositae, tribe Eupatorieae) encompasses about 430 species mainly distributed in Neotropical region. More than 200 species of this genus occur in Brazil and approximately 140 endemics. Mikania glomerata and M. laevigata, popularly known as guaco, are widely used in Brazilian folk medicine for treating respiratory diseases. Phytochemical investigations of this genus were centered in chemical markers of guaco species, as kaurene diterpenes and coumarins, and low polarity metabolites, as sesquiterpenes. However, polar compounds are less reported than terpenes. M. micrantha, which is one of the worst invasive weeds in the world, has been the most chemically investigated species, due to allelopathic effects. Nevertheless, the chemical composition of only 12 % of Mikania species has been determined. Besides, there are no chemical data of several Mikania species of Brazilian biodiversity, including endemic species. Thus, LC-MS/MS analysis can be associated to computational tools for metabolomics of this species. We performed the metabolomics of Mikania species collected from different vegetations of Atlantic Forest and Cerrado biomes. Leaves of a group of 11 Mikania species were obtained from specimens stored in herbarium of UEC. These leaves were milling to obtain powder samples. Then, samples were extracted with methanol: water and analyzed by LC-ESI-MS/MS (Ion Trap analyzer) in negative mode ionization, using a C18 column and elution with the gradient of water: acetonitrile, both with formic acid 0.1% (v/v). MS/MS data were uploaded to online platform GNPS (Global Natural Products Social Molecular Networking) to perform the Molecular Networking. Annotations of compounds were based in matches with spectral libraries of GNPS, as well chemotaxonomic data, and fragmentation patterns of NP with ESI. It was observed that chlorogenic acids are the phenolics widely distributed among the group of Mikania species, followed by feruloyl derivatives of caffeoylquinic acids. Flavonol-O-heterosides and methoxylated flavonol aglycones were annotated in the most species, while the presence of flavone-O-heterosides were restricted to M. micrantha and M. cipoensis. Caffeoyl-anhydro-deoxy-octulopyranosonic acids derivatives, found for the first time in Mikania, were verified in four species: M. phaeoclados, M. lasiandrae, M. hastato-cordata and M. campanulata. Moreover, the molecular network allowed the visualization of distribution of metabolites among species. Therefore, this work brings new chemical data to Mikania and contributes to increase the knowledge about the chemodiversity of polar compounds in this genus, as flavonoids, caffeoylquinic acid derivatives and other phenolics.

Estudo do potencial antioxidante do extrato etanólico da semente de maracujá amarelo (passiflora edulis)

https://proceedings.science/p/138951

Ricardo Alexandre dos Santos [1]; Marília Oliveira Fonseca Goulart [1]; Jadriane de Almeida Xavier [1]

[1] Instituto de Química e Biotecnologia / Universidade Federal de Alagoas

Introduction: Among the most produced fruits in Brazil, passion fruit stands out, in addition to being widely consumed due to its functional power, however, its residues are continuously discarded

(SANTOS, 2014). Therefore, to add value to waste, an evaluation of its antioxidant activity is necessary. Antioxidants are a class of substances capable of delaying or inhibiting the oxidation of an oxidizable substrate, their role is to protect healthy body cells against the oxidizing action of reactive species (SIES et al., 2017). Objective: The aim of this work was to evaluate the antioxidant activity of the yellow passion fruit seed ethanol extract. Methodology: The dried and crushed passion fruit seeds went through an extraction process with hexane and ethanol in the Soxhlet apparatus and the calculated yield was 7.9%. The applied methods were: DPPH free radical capture, determination of the FRAP iron ion reduction power and the colorimetric assay using the Folin-Ciocalteu reagent. Results: The results were obtained by measurements in a UV-vis spectrophotometer and expressed as a function of the IC50 of the standards of each method and of the analyzed sample. The FRAP and Folin assays presented the values closest to their respective standards, presenting better values than those of other brazilian fruits described in the literature. Conclusion: The study of the antioxidant activity of the compounds present in the passion fruit seed extract revealed a promising potential, thus, the use of the extract as a natural antioxidant therapy can be another way to add value to what was previously discarded, in most cases.

Estudos da interação de Maytenus ilicifolia (Celastraceae) e Xanthomonas albilineans envolvidos na formação de triterpenos quinonametídeos

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Karina Alves Pinheiro Fontanin [1]; Tatiana Maria Souza-Moreira [2]; Vania Aparecida de Freitas Formenton Macedo dos Santos [1]; Andrew Oliveira [3]; Sandro Roberto Valentini [2]; Cleslei Fernando Zanelli [2]; Rafael Guido [3]; Maysa Furlan [1]

[1] Instituto de Química / Universidade Estadual Paulista “Júlio de Mesquita Filho”; [2] Faculdade de Ciências Farmacêuticas / Universidade Estadual Paulista “Júlio de Mesquita Filho”; [3] USP - São Carlos

Quinonemethide triterpenes (QMTs), maytenin (1) and pristimerin (2) (Figure 1) show accumulation in the root bark of Maytenus ilicifolia (Celastraceae)1. These compounds show biological potential, including antimicrobial (unpublished data), antitumor and anti-inflammatory activities2. The evaluation of these metabolites against Xanthomonas albilineans, a bacterium present in the soil that infests sugarcane plantations, showed to be potentially active, being 1 (IC50 0.46 mM) twice more active than 2 (IC50 1.0 mM) and the positive control tetracycline (IC50 1.0 mM). Due to the restricted accumulation of such triterpenes in the root bark of M. ilicifolia, combined with its previous proteomic studies, which demonstrated a large number of proteins (99) involved in the response to metabolic stress, the hypothesis that QMTs 1 and 2 may have their biosynthetic pathway regulated by plant-microorganism interactions was raised. Thus, some studies of M. ilicifolia seedlings inoculated with X. albilineans were carried out to study such hypothesis. The concentrations of 1 and 2 were evaluated by high-performance liquid chromatography diode array detection (HPLC-DAD) before the infection. The concentrations of 1 and 2 in the root barks of M. ilicifolia seedlings showed variation on QMT production among three individuals. That data will set a baseline in QMT capability of production of the analyzed individuals for comparison after their inoculation with the bacteria. Expression level of genes involved in QMT production (coding for friedelin synthase and cytochrome P450) will also be analyzed before and after inoculation to evaluate the possible plant response to X. albilineans.

Estudos in silico para seleção de alcaloides com atividade de inibição da Tioredoxina Glutationa Redutase do Schistosoma mansoni (SmTGR)

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Valeria Vieira Moura Paixão [1]; Ricardo P. Rodrigues [2]; Silvio Santana Dolabella [3]; Tiago Branquinho Oliveira [4]

[1] Universidade Federal de Sergipe; [2] Universidade Estadual de Campinas; [3] Departamento de Morfologia/Universidade Federal de Sergipe; [4] Departamento de Farmácia / Universidade Federal de Sergipe

Schistosomiasis is a neglected tropical disease caused by the parasite Schistosoma mansoni and affects about 200 million people per year. The current treatment is carried out using praziquantel (PZQ) achieving cure rates of 60 to 70%, but it is not effective against its juvenile form. Thus, the development of new schistosomicidal drugs becomes necessary. In this sense, SmTGR, responsible for the parasite metabolism, was validated as a promising target for drug development. Alkaloids have a great structural diversity comprising an extensive and important group of secondary metabolites. In the present study, structure-activity relationship (SAR) models were built to identify promising alkaloids to inhibit SmTGR for the treatment of schistosomiasis. The PubChem Bioassay database (AID: 485364) was selected for the development of the models and a database of structures of 1000 alkaloids was developed for the virtual screening. After exploring the combination of 63 two-dimensional chemical descriptors with the random forest (RF), J48 tree learning, adaptive boosting (AdaBoostM1) with J48 tree learning and, supportvector machine (SVM), four classification SAR models were built. The RF model was selected after external validation (ROC = 0.97 and kappa = 0.81). Among the 46 alkaloids that were selected as potential SmTGR inhibitors are epiisopilosin and epiisopiloturine, which can be isolated from the leaves of Pilocarpus microphyllus (jaborandi), and present inhibition activity in vitro and in vivo against S. mansoni. However, the mechanism of action of these substances has not yet been elucidated. This is the first SAR-based study to discover promising alkaloids to inhibit SmTGR. This research has successfully applied different computational approaches to accelerate the identification of alkaloids with schistosomicidal activity, which when properly validated experimentally, can contribute to the advance in the discovery of drug candidates against schistosomiasis.

Evaluation of anti-Trypanosoma cruzi activity of volatile oils from Saururus cernuus and chemometric analysis using PLS-DA methods

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Juliana Brito [1]; Thais Costa-Silva [2]; Vinicius Silva Londero [1]; João Luiz Baldim [3]; Edgard Antonio Ferreira [4]; André Gustavo Tempone [5]; Joao Lago [6]

[1] Universidade Federal de São Paulo; [2] Center of Natural Sciences and Humanities / Universidade Federal do ABC; [3] Centro de Ciências Naturais e Humanas / Universidade Federal do ABC; [4] Química / Escola de Engenharia / Universidade Presbiteriana Mackenzie; [5] Centro de Parasitologia e Micologia / Adolfo Lutz / Adolfo Lutz; [6] Universidade Federal do ABC

The present study reports the molecular dereplication and the evaluation of anti-Trypanosoma cruzi activity of volatile oils from inflorescences, leaves, branches, and roots of Saururus cernuus L. (Saururaceae). Chemically, the oils showed the predominance of sesquiterpenes in inflorescences (64.04%) and branches (63.82%), with beta-sesquiphellandrene (25.50%) and (E)-caryophyllene (22.40%) corresponding to the main constituents of each oil. Furthermore, it was possible to detect

safrole as the most predominant compound in the leaves oil (49.09%). On the other hand, the oil from roots was mainly composed by monoterpenes (84.60%), with limonene in higher concentration (38.41%), followed by apha-pinene (20.19%), and camphene (14.71%). The volatile oils from S. cernuus were submitted to evaluation of the in vitro anti-T cruzi activity (trypomastigote forms) and cytotoxicity in mammalian cells (NCTC). The obtained results (Table 1) revealed that the oils from inflorescences and branches displayed higher antitrypanosomal potency with EC50 values of 7.1 and 8.8 microg/mL, respectively, followed by the oils from the roots and inflorescences, with EC50 values of 17.3 and 30.4 microg/mL, respectively. Additionally, branches and inflorescences oils displayed no toxicity in mammalian NCTC cells (CC50 > 200 microg/mL).
Using two different PLS-DA methods, it was possible to suggest that the anti-T. cruzi activity of the tested oils could be associated with the presence of beta-sesquiphellandrene, safrole, beta-elemene, and alpha-zingiberene whereas threo-austrobailignan-5, beta-sesquiphellandrene, alpha-humulene, germacrene D, and bicyclogermacrene play a role in the cytotoxicity against NCTC cells.

Friedelane-type triterpene reductase in Maytenus ilicifolia biosynthesis

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Naira Anhesine [1]; Mariana Santoni [2]; Tatiana Maria Souza-Moreira [2]; Sandro Roberto Valentini [2]; Cleslei Zanelli [2]; Maysa Furlan [1]

[1] Instituto de Química / Universidade Estadual Paulista “Júlio de Mesquita Filho”; [2] Faculdade de Ciências Farmacêuticas / Universidade Estadual Paulista “Júlio de Mesquita Filho”

The species Maytenus ilicifolia, Celastraceae, is popularly known as “espinheira-santa” and its leaves are widely used in the form of tea in folk medicine for the treatment of stomach ulcers and gastritis. Chemical and biological studies report other activities such as contraceptive, analgesic, antioxidant, among others, which are closely related to the presence of flavonoids, tannins and terpenes. The pentacyclic triterpenes (C30) is the subclass that deserves attention in species of the genus Maytenus, among them friedelin and friedelan-3-ol, which are the most abundant compounds in the nonpolar extract of M. ilicifolia leaves. From a biosynthetic point of view, friedelin is the only pentacyclic triterpene that is oxidized at carbon 3 (C-3) as a ketone and the proposed mechanism for the formation of this function does not involve the formation of an enol form. However, the concomitant accumulation of friedelin and its reduced derivative, friedelan-3-ol, raises interesting biosynthetic aspects to be investigated. In this context, the aim of this work is to identify a reductase-like enzyme capable of reducing a ketone group at the C-3 position of terpenes in its alcoholic derivatives using molecular biology and microbiology tools. Through bioinformatics analysis, four transcripts were considered promising since they bear characteristic motifs of 3-ketoreductse, a type of Short-Chain Dehydrogenase (SDR). So far, two of them (45855_i6 and 52338_i1) were cloned by Gateway Cloning Technology, sequenced and transformed into the yeast strain Saccharomyces cerevisiae KB13 containing a plasmid carrying the friedelin synthase gene (FRS) which will provide the substrate (friedelin) to the enzyme of interest. The yeast cells were galactose induced and the spent medium extracted with hexane/ethyl acetate 7:3 was analyzed by GC-MS. The chromatograms showed only the friedelin production suggesting that both transcripts don’t reduce the friedelin keto group in friedelan-3-ol. These results are of interest since could be the entry point of the friedelan derivatives biosynthetic pathway in M. ilicifolia and ultimately may provide a sustainable heterologous source of these pharmacologically important metabolites.

Identification and synthesis of male-specific cuticular compounds of Amerrhinus ynca SAHLBERG (COLEOPTERA: CURCULIONIDAE)

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Rândilla Regis Cordeiro dos Santos [1]; Palmira Neta [2]; José Inácio Lacerda Moura [3]; Diogo Montes Vidal [4]; Carla Fernanda Favaro [2]; Paulo Zarbin [1]
[1] Universidade Federal do Paraná, UFPR; [2] Universidade Estadual de Santa Cruz, UESC; [3] Centro de Pesquisa do Cacau, CEPLAC/CEPEC; [4] Universidade Federal de Minas Gerais, UFMG

The beetle Amerrhinus ynca Sahlberg, 1823 (Coleoptera: Curculionidae) causes damages to several species of palm trees, as Arecaceae family. The larvae of this beetle pierces the leaf rachis, causing an obstruction in the flow of nutrients to the plant. To date, there are no registered insecticides for the control of A. ynca. An efficient control strategy is the use of synthetic pheromones allied with integrated pest management tactics. Thus, this work aims to extract, identify and synthesize the pheromone produced by A. ynca, in order to provide a method for monitoring and/or control this pest. The cuticle compounds produced by A. ynca were collected by immersion of the adult beetles in hexane. Chromatographic analysis of cuticular extracts from males and females revealed that only males insects had specific cuticular chemical compounds. The chemical structures of two male-specific pheromone compounds were proposed by the analysis of their mass spectra (GC-MS) and infrared spectra (CG-FTIR). The structure suggested for the major component was octadecanal (1), which was confirmed by CG analysis and coinjection of synthetic standard. The second compound presented as a minor component was indicated as a methyl-branched ketone (2). Two structural proposals were designed and synthesized to identify and confirm the structure of the methyl-branched ketone as 6-methydocosan-2-one. The 6-methydocosan-2-one was obtained after fifteen steps using Wittig olefination as keys steps. A enantioselective synthesis is being developed in order to determine the absolute configuration of the methyl branch of the natural compound of A. ynca.

In vitro evaluation of alkyl long-chain p-coumaric esters from Baccharis retusa and B. sphenophylla against amastigotes forms of Trypanosoma cruzi

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Matheus Lopes Silva [1]; Anderson Ueno [2]; Thais Costa-Silva [3]; Guilherme Antar [4]; André Gustavo Tempone [5]; João Henrique Ghilardi Lago [6]
[1] Universidade Federal do ABC; [2] Universidade Federal de São Paulo; [3] Center of Natural Sciences and Humanities / Universidade Federal do ABC; [4] Universidade de São Paulo; [5] Centro de Parasitologia e Micologia / Adolfo Lutz / Adolfo Lutz; [6] Centro de Ciências Naturais e Humanas / Universidade Federal do ABC

Comprising more than 500 species distributed throughout most of South America, Baccharis is one of the most phytochemically diverse genus of Asteraceae, being composed by diterpenes and flavonoids. Chemically, Baccharis extracts are notably known to afford flavonoids and terpenoids. In the present work, was reported the isolation of one alkyl (1) and two alkenyl p-coumarates (2 – 3) from hexane extracts of aerial parts from B. sphenophylla and B. retusa. NMR and ESI-HRMS analysis allowed the identification of compounds 1 – 3 as hexacosyl p-coumarate (1), (7E,18′Z)-hexacos-18′-enyl coumarate (2) and (7Z,18′Z)-hexacos-18′-enyl coumarate (3). Searching for new molecular prototypes for the treatment of Chagas disease, compounds 1 – 3 were subject to in vitro anti-T. cruzi screening using resazurin colorimetric assay in order to evaluate 50% inhibitory concentration (IC50) against amastigotes (intracellular form) of the parasite. For determination of cytotoxicity against mammalian

cells (CC50), screening using MTT assay was performed using NCTC cells. Obtained results shown that compounds 1 – 3 displayed reduced cytotoxicity against NCTC cells (CC50 > 200 µM), though only compound 1 displayed activity against amastigotes with IC50 value of 16.9 ± 3.2 uM and a respective selectivity index of > 11.9. For comparison, the positive control benznidazole displayed IC50 value of 5.5 ± 1.0 uM and a SI > 36.4. Considering that the amastigote form of T. cruzi define the chronic phase of Chagas disease and the standard drug benznidazole is not very effective in this stage, new drug prototypes active against the intracellular forms of the parasite are of major clinical relevance. In addition, the Drugs for Neglected Disease Initiative (DNDi) preconizes a selectivity index of 10-fold more active to the parasite in relation to mammalian cells as target for the discovery of new hit compounds – a framework in which compound 1 manages to achieve. As previously demonstrated, alkyl p-coumarates were active against both epimastigote and trypomastigote form of the parasite and the size of the side-chain seem to play a role in the activity observed. In addition to this, our study reveals that a saturated side-chain of compound 1 also seems to be a necessary pharmacophoric moiety, as unsaturated compounds 2 and 3 were shown to be inactive. In conclusion, considering the SI and non-toxicity observed for compound 1, was suggested that it could be used as scaffold for the synthesis of new chemically related derivatives which in turn could shed light on alternative treatments for Chagas disease.

Isolamento cromatográfico de dois ésteres de forbol do látex de Euphorbia umbellata (janaúba) usado na medicina popular

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Gabrielle Neves [1]; Andressa L. D. Carvalho [1]; João B. F. Tostes [2]; Marcos Nakamura [2]; José Luiz Mazzei [2]; Helvécio V. A. Rocha [3]; Antonio Carlos Siani [2]

[1] Programa de Pós-Graduação Acadêmico em Pesquisa Translacional em Fármacos e Medicamentos / Instituto de Tecnologia em Fármacos / Fundação Oswaldo Cruz; [2] Departamento de Produtos Naturais / Instituto de Tecnologia em Fármacos / Fundação Oswaldo Cruz; [3] Departamento de Inovação Galênica / Instituto de Tecnologia em Fármacos / Fundação Oswaldo Cruz

Investigações do látex de E. umbellata (Pax) Bruyns (Euphorbiaceae) têm demonstrado a alta capacidade de seu conteúdo diterpênico, do tipo ésteres de forbol, em atuar como agente reversor da latência (LRA) do vírus da imunodeficiência humana (HIV) em células infectadas, abrindo a perspectiva de uma nova terapia de combate ao HIV. Tendo em vista esse potencial e a escassez de dados relativos à caracterização físico-química de extratos e frações ativas do látex de E. umbellata, o presente estudo abordou o isolamento e a caracterização de diterpenos do tipo tigliano de forma a propor marcadores químicos para monitoramento da qualidade dessa matéria-prima vegetal e dos seus intermediários de transformação tecnológica. Após a coleta (julho/2019, Barretos/SP, SisGen A3EA521), o látex foi congelado e liofilizado, resultando em um pó homogêneo, fino e branco, codificado como LLBA. Em seguida, 120 mg de LLBA foram submetidos à Extração em Fase Sólida em RP-18 (Supelco, 1000 mg/6 ml), eluídos com CH_3CN para resultar numa fração concentrada em diterpenos. Após otimização da extração, o método foi escalonado, com mesmo eluente, para atender as condições da Cromatografia Líquida de Média Pressão, na qual 1 g de material foi aplicado em coluna de sílica (40-63 µm; 23 x 2,6 cm) gerando 14 frações de 30 ml, as quais foram avaliadas por CCF em RP18 (CH_3CN) e coloração por anisaldeído sulfúrico. As frações, reunidas por similaridade de perfil em CCF, foram analisadas por CLAE-DAD (Purospher Star RP-18 250 x 4,6 mm, 5 µm, gradiente CH_3CN-H_2O). As frações ricas em diterpenos (170 mg) foram submetidas ao fracionamento em coluna de sílica gel 60 (63-200 µm, 30 x 3,0 cm, $CHCl_3$ como eluente), coletando-se cerca de 70 frações de 12,5 ml. Após avaliação por CCF em gel de sílica ($CHCl_3$-éter etílico 95:5), CLAE-DAD e da capacidade de reativar o HIV in vitro, as frações de interesse foram submetidas à CLAE semi-preparativa (Inertsil ODS-4 RP18 250 x 6,0 mm, 5 µm; CH_3CN-H_2O 60:40) para isolar as substâncias candidatas a marcadores. Entre essas, os dois ésteres de forbol mais abundantes, codificados como DA e DG, tiveram suas purezas qualitativamente checadas por CCF (RP18/CH_3CN) e CLAE-DAD (Purospher Star RP-18e). Análise por espectrometria de massas e ^1H e ^{13}C-RMN confirmaram as estruturas como sendo ésteres diterpênicos derivados do núcleo tigliano. DA e DG estão sendo testados quanto à capacidade em atuar como LRA.

MOLECULAR NETWORKING AND UHPLC-HRMS/MS ANALYSIS OF THE WILD MUSHROOM Gymnopilus imperialis (Agaricomycetes, Basidiomycota)

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Patricia Sartorelli [1]; Lhaís Caldas [1]; Cassius Stevani [2]; Douglas Mendel [2]; Nelson Menolli [3]
[1] Universidade Federal de São Paulo; [2] Universidade de São Paulo; [3] Departamento de Ciências da Natureza e Matemática (DCM), Subárea de Biologia (SAB) / Instituto Federal de Educação, Ciência e Tecnologia de São Paulo

The genus Gymnopilus, consists in a widely distributed basidiomycete fungi in tropical regions of the world. It is represented by some species such as G. spectabilis, G. junonius, G. penetrans, G. dilepis [1]. Although controversial, some of them are reported in the literature due to its toxicity and psychoactive effect caused by the alkaloids psylocibin and psilocin [2]. Considering the large number of metabolites from mushroom species that can be prospected for therapeutic purposes, fractionation and isolation of metabolites can be an arduous task. Therefore, tools for rapid identification of molecules in situ have emerged as an important method in helping to promptly identify molecules. In this matter, dereplication tools such as GNPS (Global Natural Products Social Molecular Networking), has become important in prospecting metabolites [3]. In this work extracts obtained from wild mushrooms Gymnopilus imperialis were analyzed considering their content of oligoisprenoids by using UHPLC-HRMS/MS and GNPS to prospect molecules and dereplicate analogues. It was possible to annotate 25 oligoisoprenoids, named gymnopilins, from methanol, dichoromethane and ethyl acetate extracts of G. imperialis, 4 of them from GNPS spectral library match, and 21 from prediction based on molecular network. Literature suggests that these molecules might act as a complement in the psychoactive activity of some species of the genus [4].

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Paepalanthus: a review on isolated compounds

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Laysa Lanes Pereira Ferreira Moreira [1]; Warley Borges [1]
[1] Universidade Federal do Espírito Santo

Paepalanthus belongs to Eriocaulaceae family and it is one of the most diverse genera in Brazil, with an endemism rate equivalent to 95.7%.1 It has distribution throughout territory, but the greatest center of diversity occurs in the “Cadeia do Espinhaço”.2 Despite this, few species of the genus have been chemically studied. Thus, the aim of this study is to carry out a literature review on isolated compounds in the Paepalanthus genus. Papers were accessed from six platforms such as SciFinder® and ScienceDirect. Forty papers were evaluated, within isolated and/or identified compounds. The research evidenced eighty-seven compounds from the flavonoids (64.4%) and naphthopyranones (35.6%) classes. Among the compounds of the flavonoids class were isolated derivatives of apigenin, luteolin, kaempferol, patuletin and quercetin. So far, 30 naphthopyranones and 1 naphthoquinone have been isolated from Paepalanthus species.

Pedra-ume-caá (Eugenia biflora): compostos fenólicos e potencial antidiabético.

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Edinilze Souza Coelho Oliveira [1]; Flavia Pontes [2]; Leonard Acho [1]; Bárbara Janaína Silva [1]; Alessandro Rosário [3]; Jaqueline de Araújo Bezerra [4]; Francinete Campos [5]; Emerson Lima [1]; Marcos Machado [1]

[1] Universidade Federal do Amazonas; [2] Departamento de Bioquímica e Biologia Molecular / Centro Politécnico / Universidade Federal do Paraná; [3] Engenharia Florestal, Campus Paragominas, Universidade Federal Rural da Amazônia; [4] Instituto Federal de Educação, Ciência e Tecnologia do Amazonas; [5] Departamento de Farmácia / Laboratório de Biociências e Espectrometria de Massas / Universidade Federal do Paraná

A espécie vegetal *Eugenia biflora* (L.) DC., conhecida popularmente como pedra-ume-caá, tem sido utilizada na medicina popular brasileira na forma de infusão (folhas) para o tratamento do diabetes. Tendo em vista, a necessidade do estudo químico e da comprovação do uso popular, as folhas dessa espécie foram coletadas na Área de Proteção Ambiental de Algodoal, Maracanã (PA). A infusão das folhas secas trituradas (m/v) foi seca por spray drying. A identificação dos constituintes foi realizada por LC-qTOF-MS/MS e RMN 1D e 2D. Ademais, foram realizados estudos *in vitro* para determinar os potenciais antioxidante, antiglicante e enzimático (alfa-glicosidase), bem como o ensaio de tolerância oral a carboidratos em modelo experimental *in vivo*. Onze constituintes químicos foram identificados, sendo o ácido quínico e 10 compostos fenólicos (procianidina tipo B, catequina, catequina-3-*O*-galato, miricetina-3-*O*-glicosídeo, miricetina-3-*O*-(2''-*O*-galoil)-alfa-ramnosídeo, miricitrina, guaijaverina, quercitrina, isoramnetina-3-*O*-glicosídeo e ácido metil elágico ramnosídeo). Concernente ao estudo farmacológico, o extrato de *E. biflora* inibe a glicação pela Via Não Oxidativa (CI50 22,2 ± 1,2 ug mL-1) com resposta superior ao padrão aminoguanidina (CI50 37,6 ± 0,03 ug mL−1). Além disso, o teor de fenóis totais (263,2 ± 1,9 mg GAE g-1), associado às elevadas atividades antioxidantes indicadas pelos métodos DPPH● (1475,0 ± 4,7 umol TE g-1), ABTS●+ (982,0 ± 23,6 umol TE g-1) e atividade antioxidante celular (65,53% ± 3,5 ug mL-1, 100 ug mL-1) revelam um elevado potencial antioxidante desse extrato. Além disso, esse extrato foi capaz de inibir a enzima alfa−glicosidase (CI50 = 22,2 ± 1,2 ug mL−1) com resposta superior ao padrão acarbose (CI50 = 62,2 ± 1,2 ug mL−1). O mecanismo de ação foi confirmado por meio do experimento *in vivo* com animais saudáveis hiperglicêmicos (*Mus musculus* Swiss), o qual evidenciou um declínio na curva da glicose 30 min após a dose oral de maltose em duas concentrações testadas (100 mg/kg pc e 200 mg/kg pc). O presente estudo corrobora com o uso popular dessa espécie para o tratamento do diabetes, bem como comprova a via de ação hipoglicemiante e antiglicante, bem como alicerça futuros estudos químicos e farmacológicos dessa espécie.

Peracetylation of polyphenols under rapid and mild reaction conditions

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Douglas Chaves de Alcântara Pinto [1]; Paulo Pitasse [2]; Gabriela de Souza [1]; Rosane Castro [3]; Marco Edilson Freire de Lima [1]

[1] Universidade Federal Rural do Rio de Janeiro; [2] Departamento de Química Orgânica / Instituto de Química / Universidade Federal Rural do Rio de Janeiro; [3] Departamento de Quimica / Instituto de Química / Universidade Federal de Juiz de Fora

Structure modification is an important tool on studying properties of naturally occurring polyphenols. Regarding preparation of acetyl esters, the presence of hydroxyl groups stabilized by intramolecular hydrogen bond may pose as an obstacle for the peracetylation of such polyphenols1,2. In this work we present a facile protocol for the acetylation of selected polyphenols under mild reaction conditions, by using acetic anhydride, catalytic 4-dimethylaminopyridine (DMAP) and dimethylformamide (DMF) as solvent3. Reaction conditions were adjusted for optimal formation of peracetylated polyphenols while minimizing the formation of by-products. Butyric anhydride was employed as alternative acylating agent and showed similar results. Reaction yields varied from 78–97% and products were obtained in high purity, as determined by LCMS(ESI+), 1H NMR and 13C NMR.

Primeiros compostos isolados de Sida ciliares L. (Malvaceae sensu lato)

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Wallace Amorim Machado de Queiroz [1]; Diégina Fernandes [2]; Ana Laura Cabral Sobreira [1]; Camila Macaúbas [1]; Janderson Albuquerque [2]; Abrahao Alves [3]; Yanna Teles [4]; Maria Agra [5]; Maria de Fátima Vanderlei de Souza [1]

[1] Universidade Federal da Paraíba; [2] Centro de Ciências da Saúde / Universidade Federal da Paraíba; [3] Universidade Federal de Campina Grande; [4] Centro de Ciências Agrárias / Universidade Federal da Paraíba; [5] Centro de Biotecnologia / Universidade Federal da Paraíba

The millenary medicinal use of plants to heal illnesses gave humanity a large knowledge about the therapeutic effects and the toxicitity of some species. In this context, the gender Sida ciliaris L. in the Malvaceae sensu lato family, which is popularly known as “escova peluda” and “guanxuminha” and used in the treatment of kidnet diseases. The aerial parts of the species were collected at Brejo do Cruz/PB /Brazil, in April 2021 and the botanical identification was carried out by Profa Dra Maria de Fátima Agra. A specimen voucher was kept in the herbarium Rita Baltazar de Lima, under number 7572. The material was dried in a stove at 40oC circulating air and powderer in a mechanical mill, providing 1.8 Kg of power, that were submitted to maceration with hexane, hexane/ethyl acetate (1:1) and 95% ethanol, for 72 hours each, resulting in extractive solutions, which were filtered and concentrated in a rotative evaporator, providing their respective extracts. From the chromatographic fractionation using sílica flash and/or sephadex LH-20 (Merk) as stationary phases and PA solventes as mobile phase, it was possible to isolate the compound coded as Sc-1 from the Hexane/ethyl acetate extract (1:1) and from the ethanol extract the Sc-2. The structural characterization of those, was defined after analysis of the Nuclear Magnetic Resonance spectra (NMR de H1 e 13C) Uni and Bidimencional and comparisons with models from the literature, being Sc-1 a mix of hydroxy pheophytins:132-hidroxy-(132-R)-pheophytin a (Sc-1a) and 132-hidroxy-(132-S)-pheophytin (Sc-1b) and Sc-2 as 5,7,3’,4’- tetrahydroxyflavone (luteolin), both inedits on the species S. ciliares, being thus, a S. ciliares pioneer study that will contibrute to the chemotaxonomic knowledge about the Malvaceae sensu lato family.

Putative identification of metabolites from aqueous extracts of Magonia pubescens A.St.-Hil. branches

https://proceedings.science/p/138866

Acácio Raphael Moraes [1]; Maria Simões [2]; Ezequias Pessoa Siqueira Filho [3]; Markus Kohlhoff [3]; Lucienir Duarte [1]; Antônio Alcântara [1]; Grasiely Sousa [1]

[1] Departamento de Química / Instituto de Ciências Exatas / Universidade Federal de Minas Gerais; [2] Universidade Estadual de Montes Claros; [3] Laboratório de Química de Produtos Naturais / Instituto René Rachou / Fundação Oswaldo Cruz

Magonia pubescens A. St.-Hil. is a natural species from the Brazilian savannah (Cerrado) and its fruits and seeds are employed for preparation of soaps used in the treatment of dermatitis and seborrhea[1]. In this research work, the phytochemical composition of the aqueous extracts of M. pubescens branches was analyzed for the first time.

The vegetal material was collected in Montes Claros, Minas Gerais, and the aqueous extract (EA) was obtained by decoction (60 ºC, 2 h) of 20 g of the dried branches. The extract obtained was fractioned using chemical march[2]: EA was alkalized with ammonium hydroxide until pH 10. Afterwards, extractions were performed with 100 mL of ethyl acetate and ethyl ether (3:1), three times. Both aqueous and organic fractions were acidified with HCl to approximately pH 2. After acidification, the aqueous fraction was extracted with 100 mL of a mixture of ethyl acetate and ethyl ether (3:1) three times, generating an aqueous phase (EA1) and an organic phase (EA2). The acidified organic fraction was extracted three times with 100 mL of aqueous HCl solution (pH 2), giving rise to the aqueous phase (EA3) and the organic phase (EA4). Organic solvents were eliminated using a rotary evaporator, and the aqueous extracts were lyophilized. The most polar fraction was not analyzed due to its limited solubility. EA2, EA3 and EA4 were analyzed through ultra-high performance liquid chromatography (UHPLC) with high resolution mass detection. The comparison of the experimental data and mass spectra from public database allowed to putatively identify some compounds in each fraction. From fraction EA2, 17 compounds were putatively identified, including flavonoids, triterpenes and lapachol. The total of 16 compounds, including flavonoids and triterpenes, were putatively identified in fraction EA3. They were also putatively identified 15 compounds at fraction EA4, including triterpenes, saponins and lapachol. Some compounds, as lapachol, scopoletin, glycyrrhetinic acid, quercetin, afzelin, cleomiscosin B and litseacolide L, were putatively identified in two different fractions.

In the present work, it was possible to putatively identify 53 compounds in the aqueous extract from branches of Magonia pubescens A. St.-Hil.

Química Ambiental - AMB

Estresse oxidativo em Oreochromis niloticus após exposição aguda ao arsênio

https://proceedings.science/p/138783

Aryanna Sany Pinto Nogueira Costa [1]; Maraísa Feitosa [1]; Lucas Matheus Batista Dantas Falcão [2]; Daniela Santos Anunciação [1]; Josué Carinhanha Caldas Santos [1]; Elton Lima Santos [1]

[1] Universidade Federal de Alagoas; [2] Instituto de Química e Biotecnologia / Universidade Federal de Alagoas

A toxicidade e propriedades bioacumulativas do arsênio (As) requer um controle dos níveis de concentração e avaliação dos efeitos adversos de suas espécies no ambiente natural. O presente trabalho visou a determinação da LC50 de As(III) e As(V), assim como o mecanismo de ação mediado pelo estresse oxidativo em Tilápia do Nilo (Oreochromis niloticus). Os peixes foram aclimatados durante 10 dias com sistema de aeração, filtração e monitoramento da qualidade da água. Em seguida, em cada aquário, 10 peixes foram expostos às espécies de arsênio inorgânico por 96h, em quadruplicata. Os níveis de concentração de exposição foram 5, 15, 30, 40, 60 e 80 mg L-1, para As(III) e 50, 150 e 300 mg L-1, para As(V). Para ambas as espécies, aquários sem contaminantes foram utilizados como controle. Ao longo do experimento, os peixes mortos foram contados para o estudo LC50 e após 96 h, os sobreviventes foram anestesiados e sacrificados para separação dos tecidos (brânquias, músculo e fígado), então armazenados a -20 ° C para posterior análise enzimática. Os valores de LC50 foram 42,92 mg L-1 para As(III) e 52,24 mg L-1 para As(V). O As utilizado na água dos aquários foi determinado por HG-AFS e as porcentagens de recuperação para As(III) e As(V) foram, respectivamente, 74 e 81%. Os elementos Al, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, V, Zn foram detectados na água dos aquários por ICP OES, dos quais Ca, Cd, K, Mg, Na e P foram quantificados e apresentaram, respectivamente, de 2,92; 0,146; 3,82; 2,81; 18,43 e 0,19 mg L-1. O teor de carbono orgânico foi determinado na água da torneira (<LOQ) e na água do rio (0,11 mg L-1) e este baixo teor teria pouca influência na interação da matéria orgânica natural (MON) com o As. A similaridade entre os valores de LC50 para As(III) e As(V) pode estar relacionada à conversão de As(III) a As(V), devido ao ambiente oxidante. A avaliação do mecanismo de toxicidade foi realizada nos tecidos dos peixes expostos a 30 mg L-1 de As(III) com base nas determinações de malondialdeído (MDA), superóxido dismutase (SOD), catalase (CAT) e glutationa S-transferase (GST). Com relação à atividade das enzimas, apesar da tendência à diminuição em todos os parâmetros, não houve diferença significativa entre tratamentos, para 95% de confiança. O MDA também foi utilizado como indicador de dano à membrana celular nas amostras de fígado e brânquias; e o aumento do MDA no músculo e diminuição no fígado e brânquias sugerem que o mecanismo de defesa antioxidante e detox no músculo, no tempo avaliado, indica uma modulação negativa pelo As(III). Esta modulação pode estar ocorrendo tanto pela diminuição do transporte de oxigênio para o interior das células, quanto pela inibição enzimática direta. Este aumento das espécies reativas de oxigênio biodisponíveis acarreta o dano celular, que em primeira instância se reflete no aumento de peroxidação lipídica ocasionando desde o aparecimento de doenças até a morte dos peixes expostos ao As(III).

"Aires nuevos para la primeira infância": um programa internacional para o monitoramento e gerenciamento da qualidade do ar e

https://proceedings.science/p/138769

Graciela Arbilla de Klachquin [1]; Cleyton Martins da Silva [2]; Danilo Moreira Junior [2]; João Rogério Borges de Amorim Rodrigues [1]
[1] Universidade Federal do Rio de Janeiro; [2] Universidade Veiga de Almeida

This project, related to the Sustainable Development Goals, is part of a network of 13 cities in Latin America and Caribbean, coordinated by Fundación Horizonte Ciudadano (Chile) in order to determine fine particulate matter concentrations (PM2.5). Monitoring was initiated in 2021 and data are regularly discussed by the network members. Local governments will be updated with the results in order to implement actions to improve air quality to guarantee the health of children, mainly those in the early childhood. Data are included in a free real-time air quality platform.

Low-cost monitors (Air-visual Pro) were installed in locations with high flux of children (near schools and pre-schools) in the north and west areas of the city of Rio de Janeiro. Initially, results determined using a low-cost monitor were compared with data obtained by the air quality automatic station operated by the municipal government in Irajá. Data obtained in Del Castilho, Bangu, Irajá, Campo Grande, Madureira and Tijuca showed that the median values for 24-hour means are approximately 10 µg m-3. 50% of values were in the interval 5-20 µg m-3, with values as high as 55 µg m-3. 1-hour means reached 200 µg m-3, mainly during the dry season. Simulations of air masses transport showed that the north area (Del Castilho, Madureira and Irajá) receive pollutants originating in the petrochemical complex of the Metropolitan Region of Rio de Janeiro. The west zone (Campo Grande and Bangu) receives air pollutants due to metallurgical industries and mining activities. Local and transported emissions from vehicles, mainly diesel, also affect particulate matter levels. Tijuca, is a typical urban area with high flux of vehicles.

In spite of being a pollutant of major concern, PM2.5 levels, in the city of Rio de Janeiro, are determined in only one automatic monitoring station. Low-cost monitors could provide useful information to determine the most critical areas and implement, in the future, an effective air quality plan.

A Mata Atlântica remanescente do Rio de Janeiro: a metrópole e a floresta

https://proceedings.science/p/138772

Guilherme de Sousa Dantas [1]; Bruno Siciliano Ramos Barros [1]; Cleyton Martins da Silva [2]; Graciela Arbilla de Klachquin [1]

[1] Universidade Federal do Rio de Janeiro; [2] Universidade Veiga de Almeida

The Metropolitan Region of Rio de Janeiro has approximately 16% of its territory as protected areas, mainly forest formations of the Atlantic Forest (secondary and primary). This constitutes a significant green belt for the city with a relevant role in the maintenance of biodiversity, water supplies, air quality and temperature regulation. In this project, volatile organic compounds were determined in the Tijuca Forest (National Park) and Pedra Branca, Chacrinha and Grajau State Parks to assess the impact of the urban emissions in the forest. Air samples were collected using electropolished stainless steel canisters (Silonite®) and analyzed using thermal desorption heart-cutting multidimensional gas chromatography (MDGC). The analytical system consisted on an Agilent 7890A CG with a capillary flow technology (CFT) Deans Switch, two chromatographic columns (a DB-624 and a PoraPLOT Q HT) and two detectors (a mass spectrometer and a flame ionization detector) without cryogenic.

Concentrations of isoprene, the main biogenic compound, were in the interval 0,23 to 3,99 µg m-3 . Other compounds, probably of anthropogenic origin were (concentrations in µg m-3): propane (1,42-7,01), nbutane (2,76-7,93), ethane (1,02-5,95), isopentane (1,06-5,09), n-pentane (0,83-4,18), isobutane (1,31-3,63), propene (<QL-0,47), ethene (<QL-0,71), benzene (0,29-0,55) and toluene (0,36-3.02).

Concentrations of anthropogenic compounds were lower in Tijuca and Pedra Branca forest, showing the role of dense vegetation in pollution mitigation. Levels in Grajau and Chacrinha parks were lower than concentrations currently determined in the urbanized area. These urban parks increase the connectivity between the different elements of the biodiversity and have an important role in the improvement of environmental quality. Rio de Janeiro depends on the Atlantic Forest but, also, the future of the Atlantic Forest will be defined by the way in which the city protects the natural areas.

Adsorption study of a binary mixture of salicylic acid and caffeine using activated carbon from green coconut husks

https://proceedings.science/p/138786

Bruno Salarini Peixoto [1]; Larissa Silva de Oliveira Mota [2]; Isac Marinho Dias [3]; Rafael dos Santos Caetano da Silva [3]; Marcia Cristina da Cunha Veloso [3]; Gilberto Alves Romeiro [3]; Marcela de Moraes [2]

[1] Programa de Pós-Graduação em Química / Instituto de Química / Universidade Federal Fluminense; [2] Universidade Federal Fluminense; [3] Instituto de Química / Universidade Federal Fluminense

A crescente demanda populacional vem acarretando o uso massivo de fármacos, o que se tornou uma fonte de poluição aos ecossistemas aquáticos. Os fármacos não metabolizados pelo organismo humano, ou descartados de forma inadequada, assim como os produtos de cuidados pessoas (PPCP – Pharmaceuticals & Personal Care Products), não são removidos de forma eficiente nas estações de tratamento de águas e efluentes. Este fato é observado em corpos d’água ao redor de todo o globo, embora a extensão dos efeitos danosos ainda está sendo investigada [1]. Desta forma, o desenvolvimento de novas tecnologias para a remoção destes contaminantes tornou-se necessária. Neste quesito, os carvões ativados mostram-se como excelentes candidatos para a resolução do problema. Tais materiais possuem elevada superfície específica e podem adsorver química e/ou fisicamente os contaminantes eliminando-os dos efluentes aquáticos. Por outro lado, os carvões ainda podem ser obtidos a partir de resíduos urbanos e agroindustriais, tornando-os como uma estratégia para a valorização destes rejeitos. Desta forma, o objetivo deste trabalho é a obtenção e caracterização de um carvão quimicamente ativado produzido a partir de rejeitos da casca de coco verde (Cocos nucifera) obtido por pirólise lenta. Posteriormente, foi realizado o estudo cinético e de adsorção do carvão monitorado por CLAE-DAD em uma mistura binária de ácido salicílico e cafeína, a fim de simular um efluente contaminado. A síntese do carvão foi realizada pela pirólise a 500 °C da casca do coco verde impregnado com ácido fosfórico (razão mássica 1:3). O material foi caracterizado por adsorção de N2; FTIR; PZC. O estudo cinético foi realizado utilizando 45 mg·g-1 de cada um dos adsorvatos (cafeína e ácido salicílico), individualmente e na forma de uma mistura binária a fim de estudar a interferência que a presença de outras substâncias pode causar no processo de adsorção. Uma mesma massa do adsorvente foi misturada a solução contendo o(s) contaminante(s) e agitado por diferentes tempos de contato – de 1 min a 48 h. O carvão ativado obtido mostrou ter características ácidas, com um ponto de carga zero no pH 1,96, uma grande superfície específica (1242 m2·g-1), com uma distribuição de poros distribuída entre microporos e mesoporos, e diâmetro médio de poros (BJH) de 4,44 nm. Os resultados dos ensaios de adsorção mostraram que o carvão ativado produzido é eficiente na remoção dos contaminantes modelos, embora o material apresente uma maior afinidade pela cafeína, com uma capacidade adsortiva de 40 mg·g-1 e 99 % de remoção tanto em água ultrapura quanto na mistura binária. Já a adsorção do ácido salicílico ocorreu em menor extensão (37 mg·g-1 e 85 % de remoção) em água ultrapura e sofreu uma maior influência da competição com a cafeína na mistura binária (32 mg·g-1 e 80 % de remoção).

[1] J. Borrull et al. Chemosphere 276 (2021) 130023.

AIR QUALITY IN AN URBAN SITE BEFORE AND DURING PANDEMIC

https://proceedings.science/p/138780

Aleinnys Marys Barredo Yera [1]; Camila Novais Farias [1]; Pérola de Castro Vasconcellos [1]
[1] Universidade de São Paulo

Strategies to combat air pollution are considered one of the biggest challenges all around the world. Large cities in developing world present poor air quality and less restrictive legislation allowing the population to be more exposed to the damage caused by pollutants. In order to study the source and fate of the air pollutants, field campaigns have been made in São Paulo city, Brazil. Sixty PM2.5 samples were collected from July to December 2019 just before the pandemic; other fifty samples were collected during one of the peaks of COVID-19 contamination in this city (from June to August 2020). Polycyclic aromatic hydrocarbons (PAH) and water soluble ions were determined. Concentrations of PM2.5 varied from 5 to 52 μg m-3 in 2019 samples and from 5 to 35 μg m-3 during the pandemic. The most abundant PAH were benzo(e)pyrene, benzo(b)fluoranthene and pyrene. These compounds are ubiquitous in urban atmosphere and present risks for human health. Benzo(a)pyrene equivalent over 1 indicates risk of cancer in the samples collected in 2019, before the pandemic. Sulfate, nitrate, sodium, ammonium, and potassium are the most abundant ions Figure above, shows the concentrations of the most abundant species in 2019 samples. These species are emitted by anthropogenic and natural sources, mainly vehicles, biomass burning and sea salt.

Amazonia como fonte de carbono em função do desmatamento e mudanças climáticas

https://proceedings.science/p/138779

Luciana Vanni Gatti

Amazonia hosts the Earth's largest tropical forests and has been shown to be an important carbon sink over recent decades. This carbon sink seems to be in decline, however, as a result of factors such as deforestation and climate change. Here we investigate Amazonia's carbon budget and the main drivers responsible for its change into a carbon sourceWe performed 590 aircraft vertical profiling measurements of lower-tropospheric concentrations of carbon dioxide and carbon monoxide at four sites in Amazonia from 2010 to 2018. We find that total carbon emissions are greater in eastern Amazonia than in the western part, mostly as a result of spatial differences in carbon-monoxide-derived fire emissions. Southeastern Amazonia, in particular, acts as a net carbon source (total carbon flux minus fire emissions) to the atmosphere. Over the past 40 years, eastern Amazonia has been subjected to more deforestation, warming and moisture stress than the western part, especially during the dry season, with the southeast experiencing the strongest trends. We explore the effect of climate change and deforestation trends on carbon emissions at our study sites, and find that the intensification of the dry season and an increase in deforestation seem to promote ecosystem stress, increase in fire occurrence, and higher carbon emissions in the eastern Amazon. This is in line with recent studies that indicate an increase in tree mortality and a reduction in photosynthesis as a result of climatic changes

across Amazonia.
Reference: Gatti et al., 2021 Nature, https://doi.org/10.1038/s41586-021-03629-6

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

https://proceedings.science/p/138784

Rayane Nascimento [1]; Bruna Ramos de Souza Gomes [2]; Rebeca dos Santos França [3]; Giovana Bataglion [3]; Alex Souza Moraes [2]; Jandyson Machado Santos [2]

[1] Universidade Federal Rural de Pernambuco/Departamento de Química ; [2] Universidade Federal Rural de Pernambuco; [3] Universidade Federal do Amazonas

O crescimento nas atividades antrópicas tem provocado impactos ambientais, tais como o aumento na contaminação de sistemas aquáticos por meio de descargas urbanas, atividades relacionadas ao petróleo e tráfego de navegações. Os hidrocarbonetos são amplamente utilizados como marcadores químicos ambientais, sendo os hidrocarbonetos policíclicos aromáticos (HPAs) usados para indicar diferentes fontes de contaminação, por exemplo, aquelas de origem pirogênica e/ou petrogênica. Desse modo, este estudo objetivou avaliar o nível de contaminação por HPAs em sedimentos do Rio Capibaribe, trecho dos municípios do polo têxtil de Santa Cruz do Capibaribe e Toritama, Pernambuco, empregando Cromatografia Gasosa acoplada à Espectrometria de Massas (CG/EM). Foram coletados 11 sedimentos (ST1 - ST11), abrangendo regiões com alta e baixa ocupação populacional e atividade industrial. As amostras foram secas em estufa a 60 °C/48 h e peneiradas (2 mm), em seguida, 5 g foram extraídos com diclorometano/metanol em sistema de micro-ondas. Por fim, foi realizado o fracionamento em coluna de vidro aberta utilizando hexano/diclorometano para obtenção da fração contendo os HPAs. A fração foi então analisada por CG/EM, obtendo-se a quantificação de 16 HPAs, incluindo os HPAs prioritários. Na avaliação dos resultados, para a obtenção dos níveis de contaminação, utilizou-se os parâmetros: ΣHPAs totais, Σ16 HPAs prioritários e a razão diagnóstica fluoranteno/pireno. Para o ΣHPAs totais, os sedimentos ST2, ST4 e ST10 apresentaram valores > 500 ng g-1, sendo classificados como altamente contaminados. Estes sedimentos foram coletados próximos a regiões de alta densidade populacional e atividade do setor têxtil. Quanto aos valores de Σ16HPAs, as amostras ST2, ST4 e ST10 também apresentaram os maiores valores, sendo obtido o intervalo de 100 a 1000 ng g-1, o que caracteriza regiões com contaminação moderada, possivelmente pela mesma razão anteriormente citada. Para a razão fluoranteno/pireno, todos os sedimentos apresentaram valores >1,0, o que indica a presença de matéria orgânica de fontes pirogênicas, o que aponta para uma contaminação procedente da combustão de petróleo e/ou biomassa. Dessa maneira, os resultados sugerem a existência de regiões no Rio Capibaribe impactadas por ação antrópica, devido à alta contaminação por HPAs nas amostras de sedimentos, sendo este o primeiro estudo na região envolvendo este sistema aquático, cujo trecho estudado amplia as áreas de monitoramento ambiental para além do estuário do Rio Capibaribe, trecho este amplamente estudado pela comunidade científica local.

AVALIAÇÃO DA CONTAMINAÇÃO ANTROPOGÊNICA POR ESTERÓIS DE SEDIMENTOS DO PORTO DE SUAPE, PERNAMBUCO, BRASIL

https://proceedings.science/p/138785

Ana Flávia B. de Oliveira [1]; Bruna Ramos de Souza Gomes [1]; Rebeca dos Santos França [2]; Alex Souza Moraes [1]; Giovana Bataglion [2]; Jandyson Santos [1]

[1] Universidade Federal Rural de Pernambuco; [2] Universidade Federal do Amazonas

The study and monitoring of aquatic environments with anthropogenic activities (from human activities) being responsible for large environmental degradations. The assessment of urban sewage contamination in sediments can be performed through the analysis of sterol class biomarkers, due to the sterol characteristics such as high specificity with the source of organic matter (OM), chemical stability and resistance to anaerobic degradation remaining, preserved over time.1 Herein, the study aims to assess the anthropogenic contamination through the determination of sterol class biomarkers, present in the sedimentary OM sampling on the Suape Industrial Port Complex, which is located in the Ipojuca city, Pernambuco state at Brazil. The port is very important for the state due to slowing down about 100 companies with national and international capital, in different areas as. A total of 5 surface sediment samples (0-10 cm) were collected with a Van Veen dredge and were transported to the laboratory in glass bottles at 4° C. After preliminary treatment, the samples were submitted to the process of extraction and fractionation of organic compounds following the method described by Rau et al. (2013)2 and the determination of sterols was performed using a liquid chromatography-tandem mass spectrometry (LC-MS/MS) method described by Bataglion et al. (2015).3 For eight sterols detected, the total concentration ranged between 1.510 and 40.720 ng g-1. Highlighted, the sediment located close to one of the shipyards presented coprostanol concentration (main fecal biomarker) above 500 ng g-1, which suggests a strong direct or indirect input of domestic sewage. The same sample also received an additional source of β-sitosterol, present in vegetable oils used in cooking, which indicating that sewage from the shipyard activities can compose the OM of the sediment in this region. The other four samples showed coprostanol concentrations between 100 and 500 ng g-1, indicating moderate anthropogenic contamination. Sterol ratios (as coprostanol / (coprostanol + cholestanol) pointed to classify the sediments as moderate contamination by sewage, being the sediment located near the shipyard the most contaminated, which can be from its facilities, such as bathrooms and kitchens, which have been in operation for about 14 years in its surroundings. Thus, the study shows the presence of sterol biomarkers in the sedimentary OM of Suape Port in a moderate level of contamination, which is present due to anthropogenic activities in the region. 1. Frena, M. et al. Mar. Pollut. Bull. 109, 619-623, 2016. 2. Rau, M. et al. Rev. Virtual Quim. 5 (2), 201-221, 2013. 3. Bataglion, G. A. et al. Anal. Chem, 87, 7771−7778, 2015.

Avaliação da contribuição antrópica de elementos traço em sedimentos ao longo da bacia do rio Reis Magos, ES- Brasil

https://proceedings.science/p/138787

Eldis Sartori [1]; Bruna Dalfior [2]; Carolina Scocco Provete [3]; Guilherme Yacovenco [4]; Maria Tereza Carneiro [3]; Geisamanda Pedrini Brandão [3]

[1] Instituto Federal de Ciência e Tecnologia do Espírito Santo; [2] Departamento de Química / UFES / Universidade Federal do Espírito Santo; [3] Universidade Federal do Espírito Santo; [4] UFES (Universidade Federal do Espírito Santo)

Atividades antropogênicas podem provovar impactos ambientais importantes, já que o aporte de elementos traço nos ecossistemas afetam os ciclos geoquímicos e apresentarem toxicidade para os seres vivos. Quando esses elementos são carreados para sistemas aquáticos, esses são distribuídos entre a água e os sedimentos, sendo sua maioria acumulados nos sedimentos devido aos processos de adsorção, hidrólise e co-precipitação, por conseguinte, são fontes de contaminação em potencial, pois podem redisponibilizá-los no corpo d'água. Diante disso, pesquisas com sedimentos são fundamentais para verificação da contribuição antrópica na poluição desses ecossistemas, tendo como fontes poluidoras descargas diretas de efluentes e resíduos sólidos, defensivos agrícolas, fertilizantes, deposição atmosférica e transporte de sedimentos. Com a crise hídrica o Governo do Espírito Santo (Brasil) passou a utilizar, em 2017, o Rio Reis Magos para abastecimento público, porém, essa bacia hidrográfica vem sofrendo impactos ambientais importantes, entretanto, apesar da sua importância, ainda não há dados significativos publicados referentes a sua qualidade ambiental. Com isso, o presente trabalho objetivou a quantificação das concentrações de As, Cd, Co, Cr, Cu, Ni, Pb, e Zn via ICP-MS, teor de matéria orgânica e carbonatos, pH, estudo granulométrico e cristalográficos em sedimento da Bacia do Rio Reis Magos. Para avaliar probabilidade de efeitos adversos à biota foram adotados os valores estabelecidos pelo Conselho Canadense de Ministérios de Meio Ambiente que preconizam níveis de concentração TEL e PEL. Já para aferir o grau de contribuição antropogênica foram determinados os fatores de enriquecimento (FE), de contaminação (FC) e o índice de geoacumulação (Igeo). A correlação entre as variáveis feita por PCA, mostrou uma relação direta entre o grau de poluição e proximidade do centro urbano, características mineralógicas alcalinas provocam elevação do pH e quanto maior o teor de finos e matéria orgânica maior a concentração dos elementos traços. O As (>17mgkg-1) apresentou maior probabilidade de efeitos adversos à biota, enquanto que o Cd (<0,6 mgkg-1), Cr (>90mg kg-1), Co(>11,6mgkg-1), Cu(<159mgkg-1), Ni(<45mgkg-1), Zn(<315mgkg-1) e Pb (<91,3mgkg-1) requerem certa atenção. Pela avaliação geral os sedimentos estão com graus de contaminação leves a moderados, indicando uma possível contribuição antrópica.

Avaliação da Qualidade da Água do Rio Maracanã - Rio de Janeiro

https://proceedings.science/p/138771

Cleyton Martins da Silva [1]; Lillyane Gomes de França Valle [1]
[1] Universidade Veiga de Almeida

The sources of Maracanã river are located inside the Atlantic Forest, in Tijuca National Park. Within the conservation area, its waters are clean and clear. However, following its course, the strong urbanization, which promotes irregular dumping of domestic and industrial effluents and garbage into its waters, results in the degradation of water quality along the entire river to the site of its mouth, the Guanabara Bay.
In this work, the water quality parameters of the Maracanã river (Biochemical Oxygen Demand (BOD), Total Phosphorus (TP), Nitrate (NO3), Dissolved Oxygen (DO), pH, Turbidity (T) and Thermotolerant Coliforms (TC)) for the period between 2012 and 2019, were determined in two monitoring points of the State Institute for the Environment (INEA). Data were evaluated in accordance with CONAMA Resolution No. 357/2005, which provides environmental classification and guidelines for the framing of surface water bodies, as well as establishes the conditions and standards for the release of effluents.
The obtained results, for the period considered in this study, indicate the classification of water quality for the Maracanã River as bad (years 2012, 2013 and 2016) and very bad (years 2014, 2015, 2017, 2018 and 2019). These results can be correlated with the great disorganized urbanization process in the region, with the disposal of waste and effluents in the river. The highest average value for the water

quality index (29.28) was determined in 2016, which can be attributed to local actions of the Guanabara Bay Depollution Program, carried out that year, for the Rio Olympics-2016.
This work also indicates that the region of the “Canal do Mangue sub-basin”, where the Maracanã River is located, despite its great importance in terms of its biodiversity, has most of its water resources polluted. This fact shows the government neglect in this location and highlights the urgency in taking corrective and mitigating measures, both along the entire Maracanã River and in its tributaries.

Avaliação da qualidade do ar na cidade do Rio de Janeiro usando dados obtidos por uma estação de monitoramento ambiental móvel

https://proceedings.science/p/138770

João Rogério Borges de Amorim Rodrigues [1]; Guilherme de Sousa Dantas [1]; Bruno Siciliano Ramos Barros [1]; Cleyton Martins da Silva [2]; Graciela Arbilla de Klachquin [1]
[1] Universidade Federal do Rio de Janeiro; [2] Universidade Veiga de Almeida

Data were obtained using a mobile environmental monitoring station, operated by the Municipal Department of the Environment (SMAC) from 2010 to 2018. Criteria pollutant concentrations (CO, fine particulate matter PM2.5, ozone, NO2 and SO2) were determined in the northern, southern and western areas of the city of Rio de Janeiro (16 locations). Data were displayed using boxplots and air quality levels (IQAs) were determined. For each location the pollutant of major concern was identified. The dispersion of pollutants was analyzed by comparing wind roses with HYSPLIT simulations. In downtown and the Guanabara Bay coast the most critical pollutant is PM2.5. In the northern and west zones, ozone levels are higher due to the impact of industrial emissions from the petrochemical complex (north). The identification of areas of major concern may be used to implement a plan to manage air quality in the city. The determination of ozone precursors may be a key advance to a complete understanding of ozone formation and requires substantial investment in the municipal monitoring net.

Determinação da emissão de hidrocarbonetos precursores de ozônio em veículos flex usando um método desenvolvido no Brasil

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Bruno Siciliano Ramos Barros [1]; Guilherme de Sousa Dantas [1]; Cleyton Martins da Silva [2]; Graciela Arbilla de Klachquin [1]; Tadeu Cavalcante Cordeiro de Melo [3]; Pedro Caffaro Vicentini [3]
[1] Universidade Federal do Rio de Janeiro; [2] Universidade Veiga de Almeida; [3] Petrobras

Abstract

Determination of hydrocarbons (HC) in the exhaust emissions of vehicles fueled with ethanol is a great analytical challenge. In this project a new method was implemented and optimized. A flex fuel vehicle (PROCONVE L6), using ethanol (E100) and gasoline (E22), was tested using the EPA-75 driving cycle (ABNT/NBR 6601). The exhaust was collected in Tedlar® bags and transferred to electropolished stainless steel canisters (Silonite®). The three exhaust phases (cold start, stabilized and hot start) and the dilution air of each phase were analyzed using thermal desorption heart-cutting multidimensional gas chromatography (MDGC). The analytical system consisted on a Agilent 7890A GC with a capillary flow technology (CFT) Deans Switch, two chromatographic columns (a DB-624 and a PoraPLOT Q-HT)

and two detectors (a mass spectrometer and a flame ionization detector) without cryogenic trapping. HC emissions, Ozone Forming Potentials (OFP) and Maximum Incremental Reactivities (MIR) were determined:
Weighted emissions: 0,0042 ± 0,0006 g km-1 (Gasoline E22) and 0,0057 ± 0,0008 g km-1 (Ethanol E100); MIR: 3,6 ± 0,2 (Gasoline E22) and 5,7 ± 0,3 (Ethanol E100); OFP: 0,015 ± 0,001 g O3 km-1 (Gasoline E22) and 0,032 ± 0,005 g O3 km-1 (Ethanol E100).
These results were obtained using a new method developed in Brazil and can be useful for technical discussions about ozone forming potential using Brazilian vehicles and fuels. The method showed a performance compatible with international procedures used in Europe and the United States of America.

Development of a method for determination of organophosphorus flame retardants and plasticizers in meat

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Caroline Mayara Pessoa [1]; Joyce Cristale [2]; ENELTON FAGNANI [3]
[1] Universidade Estadual de Campinas; [2] Centro de Energia nuclear de Agricultura-CENA/USP; [3] Faculdade de Tecnologia / Universidade Estadual de Campinas

OPFRs are used to prevent or to delay combustion of flammable materials. These compounds are not chemically bonded to materials and can be released to the environment and affect humans through dietary exposure. There are few studies regarding the contamination of food matrices by these compounds. The present study aims to develop an analytical method using GC-MS in order to evaluate nine OPFRs in food matrices and estimate human exposure to these compounds through the consumption of meat. Firstly, tests were carried out using classic QuEChERS to assess the method efficiency for extraction of OPFRs from meat. Spiked meat samples (500 ng g-1 for classic QuEChERS and 50 ng g-1 for modified QuEChERS) and procedural blanks were used to verify the recovery and selectivity. Furthermore, the instrumental repeatability was measured through the relative standard deviation obtained for quintuplicate injections of a standard solution prepared in the matrix extract. The instrumental repeatability ranged from 2.6% to 10%, except for tris (2-butoxyethyl) phosphate (TBOEP) with 27%. The recoveries ranged from 73% to 143%, except for Tris(2-ethylhexyl) phosphate (TEHP) with 221%, and the relative standard deviation ranged from 2.6 to 17% (except TEHP - 125%). The classic QuEChERS method for determination of OPFRs in meat using GC-MS (ion trap) resulted in limits of detection in the order of 20 to 300 ng g-1, levels that were considered high based on the levels reported for OPFRs in meat (usually lower than 20 ng g-1). Thus, some modifications in the QuEChERS method were evaluated in order to concentrate the extract for decreasing the limits of detection. Low temperature partition after acetonitrile extraction followed by concentration of the whole supernatant organic phase (acetonitrile) was evaluated. The extracts were evaporated to dryness under a gentle nitrogen stream after clean-up and redissolved with 300 µL of ethyl acetate. Additional tests were performed using different solvents (dichloromethane and ethyl acetate) for washing the sorbent after the dispersive-solid phase extraction (d-SPE) clean-up. Ethyl acetate was chosen because it showed a better recovery, ranging 61% to 118% with standard deviation ranging from 6% to 14%, except 2-Ethylhexyl diphenyl phosphate (EHDPP) and TBOEP, with standard deviation of 51% and 48%, respectively. Based on these results, we concluded that the present methodology is promising for extracting OPFRs from meat samples.

Estudo de complexação entre substâncias tipo húmicas de carvão hidrotérmico produzido a partir de subprodutos da indústria de cana-de-açúcar e Cu(II) por PARAFAC e 2D-COS-FTIR

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Bernardo Ribeiro de Moura [1]; Vinicius Sarracini Santos [1]; Gustavo Metzker [1]; Odair Pastor Ferreira [2]; Marinônio Lopes Cornélio [3]; Marcia Bisinoti [1]; Altair Benedito Moreira [1]

[1] Departamento de Química e Ciências Ambientais / Instituto de Biociências, Letras e Ciências Exatas / Universidade Estadual Paulista "Júlio de Mesquita Filho"; [2] Departamento de Física / UFC (Universidade Federal do Ceará); [3] Departamento de Física / Instituto de Biociências, Letras e Ciências Exatas / Universidade Estadual Paulista "Júlio de Mesquita Filho"

The hydrothermal carbonization of sugarcane bagasse and vinasse, which are by-products of the sugarcane industry, produces a coal called hydrochar (HC), which is a source of humic-like substances (HLS) and nutrients to the soil. HLS are complex macromolecules, extracted in alkaline medium from organic materials that have not been subjected to the natural process of humification in the soil1. HLS can increase the amount of organic matter in the soil, improving plant growth, biological activity and reducing soil erosion. Furthermore, HLS can interact with metals through the formation of complexes, indicating that these substances have potential to act as organic fertilizers, due to their ability to incorporate micronutrients such as Cu(II) and Co(II), and represent an alternative for the remediation of contaminated environments2. The objective of this work was to increase the content of HLS present in HC through the oxidation with HNO3, characterize these substances by 13C nuclear magnetic resonance spectroscopy and study their interaction with Cu(II) metal. HC was produced from hydrothermal carbonization of sugarcane bagasse, vinasse and KOH, and then oxidized with HNO3 15% for 2 hours. HLS were extracted from oxidized and non-oxidized HC, purified by centrifugation, dialysis and lyophilization. Subsequently, HLS were characterized by solid-state 13C magic angle spin nuclear magnetic resonance spectroscopy (13C CPMAS NMR). The interaction study with Cu(II) metal was performed by fluorescence quenching; the data were analyzed by parallel factor analysis (PARAFAC) and introduced to Ryan and Weber complexation model. The functional groups involved during the interaction between HLS and Cu(II) were determined by two-dimensional Fourier transform infrared correlation analysis (2D-COS FTIR).The oxidation increased the content of HLS present in HC from 6.83% to 24.30%. Relative integrated areas of 13C CPMAS NMR spectra indicated that HLS extracted from oxidized HC presented greater aromaticity and increased amount of hydrophobic compounds in its composition, represented by C-Alkyl (0-45 ppm), C-Aryl (110-140 ppm) and O-Aryl (140-160 ppm) fractions, due to the greater stabilization of organic matter caused by oxidation with nitric acid. CP/PARAFAC identified two fluorophores present in both HLS, all of then showed high affinity for metal Cu(II), behavior evidenced by the high stability constants of the metal-ligand complex (K), between 5.54 and 5.81 x 10^5. 2D-COS-FTIR analysis indicated that both HLS interacted with Cu(II) mainly through oxygenated functional groups such as hydroxyls (-OH), carboxylates (-COO-) and C-O bonds of polysaccharides. Therefore, nitric acid oxidation enhance the content of HLS present in HC, favoring its use as a soil conditioner and adding value to by-products of the sugarcane industry produced on a large scale in Brazil.

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Influence of the matrix and the radiation source on the simultaneous degradation of pharmaceuticals by the TiO2/H2O2/UV process

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Cleiseano Emanuel da Silva Paniagua [1]; Ivo Amildon Ricardo [1]; Eduardo Marson [1]; Alam Gustavo Trovó [1]
[1] Universidade Federal de Uberlândia

Under the best experimental conditions in DW and SW (pH 6.0, 150 mg L-1 of TiO2 and 6 mg L-1 of H2O2) and, in STP (pH 7.4 and 450 mg L-1 of TiO2), the influence of the radiation source (black light and sunlight) was evaluated. High degradation efficiencies were obtained for all pharmaceuticals, resulting in values below the limit of detection (LOD) (25, 3.3, and 0.76 µg L−1 for GEM, HCTZ and NAP, respectively) in all matrices evaluated under radiation with black light. However, a higher dose of energy was required with the increase in the complexity of the matrices: STP (527 kJ m-2), SW (371 kJ m-2) and DW (448 kJ m-2). Similar results were obtained with the use of sunlight, when working under the same conditions used for black light. These results show that the components of the matrices affect the degradation efficiency. This is justified by the presence of optically active substances that limit the penetration of light, the presence of inorganic anions and organic matter that compete with the target compounds for hydroxyl radicals.

Although heterogeneous photocatalysis was efficient to degrade target compounds, there was no complete mineralization. In DW, mineralizations of 75% (sunlight) and 85% (black light) were obtained after 448 kJ m-2. Using the same dose of energy, 64% (sunlight) and 72% (black light) of mineralization were obtained for the SW matrix. In STP, there was 75% mineralization for both sources of radiation after 523 kJ m-2. It is noteworthy that although a higher percentage of mineralization was obtained in DW compared to the matrices of SW and STP, the amount of organic carbon removed in mg L-1 was higher for SW and STP, since the initial DOC value in DW is 0.77 mg L-1 while in SW it is 6.7 mg L-1 and, in STP, 25 mg L-1.

Since complete mineralization was not achieved, by-products of the target compounds or from organic matter naturally present in the SW and STP matrices were formed, being necessary to evaluate the evolution of the solution's toxicity before and after treatment. In DW, the initial inhibition was 1% and increased to 99% (black light) and 83% (sunlight) when 448 kJ m-2 was applied. At the same dose of energy, in SW, the initial toxicity of the matrix (in natura and after the addition of pharmaceuticals) was 3.3% and increased to 77 and 99%, respectively, with black and sun lights (with or without the addition of pharmaceuticals). In STP, the initial matrix toxicity (with or without the addition of pharmaceuticals) was 50% and increased to 79% (fresh matrix) and 85% (addition of pharmaceuticals) with the application of 523 kJ m-2, with no significant differences being obtained with the use of sunlight. The increase in toxicity observed for DW comes from the by products generated during the degradation of pharmaceuticals.

Investigando a adsorção de micropoluentes de interesse emergente por carvões ativados em meio aquoso

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Fábio Marley de Sousa Nascimento [1]; Imisi Michael Arowojolu [1]; Fernando Fabriz Sodré [1]
[1] Instituto de Química / Universidade de Brasília

Micropoluentes de interesse emergente (ME), presentes em fármacos, produtos de higiene pessoal, formulações agroquímicas, produtos industriais, etc., surgem no ambiente em função da produção, do uso e/ou do descarte, sendo o esgoto doméstico uma das principais fontes de contaminação de águas naturais. A remoção de ME tem sido objeto de interesse recente, sendo a adsorção por carvão ativado granulado (GAC) atrativa em função do baixo custo e da existência de estações com infraestrutura já em uso. Este trabalho buscou compreender os processos envolvidos na remoção de ME por diferentes carvões ativados.

Dois GAC comerciais, DARCO (Ø 100 mesh, pHPCZ 7,5, área superficial específica - ASE 855 m2/g) e SIAL (Ø 100 mesh, pHPCZ 4,2, ASE 1339 m2/g) foram investigados. A adsorção de sulfametoxazol (SMX), sulfapiridina (SP), cafeína (CAF), triclosan (TCS), fenacetina (PHE) e paracetamol (APAP) foi determinada, separadamente, em ensaios realizados conforme norma ASTM D3860-98 para massas de adsorvente entre 1 a 40 mg e concentração de analito fixa em 35 mg/L em água destilada e pH 6,5, empregando espectrofotometria UV-Vis (Agilent Cary 8454) e quantificação de nitrogênio (NT) e carbono orgânico (COT) totais (Multi N/C 3100, Analytik Jena). Ao contrário do que preconiza a norma ASTM, as isotermas foram ajustadas em modelos não-lineares de Freundlich, Langmuir, Temkin e Dubinin–Radushkevich (DR).

As isotermas dos ME para o GAC DARCO apresentaram, para todos analitos, com exceção do APAP, formas do tipo H, onde o adsorvato tem grande afinidade inicial pelo adsorvente. Para o GAC SIAL foram observadas isotermas do tipo H para TCS, SP e SMX, isotermas do tipo L, menos intensas que as do tipo H, para CAF e PHE, e do tipo C, com disponibilidade constante de sítios ativos, para o APAP. Isotermas construídas com base em valores de NT ou COT apresentaram, em sua grande maioria, o mesmo padrão mencionado anteriormente, com exceção daquelas baseadas em NT para CAF (GAC DARCO) e para PHE (GAC SIAL), onde isotermas do tipo S, caracterizadas por interações solvente-adsorvente significativas no início do processo sortivo, foram formadas. Para ambos os carvões, as capacidades adsortivas, determinadas via modelos de Freundlich e Langmuir (parâmetro b), seguiram a ordem: TCS≅SMX>SP>PHE>CAF>APAP. O GAC DARCO apresentou valores de b (158 a 269 mg/g) similares aos obtidos para o GAC SIAL (158 a 269 mg/g), mesmo apresentando menor ASE, revelando maior capacidade adsortiva por área. Valores elevados do parâmetro n de Freundlich (8,8 a 5,9 para DARCO; 4,4 a 2,1 para SIAL), sugerem maior heterogeneidade dos sítios adsorventes, corroborada por valores de pHPCZ, já que o GAC DARCO deve possuir maior equilíbrio entre grupos ácidos e básicos em comparação ao GAC SIAL. Os valores elevados de Qui-R2 obtidos no modelo de Temkin reforçam que a adsorção dos ME é dependente de suas propriedades físico-químicas, ainda que pelo parâmetro de energia, E, do modelo de DR, os valores obtidos, menores que 8 kJ/mol, sugiram que para todos os experimentos houve prevalência de fisiossorção.

Method Validation for BTEX analysis in Marine Water and Sediments by Manual Headspace Sampling

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Jennifer do Nascimento Chaves Menezes [1]; Maria Cristina Canela [1]
[1] Universidade Estadual do Norte Fluminense Darcy Ribeiro

Petroleum is a complex mixture of several organic compounds, mainly hydrocarbons. In this group, toxicity is generally related to monoaromatic substances (BTEX-Benzene, Toluene, Ethylbenzene, and Xylenes) and polycyclic aromatic hydrocarbons (HPA). BTEX are more volatile and have more excellent solubility in water than soil; they are prejudicial to health, with benzene being the most dangerous, listed as a carcinogen by the International Agency for Research on Cancer (IARC). BTEX is dangerous even to people who work in spilled crude oil clean-up operations and may develop alterations in the hematological profile and liver function. Petroleum accident has been considered a concern for the environment. Between the years 2010 to 2019, there was an average of 1.8 oil spills per year in the world, above 700 tons each. In Brazil, in 2019, there was an oil spill of unknown origin that left oil slicks along the entire northeastern and states of Rio de Janeiro and Espírito Santo coast. This accident was considered the largest in terms of coastline, in which 11 states and 130 municipalities were affected. The effects of contamination caused by oil spills in the aquatic environment are linked to its physicochemical characteristics and toxicity. Given this theme, this work aims to determine an easy, fast and safe methodology to determine BTEX in water and marine sediments in a laboratory with few resources, without an automatic headspace analysis system with an injection to the chromatograph. The method for determining BTEX was performed and validated after primary study variables. The bath temperature for volatilization, mixer of the sample, matrix effect, and an internal standard were studied to obtain this analysis's best performed and variation coefficient. Vials containing the analytical standards of BTEX and internal standard of propylbenzene, prepared in synthetic seawater, having half of its total volume (40 mL) with the solution, were placed in a water bath at 60°C, for 22 min, and vortexed for 10 seconds in the end; then an aliquot of the gas phase was removed with a gastight micro syringe of 500 µL and injected into a gas chromatograph with a flame ionization detector (Shimadzu model 2010 Plus). The temperature and time were enough to transfer the compounds into the gas phase without leaving too high the water concentration in the gas phase, damaging the chromatography column. The vortex was used to increase the efficiency of gaseous phase interaction, but without causing imbalance, as it could affect the repeatability. This work also observed that artificial seawater to perform the analytical curve eliminates matrix effect problems since the salting-out effect is significant in analyzing the transfer of nonpolar compounds from a polar matrix. With the validated methodologies, a field collection will be carried out on beaches of the State of Rio de Janeiro and Espírito Santo to assess their bathing abilities and a study of the origin of the contaminants found.

Microsplastics as chemical transport vectors in the real fresh- and seawater

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Mariana Amaral Dias [1]; Cassiana Carolina Montagner [1]
[1] Universidade Estadual de Campinas

Batch sorption experiments were conducted to evaluate the interaction of polyamide microplastics (~106 µm) with the atrazine herbicide and hormones (progesterone and testosterone). Two different approaches were used to assess sorption, one with contaminants in seawater (SW), collected from Guarujá beach, and the other in freshwater (FW), collected from Ribeirão das Pedras source. Kinetic experiments were conducted with the contaminant solutions in water (1 mg L-1) and 20 mg of microplastics. Sorption times of 0 h, 0.5 h, 1 h, 2 h, 3 h, 6 h, 12 h, 24 h, 48 h, 72 h, 96 h, and 108 h were evaluated. Contaminant solutions and microplastics were mixed into a glass tube and placed on an orbital shaker at 19 °C and 80 rpm. After the sorption times, 1 mL of the supernatant was filtered through a 0.22 µm syringe filter and analyzed by liquid chromatography coupled to a mass spectrometer in tandem (LC-MS/MS). Sorption isotherms (Langmuir and Freundlich) were performed with contaminant solutions set as 0.01, 0.05, 0.1, 0.2, 0.5, 1.0, and 2.0 mg L-1. All experiments were performed in triplicate. Pseudo first order and pseudo second order kinetic models were applied for the three contaminants. Experimental concentration sorbed on microplastics in SW at equilibrium (qe), in mg g-1, was 0.028, 0.054, and 0.087 for atrazine, testosterone, and progesterone, respectively. Similar qe were observed in FW, 0.021, 0.058, and 0.086 for these same three compounds, respectively. Theoretical qe and constants of kinetic models (k1 and k2) were obtained using these two approaches. The experimental data fitted better to the Langmuir model for both experiments (R2 > 0.93), indicating that the microplastic surface is homogeneous and the adsorption occurs on the microplastic outer surface. Sorption efficiency of about 20% was obtained for atrazine (Figure 1 – red data), which can be associated with a lower octanol-water coefficient when compared to other compounds. On the other hand, high sorption efficiencies were observed for testosterone, ranged from 40% to 70% (Figure 1 – green data), and progesterone, higher than 80% (Figure 1 – blue data). A slight increase in sorption efficiencies (about 6%) was observed in the SW experiment, for all contaminants in seven different concentrations. The SW salinity was more than 110 times higher than FW, thus salinity may change the aqueous solubility of compounds allowing their sorption in solid phases.

OPTIMIZATION OF QuEChERS EXTRACTION FOR THE DETERMINATION OF ORGANOPHOSPHATE ESTERS IN BOVINE MILK

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AMANDA ARAÚJO DA SILVA [1]; ENELTON FAGNANI [1]; Joyce Cristale [2]
[1] Faculdade de Tecnologia / Universidade Estadual de Campinas; [2] Centro de Energia nuclear de Agricultura-CENA/USP

Organophosphate esters (OPEs) are used as flame retardants and plasticizers in electronics, plastics, textiles, furniture, and building materials. The OPEs have been added to the market to replace the polybrominated diphenyl ethers (PBDEs), which are classified as persistent organic pollutants (POPs) by the Stockholm Convention. However, recent studies have found that some OPEs can cause several problems to human health, such as cancer, endocrine, hormonal and reproductive disorders, among others. The OPEs can be transferred to food by the contact with plasticizers during production, packaging and storage processes. The dairy industry has been growing in recent years, and the presence of OPEs in milk was reported. However, there are few studies that have determined the presence of OPEs in milk. The aim of the present study is to develop an analytical method for the determination of ten OPEs in bovine milk. The method is based on QuEChERS extraction and analysis by gas chromatography coupled to mass spectrometry (GC-MS). The recovery tests were carried out using a whole milk matrix (5 mL) spiked at a concentration of 200 ng mL-1 for the classic QuEChERS, and at 20 ng mL-1 for modified QuEChERS. Evaluated modifications included the use of low temperature partition after extraction, concentration of the extract followed by additional clean-up steps using C18 or HLB cartridges, and the use of C18 associated to PSA sorbent during the dispersive solid phase extraction (d-SPE). Matrix effect was observed when comparing the analytical response obtained for the OPEs in standard solutions (prepared using pure solvent – ethyl acetate) and in standards prepared using a dried milk extract (matrix- matched standard). Thus, for these optimization experiments the recoveries were calculated based on the response factor obtained for the matrix-matched standards (milk extract spiked with OPEs) prepared at a concentration corresponding to a recovery of 100%. Preliminary results obtained with classic QuEChERS showed recoveries within the range from 62% to 116% and relative standard deviation from 3% to 29%, except for the tris (2-ethylhexyl) phosphate (TEHP). Regarding the tests using modified QuEChERS with concentration of the extract, the C18 cartridges showed the best recovery performance, which ranged from 99% to 128%, except for the 2-ethylhexyl diphenyl phosphate (EHDPHP) (381%) and TEHP (51%). The optimization of the d-SPE clean-up using PSA and C18 was also evaluated, including additional sorbent washing steps using dichloromethane, acetonitrile or ethyl acetate. The best results have been obtained with ethyl acetate, with recoveries ranging from 78 to 107% for eight out of the ten evaluated OPEs, with relative standard deviation from 4 to 17%.

Therefore, based on these results, the modified QuEChERS method is promising for the determination of OPEs in bovine milk.

Probabilistic health risk assessment of H2S emissions in areas near polluted urban rivers in the city of Salvador, Bahia

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Lícia Passos dos Santos Cruz [1]; Mateus S. Moreira [1]; Raiane S. Alves [1]; Franciele O. C. da Rocha [1]; Jullietty Cardoso Silva [1]
[1] Universidade Federal da Bahia

Rivers in urban areas are often disposal sites for domestic and industrial sewage. This causes negative impacts on air quality on a local scale, mainly related to emissions of unpleasant odors and adverse effects on human health. Under anaerobic conditions, such as those found in urban rivers polluted predominantly by domestic sewage, hydrogen sulfide (H2S) resulting from dissimilatory sulfate reduction is the main reduced sulfur compound emitted into the atmosphere and a typical pollutant that generate odors and also affects human health these areas. Thus, the objective of this study was to assess the non-carcinogenic risks (expressed as hazard quotient - HQ) for three different groups of the adult population (P1, P2, and P3) associated with exposure to H2S by inhalation in five sites near polluted rivers in the city of Salvador, Bahia, during two different periods (rainy and dry) using a probabilistic approach with Monte Carlo simulation. The Crystal Ball software (version 11.1.2.4) was used to calculate the probability distributions of these risks, and a total of 10,000 repetitions were performed to simulate the Monte Carlo method and sensitivity analysis. HQ values at the 95th percentile (adopted as the upper-bound estimate of the potential risk) were 4.28, 2.80, and 1.46 for the dry period and 3.31, 2.15, and 7.36x10-1 for the rainy period for P1, P2, and P3, respectively, i.e. the non-carcinogenic risks were higher in the dry period than in the rainy one. Furthermore, except for P3 in the rainy period, all other values were higher than the limit allowed by US Environmental Protection Agency - USEPA (HQ = 1), meaning that the risks are high considering 25 years of exposure and, therefore, the three groups of the exposed population considered may suffer adverse effects health, such as eye irritation, headache, nausea and respiratory problems. A sensitivity analysis was also performed in this study to determine the contributions of the input variables in estimating the non-carcinogenic risk values for H2S. The results revealed that H2S concentration was the most important contributing variable to the non-carcinogenic risk values, accounting for 64.9%, 81.7% and 77.4% in the dry period and 47.5%, 67.8% and 60.3% in the rainy period for P1, P2 and P3, respectively. As the contributions of H2S concentrations to sensitivity were positive values in all cases, there was a positive correlation between concentrations and non-carcinogenic risks The results obtained in this study showed the need to adopt measures to decrease the release of untreated sewage into the urban rivers in Salvador, as well as strategies to recover the rivers of this city, in order to avoid the discomfort caused by odors and reduce the health impacts of the exposed population.

Qualidade de águas subterrâneas na bacia hidrográfica do Taquari-Antas e estratégias de sustentabilidade

https://proceedings.science/p/138781

Demis Pessatto Faqui [1]; Aline Teichmann [2]; Alejandro Okroglic [3]; Eduardo Schmitt [3]; Fabiane Regina Bartz [3]; Mateus Guterres [3]; Juliana Reinke Rodrigues [2]; Eduardo Alexis Lobo Alcayaga [2]; Adilson Ben Costa [2]
[1] Programa de Pós-graduação em Tecnologia Ambiental (UNISC); [2] UNISC (Universidade de Santa Cruz do Sul); [3] Philip Morris Brasil

Water is essential to developing and maintaining successful and healthy economies and for human health and wellbeing. However, water must be used responsibly and sustainably to protect the needs of the natural environment and to ensure the ongoing availability of water as an essential resource and human right. Part of this responsibility, especially for the government, organizations and universities, is to cause no harm to the natural environment and communities and aspire to achieving a net benefit. In additional, identifying and addressing challenges and risks also provides insight into opportunities associated with good water stewardship into communities.1 Going into this direction, Philip Morris Brasil started the study of Taquari-Antas water catchment among 2021, identifying a potential natural hydrogeological risk related to excess of fluoride into well water. As well known, fluoride above national regulation2 (> 1.5 mgL-1), can cause dental fluorosis with irreversible damage. In this scenario, Santa Cruz do Sul University was involved in the work and responsible for: 1) confirm the hypothesis of fluoride > 1.5 mgL-1 into well water located at Taquari-Antas watershed (water used for human consumption by tobacco producer's families from several wells) and 2) develop a sustainable solution to reduce fluoride in water, to respect national limits. For the first stage, in the current phase of the work, 49 water samples, collected directly from tobacco producer's family's properties in their consumption points, were determined for several parameters including fluoride (applying ion-selective electrode method), in which 19 were above the limits for the national regulation. In the next stage, two bone charcoal filters previously developed and tested by the University were installed in two different properties. After filter installation, the result of fluoride concentration in these samples decreased from 3.74 mgL-1 and 3.86 mgL-1 to 0.05 mgL-1 and 0.02 mgL-1, respectively. The next stages of the work comprehend the analysis of a total of 102 samples at Taquari-Antas watershed, the installation of more filters in tobacco producer's family's properties that show fluoride concentrations above the limits and the monitoring of the general quality of the drinking water of the beneficiaries from that region. References: 1International Water Stewardship Standard, Version 2.0, 22.03.2019. 2Portaria GM/MS nº 888, from 04th May 2021

Treatment of craft beer wastewater by Advanced Oxidation Processes (AOP) employing 70% hydrogen peroxide

https://proceedings.science/p/138775

David Vasconcellos Linhares [1]; Elisson Andrade de Souza [2]
[1] Centro Universitário SENAI CIMATEC; [2] SENAI CIMATEC

With the increase in consumption and popularization of craft beer, the production of wastewater has been growing at an alarming rate. Associated with this fact, new AOP techniques have been improved with the use of H_2O_2 (70% wt.) [1,2]. At room temperature and pH 3.0, 50 mL of the craft beer wastewater were treated with 50 g/L of H_2O_2 (70% wt.) and 2 g/L Fe(II). Material degradation was

evaluated by absorbance at 409 nm because it is the wavelength of maximum absorption of the residue. Under these conditions, within 30 minutes of reaction, 80% discoloration was achieved with the Fenton process. Subsequently, the Fenton's reaction was performed with UV light (Photo-Fenton process, 370 nm cutoff filter was used; λ > 370 nm) and ultrasound (Sono-Fenton process, 80 W and 20 kHz) directly on the solution. A discoloration of 85% and 93% was achieved with the Sono-Fenton and Photo-Fenton processes, respectively. Due to its greater discoloration, a COD removal test was carried out for the Photo-Fenton process, indicating a removal of 79%. Thus, preliminary results of this work show that these techniques and reagent are promising in the treatment of effluents and mainly in the craft beer residue. Now, we are currently optimizing the data and results using chemometric analysis for better responses.

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Química Analítica - ANA

Determinação e distribuição de Cu, Fe e Zn em camapu por espectrometria de emissão óptica com plasma acoplado indutivamente

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Cecilia Correia Pereira [1]; Michelle de Souza Lemos [2]; Kelly das Graças Fernandes Dantas [2]
[1] UFPA/ PPGQ; [2] Universidade Federal do Pará

A região Amazônica apresenta diversas espécies frutíferas, dentre as quais se destaca a Physalis angulata, conhecida como camapu. Essa fruta pode ser consumida in natura ou na forma de suco. O suco do camapu é utilizado como sedativo, diurético, depurativo e antirreumático1. O objetivo deste estudo foi avaliar os níveis totais de cobre, ferro e zinco e também nos extratos proteicos, lipídicos e no resíduo final após o procedimento de extração sequencial por espectrometria de emissão óptica com plasma acoplado indutivamente (ICP OES). Primeiramente, a remoção de lipídeos foi realizada no camapu usando clorofórmio e metanol (2:1). As frações proteicas foram obtidas após extração sequencial usando quatro diferentes soluções extratoras. A amostra de camapu e as frações proteicas foram digeridas em forno de micro-ondas com cavidade com ácido nítrico diluído e peróxido de hidrogênio. Os teores totais de Cu, Fe e Zn no digerido de camapu variaram de 10,8 à 32,7 mg kg-1. Na fração lipídica foram obtidos níveis de Cu, Fe e Zn variando de 0,07 à 0,5 mg kg-1. Ferro foi encontrado em maior teor no resíduo. Elevados teores de Cu e Zn foram encontrados associados à albumina (extração com água) quando comparado aos outros extratores. Por outro lado, níveis elevados de ferro foram obtidos na fração referente às globulinas (extração com NaCl). A exatidão do procedimento de análise proposto foi avaliada utilizando o método de adição e recuperação de analito. As recuperações para Cu, Fe e Zn variaram de 88,3 a 109,6 %. Este estudo mostrou que os elementos estudados no camapu foram encontrados associados às proteínas albumina, globulinas, glutelinas-1 e glutelinas 2.

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A Green Sample Preparation Method for Elemental Impurity Determination in Oily Pharmaceutical Excipients by ICP-MS in compliance with ICH Q3D

https://proceedings.science/p/138808

Cristian Andriolli [1]; Mariele Samuel do Nascimento [2]; Paula Dalla Vecchia [1]; Eder Lisandro de Moraes Flores [3]; Erico Marlon de Moraes Flores [1]; Rochele Picoloto [1]

[1] Universidade Federal de Santa Maria/Departamento de Química; [2] BTA Aditivos/Laboratório de Química Analítica; [3] Universidade Tecnológica Federal do Paraná/Departamento de Química

The use of oily pharmaceutical excipients became important to the use of some injectable drugs.1 Among the pharmaceutical excipients available for injectable drugs, some oily excipients such as soybean oil, castor oil, corn oil, and sesame oil are commonly used.1 However, oily excipients are not completely free of elemental impurity and the quality control is mandatory. In this way, the International Council for Harmonisation (ICH) classifies the elemental impurity according to their toxicities.2 Moreover, according to the ICH guideline Q3D, the quality control of class 1 (As, Cd, Hg, and Pb) and class 2A (Co, Ni, and V) is necessary in oily excipients used in the formulation of injectable drugs.2 Despite the necessity to determine class 1 and class 2A in oily excipients, some difficulties are related to the sample preparation step mainly due to the matrix complexity and the low levels of the analytes usually present in this kind of sample. In order to overcome these limitations, in the present study, a reversed-phase dispersive liquid-liquid microextraction (RP-DLLME) method was developed for further As, Cd, Pb, Co, Ni, and V 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 analytes extraction from the organic phase (oil sample) to an aqueous phase using a dispersant/extractant (alcohol/diluted acid solution) mixture. For the RP-DLLME procedure, a water-bath (Elmasonic P 120 H, Germany), capacity of 9 L and temperature control (up to 85 °C) was used. A certified reference oil material was used for recovery experiments. Corn oil was used for the development of the proposed method. Operational parameters, such as proportion of dispersant:extractant solvents (65:35 to 15:85% v/v), extractant solvent concentration and type (0.5 to 3.0 mol L-1 HNO3 and 4.0 to 10 mol L-1 HCl), extraction solution volume (1.0 to 2.0 mL), and centrifugation time (5 to 15 min) were evaluated. A green analytical metric was used to analyze the proposed method greenness. Suitable results were obtained by using 5 g of oily excipient, a mixture of dispersant (n-propanol) and extractant (3.0 mol L-1 HNO3 solution for As, Cd, Pb, Co, Ni, and V and 6.0 mol L-1 HCl solution for Hg) solvents with proportion of 50:50% (v/v) in 2 mL, 85 °C, and 10 min of centrifugation. Due to the use of a high sample mass (5 g), diluted extraction solutions, and low detection limits (ranged from 1 to 31 ng g-1) were obtained.

A "Green" Approach for Screening Nitrosamines in Medicines by Ultrasound-Assisted Dispersive Liquid-Liquid Microextraction (UADLLME) and HPLC-UV

https://proceedings.science/p/138813

Thiago Novotny [1]; Mychelle Monteiro [2]; Soraya Ochs [2]; Patrícia Lima [2]; Fernando Antonio Simas Vaz [3]; Flávia Ferreira de Carvalho Marques [1]

[1] Universidade Federal Fluminense; [2] INCQS / Fundação Oswaldo Cruz; [3] Instituto de Química / Universidade Federal Fluminense

N-nitrosamines (NA) are carcinogenic substances that should not be present in medicines. In 2018, Regulatory Agencies detected, for the first time, the presence of NA in medicines, bringing great concern worldwide. As medicines should not pose additional risk to patients, the agencies have instructed manufacturers to monitor each batch produced. The monitoring method currently recommended is liquid chromatography coupled with mass spectrometry, posing a considerable cost to the pharmaceutical industry. Therefore, sensitive alternative methods for screening NA in medicines are highly desirable. In recent years, hydrophobic deep eutectic solvents (HDES) have emerged as a novel "green" alternative to solvents commonly used in microextraction techniques as they are biocompatible, chemically stable, biodegradable, low volatile, and cheap. The purpose of this work is the development of an UADLLME method for screening six NA (N-Nitrosodimethylamine, NDMA; N-Nitroso-N-methylamino butyric acid, NMBA; N-Nitrosodiethylamine, NDEA; N-Nitrosoethylpropylamine, NEIPA; N-Nitrosodiisopropylamine, NDIPA and N-Nitrososdibutylamine, NDBA) in "sartans" drug class samples by HPLC-UV, as a viable alternative to the pharmaceutical industry. Aside several traditional extraction solvents, some HDES combinations were evaluated. The extraction efficiencies of the HDES were assessed through their partition coefficients. Extractions were performed by sonicating adequate volumes of the HDES-aqueous sample mixtures for 15 minutes and separating the organic phase by centrifugation at 5000 rpm for 20 minutes. 20 ul of the organic phase were directly injected into the chromatograph. The NA were resolved in less than 23 min, suggesting that the proposed method is promising for the determination and monitoring of NA in medicines.

Acidic leaching of cobalt and nickel from ferronickel slag using oxidant medium

https://proceedings.science/p/138806

Vinício Francisco Ibiapina [1]; Iranildes Daniel dos Santos [2]; Julio Carlos Afonso [1]; Marta Eloisa Medeiros [1]

[1] Universidade Federal do Rio de Janeiro (UFRJ); [2] Instituto Tecnológico Vale (ITV)

The pyrometallurgical processing of lateritic nickel ores produces large amounts of FeNi slag. Its chemical composition depends on the step of the metallurgical process (smelting, refining, and desulphurization). Magnesium silicates and iron, cobalt, and nickel oxides are present in the slags. In general, cobalt is present in laterites at levels below 0.2% m/m, and a specific processing to recover this valuable metal by a pyrometallurgical route was not found in searches. Therefore, the development of routes to process this waste is fundamental to recover cobalt and nickel, strategic metals for modern technologies, and to reduce this environmental liability.

This work presents a study of the acidic leaching of FeNi slag from refining process of nickel laterites to recover cobalt and nickel. The leachants were mixtures composed of an inorganic acid (HCl 6.0 mol L-1, H_2SO_4 9.0 mol L-1, H_3PO_4 7.5 mol L-1) and H_2O_2 (2.5 mol L-1). The effects of time (2-4 h), temperature (25-75 °C), and solid/liquid ratio (50-150 g L-1) were tested.

The reproducibility of leaching was determined to be ± 4%. Hydrochloric acid had the best performance as leachant. The effect of temperature was not significant to Co and Ni leaching. Thus, it is possible to apply the method at 25°C, reducing energy consumption. Under the best experimental conditions (25 °C, 2 h, S/L ratio 100 g L-1), 99 wt.% of nickel and cobalt were leached in the presence of HCl + H_2O_2 mixtures. The mass balance showed the best yields in 3 h (> 75 % m/m). However, flame atomic absorption spectroscopy (FAAS) of the liquors indicates that Co and Ni were better leached in 2 h (≥ 99 % m/m). The leaching performance with a solid/liquid ratio of 50 g L-1 (80-84% m/m) was slightly better than at 100 g L-1 (72-75% m/m). Consequently, it is more profitable to use a less volume of acidic leach solution. X-ray powder diffraction (XRPD) analyzes indicate SiO_2 and Fe_3O_4 (HCl) and calcium salts (H_2SO_4 and H_3PO_4) as components of the insoluble matter from leaching. The X-ray fluorescence (XRF) results indicate cobalt and nickel contents below the detection limit.

Análise multielementar de óleo de copaíba (Copaifera spp.) da FLONA Carajás por ICP OES

https://proceedings.science/p/138830

Charles Miller de Souza Borges [1]; Selma Goulart [2]; Kelly das Graças Fernandes Dantas [3]
[1] PPGQ / Universidade Federal do Pará; [2] Universidade Federal Rural da Amazônia; [3] Universidade Federal do Pará

O óleo-resina de copaíba é um produto florestal não madeireiro bastante utilizado na indústria farmacêutica e cosmética, além da grande aplicabilidade como fitoterápico, principalmente na região amazônica. Sendo assim, este estudo teve como objetivo a análise multielementar de Al, As, Ca, Cd, Cr, Cu, Fe, K, Mg, Na, Ni, Pb, Sb, Se, Ti e Zn em óleo-resina de copaíba por espectrometria de emissão óptica com plasma acoplado indutivamente (ICP OES). Dez amostras de óleo de copaíba da Flona Carajás e uma amostra comercial foram estudadas. Essa amostra comercial foi estudada para fins de comparação. As amostras foram digeridas utilizando ácido nítrico e peróxido de hidrogênio em forno micro-ondas com cavidade. Para a determinação dos analitos foi utilizado um espectrômetro de emissão óptica com plasma acoplado indutivamente (ICP OES). A exatidão da etapa de preparo das amostras e da análise por ICP OES foi avaliada através do método de adição e recuperação de analito. As amostras apresentaram valores para Al, Cd, Cr, Cu, K, Pb, Sb, Se e Ti abaixo do limite de detecção (LD). O As foi encontrado na amostra A3, 0,006 mg kg-1. Para Ca, as amostras A5 e A8 não obtiveram resultados ficando abaixo do LD. Os valores de Ca obtidos foram de 0,38 a 20,09 mg kg-1. Para o ferro, a amostra A3 apresentou 0,2228 mg kg-1, enquanto as outras amostras ficaram abaixo do LD. Para o magnésio, as concentrações foram de 0,021 a 0,264 mg kg-1. Para Na, as concentrações foram de 0,11 a 0,68 mg kg-1. Níquel obteve concentrações na faixa de 0,008 a 0,026 mg kg-1. As concentrações de Zn nas amostras ficaram entre 0,009 e 0,149 mg kg-1. Este estudo mostrou que a digestão ácida por forno micro-ondas com a análise por ICP OES permitiu a obtenção da composição elementar das amostras de óleo-resina de copaíba, que é um produto florestal carente de estudos e que pode ser importante, tanto para agregar valor quanto como controle de qualidade

ASPECTO MOLECULAR DO MATERIAL INTERFACIAL ENVOLVIDO NA ESTABILIZAÇÃO DE ÁGUA PRODUZIDA / EMULSÃO DE PETRÓLEO

https://proceedings.science/p/138821

Vinícius Matos da Costa [1]; Jhonattas Carregosa [2]; Alberto Wisniewski Jr [1]
[1] Universidade Federal de Sergipe; [2] Centro de Ciências Exatas e Tecnologia / Universidade Federal de Sergipe

The formation of stable emulsions between produced water and crude oil represents, in part, one of the challenges of the crude oil production and exploitation industry. The problems related to stable oil emulsions affect both Upstream and Downstream processes. In this sense, the aim of this work was to evaluate, at the molecular level, the species that exhibit interfacial activity within these systems. For this purpose, 5 crude oils of different ^{0}API were selected, these were named OB-1 (^{0}API 23.5), OB-2 (^{0}API 7.4), OB-3 (^{0}API 11.0), OB-4 (^{0}API 15.4) and OB-5 (^{0}API 22.4). The parameters: stability time and Zeta Potential of the system were used for correlation with the chemical nature of the active species present in the Interfacial Materials (IMs). The molecular-level characterization of the IMs extracted from the oils studied was performed using an ultra-high-resolution mass spectrometer Orbitrap type, adopting APPI as the ionization source. Regarding the results of the stability test, it was observed that the OB-2 oil was the one that kept the system homogeneous for the longest time. About the zeta potential of the systems, the following values were observed: -17.1 mV, -12.2 mV, +16.5 mV, +23.7 mV, -44.3 mV, for the oils OB-1, OB-2, OB-3, OB-4 and OB-5, respectively. According to the XDLVO theory for a non-aqueous system, the closer to zero the absolute value of the zeta potential is, the greater the stability of the system formed. Thus, the zeta results corroborated the observed stability times. Considering these results, and correlating them with the mass content of the isolated interfacial materials, no linear relationships were observed, therefore, the number of active species is not the determining factor for the stability of the emulsion system, but, rather, its nature. Thus, the IMs were fractionated and characterized by APPI(+)-FT-Orbitrap MS. The majority classes were: OxSy (x = 1 or 3, and y = 1 or 2) and Nx and NxOy (x = 1 and y = 1 or 2). By performing linearization of the zeta potential with the majority classes obtained by APPI(+)-FT-Orbitrap MS it was observed that the polar (acidic) species belonging to the OxSy classes (the most abundant species) act as natural surfactants, because, they showed positive Pearson correlation coefficients, between 0.55 and 0.64, indicating moderate to high correlation. The O3S1 and O2S2 classes are associated with sulfur-containing naphthenic acids and are described as natural surfactants. On the other hand, the Nx and NxOy species act in the opposite way, that is, they provide a greater disturbance of the system because, from the negative Pearson's relationship, it was observed that the higher the intensity of the N1 and N1O1 classes, the lower the stability of the resulting system. Therefore, for the set of oils studied, oils that have acidic molecular structures composed of oxygen-sulfur-containing compounds confer greater stability to the emulsion system involving crude oils. And conversely, the greater the presence of nitrogen-containing compounds, and nitrogen-oxygen-containing compounds, the lower the stability of the resulting system.

Cloud point extraction methodology for Cd(II) extraction using magnetic peel of Moringa oleifera as adsorbent.

https://proceedings.science/p/138827

Deborah Candida Bagano Gonçalves [1]; Vanessa Alves [2]
[1] Regional Catalão / Universidade Federal de Goiás; [2] Universidade Federal de Goiás

Devido principalmente às atividades industriais, agrícolas e pecuárias, o uso e descarte de íons metálicos tem aumentado, causando contaminação do meio ambiente, alimentos e etc. Ainda que alguns metais sejam encontrados de forma natural, alguns são prejudiciais, e mesmo em baixas concentrações podem causar acúmulo, levando a problemas de saúde. Dentre esses metais pode-se citar o Pb, Cd, As, Cu, Mn, Cr, etc. Técnicas de instrumentação para análises de íons metálicos já são estabelecidas, porém algumas possuem limitações, sejam elas em relação ao limite de detecção, inserção da amostra, sensibilidade, análises de amostras sólidas e disponibilidade em laboratórios. Isso faz com que haja uma etapa que anteceda a análise, conhecida como etapa de preparo de amostras, e dentro dessa etapa os procedimentos de extração e/ou pré-concentração são bastante utilizados, tornando possível a análise em equipamentos de custo relativamente baixo e sensibilidade mais alta, como é o caso da Espectrometria de Absorção Atômica com atomização por chama (FAAS, em inglês), quando comparadas com outras técnicas de absorção e emissão. O FAAS possui vantagens por permitir análises rápidas e simples. A Extração por ponto nuvem (CPE) e Extração em fase sólida (SPE) são difundidas na química analítica, visando a extração e pré-concentração de analitos. Dessa maneira, este trabalho tem como objetivo desenvolver uma metodologia para determinação de íons metálicos, utilizando a junção dessas técnicas a fim de contribuir com o meio ambiente, utilizando menos reagentes e alcançando baixos limites de detecção e quantificação. A metodologia proposta envolve a junção da técnica CPE com a SPE. Assim, utilizando a metodologia proposta por Falahnejad et al., 2, testou-se a casca de sementes de Moringa oleífera modificada magneticamente como adsorvente e Triton x- 100 (3% v/v) como surfactante para extrair Cd(II) na concentração de 1 mg/L. A avaliação do pH no ponto de carga zero (PCZ) e análise por espectroscopia na região do Infravermelho, foram utilizadas para caracterizar o adsorvente utilizado. O pH ideal para a extração foi estudado de forma univariada, onde soluções contendo o íon Cd(II) (1 mg/L) e pH entre 4 e 11 foram preparadas e submetidas ao procedimento proposto. Posteriormente um planejamento fatorial 24, com ponto central foi realizado, onde foram avaliadas as variáveis, concentração de surfactante Triton x-100 (1 e 5 % (v/v)), tempo de sonicação e tempo de banho Maria (1 e 10 minutos), e concentração de ácido nítrico (0,1 e 1,0 mol/L). O pH 6,0 é o que mais favorece o procedimento de extração. Os resultados do planejamento fatorial apontaram que o tempo de sonicação no ultrassom, e o tempo de aquecimento são variáveis que influenciam significativamente no procedimento e necessitam de um estudo mais refinado para que suas condições ideais sejam obtidas. Até o momento, a extração do íon ocorre, fornecendo um sinal analítico em média 3 vezes maior que aquele obtido para a solução sem o procedimento de extração.

Controle da concentração de biodiesel de crambe em misturas com diesel usando PLS-DA e espectroscopia MIR

https://proceedings.science/p/138799

Anizia Furtado Durans [1]; Carlos Alface [1]; Rodrigo dos Santos [1]; Lucas Gustavo da Costa [1]; Waldomiro Borges [2]

[1] Universidade Federal de Uberlândia; [2] Instituto de Química, Universidade Federal de Uberlândia – IQ-UFU

The economic importance of fuels demand quick response tools to control their qualities, as they are subject to adulteration and/or contamination. In this context, the Partial Least Square Discriminant Analysis (PLS-DA) can be used to classify samples inside and outside a given interest, so its use is proposed for the construction of a multivariate model that discriminates samples of biodiesel blends in diesel from according to their concentrations. The model was built from 68 samples where: 34 simulate crambe methyl biodiesel blends in diesel with a content of 10.0 ± 0.5 (% v/v), our class of interest, and 34

simulate biodiesel-diesel blends in a range ranging from 1.0 to 9.0 (% v/v) and from 11.0 to 30.0 (% v/v), our non-interest class. The classification model shown in Figure 1 presented VP=1, FP=0, VN=1, FN=0 and CCM=1, managing to correctly differentiate the samples of interest and not.
Figure 1 – Samples vs. Classes provided by PLS-DA

Desafios das Principais Técnicas Espectrométricas Atômicas e de Massas – Uma Visão Profissional

https://proceedings.science/p/138804

Daniela de Miranda Rodrigues [1]; Juliano Carvalho Ramos [1]
[1] Universidade de São Paulo

O presente trabalho propõe avaliar comparativamente a utilização das técnicas espectrométricas atômicas (FAAS, GFAAS e ICP-OES) e de massas (ICP-MS), destacando as principais limitações de cada instrumentação além de fornecer um panorama atual da popularização desses equipamentos no Brasil. As três técnicas são majoritariamente utilizadas para realizar análises elementares, comumente em quantidade traço (100 ppm a 1 ppb), possuindo peculiaridades, componentes e princípios próprios. A metodologia consistiu na revisão bibliográfica de artigos científicos e livros, além de uma investigação em forma de entrevista com uma especialista profissional experiente, atuante na comercialização destas instrumentações. Na investigação, discorreu-se a respeito dos tipos de análises mais desafiadoras, destacando-se as amostras as quais possuem alto teor salino. Para os ICPs, o excesso de sais pode acarretar em entupimentos no sistema de introdução de amostras, desgaste precoce da tocha de quartzo, ocorrência de interferências, dentre outros problemas que inviabilizem as análises.
Em suma, as três técnicas vêm sendo aprimoradas, no entanto, a técnica desenvolvida mais recentemente, de ICP-MS é a que possui maior investimento, sendo que a sua aplicabilidade está em ascensão principalmente em países mais desenvolvidos. As perspectivas futuras desta técnica são de criações de um equipamento com uma interface mais intuitiva ao usuário e autônoma, além da possibilidade de uma plataforma do equipamento que seja remota, ideal para aplicações em campo (fora do espaço do laboratório). No Brasil, a linha de absorção atômica, devido ao menor custo da instrumentação e manutenção, quando comparado aos demais citados, ainda é bastante utilizada e possui um mercado de vendas de instrumentação analítica bem aquecido, com possibilidade de análises com boa relação custo-benefício, especialmente em laboratórios com recursos financeiros limitados. No entanto, seu uso em países desenvolvidos possui prenúncio de tornar-se obsoleto, em virtude da crescente demanda por
técnicas multielementares, rápidas e que possibilitem menores limites de detecção. Em relação ao ICP-OES, seu uso é particularmente significativo em relação às análises de solos, especialmente notável por ser de grande importância dentro do agronegócio, o qual possui uma crescente expansão e forte relevância no mercado brasileiro.

Desenvolvimento de um imunossensor para monitoramento de anti-asparaginase em pacientes com leucemia linfoblástica aguda (LLA)

https://proceedings.science/p/138817

Jocimara Camargo da Silva [1]; Augusto Facundes da Silva [1]; Augusto Etchegaray [1]; José Andrés Yunes [2]; Renata Kelly Mendes [1]
[1] Pontifícia Universidade Católica de Campinas - Centro de Ciências Exatas, Ambientais e de Tecnologia; [2] Centro Infantil para Investigações Hematológicas Dr. Domingos A. Boldrini

Acute lymphoblastic leukemia (ALL) is the main type of childhood cancer. Among the drugs used in the disease treatment the enzyme L-asparaginase stands out as an important therapeutic drug. It has been observed that the use of enzyme ontributes significantly for the remission of the disease, with consequent elimination of the leukemic cell. However, the organism can produce anti-asparaginase antibodies, which mitigate the pharmacological effect of the treatment. In this way, the monitoring of these antibodies in patients contributes to the efficiency of the treatment. Therefore, the development of new methods that allow this analysis using a simple, precise and selective process is of great interest. In this context, the aim of this work was the development of an electrochemical immunosensor for monitoring the antibodies in patient in treatment for leukemia. There are few immunosensors reported using asparaginase as a recognition element and it was not found electrochemical immunosensor to determine anti-asparaginase, considering the database analyzed, which makes this work innovative. For this, the L-asparaginase enzyme was immobilized on the printed carbon electrode surface using the nanocomposite formed by Fe3O4 magnetic nanoparticles modified with chitosan and glutaraldehyde. The immunosensor showed linearity for antibody between the 0.1 and 10 µg.mL-1 and the limit of detection found was 150 ng.L-1 . In addition, the device was selective and it showed reproducibility of construction (3.3%). From these results, the proposed immunosensor presented satisfactory prospects for monitoring the anti-asparaginase during the treatment of childhood leukemia.

Determinação de fluopyram em amostras de água usando LLE-LTP e HPLC-DAD

https://proceedings.science/p/138801

GLEYSSON DE PAULA TERRA [1]; Flaviano Silvério [2]; Lázaro Sicupira [1]; Lucas Victor de Freitas [3]; SILAS DE SOUZA SANTOS [4]
[1] Universidade Federal dos Vales do Jequitinhonha e Mucuri; [2] Universidade Federal de Minas Gerais; [3] Faculdade de Ciências Farmacêuticas de Ribeirão Preto - Universidade de São Paulo, FCRP-USP; [4] Instituto de Ciências Agrárias / Universidade Federal de Minas Gerais

Fluopyram is used in agriculture to control fungi and its intensive use can lead to a significant risk to living organisms.1 Therefore, monitoring this compound is important to ensure human health and preserve the environment. This work aimed to optimize and validate liquid-liquid extraction with low temperature purification (LLE-LTP) to determine fluopyram in water samples. The optimization was performed through a complete 23 factorial design, and the variables studied were: the composition of the extraction phase (acetonitrile and acetonitrile/ethyl acetate), ionic strength (0.0 and 0.2 g of NaCl) and freezing time (60 and 120 min). The method consists of adding 4.0 mL of water sample and 8 mL of extraction phase. Then, the system is homogenized by vortexing for 1 min and kept at -20°C until complete freezing of the aqueous phase. After this step, 5 mL of the liquid organic phase containing fluopyram were completely evaporated under air flow and immediately resuspended in 400 µL of acetonitrile. The optimal extraction conditions for this work were 8.0 mL of acetonitrile, freezing time of

120 min and without the addition of NaCl. All extracts were analyzed in a liquid chromatograph coupled to a diode array detector (HPLC-DAD). The recovery rate achieved in this condition was 106.29% with a relative standard deviation of 7.54%. The extraction method was selective, precise, and exact (as can be seen in Figure 1), with a linearity range between 6.0 to 200.0 µg L-1 and did not show a matrix effect. The detection and quantification limits reached were 4 and 6 µg L-1, respectively.

Determinação espectrofotométrica de Pb em resíduo de disparo de arma de fogo usando um smartphone

https://proceedings.science/p/138795

Alessandro Storck Figueira [1]; Flávia Ferreira de Carvalho Marques [1]; Wagner Pacheco [2]
[1] Universidade Federal Fluminense; [2] Instituto de Química / Universidade Federal Fluminense

Statistical data show that Brazil has a high number of homicides caused by guns. This fact gives great relevance to the ballistic study, as an instrument to clarify a criminal fact. It is known that when a gun is fired, the increase in pressure from the gases of the propellant burning material forms a cloud of smoke around the shooter's hand. Gases are condensed and solid particles called GSR (Gunshot Residue), containing Pb, are deposited in shooter's hand [1].

The objective of this work is to quantify Pb as GSR in the skin through digital image analysis. The methodology is based on the formation of the Pb-rhodizonate complex and the quantification is given by the treatment of digital images obtained from the colored complexes. The experiment was carried out in the range of 1.25 µg to 12 µg of Pb, adding in each solution 25 µL of tartrate buffer solution (0.10 g/L) at pH 2.5 plus 50 µL of sodium rhodizonate solution (0.20 mol/L).

A porcelain touch plate containing cavities was used to distinguish the color of each Pb-rhodizonate complex, according to the Pb mass in each sample (Fig.1). After the reaction, the plate was placed inside an LED (Light-Emitting Diode) box that was constructed to maintain light and focus, where digital photographs were taken with a smartphone (model iPhone-5). The images were treated in the free software ImageJ, which generated histograms containing data relating to the color intensity of each sample. The histograms provided data of the RGB (red, green and blue) channels. The green channel was the reference chosen because it is the complementary color to the red complex color (Fig.1). Absorbance values were calculated from the mean value provided by the histogram using the equation Abs= - log [P/Po]; where P= mean value in the sample; and Po= mean value in the blank. Finally, the analytical curve was constructed correlating the absorbance values with the mass of Pb. Linearity from 1 µg to 12 µg of Pb, characterized by R2 > 0.97, was verified.

Results look worthy for further studies and the next step is to apply the method on samples from shooter’s hand.

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Determination of chloride in crude oil by colorimetric analysis using a portable device and a smartphone

https://proceedings.science/p/138812

Paola de Azevedo Mello [1]; Alice Penteado Holkem [1]; Gabrielle Dineck Iop [1]; Juliano Smanioto Barin [2]; Adilson Ben Costa [3]; Gilson Helfer [4]
[1] Universidade Federal de Santa Maria; [2] Departamento de Tecnologia e Ciência dos Alimentos / Universidade Federal de Santa Maria; [3] Programa de Pós-Graduação em Sistema e Processos Industriais / Unisc / Universidade de Santa Cruz do Sul; [4] Universidade de Santa Cruz do Sul

The determination of salt content in crude oil is of great concern and the standard method from the American Society for Testing and Materials (ASTM) D 6470 is the most common for this purpose. This method is based on the extraction of salt to an aqueous solution using organic solvents, followed by chloride determination by potentiometric titration. However, several disadvantages have been reported, such as the excessive amount of reagents and waste generation, which contrasts with the recommendation of green analytical chemistry. Digital images can be an alternative approach using colorimetry on smartphones with low-cost and time-saving analyses. Thus, in this work, a digital-image-based method for chloride in crude oil was developed. The parameters for extraction (sample mass, time, temperature, and type of solvent) and for detection (ratio between silver nitrate and indicator, volume inside the vial, lighting, focal distance, number of pixels and pH effect) were evaluated. To obtain the digital images, an USB camera was attached to a homemade 3D-printed chamber with controlled light intensity by a white light-emitting diode (LED). Sample solution 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 square regression (PLS) model was obtained directly from the app. The PLS regression results were evaluated in terms of the number of samples and factors, the coefficient of determination (R2), the root mean squared error of calibration (RMSEC), the root mean squared error of cross validation (RMSECV), and the root mean squared error of prediction (RMSEP). The calibration curve (from 100 to 500 mg L-1 of Cl) was obtained using a PLS model with a R2 better 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 9.04, 31.2 and 26.1 mg L-1, respectively. The detection limit was 69 mg L-1 (0.034 mg g-1 using 10 g of sample). No differences were observed ($p < 0.05$) when comparing the results from the proposed method with the reference values obtained using ASTM D 6470. The extraction method's simplicity combined with the digital image-based colorimetric analysis allowed an easy-to-use and environmental friendly method. Other important advantages include low cost, the possibility to be portable, and high throughput in comparison to conventional methods.

Development of a Horseradish Peroxidase Catalyzed Chemiluminescence Method for Determination of Peroxides in Ozonized Oils

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Nathalia Pavan [1]; Valdecir Ximenes [1]
[1] Faculdade de Ciências / Universidade Estadual Paulista "Júlio de Mesquita Filho"

Ozone therapy is a widespread medical, veterinary, and dental procedure. The techniques are diverse and include the direct and controlled administration of ozone gas and the use of previously ozonated materials, as ozonized oils. Ozonation of oils alters the structure of fatty acids, generating peroxides,

which are the agents in wound healing and has bactericidal effects. This work aimed to develop a chemiluminescence-based analytical technique for measuring the peroxidic content of ozonized oils. Sesame oil was ozonized at different time intervals, and the presence of peroxide characterized by FTIR and the peroxide content was determined by iodometry (Peroxide Index). The chemiluminescent analytical method was developed based on the oxidation of luminol and using horseradish peroxidase (HRP) as the catalyst. Figure 1 shows the light emission profile for a reaction in the presence and absence of ozonized oil. The studied parameters were: buffer type and pH, the concentrations of HRP and luminol, and the solvent used to dissolve the ozonized oil. The best conditions were: HRP 12.5 nM, luminol 0.5 mM, and Tris buffer 50 mM, pH 9.0. Figure 2 shows the correlation between the oil concentration and the total light emission. In conclusion, the method was sensitive and adequate to measure the oxidative potential of ozonized oils.

Development of composite electrodes based on carbon black for lead quantification.

https://proceedings.science/p/138825

Suellen Fabricia Lima do Nascimento [1]; Taíssa da Silva Cabral [1]; Wagner Pacheco [2]; Rafael Machado Dornellas

[1] Universidade Federal Fluminense; [2] Instituto de Química / Universidade Federal Fluminense

Handcrafted composite electrodes consist of mixtures between, at least two phases, one insulating and one conductor, generating a conductive material with physical and chemical properties different to those from the original phases. Carbon black (CB) is a spherical nanomaterial consisting primarily of carbon. Materials based on carbon black have favorable electrical properties that make them good conductors, in addition to being easy to obtain, low cost, and can also be obtained through the recycling of organic matter. In this work, three different types of composite electrodes were developed whose conducting phase was CB powder and the insulating phase, distinct for each type of electrode, was acrylonitrile-butadiene-styrene (ABS), poly(ethylene terephthalate glycol) (PETG) and polylactic acid (PLA), named CB-ABS, CB-PETG and CB-PLA, respectively. Different proportions of carbon black and polymer were prepared in proportion range from 30 to 70% (carbon black, m/m), but only electrodes consisting of 35, 40 and 50% of carbon black showed adequate physical characteristics to be used and tested. Techniques such as cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and atomic force microscopy (AFM) were used to characterize these electrodes. CV along with EIS were used to assess the electrochemical behavior of these electrodes. For each type of optimized electrode, anodic stripping square wave voltammetry was employed for analytical purposes, being several parameters investigated to determine the optimum experimental conditions for lead quantification. The calculation of the electroactive area was performed by CV using the redox system [Fe(CN)6]-3/[Fe(CN)6]-4 and the proportions that presented the largest electroactive areas for each type of composite were CB50%-ABS50%, CB50%-PETG50% and CB50%-PLA50%, obtaining the results of 0.1056 ± 0.0011, 0.0926 ± 0.0075 and 0.1082 ± 0.0086 cm2 which corresponds to 71, 66 and 77% of the geometric area, respectively. The EIS Nyquist graph (frequencies between 0.1-5.104 Hz) showed that the smaller the semicircle diameter the bigger the carbon black content, indicating that the surface resistance of these electrodes is lower, which favors charge transfer on the surface of CB50%-ABS50%, CB50%-PETG50% and CB50%-PLA50% electrodes. The electrodes, under optimized conditions, provided limits of detection for determination of lead of 2.84E-8 mol L-1, 2.88E-7 mol L-1 and 1,14E-8 mol L-1 for CB50%-ABS50%, CB50%-PETG 50% and CB50%-PLA50%, respectively.

Effects of non-thermal processing technologies (UV-C) on the hydrolyses of β-lactoglobulin by commercial proteases: bioactive peptides and transepithelial transport across Caco-2 cell monolayers

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Keila Cavalcante [1]; Sinara T.B. Morais [1]; Jéssica Feitor [1]; Daniel Cardoso [1]
[1] Instituto de Química de São Carlos / Universidade de São Paulo

Whey proteins are relevant dairy derived products specially for the supply of high-quality protein and may relevant to reduce frailty in older adults, usually associated to low protein intake. Furthermore, whey proteins may be an important source of peptides bioactive (BPs) from food. β-lactoglobulin (β-LG) is the main protein in whey, accounting to around 80 % of the total protein content, however, β-LG is not fully digested and may, for some people, lead to an allergic response. Non-thermal processing technologies like UV-C and PEF are growing in interest for food industries to overcome the chemical changes induced by the traditional thermal processing methods like LTST pasteurization as used to reduce foodborne pathogens. UV-C light irradiation of β-LG has been shown to induce slight changes in the protein conformation due to the presence of the photoactive triads (Trp/Cys-Cys or Tyr/Cys-Cys) which led to disulfide reduction [1]. In this context, the present work investigates the effects of the UV-C light irradiation on the degree of hydrolysis (DH) by trypsin, changes in the peptidomic profile as determined by MALDI-TOF/TOF-MS, and the effect on the hydrolysates transepithelial transport across Caco-2 cell monolayers. β-LG (2 mg per ml) was photolyzed with Io = 1,81.10-10 Einstein/s for 2 hours or for comparison pasteurized by LTLT process. Native protein, UV-C irradiated, and thermo treated β-LG was afterword submitted to trypsin hydrolysis for different times up top 2 hours [2]. Different digestion times were evaluated for DH and the 2-hours hydrolysate submitted to peptidomic analysis and used to evaluate the transepithelial transport across Caco-2 cell monolayers using a static trans-well model [3]. The DH showed significant differences in digestibility for native, UV-C irradiated and thermal processed protein. UV-C light irradiated β-LG showed an increase of 3% in the DH in comparison to the native protein and an increase of almost 6% in comparison to pasteurization. The peptidomic profile as obtained by MALDI-TOF/TOF-MS shows a higher yield of bioactive peptides like the peptide ALPMHIR f(158-164) with a 4-fold increase in comparison to the native protein. The transwell assay suggested that three bioactive peptides fβ-LG (158-164; 87-91 and 57-76), are efficiently transported across Caco-2 cell monolayers with high apparent permeability. Thus, the use of UV-C as non-thermal processing technology for whey protein is a relevant alternative to thermal processing, being able to efficiently reduce foodborne pathogens and also increasing the total hydrolysis capacity by 2% and the specific hydrolysis capacity by 18% for β-LG, and in addition, increasing significantly the yield of bioactive peptides in hydrolysates by the use of commercial proteases.

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Enantioselective analysis of the pesticide imazamox in permeability study with CACO-2 cells: chiral separation optimization and method validation

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Carolina Oliveira Serpellone [1]; Maike Felipe Santos Barbetta [1]; Giulia Ballestero [2]; Nayara de Albuquerque [2]; Anderson Rodrigo Moraes de Oliveira [1]

[1] Departamento de Química / Faculdade de Filosofia, Ciências e Letras de Ribeirão Preto / Universidade de São Paulo; [2] Eleve Science Pesquisa e Desenvolvimento Ltda. / Eleve Science Pesquisa e Desenvolvimento Ltda.

Pesticides application in agricultural production is a widely resource used around the world to protect crops and reduce considerable losses caused by pests. Nevertheless, their intense use puts the environment and non-target organisms at risk. Imazamox (IMX) is a chiral herbicide used against weeds in cereal and oilseed crops in their pre- or post-emergence. The commercialization of this pesticide is allowed in several countries of the European Union, in the United States and Brazil. However, data on the exposure and enantioselective interaction of IMX with non-target organisms are scarce. In addition, there are no studies regarding the enantioselective behavior of IMX in human models. This work presents the development, through experimental design, of an enantioselective method to analyze IMX in acceptor solution to further study its permeability through CACO-2 cells. Initially, three chiral columns (Chiralpak-AD-H, Chiralcel-OD-H and Chiralcel OJ) were evaluated in polar organic and reverse modes, using 3 solvents: methanol, ethanol and acetonitrile. In the screening stage, fractional factorial planning was used by evaluating the following factors at two levels: (i) solvent proportion in mobile phase, (ii) percentage of formic acid, (iii) flow rate, (iii) temperature and (iv) volume of injection. In the optimization step, the central composite rotational design (DCCR) was used. Following the development of the enantioselective separation, the analytical validation was performed in order to analyze the IMX in permeability studies with CACO-2 cells. The following parameters were evaluated: linearity, lower limit of quantification, precision, accuracy, stability, selectivity, and residual effect. The acceptability criteria for each parameter were based on the ones described in the ANVISA validation guideline for bioanalytical methods. The final and optimized chromatographic condition was reached by using the Chiralcel OD-H column and H2O:ACN, 79:21 (v/v) was used as mobile phase. The flow rate was 0.6 mL min-1 and the column temperature was set at 30ºC. The resolution obtained was greater than 1.5 for the IMX enantiomers and the analysis time was less than 12 minutes. Based on ANVISA's bioanalytical validation guide all the parameters were satisfactory and the method was considered validated.

Enantioselective analysis of the pesticide prothioconazole and its main metabolite in liver microsomes by coupling aquiral-chiral columns

https://proceedings.science/p/138797

Icaro Salgado Perovani [1]; Maike Felipe Santos Barbetta [1]; Rodrigo Moreira da Silva [2]; Norberto Peporine Lopes [2]; Anderson Rodrigo Moraes de Oliveira [1]

[1] Departamento de Química / Faculdade de Filosofia, Ciências e Letras de Ribeirão Preto / Universidade de São Paulo; [2] Faculdade de Ciências Farmacêuticas de Ribeirão Preto / Universidade de São Paulo

Pesticide use has been increasing mainly to the increase in world population and food demand. This has been led to increased exposure to these chemicals, resulting in a harmful scenario for humans and wildlife (Carvalho, 2017). Prothioconazole (PTC) is a triazole chiral fungicide that has been found in food

samples (Gaweł et al., 2019). In addition, studies in mammals showed that PTC was converted into desthio-prothioconazole (D-PTC) after hepatic metabolism (Zhang et al., 2019). In order to evaluate the metabolism of this pesticide in a human model, the aim of this work was to analyze the pesticide prothioconazole in human liver microsomes after sample preparation optimization and method validation. The enantioseparation of PTC and D-PTC was carried out on a Chiralcel OD-3 column (100 x 4.6 mm, 3 µm) using the mixture of acetonitrile: water 60:40 (v/v) with 0.1% (v/v) formic acid as mobile phase in an LC-MS/MS system. An achiral C18 column (100 x 4.6 mm, 2.7 µm) was coupled before the chiral column to separate PTC and D-PTC. Dispersive liquid-liquid microextraction (DLLME) was used as a sample preparation technique after optimization by using a central composite design. The final condition of the DLLME comprised injecting 100 µL of the mixture butyl acetate: ethanol 1:3 (v/v) into 200 µL of the sample. After that, the sample was centrifuged and 15 µL of the butyl acetate was collected and diluted into 85 µL of ethanol before being injected into the chromatographic system. These conditions yielded an extraction efficiency of 89 and 92% for PTC and D-PTC respectively. The bioanalytical method was fully validated. The PTC method linearity comprised the range 0.0321 – 5.50 µmol L-1, for D-PTC the linear range was 0.0105 – 2.10 µmol L-1. The method was accurate and precise, and the analytes remained stable during the analysis.

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Enantioselective in vitro metabolism study of the pesticide diclofop-methyl: optimization of the chiral separation and sample preparation

https://proceedings.science/p/138802

Maike Felipe Santos Barbetta [1]; Jade Lorena Mariano Bucci [1]; Icaro Salgado Perovani [1]; Márcia Silvana Freire Franco [1]; Anderson Rodrigo Moraes de Oliveira [1]
[1] Departamento de Química / Faculdade de Filosofia, Ciências e Letras de Ribeirão Preto / Universidade de São Paulo

Diclofop-methyl (DCM) is a chiral herbicide from the aryloxyphenoxypropionate class, specially applied to wheat and barley cultures against weed. Some works have reported that this pesticide shows an enantioselective degradation in fruit and vegetables [1] and enantioselective metabolism in loach [2]. However, information about its affect in humans is scarcely. In addition, there is no data regarding its metabolism and interaction with cytochrome P450 enzymes from humans. The knowledge of those information are important in order to understand the metabolic profile of this pesticide in humans and to prevent drug-pesticide interactions. The aim of this work was to optimize an enantioselective chromatographic separation and a sample preparation technique to analyze the DCM and its main metabolite, diclofop (DC), in human liver microsomes to be further used in in vitro metabolism studies. In order to reach a suitable resolution of DCM and DC, several chromatographic parameters were evaluated, such as column temperature, flow rate, elution mode (reversed and polar organic), mobile phase composition (water, acetonitrile, methanol and ethanol) and chiral columns (Chiralcel OD-RH®, Chirobiotic TAG®, Chiralpak AD-RH® e AD-3®). Next, to extract the analytes from microsomal medium, liquid-liquid extraction was optimized and the following parameters were evaluated: (i) solvent type (ethyl acetate, chloroform and dichloromethane), (ii) solvent volume (400, 600, 800 and 1000 µL),

(iii) extraction agitation time (5, 10 and 15 min). Other parameters were kept constant: stirring speed at 1500 rpm and centrifugation at 1600 xg for 10 min at 4 °C. The best conditions for enantioseparation were obtained by using the Chiralpak AD-3® column, in which there were two possible conditions: methanol: ethanol with 0.1% of formic acid (80:20 v/v) and ethanol: aqueous solution of formic acid 0.1% v/v (70:30 v/v). Since the first condition was faster (7.5 min) it was chosen and further adapted to HPLC-MS. The final condition was: Chiralpak AD-3® column and 63% methanol: 27% ethanol: 10% water with 0.75% formic acid and 0.25% ammonium acetate was used as mobile phase. The flow rate and column temperature was, respectively, 0.8 mL/min and 30 °C. The resolution between the peaks was higher than 1.5 and the total run time was 7.5 min. The best extraction condition was accomplished by using 800 µL of ethyl acetate and extraction agitation time of 5 min. By using this condition, the recovery of the analytes was 100% and no interferents were observed either in the retention of DCM or DC.

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Estudo do efeito sequestrante PVP-Fenol na determinação do teor de proteína pelo método de Lowry

https://proceedings.science/p/138796

Daniel Vasconcelos [1]; Francisca Sobral [2]; Andrea Medeiros Salgado [2]; M Queiroz [3]
[1] UNIVERSIDADE DO ESTADO DO RIO DE JANEIRO; [2] Universidade Federal do Rio de Janeiro; [3] Laboratório Extratos Alergênicos

O método de Lowry é rotineiramente utilizado em laboratório de análise para determinação do teor de proteínas, tendo os compostos fenólicos como substancias interferentes1. Contudo, o polímero polivinilpirrolidona (PVP) pode formar complexos com compostos fenólicos, permitindo sua remoção e conferindo estabilidade à proteína. Objetivo: O presente estudo tem por objetivo avaliar o efeito do polímero PVP, como agente sequestrante de fenol em amostra proteica, mediante a quantificações pelo método de Lowry2. Metodologia: Foram construídas curvas padrão de albumina soro bovino (BSA), nas concentrações de 5, 10, 25, 50, 75, 100 µg/mL, em matriz contendo 0,032 mmol/mL de fenol e PVP-40 (3, 10, 25 % (m/m)). Os experimentos foram avaliados, observando as amostras controle padrão (ausência de fenol) em relação aos experimentos contendo: BSA, fenol e PVP-40. Resultados e Discussão: A ausência de PVP-40 impossibilitou a obtenção da densidade óptica (D.O) (Figura 1(a)) pela turvação do meio, tendo em vista a formação óxido de tungstênio e óxido de molibdênio. Para a concentração de 5 µg/mL da curva analítica, foram obtidos os menores erros relativos, nos valores de 1,8% e 5,6 %, quando submetidos aos percentuais de 25% e 3% de PVP-40, respectivamente. Esses resultados sugerem que nessas condições, houve sequestro de fenol pelo polímero, minimizando interações entre fenol e o reagente Folin-Ciocalteu (turvação). Os baixos coeficientes de correlação das curvas analíticas (Figura 2 (b), (c) e (d)) em concentrações de proteína acima de 5 µg/mL, sugerem haver interações proteína-fenol, conforme relatado por Winters e Minchin (2005). Isso justificaria a diminuindo a D.O, pela minimização da interação proteína e Folin-Ciocalteu. Esses resultados apontam que para cada concentração da curva analítica (teor de proteína) há a necessidade de ajuste do percentual em massa do polímero, (para o valor fixo de fenol, 0,032 mmol), fato que está sendo investigado em laboratório. Conclusão: A aplicação de PVP permitiu uma boa aproximação em relação a amostra sem fenol, sendo um método promissor, porém requer ainda processo de validação, etapas que ocorrerão no curso nesta pesquisa.

Evaluation of analytical performance in the determination of rare earth elements in marine sediment by ICP-MS

https://proceedings.science/p/138833

Suellen Cordeiro [1]; Geisamanda Pedrini Brandão [1]; Maria Tereza Carneiro [1]; Jefferson Rodrigues de Souza [2]

[1] Universidade Federal do Espírito Santo; [2] Universidade Estadual do Norte Fluminense Darcy Ribeiro

A utilização da matriz de sedimento, na avaliação do ecossistema aquático, destaca-se na comunidade científica por agregar informações capazes de revelar o processo de contaminação bem como sua origem. A distribuição dos elementos químicos no ecossistema, quando desequilibrada pode comprometer a biota dos rios e mares, além de acarretar danos à saúde humana. Os elementos terras raras têm sido muito utilizado em pesquisas de avaliação ambiental marinha pois são excelentes indicadores de processos geológicos, visto que, encontram-se associados em diferentes proporções nos minerais que compõem os sedimentos marinhos. Porém, devido à complexidade desta matriz, o desenvolvimento de metodologia adequada para determinação dos elementos terras raras faz-se necessário. Sendo assim, o objetivo deste estudo foi avaliar o desempenho analítico da determinação de elementos terras raras, em sedimento marinho, por espectrometria de massa com plasma indutivamente acoplado. O preparo da amostra consistiu na decomposição em forno de radiação micro-ondas, baseado no USEPA 3052 adaptado utilizando HNO3, HCl, HF e H3BO3. Para análise das amostras em ICP-MS, a faixa de trabalho foi de 0,05 µg.L-1 a 10 µg.L-1 . Foi utilizado como padrão interno (PI) o índio (In), na concentração de 5□g L-1, para elementos Pr, Nd, Sm, Eu, Gd, Tb, Dy. A linearidade, avaliada a partir dos coeficientes de determinação, obtidos durante a construção da curva analítica na determinação dos elementos terras raras foi maior que 0,999 para todos os elementos. Os valores do limite de detecção e quantificação obtidos foram adequados para detectar e quantificar os analitos em amostra real, ainda que em baixas concentrações. Para avaliação da exatidão do método foram determinados 139La, 140Ce, 141Pr, 142Nd, 152Sm, 151Eu, 160Gd, 159Tb, 162Dy, 165Ho, 166Er, 169Tm, 174Yb, 175Lu no material de referência certificado (MRC) de sedimento estuarino – BCR 667, além da realização do teste de adição e recuperação em amostra real. Os valores de recuperação obtidos, foram condizentes com a faixa aceitável estabelecida pela Association of Official Analytical Chemists (AOAC, 2016) para os diferentes níveis de concentrações estudados, que é de 80% a 100%. As concentrações determinadas no MRC BCR 667 foram comparadas com os valores certificados e, com exceção do elemento Yb, todos os outros valores apresentaram boa concordância, indicando boa exatidão do método.

Expanding Urinary Metabolite Annotation through Integrated Mass Spectral Similarity Networking

https://proceedings.science/p/138816

Fausto Carnevale Neto [1]

[1] Northwest Metabolomics Research Center / University of Washington / University of Washington

The urine metabolome constitutes a rich source of functional information reflecting physiological states that are influenced by distinct conditions and biological stresses, such as responses to drug treatments or disease manifestations. Although global LC-MS profiling provides the most comprehensive measurement of metabolites in complex biological samples, annotation remains a challenge, and

computational approaches are necessary to translate the molecular composition into biological knowledge. Here, we investigated the use of tandem MS-based enhanced molecular networks (MolNetEnhancer) to improve the metabolite annotation of urine extracts. The samples were analyzed by hydrophilic interaction chromatography (HILIC)-QTOF mass spectrometry in both electrospray (ESI) ionization modes. Consistent with other common data preprocessing software, the use of Progenesis QI led to the annotation of up to 20 metabolites based on MS2 library searches showing high fragmentation score (cosine similarity ≥ 0.7), i.e., ~2% of mass features containing MS2 spectra. Molecular networking (MN) based on library match resulted in annotation of up to 62 urinary compounds. Using a combination of unsupervised substructure discovery (MS2LDA), the in silico tool network annotation propagation (NAP), and ClassyFire chemical ontology, embedded in a multi-layered MN by MolNetEnhancer, we were able to expand the chemical characterization to ~50% of the dataset. The integrative approach led to the annotation of 275 compounds at the Metabolomics Standards Initiative (MSI) confidence level 2, as well as 459 and 578 urinary metabolites (MSI level 3) in both negative and positive ESI modes, respectively. The exhaustive MS2-based annotation outperformed similar studies applied to larger cohorts while offering the discovery of metabolites not identified by MS2 library search. This is the first work that effectively integrates orthogonal annotation methods and MS2-based fragmentation studies to improve metabolite annotation in urine samples.

Extração e pré-concentração de agrotóxicos em suco de maçã empregando microextração por sorvente empacotado (MEPS)

https://proceedings.science/p/138810

Wagner Aires de Oliveira Júnior [1]; Silvia de Sousa Freitas [1]
[1] Instituto de Química / Universidade Federal de Catalão

A técnica de microextração por sorvente empacotado (microextraction by packed sorbent, MEPS) é uma miniaturização da extração em fase sólida e opera com consumo reduzido de reagentes, amostra, solvente e fase sólida, resultado em uma redução no tempo de preparo de amostra. Nesta técnica, a amostra é aspirada por uma seringa preenchida com uma fase sólida, em vários ciclos, promovendo a remoção dos analitos da amostra para posterior determinação cromatográfica. Neste trabalho, MEPS foi utilizada para a extração e pré-concentração dos agrotóxicos diuron, parationa metílica e clorotalonil de amostras de suco de maçã, com determinação por HPLC-UV. O dispositivo MEPS usado é formado de 3 partes desmontáveis (base, corpo e tampa) de politetrafluoretileno e 2 filtros de aço inoxidável porosos contendo cerca de 5 mg do sorvente C18, acoplados a uma microsseringa de agulha removível (HAMILTON, 500 µL). As etapas do procedimento MEPS foram: (1) limpeza do sorvente com 300 µL de acetonitrila (3 ciclos); (2) condicionamento com 300 µL de água deionizada (2 ciclos); (3) carregamento da amostra; (4) eluição dos analitos em 100 µL de uma mistura de acetonitrila/água (1:1, v/v) (10 ciclos). A etapa de carregamento foi avaliada para 2 diferentes volumes de amostra: 100 e 300 µL. Assim, em cada ensaio, este volume de amostra foi aspirado na seringa e dispensado em um descarte e este procedimento foi repetido (5 ciclos). Todos os ensaios foram feitos em quadruplicata, usando amostra de suco de maçã fortificada com os agrotóxicos (diuron: 0,1 mg L-1, parationa metílica: 0,2 mg L-1 e clorotalonil: 0,5 mg L-1). Os analitos eluídos foram analisados em HPLC-UV (coluna e pré-coluna C8, fase móvel: metanol/água, 62:38 (v/v), vazão 1 mLmin-1, □ = 254 e 280 nm). Após o MEPS, a resposta cromatográfica dos compostos foi significativamente aumentada. O fator de concentração (área do composto após MEPS)/área da solução padrão) foi usado para avaliar a eficiência do processo. Conforme o volume de amostra aumentou de 100 para 300 µL no procedimento, o fator de concentração médio

aumentou de 3,34 0,25 para 9,74 0,29. A quantidade de C18 no dispositivo de extração é muito pequena e, mesmo com aumento no volume de amostra, o dispositivo foi capaz de aumentar proporcionalmente sua eficiência de extração, sendo observado ótima reprodutibilidade nesta condição (desvio padrão relativo de 2,93%). Assim conclui-se que o procedimento MEPS proposto foi capaz de determinar os agrotóxicos em uma amostra complexa de modo simples, rápido e utilizando pequenas quantidades de solventes.

Geoquímica Forense Molecular: especiação de óleos brasileiros no setor petrolífero e em crimes ambientais

https://proceedings.science/p/138822

Flavia Rodrigues Alvares [1]; Gleicielle Wurzler [1]; Gabriela Vanini [1]
[1] Universidade Federal do Rio de Janeiro

The growing 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 aims 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 (39.38%), aromatic (14.42%), and polar (36,99%) 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. 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], N2[H], O3[H], O[H], O2[H], NO2[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 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 C12 to C58 and a highest abundance of nitrogen compounds in DBE = 8 to 10. In intermediate samples, CN was C12 to C67 and DBE between 6 to 10. In heavy samples, CN was C12 to C59 and DBE between 6 to 9. These results are preliminary, and the next step will be to calculate the geochemical parameters and 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.

1. VANINI, G. et al. Characterization of Nonvolatile Polar Compounds from Brazilian Oils by Electrospray Ionization with FT-ICR MS and Orbitrap-MS. Fuel 282 (2020) 118790
2. WANG, Z. et al. Forensic Fingerprinting of Biomarkers for Oil Spill Characterization and Source Identification. Environmental Forensics, 7:105-146, 2006.

Green and Sustainable Chemistry in Papers Published by Química Nova (2010-2020): Trends and recommendations

https://proceedings.science/p/138829

Carlos Alberto da Silva Júnior [1]; Andrea do Oriente Lino [1]; José Renato Gomes Lopes [1]; Nara Karoline Ferreira Dias [1]
[1] Instituto Federal de Educação, Ciência e Tecnologia da Paraíba

Since the 12 principles of Green Chemistry (GC), postulated by Paul T. Anastas and John C. Warner [1] in the 1990s, the scientific world was never the same again. New product development processes have emerged with a more sustainable perspective. Evidently, the impacts of GC on the environment and population are growing in the literature. Química Nova (QN) is a prestigious Brazilian journal that covers the traditional fields of chemistry (e.g. chemical education, analytical chemistry). QN is responsible for publishing the first works on GC in Portuguese. The overview of the previously published works on QN was based on keywords (e.g. green chemistry, green sustainability, greener process) and on previous categories: area of knowledge and purpose of the proposal. The papers were selected from the period 2010 to 2020. The authors analysed 49 papers. The development of new procedures for hazardous material elimination is crucial. Approaches with benign solvents are in the frontiers of GC [2]. Green Chemistry Education (GCE) was described in 27 papers which address techniques for introducing the concepts of GCE into the Teaching Laboratory. In this context, GCE received increasing attention [3]. Nonetheless, one of the greatest challenges is the development of integrative approaches in GCE. Currently, there is a lack of reports in the national literature. However, Brazil has immense potential to lead in this scenario, providing new methods to introduce the 12 principles of GC in basic education. In conclusion, an outline of potential research areas for academic researchers with an overview of current trends on Química Nova were reported. As perspectives, new literature reviews in other national journals (e.g. Journal of the Brazilian Chemical Society, Química Nova na Escola) should be performed. The way of creating a sustainable future is contained in the present.

Isotopic Analysis of Mg in Crude Oil using Multi-Collector Inductively Coupled Plasma-Mass Spectrometry (MC-ICP-MS)

https://proceedings.science/p/138815

Erico Marlon de Moraes Flores [1]; Alessandra Schneider Henn [1]; Paola de Azevedo Mello [1]; Vitoria Cauduro [1]; Stepan Chernonozhkin [2]; Frank Vanhaecke [3]
[1] Universidade Federal de Santa Maria; [2] Ghent University; [3] Ghent University – Belgium / Ghent University– Belgium

Information related to the geological formation processes, degree of evolution of certain fluids and rocks, origin, type and migration of crude oil is imprinted in the isotopic composition of certain proxy elements in crude oil. Mg has been used as isotopic proxy in geochemical, environmental and/or biomedical applications. The isotopic analysis of Mg has been performed in many matrices already, including environmental samples, geological and archeological materials, biological fluids and tissues. However, no papers have reported Mg isotopic analysis of crude oil so far. As a result, information on the isotopic composition of this element in crude oil is still lacking. Thus, the goal of the present work was to develop a method for Mg isotopic analysis of medium crude oil using high-precision multi-collector inductively coupled plasma-mass spectrometry (MC-ICP-MS) to provide the community with

analytical tools for oil provenancing and tracing of the oil deposit formation. 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 HNO3 (75 min, temperature up to 250 °C). On the other hand, the ASTM based method does not require any sophisticated equipment or the use of halogenated solvents. With this method up to 10 g of oil can be dissolved in toluene and filtered through a nylon membrane. Elements present as inorganic solids, such as Mg, are retained on the nylon membrane and can be easily recovered in water. Isolation protocols were fine-tuned to the composition of crude oil solutions obtained upon MAWD-PDC and solubilization. Mg isolation was successfully carried out using the cation exchange resin AG 50W-X8. Both sample preparation methods were shown to be suitable for subsequent determination of Mg concentration and isotope ratio. A proof-of-concept study showed that the Mg isotopic composition of the Brazilian crude oils was within the range observed for seawater and the deposit bedrock, suggesting that the methods developed can be considered as promising tools to decipher the formation history of oil reservoirs.

Mixture design in the optimization of a procedure for rare earth elements determination in environmental samples rich in silicates

https://proceedings.science/p/138807

Rafael Mantovaneli [1]; Suellen Cordeiro [1]; Matheus Barbosa Rasch [1]; Bruna Dalfior [2]; Vinicius Câmara Costa [1]; Geisamanda Pedrini Brandão [1]; Joaquim Araújo Nóbrega [3]; Maria Tereza Carneiro [1]
[1] Universidade Federal do Espírito Santo; [2] Departamento de Química / UFES / Universidade Federal do Espírito Santo; [3] Universidade Federal de São Carlos

A determinação de elementos terras raras (RRE) em amostras ambientais vem sendo cada vez mais utilizada, tendo em vista as importantes informações que podem ser extraídas a partir da distribuição desses elementos. Contudo, quando amostras ricas em silicato são o alvo da análise, o uso de ácido fluorídrico é recomendado para o preparo das amostras. A necessidade de utilização de reagentes de elevada toxicidade, como o ácido fluorídrico (HF), pode trazer riscos ao analista e ao meio ambiente[1]. Assim, a substituição do HF pelo ácido tetrafluorbórico (HBF4) vem sendo estudada2. Dessa forma, o objetivo deste trabalho foi otimizar um procedimento para a decomposição de sedimentos ricos em silicatos utilizando o HBF4 em substituição ao HF, visando a determinação de RRE por espectrometria de massas com plasma indutivamente acoplado (ICP-MS). Um planejamento de misturas foi realizado para a determinação da proporção ótima entre os ácidos empregados na decomposição das amostras de sedimento marinho. Para a realização dos experimentos, foi utilizada massa de amostra de 0,250 g e as variáveis investigadas foram os volumes de HNO3 (4 a 8 mL), HCl (1 a 3 mL) e HBF4 (1 a 3 mL), todos concentrados. Foram realizados um total de 12 experimentos, sendo 4 réplicas de um dos experimentos, para cálculos estatísticos. Para a obtenção da proporção ótima entre os ácidos, foi adotado o modelo quadrático, que apresentou erro puro baixo (1,2090), $R^2 = 0,9420$ e Fcal de 19,4723, indicando boa adequação do modelo. A equação encontrada foi Y = 22,9059 (±1,9923) x1 + 53,4627 (±12,2904) x2 + 6,1924 (±12,2904) x3 - 52,5088 (±21,9400) x1x2 + 10,9187 (±21,9400) x1x3 - 22,5213 (±31,0278) x2x3, onde x1, x2 e x3 representam o volume de HNO3, o volume de HCl e volume de HBF4, respectivamente. A função de desejabilidade foi utilizada para a obtenção da proporção ótima, sendo obtidos os volumes de 5,3 mL de HNO3, 3,0 mL de HCl e 1,7 mL de HBF4. A exatidão do método foi avaliada pelo uso do material de referência certificado BCR 667 (sedimento estuarino) e os resultados indicaram uma boa concordância entre as concentrações determinadas e as concentrações certificadas. Desta forma, o planejamento de misturas mostrou-se adequado para otimização da proporção entre reagentes e o uso de HBF4 representa uma alternativa viável, substituindo o HF na decomposição de matrizes ricas em silicatos, atendendo os princípios da química verde.

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

https://proceedings.science/p/138826

Alessandro Freitas Barbosa [1]; André Henrique Barbosa de Oliveira [1]; Paloma Gonçalves Silva [1]; Tayná Ferreira dos Santos [1]; Kamylla Mesquita Machado Bezerra [1]; Natália Solange Lima Silva [1]; Ana Caroline Sousa Santos [1]

[1] DQAFQ - Departamento de Química Analítica e Fisico-Química / UFC (Universidade Federal do Ceará) / UFC (Universidade Federal do Ceará)

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 %Organic 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.

Optimization and Validation of LLE-LTP for determination of Florpyrauxifen-benzyl in water samples by HPLC-DAD

https://proceedings.science/p/138803

Luis Henrique Silva Vieira [1]; Flaviano Silvério [2]; Lázaro Sicupira [3]
[1] PROGRAMA DE PÓS-GRADUAÇÃO EM PRODUÇÃO VEGETAL / Instituto de Ciências Agrárias / Universidade Federal de Minas Gerais; [2] Instituto de Ciências Agrárias / Instituto de Ciências Agrárias / Universidade Federal de Minas Gerais; [3] Universidade Federal dos Vales do Jequitinhonha e Mucuri

O florpirauxifen-benzil é um herbicida sistêmico, que atua em plantas daninhas de ocorrência comum em áreas de cultivo de arroz utilizando sistema alagado ou de sequeiro. Em 2019, a Agência Nacional de Vigilância Sanitária (ANVISA) autorizou a comercialização desse defensivo agrícola. Entretanto, a agencia ainda não estabeleceu diretrizes com método de extração e quantificação de resíduos desse composto como forma de monitoramento ambiental. O presente estudo objetivou-se otimizar e validar a extração líquido-líquido com partição em baixa temperatura (LLE-LTP) para determinação do florpirauxifen-benzil em amostras de água por cromatografia líquida de alta eficiência com detecção por arranjo de diodos (HPLC-DAD). Na análise cromatográfica, os parâmetros de temperatura, tipo de coluna, comprimento de onda, composição e fluxo da fase móvel foram avaliados de modo univariado. A LLE-LTP foi otimizada por meio de experimento fatorial completo (23), tendo como fatores: fase extratora (8,0 mL de acetonitrila e 6,5 mL de acetonitrila+1,5 mL de acetato de etila), força iônica (0,0 e 0,1 g de NaCl) e tempo de congelamento (60 e 120 min). A melhor condição cromatográfica para determinação de florpirauxifen-benzil foi obtida em coluna C18 (Poroshell 120) mantida a temperatura de 30 °C, com fase móvel composta por acetonitrila a um fluxo de 0,4 mL min-1 e detecção em comprimento de onda a 243 nm (Figura 1a). Para a LLE-LTP, as porcentagens de recuperação do analito variaram entre 95,84-105,4% com desvio padrão relativo inferior a 1,5. O maior resultado, 105,4%±1,316, foi observado no experimento com a combinação de fase extratora composta por 8,0 mL de acetonitrila, força iônica de 0,1 g de NaCl e tempo de congelamento de 120 min (Figura 1b). Na validação, a LLE-LTP foi seletiva, precisa, exata, linear na faixa de 4,00 a 150 µg L-1 e o limite de quantificação do analito de 4,00 µg L-1. A LLE-LTP acoplada à HPLC-DAD apresentou-se como um método simples, fácil e eficiente de extração e análise deste em amostras de água.

Optimization of the liquid-solid extraction method with low-temperature purification for determination of florpirauxifen-benzyl in soil by HPLC-DAD

https://proceedings.science/p/138805

Junai Carvalho de Souza Lopes [1]; Lázaro C. Sicupira [2]; Flaviano Oliveira Silvério [3]
[1] Instituto Federal de Educação, Ciência e Tecnologia do Norte de Minas Gerais; [2] Universidade Federal dos Vales do Jequitinhonha e Mucuri; [3] Universidade Federal de Minas Gerais

The florpirauxifen-benzyl is a herbicide classified as toxicological III, which belongs to the arylpicolinate group in the synthetic auxin class. This compound was recently released in Brazil for the usage in rice, corn and soy cultures. Considering this recent release, it´s important that the extraction and quantification methods of this compound are well consolidated, contributing to the mitigation of possible damage. This work aimed to optimize the solid-liquid extraction with low temperature purification (ESL-PBT) for the determination of florpirauxifen-benzyl in soil samples through a high efficiency liquid chromatography with a diode arrangements detector (HPLC-DAD). The extraction method is based on using 4.0 g of soil and 4.0 mL of water. Then 8 mL of the extraction phase is added.

The obtained system is homogenized in vortex for 1 min and kept at -20 ºC until the complete freezing of the soil and water mixture. After this step, 5 mL of the organic phase containing the florpirauxifen-benzyl were completely evaporated under an air flow and immediately resuspended in 400 µL of acetonitrile. The ESL-PBT optimization was performed through a complete 23 factorial design, the studied variables were: extraction phase (8 mL of acetonitrile and 1.5 mL of ethyl acetate + 6.5 mL of acetonitrile); freezing time (60 and 120 min) and ionic strength (0 and 0.2 g of NaCl). The used chromatographic conditions were: 243 nm wavelength, mobile phase composed of 100% acetonitrile, 30 ºC column temperature, 20.0 µL injection volume, 0.4 mL min-1 mobile phase flow, EC-C18 120 Poroshell column (4.6 x 50 mm, 2.7 µm, Agilent Technologies). The compound signal occurred at the 1.5 minutes retention time. The obtained results demonstrated that the increase in the freezing time reduced the standard deviation. The NaCl addition increased the ionic strength of the system, however, it made it more difficult the formation of a single phase, reducing the extraction percentage of the compound. The polarity reduction of the extraction phase by the addition of ethyl acetate to the acetonitrile provided an extraction percentage superior to 100% and a <10% standard deviation, with a lower baseline elevation, showing a better chromatographic response. This behavior can be explained by the high solubility of the compound in the ethyl acetate solvente (120 g L-1). For this work, the optimal extraction conditions were 8 mL of acetonitrile, without the addition of salt and freezing time of 120 min. This metodology will be submitted to the validation step using the main merit figures: linearity range, detection and quantification limits, selectivity, accuracy and precision.

Polymer monolithic columns constructed in alternative supports for protein separations by diverse liquid chromatography retention modes

https://proceedings.science/p/138798

Jorge Masini [1]; Fernando Nascimento [2]

[1] Química Fundamental / Instituto de Química / Universidade de São Paulo; [2] Universidade de São Paulo

Polymeric monolithic columns have been valuable tools in bioanalysis by efficiently separating intact proteins, viruses, nucleic acids, etc. Monoliths were first prepared by free radical thermal polymerization in 4.6 - 8.0 mm i.d. inox tubes to separate proteins at high flow rates. The growing demand for the hyphenation of liquid chromatography with mass spectrometers motivated the columns' miniaturization. Nowadays, analytical monoliths are primarily prepared in fused silica capillaries (> 100 µm i.d.), requiring a drastic reduction of extra-column volumes of the chromatographic system. There is a growing interest in semi microcolumns (0.5 to 2.0 mm i.d.) to fill the gap between the capillaries and regular 4.6 mm i.d. columns. Here, we describe the construction of polymer monolithic columns inside 2-mm i.d. fluorinated ethylene propylene (FEP), polypropylene (PP), and fused silica stainless steel (FSSST) tubes for separation of proteins by reversed-phase (RP)1, ion exchange (IEX)2 and Immobilized Metal Ion Affinity Chromatography (IMAC)3. Columns prepared inside FSSST were based on the copolymer formed by free-radical polymerization of glycidyl methacrylate (GMA, functional monomer) and ethylene glycol dimethacrylate (EDMA, crosslinker) in a mixture of 1-propanol and 1,4 butanediol as the porogenic solvents using azobisisobutyronitrile (AIBN) as initiator. The polymerization proceeded for 24 h at 60 C. After the polymerization and washing out of the unreacted monomers, the free epoxy groups in the P(GMA-co-EDMA) were functionalized with Na2SO3 and iminodiacetate (IDA), forming strong and weak cations exchangers. The P(GMA-co-EDMA)-IDA column saturated with Cu(II) formed columns to separate proteins by IMAC. While the free radical thermal polymerization takes several hours to achieve suitable yield and reproducibility, UV-assisted polymerization takes only 20 min. Exploring UV-polymerization, lauryl methacrylate (LMA) was used to construct P(LMA-co-EDMA) monoliths inside 2 mm FEP tubes for RPLC and P(GMA-co-EDMA) columns modified with Na2SO3 and IDA inside PP tubes from ink pens for IEX. All tubes (FSSST, FEP and PP) require vinylization of the internal walls to bind the monolith covalently, thus keeping stable the chromatographic bed at backpressures at around 7 MPa without the need for retention frits. The separation of ovalbumin and lysozyme in egg-white samples by RPLC and IEX and myoglobin in urine by RPLC demonstrated the applicability of the columns to complex matrices. 1 F.H. do Nascimento, A.H. de Moraes, C.R.L. Trazzi, C.M. Velasques, J.C. Masini, Talanta 217 (2020) 121063 2 F.H. do Nascimento, C.R.L. Trazzi, A.H. de Moraes, C.M. Velasques, D.M. de Souza Costa, J.C. Masini, Journal of Separation Science 43 (2020) 4123-4130 3 F.H. do Nascimento, J.C. Masini, Analytical Letters 53 (2020) 522-535

Preparo de amostras usando ácido nítrico diluído para determinação multielementar em casca, polpa e semente de pupunha por ICP OES

https://proceedings.science/p/138823

Kelly G. Fernandes Dantas [1]; Michelle de Souza Lemos [1]; Adriano Lima [1]; Allan Cruz [2]; Fábio Carvalho [3]
[1] Instituto de Ciências Exatas e Naturais / Universidade Federal do Pará; [2] Campus de Salinópolis / Universidade Federal do Pará; [3] Campus Parauapebas / Universidade Federal Rural da Amazônia

A pupunha (Bactris gasipaes) é um fruto muito procurado pela população da região Norte devido principalmente à facilidade de cultivo e ao seu alto valor nutricional1. Diferentes partes da pupunha (casca, polpa e semente) cozidas e in natura foram submetidas à procedimentos de digestão utilizando ácido nítrico em diferentes concentrações (3,5; 7 e 14 mol L-1) e peróxido de hidrogênio (30% m m-1) em um forno de micro-ondas com cavidade. Os teores de Ca, Cu, K, Mg, Mn, P, Se e Zn foram determinados por espectrometria de emissão óptica com plasma acoplado indutivamente (ICP OES). A análise de componentes principais (PCA) e análise hierárquica de agrupamento (HCA) foram aplicados para realizar uma avaliação mais completa dos dados originais. A eficiência dos procedimentos foi avaliada comparando os teores de carbono residual e as concentrações obtidas nas amostras. O procedimento usando ácido nítrico 7 mol L-1 foi efetivo apresentando um teor de carbono residual adequado (casca: 6,66%; polpa: 5,13% e semente: 7,80%) se comparado aos outros procedimentos. A exatidão foi avaliada usando os materiais certificados de referência GBW 07604 (poplar leaves) e 1570a (spinach leaves) e as recuperações variaram de 81% a 118%. As amostras cozidas apresentaram menores teores dos elementos estudados em relação as amostras in natura. Dentre os analitos estudados, Cu, K e Mg foram os mais abundantes em todas as amostras, sendo que as cascas da pupunha apresentaram as maiores concentrações. Além disso, o PCA explicou 66% da variância total, enquanto o HCA confirmou as correlações encontradas no PCA, permitindo a avaliação do grau de similaridade entre as amostras estudadas.
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Preparo de fases estacionárias monolíticas para aplicações em eletrocromatografia capilar

https://proceedings.science/p/138828

Isabela de Paula Lima [1]; Flávia Ferreira de Carvalho Marques [2]; Fernando Antonio Simas Vaz [1]
[1] Instituto de Química / Universidade Federal Fluminense; [2] Universidade Federal Fluminense

Among the existing separation techniques, liquid chromatography (LC), gas chromatography (GC) and capillary
electrophoresis (CE) stand out. The combination of chromatographic and/or electrophoretic mechanisms in
analytical separations constitutes electrochromatography, which gives rise to capillary electrochromatography
(CEC). Much of the development of CEC is due to the use of MSP which emerged as an alternative to conventional
particulate stationary phases (SP). MSP consist of a single piece of porous material, such as organic polymers,
inorganic substances or a combination of both, which allow a
wide range of innovations, with diverse functionalities and
applications, at a lower cost. The objective of this work was to
improve the manufacturing process of FEM for diverse
applications in CEC. For this, first it was necessary to build (in
the laboratory) a photoreactor chamber used for polymerization
of FEM (Fig. 1) and a device for inserting the reagents into the
capillary. Different compositions and types of porogenic
solvents were studied.
The MSPs with the best characteristics were prepared by polymerizing the 3-(methacryloxypropyl) trimethoxysilane
monomer through two processes: (i) sol-gel and (ii) photoinitiated free-radical addition. The photopolymerization was
carried out in situ (in the photoreactor chamber) in fused silica capillaries with an internal diameter of 100 μm,
transparent to ultraviolet radiation (UV).
The produced columns have been inserted on a capillary electrophoresis system with UV-VIS detection and used in
the separation of PAHs (naphthalene, acenaphthene, fluorene,
phenanthrene e anthracene), neutral compounds which separation
indicates the presence of MSP. The electrophoretic conditions for
analysis were: thiourea as the flow marker, ammonium acetate 16.7
mmol L-1 pH 7.0 : acetonitrile (60:40 % v/v) as mobile phase; - 20
kV; 20 °C; - 25 mbar por 20 s; 220 and 250 nm. The preliminary
results show partial separation of the tested compounds (Fig. 2).
However, efforts are being made to improve both the composition
of MSP and mobile phase for a complete separation. It is
noteworthy that other materials for composition or functionalization
of columns will also be tested.

Produção de pó magnético para revelação de impressão digital latente

https://proceedings.science/p/138819

Barbara Dias de Cordeiro de Castro [1]
[1] Instituto de Química / Universidade Federal Fluminense

One of th most values evidences found at the crime scene it's the finger print. If the fingerprint it is in the latente form (invisible), it is necessary to apply fingerprint revealing material to make it visible. It's importante to note that there is no universal revealing material, there are different types os materials and the correct choice takes in consideration several factors, like the substract factor, porosity, color, umidity, among others.

The main objective of this work is the production of one of these materials, the magnetic powder. This material is of great importance in the field of forensic sciences and in this case it's elaboration will be made from magnetic nanoparticles obtained from industrial waste, ensuring that the product is formed in a sustainable and economically advantageous manner. To do this, it will be necessary to produce the nanoparticles from standard iron solution, then adapt them to the characteristics os revealing material, in particular coloring and adhesion. And finally, the use of industrial waste as na iron precursor. In this summary, the result of the first two parts is presented.

Salting-out Induced Liquid–liquid Microextraction for antiemetic residues in sediment samples using liquid chromatography coupled to mass spectrometry

https://proceedings.science/p/138831

Darliana Mello Souza [1]; Dinara da Silva Rodrigues [1]; Petronio Silva Zinn [1]; Paola de Azevedo Mello [1]; Ayrton Figueiredo Martins [1]; Erico Marlon de Moraes Flores [1]
[1] Universidade Federal de Santa Maria

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 5 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.

SILICA MODIFIED WITH TI AND PMODS FOR SOLID PHASE EXTRACTION OF ORGANIC POLLUTANTS

https://proceedings.science/p/138800

Patryck Sassaki [1]; Carla Grazieli Azevedo da Silva [1]
[1] Departamento de Química / Instituto de Ciências Exatas e da Terra/ Universidade Federal de Mato Grosso

The aim of this work was the preparation and characterization of a new sorbent material for solid phase extraction (SPE) from silica metallization with Ti and thermal immobilization of poly(methyloctadecylsiloxane)(PMODS) under three experimental conditions: 80 ºC for 8 h, 100 ºC for 17.36 h and 120 ºC for 16 h. The results of physicochemical characterization showed that Ti was incorporated at silica support with 33.2% (w/w), and the efficiency of immobilization of PMODS onto the surface of the metallized support in all three conditions (Figure 1). The determination of breakthrough volume (Vb), using aqueous media fortified with the pesticides methomyl, imidacloprid, carbofuran, diuron, tebuconazole, carbosulfan, by the construction of the Vb curves, showed a good sorptive capacity for solid phase extraction of the analytes, with good retentivity, especially in the condition 100 ºC for 17.36 h (Figure 2), where the Si-Ti(PMODS) phase shows adequate recovery for most analytes studied according to ANVISA criteria (ANVISA, 2017).

Síntese e caracterização de um polímero molecularmente impresso (MIP) para extração seletiva de escopolamina para potenciais aplicações forenses

https://proceedings.science/p/138818

Weida Rodrigues Silva [1]; João Flávio da Silveira Petruci [1]
[1] Universidade Federal de Uberlândia

A determinação de fármacos e drogas de abuso em fluídos corporais, como urina, saliva e sangue têm se mostrado importante em diversos cenários, como toxicologia forense e clínica, entre outras. Essas matrizes possuem uma variedade de constituintes que podem ser possíveis interferentes para a identificação do analito. Portanto, a preparação adequada da amostra é uma etapa determinante na identificação e quantificação de drogas de abuso em matrizes biológicas, por exemplo. Os métodos de extração em fase sólida (SPE) tradicionais muitas vezes não são seletivos para o analito medido. Com isso, os polímeros molecularmente impressos (MIP's) representaram um avanço importante nas técnicas de preparo de amostras, pois essa técnica é capaz de produzir polímeros com sítios específicos de reconhecimento, moldados a partir de uma molécula molde, possuindo a capacidade de reconhecer e se ligar ao alvo molecular desejado. Assim, este trabalho consistiu na síntese de um MIP para a escopolamina – um alcaloide que quando misturado ao álcool é conhecido popularmente como "boa noite Cinderela" – droga que causa a dopagem de vítima de assalto ou abuso sexual. Para a síntese do MIP utilizando a escopolamina como molécula molde, foram avaliados três monômeros funcionais: Acrilamida (ACR), ácido acrílico (AAC) e ácido metacrílico (MAA). Etilenodimetacrilato como reagente de ligação cruzada, 1,1′-Azobis (ciclohexanocarbonitrila) como iniciador radicalar e metanol como solvente porogênico foram utilizados. Polímeros não impressos (NIP) foram sintetizados pelo mesmo método, mas sem adição do molde de impressão. As capacidades adsortivas foram determinadas para cada um dos polímeros sintetizados, para o MIP – ACR o valor obtido foi de 4,05 mg g-1 e para o NIP – ACR de 1,25 mg g-1. Os polímeros obtidos a partir do ácido acrílico apresentaram as capacidades adsortivas MIP – AAC igual 2,4 mg g-1 e para o NIP-AAC foi de 2,0 mg g-1. Outro polímero avaliado foi o obtido do ácido metacrílico, sendo que os valores encontrados foram MIP-MAA 2,6 mg g -1 e NIP-MAA 2,3 mg g-1. Em seguida o fator de impressão (IF) molecular foi determinado. Este parâmetro estabelece uma relação entre as capacidades adsortivas do MIP e do NIP. Os valores encontrados foram 3,2, 1,2 e 1,1, respectivamente, para os polímeros sintetizados com acrilamida, ácido acrílico e ácido metacrílico. Técnicas de caracterização como FT IR, MEV e BET foram utilizadas para identificar os principais grupos funcionais, morfologia e tamanhos de poros. Um teste de seletividade foi empregado para o MIP-ACR, pois apresentou o melhor resultado do IF. O fator de seletividade () foi estabelecido relacionando o IF obtido para a escopolamina com os IFs obtidos para as moléculas análogas. Os valores encontrados foram 5,25 e 3,40, hioscina e atropina respectivamente. Valores altos para esse fator de seletividade implica que o reconhecimento das cavidades do MIP foi maior para a escopolamina. O MIP sintetizado se apresentou satisfatório para a religação com a escopolamina, portanto esse adsorvente pode ser empregado no desenvolvimento de métodos de SPE para determinação desse analito.

The influence of N-alkyl chain in benzoylthioureas in the urease inhibition: exploring biophysical and soil studies in the mechanism evaluation

https://proceedings.science/p/138814

Maria Célia Tavares [1]; Josué Carinhanha Caldas Santos [1]; Thiago Mendonça de Aquino [2]; Ângelo de Fátima [3]; Igor José dos Santos Nascimento [4]
[1] Universidade Federal de Alagoas; [2] Chemistry and Biotechnology Institute, Federal University of Alagoas, Maceió, AL, Brazil; [3] Universidade Federal de Minas Gerais; [4] Instituto de Química e Biotecnologia / Universidade Federal de Alagoas

Urease catalyzes urea hydrolysis in NH3 and CO2. In the soil, urease activity can result in nitrogen losses. Thus, a urease inhibitor associated with fertilizer is an alternative to reduce the losses of N by volatilization. In this sense, biophysical studies were carried out to evaluate the influence of the N-alkyl chain in benzoylthioureas (Fig. 1) on urease enzyme inhibition. Screening evaluation based on IC50, binding constants (Fig. 2 A-B), and theoretical studies showed that BTU1 more is more active compared to other BTUs; thus, the magnitude of the interaction was determined as BTU1 > BTU2 > BTU3 > BTU4 > BTU5. Thus, BTU1 was selected for interaction and soil application tests. The binding constants (Kb) for the supramolecular urease-BTU1 complex ranged from 7.95 to 5.71×103 M-1 at different temperatures (Fig. 2C-E), indicating that the preferential forces responsible for the stabilization of the complex are hydrogen bonds and van der Waals interactions ($\Delta H < 0$ and $\Delta S < 0$). Studies by UV-vis, 3D, and synchronized fluorescence indicated conformational changes in urease in the presence of BTU1. Theoretical and experimental results (thermodynamics, synchronous fluorescence, and competition assay) agree and indicate that BTU1 is a mixed inhibitor. Finally, urease inhibition was evaluated in the soil, where BTU1 was as efficient as NBPT (95% confidence). Thus, increasing the N-alkyl chain in benzoylthioureas is not a good strategy for developing urease inhibitors.

The protective role of Se against accumulation of Cd, Hg, and Pb in white oyster (Pleurotus ostreatus) and pink oyster (Pleurotus djamor) mushrooms

https://proceedings.science/p/138834

Aline Pereira de Oliveira [1]; Juliana Naozuka [1]; Julio Alberto Landero-Figueroa [2]
[1] Universidade Federal de São Paulo; [2] University of Cincinnati

Mushrooms have been used to elemental enrichment procedures or bioremediation purposes, due to their elemental accumulative ability. It is known that co-exposure Se can provide a protective role against toxicity of metals in some organisms. Thus, this study aimed to study the protective effect of SeO32- (Se(IV)) and SeO42- (Se(VI)) on Cd, Hg, and Pb uptake and accumulation by mushrooms. This effect was evaluated determining elemental concentration by ICP-MS and evaluating proteins distribution and Cd, Hg, and Pb incorporated into compounds of different molecular weights by SEC-UV-ICP-MS. Co-exposure to Hg + Se(IV) or Se(VI) produced mushrooms morphologically more similar to the control group, when compared to Hg-contaminated substrate in the absence of Se. Pink oyster mushrooms showed greater ability to bioaccumulate Se(IV), Se(VI) and toxic metals.
The protective effect of Se against Cd and Hg accumulation was opposite to that observed for Pb. The addition of Se(IV) in the substrate decreased Cd (3 to 52%) and Hg (64 to 95%), while Se(VI) increased the Pb (70 to 194%) uptake and accumulation. For proteins distribution and elements associated with proteins, a fast and efficient protein extraction procedure has been optimized to evaluate the effects of enrichment on Se, Cd, Hg, and Pb-related protein distribution. It was found that Se(VI) cultivation favored the Se interaction with proteins of medium molecular weight (17 - 44 kDa), when compared to cultivation with Se(IV). Supplementation, mainly with Se(IV), favored the Cd association with low molecular weight entities (<1.4 kDa) increasing 165% in white oyster mushrooms. However, the supplementation with both Se species increased the Pb levels associated with high and medium molecular weight compounds (>17 kDa) while an opposite trend was verified for the white oyster mushroom. Additionally, the results suggest an interaction of Se(VI) with Hg in medium molecular weight compounds (17 - 44 kDa) in pink oyster mushrooms.

The Spectral Interferences Evaluation of NADES application in the Sample Treatment and its Compatibility with the GFAAS Technique.

https://proceedings.science/p/138824

William Endo [1]
[1] Departamento de Química / Setor de Exatas / Universidade Federal do Paraná

Deep Eutectic Solvents (DES) have accumulated a wide variety of publications in the most varied areas.

The reason for this attention is due to the simplicity and fast synthesis, low cost and toxicity, and high modeling capacity, allowing it to be adaptable and optimizable according to the specific purposes. Natural deep eutectic solvents (NADES), being one of the recent groups of (DES) employing as precursors naturally occurring chemical compounds such as organic acids, amino acids, sugars, and alcohols that have been gaining attention in agreement with the Green Chemistry concept, being remarkable versatility in several applications, such as in the Sample Preparation. In the present study, the use of NADES based on citric acid (CA), lactic acid (AL), choline chloride (ChCl), and glucose (GLU) as an extracting solvent in the sample preparation for the determination of As and Pb, elements whose toxicity well-known in humans, has been evaluated. In these studies, the compatibility evaluation of the NADES, with the Graphite Furnace Atomic Absorption Spectrometry (GFAAS) through evaluation of spectral and/or non-spectral interferences from reaction/instrumental conditions were studied. NADES (AL-GLU) and (ChCl-AC) were efficient in extracting analytes from plant/animal tissues. It can also be verified, that the NADES (ChCl-AC) promoted the volatilization of analytes by their respective volatile chlorides, however, this effect can be reduced by dilution of the mixture containing NADES/samples (20-fold dilution), still suitable for the level of detectability of the GFAAS. Significant spectral interferences in the As signal (193.7 nm) were observed in both NADES employed. For the Pb, the NADES not showed interferences, reaching recovery values of (70-90% for Pb and 70-120% for As). The application of factorial designs was suitable to evaluate the occurrence of the spectral and/or non-spectral interferences, based on the response of the following parameters: characteristic mass values (m0), signal-background-ratio (SBR), and analyte recovery values. The factorial design is an important statistic tool that allows elucidating the significance of the factors, as well as evaluating their possible interaction effects. This study was mandatory for a better understanding of reactional/instrumental conditions in the analysis by GFAAS, when the NADES were employed, taking into account the organic content and the viscosity of the NADES, different when compared to the mineral acids, commonly used.

Titulação de retorno ácido-base aplicada no doseamento de carbonato de lítio em formulações farmacêuticas

https://proceedings.science/p/138811

Beatriz Picolo de Castilho [1]; Valéria Almeida Alves [1]; Luís Antônio da Silva [1]; Pedro Henrique Machado Pereira Lima [1]
[1] Universidade Federal do Triângulo Mineiro

O íon lítio é utilizado na prevenção de doenças maníaco-depressivas, estando presente na composição de fármacos na forma de carbonato de lítio (Li2CO3). Apesar dos seus benefícios, o Li traz riscos à saúde, se consumido em grande dosagem. A relevância do presente trabalho consiste na aplicação de metodologia analítica na determinação de carbonato de lítio em amostras reais (medicamentos antidepressivos), avaliando as suas potencialidades, com vistas à utilização nas aulas práticas de Análise Instrumental no Ensino Superior, para o processo de ensino e aprendizagem de diversos conceitos fundamentais nessa área da Química. Determinou-se a concentração de carbonato de lítio em comprimidos das marcas A, B e C, por meio da titulação de retorno ácido-base, conforme recomendado pela Farmacopeia Brasileira (FB).1 O procedimento descrito na FB foi adaptado, da seguinte forma: a) o número de comprimidos pulverizados, 20, seguiu o procedimento para dosagem de ácido acetilsalicílico (AAS) em comprimidos, descrito na FB (p. 52).1 Isso porque o procedimento descrito na FB (p. 319)1 para doseamento de Li2CO3 não informou o número de comprimidos a ser pulverizado; b)transferiu-se quantidade do pó equivalente a 0,5000 g de amostra para Erlenmeyer de 125 mL e adicionou-se 25,00 mL de solução de HCl 0,4836 mol L-1 (previamente padronizada com Na2CO3); c) titulou-se o excesso de HCl com solução de NaOH 0,4989 mol L-1(previamente padronizada com HK(C8H4O4)), utilizando-se alaranjado de metila como indicador. Considerando-se a equação química que representa a reação química que ocorre entre o analito (Li2CO3) e o ácido clorídrico adicionado em excesso, Eq. (1), obteve-se que cada mL de HCl 0,4836 mol L-1 equivale a 17,866 mg de Li2CO3.

Li2CO3(aq) + 2HCl(aq) ⇌ 2LiCl(aq) + H2O(l) + CO2(g) (1)

Os resultados obtidos (Quadro 1) mostram que as quantidades de carbonato de lítio obtidas estão de acordo com as descritas nas bulas dos medicamentos, e que o método analítico descrito pela FB apresentou precisão e exatidão. Ao utilizar uma abordagem contextualizada no processo de ensino e aprendizagem, mostrando que a Química Analítica tem um papel essencial no controle de qualidade de medicamentos, acredita-se que as aulas possam se tornar mais atrativas e relevantes para os alunos, potencializando esse processo.

Quadro 1. Consolidação dos resultados obtidos para as amostras analisadas.

Marca da amostra	mLi2CO3 média (experimental) ± s/ mg	sr / %	mLi2CO3 média (esperada) / mg	Er médio / %
A	366,551 ±3,258	0,89	373,770	-1,93
B	357,082 ± 1,149	0,32	365,878	-2,40
C	359,762 ± 6,086	1,69	366,000	-1,70

Fonte: Elaborado pelos autores.

Uso de espectroscopia MIR e siPLS na determinação do teor de biodiesel de mafurra em diesel

https://proceedings.science/p/139160

Carlos Jose Domingos Alface Alface [1]; Lucas Gustavo da Costa [2]; Anizia Furtado Durans [2]; Rodrigo dos Santos [2]; Waldomiro Borges [3]

[1] Quimica / Instituto de Química / Universidade Federal de Uberlândia; [2] Universidade Federal de Uberlândia; [3] Instituto de Química, Universidade Federal de Uberlândia – IQ-UFU

A espectroscopia no infravermelho médio com regressão por mínimos quadrados parciais (PLS) é o método convencional para determinar a quantidade de biodiesel presente no diesel comercial brasileiro, porém este método utiliza solventes e um grande número de amostras para a construção das curvas de calibração. Para desenvolver um método não destrutivo, reduzir o número de amostras na curva de calibração e o número de variáveis, utilizou-se a análise por siPLS (mínimos quadrados parciais de intervalos sinérgicos) para determinar o teor de biodiesel metílico de mafurra em misturas com óleo diesel na faixa de concentração de 1 a 30% (v/v). O modelo gerado através da utilização de duas bandas do espectro total mostradas na Figura 1, obteve RMSECV = 0,20% (v/v), RMSEC = 0,42% (v/v), RMSEP = 0,46% (v/v) e R = 0,9993, com leitura direta das amostras e boa concordância entre os valores medidos e previstos, sendo o método proposto uma alternativa no controle de qualidade deste combustível..

Microwave-assisted synthesis of W-BiVO4/WO3 heterojunctions for photoelectrochemical water splitting

https://proceedings.science/p/138853

Barbara Scola Rodrigues [1]; Juliana dos Santos de Souza [1]
[1] Universidade Federal do ABC

Heterojunctions formed by tungsten-doped bismuth vanadate and tungsten oxide (W-BiVO4/WO3) are promising for water photosplitting, due to their physical and chemical properties [1]. However, aspects such as crystalline structure and morphology can be modulated through the synthesis conditions; being essential for tuning the efficiency of photoelectrocatalysts. Hereby, we report the synthesis WO3 and W-BiVO4 via a microwave pathway; since this method ensures the reduction of reactional time [2]. WO3 was synthesized directly onto FTO; W-BiVO4 was synthesized varying the solvent between ethanol (W-BiVO4(EtOH)) and ethylene glycol (W-BiVO4(EG)), then the materials were suspended, drop casted on WO3 and annealed at 500°C. SEM images (Figure 1a and 1b) show significant differences in the morphology of both materials. Photoelectrochemical measurements show that the activity of W-BiVO4(EG)/WO3 (Figure 1a) is at least 16 times higher than W-BiVO4(EtOH)/WO3 (Figure 1b) at 0.5 V vs. NHE. Unexpectedly, SI-SECM (Figure 1c) shows that W-BiVO4(EtOH)/WO3 has higher surface coverage of reactive oxygen species, therefore this material may be suitable for other reactions.

Adsorção da proteína BSA em filmes nanoestruturados de prata caracterizada por espectroscopia SERS

https://proceedings.science/p/138859

Hugo Belgo [1]; Antônio Carlos Santana [1]
[1] Universidade Federal de Juiz de Fora

Different mechanisms of interaction between bovine serum albumin (BSA) and silver nanoparticles (AgNPs) were investigated by using Surface-Enhanced Raman Scattering (SERS) spectroscopy. The Localized Surface Plasmon Resonance (LSPR) of the synthesized silver nanoparticles was monitored through UV-VIS-NIS spectroscopy. The size distribution was investigated by Dynamic Light Scattering (DLS), and the average size was determined at 22 nm. The zeta potential was measured at -40.9 mV by, indicating the surface charge stabilizes the colloidal suspension. The nanostructured silver films (AgNF) were built on glass slides and the metallic surfaces were modified with 2-mercaptoethanol (ME). In the presence of such a hydrogen-bonding surface modifier, BSA adsorbed preserving a SERS spectral pattern. In the absence of ME, the BSA protein presented different adsorption geometries and, therefore, different SERS spectral patterns, indicating that several ME molecules anchor the macromolecule on the silver surface.

Biocomposites of Eu3+-doped gellan gum and nanocellulose for 3D printing

https://proceedings.science/p/138871

Francisco Recco Torres [1]; Hernane da Silva Barud [2]; José Maurício Almeida Caiut [1]
[1] Departamento de Química / Faculdade de Filosofia Ciências e Letras de Ribeirão Preto (FFCLRP) / Universidade de São Paulo (USP); [2] Universidade de Araraquara

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. Several structural groups from this biomaterial may be available as coordination site for lanthanide ions, well-known for their luminescent properties; specifically, the Eu3+ ion was used herein as a luminescent probe, with emission profiles shown in Figure 1 (a), 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. However, the polysaccharide structure could also induce a quenching way for the luminescence, so, the strategy in this work to avoid that was to use the ligand TTA (2-thenoyltrifluoroacetone), in different proportions for each of the Eu3+ concentrations, which act as a sensitizer for the Eu3+ ions resulting in a material with a strong emission. Obtaining GG hydrogels with the addition of Eu3+ in their preparation showed that the lanthanide ion promoted the crosslinking of the polysaccharide chain and gradually changed the viscoelastic properties of the material, and oscillatory rheology studies indicated that the presence of the ion in the polymeric network decreases its reticular strength, but maintained the gel structure behavior, even in tests at body temperature, as shown in the rheogram in Figure 1 (b). Such properties are already favorable to the generation of three-dimensional structures from 3D printing. This work also aims to reinforce these obtained materials with cellulose nanocrystals, which have the potential to improve the mechanical properties of polymer composites.

Bismuth niobate/zinc oxide heterojunctions with application as photoanodes for water splitting

https://proceedings.science/p/138856

Maria Kuznetsova [1]; Juliana dos Santos de Souza [1]
[1] Universidade Federal do ABC

Bismuth niobate (BiNbO4) has been widely used as photoelectrocatalyst for water splitting due to its physical and chemical properties, however, it exhibits poor conductivity. Zinc oxide (ZnO) has suitable properties for photoelectrochemical applications. Nevertheless, its use is not adequate for water splitting using visible sunlight. The BiNbO4 /ZnO heterojunction formation is a way to overcome these drawbacks.
In this work, BiNbO4 nanomaterials with controlled morphology and crystalline structure were synthesized using a microwave-assisted hydrothermal methodology,1 where the pH, irradiation power and temperature were varied. ZnO films were prepared using a two-step method; first, the seed layer was spin-coated on an FTO glass, second ZnO nanorods were grown under microwave-assisted hydrothermal conditions, controlling temperature and varying time and irradiation power. The alignment of the obtained materials showed a strong correlation with the reactional conditions. To

prepare the BiNbO4/ZnO heterojunction BiNbO4 suspensions were drop-casted on the ZnO films, and the resultant photoanodes show a homogeneous dispersion. Chopped light linear sweep voltammetry was obtained under dark and simulated sunlight.

Bisphenol A adsorption using hydrocarbonized pine nuts from Araucaria angustifolia: an efficient and ecologically friendly alternative

https://proceedings.science/p/138920

Rogério dos Santos Maniezzo [1]; Hugo Henrique Carline de Lima [1]; Maria Egenia Grego Llop [1]; Murilo Pereira Moisés [2]; Vanderly Janeiro [3]; Pedro Augusto Arroyo [4]; Marcos Rogerio Guilherme [5]; Andrelson Wellington Rinaldi [1]

[1] Rinaldi Research Group/Departamento de Química / Centro de Ciências Exatas / Universidade Estadual de Maringá; [2] Câmpus Apucarana / UFTPR; [3] Departamento de Estatística / Universidade Estadual de Maringá; [4] Adsorption and Ion Exchange Laboratory - Lati - Departamento de Engenharia Química / Universidade Estadual de Maringá; [5] Faculdade de Engenharia e Inovação Técnico Profissional / FEITEP

Bisphenol A, a monomer widely used in the manufacture of various types of plastics, e.g. polycarbonate, has high toxicity in humans, being a substance that disrupts the endocrine system. The technique of obtaining carbons by hydrothermal process (HTC) shows promise, because it uses low temperature in the process (between 453 K – 523K) and allied to chemical activation, increases the porosity of the material surface, showing promise in the adsorption of this emerging pollutant. Three activated hydrochars were developed for the mentioned studies AHPN 24, AHPN 48 and AHPN 72. The material was characterized by the N2 physisorption process (Table 1), presenting a surface area of 2220 m²g-1. Other characterizations were performed, such as FTIR-ATR, Raman Spectroscopy, SEM, Boehm Titration. In the adsorption study, the best hydrocarbon was AHPN 72, which had a qmax of 746.00 mg g-1. This value is explained by the hydrocarbonization time, which promoted a better arrangement of specific groups on its surface.

In general, the activated hydrocarbons produced with the seed shells of Araucaria angustifolia have shown great promise in the adsorption of Bisphenol A from effluents, being a cheap and environmentally friendly alternative for the process.

Caracterização estrutural e luminescente do luminóforo vermelho SrY2O4:RE3+ (RE3+ = Eu3+, Ce3+) para protótipos de LEDs brancos quentes

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Leonardo Figueiredo Saraiva [1]; Airton Bispo [2]; Fabiano Praxedes [3]; Silvania Lanfredi [4]; Ana Maria Pires [1]; Sergio A Marques de Lima [1]

[1] Faculdade de Ciências e Tecnologia / Universidade Estadual Paulista "Júlio de Mesquita Filho"; [2] Instituto de Química / Universidade Estadual Paulista "Júlio de Mesquita Filho"; [3] Instituto de Biociências, Letras e Ciências Exatas / Universidade Estadual Paulista "Júlio de Mesquita Filho"; [4] Química e Bioquímica / Faculdade de Ciências e Tecnologia / Unesp (Universidade Estadual Paulista)

Nowadays, the main technology within solid-state lighting (SSL) is based on phosphor-converted white light-emitting diodes (PC-WLEDs). However, the mechanism of white light generation produces a bluish-white light dangerous to humans at night considering the regulation of human circadian rhythm1. Therefore, this study introduces the red-emitting Ce3+ (2 at. %), Eu3+ (1, 3, 5 at. %) co-doped SrY2O4 phosphor synthesized by Pechini modified method2, aiming the application in warm WLEDs ideal for night lighting 1. Eu3+ and Ce3+-single and -co-doped samples were synthesized by a precursor resin

obtained from metal solution precursors, which was fired at 1100 °C upon CO reducing atmosphere. Both Ce3+-single doped, and Ce3+, Eu3+ co-doped samples were obtained as SrY2O4 single phase whereas SrY2O4:Eu3+ was a mixture of SrY2O4/Y2O3 quantified by Rietveld's, refinement. The refinement of the Ce3+-doped sample revealed distinct lattice parameters in comparison with the mixture and the disposition of two Y3+ sites in the structure. FTIR also showed the broadening and shifting of the v(Sr-O) band in the co-doped sample, which suggests the substitution of Sr2+ local sites by Ce3+ and/or Eu3+. However, XPS data showed that there is a proportion of Ce4+ and Ce3+ in the Eu3+ 3% co-doped sample (≈70 % and ≈30 %, respectively), which probably can be taking an important role in the SrY2O4 phase stabilization. Upon 370 nm excitation, the SrY2O4:Ce3+, Eu3+ emission spectrum is a set of broad emission bands within the orange-red spectral region characteristic of Eu3+ while the most intense band was assigned to the one coming from the 5D0 → 7F2 transition. The 5 % Eu3+-doped sample displays the highest emission intensity among the others, implying the insertion of a great quantity of Eu3+ into low-symmetry sites lacking an inversion center. Thus, the phosphor was successfully synthesized as proposed, and Ce3+-doping favors the single-phased system, while the combination of dopants (Eu3+ and Ce3+) yields a red-emitting phosphor upon near-UV excitation. The obtained data suggest the phosphor is a potential candidate for the development of warm WLED prototypes.

Characterization of AgBr/Ag3BiO3 nanocomposite with enhanced photocatalytic under visible light

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Roman Alvarez Roca [1]; Edson T. de Jesus [1]; Mayara de Sá [1]; Luciana Dias [1]; Gilmar da Silva [1]
[1] Instituto Federal de Educação, Ciência e Tecnologia do Maranhão

The discharge of large amount of organic pollutants and antibiotics has seriously contaminated the water environment, which poses a serious threat to human health. In recent years, photocatalytic nanomaterials have become a research hotspot in the environmental remediation [1-3]. In this paper, we report on the photocatalytic properties of AgBr/Ag3BiO3 composite, prepared using an ionic exchange method. The structure of the synthesized composite was investigated by X-ray diffraction (XRD) and Fourier transform infrared (FT-IR) spectroscopy. The UV-Vis diffuse reflectance spectroscopy (UV-vis) was used to examine the optical behavior. The photocatalytic activity was tested by degrading of Rhodamine B (RhB) cationic dye and methyl blue (MB) anionic dye using visible-light (VL), and the result indicated that the photodegradation rate for both dyes was improved compared to pure Ag3BiO3 and AgBr (86% and 90 % for RhB and MB, respectively, at 60 min of degradation). A comparative study with different kinetic models has been carried out for studying the photocatalytic degradation kinetics of both dyes. The enhanced photocatalytic performance could be attributed to the the effective formation of heterojunction between Ag3BiO3 and AgBr which significantly inhibited the recombination of light-induced electron-hole pairs in the semiconductor composite. Also, surface plasmon resonance (SPR) effect, due to the introduction of Ag nanoparticles on the surface of the catalyst, could be considered [2,4]. These results demonstrated that the AgBr/Ag3BiO3 composite photocatalyst could be widely used in the treatment of environmental pollution and in the antibacterial field.

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Chitosan-supported Zeolite NaA beads for water softening

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Conceição Alves [1]; Armando Freitas [1]; Carlos Rhamon do Nascimento Ferreira [1]; Ingrid Azevedo [1]; Sílvio Oliveira [1]; Lara Ramos [1]; Jeanny Maciel [1]; Adonay Loiola [2]
[1] Departamento de Química Orgânica e Inorgânica / Centro de Ciências / Universidade Federal do Ceará; [2] UFC

The development of methodologies for hard water treatment, i.e., the removal of calcium and magnesium ions, is highly demanded. In this sense, the use of ion-exchange materials stands out as a low cost-benefit strategy. Zeolites are well-known cation-exchangers, but that, due to their powder nature, present some drawbacks related to mass transfer and its recovery after use. To overcome such limitations, the preparation of hierarchical composites by adding a second class of pores appears as a viable alternative.[1] In this work, we present the development of chitosan-supported composites (CS_2-ZA_1-GA) containing zeolite NaA (ZA). This zeolite was synthesized via hydrothermal route using coal fly ashes as starting materials. The composites were prepared by dispersing the ZA in chitosan (CS) solution followed by gelation process. [2] The obtained materials were characterized using X-ray powder diffractometry, Fourier-transform infrared spectroscopy and scanning electron microscopy. The results indicate the successful preparation of porous composites containing zeolite NaA dispersed homogeneously in chitosan. Preliminary results of water softening showed that the composites present up to 60% of the zeolite NaA efficiency in the removal of Ca2+ ions from aqueous media.

Cobalt-doped Iron oxides derived from ZIF-67 applied as electrocatalysts in oxygen evolution reactions (OER)

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João Pedro Gonçalves de Souza Soares [1]; Vinícius Dias Silva [2]; Annaíres de Almeida Lourenço [3]; Rodolfo Bezerra da Silva [4]; Daniel Araújo de Macedo [2]; Fausthon Fred da Silva [3]
[1] Departamento de Engenharia Química / Centro de Tecnologia / Universidade Federal da Paraíba; [2] Departamento de Engenharia de Materiais / Centro de Tecnologia / Universidade Federal da Paraíba; [3] Departamento de Química / Centro de Ciências Exatas e da Natureza / Universidade Federal da Paraíba; [4] Departamento de Física / Faculdade de Ciências Exatas e Naturais / Universidade do Estado do Rio Grande do Norte

Hydrogen (H2) is a green fuel, synthesized usually by water electrolysis. However, a large amount of energy is required in this process and electrocatalysts are needed, especially for the half-reaction so-called Oxygen Evolution Reaction (OER), which request a high overpotential to occur. In this context, this work reports new cobalt-doped iron oxides derived from Zeolitic Imidazolate Framework-67 (ZIF-67) as potential electrocatalyst for OER. The materials were obtained via impregnation of Fe2+ ions into ZIF-67 using methanol or ethanol as solvent, follow by calcination at 350°C. Bimetallic oxides were named here Fe/O/Co(M) and Fe/O/Co(E). The electrocatalysts were characterized by XRD, FT-IR and SEM-EDS. The electrochemical properties for OER were investigated using linear sweep voltammetry (LSV) in KOH 1 mol L-1.
Figure 1: Experimental diffraction pattern ((a) and (b)) and (c) LSV data for cobalt-doped iron oxides

electrocatalysts. (Attached in the PDF document)
XRD data indicates the formation of two crystalline phases (Fe2O3 + Fe3O4) for the material obtained in ethanol and one phase (Fe2O3) for the sample synthesized in methanol. The presence of cobalt into the iron oxides were confirmed by the shifts in the XRD signals and using EDS spectroscopy. Signals of Fe-O and Co-O vibrational modes were also observed in the FT-IR spectra. SEM images shows irregular morphologies for both materials. The electrocatalytic activity for the OER was evaluated in alkaline medium and both materials show overpotential of 273 to produce a current density of 10 mA cm-2. These results are similar or superior to those ones reported in the literature.

Conductive ink based on PEDOT nanoparticles dispersed in water without organic solvents, passivant agents or metallic residues

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Matheus Felipe Fagundes das Neves [1]; João Paulo Vita Damasceno [2]; Aldo José Gorgatti Zarbin [3]; Lucimara Stolz Roman [1]
[1] Universidade Federal do Paraná / Departamento de Física; [2] Instituto de Química / Universidade Estadual de Campinas; [3] Universidade Federal do Paraná / Departamento de Química

Poly(3,4-ethyledioxythiophene), PEDOT, is a well-known polymer used in organic electronics due to its high electrical conductivity, flexibility and optical transparency. This study reveals a simple and fast method to obtain a conductive ink based on PEDOT aqueous dispersion. The ink remains stable for months without surfactants, polymers or additives and it is formed by polymer nanoparticles with low metallic content residue from the synthesis. PEDOT was obtained by oxidative polymerization of the monomer with anhydrous iron (III) chloride in acetonitrile. The obtained solid was washed in two steps, being the first with acetonitrile followed by water, and the residues content is decreased to lower than 0.5 %. Fresh polymerized and wet PEDOT was sonicated in water and resulted in aqueous ink with concentration up to 1.145 g/L, which is high for lyophobic dispersions. This conductive ink was deposited on glass substrates via air-brush technique, resulting in transparent and conductive thin films with sheet resistances of 1 and 20 kΩ/sq and optical transmittances at 550 nm of 50 and 80 % respectively. Those samples have PEDOT distributed over macroscopic distances and covering the entire substrates, which shows the great potential of the aqueous PEDOT ink to be used as electrode in organic electronic devices.
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Desenvolvimento de cartuchos à base de carbonos porosos para processos de purificação de biogás

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Ingrid Aragão Lima Azevedo [1]; Conceição Alves [2]; Adonay Loiola [3]; Antoninho Valentini [4]
[1] Departamento de Química Orgânica e Inorgânica / Centro de Ciências / Universidade Federal do Ceará - UFC; [2] Departamento de Química Orgânica e Inorgânica / Centro de Ciências / Universidade Federal do Ceará - UFC; [3] UFC; [4] Departamento de Química Analítica e Físico-Química / Centro de Ciências / Universidade Federal do Ceará - UFC

A geração de gases responsáveis pelo efeito estufa, em decorrência de ações antropogênicas, está diretamente relacionada ao aquecimento global. Neste sentido, o biogás produzido no processo de decomposição da matéria orgânica de resíduos urbanos chama atenção. O impacto do metano (CH_4), principal componente do biogás, no efeito estufa é superior ao do dióxido de carbono (CO_2) e por apresentar elevado poder calorífico mostra-se uma fonte de energia renovável com o potencial de substituir combustíveis fósseis para a produção de energia elétrica. Contudo, visto que seu uso demanda processos de purificação, faz-se necessário o desenvolvimento de técnicas com bom custo benefício e com baixa produção de resíduos. Assim, a técnica de adsorção por pressão balanceada (PSA) se destaca pelo uso de materiais adsorventes sólidos com elevada capacidade adsortiva e capacidade de regeneração. Recentemente, materiais à base de carbonos porosos têm sido empregados como adsorventes de CO_2 nessa técnica,
pois em comparação aos adsorventes convencionais, como as sílicas, esses materiais apresentam elevada área superficial, alta capacidade de adsorção, além da possibilidade de serem obtidos a partir de subprodutos da agroindústria. Nesse contexto, o presente trabalho apresenta o desenvolvimento de cartuchos à base de carbonos mesoporosos a partir de subprodutos agrícolas: amêndoa da manga Tommy atkins e caroço do abacate Persea americana. A obtenção desses materiais consistiu na limpeza, carbonização e oxidação para posterior funcionalização. Os materiais obtidos foram caracterizados por espectroscopia na região do infravermelho, microscopia eletrônica de varredura e análises termogravimétricas. Os resultados preliminares apontam que os materiais porosos de carbono apresentam características, em termos de composição, estabilidade térmica e morfologia, adequadas para terem seu desempenho avaliado como adsorventes no tratamento de biogás.

Estudo das propriedades magnéticas de nanocubos e nanofios de céria

https://proceedings.science/p/138893

Eduardo Magalhães Rodrigues [1]; Odivaldo Alves [2]; Júlio César Martins Silva [2]; Jilder P. Serna [3]; Juliana Pires de Souza [2]; Raquel Checca [4]

[1] Universidade Federal Fluminense; [2] Instituto de Química / Universidade Federal Fluminense; [3] CBPF / Centro Brasileiro de Pesquisas Físicas; [4] Centro Brasileiro de Pesquisas Físicas

Nanomateriais de óxido de cério IV, também chamado de céria, podem ser empregados em spintrônica sendo responsáveis por maior armazenamento e velocidade de processamento de dados nos computadores atuais, graças ao seu comportamento ferromagnético a temperatura ambiente.1 Diferentes morfologias de céria apresentaram diferentes concentrações de vacâncias de oxigênio e, portanto, influenciando no comportamento magnético do material.2 Neste trabalho nanofios e nanocubos de céria foram submetidos a caracterização magnética com medidas de magnetometria por curvas de suscetibilidade magnética ZFC/FC (Zero Field Cooling/Field Cooling), curvas de magnetização em função do campo magnético M(H) e por espectroscopia de ressonância paramagnética eletrônica (EPR – electron paramagnetic ressonance) a temperatura de ambiente. Através das curvas de magnetização ZFC/FC foi constatado que ambas morfologias apresentam uma separação da curva FC e ZFC em baixas temperaturas, indicando a presença de partículas orientadas magneticamente possivelmente associadas a anisotropia magnética cristalina ou de forma, presentes em maior quantidade em nanofios, que apresentam maior separação entre as curvas. As curvas de magnetização M(H) realizadas nas temperaturas de 100, 200 e 300 K apresentam comportamento histerético, e através das mesmas foi possível determinar os valores de magnetização de saturação, campo coercivo e magnetização remanescente. Notou-se uma diminuição dos valores de magnetização de saturação e campo coercivo com o aumento da temperatura característico de sistemas nanometricos. Nos espectros de EPR a temperatura ambiente foi observada a combinação de dois tipos de sinais, sinais largos característicos de sistemas ferromagnéticos e sinais estreitos característicos de sistemas paramagnéticos. Nanocubos apresentam maior contribuição ferromagnética do que nanofios. Para identificação das espécies paramagnéticas foram utilizadas simulações de sinais de EPR para cada morfologia em um intervalo de 3000 a 4000 G, ambas morfologias apresentaram sinal paramagnético em g1~ 1,97 e g2~ 1,94 característico para o íon Ce3+, para a morfologia nanocubo foi observado um sinal isotrópico com desdobramento em seis linhas devido ao spin nuclear 5/2 atribuído ao íon Mn2+ um contaminante comum em amostras de céria. Para a morfologia nanofio foram observados sinais em g1~ 2,07, g2~ 2,05 e g3~ 2,02 associados ao O2 adsorvido nas vacâncias, e um sinal em g~ 2,06 associados a vacâncias de oxigênio isoladas. A origem do comportamento ferromagnético em nanoparticulas de céria é extensivamente discutido na literatura, nesse trabalho apresentamos evidencias que o mesmo depende da morfologia das nanopartículas.

Filmes nanoestruturados de pontos quânticos de carbono como sensor de íons Fe3+ e Cu2+

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Ana Carolina Cunha Serafim [1]; Adriano Siqueira [1]; Camila Gonçalves Minetuma [1]; Eralci Moreira Terézio [2]; Ailton José Terezo [1]

[1] Departamento de Química, Universidade Federal de Mato Grosso; [2] Instituto de Física, Universidade Federal de Mato Grosso

Carbon dots (CDs) are luminescent carbon nanoparticles with dimensions close to 10 nm. These nanoparticles were discovered in 2004 since that, they have attached interest due to their properties like photoluminescence, abundant sources, water solubility, and low toxicity. CDs synthesis is made from organic sources, therefore, they started being produce using wastes like peels, sludges, and biomass. The use of these resources is cheap, green and, an alternative to waste disposal, promoting the development of sustainable materials. Herein, CDs were synthesized from swine farm effluent, then nanostructured CDs films were made up via solution casting approach using poly (vinyl alcohol) (PVA) as a matrix, for Cu2+ and Fe3+ ions sensing in water. The characterization and optical properties of PVA/CDs films were reported by using UV-vis spectroscopy, photoluminescence spectroscopy (PL), and thermogravimetry-differential thermal analysis (TG-DTA). These analyzes demonstrated the interaction of PVA and CDs. Despite the interaction, PVA/CDs films maintained the luminescence of CDs, even after the drying process, as shown in Fig. 1. Sensing application of PVA/CDs films was demonstrated using Cu2+ and Fe3+ ions based on decreasing luminescence. The ions were tested with solutions of concentrations from 1.10-6 to 1.10-2 mol L-1. As shown in Fig. 2 and Fig. 3, with the increase of ion concentration, the luminescence decreases indicating that the film works as a sensor for these metals. Furthermore, the luminescence intensity decreased 82,9 and 81,9%, for Cu2+ and Fe3+, respectively, from a concentration 0 to 1.10-2 mol L-1.

Funcionalização de carbon dots com peptídeo antimicrobiano ecPis-4s

https://proceedings.science/p/138868

Aniely Pereira de Souza [1]; João Paulo de Mesquita [1]
[1] Universidade Federal dos Vales do Jequitinhonha e Mucuri

The methodology of carbon dots (CDs) preparation was performed by dehydration and oxidation reactions of cotton cellulose. The surface modification reaction of the CDs was carried out based on the concentration of superficial oxygenated functional groups. 50 mg of carbon dots were mixed with EDAC at 45 ºC under constant agitation. After 30 minutes of reaction, was added OxymaPure® and then a solution of the peptide. The materials obtained were characterized through different techniques, including Fourier Transform Infrared Spectroscopy (FTIR) (Figure 1) 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. The results of the antimicrobial activity, 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). 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 in a membrane mimetic medium (Figure 2).

Growth of leaf-and-flower-like structures on screen-printed carbon electrodes by template-free electrodeposition

https://proceedings.science/p/138917

Larissa Leffa Fernandes [1]; Filomeno Inroga [1]; Jacqueline Arguello [1]; Vladimir Lavayen [1]
[1] Universidade Federal do Rio Grande do Sul

Electrodeposition is an efficient and widely used technology with applications ranging from functional, protective, and decorative coatings with precious metals, oxides, metal alloys, and polymers. Different morphologies, sizes, and thicknesses can be achieved by controlling or varying the potential/current [2]. The mechanism behind the formation of gold microstructures involves a sequence of nucleation, adsorption, growth, and branching [3]. In this work, two different morphologies were grown on a screen-printed carbon electrode (SPCE) by performing the electrolysis through constant applied potential and cyclic voltammetry. The experiments were carried out with a potentiostat/galvanostat Autolab PGSTAT128N, connected to a computer with NOVA 2.1 software. The electrolyte solution consisted of 0.1 M Na2SO4 and 30 mM HAuCl4. By applying a constant potential of 0.6 V for 600 s, dendritic microstructures were obtained with leaves shape. On the other hand, by applying twenty consecutive cycles by cyclic voltammetry, at 200 mV s-1, flowers-like microstructures were obtained. Figure 1 shows the images obtained by scanning electron microscopy (SEM), where the changes in morphologies can be observed. The effect of the modification was evaluated by cyclic voltammograms before and after electrodeposition using potassium hexacyanoferrate (III) as a probe molecule.

Influence of pH on the preparation of microcapsules formed by casein and carboxymethylcellulose

https://proceedings.science/p/138962

Davi Siqueira da Silva de Souza [1]; Maria Paula Garofo Peixoto [2]; Osvaldo de Freitas [2]; Kelly Francisco [1]
[1] DCNME / Centro de Ciências Agrárias / Universidade Federal de São Carlos; [2] Faculdade de Ciências Farmacêuticas de Ribeirão Preto (FCFRP), Universidade de São Paulo (USP)

Obtaining microcapsules from biopolymers in aqueous systems is strategic for the development of new biodegradable and biocompatible products to be used in the controlled release and storage of natural dyes for food industries. In this work, microcapsules of casein (CA) and carboxymethylcellulose (CMC) in a proportion of 1:1 were prepared by complex coacervation technique at different pH values (4.0, 5.0, 6.0 and 7.0). The systems were crosslinked with 0.300 mol of glutaraldehyde for each 1g of casein, centrifugated and the precipitate was collected and dried in an oven at 40°C for 24h. The chemical composition of materials was characterized using Fourier transform infrared spectroscopy (FTIR) and X Ray Diffraction (XRD). FTIR spectra showed bands around 3300 cm-1 and 2945 cm-1 related to -OH and -CH2 groups, respectively. Bands at 1650 cm-1 and 1543 cm-1 were due to the amide I and amide II, in that order. Bands in the region of 1270-1250 cm-1 were related to the C-N stretching and N-H bending [1]. Bands at 1715 cm-1 became stronger with the increment of the pH, indicating the formation of complexes can be described by chemical bonds between COO- with the amide I groups of CMC and CA, respectively [1,2]. Bands around 1060 cm-1 were correspondent to the stretching of C-O groups in CMC chains, being more intense for materials obtained at pH values of 5 and 6. Microcapsules are mainly amorphous and its size decrease with the increment of the pH values of the systems. These results suggested a higher efficiency in obtain the biopolymer complexation microcapsules increasing the pH values of the coacervations systems. Also, electrostatic interactions between the polymeric chains played an important role to produce CMC/CA microcapsules.

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Materiais cerâmicos Zn2GeO4 preparados por reação em estado sólido assistida por radiação microondas

https://proceedings.science/p/138902

Jéssica Viegas [1]; Anderson Dias [2]; Roberto Moreira [3]
[1] Departamento de Química / Instituto de Ciências Exatas / Universidade Federal de Minas Gerais; [2] Departamento de Química / Instituto de Ciências Exatas / Universidade Federal de Minas Gerais; [3] Departamento de Física / Instituto de Ciências Exatas / Universidade Federal de Minas Gerais

Zinc orthogermanate (Zn_2GeO_4) is a semiconductor material with bandgap in the range 4.3-4.7 eV. This ceramic material is isostructural with willemite compounds (Zn_2SiO_4), which belongs to the rhombohedral R3 space group (#148). Due to their photocatalytic properties, Zn_2GeO_4 ceramics has been applied in CO_2 reduction experiments, as well as in water splitting and organic compounds decomposition. In this work, Zn_2GeO_4 was obtained by microwave-assisted solid-state reaction using stoichiometric amounts of ZnO and GeO_2. The powders were obtained at 900°C, for 2 h, followed by

sintering at 1000°C, for 4 h. Cylindrical pucks of about 5 mm height and 12.5 mm diameter were obtained. The structural and morphological properties of the synthesized ceramics were evaluated using X-ray diffraction and transmission electron microscopy techniques. The optical-vibration properties of Zn2GeO4 ceramics were investigated by polarized Raman scattering and infrared spectroscopic measurements. Sintered Zn2GeO4 ceramics exhibited flat, very large grain microstructure (50–350 µm), with small pores, easily visible with an optical microscope. These characteristics were the motivation to study the light polarization effects in this polycrystalline material, only previously investigated in the point of view of a single crystal. By this study, it was possible to observe and assign the most relevant vibrational modes foreseen by group theory analysis. Also, the frequencies and damping constants of the transversal and longitudinal branches were determined, as well as its related dielectric response.

Metal driven self-assembly of a Imidazole Functionalized Pillar[5]arene for adsorption and separation applications

https://proceedings.science/p/138907

Tamires Soares Fernandes [1]; Carolina Bastos Pereira Ligiero [1]; Dayenny Louise D'Amato Leite [1]; Isabela Alves de Albuquerque Bessa [1]; Catiúcia R. M. O. Matos [1]; Thiago Custódio dos Santos [2]; Filipe Barra de Almeida [1]; Guilherme Pereira Guedes [1]; Vanessa do Nascimento [1]; Célia Machado Ronconi [3]

[1] Universidade Federal Fluminense; [2] Universidade Federal do Rio de Janeiro; [3] Química Inorgânica / Instituto de Química / Universidade Federal Fluminense

Pillar[n]arenes are a class of macrocyclic compounds reported in 2008 by Ogoshi and coworkers, formed by hydroquinone derivatives connected in the 2,5-positions by methylene bridges.1 Due to its high yield synthesis, easy modifications, and electron-rich cavity, these macrocycles are excellent materials for a wide range of applications, such as isomer separation2, gas capture3, drug delivery systems4. Imidazole group is well-known for its interaction with CO2.5 In this scenario we explore the electron-rich cavity combined with an imidazole functionalization for gas adsorption and xylene isomer separation. The P[5]Im in its amorphous form has been synthesized in 3 reactional steps following a procedure previously described in literature.6 The ^{1}H NMR spectra confirmed the structure of P[5]Im intermediates and the final product (Figure 1a). Single crystals of pure P[5]Im were obtained as transparent needles by slow evaporation of CH3CN:H2O solution in the presence of different cations (Na(I), Ca(II), Sr(II), Ba(II), Mg(II) and Sm(III)) (Figure 1b,c). Although low BET surface area of P[5]Im, 0.062 m2 g-1, (Figure 1d), the material showed a good CO2 adsorption capacity (11 mmol g-1 = 484 mg of CO2/g) at 25°C and high pressure regime (40 bar). The material can also separate xylene isomers.

Nanobiosensor based on gold nanoparticle and horse-pAb for the fast detection of SARS-CoV-2 spike protein

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Carolina Bastos Pereira Ligiero [1]; Célia Machado Ronconi [2]; Tamires Soares Fernandes [1]; Dayenny Louise D'Amato Leite [1]; Francisco Gaspar [3]; Ana M. Percebom [4]; Camilla Djenne Buarque Müller [4]; Bráulio Soares Archanjo [5]; Marcelo Abrahão Strauch [6]; Patricia Bento Silva [7]; B. Ricardo Azevedo

[1] Universidade Federal Fluminense; [2] Química Inorgânica / Instituto de Química / Universidade Federal Fluminense; [3] Instituto de Pesquisa de Produtos Naturais / Universidade Federal do Rio de Janeiro; [4] Pontifícia Universidade Católica do Rio de Janeiro (PUC-Rio); [5] Divisão de Metrologia de Materiais / Instituto Nacional de Metrologia, Qualidade e Tecnologia / Inmetro; [6] Instituto Vital Brazil / Instituto Vital Brazil; [7] Universidade de Brasília

Since the emergence of COVID-19 pandemic there were near 22 million cases in Brazil, causing at least 594 thousand deaths.1 Despite the impressive development of diagnostic tests, there is still a lack of rapid antigen tests.2 We used previously purified horse polyclonal antibodies anti-S (a,b) covalently bonded to spherical gold nanoparticles (c,d,e), to prepare a nanobiosensor IgG@AuNP (c). This bioconjugate was employed in the identification of SARS-CoV-2 spike protein by monitoring the increment in the hydrodynamic diameter (ΔHD) determined by Dynamic Light Scattering (f) in an immunoassay. The present method is sensible, fast, inexpensive, and can potentially be applied to detect the virus in patients suspected of SARS-CoV-2 infection.

Nanoparticles of low-functionalized fullerenols as stable radicals: towards dispersed nanocapacitors and nanobatteries?

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João Paulo Vita Damasceno [1]; Lauro Tatsuo Kubota [1]

[1] Instituto de Química / Universidade Estadual de Campinas

In this work, we have prepared a stable organic dispersion of fullerenols with low degree of modification and without passivant agents and a metastable aqueous dispersion with the same material. Fullerenols were prepared by reacting pristine fullerene C60 with potassium hydroxide in organic medium under inert atmosphere. In this step, radicals of fullerene and fullerenols are formed. Air exposition promotes oxidation of most of those charges and induce material aggregation as nanoparticles in organic liquid, which are indefinitely stable due to electrostatic and solvation interactions. Fresh oxidized mixture was transfer to water and resulted in metastable aqueous dispersions. The prepared organic and aqueous dispersions are formed by fullerenol nanoparticles with mean hydrodynamic sizes of 74 and 86 nm (both polydispersed) and zeta potentials of -60 and -34 mV, respectively. Additional characterization provided evidences for fullerene modification with hydroxyl groups and approximately stoichiometry of K1.59[C60(OH)13.15] for those nanoparticles. Even being sensible to oxygen, some of those radicals remain stable in the fullerenol nanoparticles as probed by electron paramagnetic resonance spectroscopy (EPR). We postulate that these stable radicals are responsible for the measured zeta potential and for the electrostatic interactions in organic liquid. Fullerenol aqueous dispersion was deposited by drop casting on glassy carbon electrode and dried at room temperature. Cyclic voltammetry (CV) in KCl presents one peak in the cathodic region, which is present in similar samples and it is attributed to one-electron reduction. No correspondent oxidation peak was observed, indicating charge stabilization. CV results also suggest that the materials surface is not highly modified

by hydroxyl groups corroborating with the previous analysis, and that those charges formed in KCl affects the response specially using negatively charged redox probes. Since fullerenol nanoparticles have remaining radicals, we have been carried out experiments to use this reservoir of electrical charges in chemical reactions or to perform useful work, therefore such nanoparticles could be further explored as dispersed nanocapacitors and/or nanobatteries.

Oxidação fotoeletroquímica da água usando fotoanodos BiVO4 / V2O5 formados a partir da reação de estado sólido entre Bi2O3 e V2O5

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Antero Ricardo Santos Neto [1]; Marcio Cesar Pereira [1]
[1] Universidade Federal dos Vales do Jequitinhonha e Mucuri

Increasing the light absorption and charge separation of semiconductor films are challenges that must be addressed to increase the performance of photoanodes for photoelectrochemical water oxidation. Here, a mixture of Bi2O3 and V2O5 was deposited onto conductive FTO substrates by drop-coating and calcined at 500 oC to produce heterostructured BiVO4-V2O5 photoanodes. The solid-state reaction between Bi2O3 and V2O5 leads to the formation of BiVO4-V2O5 heterojunctions that were highly efficient for the water oxidation reaction. In 1 M Na2SO4 electrolyte, the BiVO4-V2O5 photoanode produced a photocurrent of 6.83 mA cm-2 at 1.23 V vs. RHE, which is one of the highest photocurrents ever reported for BiVO4-based photoelectrodes. This synthesis approach provided better photoelectrochemical performance due to increased light absorption due to the use of two absorbers with complementary bandgap energies and greater separation and transfer of photogenerated charges in the bulk of the film due to the formation of heterojunctions. Thus, the results support a simple and innovative strategy to design an efficient visible-light photocatalyst, bringing original perspectives to solar energy technologies.

Polyacrylamide Nanocomposite Hydrogels for Advanced Oil Recovery

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Aline Ingrid Alves dos Reis Almeida [1]; Marcelo Machado Viana [1]; Sthéfany Z S do Amparo [1]; Cláudia K. B. de Vasconcelos [2]; Laryssa E. B. Sena [1]; Glaura Goulart Silva [1]; Hállen Daniel Rezende Calado [1]
[1] Departamento de Química / Instituto de Ciências Exatas / Universidade Federal de Minas Gerais; [2] Pontifícia Universidade Católica de Minas Gerais - PUC Minas

Oil recovery rates in mature fields can be increased by using conformance control techniques. Conformance control using polymeric gels makes the sweeping of a reservoir more uniform, which allows the recovery of oil from less permeable regions, reducing excessive water co-production [1]. Blocking the zones preferably using polymeric gels causes the injected fluids to travel through previously unscanned areas [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 blocking gels. Polyethyleneimine (PEI) is currently the most investigated organic compound for crosslinking systems, mainly because it is ecologically correct and possesses a high nucleophilic character [2]. The incorporation of carbon nanomaterials such as oxidized carbon nanotubes (OCNT) and graphene oxide (GO) in hydrogel matrices has been shown to be important in obtaining polyacrylamide nanocomposite hydrogels with

improved properties. In this work, polyacrylamide nanocomposite hydrogels were obtained in saline solutions with ionic strength μ = 0.6 from the incorporation of 1.0% wt. of OCNT and GO in relation to PAM. PEI was used as a crosslinker in the formation of the three-dimensional structure of the gel.
The gelling solutions obtained from the 9:3 PAM/PEI mass ratio (P3) with the addition of OCNT and GO, showed a slight increase in viscosity (Fig. 1a) in relation to the P3 reference, as a result of the physicochemical interactions promoted between the nanofillers and macromolecules. Fig. 1b shows that after 40 days of storage in an oven at 70 °C, the G' modules are superior to the G" modules in the entire frequency range analyzed, revealing the dominance of the elastic character of the gels. The P3-OCNT and P3-GO gels have lower G' values compared to the P3 gel, which can be explained by the fact that the interaction of PEI with the functional groups present on the surface of oxidized carbon nanomaterials [3] a smaller amount of active sites on the PEI available for PAM crosslinking, which can avoid excessive crosslinking and make the gels more stable [2].

Fig. 1: a) Viscosity as a function of shear rate for the gels obtained; b) Log. of G′ and G″ modules as a function of angular frequency; c) Percentage of syneresis of the gels obtained.

This behavior is also evidenced in the syneresis results presented for these gels in Fig. 1c, where it is possible note that the addition of nanofillers considerably reduces the percentage of water loss from the gel structure. Therefore, our group considers the use of carbon nanomaterials very promising for application in nanocomposite hydrogels for advanced oil recovery.

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Preparação de substratos SERS por deposição de nanopartículas de ouro em filmes finos de PS-b-P2VP

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Moyra Freitas Vieira [1]; Celly Mieko Shinohara Izumi [1]; Gabriela Cristina Mendonça Calisto [1]
[1] Universidade Federal de Juiz de Fora

In this work, thin films of PS-b-P2VP thermally annealed at 150 °C for 1.5 h were used as templates for large areas of site-specific AuNPs assembly. Deposition of AuNPs were performed by immersion of PS-b-P2VP in Au colloidal suspension for 6 hours. In an aqueous environment (pH≈6), P2VP microdomains are protonated and act selectively as a biding site for the negatively-charged AuNPs through electrostatic interactions. BCPs with different Mw and PS/P2VP blocks ratio were used. The density of NPs deposited on the films can be controlled by the immersion time in Au colloid. The SERS activity was tested using the Nile Blue (NB) dye as a molecular probe. Fig. 1 shows the AFM images and SERS mapping of the AuNP/PS-b-P2VP thin films. As can be observed with the increase of the P2VP domain; thereby increasing the protonated pyridine groups available for the electrostatic assembly, an increase in AuNP aggregation was observed, resulting in the intensification of the SERS signal due to the formation of more hotspots. These results show that the Mw, PS/P2VP blocks ratio of the BCPs strongly influence the NPs dispersion and that the synthetized nanocomposties have homogeneous and tunable SERS enhancement.

Preparation of a reusable SERS substrate of Au nanoparticles on polyaniline/cellulose film

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Bismark Nogueira da Silva [1]; Celly Mieko Shinohara Izumi [1]
[1] Universidade Federal de Juiz de Fora

Surface-enhanced Raman spectroscopy (SERS) is a technique that consists of the enhancement of the Raman scattering intensity by molecules next to plasmonic nanostructures such as Au and Ag [1]. The fabrication of cost-effective, easy to synthesize, and reusable SERS substrates is a relevant topic in the field [2]. In this work, a plastic polymeric blend film (polyaniline nanofibers/cellulose acetate) was prepared and immersed in HAuCl4 (0.01 mol L-1) solution for 24 h to reduce Au3+ by polyaniline. The prepared composite SEM image (Figure 1a) shows Au nanoparticles with wire and strip morphology on the blend film. Then, this film was used as SERS substrate to detect the Nile blue dye molecules (10-4 mol L-1). For this purpose, the composite film was immersed in the dye solution for 24 h. The SERS mapping of the 591 cm-1 Nile blue band shows regions of signal enhancement throughout the substrate (Figure 1b). After this first SERS measurement, the film was washed with ethanol and the second SERS mapping (Figure 1c) shows the dye removal. Afterward, the substrate was again immersed in the dye solution. The SERS mapping after the second immersion shows regions of Nile blue characteristic band intensification (Figure 1d) again. Thus, the polyaniline nanofibers/cellulose acetate polymer blend film is able to reduce Au3+ ions forming metallic nanoparticles. In addition, the composite formed has SERS activity and can be reused after the washing process.

Figure 1 – a) Au nanoparticles SEM image. SERS mapping of the band 591 cm-1 after b) first immersion in the dye, c) first ethanol washing, and c) second immersion in dye.
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Preparation of MCM-41 Silica Nanoparticles with Different Morphologies for Drug Delivery System

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Aline Farias Moreira da Silva [1]; Thiago Custódio dos Santos [2]; Bráulio Soares Archanjo [3]; Célia Machado Ronconi [1]
[1] Química Inorgânica / Instituto de Química / Universidade Federal Fluminense; [2] Química Inorgânica / Instituto de Química / Universidade Federal do Rio de Janeiro; [3] Divisão de Metrologia de Materiais / Instituto Nacional de Metrologia, Qualidade e Tecnologia

Mesoporous silica nanoparticles (MSN) exhibit desirable features for drug delivery system (DDS) fabrication. Nanovalves are a type of DDS in which drugs are stored inside the nanoparticle pores and can be released under different stimuli. Several studies have focused on the size of MSN and do not exploit the effect of particle morphology in drug carriers. However, some authors have demonstrated that nanorods exhibit higher cellular uptake than those spherical ones. In this work, we prepared three different types of MSN aiming to fabricate several nanovalve reservoirs (Figure 1). Spherical and rod-shaped mesoporous silica can be synthesized controlling the reagent ratio of hexadecyltrimethylammonium bromide, water, tetraethyl orthosilicate and the solution pH. Also, for the synthesis of mesoporous silica nanorods, BuOH was used as co-solvent. Scanning electron microscopy

(SEM) shows spherical (~ 85 nm) and nanorods with lengths about 100 nm (short) and 500 nm (long). N2 isotherms of MSN are of type IV for all materials, suggesting the presence of cylindrical mesopores. Short and long nanorods exhibit, respectively, surface areas of 1017 and 1020 m2 g-1, pore volumes of 1.00 and 1.02cm3 g-1 and narrow pore distribution of 2.7 nm (BJH method). Further spectroscopic analyses are in progress. As perspectives, we will work on with chemical modification of MSN followed by drug loading and pore closing of these systems. The effect of these MSN shapes and sizes of the final devices (nanovalves) on cellular uptake will be evaluated by biological assays.

Produção de silicato de potássio líquido e sólido a partir de rejeito de mineração de ferro usando rotas hidrotérmica e sólida

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Lucas Lorenzini [1]; Paula Sevenini Pinto [2]; Ana Paula de Carvalho Teixeira [1]
[1] Departamento de Química / Instituto de Ciências Exatas / Universidade Federal de Minas Gerais; [2] Universidade do Estado de Minas Gerais

The iron mining is one of the most important activities in Brazil, however it can generate 150 million ton of iron mining tailings per year. The sandy tailings, from the iron ore beneficiation process, have high levels of silica in its composition. By reacting with an alkaline base, the silica present in the tailings can be extracted as silicate from the corresponding alkali metal, producing a valuable product. Although many studies have been reported using NaOH to react with silica, there is a lack of studies assessing the influence of time and amount of KOH in this reaction. In this work, two different routes were used to obtain potassium silicate from iron mining tailings, the hydrothermal route and the solid route. For the hydrothermal route, 12 g of iron ore tailings were mixed with 15 g of KOH and 30 g of distilled water. The materials were kept under stirring, and then transferred to a Teflon-coated steel autoclave which statically reacted at 200°C. Different times (4, 6, 8 and 24 hours) and amount of KOH (12, 15 and 18 g) were tested in order to understand the influence of time and KOH concentration in the yield of silicate. After reaction it is expected to obtain liquid potassium silicate. In the solid route, 12, 15 and 18 g of KOH were solubilized in 30 g of distilled water, respectively. After, 12 g of iron ore tailings were added to each mixture and the system was kept under heating and stirring until complete drying. The resulting solid was placed in a muffle at 500 °C for 3 hours. After reaction it is expected to obtain solid potassium silicate. The K2O and SiO2 contents in the resulting materials were quantified by titration. The titration results showed 7.6, 7.9 and 8.8 wt% SiO2 in the solutions after 2, 6 and 8h of reaction, respectively, indicating that these times had the same impact in the dissolution of silica. Although, when performing the reaction for 24h, the greatest dissolution was obtained for the hydrothermal route, ca. 14.7 wt% SiO2. The variation in the amount of KOH did not significantly change the silica content, ca. 14.08, 14.65 and 13.27 wt% SiO2 when using 12, 15 and 18 g of KOH, respectively. For the solid route, it was observed that increasing the amount of KOH, the dissolution of silica was also increased. The final solid had a content of 35.6 wt% SiO2. XRD, TG, SEM and XRF analysis are ongoing in order to understand the transformations in the solid and to quantify the amount of potassium silicate. This work showed the possibility to produce liquid and solid potassium silicate from iron mining tailings at different conditions. When using the hydrothermal route, the time was the most important parameter in the dissolution of silica, whereas 24 h was the best condition. Moreover, among the two routes, solid was the most efficient route.

Propriedades Estruturais e Fotoluminescentes de Nanopartículas de Ortofosfato/Carbonato de Cálcio

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Carlos Eduardo Zanardo [1]; Valtencir Zucolotto [2]; Thales Machado [3]; Lucas Trindade [1]

[1] USP - São Carlos; [2] Universidade de São Paulo; [3] Departamento de Química / Universidade Federal de São Carlos

Calcium phosphates (CaPs) are highly biocompatibility biomaterials widely applied in bones and teeth repair, and tissue engineering. In the form of nanoparticles (NPs), these materials have attracting attention in the field of nanomedicine due to their potential application in fluorescence imaging diagnostics and theragnosis, highlighting the use of intrinsically luminescent hydroxyapatite (HA) NPs [1,2]. Amorphous calcium phosphate (ACP) NPs are candidate materials for nanomedicine due to its easy and rapid preparation procedure, in which the autofluorescence by defects and impurities can be thermically induced [3]. In this study, we investigated the effect of carbonate impurities on the PL properties of chemically precipitated ACP NPs submitted to heat treatment in a programmed furnace for 4 h in air at 400°C. Structural, compositional, and optical properties were analyzed herein. The ACP NPs were characterized by Fourier Transform Infrared Spectroscopy (FTIR), Thermogravimetric Analysis (TG), UV-Vis Spectroscopy, and by PL Spectroscopy. When excited at λexc = 405 nm the PL intensity and profile of ACP NPs changed according to different concentrations of carbonate groups before and after the heat treatment, which indicates the influence of such impurity on the PL of these nanomaterials. References: [1] C. Qi, et al. Chem. Soc. Rev., 47, 357-403, (2018) [2] T.R. Machado, et al. Mat. Today Chem., 14, 100211, 2019. [3] T.R. Machado, et al. J. Solid State Chem., 249, 64-69, 2016.

Salicylic Acid acts as a co-catalyst in TiO2-Mediated Photodegradation of Paracetamol

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Matheus Ruffo Peres [1]; Valdecir Ximenes [2]

[1] Departamento de Química / Faculdade de Ciências / Universidade Estadual Paulista "Júlio de Mesquita Filho"; [2] Faculdade de Ciências / Universidade Estadual Paulista "Júlio de Mesquita Filho"

Titanium dioxide (TiO2) is one of the most used catalysts in photodegradation. Paracetamol and salicylic acid are widely used as pharmaceutical drugs. We found that paracetamol (PCT) is less susceptible to photodegradation than salicylic acid (SAA). From a chemical perspective, this was unexpected since paracetamol is more vulnerable to chemical oxidation. Aiming the comprehension of the phenomenon, studies were performed comparing the efficiency of photodegradation of paracetamol versus salicylic acid and acetophenone versus 4-aminoacetophenone. The presence of the amino/amide group in the studied molecules was shown to be responsible for the lower susceptibility to degradation, as demonstrated to paracetamol versus salicylic acid and 4-aminoacetophenone versus acetophenone. It was also shown that salicylic acid increased the degradation of paracetamol and, consequently, was partially recycled. In other words, as a co-catalyst. The lower efficiency of photodegradation of the amino-based compounds seems to be related to the deactivation of the excited states of the TiO2.

Síntese de nanoestruturas de carbono por processo CVD usando rejeito de mineração e sua aplicação na remoção de corantes em água

https://proceedings.science/p/138919

Thaís Cristina de Oliveira Cândido [1]; Paula Sevenini Pinto [1]; Rafaela Fernandes Ribeiro [1]; Ana Paula de Carvalho Teixeira [2]; Marden Pires Moura [1]
[1] Universidade do Estado de Minas Gerais; [2] Departamento de Química / Instituto de Ciências Exatas / Universidade Federal de Minas Gerais

Activities such as iron mining and the textile industry are important for the economy, but their practices may be related to significant environmental problems, including the generation of tailings and contaminants in the water, respectively. This work aimed the synthesis of carbon nanostructures through the CVD process using iron mining tailings as catalyst and support, for further application in the removal of methylene blue and carmine indigo contaminants by adsorption. For the synthesis, the tailings were heated at a rate of 10 oC/min to 900 oC, under a methane atmosphere at 100 mL/min, remaining at the final temperature for 3 hours. The materials generated from this synthesis were named as R01CVD900, where R = A (sand) or L (mud). The materials were characterized by SEM, Raman, TGA, XRD, Mössbauer, EDS and ICP. Adsorption experiments were carried out with 20 mL of an aqueous dye solution (5 mg.L−1) and 20 mg of the adsorbent at pH7. After 24 h of contact, the mixture was centrifuged and the solution analyzed by a spectrophotometer UV-Vis monitoring the bands 609 and 664 nm to quantify the removal of methylene blue and carmine indigo, respectively. The chemical composition of the tailings was obtained by ICP analysis and indicated the presence of 19.2 wt% Fe and 71 wt% SiO2 for A01, and 50.2 wt% Fe and 14 wt% SiO2 for L01. The DRX and Mossbauer data showed that the iron oxides present in the A01 and L01 tailings were completely transformed into □-Fe and □-Fe(C). Moreover, peaks of carbon in 2□ at 26.5o confirmed the formation of carbon during the CVD process. The thermogravimetric analysis indicated 38 and 66 % of carbon for A01CVD900 and L01CVD900, respectively. Raman spectroscopy was performed in order to understand the quality of carbon nanostructures formed. As known, the D band is related to a disordered carbon, while the G band is related to a organized type of carbon. Raman spectra revealed the presence of D and G bands for both materials produced, the latter being more intense than the former. The ratio ID/IG were calculated for both samples and indicated that L01CVD900 have a more organized graphitic structure and has fewer defects compared to the material A01CVD900. The adsorption results showed that both materials were capable to adsorb methylene blue and carmine indigo dyes in aqueous solution, ca. 4.23 and 2.53 mg.g-1 for A01CVD900, while 3.79 and 2.63 mg.g-1 for L01CVD900. This means that while for methylene blue the removals a maximum of 85 %, for carmine indigo it was around 52 %. These results indicated that the materials adsorb methylene blue better and also that A01CVD900 is the best material. Adsorption isotherm studies, kinetics, pH effect and other studies are ongoing in order to understand the differences in the removal percentages of materials of for each dye. Nevertheless, these results demonstrated that iron mining tailings that is currently discarded and unused can be used to produce materials with carbon nanostructures capable of acting in the removal of water contaminants.

Sintese de Silicato de Cádmio vareando os precursores de cádmio e as rotas sintéticas

https://proceedings.science/p/138963

ELENA SANTOS [1]; Flavio Maron Vichi [2]
[1] Universidade de São Paulo; [2] Química Fundamental / Instituto de Química / USP

Materials with Persistent luminescence attract great interest due to its vast application range(1). Cadmium Silicate is one of these luminescent materials that have been arising interest. These are normally synthesized via a solid state route, but the implementation of different methods of synthesis can open paths to the attainment of silicates in low temperatures of calcination and with sizes and shapes of interest(2-3).The samples were characterized using x-ray diffraction (drx). The use of different cadmium precursors such as cadmium nitrate, cadmium acetate and cadmium chloride in the same synthesis method shows a dependence between the cadmium source and the silicate formation. With different conditions providing different silicate phases of metasilicate CdSiO3, orthosilicate Cd2SiO4 and oxyorthosilicate, Cd3SiO5 . In the Sol-Gel method, for example, the same conditions of synthesis with cadmium acetate generates a mixture of the three possible phases, while cadmium nitrate yields cadmium metasilicate as the only phase.

The different synthetic routes, on the other hand, have a range of aspects to be considered. Such as pH in the Hydrothermal route or the Sol-Gel route.The use of acid pH issues cadmium metasilicate while the basic pH favors the formation of impurities.

Síntese do óxido de grafeno: A primeira etapa de obtenção de um material poroso para a captura de CO2

https://proceedings.science/p/138956

Matheus Grohs Ribeiro [1]; Aline Farias Moreira da Silva [2]; Thiago Custódio dos Santos [3]; Célia Machado Ronconi [2]

[1] Universidade Federal Fluminense; [2] Química Inorgânica / Instituto de Química / Universidade Federal Fluminense; [3] Instituto de Química / Universidade Federal do Rio de Janeiro

A captura de CO2 utilizando grafenos porosos e dopados com átomos de nitrogênio (N-grafeno) é uma tecnologia com grande potencial devido às altas quantidades de gás adsorvidas e baixos valores de energias requeridas na fase de regeneração. Os valores elevados de área específica permitem um grande número de interações entre o CO2 e os nitrogênios distribuídos na estrutura do N-grafeno. Estes materiais podem ser fabricados a partir de óxido de grafeno (GO), uma amina e KOH como ativante1. Desta forma, este trabalho tem como objetivo sintetizar o GO e utilizá-lo para a obtenção de N-grafeno que será empregado na captura de CO2. Pretende-se investigar diferentes ativantes (K2CO3, ZnCl2 e FeCl3) e diferentes aminas para verificar o efeito tanto na área como na quantidade de nitrogênio. A síntese do GO foi realizada por um método de Hummers modificado, que iniciou-se por uma etapa de pré-oxidação com o grafite em flocos sendo adicionado a uma solução de H2SO4 (conc.) com P2O5 e K2S2O8. Em seguida, foi realizada a etapa de oxidação adicionando o grafite pré-oxidado em ácido sulfúrico contendo NaNO3 e KMnO4, o qual foi deixado em agitação magnética por 4h. Após, seguiram-se etapas de lavagem com HCl e H2O2. A Fig. 1(a) mostra a presença de grupos funcionais oxigenados com bandas de absorção localizadas em 3348, 1752, 1573 e 1076 cm-1, atribuídas aos estiramentos das ligações O-H, C=O, C=C e C-O. A curva de análise termogravimétrica apresenta perda de massa entre 190 e 300 °C referente à remoção dos grupos oxigenados e outra perda acima de 322 °C devido à decomposição da estrutura de carbono2. O difratograma de raios X mostrou um pico de difração alargado em 2□ = 24,5° (distância interlamelar = 3,6 Å) característico da estrutura de empilhamento π-π das folhas de carbono e outro pico de difração em 2□ = 11,4° (distância interlamelar = 7,8 Å), indicando a que a etapa de oxidação foi realizada com sucesso devido ao aumento da distância interlamelar em relação ao grafite. Nas próximas etapas, GO será impregnado com aminas e submetido ao processo de ativação química para a dopagem com nitrogênio e aumento de área específica.

SÍNTESE E CARACTERIZAÇÃO DE SULFATOS TRI E TETRA BÁSICO DE CHUMBO E APLICAÇÃO EM ACUMULADORES CHUMBO-ÁCIDO

https://proceedings.science/p/138882

Erilene Ribeiro [1]; Euzébio Skovroinski [2]; Andre Galembeck [1]
[1] Universidade Federal de Pernambuco - UFPE; [2] Instituto de Tecnologia Edson Mororó Moura / ITEMM

Um dos principais desafios da tecnologia Pb-A é torná-la mais atraente com o aumento da capacidade específica, aumento da energia específica e aumento do ciclo de vida. Estes aspectos são cruciais para que essa tecnologia se mantenha competitiva frente a outras, como as baseadas em lítio e seja utilizada em veículos elétricos ou híbridos. As limitações do ciclo de vida útil são decorrentes de fatores como corrosão do coletor de corrente positivo, queda de massa do eletrodo positivo, sulfatação do eletrodo negativo e perda de água por eletrólise (PAVLOV, 2011; GARCHE et al., 2015), além da elevada densidade dos componentes principais, as limitações de capacidade e energia específicas, são decorrentes também da baixa eficiência de utilização do material ativo, pois, apenas cerca de 50% do material eletroquimicamente ativo utilizado na confecção dos eletrodos é efetivamente utilizado para armazenar/liberar energia e ainda ocorre que processo de produção convencionalmente utilizado nas indústrias, resulta em uma massa com uma variação quantitativa relativamente grande de seus componentes. Como consequências, os acumuladores produzidos tendem a apresentar características de desempenho desuniformes (PAVLOV, 2011). Diante disso, é estudada a hipótese de uma síntese prévia de 3BS e 4BS para só então produzir o eletrodo. O método tem como objetivo de produzir dispositivos com características de desempenho mais uniforme; aumentar a eficiência na utilização do material ativo e da vida útil do acumulador a partir do ajuste quantitativo da composição da massa a ser empastada no eletrodo. Tanto o 3BS, como o 4BS estão sendo produzidos a partir da reação de óxidos de chumbo e ácido sulfúrico em meio aquoso, com proporções estequiometricamente calculadas e condições de temperatura controladas, de modo a otimizar a produção de cristais com alto grau de pureza. Os produtos das reações estão sendo caracterizados por difratometria de raios-x (DRX), microscopia eletrônica de varredura (MEV). Referências PAVLOV, D. Lead-Acid Batteries: Science and Technology. Elsevier Science, 2011. GARCHE, J.; MOSELEY, P. T.; KARDEN, E. Lead–acid batteries for hybrid electric vehicles and battery electric vehicles. Energy, 2015.

Stepwise Isothermal Thermogravimetric Analysis of Graphene Oxide

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Tiago Serodre [1]; Danilo Roberto Carvalho Ferreira [2]; Jefferson P. Nascimento [3]; Pedro L. Gastelois [1]; Clascidia Aparecida Furtado [1]
[1] Comissão Nacional de Energia Nuclear; [2] Centro de Desenvolvimento da Tecnologia Nuclear; [3] Instituto de Pesquisas Tecnológicas

Stepwise isothermal thermogravimetric analysis allows the resolution of decomposition events that occur at neighbouring temperatures, by allowing each mass loss event to go to completion at a fixed temperature before subsequent temperature increment. In this work, we applied this technique to a sample of graphene oxide (GO) synthetised by our research group.
GO is a complex material containing multiple oxygenated groups on the surface of graphene flakes, each

in a slightly different chemical environment. Conventional thermogravimetric analysis of GO carried out in nitrogen atmosphere evidences an important mass decomposition event taking place between around 120 and 220 °C. This temperature range corresponds to the decomposition of most of the oxygenated groups present on the surface of the carbon skeleton, which goes on to be slowly decomposed as the temperature increases.
The stepwise technique is able to resolve this event in three distinct events at 126, 150 and 178 °C respectively, and by interrupting the analysis after each of these steps, we were able to collect samples for chemical analysis, in order to determine which groups are decomposed at each temperature. These samples were analysed by X-ray photoelectron spectroscopy and Fourier-transform infrared spectroscopy, which showed the evolution of the chemical composition of GO. We expect this technique to become relevant not only in the characterization of GO samples and other graphene derivatives, but also, for example, in the determination of which groups participate in functionalisation reactions, for example.

Synthesis of mesoporous silica/hydroxyapatite nanocomposite for biomedical applications

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Isabela Alves de Albuquerque Bessa [1]; Aline Farias Moreira da Silva [2]; Tamires Soares Fernandes [1]; Carolina Bastos Pereira Ligiero [1]; Alexandre Malta Rossi [3]; Célia Machado Ronconi [2]
[1] Universidade Federal Fluminense; [2] Química Inorgânica / Instituto de Química / Universidade Federal Fluminense; [3] Centro Brasileiro de Pesquisas Físicas - CBPF

Mesoporous silica nanoparticles (MSNs) have been widely explored as therapeutic cancer treatment due to its high surface area and, which leads to an elevated drug-loading efficiency. In our research group, MSNs was already employed as a gated nanocarrier, using the macrocycle pillar[5]arene as the nanogate1. However, some drawbacks on using MSNs due to their low degrability and bioaccumulation2. In order to improve MSNs safety, one of the strategies used is to incorporate biodegradable materials. In this scenario, we proposed a new gated nanocarrier based on MSN and hydroxyapatite core-shell for cancer treatment. Hydroxyapatite (HAP) can, as the major inorganic compound of bone tissues, dissolve in the acid environment of tumor cells. Therefore, the hydroxyapatite presence increases both drug release and biocompatibility. The nanocomposite synthesis was performed following procedure previously described in literature with modifications3. The PXRD pattern showed good correspondence hydroxyapatite's phase and also presents a peak in 2 = 2o referring to the mesoporous structure of silica (Figure 1a). The FTIR spectra presents a band overlapped in 1040 cm-1, referring to Si-O and phosphate groups stretching modes of MSN and HAP, respectively (Figure 1b). The nanoparticles showed a hydrodynamic diameter of 189 nm (Figure 1c). To confirm the core-shell structure, transmission electron microscopy analysis will be carried out.

UNDOPED TETRAGONAL ZrO2 APPLIED ASADSORBENT FOR ENVIRONMENTAL REMEDIATION

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João de Jesus Maurício [1]; Ieda Maria Garcia dos Santos [2]
[1] Departamento de Química / Centro de Ciências Exatas e da Natureza / Universidade Federal da Paraíba; [2] Universidade Federal da Paraíba

The ecological equilibrium has been impaired due to contamination of aquatic media by industrial effluents such as methylene blue (MB).[1] In order to minimize environment impacts of that practice, this research aimed at performing decolorization of solutions containing MB using zirconium dioxide (ZrO2). The material was synthesized by the modified Pechini method using Zirconium Butoxide as precursor.[2] Zirconia was obtained as final product of the synthesis, as indicated by the X-ray diffraction pattern (Figure 1a), which presents intense peaks assigned to the tetragonal phase and low-intensity peaks assigned to the monoclinic phase. The presence of tetragonal structure occurs in spite of being a high temperature phase, probably due to the small particle size, as previously reported.[2] The zeta potential of the material was analyzed and a negative surface was identified whatever the pH of the suspension and a greater negative electrical density was observed for higher pH values. ZrO2 was added into a quartz reactor containing 100 mL of MB solution at 10 ppm and subjected to irradiation with three UVC lamps under constant stirring for 24 h. The pH of the MB solution was adjusted to 2, 5, 7 or 10 using buffer solutions.[3] After irradiation, ZrO2 was separated from suspension by centrifugation and all solutions were analyzed by UV-Visible spectroscopy, in the wavelength range from 400 to 700 nm, obtaing the MB spectrophotometric profile (Figure 1b). The average concentrations of the dye solutions were quantified by an analytical curve (Figure 1c) previously produced according to the intensities of the UV-Vis spectra at 663 nm at concentrations of 1, 2, 4, 6, 8 and 10 ppm. It was observed that different decolorization values were obtained depending on the pH of the suspension, as indicated in Figure 1d. The biggest decolorization was attained at pH 2 with 94,4%, due to the positive charge of the MB dye, which favored the adsorption process. At pH 10 a high decolorization of 82,5% was also attained, probably due to the highly negative surface of ZrO2. Moreover, the appearance of a light blue color in the zirconia powder after irradiation proved that MB dye adsorbed on its surface, without degradation by photocatalytic processes in spite of the long exposition time. Finally, it is concluded that zirconia favored the decolorization of Methylene Blue solutions by adsorption, as ZrO2 is an insulating material with large band gap, being the pH 2 suspension most efficient to minimizing the ecological impacts.

Figure 1: (a) XRD pattern (ZrO2), (b) UV-Vis spectra of the MB, (c) zeta potential and (d) graphic of decolorization vs solution pH.

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Valorização da Biomassa Lignocelulósica por Desconstrução em Moinho de Bolas

https://proceedings.science/p/138967

Michelle Ramos Cavalcante Fortunato [1]; Ricardo Sposina Sobral Teixeira [1]; Rosane Aguiar da Silva San Gil [2]; Viridiana Santana Ferreira Leitão [3]
[1] Universidade Federal do Rio de Janeiro; [2] Departamento de Química Orgânica (DQO) / Instituto de Química (IQ) / Universidade Federal do Rio de Janeiro; [3] Int

The successful transition to cleaner energy depends on the efficient use of renewable resources such as lignocellulosic biomass, that have the potential to meet the world's long-term energy demands. However, processing these biomasses is not trivial. The biomolecules present are often part of recalcitrant cell structures, and pre-treatment steps are necessary, aiming at the deconstruction of the structure and consequente increase in the accessibility of enzymes, which is used in subsequent processing steps. Among the various pre-treatments available for structural deconstruction, the physical method by ball milling stands out, which has attracted attention for its various benefits in the context of biorefineries. It is a greener, more versatile pretreatment that, for example, improves the efficiency of the enzymatic conversion of polysaccharides to monosaccharides in the context of second generation ethanol production. The deconstruction of the supramolecular structure of lignocellulose is promoted by the energy generated by mechanical forces during the milling process (LIU et al., 2019). The pre-treatment by grinding balls, in addition to reducing the particle size, promotes mechanochemical reactions, and induces a reduction in the crystallinity and degree of polymerization of cellulose (SHEN et al., 2020). In this communication, the effects of that pretreatment could be successfully monitored by solid state nuclear magnetic resonance spectroscopy (13C CPMAS NMR) through the areas of characteristic carbon signals of cellulose, hemicellulose and lignin.

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Química Inorgânica - INO

A cobalt(II) aminoacid complex: a material for reversible water capture

https://proceedings.science/p/138888

Dayenny Louise D'Amato Leite [1]; Catiúcia R. M. O. Matos [1]; Carolina Bastos Pereira Ligiero [1]; Acácio Silva de Souza [1]; Sérgio Pinheiro [1]; Célia Machado Ronconi [2]
[1] Universidade Federal Fluminense; [2] Química Inorgânica / Instituto de Química / Universidade Federal Fluminense

Reversible water capture directly from atmospheric humidity can be used for both produce safe and

clear water and humidity control1. Today, commercial sorbents, such as silica gel or zeolites are widely used despite having high-energy consumption and low recyclability due to their high affinity towards water molecules. Therefore, the development of new adsorption materials that can outperform traditional desiccants proves to be important2. Herein, we report the synthesis and characterization of a Co(II) coordination complex that can be used as a candidate for atmospheric water harvesting. The complex was synthesized adding a MeOH solution of Co(CH3COO)2.4H2O into a solution of an aminoacid ligand3 in 1:1 MeOH:H2O using a metal-ligand ratio 1:2. Single crystal X-ray diffraction revealed that the complex crystallizes in a monoclinic P21/n space group, with two ligand molecules coordinated in the equatorial plane and two water molecules completing the octahedral sphere. The crystalline structure is stabilized by hydrogen bonding between the complex units and uncoordinated water molecules in the asymmetric unit of the compound (Figure 1a). Water absorption/dessorption properties were studied by thermogravimetric analysis (TGA), shown in Figure 1b. The material was first heated at 155°C/ 30 min to complete water removal, which is accompanied by crystal color change. After crystal dehydration, three water capture tests were carried out: i) capturing water from air humidity, ii) from liquid water and iii) from water vapor at 60 °C. The results of these experiments were analyzed by TGA, which showed a maximum of 18 % of water uptake, e.g, an amount close to the initial water capacity of the complex. These absorption studies combined to the color change (Figure 1c) strongly indicate that the Co(II) complex hows a potential material for atmospheric water harvesting or dehumidification agent.

Ab initio and DFT theoretical methods for geometry evaluation of inorganic compounds with first series transition metals

https://proceedings.science/p/138960

João Madureira; Bruno Moynier [1]
[1] Universidade Federal Fluminense

The lack of enough experimentally resolved equilibrium structures (reexp) for organometallics or coordination compounds undermines any serious attempt to evaluate ab initio and DFT prediction ability about such compounds. When such studies are performed three strategies are typically used: either they are performed using benchmarks based on non-metal compounds, or benchmarks that include inorganic compounds with more common experimentally related structures, like r0, rα, rg, etc, that are most probably still significantly far from equilibrium structures. A third approach is based on high quality calculated structures, at CCSD(T) level or above, with QZ and 5Z basis-sets, that are too expensive and slow to achieve convergence, and are still far from CBS.
We performed an extensive literature study to build a database of experimentally resolved equilibrium structures of inorganic compounds with a metal center, with nearly 1000 references. Such database is still growing and is available for any interested researcher (please e-mail the main author).
Based on a selected number (30) of inorganic diatomics, with a first-series transition metal, 14 ab-initio/DFT methods on a typical Jacob ladder approach, with def2-triple zeta basis-sets, were evaluated for the hydride, chloride and carbide series. Preliminary results indicate that GGA (BP86-D3 and BPE-D3) and meta-GGA (TPSS) have the best prediction ability based on MAD and RMSD statistics.
Carbide series gave worst results, which was determined to be caused by almost degeneracy of the fundamental states and its multiconformational nature, according to the B1-test proposed by Truhlar and collaborators,1 since DFT methods are fundamentally uniconformational. Such difficulties also apply to the experimental studies, since only NiC and FeC reexp are known, while hydride and chloride

series are almost complete.
The inclusion of the relativistic effect in the studied ML compounds, according to the Douglas-Kroll-Hess approach (DKH2), significantly improves the MAD and RMSD results, with almost 50% decrease in the deviation; and is recommended even in the transition metals first series.
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Análise termoquímica, energia de decomposição e NBO de complexos de zinco contendo ligantes xantatos

https://proceedings.science/p/138908

Daniella Brito de Miranda [1]; Susana Quintal [1]; Gláucio Braga Ferreira [1]
[1] Universidade Federal Fluminense

Xanthates are compounds of great interest in coordination chemistry due to the presence of the OS2 group in their structure, which establishes different forms of coordination with the metallic center. In addition, this class has applicability in the biological, environmental and technological areas. In this work, thermochemical, NBO and EDA analyzes of zinc complexes C1-C4 with propyl (L1), butyl (L2), amyl (L3) and 2-ethoxyethylxanthates (L4) were performed. The density functional theory through the M06L method was used associated with the base functions 6-311++ G ** for the atoms of S, C, O and H and LANL2TZ with pseudopotential for zinc. The thermochemistry was analyzed for the zinc complexes from the first and second substitution of water molecules by the xanthate ligands. Furthermore, the complexes were analyzed in their bidentate form and also for their cis/trans isomerism. It is possible to observe an increase in stability, which is proportional to the increase in the chain from L1 to L3. This trend can be explained by the better neutralization of the metal's dicathionic charge through the increase in the electron density in the sulfur atom, from the carbon chain donor atoms. Besides, the M-S bond occurs through density donation from the sulfur p character orbital and density reception by the zinc s orbital. The data obtained in this study confirm that xanthate complexes can have different coordination spheres. The complexes trans-C1-C4 have M-L bond predominantly ionic.

Complexos antitumorais promissores de Pt (II) com derivados de 1,3,4-oxadiazol e piperazina

https://proceedings.science/p/138904

Antônio Augusto de Oliveira Neto [1]; Heveline Silva [1]; Mara Rubia Costa Couri [2]; Camille Carvalho de Mendonça [2]
[1] Universidade Federal de Minas Gerais; [2] Universidade Federal de Juiz de Fora

The beginning of the use of platinum (II) complexes in the chemotherapy treatment of cancer took place after the discovery of the antitumor activity of cisplatin by Rosenberg in the 60s.[1However, the side effects and cell resistance lead scientists look for new complexes. Ligands play a role in addition to the central metallic species, such as synergism, modulation of the lipophilic and hydrophilic character and lability.
In this work, we have combined N-alkylated piperazine and phenyl substituted 1,3,4-oxadiazole moieties as ligand, and varying the side carbon chain length (figure 1). Piperazine derivatives showed

antibiotic and antitumor activities as well 1,3,4-oxadiazole derivatives showed even more antiparasitic, antidepressant and anti-HIV activities.[2] Three new platinum(II) complexes were synthesized using the same conditions as described in figure 1. The complexes were analyzed by IR, NMR 1H, 13C, MS-Maldi, TG, molar conductivity and CHN. The analyses suggested the Pt were coordinated to the sulfur atom of oxadiazole and to the nitrogen of piperazine. For all three complexes, IR spectra showed C=S and C-N shifted, NMR spectra showed N-CH2-N shifted, MS-MALDIpresented 1 [M-C12H26N2]+, 2 [M-C2H6]+, 3 [M-H]+, TG present two mass lost and residue (PtCl2), molar conductivity in DMF showed the neutral and CHN showed values with <5% error.

Cytotoxic assays using tumor cells and non tumor cells are ongoing and IC50 and selectivity will be assessed to help conclusion about structure activity relationship of this complexes, also compared to free ligands.

Complexos ciclopaladados derivados da 2,6-lutidina como potenciais agentes antitumorais

https://proceedings.science/p/138901

Renan Diego Zanetti [1]; Adelino Vieira de Godoy Netto [1]; Mariete Barbosa Moreira [2]; María Sol Brassesco Annichini [3]

[1] Instituto de Química / Universidade Estadual Paulista “Júlio de Mesquita Filho”; [2] Departamento de Química / Centro de Ciências Exatas / Universidade Estadual de Londrina; [3] Departamento de Biologia / Faculdade de Filosofia, Ciências e Letras de Ribeirão Preto / Universidade de São Paulo

Cancer represents one of the most deadly diseases in the world. Among the various forms of treatment available, the chemotherapy regimes based on cisplatin stand out as one of the most applied. However, its toxicity added to increasing drug resistance (MDR) make its use less effective. Thus, in this context, four palladium complexes containing N,N-Dimethyl-1-phenylethylamine (dmpa) and 2,6-Lutidine were prepared as potential antitumor candidates. These compounds were properly characterized by NMR ^{1}H and IR spectroscopy. Chemical stability studies in solution were initially investigated by UV-Vis over 48h and the cytotoxic activity of cyclopalladated complexes determined for glioblastoma cell lines (U251 and T98G) and human malignant melanoma cell lines HT144 and LB373. Binding studies with targets of interest such as DNA and human serum albumin (HSA) by circular dichroism (CD) and fluorescence were carried out using the most cytotoxic complex.

Compostos de coordenação derivados da quinolina e Eu3+: propriedades luminescentes e estruturais

https://proceedings.science/p/138864

Nathália Maria Moraes Fernandes [1]; Izilda A. Bagatin [1]

[1] Universidade Federal de São Paulo

OLEDs (organic light-emitting diodes) have become a viable alternative to the current technology market due to their lightness, low cost, and high image quality in displays. Consequently, our research group aims to synthesize and characterize coordination compounds based on quinoline ligands and study their luminescent properties. Initially, Eu(CF3SO3)3 soluble salt was used for the synthesis, and 8-hydroxyquinoline, 5-SO3-8-hydroxyquinoline (1), and 5-Cl-7-I-8-hydroxyquinoline (2), which are suitable coordinating ligands and have excellent luminescent properties. Then, four compounds were synthesized: [Eu(5-SO3H-8-hydroxyquinoline)3(H2O)2] (3), [Eu(5-SO3H-8-hydroxyquinoline)4] (4), [Eu(5-Cl-7-I-8-hydroxyquinoline)3(H2O)2] (5) and [Eu(5-Cl-7-I-8-hydroxyquinoline)4]. Finally, characterizations by spectroscopies techniques, such as UV-Vis, infrared (FTIR), NMR, and luminescence, were performed. Preliminary results are auspicious and indicate complexation, the probable conformation of the complexes, and their respective luminescence.

Degradação Oxidativa do Herbicida Atrazina Catalisada por Porfirinas de Manganês como modelo biomimético do Citocromo P450

https://proceedings.science/p/138965

Iasmin Tavares Resende [1]; Bruno José Rocha da Silva [1]; Mirra Angelina Neres da Silva [1]; Dayse Carvalho da Silva Martins [2]

[1] Departamento de Química / Instituto de Ciências Exatas / Universidade Federal de Minas Gerais; [2] Departamento de Química / Instituto de Ciências Exatas / Universidade Federal de Minas Gerais

Os agrotóxicos são substâncias utilizadas em todo mundo para o controle de pragas em plantações agrícolas e começaram a se destacar no início da década de 1940, com a produção dos pesticidas sintéticos, o dicloro-difenil-tricloroetano (DDT) e o ácido diclorofenóxiacético (2,4-D), que foram amplamente utilizados durante a segunda guerra mundial. Ainda que estes produtos tenham muitos benefícios para os seres humanos na agricultura e no comércio, do ponto de vista ambiental, há uma grande preocupação com o destino deles. Após utilizados na atividade agrícola, estas substâncias podem se adsorver em partículas do solo ou ainda se dissolver em águas superficiais e subterrâneas, podendo persistir no ambiente e causar danos ecológicos. Com isso, maneiras de degradar os agrotóxicos para minimizar seus impactos passaram a ser investigadas ao longo de todo mundo e, entre elas, pode-se destacar o uso de metaloporfirinas como modelo biomimético do citocromo P450, que é uma família de enzimas responsável pela oxidação de substâncias xenobióticas em diversos organismos vivos. O presente trabalho teve como objetivo a degradação do herbicida atrazina catalisado por duas porfirinas de manganês, aplicando-se dois oxidantes mais comumente empregados na literatura: iodosilbenzeno (PhIO) e iodobenzeno diacetato (PhI(OAc)2), em acetonitrila. Utilizou-se uma razão molar para catalisador:oxidante:substrato de (1:100:10) e foi possível obter uma porcentagem de degradação de atrazina de até 51%. Foram estudados também sistemas com outros oxidantes mais ambientalmente amigáveis, como peróxido de hidrogênio e oxone®, obtendo-se porcentagem de degradação máxima de 36% e 41% respectivamente. Diante do fato de que a atrazina é um poluente emergente persistente, o sistema de degradação deste composto é bastante eficiente obtendo-se resultados satisfatórios e que estimulam o estudo das condições de reação de forma a otimizar a degradação desse agrotóxico.

Desenvolvimento de fotocatalisadores baseados em nanoestruturas hibridas de BiVO4 e nitreto de carbono grafítico

https://proceedings.science/p/138858

Caroline Claudino [1]; Juliana Souza [1]; Bárbara Rodrigues [1]; Carolyne Martins Branco [1]

[1] Centro de Ciência Naturais e Humanas, Universidade Federal do ABC (UFABC)

Bismuth vanadate (BiVO4) is considered one of the most promising materials for the development of

visible-light sensitive photocatalysts. However, this material exhibits high recombination rates and relatively low stability, which limits its applicability. Therefore, this system shows limitations and do not reach their full potential. The incorporation of the organic semiconductor polymer carbon nitride graphitic (C3N4) to the BiVO4 is also a well-succeed strategy to increase the activity of the material. Here we describe the synthesis, characterization and photocatalytic activity of the hybrid organic-inorganic BiVO4/g-C3N4 material. BiVO4 was synthesized through a facile microwave-assisted method that takes only 12 min, for the synthesis of HPZ-BiVO4 urea was added to a round-bottom flask and BiVO4 was added to a Schlenck, the system was placed into a muffle and heated at 400°C for 30 minutes. The material was characterized by Scanning Electron Microscopy (SEM), Raman spectroscopy, diffuse reflectance spectra, vibrational spectroscopy in the infrared region, zeta potentials, energy dispersive spectroscopy analysis and thermal analysis experiments to evaluate the quantity and degree of crystallinity of the HPZ. The catalytic activity of HPZ-BiVO4 was evaluated through the degradation of three different dyes: rhodamine B, methyl orange and methylene blue, simulated sunlight was used for these tests, in addition to different suppressors: superoxide radical suppressor, hydroxyl radical, holes and visible light. Raman spectroscopy analysis revealed that with HPZ the peaks are wider, which indicates a decrease in the degree of crystallinity of the material, there was an increase in the band-gap energy when the HPZ is incorporated into BiVO4, the material presents a good thermal stability and with the thermal analysis it was possible to indicate that the presence of the polymer interferes in the oxide degradation/stability curve. In photocatalysis the experiment in methylene blue shows better results, these results lead us to believe that there is a reaction between the formed radical species, which leads to an increase in photocatalytic activity when some species is suppressed.

Design e docking molecular de novo material fotoluminescente à base de Eu3+ combinado com o fármaco Nitazoxanida

https://proceedings.science/p/138959

Andrei Marcelino Sá Pires Silva [1]; Jorge Fernando Silva de Menezes [1]; Aluísio Marques da Fonseca [2]
[1] Universidade Federal do Recôncavo da Bahia; [2] ICEN / Unilab

A Síndrome Respiratória Aguda por Coronavírus (SARS-CoV-2) é uma infecção viral recente e gerou um dos maiores problemas de saúde pública mundial, e tem despertado interesse da comunidade acadêmica científica na busca por um maior conhecimento sobre o mecanismo de ação viral. Não há evidências científicas e ensaios clínicos que indiquem que possíveis terapias tenham mostrado resultados em pacientes suspeitos ou confirmados de ter contraído a doença, além do uso de imunizações. Diante do exposto, algumas substâncias estão sendo estudadas para aplicação no sentido de conter sua disseminação e maiores danos. Assim sendo, o presente trabalho tem como objetivo a síntese e estudo fotoluminescente de um novo material envolvendo a combinação de um precursor do tipo, Eu(DBM)3.2H2O (DBM=dibenzoilmetanato), que tem a molécula de água (oscilador de alta frequência inibidor de emissão) substituída pelo pró-fármaco nitazoxanida (NTZ), e a realização de estudo de in silico com intuito de utilizar o mesmo como biomarcador através de sua interação com a proteína spike Glicoprotease. A reação do sal de lantanídeo hidratado com o ligante NTZ originou um complexo sólido, Eu(DBM)3.NTZ, em forma de pó amarelo, com perfil cristalino fortemente luminescente sob excitação UV. Analisando os espectros vibracionais na região do infravermelho (IV) pode-se constatar a evidência da ocorrência de coordenação envolvendo o íon európio, Eu3+. O espectro IV de NTZ, revela quatro bandas de estiramento características em 3357, 1774, 1661 e 1604 cm-1 atribuídas para éster v(NH), v(C = O), v(C = O) amida e v(C = N) tiazol. Após a quelação, o modo v

(NH) é deslocado para comprimentos de onda mais altos, o que elimina o envolvimento do grupo funcional -NH- na esfera de coordenação do íon Eu3+. 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 5D0 para o fundamental 7FJ (J = 0, 1, 2, 3 e 4). A amostra apresenta a emissão, 5D0→7F0, indicando que o centro metálico pode possuir uma simetria Cnv, Cn, ou Cs. A única linha de emissão na transição 5D0→7F0 em 580 nm pode ser atribuída à existência de um único sítio de simetria em torno do íon Eu3+. A característica proeminente notada no espectro de emissão é a alta intensidade da transição 5D0→7F2, em torno de 612nm (a maior intensidade da transição 5D0→7F2 em relação à 5D0→7F1, indica a ausência de centro de simetria). O novo material luminescente usado na simulação foi criado no programa Chem3D e sua adicional parametrização foi elaborada pelo aplicativo LUMPAC. O estudo foi realizado utilizando o AutoDock Vina com modelo genético lamarckiano (GA) combinado com a estimativa de energia baseada em grade, conformação rígida e flexível. Este estudo em sua fase inicial aponta para construção de protótipo de sonda luminescente para rastrear mecanismo de ação de fármacos principalmente aqueles que são usados para minimizar efeitos de agentes virais como o Sars-CoV-2, que é o caso da molécula de nitazoxanida.

Development of biofilms containing a metal complex as active compound for food applications.

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Rafael Cavalieri Marchi [1]; Sara Limbo [2]; Rose Maria Carlos [1]
[1] Departamento de Química / Universidade Federal de São Carlos; [2] Department of Food, Environmental and Nutritional Sciences / Milan University / Milan University

This work explores the potential of active packaging containing Mg(II)-polyphenol complex for application in food protection. The polymeric films were produced from tapioca starch or gelatin containing a complex of Mg(II) with ferulic acid (Fer) and phenanthroline (Phen; MgPhenFer). The investigated metal complex is obtained with a high degree of purity without the need for purification and using a low-cost methodology.
Reactive oxygen species such as singlet oxygen (1O2) and the hydroxyl radical (OH•) are responsible for food deterioration because they start the lipid peroxidation process. Studies carried out to evaluate the antioxidant potential of complexes show a total inhibition of 1O2 at a concentration of 1.65 µg.mL-1 and 5.00 µg.mL-1 for peroxyl radical.
The bactericidal activity of the complex against the bacteria related to meat deterioration such as L. innocua, L. monocytogenes, St. aureus, Samonella ssp, E. coli, Ps. putida, Ps. fluorescens S8, Ps. fluorescens S9 was investigated at concentrations ranging from 0.1 mg.mL-1 up to 5 mg.mL-1. The MgPhenFer complex inhibited the growth of all analyzed bacteria at a concentration of 1.0 mg.mL-1.
The antifungal activity of the complex was also evaluated for the pathogens A. niger, P. notatum e Rh. oryzae. In these studies, the MgPhenFer at a concentration of 0,1 mg. mL-1 inhibited 100% of the growth of the molds in relation to the control.
The presence of complexes in gelatin or starch films did not interfere with the transparency of the material obtained, having similar transparency to commercial PET films. Gelatin films showed greater efficiency in the oxygen barrier properties in compared to the starch film. The prevention of the browning process in apple pulps using the starch film containing the complexes was evidenced since the film with MgPhenFer decrease the enzymatic oxidation process.
The films containing the complex have high application potential, MgPhenFer when used freely or in

plastic films are promising alternatives to the commercial antioxidant.

Development of multifunctional metalloporphyrin-based layered-magnetic solids for Tandem-assisted catalytic reactions

https://proceedings.science/p/138889

Everton Henrique dos Santos [1]; Fernando Wypych [2]; Vanessa Prevot [3]; Claude Forano [3]; Shirley Nakagaki [4]
[1] Departamento de Química / Programa de Pós Graduação em Química / Universidade Federal do Paraná - Campus Centro Politécnico; [2] Universidade Federal do Paraná – Campus Centro Politécnico; [3] Institut de Chimie de Clermont-Ferrand / Université Clermont Auvergne; [4] Departamento de Química / Setor de Exatas / Universidade Federal do Paraná – Campus Centro Politécnico

Synthetic metalloporphyrins (MP) are bioinspired molecules on Iron Protonporphyrin IX, which is present in all living-being species. MP are known for great catalytic and selective efficiency towards a scope of reactions, whereby results in products of chemical and pharmaceutical interest, for instance: ketone, alcohol, epoxide, and CO2-fixation products [1]. When evaluating MP as a catalyst in homogeneous medium, some issues can commonly be observed, such as biomolecular interactions leading to catalyst deactivation, and difficulty on catalyst recovering since it is solubilized in the reaction medium. Therefore, immobilizing MP onto solids support comes as an alternative for overcoming such drawbacks since the side reactions are avoided and the catalyst is easily recovered by centrifugation, for example [2]. At the same time, most of the catalytic studies regarding these solids take place in a single-step catalytic reaction which makes expensive the catalyst reuse and contributes to reactant wastes. Considering these points, sequential reactions arise as a more efficient usage of catalyst and reactants involved in the process [3]. Consequently, idealizing solids support becomes important since the combination of specific compounds can bring new properties to the final catalytic solid. Hereby is reported the preparation of core@shell solid types, mainly composed by magnetite (Fe3O4) as core and layered solids, such as layered double hydroxides (LDH) or layered hydroxide salts (LHS), as shell, evaluating diverse conditions of preparation, for further different MP e.g. [M(TDFSPP)] (Figure), where M = Fe3+ (Figure), Mn3+, Zn2+ or Mg2+ immobilization. The solid supports were analyzed by XRD, TEM, SEM, TGA techniques. These solids will be studied in different single and sequential reactions, such as cycloalkene oxidation followed by CO2 cyclic addition.

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Hybrid materials obtained from kaolinite and phenylalanine complexed to Eu3+ ion as luminescent sensor of caffeine

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Denis Talarico de Araujo [1]; Vinilson Gouveia Peixoto [1]; Eduardo José Nassar [2]; Kátia Ciuffi [3]; Miguel Angel Vicente [4]; Raquel Trujillano Hernández [4]; Vicente Rives [4]; Emerson Henrique de Faria [3]
[1] Universidade de Franca; [2] UNIFRAN; [3] Sol-gel / Universidade de Franca / Universidade de Franca; [4] Universidad de Salamanca

With the advancement of economic and social development in recent decades, thousands of chemical compounds are dumped into natural effluents, posing a risk to both the environment and human health. The lack of knowledge about the behavior of these contaminants in the environment, as well as the emergence of new substances by mixing these pollutants, is an aggravating factor for this problem. Aiming to overcome this problem, a hybrid material to be used as a luminescent sensor for the contaminant caffeine was prepared from kaolinite functionalized with phenylalanine and used for complexing Eu3+ ions by (i) a conventional route already widely used in the literature, and (ii) a new route catalyzed by boric acid, for application. The lanthanide ion has unique optical properties such as thin emission bands with high lifetimes, bringing sensitivity and selectivity, essential properties for this application. The amino acid has a high molar absorptivity and offers greater structural rigidity to the complex, maximizing energy transfer to Eu3+, and increasing its radiative emission yield, while kaolinite offers thermal resistance and increases the dispersion of the complex, decreasing luminescence suppression. The secondary ligand tenoyltrifluoroacetonate was added to the complex to improve energy transfer to the Eu3+ ion and to remove water molecules in the first coordination sphere. The material was characterized by powder X-ray diffraction, infrared molecular spectroscopy, thermal analysis, scanning electron microscopy and luminescence spectroscopy. The presence of symmetric and antisymmetric stretch vibration bands of the COO- group of amino acids (1300 – 1600 cm-1) and modification of the kaolinite OH stretch bands was verified, showing the interaction and formation of the hybrid materials, also concluded from the increase in the kaolinite basal space from 0.7 nm to 7.9 nm evidenced by X-ray diffraction. The samples presented 0.2 mol of organic matter per kaolinite unit cell and pseudo-tubular morphology. The sample obtained by the boric acid-catalyzed route showed better optical properties with 1 water molecule complexed and 42 % internal radiative emission yield. The adsorption kinetic study of the sensor with the contaminant showed selectivity at concentrations below 25 mg/g and pseudo second order kinetics, attributed to materials with multiple adsorption sites with strong interactions between the contaminant and the hybrid material.

Mechanochemical synthesis of complexes with europium (III) ions and N-tosylacetamide

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Jéssika Cavalcanti de Lima [1]; Ivani Malvestiti [2]; Ricardo Luiz Longo [2]
[1] Universidade Federal de Pernambuco; [2] UNIVERSIDADE DE PERNAMBUCO

Trivalent lanthanide complexes attract great interest due to their diversity of applications, which include catalysis, contrast agents for NMR imaging, photo and electro-luminescent devices. However, the complexes with lanthanides (III) and β-diketones has a disadvantage about their photo-stability, it improve the interesting related to discovery new ligands. In this context, is important the evaluation of analogues ligands to β-diketones to understand this phenomena. The mechanochemistry is an interesting tool that allows the develop of synthesis methodology more green, since reduces or eliminate the use of bulk solvents, although this technique is little used in syntheses of lanthanide complexes. In this sense, the present work developed an unprecedented complex from Eu3+ and the ligand N-tosylacetamide. Were tested two mechanochemistry conditions, in two steps (M1) and in single step (M2).The syntheses of the complexes were carried out in mixer mill Restch MM200 with liquid-assisted grinding (LAG) in 10 mL Teflon jars, two 5 mm zirconia sphere and 25 Hz grinding frequency. The methodology M1 can be divided in two parts: i) abstraction of the N-tosylacetamide (0, 9 mmol) proton with NaOH (0, 9 mmol) and water (25 l) for 30 min; ii) followed by the addition of

EuCl3·6H2O(s) (0,3 mmol) and another 60 min of grinding. In M2 the stoichiometry of M1 was maintained, but all components were added in a single step and the grinding lasted 90 min. The solids were washed with water and the yields were determined by tritation, the result for both synthesis is 79%. The emission spectra obtained by excitation in the ligand present the transitions 5D0 → 7FJ (J = 1,2,3 e 4) and not differ from each other, it indicates the obtaining of the same complex. Therefor, the methodology M1 is more advantageous for being one-pot.
This result shower the formation of the complexe and
the efficiency of mechanochemistry in this kind of
synthesis.

Multiplicidade de estereoisômeros e reconhecimento da quiralidade de coordenação em complexos de íons lantanídeos pelo software Complex Build

https://proceedings.science/p/138918

Gabriel Henrique Lima Munguba [1]; Gabriel Urquiza [1]; Frederico Teixeira Silva [2]; Alfredo Mayall Simas [1]
[1] Universidade Federal de Pernambuco; [2] Hilab

Complexos de íons lantanídeos podem apresentar altos números de coordenação, o que leva a uma rica estereoisomeria. De fato, ao aumentar o número de coordenação de um complexo heteroléptico octaédrico com 6 ligantes monodentados para 7, levando a uma bipirâmide pentagonal, já se aumenta em dezoito vezes o número de estereoisômeros de coordenação possíveis: de 30 para 540.1 No entanto, nos trabalhos, é comum considerar apenas um dos estereoisômeros, tanto em cálculos teóricos, quanto na interpretação de resultados experimentais; desconsiderando, portanto, esta multiplicidade de possíveis estereoisômeros, bem como a possibilidade de ocorrência de quiralidade de coordenação. Como exemplo, vamos considerar o complexo $Er(C_{18}H_{37}PN_2O_5)_2(H_2O)(NO_3)_3$ de geometria Muffin (MFF-9), encontrado no Cambridge Structutral Database (CSD) pelo código de referência DOGKEP. Dos 682 estereoisômeros quirais possíveis do grupo pontual C1, há pelo menos 3 agrupamentos possíveis na representação de seus potenciais de ionização versus suas energias de repulsão dos caroços, a partir de cálculos RM1. Isto indica que o cálculo de um único estereoisômero não é representativo do conjunto de estereoisômeros possíveis. É necessário considerar o conjunto completo. Para isto, foi desenvolvido o software Complex Build, que além da identificação, descrição, construção e visualização desses estereoisômeros (incluindo reconhecimento de quiralidade de coordenação), produz arquivos de entrada pré-otimizados de suas geometrias para vários outros softwares de química computacional (ORCA, Gaussian, MOPAC, LUMPAC, Gamess, etc.) para cálculos posteriores. O software pode ser obtido de forma livre, a partir de nossa página https://complexbuild.sparkle.pro.br/./.

Nanopartículas superparamagnéticas tioladas como potenciais veículos biológicos

https://proceedings.science/p/138969

Tatiane Britos [1]; Camila Silva Chagas [2]; Fabio Furlan Ferreira [3]; Fernando Luiz A. Fonseca [4]; Paula Silvia Haddad Ferreira [1]
[1] Universidade Federal de São Paulo; [2] Faculdade de Medicina do ABC / Faculdade de Medicina do ABC; [3] Universidade Federal do ABC; [4] Faculdade de Medicina do ABC

Superparamagnetic iron oxide nanoparticles (SPIONs), such as magnetite (Fe3O4), are known for their biocompatibility and applications in several areas of medicine1. The present research is focused on the synthesis, characterization, and biological application of SPIONs. Magnetite nanoparticles (Fe3O4 NPs) were synthesized by co-precipitation of iron salts and coated with biocompatible molecules such as L-cysteine (CYS)2 and Glutathione (GSH), making thioled-nanoparticles as Fe3O4-CYS and Fe3O4-GSH NPs, respectively. The physicochemical, structural, and magnetic properties were characterized by different experimental techniques, such as X-ray diffraction (XRD), Fourier transforms infrared (FTIR), and ultraviolet-visible (UV-vis) spectroscopies, SQUID magnetic measurements, and dynamic light scattering (DLS). The results showed that these nanoparticles have a mean diameter about of 15 nm, at a solid-state and good size for biological applications in aqueous dispersion, the average hydrodynamic sizes of these NPs were about 80 nm and has a superparamagnetic behavior at room temperature and the residual magnetization and coercive force were found to be zero. The titration with 5,5′-dithiobis (2-nitrobenzoic acid) molecule (DTBN) was used to quantify free thiol (-SH) groups on the surface of nanoparticles, we found a value of (0.122 ± 0.06) mmol.g−1 of -SH in Cys-Fe3O4. To evaluate their applicability in nanomedicine we evaluated their toxicity using Balb/C mice. Taken together the results suggest that coating magnetite nanoparticles with CYS lead to the formation of a stable aqueous dispersion of thiolated superparamagnetic nanoparticles synthesis was well succeeded which shows great potential as biomedical vehicle. 1 P.S. Haddad, T.N. Britos, L.M. Li, L.D.S. Li. Journal of Physics. Conference Series, v. 617, p. 012002, (2015). 2 T.N. Britos, C.E. Castro, B.M. Bertassoli, G. Petri, F.L.A. Fonseca, F.F. Ferreira, P.S. Haddad, Mater. Sci. Eng. C 99, 171 (2019).

PMMA and PVDF luminescent films containing Eu(III) and Tb(III) tetrakis complexes as candidates for phosphor-converted UV LED application

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Ariane Caroline Ferreira Beltrame [1]; Felipe Canisares [2]; Airton Germano Bispo Júnior [3]; Edson Laureto [4]; Sergio A Marques de Lima [2]; Ana Maria Pires [2]

[1] Instituto de Biociências, Letras e Ciências Exatas / Universidade Estadual Paulista “Júlio de Mesquita Filho”; [2] Faculdade de Ciências e Tecnologia / Universidade Estadual Paulista “Júlio de Mesquita Filho”; [3] Universidade Estadual de Campinas; [4] Universidade Estadual de Londrina

In the search for lighting devices application, the aim of this study was the synthesis and characterization of films via the drop-casting method based on tetra substituted complexes of europium(III) with dibenzoylmetanate (Hdbm), for red emission, and terbium(III) with acetylacetonate (Hacac), for green one, using the polymers polymethyl-methacrylate (PMMA) and polyvinylidene fluoride (PVDF). The tetrakis complexes Q1[Eu(dbm)4], where Q1 = Didodecyldimethylammonium (C26H56N+) and Na[Tb(acac)4] were successfully obtained without water molecules in the coordination sphere, having their molecular properties and structural (FTIR, TGA, MALDI-TOF, elemental analysis) and optical (UV-Vis and photoluminescence) fully elucidated. In the case of the Q1[Eu(dbm)4] complex, films supported on PMMA or PVDF, in concentrations of 0.1%, 0.25%, 0.5%, 0.75%, 1%, 2% and 5% were produced. As for the Na[Tb(acac)4] complex, for both PMMA and PVDF films, the concentrations used were 0.5%, 0.75%, 1%, 2% and 5%. All films had their luminescent properties evaluated and it was observed that the concentration of the complexes embedded in the two polymers modifies the analyzed photophysical parameters (lifetime, intrinsic quantum yield and absolute quantum yield), but not uniformly, as at high complexes concentrations tend to form clusters. Among the series of red-emitting polymeric films, both in PVDF and in PMMA, those with a concentration of 1% of the Eu(III) complex were considered the most promising candidates for manufacturing LED prototypes. In the case of green-emitting films, the 5% concentration of terbium(III) tetrakis complex results in a more suitable system to be used in the production of lighting devices. Therefore, the red and green luminescent films produced can be used to produce phosphor-converted UV LED devices.

Preparation of Li/Al layered double hydroxides (LDH) for catalytic purposes: investigation of different synthesis methods

https://proceedings.science/p/138892

Shirley Nakagaki [1]; Gabriela Bosa [2]; Fernando Wypych [3]
[1] Departamento de Química / Setor de Exatas / Universidade Federal do Paraná – Campus Palotina; [2] Universidade Federal do Paraná; [3] Universidade Federal do Paraná – Campus Centro Politécnico

The layered double hydroxides (LDHs) are materials made up by stacking layers that interact to each other by van der Waals or electrostatic interactions between the layers and ions intercalated. These structures can be thought of as a replacement of some Mg2+ cations of the neutral layered mineral brucite (Mg(OH)2) with trivalent cations, creating positively charged layers. To achieve the structure electroneutrality, the interlayer space is filled with charge compensating anions and solvation molecules, resulting in an anionic exchange layered compound, in this case an LDH. Usually the LDHs contain layers composed by divalent M2+ and trivalent M3+ metallic cations with a general formula that may be written as [M2+1-xM3+x(OH)2]x+ Am-x/m·nH2O, where Am- represents an intercalated hydrated anion with m- charge [1]. Some literature shows that LDHs may also contain M+, or M4+, but these materials are less common than the ones with di- and trivalent cations combined [1,2]. A notable example of LDH is one derived from the layered compound gibbsite (aluminum hydroxide, γ-Al(OH)3) with Li+ ions inserted in the hydroxide layers, occupying octahedral sites of the gibbsite [1,3]. That is because the gibbsite structure is dioctahedral, where one third of the octahedral sites of the layers are originally unoccupied and, in the LDH, the Li+ ions most likely occupy these vacant sites. Hydrated anions, such as halide ions, intercalate in the interlayer space, resulting in an LDH with formula [LiAl2(OH)6]A·nH2O (A = anions) [1,4]. LDHs present properties that lead to several potential uses, such as electronic, photonic, magnetic, medical and catalytic applications [1,2]. Specifically the hexagonal [LiAl2(OH)6]Cl·H2O has been reported to have potential use as a preferential ion-exchange intercalation LDH, also capable of incorporating large anions in the interlayer space, such as metalloporphyrins, what can be interesting for catalytic applications. Considering the growing development of studies on this material, in this work different conditions for the preparation of Li/Al LDH using gibbsite as Al precursor is reported. The different methods were essentially based on gibbsite heating in a LiCl solution, differing mainly in the LiCl concentration [4,5]. The solids were characterized by PXRD and other techniques in order to observe the influence of the different synthetic conditions on the LDH production. The analysis indicated that the Li-Al LDH was obtained with the method based on LiCl concentration near saturation and heating [5].

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Quimiossensores para identificar espécies tóxicas ao meio ambiente

https://proceedings.science/p/138863

Janail Rodrigues da Silva [1]; Izilda A. Bagatin [1]
[1] Universidade Federal de São Paulo

The industrialization process has increased because of the population increase, and tons of solid, liquid, and gaseous waste is produced and can cause severe environmental and human health problems if released to the environment without proper treatment1. Therefore, the search for simple methods to identify them and, if possible, extract them from the environment has become an attractive field in recent years. In this scenario, it was synthesized chemosensors to identify such hazardous species. The synthesis of 2-Bromo-N-(thiazole-2-il) acetamide (1) was made with the goal of anions interacting due to the pairs of free electrons of nitrogen and sulfur and H of group NH. The characteristic was performed employing 1H-NMR, showing the following signals: (δCDCl3 300 MHz) 4.08 ppm (s, 2H, CH2),7.08 (d, 1H, S-CH),7.55 ppm (d, 1H, N-CH) and 10.97 (sl, NH). The UV-Vis spectrum of this ligand has bands at 217 nm and 274 nm, characteristic of typical $\pi \rightarrow \pi$ * transitions. The ligand (1) was functionalized in the calixarene matrix, originating the ligand (2). The characterization of this new species was made employing 1H-NMR, showing the following signs: (δCDCl3) 1.18 and 1.25 ppm (2s, 36H, tBu), 3.54 ppm (d, 4H, Spin AB), 4.26 ppm (d, 4H, Spin AB) 4.83 ppm (s, 4H, CH2),7.06 ppm (1s, 8H, m-ArH), 7.10 ppm (d, 2H, S-CH),7.38 ppm (d, 2H, N-CH),8.83 ppm (s, 2H, OH) 12.36 ppm (sl, 2H, NH). The spectrum of UV-Vis of this composition presents bands in 272 nm, 283 nm, and 290 nm characteristics of bands of type $\pi \rightarrow \pi^*$. Ligand (1) presented a good interaction with the anions F-, Ac- and PO43- via UV-vis by decreasing 272 nm band and the emergence of 318 nm band. The hydrogen bond of the NH group with the F- anion without intermediates were observed in the spectrum of 1H-NMR. Similarly, ligand (2) with ions F- interacting was observed in approximately 303 nm. The same effect is also observed in the spectra of interaction with Acetate and dihydrogen phosphate. The ligands (1) and (2) interactions with the anion's fluoride, phosphate, and acetate are potential ionic chemosensors.

Redes tridimensionais Metal-Orgânicas baseadas em colágeno

https://proceedings.science/p/138968

Priscilla Rodrigues [1]; João Paulo de Mesquita [1]; Wanessa Lima de Oliveira [1]; Everton L. Paula [2]
[1] Universidade Federal dos Vales do Jequitinhonha e Mucuri; [2] Departamento de Ensino à Distância, UFVJM

As estruturas híbridas metal-orgânicas (MOFs, do inglês metal-organic frameworks) tem sido amplamente estudadas como material poroso para as mais diversas aplicações [1]. Dentre essas aplicações destacam-se o uso em separação, armazenamento e adsorção de gases (CO2, H2), purificação de água, sensores químicos entre outras [2]. Aqui nós reportamos sobre os estudos iniciais do desenvolvimento de redes tridimensionais metal-orgânicas baseadas em colágeno hidrolisado. A estrutura do colágeno apresenta, além dos grupos N e C-terminais, grupos funcionais nas cadeias laterais dos resíduos de aminoácidos que podem ligar-se aos íons metálicos que na presença de agentes complexantes podem formar uma rede tridimensional metal-orgânica com características únicas [3]. Os compostos baseados em colágeno foram produzidos pela adição 500 µL de solução de colágeno em água com concentração de 0,3 g/mL em 5 mL de soluções de NiSO4 e CoCl2 em etanol com concentrações de 0,1g.L-1 e 0,4g.L-1 respectivamente em temperatura ambiente por 5h. As amostras foram caracterizadas com Microscopia eletrônica de varredura (TESCAN modelo VEGA3 LMH.), Energia dispersiva de raios X e difração de raios X (SHIMADZU modelo XRD-6000). Na Figura 1 são mostradas as imagens das amostras de colágeno puro e colágeno precipitado com Ni2+ e Co2+. Como pode ser observado, a precipitação do colágeno com os metais leva a formação de aglomerados formados por partículas sem uma forma definida, principalmente na presença de do Co2+. Este resultado sugere indícios da possibilidade da formação de cristais com morfologias definida. Os resultados da composição elementar obtidos para as amostras de colágeno puro e colágeno com os metais Ni2+ e Co2+ mostram que o percentual de metal presente na estrutura do biopolímero foi muito pequeno. Em adição, nas condições experimentais realizadas, os difratogramas de raios X não mostraram alterações significativas entre a amostra de colágeno e as amostras complexadas com Ni2+ e Co2+. Os resultados iniciais mostram que a adição dos íons metálicos induz a formação de aglomerados formados com partículas ainda sem uma morfologia definida, a qual pode estar relacionada a baixa concentração dos íons metálicos na amostra. Apesar de indícios de uma possível cristalização, os resultados mostram a necessidade de uma ampla otimização da síntese, especialmente com relação a concentração dos íons metálicos.

Syntheses and structural characterization of pyridyldicarboxamide-based multinuclear copper(II) complexes

https://proceedings.science/p/138923

Ana Júlia Londero [1]; Vinícius da Silva Matos [2]; Vânia Denise Schwade [2]; Ernesto Schulz Lang [2]
[1] Universidade Federal de Santa Maria ; [2] Universidade Federal de Santa Maria

Derivatives of 1,3,4-thiadiazoles exhibit a several applications in the chemical, pharmaceutical and agrochemical industries1. The pyridine carboxamide derivatives as ligands provide several N- and O-donor sites. This fact make them attractive for the preparation of polynuclear complexes with novel structural topologies2. Such ligands in their deprotonated form generate a pincer cavity via two N-amidate groups and an anchoring pyridine ring that strongly hold a metal ion, while the thiadiazole groups are positioned to create a secondary coordination sphere3. Considering these aspects, we decided to prepare a ligand which contains a 2,6-dicarbonilpyridine ring and 5-(methylthio)-1,3,4-thiadiazole (H2L) for the preparation of multinuclear CuII complexes. The ligand was confirmed through infrared spectroscopy, single-crystal X-ray diffraction and 13C and 1H NMR. Complexes {[Cu4(μ3-OH)2(μ2-Cl)2(L)2]·2DMF} (1) and {[Cu5(μ3-OH)2(L)3(Lb)(dmf)]·DMF·H2O} (2) were obtained in N,N-dimethylformamide (DMF) solution in presence of triethylamine. In complex 2 one of the ligands suffered partial hydrolysis in the amide group, [Lb]2-. The single-crystal X-ray structures of 1 and 2 show that each copper(II) centre is five-coordinated in an approximately square pyramidal geometry.

Synthesis and characterization of new organogold(III)-dithiocarbamates as potential anticancer agents

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Ana Luiza de Andrade Querino [1]; Heveline Silva [2]
[1] Departamento de Química / Instituto de Ciências Exatas / Universidade Federal de Minas Gerais; [2] Universidade Federal de Minas Gerais

Metal-based compounds, as cisplatin and auranofin, are widely known and used for biological

applications, e.g. anticancer and antiarthritis. Gold(III) complexes are a current focus of research due to their potential anticancer activity. Structurally, a wide spectrum of gold compounds is being investigated but their mechanism of action is not fully elucidated. In the design of new bioinorganic compounds, one strategy relies on the bioactivity presented by free ligands, aiming to achieve synergy. Dithiocarbamates have been investigated for their structural versatility and broad bioactivity. They are also capable of efficiently stabilize gold(III) centers and have been useful in the synthesis of drug candidates1,2.
In this work, a series of gold(III) complexes were synthesized, combining the stabilization provided by cyclometallated C^N bonds with gold and the biological properties of the dithiocarbamate moiety. Infrared spectra are consistent with successfully synthesis of compounds. Also, elemental analyses are in good agreement with the calculated vaues. 1H, 13C and 31P NMR spectra were acquired in DMSO-d6 and complexes proved to be stable in this solvent for at least 10 days. The series is being tested in vitro against a panel of human cancer cell lines by us. Bioactive compounds will have their mode of action investigated in assays against target biomolecules, for instance DNA, GSH and BSA.

Tuning the red emission of doped iridium(III) complex in PMMA films under Near-UV to Green excitation to improve efficiency of c-Si solar cell

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Sergio A Marques de Lima [1]; Renan Silva [1]; Felipe Canisares [1]; Ana Maria Pires [1]
[1] Faculdade de Ciências e Tecnologia / Universidade Estadual Paulista "Júlio de Mesquita Filho"

Introduction: Nowadays, there is a demand to improve the efficiency of photovoltaic (PV) solar cells as they have limits on the power conversion efficiency (PCE). The PCE of c-Si PV cell is close to the theoretical maximum limit established by Shockley-Queisser [1] of 32% due to the overlap mismatch between the solar spectrum and the c Si bandgap, which higher External Quantum Efficiency (EQE) is at 1.12 eV (1,107 nm) [2]. Luminescent Solar Concentrators (LSCs) are devices coupled to PV cells capable of absorbing incident sunlight (AM1.5G) and emitting in the region in resonance with the maximum EQE [3]. Ir(III) complexes are excellent candidates for LSCs, as they exhibit high absorptivity in the UV to full visible, high quantum yield (Φ), and the excited-state population at the hybrid tuned emissive level, showing efficient luminescence in the deep-red and NIR approaching to the maximum c-Si EQE.
Complex Ir(pb): Yield (83.6%). MALDI–TOF calc/found (m/z): 883.2/883.1. UV-Vis (in DMSO 1.0x10-5 mol·L-1); □nm (ε, M-1 cm 1): 269 (42220), 307 (20147), 372 (14000), 413 (4419), 480 (1015). Quantum Yield (Φ): 24.2%.
Fabrication of PMMA films: Ir(pb) was immobilized in PMMA films varying the doping concentration by 0.10, 0.25, 0.50, 0.75, and 1.0 wt%. PMMA and the complex were dissolved in DCM, the solution was then dropped cast over a glass substrate. Films were dried at room temperature under a saturated DCM atmosphere.
Results: The structure of the complex has been confirmed and the photophysical characterizations in DMSO solution indicated suitable luminescence properties. Photoluminescence spectra of all films exhibit intense and broader excitation bands from 250-600 nm. Films were excited in the Near-UV (372 nm, Figure 2a) and in green (510 nm, Figure 2b), displaying intense emission in the deep red (600-800 nm,1.0wt%). Both excitations generate emissions with an interesting bathochromic shift of the band maximum, that varied from 630-660 nm as the doping concentration increased. We conclude that Ir(pb) complex is a promising candidate for a luminescent layer in LSC. Images of films emitting in deep red are shown in Figures 2(c) and 2(d).
Reference: [1] J. Appl. Phys. 32 (1961) 510–519. [2] ACS Appl. Mater. Interfaces, 9 (2017)

12540–12540. [3] J. Mat. Chem. A. 2 (2014) 5580–5596. [4] Bull. Chem. Soc. Jpn. 47 (1974) 767–768.

Química Medicinal - MED

A busca por inibidores da RdRp de SARS-CoV-2 em uma quimioteca com ampla diversidade estrutural: uma abordagem in silico

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Gabriel F. S. Gomes [1]; Priscila G. Camargo [1]; Kaio M. de Santiago-Silva [1]; Ana Paula S. S. Ribeiro [2]; Camilo Lima [2]; Alexandre Orsato [1]; Marcelle de Lima Ferreira Bispo [1]; Carla Cristina Perez [1]
[1] Departamento de Química / Centro de Ciências Exatas / Universidade Estadual de Londrina; [2] Departamento de Química Orgânica / Instituto de Química / Universidade Federal do Rio de Janeiro

COVID-19 (Coronavirus Disease 19) is caused by the novel coronavirus (SARS-CoV-2), which emerged in 2019 and has exceed 230 million confirmed cases and more than 4.7 million fatal victims worldwide.1 These alarming data has led efforts of the scientists around the world in the search for effective treatments and cure for this disease. Therefore, this study performed a virtual screening based on molecular docking aiming to identify inhibitors of the RNA-dependent RNA polymerase (RdRp) enzyme, a known molecular target for the treatment of COVID-19 and a keypoint in the replication and manufacturing process of new viral particles.2 LaSMMed Chemical Library counts 313 substances that were evaluated against the RdRp of SARS-CoV-2 (PDB code 7BV2, resolution 2.50 Å)2. Molecular docking was performed with GOLD v. 2020.1 program applying ASP score function and the protocol validation was made by redocking considering RMSD value < 2.0 Å (Figure 1 – A). The best compounds were selected based on the Fitness Score (FS) and their interactions with the target. After detailed analysis of the interactions, also in silico studies of ADME-Tox properties, Compounds LMed-052, LMed-250 and LMed-087, with FS between 35.5 and 30.4, presented the most relevant interactions on the active site of RdRp, mainly with nucleotides (U10, A11, A19 and U20), amino acid residues (Asp 623, Ser 682, Asp 760) and Mg2+ ions. These interactions could be helpful to reduce the enzyme's catalytic function or inhibit this target as well.

An on-flow high throughput assay to screen Leishmania donovani Nucleoside hydrolase' inhibitors

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Pamella Christina Ortega de Oliveira [1]; Millena Santana Ceroullo [2]; Mayane Barbosa dos Santos [1]; Rodrigo Costa da Silva [1]; Pedro Batalha [2]; Maria Cecília Bastos Vieira de Souza [2]; Fernanda da Costa Santos Boechat [2]; Luzineide Tinoco [3]; Gilberto Alves Romeiro [2]; Marcela de Moraes [2]
[1] Programa de Pós-Graduação em Química / Instituto de Química / Universidade Federal Fluminense; [2] Departamento de Química Orgânica / Instituto de Química / Universidade Federal Fluminense; [3] Universidade Federal do Rio de Janeiro

Acting in the formation of the parasite's DNA and RNA, the enzyme Nucleoside hydrolase (NH) plays an essential role for the protozoa survival.1 Leishmania donovani is the causative agent of visceral leishmaniasis, a lethal form of this disease that remains with few options of treatment. Therefore, it is crucial to continually search for potential inhibitors. This work proposes a high throughput assay by the direct and automated on-flow quantification of the formed hypoxanthine using a HPLC system, as shown in Figure 1. Firstly, LdNH was covalently immobilized on magnetic particles (MPs). After that, using a syringe pump, the resulting LdNH-MPs were trapped in a PTFE tube (10 cm) coupled to a magnets sequence in a quadrupole arrangement (4 units of 1 × 1cm), producing the LdNH microreactor. The following step was to optimize chromatographic conditions to separate substrate (inosine)/product (hypoxanthine). Chromatography separation of inosine and hypoxanthine was achieved by using an octyl column (Eclipse XBD C18 Agilent 5 µm, 15 × 0.46 cm) and, as the mobile phase in pump B, a solution containing triethylamine (1% in water, v/v, acidified with AcOH pH 6.0):MeOH (95:5), at flow rate 0.8 mL.min-1. For the microreactor, PBS (20 mM, pH 7.4, 300 mM NaCl) was used as mobile at a flow rate of 0.02 mL.min-1.

The developed method was validated, yielding the analytical curve (y = 16061x – 3497.3, R2 = 1). Kinetic studies furnished the Michaelis constant (KM) for the inosine substrate (2079.2 ± 87.1 µM). To validate this on-flow assay for screening purposes, a novel oxoquinoline ribonucleoside, named 17a, was evaluated. LdNH microreactor showed a concentration dependent response to this compound, with an IC50 of 42.3 ± 3.1 µM. Therefore, the proposed on-flow assay can be applied in inhibitors screening.

Carajurina: uma antocianidina da Arrabidaea chica como um potencial marcador biológico com atividade antileishmanicida

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Katia Calabrese [1]; Celeste S.f. de Souza [2]; Kerolain Faoro Teixeira [3]; João Victor Silva-Silva [4]; Carla Tellis [5]; Maria do Socorro Chagas [1]; Paulo Victor R. Souza [2]; Davyson L. Moreira [2]; Arthur Ribeiro Cenci [3]; Aldo Oliveira [3]; Fernando Almeida-Souza [1]; Maria D. Behrens [2]

[1] Fundação Oswaldo Cruz - Fiocruz; [2] Oswaldo Cruz Institute / Oswaldo Cruz Foundation; [3] Departamento de Ciências Exatas e Educação / Centro de Blumenau / Universidade Federal de Santa Catarina; [4] Laboratory of Immunomodulation and Protozoology / Oswaldo Cruz Institute / Oswaldo Cruz Foundation; [5] Departamento de Produtos Naturais / Instituto de Tecnologia em Fármacos - Farmanguinhos / Fundação Oswaldo Cruz - Fiocruz

Leishmaniasis is a group of neglected tropical diseases whose treatment with antimonials bears limitations and has changed little in over 80 years. This study examined the leishmanicidal activity of a crude extract (ACCE), an anthocyanidin-rich fraction (ACAF), and three isolated anthocyanidins from A. chica: carajurin, 3′-hydroxy-carajurone, and carajurone. We evaluated the antileishmanial activity against promastigote and intracellular amastigote forms of Leishmania amazonensis and determined cytotoxicity in BALB/c peritoneal macrophages, as well as nitrite quantification, using the Griess method. All compounds were active against promastigotes after 72 h, with IC50 values of 101.5 ± 0.06 µg/mL for ACCE and 4.976 ± 1.09 µg/mL for ACAF. Anthocyanidins carajurin, 3′-hydroxycarajurone, and carajurone had IC50 values of 3.66 ± 1.16, 22.70 ± 1.20, and 28.28 ± 0.07 µg/mL, respectively. Carajurin showed the highest selectivity and activity against the intracellular promastigote and amastigote forms of the parasite, changing all infection parameters in vitro. Molecular docking studies suggest an increase in nitric oxide production, observed in the other experiments reported, by activating nitric oxide synthetase (PDB 1DF1) by the interaction of carajurin (represented in blue) and the residues serine and arginine, as shown in figure. The results compiled in this work suggest that carajurin is a biological marker of A. chica.

CYTOTOXICITY OF NITRIC OXIDE RELEASING HYDROGEL CONTAINING HYALURONIC ACID AND SILICA NANOPARTICLES AGAINST TUMOR CELLS

https://proceedings.science/p/138881

Bianca de Melo Santana [1]; Joana Claudio Pieretti [1]; Rafael Nunes Gomes [1]; Giselle Cerchiaro [1]; Amedea Barozzi Seabra [1]

[1] Universidade Federal do ABC

Although several advances in cancer treatment has been achieved, there are many problems to overcome. In this context, several papers drescribe promising uses of nitric oxide (NO) in cancer therapies, mainly because NO actuates as a chemotherapeutic sensitizer. However, it's action is limited by time, concentration and application site. Due to its short half-life (0.5 s), NO donors species with highest stability are used to carry and delivery NO, such as S-nitrosothiols (RSNOs). RSNOs have been incorporated into polymer matrices to enhance the sustained NO release. Hyaluronic acid (HA) have been used to cancer targeting therapies, because of its strong affinity to the CD44 glycoprotein, overexpressed in cancer cells membrane. Also, silica nanoparticles (SiO2 NPs) have been shown to be an excellent drug carrier, due to their porosity that allows the incorporation of chemotherapeutics, for example. Thus, the aim of this study was to synthesize, characterize and evaluate the cytotoxicity of NO releasing Pluronic-F127 hydrogel containing hyaluronic acid and SiO2 NPs against tumor cells. Firstly, SiO2 NPs were synthesized and chacarterized by several techniques. The obtained nanoparticles showed an average hydrodinamic size of 197.53 ± 6.0 nm, polydispersity index of 0.144 ± 0.044 and a zeta potential of -27,37 ± 0.51, indicating stability in aqueous suspension. After, reduced glutathione was nitrosated leading to the formation of S-nitrosoglutathione (GSNO), the NO donor. GSNO was incorporated to Pluronic-F127 hydrogel, as well as SiO2 NPs and HA. The kinetics of NO release from hydrogel matrix revealed a spontaneuos and sustained release of NO at milimolar range for at least 24h under physiological temperature. The cytotoxicity of the hydrogel was evaluated against epithelial adenocarcinoma cells (MDA-MB-231), which are highly aggressive, invasive and poorly differentiated. Results showed a concentration-dependent cytotoxicity (1000 to 3000 µmol L-1 in terms of GSNO). Interestingly, treatments with GSNO and SiO2 almost halved cell viability when compared to treatments without these compounds over 1000 µmol L-1, highlighting the potential uses of this drug delivery system for anticancer therapies.

Descoberta de potenciais inibidores da protease principal (Mpro) do SARS-CoV-2 por meio de triagem virtual baseada em docking molecular e estudos in silico ADME-tox

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Kaio M. de Santiago-Silva [1]; Ana Paula S. S. Ribeiro [2]; Priscila G. Camargo [1]; Gabriel F. S. Gomes [1]; Alexandre Orsato [1]; Carla C. Perez [1]; Camilo Lima [2]; Marcelle de Lima Ferreira Bispo [1]

[1] Departamento de Química / Centro de Ciências Exatas / Universidade Estadual de Londrina; [2] Departamento de Química Orgânica / Instituto de Química / Universidade Federal do Rio de Janeiro

The coronavirus disease-2019 (COVID-19) pandemic, caused by the novel SARS-CoV-2 (severe acute respiratory syndrome-coronavirus-2), was responsible for more than 225.024.781 confirmed cases of infected people and 4.636.153 deaths worldwide, being the biggest public health crisis today.1. Faced with the need for new drugs to combat COVID-19 this study employed a virtual screening approach based on molecular docking to identify possible inhibitors for SARS-CoV-2 Mpro, an important

molecular target for viral replication.2 Therefore, the LaSMMed Chemical Library of 313 compounds were evaluated against two tertiary structures of SARS-CoV-2 Mpro obtained from RCSB PDB server (6LU72 and 6Y2F3). The molecular docking simulations were carried out with Autodock Vina and Autodock 4.2 and the best compounds were selected by averaging binding affinity score (kcal/mol). The LMed-136, LMed-137, LMed-110, and LMed-117 showed averaging score between -8.250 - -8.010 kcal/mol. These compounds showed H-bond interactions mainly with His164, Glu166, and Gln189, important amino acid residues present at the active site that can contribute to Mpro inhibition (Figure 1). The drug-likeness, oral bioavailability, toxicity, and hepatotoxicity were evaluated using the SwissADME and the OSIRIS Property Explorer. The prediction of the ADMET profile suggested that LMed-136 and LMed-137 have drug-like characteristics without toxicity and better pharmacokinetic properties. Therefore, the present study suggests that these compounds could be inhibitors of SARS-CoV-2 Mpro.

DESENVOLVIMENTO DE INIBIDORES ENZIMÁTICOS MULTIALVO PARA O TRATAMENTO E VÍTIMAS DE ACIDENTES OFÍDICOS: EXPLORANDO SERINA PROTEASES

https://proceedings.science/p/138895

SARAH LOUZADA [1]; Carlos Sant Anna [1]; Arthur Kummerle [2]
[1] Universidade Federal Rural do Rio de Janeiro; [2] Programa de Pós-Graduação em Química / INSTITUTO DE QUÍMICA / Universidade Federal Rural do Rio de Janeiro

Snakebite poisonings are currently considered neglected tropical diseases by the World Health Organization (WHO), affecting up to 2.7 million people annually. Among the main components of snake venom, there are serine proteases (SP), metalloproteases (MP) and phospholipases A2 (PLA2), which work together to cause the venom's severe toxic effects. In this work, we studied a group of semicarbazones and thiosemicarbazones of general structure shown in figure 1, which have been previously shown by us1 to present inhibitory activity on an isolated Bothrops pauloensis venom's MP, in addition to anti-hemorrhagic in vivo effect. The objective of the present work is to evaluate by theoretical methods the possibility of these compounds acting also as SP inhibitors, proposing structural changes if necessary. The target SP is from B. jararaca whose sequence was collected on the UniProt Knowledgebase server (UniProtKB), code P81661. A 3D model of the enzyme was made by homology modeling on the Swiss-Model server. The compounds were constructed and energy-minimized with the PM6 semi-empirical method of Spartan'14 (Wavefunction, Inc.). They were then used for a molecular docking study with GOLD 5.7 (CCDC) to determine probable interaction modes with the SP model. The Deep View 4.1 program was then used to select the binding site containing the ligand molecules. Enthalpies of the ligand, empty site and enzyme-ligand complex were calculated for these simplified systems with Mopac2016 and the results were used to calculate the interaction enthalpy (ΔHint). This process was carried out considering the system in an aqueous environment with a continuum model. The results obtained so far are very promising and indicative of favorable interactions between candidate inhibitors and the target SP site. Table 1 presents the five best candidates as SP inhibitors, considering the value of ΔHint in the aqueous environment, where all studied molecules have shown favorable results. Since 5a is also an inhibitor of a snake venom's MP, this result is indicative of a possible dual MP/SP inhibitor profile for this compound.

Docking and molecular dynamics of phythochemicals from Hypericum perforatum and Banisteriopsis caapi in the treatment of depression

https://proceedings.science/p/138880

Micael Davi Lima de Oliveira [1]; Kelson Mota T Oliveira [1]; Jonathas Nunes da Silva [1]
[1] Universidade Federal do Amazonas

Depression is a disease that affects millions of people but unfortunately is neglected. In addition, many drugs have the risk of dependence or do not show remission of symptoms, which poses major challenges for science. Thus, we seek through theoretical approaches of docking and molecular dynamics to understand the mechanism of the compounds that make up St. John's wort and the tea known as Ayahuasca. Docking protocols were determined using the GOLD genetic algorithm (version 5.8.1). All receptors were previously prepared using the Schrodinger Maestro 2021-2 software, where the missing hydrogen atoms in the structures were added. We exploit all the conformational degrees of freedom of the ligand along with the partial flexibility of the protein in the amino acids closest to the binding site. Among the functions available in GOLD, the ChemPLP empirical scoring function was used. We performed Molecular Dynamics (MD) simulations using the Desmond algorithm integrated to the Schrodinger Maestro 2021-2 software. We used the integration time at 2 fs so that the trajectories were produced over 10 ns. Initially, we performed the docking with drugs of reference and already consolidated in the treatment of depression, such as escitalopram and aripiprazole. In this we obtained the value of -79.8967 kcal/mol for the 5-HT1B receptor (PDB ID: 4IAQ) when interacting with escitalopram, while aripiprazole presented -89.6657 kcal/mol with the same receptor. From the simulations, we came to important indications that the compound Adhyperforin from the species Hypericum perforatum expresses great affinity with 5-HT1B, where we obtained an affinity of -94.7333 kcal/mol. On the other hand, N,N-Dimethyltryptamine from the species Banisteriopsis caapi appeared not interacting remarkably with 5-HT1B and 5-HT1A (PDB ID: 7E2Z) receptors with affinity value of -54.0776 kcal/mol and -44.0687 kcal/mol, respectively. From the molecular dynamics, we noticed a predominance of structural stability in the complex with Adhyperforin, measured by low values of protein RMSD (4.541Å), RMSF (1.779Å) and Radius of Gyration (27.439Å), which reflects a greater interaction in the protein-ligand complex. In addition, we found that the amino acid Trp48 was predominant in the interaction between Adhyperforin and the 5HT-1B receptor. This behavior not occurred in the ligand N,N-Dimethyltryptamine with not so expressive affinity for the 5HT-1B receptor with protein RMSD (7.584Å), RMSF (11.542Å) and Radius of Gyration (27.688Å) with many fluctuations. Therefore, reinforcing the data in the literature that its main mechanism of action of N,N-Dimethyltryptamine is in the interaction with the MAO enzyme. Therefore, the plant St. John's wort, in addition to being easily found, has great theoretical potential with central nervous system receptors and antidepressant effect.

Drug repurposing and computational modeling for discovery of inhibitors of the main protease (Mpro) of SARS-CoV-2

https://proceedings.science/p/138852

Fábio Alberto de Molfetta [1]; José Silva [2]
[1] Instituto de Ciências Exatas e Naturais / Universidade Federal do Pará; [2] Universidade Federal do Pará

The main protease (Mpro or 3CLpro) is a conserved cysteine protease from the coronaviruses and started to be considered an important drug target for developing antivirals, as it produced a deadly outbreak of COVID-19. Herein, we used a combination of drug reposition and computational modeling approaches including molecular docking, molecular dynamics (MD) simulations, and the calculated binding free energy to evaluate a set of drugs in complex with the Mpro enzyme. Particularly, our results show that darunavir and triptorelin drugs have favorable binding free energy (-63.70 and -77.28 kcal.mol-1, respectively) in complex with the Mpro enzyme. Based on the results, the structural and energetic features that explain why some drugs can be repositioned to inhibit Mpro from SARS-CoV-2 were exposed. These features should be considered for the design of novel Mpro inhibitors.

Estudo das interações entre o disruptor endócrino glifosato (e seus metabólitos) e três receptores hormonais

https://proceedings.science/p/138874

Milton Alves [1]
[1] Universidade de São Paulo

Glyphosate is the most used herbicide worldwide1 and, consequently, there is various concerns about its use worldspread and its effects in the human body, especially in the hormonal pathways. Some experimental data indicates that glyphosate have indeed a disruptor action2,3. However, its mode of action is not yet well documented4. So, this study has the objective to better understand the interaction between the glyphosate and its possible metabolites onto the three hormonal receptors: estrogen receptor alpha (ERα), estrogen receptor beta (ERβ), and androgen receptor (AR). First, we used the software GloryX5 to find possible metabolites of glyphosate, because the toxicity related to this chemical may be associated with a metabolite instead of itself. Afterwards, we performed redocking and docking simulations, using the GOLD software6, to analyze the main interactions between glyphosate and the metabolites. Finally, we carried out calculations on ADMET properties of these molecules using the software SwissADME7. From the obtained results, we can conclude that the glyphosate has a week and unstable interaction at the three LBDs of the different receptors under study. Furthermore, glyphosate also has a high-predicted clearance in human body, which may reduce the time of circulation in the organism.

Estudo de docking molecular e síntese de aceptores de Michael dipeptídeos miméticos com potencial atividade antiviral

https://proceedings.science/p/138932

Ruth Pereira Paulino [1]; Rossimiriam Freitas [1]; Rosemeire Brondi Alves [1]
[1] Universidade Federal de Minas Gerais

Devido à recente epidemia mundial causada pelo novo coronavirus, SARS-CoV-2, diversos estudos surgiram com o intuito de combater o vírus causador da COVID-19. Uma das estratégias planejadas consiste na inibição da proteína principal (Mpro) do vírus por substâncias que possam realizar interações com o resíduo de cisteína e, assim, diminuir a sua taxa de replicação. Neste contexto, a ferramenta de docking molecular surge como uma alternativa para prever quais interações entre a Mpro e ligantes terão maior afinidade, a partir de um score de interação. Um estudo publicado em 2020

indicou que aceptores de Michael seriam capazes de realizar uma ligação covalente com o resíduo de aminoácido (Cys145) presente na proteína principal do vírus. No presente trabalho, foi realizado um estudo de docking molecular entre a Mpro do SARS-CoV-2 e 15 novos dipeptídeos derivados da isoleucina, com o objetivo de analisar a força da interação entre o par proteína-ligante frente a um inibidor já conhecido na literatura (N3).

Estudo de seletividade in silico de tiossemicarbazonas frente às metaloproteases MMP9 e MMP1

https://proceedings.science/p/138943

Bruno H. M. Mendes [1]; Carlos Sant Anna [1]; Arthur E. Kümmerle [1]
[1] Universidade Federal Rural do Rio de Janeiro

Metaloproteases de matriz ou MMP são uma família de 25 endopeptidases dependentes de zinco altamente similares entre si, responsáveis pela degradação dos componentes da matriz extracelular. Seu envolvimento com doenças como câncer, artrite e doença obstrutiva pulmonar crônica faz com que essa classe seja um alvo promissor para o desenvolvimento de fármacos. O objetivo deste trabalho é utilizar métodos teóricos para estudar os modos de interação proteína-ligante entre uma série de tiossemicarbazonas (TSC) (figura 1) sintetizadas pelo nosso grupo, as quais tiveram ação inibitória contra outro grupo de MPs, no intuito de projetar novos inibidores seletivos. Para tal, utilizou-se duas MMPs neste estudo, a MMP1 e a MMP9, pois sabe-
se que a inibição simultânea das MMPs causa efeitos adversos como a síndrome muscoesqueletal e inflamações. As estruturas das TSC foram construídas com o programa Spartan'14 (Wavefunction,Inc) e suas energias foram minimizadas usando o método semi-empírico PM6. As estruturas cristalográficas da MMP9 e MMP1 (código no PDB 1GKC e resolução de 2,3 Å, e 1HFC, 1,5 Å, respectivamente) foram usadas em um procedimento de docagem molecular com o programa GOLD 2020 (CCDC). Em seguida, procedeu-se a docagem em triplicata dos compostos no sítio catalítico das MMPs com a função GoldScore (RMSD= 0,52 Å para MMP9 e 0,57 Å para MMP1, para os ligantes co-cristalizados) usando o cátion Zn2+ como centro da cavidade de interação, de raio 10 Å. Os valores médios da triplicata da pontuação estão descritos na tabela 1. Pode-se observar que os compostos 23, 24, 25, 26 e 27 possuem maiores valores de pontuação frente à MMP9 quando comparados com a MMP1, o que pode indicar um perfil de inibição seletivo para MMP9. Nota-se que a adição de grupos substituintes na fenila desfavorece a interação com a MMP1. Analisando os sítios em que as moléculas se ancoram (S1’), observa-se que a MMP1 possui um sítio de volume menor que o da MMP9, o que confere impedimentos de caráter estérico no caso da primeira enzima, explicando os resultados obtidos.

Expedient Microwave-Assisted Synthesis of Bis(n)-Lophine Analogues as Selective Butyrylcholinesterase Inhibitors: Cytotoxicity Evaluation and Molecular Modelling

https://proceedings.science/p/138877

Viktor Saraiva Câmara [1]; Brunella Biscussi [2]; Ana Julia Soares [1]; Isabella Alvim Guedes [3]; Laurent Dardenne [3]; Ana Paula Murray [4]; Aline R. Zimmer [1]; Thaís Ruaro [1]; Marco Antonio Ceschi [1]

[1] Universidade Federal do Rio Grande do Sul; [2] Departamento de Química / Intituto de Química del Sur / Universidad Nacional del Sur; [3] Laboratório Nacional de Computação Científica (LNCC); [4] Intituto de Química del Sur / Universidad Nacional del Sur

In the brain of patients with chronic Alzheimer's Disease (AD), the butyrylcholinesterase (BuChE) levels rise while the acetylcholinesterase (AChE) levels decrease.1 Therefore, development of new selective BuChE inhibitors is of vital importance.2 In this work, a series of bis(n)-lophine analogues was designed to have two lophine derivatives connected by a methylene chain. The bis(n)-lophine analogues were synthesized through one-pot four component reaction between pyridinecarboxaldehydes, 1,n-alkanediamines, benzil, and ammonium acetate. The reactions were performed in a microwave reactor in one step for symmetrical bis(n)-lophines, and in two steps for unsymmetrical bis(n)-lophines. The inhibition was found to be highly selective to BuChE since none of the bis(n)-lophine analogues were active against AChE, at the tested concentrations. The compounds displayed potent inhibitory activity against BuChE at a micromolar and sub-micromolar range (IC50 32.25–0.03 µM). The enzyme kinetic and docking studies suggest that the compounds act as a dual binding site inhibitors, binding into the bottom of the gorge and in the peripheral anionic site (PAS) of BuChE cavity. The bis(n)-lophine analogues were evaluated for their cytotoxicity against cellular models of VERO (kidney), HepG2 (hepatic), and C6 (astroglial) cell lines, which are widely used as experimental models for seeking information about nephrotoxicity, hepatotoxicity, and neurotoxicity, respectively. The compounds tested showed no or slightly cytotoxic effects in all cellular models.

In silico and in vitro Analyses Using a Set of Neolignans from N. leucantha

https://proceedings.science/p/138915

Sheila Cruz Araujo [1]; Thais Costa-Silva [2]; Simone dos S. Grecco [3]; Fernanda Sousa [4]; André Gustavo Tempone [5]; Joao Lago [1]; Kathia Maria Honorio [6]

[1] Universidade Federal do ABC; [2] Center of Natural Sciences and Humanities / Universidade Federal do ABC; [3] Biotechnology and Innovation in Health / Universidade Anhanguera de São Paulo; [4] Instituto de Ciências BIológicas / Universidade Federal de Minas Gerais; [5] Centro de Parasitologia e Micologia / Adolfo Lutz / Adolfo Lutz; [6] Universidade de São Paulo

In the present study, the phytochemical study of the n-hexane extract from flowers of Nectandra leucantha (Lauraceae) afforded six known neolignans (1–6) as well as one new metabolite (7), which were characterized by analysis of NMR, IR, UV, and ESI-HRMS data. The new compound 7 exhibited potent activity against the clinically relevant intracellular forms of T. cruzi (amastigotes), with an IC50 value of 4.3 µM and no observed mammalian cytotoxicity in fibroblasts (CC50 > 200 µM). Based on the results obtained and our previous antitrypanosomal data of 50 natural and semisynthetic related neolignans, HQSAR, CoMFA and CoMSIA techniques (Table 1) were employed to help the design of new neolignan-based compounds with higher activity. The results obtained from the models were important to understand the main structural features related to the biological response of the neolignans and to aid in the design of new neolignan-based compounds with better biological activity.

In silico comparative approach among caissarone, caffeine and other human A2A receptor ligands

https://proceedings.science/p/138862

Camila Fonseca Amorim da Silva [1]; Tânia Araújo Viel [1]; Kathia Maria Honorio [1]
[1] Universidade de São Paulo

This study investigates the main protein-ligand interactions between human adenosine receptor subtype A2A (hA2Ar) and caissarone, caffeine, besides other hA2Ar ligands. In the central nervous system (CNS), hA2Ar is highly expressed in basal ganglia. The receptor is activated by adenosine, a negative modulator of dopaminergic signaling, involved in sleep regulation and memory retention; hA2Ar is up-regulated by adenosine in CNS complications. Conversely, hA2Ar can be inhibited by antagonists that block the basal ganglia indirect pathway, increasing dopaminergic signaling and resulting in wakefulness and improved memory. Certain molecules are hA2Ar inhibitors, such as caffeine, and have been studied against some neurological diseases due to neuroprotective properties. Other compounds have also been explored, namely, caissarone, found in Bunodossoma caissarum. Therefore, comparisons among caissarone and other hA2Ar ligands were performed in this work to understand their binding characteristics and evaluate the biological potential of caissarone comparatively to more known compounds (Figure 1). For this, docking simulations using GOLD and calculation of ADMET properties for these molecules were carried out. All the molecules under study shared some superposition on the binding site of the studied target, particularly caffeine and caissarone. Moreover, caissarone seems to be similar to caffeine regarding blood-brain barrier (BBB) permeability and interactions with hA2Ar. Although caissarone shares structural similarities with caffeine, it might demand structural optimization and/or a specific formulation to enhance desirable attributes and minimize toxicity risks, so that it can be further explored in future studies.

In silico methods applied to understand toxicological properties of amphetamine-like within the forensic issue

https://proceedings.science/p/138914

Caio Henrique Pinke Rodrigues [1]; Aline Bruni [1]; Jade Castro [1]; Eduardo de Melo [2]
[1] Departamento de Química / Faculdade de Filosofia, Ciências e Letras de Ribeirão Preto / Universidade de São Paulo; [2] Universidade Estadual do Oeste do Paraná

In the forensic context, there are many challenges concerning new psychoactive. The lack of data can affect characterization and risk assessment. With the increase of new structures over the years, experimental procedures cannot provide data about them. The use of in-silico methods has proven to be an essential ally to supply information more quickly about these compounds. This work used free and paid software to obtain toxicological information and physical-chemical properties about amphetamine-like structures. We applied unsupervised (Principal Component Analysis - PCA) and supervised (Soft Independent Modeling of Class Analogy - SIMCA) to evaluate data. As a main result, we observed that both chemometric tools were able to identify different classes regarding amphetamines and cathinones. PCA showed solubility indicators as an important role in discriminating amphetamines and cathinones. SIMCA methods reproduced those clusters observed in PCA. Solubility indicators also showed the most discriminating power. However, results for classification reported similar behavior for some molecules in different classes, indicating that there are structures that can be confused regarding toxicological and physical-chemical properties. It can provide a warning about molecules, showing that they need careful

attention when evaluated. These results can drive decision-making about these substances, guiding public policies regarding the prohibitions and actions aimed at medical intervention in critical cases of abuse.

Modelagem Molecular na busca de moléculas ativas frente ao Covid-19

https://proceedings.science/p/138875

Julliane Yoneda Huguenin [1]; Izabella Rodrigues [1]; Yuri Marques [1]
[1] Universidade Federal Fluminense

The Covid-19 pandemic, caused by SARS-Cov-2, is responsible for millions of deaths worldwide. Despite vaccines has already been developed, until date there is no specific therapeutic agent for this disease and hence, the scientific community is searching for potential antiviral agents against this virus. The main protease (Mpro) of SARS-Cov-2 is considered one of the important drug targets for treating Covid-19, since it plays a crucial role in the viral replication and transcription. A recent study showed that anisotine (1), which is one of some alkaloids from Justicia adhatoda and exhibits antiviral activity against herpes simplex virus (HSV), should be a potent Mpro inhibitor according to docking and molecular dynamic studies. In the present work, comparative molecular docking simulations of anisotine (1) and four oxoquinoline-acylhydrazone derivatives (2-5), were carried out in order to access their binding properties in the proposition of new potential candidates to Mpro inhibitors. Compounds 2, 3 and 4 have already been synthesized and showed anti-HIV-1 activity. They also have been tested in silico against HSV-1 DNA polymerase by our group, and compound 5 was proposed as a potential candidate to be a dual anti-HIV/HSV agent.
The outcomes of the docking generated by AutoDock Vina revealed that compound 4 has a good binding affinity with Mpro (-7,8 kcal/mol) when compared to anisotine (-7,9 kcal/mol). Furthermore, both of them interact with the catalytic residue Cys145. In addition to that, compound 4 had a higher number of intermolecular hydrogen bonds than anisotine, suggesting that it is a potential candidate to Mpro inhibitor such as anisotine. Analyzing the binding mode of compound 4 into the active site of Mpro, it was found that it interacts with at least three subsites similarly to Mpro's substrate. The pharmacokinetic properties were evaluated using SwissADME online server and showed that none of the four compounds studied had Lipinski's rules violation, which means that they probably will have good oral bioavailability.

Molecular Modeling and Virtual Screening studies of potential inhibitors of SARS-COV-2: a multi-target approach

https://proceedings.science/p/138876

Amanda Moraes Vitor Pinto [1]; Joyce Sobreiro Francisco Diz de Almeida [1]; Tanos Celmar Costa França [1]; Samir Frontino de Almeida Cavalcante [2]
[1] Instituto Militar de Engenharia; [2] Instituto de Defesa Química, Biológica, Radiológica e Nuclear - IDQBRN, Centro Tecnológico do Exército - CTEx

In 2019, a new virus strain belonging to the Coronavirus family was detected in the Wuhan province, China1. The virus, named SARS-CoV-2, causes a severe acute respiratory syndrome, and has infected thousands of people around the world in a short period of time, prompting the World Health

Organization (WHO) to declare a pandemic state in early 20202. Since than immense efforts have been directed world wide to the development of vaccines and the discover of potential drugs against COVID-19. On the context of drug discovery, the repositioning of approved drugs available in commercial libraries sounds like the fastest way to achieve an efficient anti COVID-19 drug. Following this approach, we performed in this work, receptor-based virtual screening (RBVS) of a library of 51 derivatives of rilpivirine, chloroquine, cinnamic acid and isatin on several molecular targets of SARS-CoV-2(PDB codes: 6LU7, 6M03, 6M17, 6NUR, 6W9C e 6W4C). Using the software Molegro Virtual Docker®, the region of interest of each target was initially identified according to the cavity with greatest volume, and then the 25 poses with lower energy and higher number of interactions with each region of interest were selected. Results showed that among all ligands, those that are derived from isatin presented the best results against all selected targets.

Pharmacophore-based virtual screening of New Delhi Metallo-β-lactamase1 (NDM-1) inhibitors.

https://proceedings.science/p/138953

Catharine Teles Amorim Coelho da Silva [1]; Humberto de Freitas [1]
[1] Universidade Federal da Bahia

New Delhi Metallo-β-lactamase 1 (NDM-1), an enzyme that catalyzes the inactivation of β-lactam antibiotics, is one of the main causes of bacterial resistance due to its widespread worldwide and lack of clinically useful inhibitors. Aiming at screening NDM-1 inhibitors, we created pharmacophoric models from 110 molecules evaluated against the enzyme (IC50 from 0.5 to > 300 μM) previously cataloged. The 19 most potent and structurally different molecules (training set) were aligned to an inhibitor structure (IC50 = 4.6 uM) co-crystallized with NDM-1 (PDB: 6LJ1) in the Surflex-Sim module (Sybyl-X 2.1) and submitted to the Pharmagist server for generation of pharmacophoric models. The remaining molecules (test set) were used to create decoys and models evaluation. A total of 20 models were generated and evaluated on the Pharmit server, 10 models showed acceptable predictability (MCC > 0), performance (AUC ≥ 0.64), and enrichment factor (EF100% > 10). The best model (MCC = 0.18, EF100% = 15.4 and AUC = 0.81) identified 42% of potent inhibitors (IC50 < 10 uM) and only 8% of inactive molecules (IC50 > 300 uM). For virtual screening, the best model identified 603 drug-like compounds (0.001% from the ZINC and Mcule database). According to principal component analysis (PCA), only 17 molecules have physicochemical and topological features similar to the most potent NDM-1 inhibitors (IC50 < 2 uM). Screened molecules will be evaluated in vitro using phenotypic and enzymatic assays. The steps from the model's generation to the molecule's selection are depicted in Figure 1.

Purine nucleoside phosphorylase-coated magnetic particles for a new ligand screening assays

https://proceedings.science/p/138955

Isabella Sant'Anna [1]; Renato Lessa [2]; Walter de Souza [1]; Rafaella Aredes [1]; Marcela de Moraes [1]
[1] Universidade Federal Fluminense; [2] Programa de Pós-Graduação Mestrado e Doutorado / Universidade Federal Fluminense

Purine nucleoside phosphorylase (PNP) plays a central role in purine recycling and salvage pathway and has been considered an attractive chemotherapeutic target for several diseases. In this work, PNP from Mycobacterium tuberculosis (MtPNP) was covalently immobilized on magnetic particles and employed in the development of activity- and affinity-based assays. In the activity-based assays, the quantification of the formed hypoxanthine was conducted by LC-DAD to monitor the MtPNP activity. The immobilized MtPNP retained its catalytic activity for over six months. The KM values for the substrates inosine and phosphate were assessed (88.7 ± 9.24 µmol.L-1 and 1853 ± 52.87 µmol.L-1, respectively). In the inhibition assays, a fourth-generation Immucillin derivative (DI4G), a known inhibitor of other PNPs, was used to validate the use of this assay for screening purposes. It was determined IC50 value for this inhibitor of 9.14 ± 1.2 nmol.L-1, with concentration-dependent response through a competitive inhibition mechanism. Ligand fishing assay, an affinity-based screening model, was developed using DI4G as a probe to modulate the optimal experimental conditions. An UHPLC-MS/MS method was developed and validated to quantify isolated DI4G. The established ligand fishing assay conditions were: 12.5 µg of the MtPNP-coated magnetic beads were incubated with the probe for 1 minute, and the retained ligands were eluted with 5 mM ammonium acetate pH 7.4: acetonitrile (8:2) for 1 minute. Therefore, this study demonstrates the versatility of using magnetic particles as a solid support for the immobilization of proteins of clinical interest for the development of new screening assays.

Synthesis of anthranilic phenylhydrazides and evaluation of antileishmanial and anti-inflammatory activities

https://proceedings.science/p/138921

Evanoel Crizanto de Lima [1]; Patrick Pedro Pimentel [1]; Luiz Octavio Pereira Branco [2]; Tiago Rodrigues Navarro [2]; Barbara Hild de Jesus [3]; Edson Roberto da Silva [3]; Claudia do Carmo Maquiaveli [3]; João Pedro Barros de Paiva [4]; Millena Santos Cordeiro [4]; Patricia Dias Fernandes [4]

[1] Universidade Federal do Rio de Janeiro; [2] Laboratório de Catálise e Síntese de Substâncias Bioativas, Pólo Ajuda, Centro Multidisciplinar UFRJ-Macaé; [3] Laboratório de Farmacologia e Bioquímica, Faculdade de Zootecnia e Engenharia de Alimentos, USP; [4] Laboratório de Farmacologia da Dor e da Inflamação, Instituto de Ciências Biomédicas, CCS-UFRJ

Based in our previously results obtained with the N-acetyl α-α-difluorophenyl hydrazides series, new compounds were designed employing molecular simplification from the phenylhydrazide characterized as pharmacophoric group necessary for the antileishmanial activity. The Scheme 1 illustrates the use of the phenylhydrazide and aminophenyl groups in the new compounds suppressing acetyl and CF2 groups. These modifications left the synthesis shorter and without the need to manipulate reagents that require caution in handling like the fluorination agent DAST. The molecular simplification approach was employed as well to obtain compounds to evaluation of anti-inflammatory activity.
Anthranilic hydrazides were prepared using experimental procedure previously reported in which improvements were achieved. The reactions were carried out without the use of catalyst and good yields were obtained (45-80%). In a screening of L. amazonensis, promastigote cultures all compounds showed inhibition above 50% at 100 µM. We then screened again at 10 µM and selected four compounds to determine the IC50. However, INL09 showed myelotoxicity in an animal model performed at UFRJ. Thus we determined the IC50 for compounds INL07, INL18 and INL22. Compound INL22 was the most potent with an IC50 of 1.3 µM. Promastigote culture test results showed that the anthranilic hydrazides series were superior to the prototypes α-α-difluorohydrazides compounds. Additionally INL06 and INL07 inhibited leukocyte migration at 30 and 100 µmol/kg doses. Preliminary data suggest these compounds as promisors to further evaluation.

Triagem virtual de flavonoides na busca por estruturas antimaláricas

https://proceedings.science/p/138928

Adriana Fernandes [1]; Marcus Batista [1]; Ricardo P. Rodrigues [2]; Juliane Xavier dos Santos [1]; Aurélia Santos Faraoni [1]; Tiago Branquinho Oliveira [3]
[1] Universidade Federal de Sergipe; [2] Universidade Federal do Espírito Santo; [3] Departamento de Farmácia / Universidade Federal de Sergipe

Malaria is an infectious disease caused by protozoa from the Plasmodium genus, with Plasmodium falciparum being the main agent of the severe cases and deaths. Although there is a wide range of drugs for its treatment, the main first-line drugs have considerable adverse effects and several reports of resistance. This might be associated with the fact that most of these compounds are of synthetic or mixed origin, which leads to the search for less expensive natural products to avoid resistance build-up. Among them, flavonoids are interesting compounds due to their diversity of biological activities, ranging from anti-inflammatory to antiparasitic. Still, little is known about the actual capacity of flavonoids to bind to Plasmodium's proteins. Therefore, the aim of this work was to perform a virtual screening of inhibitory flavonoids and assess their binding affinity with proteins from the fatty-acid synthesis pathway. The enzymes chosen as receptors were FabG, FabZ, FabI, and FP-2, as well as P. berghei's FabI, gathered on the PDB repository. The flavonoids were collected from ChEBI and Phenol-Explorer databases. We used the software GOLD to perform the redocking and docking steps based on the ChemScore scoring function. From 183 ligands, 49 showed very high scores, ranging from 27.9145 to 55.4388. Therefore, this could make them possible candidates for posterior synthesis and/or repurposing.

Química Orgânica - ORG

5-Amino-7-(trifluorometil)pirazolo[1,5-a]pirimidina: síntese mediada por líquido iônico, estudo teórico e potencial atividade antiglioma

https://proceedings.science/p/138727

Cinara Teiroba de Ávila [1]; Taís Goulart [2]; Adriana das Neves [2]; Melinda Gomes Victor [3]; Larissa de Moura [3]; Nathalia Pedra [3]; Roselia Spanevello [3]; Robson Oliboni [3]; Wilson Cunico [3]
[1] Universidade Federal de Pelotas/ Centro de Ciência Química, Farmacêutica e de Alimentos (CCQFA); [2] Universidade Federal do Rio Grande; [3] Universidade Federal de Pelotas

For optimization of reaction conditions, we prepared the pyrazolo[1,5-a]pyrimidine 3c from β-enaminone 1c and 3-amino-5-methylpyrazole 2. The best resulted was using 1 mmol of β-enaminone 1, 2 mmol of 3-amine-5-methyl-pyrazole 2 and 1 mmol the ionic liquid ([BMIM][PF6]) without a solvent at 100 ºC for 24 hours with yield in 74%. So, the pyrazolo[1,5-a]pyrimidines 3a-j were synthesized using this methodology with moderate to good yields (Scheme 1) and were characterized by CG/MS and NMR (1H and 13C).

Scheme 1

The β-enaminone 3j and the 3-amine-5methylpyrazol 2 were optimized structures of at the B3LYP/def2-TZVP of level theory and also it was calculated the reaction energy diagram to form compound 3. The obtained Gibbs free energy was not different when comparing ethanol and the ionic liquid. Thus were suggesting that there is an influence by temperature, due to the possibility of the products 3 being thermodynamic and the ionic liquid when using to promote of the mediator from reaction.
The present study showed growth inhibitory potential of four pyrazole[1,5-a]pyrimidines (3b, 3g, 3f and 3i) against C6 cells in a dose depending on dose. The results of the screening at 25, 50, 100, 175 and 200 μM in 72h, as percentage of cell viability considering the mean of DMSO control group as 100%. The compound 3i (20%) was the only one that showed statistical difference from the positive control DMS in 25 μM. However compounds 3b (30%), 3f (25%) and 3g (25%) also showed inhibitory activity on tumor cells in 100 μM. Furthermore, it was evaluated the cytotoxic effect of all compounds through the MTT assay in primary astrocyte cells. our compounds (3b, 3g, 3f and 3i) statistical differences were not found in from DMSO in 72h at 250 μM.
In conclusion, we report the synthesis of nine pyrazolo[1,5-a]pyrimidines mediated by ionic liquid in good yields and supported by computational studies, suppose that the ionic liquid is mediated by the reaction and propose a possible mechanism. Additionally, we have shown that four compounds presented antiglioma activity and low cytotoxicity to primary astrocyte cell line. These preliminary results will guide us for further modifications.

Aminocalcogenação ecologicamente correta de alcenos: uma alternativa verde para a obtenção de compostos com potencial aplicação contra a COVID-19

https://proceedings.science/p/138743

Luana da Silva Gomes [1]; José S. S. Neto [2]; Iris Di Leo [3]; Claudio Santi [4]; Vanessa do Nascimento [5]
[1] Programa de Pós-Graduação Mestrado e Doutorado / Universidade Federal Fluminense; [2] Universidade Federal de Santa Catarina; [3] Instituto de Química / Universidade Federal Fluminense; [4] Department of Pharmaceutical Sciences / Department of Pharmaceutical Sciences / University of Perugia; [5] Universidade Federal Fluminense

Organochalcogen compounds (with C-E bonds; E = S, Se and Te) have been widely studied due to the large number of synthetic and biological applications. On the other hand, the benzotriazolic nucleus constitutes a variety of compounds that also have relevant biological properties. Thus, the combination of both in the same molecule, could be a powerful alternative to achieve a promising class for treatment of various diseases.1 In this context, the chalcogenfunctionalization of alkenes, using benzotriazole as a nitrogen source, offers an excellent perspective in organic synthesis, since the products are versatile and, still, little investigated. Therefore, in this work, the objective is the regioselective aminochalcogenation of alkenes, using benzotriazole as a nitrogen source, through an environmentally appropriate methodology.
The best condition found, under microwave irradiation (MW), was 20 mol% of iodine, 2 equivalents of DMSO at 65 °C and 100 W. The desire product was obtained in 89% yield. After determining the optimized conditions, the scope and limitations of the proposed methodology were investigated. Thus, a variety of β-amino selenides, sulfides and tellurides was developed, with yields ranging from 16-89% and which can be considered a promising alternative in the development of new drugs (Scheme 1).
After successful reactions, twenty-one compounds were sent for evaluation of potential biological activity against the new coronavirus, SARS-CoV-2, and six of them presented positive results.
In conclusion, we have developed a fast and sustainable approach to the aminochalcogenation of alkenes, using an oxidative catalytic system composed of I_2/DMSO.

An ecofriendly approach for the synthesis of pyrido[2,3-d]pyrimidine derivatives

https://proceedings.science/p/138741

Luan Alves Martinho [1]; Carlos Kleber Z. Andrade [1]
[1] Instituto de Química, Laboratório de Química Metodológica e Orgânica Sintética (LaQMOS), Universidade de Brasília

The multicomponent reactions between 6-aminouracil, aromatic aldehydes, and malononitrile to yield pyrido[2,3-d]-pyrimidine derivatives were carried out in glycerol as green solvent under microwave heating (Table 1). This method provided good to excellent yields for a variety of aldehydes with electron-withdrawing substituents on the aromatic ring. Lower yields were observed for some electron-donating aldehydes. This approach has some advantages in comparison to other methods reported in the literature including shorter reaction times, easy work-up procedure and absence of volatile organic solvents.

Biomimetic Bromofunctionalization of aromatic and heteroaromatic compounds catalyzed by selenium tetrachloride

https://proceedings.science/p/138734

Bruno Rita [1]; Cristiano Raminelli [1]
[1] Universidade Federal de São Paulo

Halogenated organic compounds are versatile building blocks in preparative organic chemistry, with application in syntheses of natural products and preparations of functional materials.1 In addition, a considerable number of halofunctionalized compounds are active pharmaceutical ingredients or important substances in diagnostic medicine.2 Therefore, the development of greener methods for the halogenation of organic substances may be considered a relevant topic in preparative organic chemistry. In this context, inspired by an iodofunctionalization reaction developed in our research group,3 we are exploring the bromofunctionalization of aromatic and heteroaromatic compounds (1) employing NaBr as bromine source, H2O2 (30%) as oxidant, and SeCl4 as catalyst, in water without a co-solvent, which allowed the formation of brominated aromatic and heteroaromatic compounds (2) in yields from 51% to 98% (Table 1).
The scope of the biomimetic bromination reaction presented in Table 1 is being evaluated. Aside from brominated pyrazoles (2k-n), we intend to obtain other brominated heteroaromatic compounds.

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Catalytic Oxidative Cyclization of BINOL to Peri-Xanthenoxanthene (PXX)

https://proceedings.science/p/138731

Marcelo Cosme Vasconcelos Silva [1]; Simon John Garden [1]
[1] Universidade Federal do Rio de Janeiro

In situ generated catalytic systems based on copper or manganese salts in the presence of

N-methylimidazole (NMI) efficiently converted BINOL into PXX. Copper-based catalysts completely consumed BINOL to give PXX as the only isolable product within 3h. When the copper salt/NMI catalyst was previously prepared the reaction consumed the BINOL within 2h. The manganese catalyst was slower but also completely consumed the BINOL within 9h.

Chemoselective transfer hydrogenation of biomass derivatives for the synthesis of nitrogen compounds using Ru pincer complexes

https://proceedings.science/p/138747

Danielle Pinheiro [1]
[1] Danmark Tekniske Universitet

In this work, transfer hydrogenation catalyzed by Ru-MACHO or Ru-MACHO-BH is used for the synthesis of furfurylamines and a-amino acids in two different transformations. For both transformations, green alcohols are used as H-donor and solvent and low catalyst loading (0.5-0.1 mol%) is required. A scope of substrates demonstrates the good tolerance of the method. For the synthesis of furfurylamine is used a reductive amination from furans without the presence of base. The synthesis of amino acids was afforded from the chemoselective transfer hydrogenation of enamides using bot EtOH and iPrOH as H-donor. The one-pot version of this method and the gram scale was also demonstrated. The application of the method and mechanistic studies was also conducted.

Copalic acid as a green, raw material, waste from the Amazonian essential oils' agroindustry, for synthesis of bioactive amides

https://proceedings.science/p/138723

Yuri Campello [1]; Samir F A Cavalcante [2]; Valdir Veiga Junior [1]
[1] Instituto Militar de Engenharia; [2] Instituto de Defesa Química, Biológica, Radiológica e Nuclear (IDQBRN-CTEx)

The structural modification of bioactive molecules is explored aiming at the optimization of a specific pharmacological activity from functionalized molecules. Acid diterpenes are not commercially available and their derivatives have been little explored in studies that improve their pharmacological activity and bioavailability. The present work aimed to generate semi-synthetic amides from ACOP extracted from industrial residues from the distillation of copaiba oil in order to enhance their biological activities. For ACOP purification, extraction procedures were performed on an ion exchange column (SiOH-KOH) at different pH ranges and purification by flash chromatography was applied. Semisynthesis of the new amide derivatives of copalic acid were based on peptide chemistry by adopting stoichiometric conditions (1:2.82:3:0.1 ACOP:amine:DCC:DMAP, respectively) optimized for unprecedented use of irradiation by microwave (MW) in a sealed tube at 80°C for 15 minutes. All products obtained were isolated and satisfactorily characterized by GC-MS as shown in figure 1. Purification of amides derived from ACOP is ongoing for biological assays.

Cytotoxic activity of 4-(butylselanyl)mandelonitrile derivatives

https://proceedings.science/p/138739

Maria Clara da Silva Durigon [1]; Leandro Piovan [2]; Bruna Renata Caitano Visnheski [3]; Fernanda Simas [3]; Juliana Thomas [4]

[1] Programa de Pós-Graduação em Química / Universidade Federal do Paraná; [2] Departamento de Química/Universidade Federal do Paraná; [3] Departamento de Biologia Celular / Universidade Federal do Paraná; [4] Instituto de Química, Departamento de Química Orgânica / Universidade Federal do Rio Grande do Sul

The biological application of selenium containing organic compounds is a growing field of study, being reported a number of selenocompounds with antioxidant, anticancer, antimicrobial, among other biological activities.1,2 In this work the syntheses of selenocompounds MC03-06 were achieved using classical methodologies for the derivatization of the cyanohydrin moiety with isolated yields ranging from 26 to 68% (Figure 1). Figure 1 – Synthetic route for cyanohydrin derivates MC03-06 MC03-06 were then tested as cytotoxic agents, via neutral red uptake and crystal violet assays, utilizing BALB/3T3 fibroblasts cell line, with incubation times of 24, 48 and 72 h and concentration varying from 10 to 50 µg mL-1 in four independent studies. Results demonstrated that compounds were not cytotoxic in the tested parameters. Besides that, it was observed an increase in cell proliferation when treated with MC03 and MC04, compared with the control, as exemplified with MC03 in Figure 2. Figure 2 – Relative cell viability after 72 h of incubation when treated with 10, 20, 30 and 50 µg/mL of MC03 (a) and cell proliferation in the same parameters (b). In summary, MC03-06 demonstrated a lack of cytotoxicity in the developed assays, presenting potential for biological application including antitumoral assays. 1. Jain, V. K.; Priyadarsini, K. I. Organoselenium Compounds in Biology and Medicine; Royal Society of Chemistry, 2018. 2. Kuršvietienė, L.; Mongirdienė, A.; Bernatonienė, J.; Šulinskienė, J.; Stanevičienė, I. Antioxidants 2020, 9, 80–91.

Desenvolvimento de uma metodologia sintética one-pot para obtenção de derivados 4-oxoquinolínacarboxamídicos

https://proceedings.science/p/138756

Thiago Mota [1]; Joice Cristina Andrade [2]; Pedro Batalha [2]; Maria Cecília Bastos Vieira de Souza [1]; Fernanda da Costa Santos Boechat [3]

[1] Instituto de Química / Universidade Federal Fluminense; [2] Universidade Federal Fluminense; [3] Departamento de Química Orgânica / Instituto de Química / Universidade Federal Fluminense

As 4-oxoquinolinacarboxamidas são substâncias orgânicas, derivadas das 4-oxoquinolinas, muito utilizadas na química medicinal. O grupamento funcional carboxamida vem sendo amplamente estudados, estando presente na estrutura de 25% dos medicamentos produzidos1, ficando 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. Como resultado foram obtidos 15 derivados 4-oxoquinolinacarboxamídicos, 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.

Development of an environmentally suitable process to obtain a series of selanyl-2,,3-dihydrobenzofurans

https://proceedings.science/p/138758

Amanda Rebelo de Azevedo [1]; Vanessa do Nascimento [1]; Luana da Silva Gomes [2]; Nathália Lessa Botelho [1]; Pâmella da Silva Cordeiro [2]; Antonio Braga [3]; José S. S. Neto [4]
[1] Universidade Federal Fluminense; [2] Programa de Pós-Graduação Mestrado e Doutorado / Universidade Federal Fluminense; [3] Departamento de Química / Centro de Ciências Físicas e Matemáticas / Universidade Federal de Santa Catarina; [4] Universidade Federal de Santa Catarina

Organochalcogens and the 2,3-dihydrobenzofuran nucleus, a heterocyclic found in a large number of natural products, have been the target 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 of great interest. Thus, a new synthesis methodology for selanyl-2,3-dihydrobenzofurans was evaluated and with the optimized conditions the products were obtained with yields ranging from 44-100%. The reactions were carried out under microwave irradiation, for only 15 minutes, and performed from 1 equivalent of allylphenols/naphthols and 1.5 equivalents of diorganoyl diselenides, without the use of solvents, with 30 mol% of molecular iodine and 2 equivalents of DMSO. Finally, compared to traditional methods, the developed methodology is a simple and practical tool free of solvents, metals, for the oxycalcogenilation of 2-allyl-phenols / naphthols derivatives.

Do organochalcogenides apply for affinity chromatography applications?

https://proceedings.science/p/138763

Samuel santos de Oliveira [1]; Rodrigo Cunha [1]; Ricardo Torquato [2]; Diogo Silva [3]; Marcelo Icimoto [2]; Maria Aparecida Juliano [2]; Gustavo Nascimento [1]
[1] Universidade Federal do ABC; [2] Universidade Federal de São Paulo; [3] Instituto de Ciências Ambientais, Químicas e Farmacêuticas / Universidade Federal de São Paulo - Campus Baixada Santista

The enzymatic inhibition promoted by hypervalent species of selenium and tellurium is widely known in the literature. Thereby this work brings new perspectives for a more detailed study of the interaction between chalcogenides with thiols. To achieve this goal, it was synthesized two different classes of organochalcogenides derived from 4-(phenyltellanyl)benzaldehyde (class I and class II). Furthermore, the preparation route of the class I (no cationic ligand) ligands involved a six-step synthetic sequence in overall yields of 26% and 19%, and the Class II (cationic ligand) ligands were prepared in a two-step sequence in global yields of 43% and 22% of the selenides and tellurides, respectively. After synthesis, the ligands contain a phenylchalcogenide moiety, a polyether spacer group functionalized with an amino

group to attach it to an agarose substrate, was immobilization on to agarose as ligands in affinity chromatography affinity technique, and finally, it was demonstrated that organochalcogenide-modified agarose is a new class of functional materials for the retention and release of biothiols presenting a "catch & release" functionality

Enantioselective Bromoaminocyclization Reactions Promoted by Organocatalysts Derived from Cinchona Alkaloids

https://proceedings.science/p/138751

Jullyane Emi Matsushima [1]; Elisângela Vinhato [1]; Alessandro Rodrigues [1]
[1] Universidade Federal de São Paulo

In 2016 Pan and coworkers1 reported the development of a methodology for enantioselective bromoaminocyclization reactions of several carbamates promoted by Sc(OTf)3 catalysts. The present work aims the development of an organocatalyzed alternative to the reactions reported by Pan, considering the use of metals and the high cost of the reagents used. The optimization of the bromoaminocyclization reactions used carbamate 1 as a model and the reactions were carried out on a 0.1 mmol scale. A series of organocatalysts derived from Cinchona alkaloids had their efficiency evaluated along with the variation of temperature, solvent, concentration, and bromine source. Among the organocatalysts that were evaluated, organocatalyst I was the most efficient, in the presence of PhMe:CHCl3 (1:1) as solvent and NBS (1.2 eq.) as bromine source at -50 °C, providing exclusively the six-membered cyclic carbamate 1a with an enantiomeric excess of 60% (Scheme 1a). After the optimization step a series of structurally more complex allyl carbamates (Scheme 1b) were synthesized to evaluate the methodology. At the present moment the reaction scope is under way, and preliminary results indicated that the substituent affects the reaction regioselectivity, as carbamates 2, 3 and 12 provided the corresponding five membered heterocycle 2a, 3a and 12a in 70%, 37% and 35% respectively.

ESTUDO DA SÍNTESE DE UM ESQUELETO HÍBRIDO ESTILBENO-QUINONA VIA REAÇÕES DE MIZOROKI-HECK EM PEG-400 SOB IRRADIAÇÃO DE MICROONDAS

https://proceedings.science/p/138761

Thais Pereira [1]; Chaquip Daher Netto [1]; Felipe Demidoff [1]
[1] Universidade Federal do Rio de Janeiro

Estilbenos e quinonas são duas classes de produtos naturais bioativos, dotadas de diversas atividades biológicas, entre elas antitumoral, antiparasitária (FERREIRA, et al.)1 e antimicrobiana (SHEN, et al, 2009)2. Com base no potencial farmacológico destas substâncias, uma série de híbridos hidróxi-estilbeno-quinona foi planejada e sintetizada pelo nosso grupo de pesquisa, por meio de reações de Mizoroki-Heck entre a 3-iodolausona e uma série de estirenos (DEMIDOFF et al., 2017)3. Em ensaios farmacológicos preliminares, estes compostos exibiram atividade antimicrobiana promissora, estimulando-nos a buscar meios de otimizar sua síntese. O objetivo desse trabalho é o estudo da síntese da hidróxi-estilbeno-quinona (LQ-01) sob irradiação de micro-ondas. A otimização das condições reacionais foi realizada utilizando a 3-iodolausona e o estireno como substratos modelo. A 3-iodolausona foi obtida através da reação entre lausona e o complexo iodo-morfolina, de acordo com o método descrito na literatura, e o estireno adquirido de fontes comerciais. Ao utilizarmos as melhores condições determinadas em um estudo prévio com aquecimento convencional (3 equiv. NaOH, 10 mol% Pd(OAc)2, 90 °C, 15 min.) (DEMIDOFF et al., 2017)3, a hidróxi-estilbeno-quinona LQ-01 foi obtida sob irradiação de micro-ondas em rendimento muito inferior (59%, , versus 81%). Quando a base foi substituída por KOH, NaOAc, Na2CO3 e Et3N os rendimentos da LQ-01 foram substancialmente mais baixos (3-30%). Os melhores resultados foram alcançados com o emprego de 3 equiv. de K2CO3, produzindo a LQ-01 em 88% de rendimento. A redução da carga catalítica de Pd(OAc)2 para 5 e 1 mol% manteve o rendimento entre 55-60%. Em todos os experimentos a estilbeno-quinona foi obtida com a configuração E, confirmada através da constante de acoplamento dos hidrogênios olefínicos (d, J = 16,7 Hz em 7,97 e 7,40 ppm) no espectro de RMN-1H. Esse trabalho demonstrou que o rendimento da estilbeno-quinona em micro-ondas superou o de aquecimento convencional, apresentando um aumento no rendimento de 81% para 88%. Outro ponto importante apresentado foi que mesmo reduzindo a carga catalítica de Pd(OAc)2 para 5 e 1 mol% o produto foi obtido entre 55-60% de rendimento. Em vista disso, levando em conta o alto custo do catalisador de paládio, pode-se considerar economicamente mais vantajosa a diminuição da carga catalítica, mesmo provocando uma queda de 20% no rendimento.

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Estudos visando a síntese de biflavonoides naturais a partir de materiais de partida de biomassa

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Mauricio Victor [1]; Juliana Lago Leite [1]
[1] Universidade Federal da Bahia

A flavona crisina (1) é um produto natural obtido a partir da Passiflora coerulea (maracujá), própolis e mel, e foi obtida de fontes comerciais. Já a apigenina (3) foi obtida a partir da naringina (2) do albedo de grapefruits (Citrus x paradisi). Estes flavonoides foram protegidos como seus éteres benzílicos e metílicos, e posteriormente halogenados seletivamente nas posições C6 e C8. Estes flavonoides serão utilizados para a síntese da agastiflavona, através da borilação do flavonoide apigenina halogenada em C8, seguida de reação de acoplamento cruzado do tipo Suzuki-Miyaura. A primeira síntese total do produto natural será então alcançada pela total remoção dos protetores do tipo éter.

Experimental and theoretical studies of 1H NMR spectra of deep eutectic solvents based on quaternary ammonium salts

https://proceedings.science/p/138762

Rachel Azevedo Maia [1]; Isadora Maria Gouveia Andrade [2]; Carlos Vital dos Santos Júnior [1]; Cláudio Gabriel Lima Júnior [1]; Dayse das Neves Moreira [2]; Renaldo Moura Jr [3]
[1] Universidade Federal da Paraíba; [2] Universidade Federal da Paraíba – Campus Areia; [3] Centro de Ciências Agrárias / Universidade Federal da Paraíba

Deep Eutectic Solvents (DES) is a class of green solvents also known as 3rd generation Ionic Liquids, generally composed of a quaternary ammonium salt and one or more hydrogen bond donors that generally form liquids at room temperature with melt smaller than its individual components.[1] The interaction between DES components affects their physical properties, especially due to the presence of hydrogen bonds. However, a limited number of works have studied the theoretical aspects of those solvents. In this context, we present herein an experimental and theoretical investigation from 1H NMR spectroscopy data of different deep eutectic solvents based on the mixture of benzalkonium chloride and oxalic acid, citric acid or glycerol (Table 1). The DES were synthesized in a conventional way with heating and continuous stirring until the formation of a viscous and homogeneous liquid. The geometry optimizations, vibrational frequencies and nmr were performed for different conformations at the CAM-B3LYP/6-311++g(d,p) theory level in the Gaussian16 program. 1H NMR spectra were recorded on a Bruker Advance DPX-300 spectrometer. The results indicated that the simulated 1H NMR spectra of the optimized structure greatly reproduce the experimental spectra. In particular, the difference in the 1H NMR shift for the selected hydrogen atoms between the simulation and observation is less than 0.62 ppm.

Green Syntheis and Investigation of the Antibacterial Activity of of 5-amino-pyrazole-4-carbonitrile and its Derivatives

https://proceedings.science/p/138732

Yasmine Queiroz [1]; Loraine Morete Dutra Xavier [1]; Juliana Morais [1]; Jhonathan Santos [2]; Luciana Machado Ramos [1]
[1] Universidade Estadual de Goiás; [2] Departamento de Química / Universidade Federal de São Carlos

Pyrazoles are part of the class of aromatic N-heterocycles and have recognized biological activities such as: cytotoxic1, anticandidal2, among others3 and can be synthesized via multicomponent reactions (MCRs). In this perspective, 5-amino-pyrazol-4-carbonitrile derivatives were catalyzed by an ionically labeled synthetic enzyme (PEI.IL)4 and as a solvent if IL (BMI.BF4) (Scheme 1). Subsequently, compounds 4a-j were submitted to the broth microdilution test against S. aureus (ATCC 25923) and K. pneumoniae (ATCC 700603) strains. The developed method allowed to obtain 10 examples of 5-amino-pyrazole-4-carbonitrile derivatives with yields between 54-94%. The 4a-j derivatives showed interesting bacteriostatic activities against the strains under study and two of these derivatives with a value of 250 μg mL-1 for the S. aureus strain (ATCC 25923).

Heterocíclicos Nitrogenados de Selênio e Telúrio como potenciais agentes antivirais

https://proceedings.science/p/138753

Thiago Puccinelli [1]; Bruna Brocardo Ferreira [2]; Leandro Piovan [3]

[1] Química / Departamento de Química / Universidade Federal do Paraná; [2] Departamento de Química / Departamento de Química / Universidade Federal do Paraná; [3] Universidade Federal do Paraná

Viruses are considered infectious agents, composed of one or more nucleic acid molecules (DNA and/or RNA). A biological effect caused by these agents is oxidative stress, which causes an imbalance of reactive oxygen (ROs) and nitrogen (ERS) species. Thus, Se and Te organic compounds that have antioxidant activity can be characterized as an alternative to their therapeutic potential, and also, hypervalent compounds have a history of inhibiting several enzymes.3 Below, in scheme 1 a compilation of the results until now. The first synthetic step was a SNAr reaction employing 1 as electrophile and lithium butylchalcogenolate (BuYLi, Y = Se, Te) as nucleophile, leading to 2-(BuSe)-benzaldehyde 2 and 2-(BuTe)-benzaldehyde 3 in 65

and 25% isolated yield, respectively. Chalcogen amines 4 (Se) and 5 (Te) were obtaibed in 51 and 21% isolated yields after reductive amination of 2 and 3. Finally, SO2Cl2 oxidation-cyclization one pot reaction led to Se-N (6) and Te-N (7) heretocycles in 21 and 33% isolated yield. 2-Butylchalcogen benzaldehydes 2 and

3 were also oxidized to hypervalent congeners in 25% (Se) and 33% (Te) isolated yield, respectively. In the end, the compounds will be sent for evaluation of antiviral activity.

Metabolic fingerprinting of gastric cancer patient's tissue

https://proceedings.science/p/138726

Renato Ferreira Hosanah [1]; Priscila F. Aquino [2]; Luana Quadros de Souza Leao [1]; Wagner Moreira [1]; Sofia Angiole Cavalcante [3]; Sidney Chalub [4]; Leonardo Guimarães [5]; Luciana Fujimoto [6]

[1] Departamento de Química / Instituto de Ciências Exatas / Universidade Federal do Amazonas; [2] Research / Instituto Leônidas e Maria Deane / Fundação Oswaldo Cruz; [3] ILMD (Instituto Leônidas e Maria Deane) / Fiocruz (Fundação Oswaldo Cruz); [4] Departamento de Cirurgia Digestiva / Faculdade de Medicina / Fundação Centro de Controle de Oncologia do Estado do Amazonas; [5] Departamento de Cirurgia / Faculdade de Medicina / Hospital Universitário Getúlio Vargas (HUGV); [6] Departamento de Patologia e Medicina Legal/ Faculdade de Medicina / Universidade Federal do Amazonas

Gastric cancer is the 3rd cause of cancer-related death around the world. Its high mortality rate is due to frequent diagnosis at advanced stages and few treatment options. Metabolomics is a recent approach used in oncology to improve the molecular understanding of cancer through metabolite profile study. In this work, our objective was to analyze the metabolic profile of gastric adenocarcinoma patient's tissues using mass spectrometry. For this, we collected fresh tissue samples of the tumor, resection margins, and metastasis from surgery biopsies; then, 25 mg of tissue was macerated and submitted to extraction with methanol for 18 hours. The samples were analyzed by direct infusion in a TSQ QuantumTM (Thermo-Scientific) using electrospray ionization in positive ion mode full-scan (ESI+). The data analysis consisted of a Principal Component Analysis (PCA) and a Hierarchical Cluster Analysis (HCA). In our results, samples showed great peak intensity between 600-900 m/z region (figure 1). The hypothesis for this can be the presence of glycerophospholipids, molecules related to energy production and energy metabolism that might be associated with cell proliferation, a hallmark of cancer progression. In PCA analysis, the sample groups were distinguished (figure 2). In HCA analysis, the results also show the

tissue types being effectively differentiated (figure 3). Additionally, the tumor and metastasis samples clustered, suggesting metabolic similarities between the primary tumor and the secondary tumor sites. Thus, complementary analyzes are needed to identify the main discriminating compounds. Therefore, metabolomic analysis
using mass spectrometry, even at low resolution, can be a potential tool to improve the molecular understanding of gastric cancer.

Meyer-Schuster-type rearrangement for the synthesis of α-iodo-α,β-unsaturated thioesters

https://proceedings.science/p/138744

José Louzinho Lopes [1]; Lucas Baldassari [1]; Diogo Lüdtke [1]
[1] Universidade Federal do Rio Grande do Sul

α,β-unsaturated thioesters are valuable compound of biologically molecules that can be founded in all living organism, which is ubiquitous in biochemistry process. They are steadily gaining strong attention not only as an important biological active group, but also as an useful intermediate building block for new bond formation. Due their application in several areas, numerous methods for their preparation were developed, such as cycloaddition and olefinations. , However, many of these methods present regioselectivity problems and form complex mixture of products. In this context, Meyer-Schuster rearrangement became valuable alternative, as it favours the formation of α, β-unsaturated carbonyl compound. Recently, our research group applied the Meyer-Schuster rearrangement to transform propargyl thioalkyne in α-selanyl-α,β-unsaturated thioesters in presence of an electrophilic selenium species. Herein, we aim to explore the potential reactivity of propargyl thioalkyne for access α-iodo-α,β-unsaturated thioesters using halonium electrophilic species. Our preliminary study revealed that the employment of 5 mol % Ag2O at thioalkyne 1a, in CH3CN solvent, at room temperature (rt) and under inert environment, using N-iodosuccinimide (NIS) (1,5 equiv.), lead to formation of α-iodo-α,β-unsaturated thioesters in excellent yield (94 %). With the optimal reaction condition in hand, were synthesized 7 examples (2a-g) with good to excellent yields ranged from 52 to 94 %.

O ENSINO METODOLÓGICO DA QUÍMICA ORGÂNICA ATRAVÉS DA PLATAFORMA DIGITAL INSTAGRAM

https://proceedings.science/p/138724

Iury Garske Baum [1]; Ariele Machado [1]; Jéssica Erd [1]; Maria Nepomuceno [1]; Juliano Braun de Azeredo [1]
[1] Universidade Federal do Pampa

A química orgânica é a área de química responsável pelo estudo dos compostos que apresentam o carbono como seu principal constituinte. Esses compostos estão presentes em nosso cotidiano e conforme a evolução da ciência, sofreram modificações essenciais para a transformação social da nossa sociedade. Gradativamente, o modelo pedagógico de ensino vem sofrendo modificações, e com isso, a tecnologia se tornou uma aliada essencial no processo de ensino e aprendizagem, implementando-a na educação e possibilitando as suas diversas alternativas de aplicação. Diante disso, tem-se como objetivo principal a utilização do Instagram como ferramenta de ensino metodológico para a química orgânica através do uso de linguagens mais acessíveis e didáticas, que possibilitem a compreensão mais clara do aluno, além de, auxiliar a correlação da disciplina com o cotidiano. Como metodologia empregou-se o programa ChemDraw para o desenvolvimento das estruturas químicas, o Canva para a elaboração dos posts e o Instagram como ferramenta de divulgação de conteúdos programáticos para a Química Orgânica sendo que, posteriormente, foi elaborada uma pesquisa de opinião que contou com a participação de 155 pessoas. Como resultados, pôde-se observar que os conteúdos com maior compreensão e aprendizado através do Instagram foram os compostos orgânicos e funções orgânicas, reações orgânicas, conceitos iniciais sobre a química orgânica juntamente com a classificação de cadeias e ligações químicas em moléculas orgânicas, estes conteúdos apresentaram 72,3%; 71,6%; 70,3% e 69,7% de índice de compreensão em relação aos conteúdos abordados, respectivamente. Além disso, 49,7% dos entrevistados acreditam que os posts, IGTVS e stories são ferramentas relevantes para o aprendizado da química orgânica e 81,3% acreditam que a linguagem utilizada é acessível, compreensível e didática. Diante desses resultados, pode-se concluir que a utilização do Instagram como ferramenta de ensino de química orgânica é de extrema valia, uma vez que, contribui para o aperfeiçoamento de informações estudadas em sala de aula e a possibilidade de correlacionar os assuntos vistos com o cotidiano, além de facilitar acesso dos conteúdos por acadêmicos de diversos cursos e do público em geral.

Planejamento e Síntese de Selenonaftoquinonas -1,2,3- Triazólicas com Potencial Aplicação contra Tuberculose

https://proceedings.science/p/138755

Nathália L. B. Santos [1]; Luana S. Gomes [1]; Ingrid C. Chipoline [1]; Ruan C. B. Ribeiro [1]; José S. S. Neto [2]; Vitor F. Ferreira [1]; Fernando de Carvalho [1]; Vanessa Nascimento [1]
[1] Universidade Federal Fluminense; [2] Universidade Federal de Santa Catarina

Os compostos organocalcogênios tem sido de grande interesse para os químicos sintéticos e medicinais devido às suas notáveis propriedades biológicas.1 As quinonas, em particular, as naftoquinonas, bem como os derivados do núcleo 1,2,3 triazólicos possuem uma vasta aplicabilidade terapêutica.2,3 O variado perfil biológico dessas classes são incontestáveis, e como relatado em trabalhos anteriores, esses núcleos apresentam atividade antituberculostática promissoras.4,5,6 Nessa perspectiva, a conjugação desses núcleos em uma única estrutura pode ser considerada uma boa estratégia para a síntese de substâncias com poderosas bioatividades, sendo este o objetivo desse trabalho. Por outro lado, de acordo com a Organização Mundial de Saúde, a tuberculose está no topo mundial como principal causa de morte por doenças infecciosas7 e, sendo assim, há a constante necessidade do desenvolvimento de novas drogas para o seu tratamento. Nesse sentido, nosso grupo de pesquisa vem trabalhando com sucesso na busca de moléculas contendo selênio com promissora atividade contra essa doença.6 Para este trabalho, a metodologia empregada na síntese dos compostos alvos, selenonaftoquinonas -1,2,3- triazólicas, se inicia com a menadiona (1) comercial.8,9,10 Os produtos finais (3a-f) foram obtidos a partir de uma reação de cicloadição 1,3-dipolar entre a azida e alcino catalisado por Cu (I), com rendimentos que variaram de 7 a 83% (Esquema 1). Em conclusão, foi desenvolvida uma metodologia eficiente para obteção de uma série inédita de selenonaftoquinonas 1,2,3-triazólicas. A próxima etapa será variar o escopo da reação, além de analisar a potencial atividade contra tuberculose desses compostos.

Preparo de Maleimidas 3-Metiltio 4-Substituídas Fluorescentes Através do Rearranjo de Tiazolidina-2,4-dionas 5-Substituídas

https://proceedings.science/p/138729

Luan Vanelli Meirelles [1]; Pedro Pôssa de Castro [1]; Saulo Passos [2]; Bernardo Basbaum Portinho de Puga Carvalho [1]; Chris Hebert de Jesus Franco [1]; José Corrêa [2]; Brenno A. D. Neto [2]; Giovanni Amarante [1]
[1] Universidade Federal de Juiz de Fora; [2] Universidade de Brasília

The preparation of 3-methylthio-4-arylmaleimides presents several synthetic drawbacks, such as the use of transition metals, the need of various reaction steps for its preparation and the formation of hazardous side-products. In this context, the development of a transition metal-free protocol for the preparation of 3-methylthio-4-arylmaleimides in a single step through the rearrangement of thiazolidine-2,4-diones is hereby described. After a careful optimization of the reaction conditions, we found a protocol that allowed the preparation of a broad scope of derivatives in up to 97% yield. The reaction tolerated several aryl-substituted groups, including challenging to prepare pyridyl-containing derivatives. The structure of derivative 1c was unambiguously confirmed by the X-ray crystallographic analysis. To demonstrate the synthetic utility of the prepared derivatives, the oxidation of the sulfide, as well as the N-alkylation of the imido group, were demonstrated affording the desired compounds in up to 97% yield.
A series of control experiments, including isotopic labelling and the use of selenated substrates, strongly suggested that the rearrangement involves a key isocyanate intermediate, as well as a further reaction with in situ generated methylthiomethyl acetate.
Moreover, some of the synthesized compounds proved to be fluorescent and had their photoproperties investigated. Since these derivatives presented promising emissive properties, their application in cell-imaging experiments was also carried out, revealing that some of these compounds are capable of selectively staining the perinuclear region of the cells.

Reações de oxidação seletivas na síntese de diterpenos naturais complexos

https://proceedings.science/p/138725

Victor Camargo Stork Santana [1]; Julian Pavan [2]; Vladimir Constantino Gomes Heleno [3]; Emilio Carlos de Lucca Junior [1]
[1] Universidade Estadual de Campinas; [2] Organic Chemistry / UNIFRAN (Universidade de Franca) / UNIFRAN (Universidade de Franca); [3] UNIFRAN - Universidade de Franca

Incorporation of oxygen atom in organic molecules causes significant changes in chemical and biological properties. In this way, we aim to synthetize natural products by increasing the oxidation level of complex diterpenes like the ent-kaurane kaurenoic acid (1) and the ent-beyerane isosteviol (9). The dihydroxylation of 1 using OsO4 and NMO gave 5 in 65%. The selective acetoxylation of 5 delivered 6 in 84%. Allylic oxidations of 1 and 2 with Py2Se2 and PhIO2 gave 7 and 3 in 35% and 55% yield, respectively. Enones 7 and 3 were submitted to dihydroxylation, delivering 8 and 4 in 44% and 75% yield, respectively. To the best of our knowledge, these are the first syntheses of natural products 4, 6, and 8.
While the remote oxidation of ent-kaurenes using Mn(CF3PDP) gave a complex mixture of oxidized products, ent-beyerane isosteviol methyl ester (10) as starting material delivered compounds 11 and 12 under the conditions developed by the White research group.

Regioselective Iodination of Remdesivir's Nucleobase via C-H Activation

https://proceedings.science/p/138733

Taniris Braga [1]; Juliana Alves dos Santos [1]; Adilson David da Silva [1]; Giuliano Cesar Clososki [2]; Giovanni Amarante [1]
[1] Universidade Federal de Juiz de Fora; [2] Faculdade de Ciências Farmacêuticas de Ribeirão Preto (FCFRP), Universidade de São Paulo (USP)

Remdesivir was the first emergence treatment for COVID-19 allowed by Anvisa. Our research group has described improvements of Klein's route for obtaining Remdesivir's nucleobase in 3 steps and 39% overall yield (Scheme 1).1 In this present work, after the amine protection step,2 we developed a methodology that allows the regioselective iodination of this nucleobase through a C-H activation promoted by the Knochel-Hauser base TMPMgCl.LiCl. The developed process consists of an initial magnesiation step followed by the electrophile (I2) attack. During our studies, the temperature, was evaluated and 0 °C showed to be the best (Table 1- entries 1 and 2). In addition, an excess of TMPMgCl.LiCl and iodine (4 equiv.) were important to improve the formation of the product (Table 1- entry 4). In conclusion, the iodide nucleobase was synthesized in 15% overall yield in mild reaction conditions via C-H activation. For future works, we desire to evaluate the glycosylation step using this advanced intermediate.

Regioselective synthesis of fluorinated nitrile-based building blocks with 2,2,6,6-Tetramethylpiperidyl bases

https://proceedings.science/p/138749

Thiago dos Santos [1]; Henrique Pereira Orenha [1]; Valter Eduardo Murie [1]; Ricardo Vessecchi [2]; Giuliano Cesar Clososki [1]
[1] Faculdade de Ciências Farmacêuticas de Ribeirão Preto (FCFRP), Universidade de São Paulo (USP); [2] Universidade de São Paulo

The 2,2,6,6-tetramethylpiperidyl (TMP) bases TMPMgCl.LiCl and (TMP)2Zn.2MgCl2.2LiCl have found application in the regioselective deprotometalation of diverse substrates.1 The obtained functionalized molecules via such strategy can be further employed in the construction of potential bioactive heterocycles. Fluorinated nitriles are valuable building blocks for the synthesis of important N-heterocyclic motifs such as benzo[d]imidazo[2,1-b]thiazoles,2 indazole,3 and dibenzoxazepinamines.4 Therefore, considering the ortho¬-directing properties of fluoro and cyano groups from these nitriles and their synthetic applicability in heterocyclic chemistry, we decided to assess their selective metalation with TMPMgCl.LiCl and (TMP)2Zn.2MgCl2.2LiCl and sequential functionalization with various electrophiles. We obtained 47 highly functionalized nitriles with the exploration of new and scarcely studied metalation sites (See Scheme 1 for examples). The yields ranged from 48 to 95%. Additionally, we performed a difunctionalization of 4-fluorobenzonitrile leading to 2f (80% yield) and used 2l as building block for the synthesis of the dibenzoxazepinamine 3 (84% yield), respectively.

Seleno-functionalization of BODIPY core: Synthesis and Characterization

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Beatriz dos Santos Cugnasca [1]; Alcindo Aparecido dos Santos [2]
[1] Química / iQ (Instituto de Química) / Universidade de São Paulo; [2] Universidade de São Paulo

The study of several fundamental biological processes requires the use of direct, reliable and sensitive methods that allows a rapid and efficient detection of diverse analytes. Recently, the design and synthesis of fluorophores with emission of fluorescence in the region of near-infrared (NIR) contribute to the development of new analytical techniques for obtaining in vivo images by fluorescence, allowing the study of physiological important processes, related to various diseases. In this context, BODIPY is a class of chromophores that is gaining a lot of relevance due to its excellent properties. Due to their promising features, BODIPYs have become synthetic targets for obtaining new fluorescent sensors in recent decades. The most commonly reported methods to introduce selenium into the BODIPY core consists of the metal-catalyzed cross-coupling reaction, radical mechanisms, or nucleophilic substitution reactions.
In this work, the synthesis of new seleno-BODIPYs is presented. The synthesis strategy was focused on the preparation of 2,6-dihalogenated BODIPYs, aiming to perform the nucleophilic substitution reaction in order to replace the halogen by the chalcogen residue. Instead, performing this reaction, it was observed the maintenance of halogens and the insertion of “PhSe” groups in the 3 and 5 positions. The procedure consisted on a reaction of 2,6-dibrominated BODIPY with PhSeH, generated in situ (Ph2Se2/NaBH4 system), under N2 atmosphere, at room temperature. The products were completely characterized by NMR and HRMS spectrum. After a mechanistic investigation it was possible to conclude that the main mechanism that was governing the reaction was the Oxidative Nucleophilic Hydrogen Substitution (ONHS). Thus, new compounds containing bromine and selenium were obtained (Figure 1) in high yields (77%) through a simple and fast procedure.

SEMI-SÍNTESE DE NOVAS BACTERIOCLORINAS USADAS NA FOTOINATIVAÇÃO DE MICRORGANISMOS

https://proceedings.science/p/138730

Marciana Pierina Uliana [1]; Andréia da Cruz Rodrigues [1]; Clovis Wesley Oliveira de Souza; Michel Rodrigo Zambrano Passarini [1]; Matheus A. dos Santos [1]; Luciano E. Fernandes [1]; Kleber Thiago de Oliveira [2]
[1] Universidade Federal da Integração Latino Americana; [2] Universidade Federal de São Carlos

Bacteriochlorophyll derivatives were semi-synthetized, initially extracted from the bacterium Rhodopseudomonas faecalis, and structurally modified in order to improve the solubility in physiological media (Scheme 1).1 Two bacteriochlorins (Bac Metoxi and Bac Trizma) were evaluated against photodynamic inactivation of Staphylococcus aureus (Figure 1). Three concentrations of photosensitizers were evaluated 1 μM, 15 μM and 30 μM with a light dose of 20J/cm2. At concentrations of 15 and 30 μM the microorganism was completely inactivated. We can conclude that the new bacterioclorin derivatives are effective in photoinactivating against S. aureus.

Síntese de derivados de 1,2,3-triazol 4-funcionalizados com aminas primárias e ácidos carboxílicos com potencial ação antimicrobiana

https://proceedings.science/p/138737

David Rodrigues da Rocha [1]; Douglas Galdino dos Santos [1]; Rosana Freitas [2]; Fernando de Carvalho [2]
[1] Instituto de Química / Universidade Federal Fluminense; [2] Universidade Federal Fluminense

Heterocyclic compounds containing the 1,2,3-triazole nucleus have received special attention in the field of synthetic chemistry since there are many possibilities of application as starting materials and in biological and material areas, like antimicrobial1 and antibacterial action2. In this scenario, the objective of this work is the synthesis of 4-functionalized 1,2,3 triazolic amines and carboxylic acids with novel structures.

The amines (5) were obtained through a four-step linear synthesis and 1,2,3-triazole 4-carboxylic acids (6) in three-step linear synthesis (Scheme 1). Firstly, functionalized anilines (1) underwent a diazotization reaction in the presence of sodium nitrite (NaNO2), hydrochloric acid (HCl) and sodium azide (NaN3) at 0 °C to generate the corresponding azides (2)3 in 96% yield. Then, the azides and the propargyl alcohol reacted in a Copper-catalyzed azide-alkyne cycloaddition (CuAAC) reaction to build exclusively the 1,4-disubstituted 1,2,3-triazole ring with a primary alcohol (3) in tert-butanol and water at room temperature4 in 85% yield. The aldehydes were obtained through partial oxidation of primary alcohols (4) by adding IBX in dimethylsulfoxide (DMSO) at room temperature5, with 95% yield. Then, the amines were obtained by reductive amination of aldehydes (5) in presence of ammonium hydroxide (NH4OH) with Zinc-Modified Cyanoborohydride, prepared mixing sodium cyanoborohydride (NaBH3CN) and anhydrous zinc chloride (ZnCl2), in methanol6 (25%). In parallel, the triazole alcohol was completely oxidated to corresponding carboxylic acids with 90% yield, using KMnO4 in tert-butanol and water at room temperature7.

Therefore, the molecules were obtained in excellent yields and with classical and reproducible synthetic methodologies. As a perspective, the final products will be sent for biological testing to assess the potential antimicrobial action.

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Síntese de derivados ribonucleosídeos quinolônicos e sua investigação como ligantes para inibição da enzima LdNH

https://proceedings.science/p/138754

Mayane Barbosa dos Santos [1]; Marcela de Moraes [2]; Pamella Christina Ortega de Oliveira [1]; Pedro Batalha [2]; Luzineide Tinoco [3]; Maria Cecília Bastos Vieira de Souza [4]; Fernanda da Costa Santos Boechat [5]

[1] Programa de Pós-Graduação em Química / Instituto de Química / Universidade Federal Fluminense; [2] Universidade Federal Fluminense; [3] Universidade Federal do Rio de Janeiro; [4] Instituto de Química / Universidade Federal Fluminense; [5] Departamento de Química Orgânica / Instituto de Química / Universidade Federal Fluminense

A leishmaniose, principalmente em sua forma visceral, é uma doença grave devido seu alcance mundial e alta letalidade. Os fármacos já existentes para o tratamento desta parasitose geralmente são caros, apresentam alta toxidade para o paciente e estão sujeitos ao surgimento de resistência dos parasitas, e diante deste fato, torna-se necessário o desenvolvimento de novos agentes leishmanicidas e investigação de novos alvos terapêuticos, na busca de fármacos mais eficazes. Neste trabalho foram sintetizados uma série de derivados ribonucleosídeos quinolônicos como potenciais inibidores da LdNH, enzima chave na via de recuperação de purinas e importante para a biossíntese do DNA e RNA do parasita. Inicialmente, as quinolonas 1, previamente sintetizadas pelo nosso grupo de pesquisa, foram sililadas com BSTFA contendo 1% de CTMS, seguido da adição de ribose e TMSO-Tf, resultando assim nos ribonucleosídeos quinolônicos protegidos 2. A desproteção seletiva para obtenção de 3, seguida de reação de hidrólise básica leva à obtenção dos ácidos carboxílicos do tipo 4. Estes derivados foram caracterizados por métodos físicos de análise e estão sendo avaliados frente à atividade inibitória da enzima nucleosídeo hidrolase do Leishmania donovani (LdNH). Ensaios preliminares indicaram que o ribonucleosídeo 4a foi capaz de exibir atividade inibitória de LdNH, com IC50= 2,66 µmol.L-1.

Síntese de novas carboxamidas derivadas da 6-sulfonamida-4-oxoquinolina como potenciais inibidores colinesterásicos.

https://proceedings.science/p/138740

Mayra Silva Coutinho [1]; Maria Cecília Bastos Vieira de Souza [2]; Fernanda da Costa Santos Boechat [3]; Pedro Batalha [1]

[1] Universidade Federal Fluminense; [2] Instituto de Química / Universidade Federal Fluminense; [3] Departamento de Química Orgânica / Instituto de Química / Universidade Federal Fluminense

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-oxoquinolínico 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. As substâncias dos tipos 3 e 4 são inéditas na literatura científica, e tiveram suas estruturas confirmadas por métodos espectroscópicos de análise (IV, RMN de 1H e de 13C), e seus pontos de fusão foram determinados. Como perspectiva futura, espera-se expandir esta coleção de substâncias variando-se os substituintes destacados R e R1, 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.

Síntese de Novos Tioéteres Derivados 1,4 naftoquinonas Catalisada por Glicerol

https://proceedings.science/p/138748

Vinicius Sodré Pereira [1]; David Rodrigues da Rocha [2]; Thaís Santos [1]; Fernando de Carvalho [1]
[1] Universidade Federal Fluminense; [2] Instituto de Química / Universidade Federal Fluminense

As naftoquinonas são substâncias comuns a diversos organismos na natureza, que devido aos seus efeitos biológicos, se tornaram foco de vários estudos na comunidade científica1. Estes metabólitos, encontrados em arvores da família Bignoniaceae, apresentam várias atividades biológicas como antibacteriana, antimalarial, moluscicida e antifúngica2. Da mesma forma, tioéteres são muito ativos em diversos processos biológicos importantes, o que pode ser exemplificado pela presença de diversos sulfetos benzílicos em muitas substancias com comprovada habilidade antitumoral. Desta maneira, este projeto busca unir esses dois blocos sintéticos utilizando como ferramenta a reação de tióis com alcenos catalisada por glicerol. A metodologia em questão, ao contrário dos diversos estudos já descritos para esta síntese, emprega componentes menos agressivos, obtendo produtos de adição anti-markovnikov.3. Com este intuito, a estratégica sintética aplicada parte da inserção da alil-amina (2) na 1,4 naftoquinona (1), onde o produto (3) obtido participará reação com uma variedade tióis, catalisada por glicerol formando os tioéteres (4) como mostrado no esquema 1 abaixo

Síntese de novos tioéteres derivados da α-xiloidona

https://proceedings.science/p/138745

Thaís Santos [1]; Vitor Ferreira [2]; David Rodrigues da Rocha [2]
[1] Universidade Federal Fluminense; [2] Instituto de Química / Universidade Federal Fluminense

As piranonaftoquinonas são uma classe de substâncias encontradas na natureza e bem exploradas na literatura, principalmente por causa de seus diversos perfis biológicos, com destaque para as xiloidonas e lapachonas.[1] No entanto, a funcionalização desses compostos no anel pirânico se baseia, quase que exclusivamente, de modificações utilizando as lapachonas como precursores, ainda que as xiloidonas possam ser usadas como plataformas sintéticas. Essa abordagem ainda é restrita a reações de hidrogenação, formação de diol, haloidrina ou epóxido,[2] levando inicialmente à formação de lapachonas mais simples, necessitando de reações subsequentes para a obtenção de seus derivados mais complexos estruturalmente. Nesse sentido, o objetivo deste trabalho consiste na obtenção de novos tioéteres, a partir da funcionalização direta da α–xiloidona. A estratégia sintética se inicia pela obtenção da α–xiloidona (1) através da reação de condensação de Knoevenagel entre lausona (2) e aldeído α,β-insaturado 3, seguida de uma ciclização intramolecular.[3] Então, os tioéteres (4) são obtidos através da adição direta de diferentes tióis comerciais a α–xiloidona (1), em etanol, resultando em dez novos derivados do tipo 4 com rendimentos moderados a bons (Esquema 1).

Síntese de potenciais fluoróforos baseados em naftil- e pirenilpirazolinas tiocarbamoil-substituídas

https://proceedings.science/p/138759

Clara Amorim da Silva [1]; Yasmin Lima Santos [1]; NATALI FAGANELLO [2]; Gleison Antônio Casagrande [2]; Lucas Pizzuti [3]

[1] Universidade Federal da Grande Dourados; [2] Universidade Federal de Mato Grosso do Sul ; [3] Faculdade de Ciências Exatas e Tecnologia / Universidade Federal da Grande Dourados

A síntese de compostos de coordenação baseados em ligantes orgânicos heterocíclicos vem recebendo atenção pois muitas das estruturas resultantes possuem propriedades luminescentes, tornando possível aplicá-las em tecnologia
de iluminação, marcadores biológicos ou pigmentos. Nosso grupo de pesquisa tem publicado trabalhos que descrevem a síntese de ligantes pirazolínicos e sua coordenação com vários metais de transição. Complexos de ouro(I) com tiocarbamoil-pirazolinas serviram de excelentes modelos de moléculas bioativas e foram suficientemente luminescentes para serem monitoradas através da técnica de bioimageamento celular no citoplasma de células de adenocarcinoma mamário humano. Neste sentido, o objetivo deste trabalho é obter pirazolinas substituídas tanto por grupos comprovadamente luminescentes quanto grupos que contenham sítios doadores de elétrons capazes de se coordenar com metais. Deste modo, foram preparadas naftil- e pirenilchalconas (4a-f e 5b-f) a partir da condensação da 2-acetonaftona (1) ou do 2-acetilpireno (2) com os benzaldeídos 3a-f com rendimentos de 42 a 85%, conforme o esquema abaixo. As chalconas foram convertidas nas tiocarbamoilpirazolinas (6a-f e 7b-f) pela ciclondensação com
tiosemicrabazida em rendimentos de 47 a 89%. Todas as chalconas e pirazolinas tiveram suas estruturas confirmadas por RMN de 1H e 13C. As pirazolinas obtidas terão suas propriedades fotofísicas estudadas e serão empregadas como
ligantes para coordenação com metais de transição, visando à síntese de complexos.

Síntese e Caracterização de derivados Quinolínicos com potencial utilização como sondas fluorogênicas

https://proceedings.science/p/138735

JULIA LOPES RODRIGUES [1]; Giovanny C. dos Santos [1]; Luiz Carlos da Silva-Filho [1]

[1] Universidade Estadual Paulista “Júlio de Mesquita Filho”

Quinoline derivatives are among the aza-heterocyclic compounds that arouse the interest of the scientific community for their biocompatible properties, being used in several medicinal applications.

The objective of this work is promote the synthesis of hydroxyquinoline derivatives and studies the phosphorylation of hydroxyl groups present in quinoline derivatives, to verify their potential application as fluorogenic probes. The insertion of phosphate groups aims to facilitate the transport of quinoline derivatives in the organism, as well as the participation in protein regulation mechanisms.
In this work we describe the synthesis of different hydroxyquinoline derivatives using NbCl5 as promoter by multicomponent reaction, with good yields and reaction times. All hydroxyquinolines synthesized were submitted a solvatochromism study in different solvents, with good results for potential applications as fluorescence probe. In figure 1 is showed the results from hydroxyquinoline obtained from p-hydroxybenzaldehyde, p-nitroaniline and phenylacetilene.

Síntese e caracterização de novos análogos de aciclonucleosídeos fosfonatos derivados de ácidos 4-quinolono-3-carboxílicos (ANPs)

https://proceedings.science/p/138742

Alan Gonçalves de Souza [1]; Claudio Santana Viana Junior [2]; Thaís Apolinário Tavares [2]; Letícia Villafranca Faro [2]; Marcos Costa de Souza [2]; Fernanda da Costa Santos Boechat [3]; Maria Cecília Bastos Vieira de Souza [2]
[1] Programa de Pós-Graduação Mestrado e Doutorado / Universidade Federal Fluminense; [2] Instituto de Química / Universidade Federal Fluminense; [3] Departamento de Química Orgânica / Instituto de Química / Universidade Federal Fluminense

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 1H e de 13C, por espectroscopia na região do IV, e se encontram sob investigação de sua atividade antiviral.

Synthesis of 1,2,3-triazole selenides with potential anti-T. cruzi activity

https://proceedings.science/p/138760

Ingrid Cavalcanti Chipoline [1]; Beatrice Faria de Almeida Barboza Brasil [1]; Marilia Valli [2]; Aldo Oliveira [3]; José Mortara San Martin [2]; Vanessa do Nascimento [1]
[1] Universidade Federal Fluminense; [2] Universidade de São Paulo; [3] Departamento de Ciências Exatas e Educação / Centro de Blumenau / Universidade Federal de Santa Catarina

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 drugs 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 with two classes of compounds that have been highlighted in the literature: organoselenium and 1,2,3-triazoles, to design new 1,2,3-triazole selenides and evaluate their biological potential against T. cruzi. Both have biological activities described 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. A bioisosterism approach was applied to compound 3o, synthesized with the S atom instead of Se, to have a Structure activity relationship comparison.

The ability of these compounds in relation to the potential to inhibit cruzain, a validated target and an essential enzyme for T. cruzi,3 was investigated. In general, the compounds did not show potent activity, 0.2-28.1% (Table 1). 4 In vitro tests of antiprotozoan activity are being carried out in parallel with tests involving phenotypic activity with T. cruzi, in addition to the in silico investigation of ADME parameters, which are important for the development of new compounds with antichagasic activity. In conclusion, a series of new hybrid molecules with triazoles and chalcogenic fractions were synthesized, with investigative activity for the development of a new drug against Chagas disease.

Synthesis of 2-(5-amino-2-(5-amino-3-bromo-2-hydroxyphenyl)-2,3-dihydro-1,3,4-oxadiazole-3-carbonyl)benzoic acids

https://proceedings.science/p/138722

Letícia Oliveira de Magalhães [1]; Barbara Vasconcellos da Silva [1]; Roberta Katlen Fusco Marra [1]
[1] Universidade Federal do Rio de Janeiro

In this study, we described the synthesis of two novel oxadiazole derivatives. At first, the salicylaldehyde nitration reaction was carried out in microwave for 70 seconds, generating a mixture of ortho (2%) and para (20%) regioisomers, wich was separated by the difference in solubility of the phenolates in aqueous solution.[2] Then, semicarbazide hydrochloride and 5-nitrosalicyaldehyde (2) have been used for the synthesis of semicarbazone (3) in 89% yield. In the next step, the semicarbazone obtained previously reacted, in a medium containing glacial acetic acid and sodium acetate under constant agitation – with a solution of bromine in acetic acid to furnished the 2,3-dihydro-1,3,4-oxadiazole (4) in 48% yield.[3] Finally, reaction of 1,3,4-dihydro-oxadiazole with maleic (10 min.) or phthalic (1 h) anhydrides in THF at room temperature led to the formation of (5) and (6) in 68% and 11% yields, respectively. In both reactions, DMAP was used as a catalyst. All structures were characterized by 1H and 13C nuclear magnetic resonance spectroscopy (NMR) technique.

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Synthesis of Coumarin-Triazole Hybrids with potential antitumor activity

https://proceedings.science/p/138750

Amanda de Andrade Borges [1]; Acácio Silva de Souza [1]; Vitor Ferreira [2]; Fernando de Carvalho [1]; Luana Forezi [1]

[1] Universidade Federal Fluminense; [2] Instituto de Química / Universidade Federal Fluminense

The search for new bioactive molecules begins with its relevance in the literature, such as coumarin and 1,2,3-triazole systems, which have numerous individual biological properties, especially against cancer. Thus, the objective of this work is to obtain new coumarin-triazole hybrids, seeking a good relationship between structure and antitumor activity. It is intended to investigate how the junction of such systems can influence the activity of these new molecules, more specifically in relation to oral squamous cells (OSCC). To obtain hybrids 6, it was initially necessary to synthesize intermediates 3, 4a-d and 5a. The azide compounds 3 were obtained from 4-hydroxycoumarin (1) in an alkylation reaction with dibromoalkane and followed by a nucleophilic bimolecular substitution with sodium azide. Compounds 3 were obtained in good yields (72-74%). Propargylated naphthoquinones 4a-d were obtained via propargylation with propargyl bromide or propargylamine from commercial naphthoquinones obtaining the derivatives in moderate yields (40-80%). Propargylated coumarin 5a was obtained in 89% yield via propargylation of 4-hydroxycoumarin with propargyl bromide. Intermediates 3 were reacted with alkynes 4a-d, 5a, 5b-d (commercial) through a 1,3-dipolar cycloaddition reaction catalyzed by Cu(I) obtaining 16 hybrids 6 with yields varying from 30-65 %. Their structures were confirmed using different physical analysis methods - NMR, IR and HRMS. Subsequently, the substances will have their biological activity evaluated against oral squamous cell carcinoma (OSCC).

Synthesis, antimicrobial evaluation and structure–activity relationship of isoxazol-5(4H)-ones derivatives

https://proceedings.science/p/138721

Yasmine Queiroz [1]; Juliana Morais [1]; Luciana Machado Ramos [1]; Yasmin Alves de Freitas [1]; Luciano Ribeiro [1]

[1] Universidade Estadual de Goiás

The isoxazol-5(4H)-ones they stand out in organic synthesis for demonstrating antibiotics and analgesics[1]. The microdilution method has the advantage of sensitivity, reproducibility and low cost[2]. The use of MAI.Cl- acid catalyst was tested in the reaction, and various aromatic aldehydes to form 3,4-disubstituted isoxazol-5(4H)-one derivatives (Scheme 1). The minimal inhibitory concentration (MIC) and minimal bactericidal concentration (MBC) of the compounds against Staphylococcus epidermidis (ATCC 12228) and Escherichia coli (ATCC 25312) bacteria were evaluated. Density Functional Theory (DFT) method at the theory level M062X/6-311++G(d,p) was used to calculate a set of molecular properties of all studied compounds. Principal Component Analysis (PCA) of the molecular descriptors discriminated the compounds into active and inactive. With application of the PCA method, the active molecules in blue were obtained, being those molecules that presented moderate to good antibacterial activity against the strains. With a MIC between 250 - 500 µg/ml for E. coli and < 15.62 - 250 µg/ml for S. epidermidis.

Use of site-directed mutagenesis to determine key positions in friedelin synthase (FRS), a monofunctional enzyme from Monteverdia ilicifolia

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Weslei Bruno Botero [1]; Tatiana Maria Souza-Moreira [1]; Melissa Remlinger [2]; Cleslei Zanelli [2]; Sandro Roberto Valentini [2]; Maysa Furlan [1]
[1] Instituto de Química / Universidade Estadual Paulista "Júlio de Mesquita Filho"; [2] Universidade Estadual Paulista "Júlio de Mesquita Filho" - Campus Araraquara

Monteverdia ilicifolia is a native Brazilian plant with a rich ethnopharmacological background. Popularly known as "espinheira-santa", the species is widely used due to its anti-inflammatory, gastroprotective and anti-cancer activities. Those biological potential comes from its flavonoids, tannins and triterpenes including quinonemethide triterpenes (QMTs). Friedelin is the only triterpene in the isoprenoid biosynthesis with a ketone group at C-3, instead of an alcohol. In addition, friedelin is the precursor of the QMTs (celastrol, pristimerin and maytenin). Despite their potential, those metabolites are produced in small amount in the host3. A way to increase the production is to understand friedelin synthase activity and improve its production in a heterologous organism such as yeast. The aim of this work was to evaluate the production of the wild friedelin synthase (FRS) in Saccharomyces cerevisiae and some key enzyme mutants. We selected key positions for the site-directed mutations in the primary structure, including the residues Phe-183, Cys-369, Asp-484 and Trp-612. In comparison with the wild enzyme, the mutation Phe-183-Leu resulted in an increase in the production of friedelin and also the production of α-amyrin and β-amyrin. However, the mutation Cys-369-Ala showed a decrease in the production of the target triterpene, while the mutations Asp-484-Glu and Trp-612-Phe did not produce any amount of friedelin.

Using Diversity Oriented Synthesis (DOS) as a Strategy for the Discovery of New GPCR ligands

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Alisson Richard Novais [1]; Alisson Meza [2]; Dênis Pires de Lima [1]; Adilson Beatriz [1]
[1] Universidade Federal de Mato Grosso do Sul; [2] Universidade Federal do Amazonas

The GPCR participates in several physiological processes, and its dysfunction is related to many pathologic disorders [1]. In this way, the discovery of ligands that can bind to such receptors selectively is of considerable importance in developing new drugs. The Molispiration software calculated excellent bioactivity scores for three new molecules as GPCR ligands 4-6. As part of our goal to use the diversity-oriented synthesis (DOS) as a strategy to create a structurally complex organic molecules database [2] from the Diels-Alder adduct tricyclo[6.2.1.02,7]-undeca-4,9-diene-3,6-dione (1), we have synthesized the advanced intermediate 3 from a key step 1,3-dipolar cycloaddition [3] between the nitrone 2 and the dipolarophile obtained from 1 after treatment with Zn/HCl (Scheme 1). The potential ligands 4-6 will be prepared after some chemical modifications in cyclohexanedione moiety present in 3. The isoxazolidine 3 was characterized by 1H and 13C NMR spectroscopy. Scheme 1. Synthesis of new GPCR ligands References: [1] Hauser, A. S.; Chavali, S.; Masuho, I.; et al. Cell 2018, 172, 41. [Crossref] [2] Schreiber, S. L. Science 2000, 287, 1964. [Crossref] [3] Reddy, D. S.; Reddy, G. G.; Beatriz, A.; Corey, E. J. Org. Lett. 2021, 23, 5445. [Crossref]

Uso do peróxido de hidrogênio-ureia (UHP) na síntese de 3-selenil-indóis

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Julia Rosa Menezes [1]; Fabiola Caldeira [1]; Juliano Alex Roehrs [2]; Juliano Azeredo [1]
[1] Universidade Federal do Pampa; [2] Química / IFSul-Campus Pelotas / Instituto Federal de Educação, Ciência e Tecnologia Sul-rio-grandense

A formação da ligação carbono-selênio empregando o núcleo indólico como substrato vem se estabelecendo como um importante alvo de estudo em razão das propriedades terapêuticas atribuídas aos compostos heterocíclicos e organoselenilados. Geralmente, a selenilação direta do indol demanda a utilização de catalisadores metálicos, longos tempos reacionais ou oxidantes tóxicos e de difícil manipulação. Nesse contexto, o uso de peróxido de hidrogênio-ureia (UHP) torna-se uma alternativa interessante pois trata-se de um aduto sólido e estável e que fornece uma fonte anidra de peróxido de hidrogênio, o que evita problemas relacionados a toxicidade, dificuldade de manipulação e formação de subprodutos geralmente relacionados ao peróxido de hidrogênio em solução aquosa. Neste contexto, o presente trabalho trata-se da síntese do 3-selenil-indóis e seus derivados, através da realização da clivagem oxidativa realizada pelo UHP na ligação Se-Se dos disselentos. O trabalho já está em estudo no grupo de pesquisa e tem sua condição otimizada bem definida com uma reação de 4 horas, sob um aquecimento de 80 °C, utilizando acetonitrila como solvente na presença de 1 equivalente iodeto de potássio e 1 equivalente de UHP. Com essa condição foi possível fazer a variação dos substratos afim de obter os produtos desejados em rendimentos de até 84%.

XPS Study of Polystyrene-Immobilized Ionic Liquid Phases Containing Scandium(III) Triflate as Lewis Acid

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Gabriela Franco Domingos dos Santos [1]; Ana Rute Santos [2]; Peter Licence [2]; Luiz S. Longo Jr. [1]
[1] Universidade Federal de São Paulo; [2] School of Chemistry / The University Of Nottingham

Kim et al. investigated the anion exchange between Sc(OTf)3 and imidazolium-based ILs immobilized on polystyrene resin containing weakly coordinating anions such as [SbF6]—. The formation of the new catalytic species of Sc3+ was evidenced by 19F NMR. In our work, we prepared ILs phases covalently immobilized on polystyrene (Merrifield resin) with subsequent adsorption of Sc(OTf)3. XPS was then used to evaluate the ion exchange between the IL and Sc(OTf)3, which ultimately could promote an increase in the Lewis acidity of Sc3+. Among the high-resolution spectra obtained for each element, the region of Sc 2p photoemission line stands out, since we are interested in verifying the presence of new Sc3+ species in the material. A -1.6 eV binding energy shift was observed for the Sc 2p3/2 and Sc 2p1/2 doublet of the commercial Sc(OTf)3, compared to values observed for PS-[C8Im][SbF6]/Sc(OTf)3 (Table 1). Thus, the Sc present in the new catalytic species, formed through ion exchange between Sc(OTf)3 and [SbF6]-IL, is more electropositive and, therefore, more Lewis acidic. The binding energies were also compared with literature data for Sc(OTf)3.