

Janković, B., Manić, N., Stojiljković, D., Jovanović, V.
TSA-MS characterization and kinetic study of the pyrolysis process of various types of biomass based on the Gaussian multi-peak fitting and peak-to-peak approaches
(2018) Fuel, 234, pp. 447-463.

<https://doi.org/10.1016/j.fuel.2018.07.051>

ABSTRACT: Slow pyrolysis characterization and kinetic modeling study of five different biomasses (corn brakes (CB), wheat straw (WS), hazelnut shell (HS), sawdust (Beech), and sawdust chemically treated (SDCT)) were performed in this work, using STA-MS techniques. Thermal decomposition of these samples was divided into three stages corresponding to removal of water, devolatilization, and formation of bio-char. Mass spectrometry (MS) showed that H₂, CH₄, H₂O, CO₂ (C₃H₈), CO, and C₂H₆ were the main gaseous products released during the pyrolysis of biomasses. It was found that H₂O, CO and CO₂ evolutions for all biomass samples arise from lignin source in biomass, followed by the cellulose, and hemicelluloses. It was established that the pseudo-component fraction estimated by the theoretical calculations is dependent on the heating rate. Using Gaussian multi-peak fitting and peak-to-peak approaches, regardless of the type of biomass, it was found that decomposition of lignin occurs independently of decomposition of remaining two pseudo-components and that there is no interaction between them. Namely, it was assumed that during pyrolysis process of biomasses, carbohydrate (hemicelluloses + cellulose)-lignin chemical structures most likely exist, where the variety of lignin structure units in different types of biomass affects on the level of energy required for its decomposition. © 2018

Oliveira, R.C.P., Milikić, J., Daş, E., Yurtcan, A.B., Santos, D.M.F., Šljukić, B.

Platinum/polypyrrole-carbon electrocatalysts for direct borohydride-peroxide fuel cells

(2018) Applied Catalysis B: Environmental, 238, pp. 454-464.

<https://doi.org/10.1016/j.apcatb.2018.06.057>

ABSTRACT: Polypyrrole-carbon (PPy-C) composites having different amounts of carbon (5-35 wt.%) decorated with platinum nanoparticles (Pt/PPy-C) were prepared and investigated for borohydride oxidation reaction (BOR) in alkaline medium and for hydrogen peroxide reduction reaction (HPRR) in acidic medium. Structural and morphological properties and composition of these electrocatalysts were determined by FTIR, Raman, XPS, SEM/EDS, TEM and ICP-MS analyses. Pt/PPy-C electrocatalysts were evaluated for BOR and HPRR by cyclic voltammetry and chronoamperometry. Faradaic and kinetic parameters, such as the number of exchanged electrons, n , charge transfer coefficient, α apparent activation energy, $E_{a,app}$, and order of reaction, β were calculated. n for BOR ranged from 6.0 to 7.6, while n for HPRR ranged from 1.0 to 2.0. $E_{a,app}$ was found to range from 10 to 18 kJ mol⁻¹ for BOR and from 8 to 14 kJ mol⁻¹ for HPRR. The BOR was found to be a 1st order reaction with respect to BH₄⁻. Pt/PPy-C35% electrocatalyst showed the best activity for both reactions. Fuel cell tests were done with Pt/PPy-C electrodes as anode, as cathode and as both anode and cathode in a direct borohydride-peroxide fuel cell (DBPFC). DBPFC with Pt/PPy-C35% as anode electrocatalyst gave the highest peak power

density of 1432 W gPt⁻¹ at current density of 2046 A gPt⁻¹ and cell voltage of 0.70 V. © 2018 Elsevier B.V.

Milovanović, B., Petković, M., Etinski, M.
Raman spectra of aqueous uracil stacked dimer: First principle molecular dynamics simulation
(2018) *Chemical Physics Letters*, 713, pp. 15-20.

<https://doi.org/10.1016/j.cplett.2018.10.015>

ABSTRACT: Raman spectra of aqueous uracil stacked dimer have been studied by employing density functional theory based molecular dynamics simulation together with the maximally localized Wannier functions. The unpolarized spectra are in a reasonable good agreement with the available experimental spectrum. The discrepancies are attributed to the used density functional approximation. Static quantum chemical calculations reveal that the coupling of the carbonyl stretching modes is significantly weaker than the one of the amide modes. The noncoincidence effect of the ring breathing mode is explained in terms of repulsive steric interactions. © 2018 Elsevier B.V.

Pašti, I.A., Janošević Ležaić, A., Gavrilov, N.M., Ćirić-Marjanović, G., Mentus, S.V.
Nanocarbons derived from polymers for electrochemical energy conversion and storage - A review
(2018) *Synthetic Metals*, 246, pp. 267-281.

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ABSTRACT: Energy demands of modern society require efficient means of energy conversion and storage. Nanocarbons have been identified as versatile materials which combine many desirable properties, allowing them to be used in electrochemical power sources, from electrochemical capacitors to fuel cells. Efficient production of nanocarbons requires innovative and scalable approaches which allow for tuning of their physical and chemical properties. Carbonization of polymeric nanostructures has been demonstrated as a promising approach for production of high-performance nanocarbons with desired morphology and variable surface chemical properties. These materials have been successfully used as active electrode materials in electrochemical capacitors, as electrocatalysts or catalyst supports. Moreover, these materials are often found as parts of composite electrode materials where they play very important role in boosting materials performance. In this contribution we shall review developments in the field of application of polymer-derived nanocarbons for electrochemical energy conversion and storage applications, covering the last decade. Primary focus will be on polyaniline and polypyrrole but carbons derived from other polymers will also be mentioned. We shall emphasize the link between the physical and chemical properties of nanocarbons and their performance in electrochemical power sources with an attempt to derive general guidelines for further development of new materials with improved performances. © 2018 Elsevier B.V.

Korać, J., Stanković, D.M., Stanić, M., Bajuk-Bogdanović, D., Žižić, M., Pristov, J.B., Grgurić-Šipka, S., Popović-Bijelić, A., Spasojević, I.

Coordinate and redox interactions of epinephrine with ferric and ferrous iron at physiological pH
(2018) Scientific Reports, 8 (1), art. no. 3530, .

<https://doi.org/10.1038/s41598-018-21940-7>

ABSTRACT: Coordinate and redox interactions of epinephrine (Epi) with iron at physiological pH are essential for understanding two very different phenomena - the detrimental effects of chronic stress on the cardiovascular system and the cross-linking of catecholamine-rich biopolymers and frameworks. Here we show that Epi and Fe³⁺ form stable high-spin complexes in the 1:1 or 3:1 stoichiometry, depending on the Epi/Fe³⁺ concentration ratio (low or high). Oxygen atoms on the catechol ring represent the sites of coordinate bond formation within physiologically relevant bidentate 1:1 complex. Redox properties of Epi are slightly impacted by Fe³⁺. On the other hand, Epi and Fe²⁺ form a complex that acts as a strong reducing agent, which leads to the production of hydrogen peroxide via O₂ reduction, and to a facilitated formation of the Epi-Fe³⁺ complexes. Epi is not oxidized in this process, i.e. Fe²⁺ is not an electron shuttle, but the electron donor. Epi-catalyzed oxidation of Fe²⁺ represents a plausible chemical basis of stress-related damage to heart cells. In addition, our results support the previous findings on the interactions of catecholamine moieties in polymers with iron and provide a novel strategy for improving the efficiency of cross-linking. © 2018 The Author(s).

Nikolić, V.N., Vasić, M., Milić, M.M.

Observation of low- and high-temperature CuFe₂O₄ phase at 1100 °C: The influence of Fe³⁺ ions on CuFe₂O₄ structural transformation
(2018) Ceramics International, 44 (17), pp. 21145-21152.

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ABSTRACT: Samples containing CuFe₂O₄ and CuO nanoparticles were synthesized by coprecipitation method and subjected to thermal treatment at 300 °C, 500 °C, 700 °C, 900 °C and 1100 °C. Depending on the synthesis conditions, high-temperature treatment of the prepared samples brought to the formation of CuFe₂O₄ with a tetragonal or cubic structure, which was confirmed by X-ray diffraction analysis. The influence of formation mechanism onto the crystallite sizes of nanoparticles and structural transformation of CuFe₂O₄ is discussed. For the first time it was shown that variations of the initial amount of Fe³⁺ and Cu²⁺ ions precursors resulted in the formation of low- and high-temperature CuFe₂O₄ phase at the same annealing temperature, 1100 °C. © 2018 Elsevier Ltd and Techna Group S.r.l.

Božić, B., Korać, J., Stanković, D.M., Stanić, M., Romanović, M., Pristov, J.B., Spasić, S., Popović-Bijelić, A., Spasojević, I., Bajčetić, M.

Coordination and redox interactions of β-lactam antibiotics with Cu²⁺ in physiological settings and the impact on antibacterial activity
(2018) Free Radical Biology and Medicine, 129, pp. 279-285.

<https://doi.org/10.1016/j.freeradbiomed.2018.09.038>

ABSTRACT: An increase in the copper pool in body fluids has been related to a number of pathological conditions, including infections.

Copper ions may affect antibiotics via the formation of coordination bonds and/or redox reactions. Herein, we analyzed the interactions of Cu^{2+} with eight β -lactam antibiotics using UV-Vis spectrophotometry, EPR spectroscopy, and electrochemical methods. Penicillin G did not show any detectable interactions with Cu^{2+} . Ampicillin, amoxicillin and cephalexin formed stable colored complexes with octahedral coordination environment of Cu^{2+} with tetragonal distortion, and primary amine group as the site of coordinate bond formation. These β -lactams increased the solubility of Cu^{2+} in the phosphate buffer. Ceftazidime and Cu^{2+} formed a complex with a similar geometry and gave rise to an organic radical. Ceftriaxone- Cu^{2+} complex appears to exhibit different geometry. All complexes showed 1:1 stoichiometry. Cefaclor reduced Cu^{2+} to Cu^{+} that further reacted with molecular oxygen to produce hydrogen peroxide. Finally, meropenem underwent degradation in the presence of copper. The analysis of activity against *Escherichia coli* and *Staphylococcus aureus* showed that the effects of meropenem, amoxicillin, ampicillin, and ceftriaxone were significantly hindered in the presence of copper ions. The interactions with copper ions should be taken into account regarding the problem of antibiotic resistance and in the selection of the most efficient antimicrobial therapy for patients with altered copper homeostasis. © 2018 Elsevier Inc.

Romanovski, V.G., Han, M., Maćešić, S., Tang, Y.

Dynamics of an autocatalator model

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<https://doi.org/10.1002/mma.4949>

ABSTRACT: We study the dynamics of an autocatalator model, which is described by a 3-dimensional autonomous cubic differential system. We analyze the number and local properties of equilibrium points of the system using methods of the qualitative theory of ordinary differential equations. We also investigate small-amplitude limit cycles bifurcating from an equilibrium state of the system. Some numerical simulations illustrating the obtained theoretical results are presented. Copyright © 2018 John Wiley & Sons, Ltd.

Vasić, M.M., Žák, T., Pizúrová, N., Roupcová, P., Minić, D.M., Minić, D.M.

Thermally induced microstructural transformations and anti-corrosion properties of $\text{Co}_{70}\text{Fe}_{5}\text{Si}_{10}\text{B}_{15}$ amorphous alloy

(2018) *Journal of Non-Crystalline Solids*, 500, pp. 326-335.

<https://doi.org/10.1016/j.jnoncrysol.2018.08.017>

ABSTRACT: The amorphous $\text{Co}_{70}\text{Fe}_{5}\text{Si}_{10}\text{B}_{15}$ alloy was studied in terms of thermal and corrosion resistance as well as thermally induced structural transformations, using several structural and thermal analysis techniques and electrochemical measurements. It was shown that the alloy is thermally stable up to around 510 °C. Anodic polarization curves of the as-prepared alloy revealed its high corrosion resistance in 0.5 M NaCl, HCl and NaOH solutions. Multistep structural stabilization through the crystallization is manifested as two well defined DSC peaks corresponding to formation of fcc Co, hcp Co, Co_{23}B_6 , and Co_2Si phases, whose microstructural parameters were studied after

thermal treatment at different temperatures in the range 25–800 °C. TEM and EDX analyses suggested the presence of minor Co-Si phases as well in the crystallized alloy and deformation twinning in the Co₂₃B₆ grains. The microstructural transformations exhibited significant influence on the magnetic moment of the alloy. Kinetics of non-isothermal crystallization was studied on the bases of isoconversional principle. Determination of kinetic triplets of individual crystallization steps, based on deconvolution of the complex DSC peaks applying Fraser-Suzuki function, enabled assessment of thermal stability of the alloy and kinetic predictions at different temperatures. © 2018 Elsevier B.V.

Dimić, D.

The importance of specific solvent-solute interactions for studying UV-vis spectra of light-responsive molecular switches
(2018) *Comptes Rendus Chimie*, 21 (11), pp. 1001-1010.

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ABSTRACT: Short-range interactions between solvents and molecular switches influence their structure, electronic transitions, and stability. The explicit solvent interactions between water and N'-[1-(2-hydroxyphenyl)ethylidene]isonicotinoyl hydrazone, as a representative of the light-responsive molecule, were investigated by quantum chemical techniques, density functional theory, natural bond orbital, and quantum theory of atoms in molecules. On the basis of the preliminary spectra obtained with the polarizable continuum solvent model, the most probable groups for the formation of specific interactions were determined. The experimental UV-vis spectrum was reproduced with the addition of five molecules of water and interactions between solvent and solute are discussed in detail. The number of water molecules was reduced to one and it was proven that this can be sufficient for the reproduction of the experimental spectra if solvent molecules are placed in the right position. Quantum theory of atoms in molecules analysis gave better insight into the change of bond critical point parameters with distance, especially for the formed hydrogen bonds. © 2018 Académie des sciences

Vujković, M., Bajuk-Bogdanović, D., Matović, L., Stojmenović, M., Mentus, S.

Mild electrochemical oxidation of zeolite templated carbon in acidic solutions, as a way to boost its charge storage properties in alkaline solutions
(2018) *Carbon*, 138, pp. 369-378.

<https://doi.org/10.1016/j.carbon.2018.07.053>

ABSTRACT: Coulombic capacity of zeolite-templated carbon (ZTC) measured in alkaline solution was roughly doubled by a previous potentiodynamic treatment in sulfuric acidic solution. In order to explain the reasons of this capacity improvement, the changes in chemical composition of ZTC surface during its pretreatment in sulfuric acid either by simple immersion, or by potentiodynamic polarization, and during subsequent potentiodynamic polarization in KOH solutions, were studied by means of TG/DTA, FTIR spectroscopy and Raman spectroscopy. The results of this study open some novel insights in understanding of very peculiar carbon

electrochemistry. The observed changes in surface chemistry include i) fast adsorption of H₂O and formation of OH⁻ and epoxide groups on immersion in sulfuric acid, ii) the multiplication of concentration of H₂O/OH⁻ and epoxide groups during potentiodynamic cycling in sulfuric acid and iii) the ring-opening of epoxide groups (formed during potentiodynamic cycling in acidic solution) upon its potentiodynamic cycling in alkaline solution, according to a SN₂ type mechanism, which results in the formation of aromatic OH-containing diol compounds. © 2018 Elsevier Ltd

Waisi, H., Janković, B., Nikolić, B., Dragičević, V., Panić, I., Tosti, T., Trifković, J.

Influence of various concentrations of 24-epibrassinolide on the kinetic parameters during isothermal dehydration of two maize hybrids (2018) South African Journal of Botany, 119, pp. 69-79.

<https://doi.org/10.1016/j.sajb.2018.08.006>

ABSTRACT: 24-epibrassinolide (24-EBL) is plant steroid hormone that can regulate several physiological effects in plants, including promotion of cell growth and induction of heat stress tolerance. The purpose of this work is to investigate the influence of various concentrations of 24-EBL on the dehydration mechanism of seedlings of two maize hybrids (ZP434 and ZP704). Control and treated samples were subjected to isothermal conditions for dehydration processes. The effects of carbohydrates and mineral contents on the possible changes in the dehydration mechanism (from kinetics standpoint) were investigated. Comparing control samples to samples treated with 24-EBL, it was found that different dehydration mechanisms exist. The differences arise from the influence of 24-EBL, that causes a significant increase of phosphorus values for ZP704, whilst the reverse was identified for ZP434. It was assumed that the plumule sensitivity to dehydration stress originates from the interaction of water with primary amino groups as cations in polyamines, for lower concentrations of 24-EBL. It was found that the temperature variation (105-130 °C) leads to situations where trehalose does not arrive fast enough to "replace the water" because its handicap to binds (by hydrogen bonds) to biomolecules instead of water. It was found that 24-EBL cause changes of carbohydrates properties, which are important for the defense mechanism from environmental stresses. © 2018 SAAB

Jovanović, A., Petković, M., Pašti, I.A., Johansson, B., Skorodumova, N.V.

Tuning the electronic and chemisorption properties of hexagonal MgO nanotubes by doping - Theoretical study (2018) Applied Surface Science, 457, pp. 1158-1166.

<https://doi.org/10.1016/j.apsusc.2018.07.041>

ABSTRACT: Oxide materials offer a wide range of interesting physical and chemical properties. Even more versatile behavior of oxides is seen at the nanoscale, qualifying these materials for a number of applications. In this study we used DFT calculations to investigate the physical and chemical properties of small hexagonal MgO nanotubes of different length. We analyzed the effect of Li, B, C, N, and F doping on the properties of the nanotubes. We find that all dopants favor the edge positions when incorporated into the nanotubes. Doping results in

the net magnetization whose value depends on the type of the impurity. Using the CO molecule as a probe, we studied the adsorption properties of pristine and doped MgO nanotubes. Our results show that the dopant sites are also the centers of significantly altered chemical reactivity. While pristine MgO nanotubes adsorb CO weakly, very strong adsorption at the dopant sites (B-, C-, and N-doped nanotubes) or neighboring edge atoms (F- and Li-doped nanotubes) is observed. Our results suggest that impurity engineering in oxide materials can be a promising strategy for the development of novel materials with possible use as selective adsorbents or catalysts. © 2018 Elsevier B.V.

Beljic Durkovic, B.B., Jovanovic, J.D., Adnadjevic, B.K.
Comparative kinetics of the alkali-catalyzed sunflower oil methanolysis with co-solvent under conventional and microwave heating with controlled cooling
(2018) Green Processing and Synthesis, 7 (5), pp. 441-452.

<https://doi.org/10.1515/gps-2017-0038>

ABSTRACT: The kinetics of the alkali-catalyzed transesterification of sunflower oil with methanol in the presence of co-solvent (TSMPC) were investigated. The kinetics curves of the alkali-catalyzed TSMPC, in the temperature range of 26°C-55°C, were measured for conventional heating (CH) and microwave heating with controlled cooling. The results showed that for both heating modes, the kinetics of the alkali-catalyzed TSMPC reaction can be described with the kinetic model of the pseudo first-order reaction with respect to the concentration of the triglycerides. The values of apparent reaction rate constants, activation energies, and pre-exponential factors are also calculated. The existence of a linear correlation (compensation effect) between the values of apparent kinetic parameters determined for CH and microwave heating with controlled cooling conditions is established. The results confirmed that the increase in the transesterification rate in the microwave heating with controlled cooling conditions is not caused by overheating nor by the existence of hotspots. The model of mechanism of the impact of microwave heating on the kinetics of transesterification is hereby proposed. © 2018 Walter de Gruyter GmbH, Berlin/Boston.

Mitić, M., Milovanović, M., Ranković, R., Jerosimić, S., Perić, M.
Topological study of nonadiabatic effects in Π electronic states of tetra-atomic molecules
(2018) Molecular Physics, 116 (19-20), pp. 2671-2685.

<https://www.scopus.com/inward/record.uri?eid=2-s2.0->

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ABSTRACT: In this study, we investigate the topological structure of the adiabatic potential energy surfaces and nonadiabatic matrix elements in the framework of a simple model for handling the Renner-Teller effect in tetra-atomic molecules. The reliability of the transformation from the adiabatic to diabatic electronic basis functions is discussed. As a concrete example, we consider the $X^2\Pi_u$ electronic state of $C_2H_2^+$. © 2018, © 2018 Informa UK Limited, trading as Taylor & Francis Group.

Milikić, J., Vasić, M., Amaral, L., Cvjetičanin, N., Jugović, D., Hercigonja, R., Šljukić, B.

NiA and NiX zeolites as bifunctional electrocatalysts for water splitting in alkaline media

(2018) International Journal of Hydrogen Energy, 43 (41), pp. 18977-18991.

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ABSTRACT: NiA and NiX zeolites were prepared and characterised using XRD, FTIR and SEM, and subsequently tested as electrodes for hydrogen (HER) and oxygen (OER) evolution reactions in alkaline media. Linear sweep voltammetry and chronoamperometry techniques showed that NiA has higher catalytic activity for these two reactions, as evidenced by higher current densities, which can be correlated with a higher weight fraction of Ni in this electrocatalyst than in the NiX and with its higher conductivity. HER and OER kinetic parameters, including Tafel slope, exchange current density and apparent activation energy were evaluated. Electrochemical impedance spectroscopy analysis yielded values of the resistance of the solution, charge transfer and mass transfer, as well as double layer capacitance and pseudo-capacitance of the working electrode, at different potentials and temperatures. Unlike the HER, during which the mass transfer resistance of the adsorbed intermediate is dominant in the case of NiA, the OER impedance response is controlled by the charge transfer process itself at the potentials of interest for these process. The overall resistance related to the HER is lower for NiA than for NiX. © 2018 Hydrogen Energy Publications LLC

Radojević, M., Janković, B., Jovanović, V., Stojiljković, D., Manić, N. Comparative pyrolysis kinetics of various biomasses based on model-free and DAEM approaches improved with numerical optimization procedure (2018) PLoS ONE, 13 (10), art. no. e0206657, .

<https://doi.org/10.1371/journal.pone.0206657>

ABSTRACT: The pyrolysis process of various types of biomass (agricultural and wood by-products) in non-isothermal conditions using simultaneous thermal analyses (STA) was investigated. Devolatilization kinetics was implemented through combined application of model-free methods and DAEM (distributed activation energy model) using Gaussian distribution functions of activation energies. Results obtained were used in the curve prediction of the rate of mass loss against temperature at various heating rates by numerical optimization. The possible calculation of biomass samples behavior under pyrolytic conditions as the summation of their pseudo-components, hemicelluloses, cellulose, and lignin is also explored. The differences between experimental and calculated data are less than 3.20% offering a quality test of applicability of proposed model on the kinetic studies of a wide range of biomass samples. It seems that the most physically realistic model is the decomposition of biomass in three reactions, depending on the composition of the biomass regarding hemicelluloses, cellulose, and lignin. Kinetic model applied here may serve as a starting point to build more complex models capable of describing the thermal behavior of plant materials during thermochemical processing. © 2018 Radojević et al. This is an open access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.

Kučírková, T., Stiborek, M., Dúčka, M., Navrátilová, J., Bogdanović Pristov, J., Popović-Bijelić, A., Vojvodić, S., Preisler, J., Kanický, V., Šmarda, J., Spasojević, I., Beneš, P.

Anti-cancer effects of wedelolactone: interactions with copper and subcellular localization

(2018) *Metallomics*, 10 (10), pp. 1524-1531.

<https://doi.org/10.1039/c8mt00191j>

ABSTRACT: Wedelactone (WL), a plant polyphenolic derivative of coumestan, represents a promising anti-cancer agent. The underlying mechanisms of its action are not fully understood and appear to involve interplay with copper ions. Herein, we examined coordination and redox interactions of WL with Cu²⁺ in phosphate buffer (pH 7), and in two breast cancer cell lines. EPR, UV-Vis and fluorescence spectroscopy showed that WL and Cu²⁺ build a coordination complex with 2:1 stoichiometry and distorted tetrahedral geometry. WL showed strong fluorescence that was quenched by Cu²⁺. The sequestration of the intracellular copper pool with neocuproine led to a significant drop in the cytotoxic effects of WL, whereas the co-application of Cu²⁺ and WL and the formation of an extracellular complex suppressed both the cytotoxic effects of WL and copper loading. Fluorescence microscopy showed that WL is mainly localized in the cytosol and significantly less in the nuclei. WL fluorescence was stronger in cells pretreated with neocuproine, implying that the complex of WL and Cu²⁺ is formed inside the cells. WL caused a two-fold increase in the lysosomal level of copper as well as copper-dependent lysosome membrane permeabilization. On the other hand, the protective effects of overexpression of thioredoxin 1 imply that WL exerts the main oxidative impact inside the nucleus. The interactions of WL with copper may be essential for therapeutic performance and selectivity against cancer cells, taking into account that a number of cancer types, including breast cancer, exhibit increased intratumoral copper levels or altered copper distribution. © The Royal Society of Chemistry.

Gavrilov, N., Momčilović, M., Dobrota, A.S., Stanković, D.M., Jokić, B., Babić, B., Skorodumova, N.V., Mentus, S.V., Pašti, I.A.

A study of ordered mesoporous carbon doped with Co and Ni as a catalyst of oxygen reduction reaction in both alkaline and acidic media

(2018) *Surface and Coatings Technology*, 349, pp. 511-521.

<https://doi.org/10.1016/j.surfcoat.2018.06.008>

ABSTRACT: The incorporation of trace amounts (<0.2%) of Co and Ni noticeably enhanced the catalytic activity of nitrogen-free ordered mesoporous carbon (OMC) towards oxygen reduction reaction (ORR). (Co,Ni)-doped OMCs were characterized by N₂-adsorption measurements, X-ray powder diffraction, field emission scanning electron microscopy and Raman spectroscopy methods, and their ORR activity was estimated by voltammetry on rotating disk electrode in acidic and alkaline media. (Co,Ni)-doped OMCs show modest activities in acidic media, while the catalytic activity in alkaline media is rather high. The measured activities are compared to the Pt-based and Pt-free ORR catalysts reported in the literature. The number of electrons consumed per O₂ in

metal-doped OMCs was found to vary between 2 and 4, which is advantageous in comparison to metal-free OMC. Also, the mass activities of metal-doped OMCs were found to be up to 2.5 times higher compared to that of metal-free OMC. We suggest that the ORR activity is governed by a balance between (i) textural properties, which determine the electrochemically accessible surface of the catalyst and which are influenced by the addition of a metal precursor, and (ii) novel active sites formed upon the introduction of metals into the carbon structure. In particular, our Density Functional Theory calculations suggest that Co and Ni atoms embedded into the single vacancies of graphene can activate the O₂ molecule and contribute to the decomposition of peroxide. © 2018 Elsevier B.V.

Petković, M., Nakarada, Đ., Etinski, M.

When hydroquinone meets methoxy radical: Hydrogen abstraction reaction from the viewpoint of interacting quantum atoms
(2018) *Journal of Computational Chemistry*, 39 (23), pp. 1868–1877.

<https://doi.org/10.1002/jcc.25359>

ABSTRACT: Interacting Quantum Atoms methodology is used for a detailed analysis of hydrogen abstraction reaction from hydroquinone by methoxy radical. Two pathways are analyzed, which differ in the orientation of the reactants at the corresponding transition states. Although the discrepancy between the two barriers amounts to only 2 kJ/mol, which implies that the two pathways are of comparable probability, the extent of intra-atomic and inter-atomic energy changes differs considerably. We thus demonstrated that Interacting Quantum Atoms procedure can be applied to unravel distinct energy transfer routes in seemingly similar mechanisms. Identification of energy components with the greatest contribution to the variation of the overall energy (intra-atomic and inter-atomic terms that involve hydroquinone's oxygen and the carbon atom covalently bound to it, the transferring hydrogen and methoxy radical's oxygen), is performed using the Relative energy gradient method. Additionally, the Interacting Quantum Fragments approach shed light on the nature of dominant interactions among selected fragments: both Coulomb and exchange-correlation contributions are of comparable importance when considering interactions of the transferring hydrogen atom with all other atoms, whereas the exchange-correlation term dominates interaction between methoxy radical's methyl group and hydroquinone's aromatic ring. This study represents one of the first applications of Interacting Quantum Fragments approach on first order saddle points. © 2018 Wiley Periodicals, Inc. © 2018 Wiley Periodicals, Inc.

Milojević-Rakić, M., Bajuk-Bogdanović, D., Nedić Vasiljević, B., Rakić, A., Škrivanj, S., Ignjatović, L., Dondur, V., Mentus, S., Čirić-Marjanović, G.

Polyaniline/FeZSM-5 composites - Synthesis, characterization and their high catalytic activity for the oxidative degradation of herbicide glyphosate
(2018) *Microporous and Mesoporous Materials*, 267, pp. 68–79.

<https://doi.org/10.1016/j.micromeso.2018.03.019>

ABSTRACT: Semiconducting composites of nanostructured and granular polyaniline (PANI) with FeZSM-5 zeolite were synthesized by the oxidative polymerization of aniline with ammonium peroxydisulfate in water, without added acid and in an aqueous H₂SO₄ solution, in the presence of FeZSM-5, by using initial weight ratios aniline/FeZSM-5 of 1/1 and 1/5. These novel composite materials, in their as-synthesized (protonated) and deprotonated forms, were characterized by elemental, thermogravimetric and differential thermal analysis, scanning electron microscopy, FTIR and Raman spectroscopy, X-ray powder diffraction and conductivity measurements. The catalytic activity of the PANI/FeZSM-5 composites towards the oxidation of herbicide glyphosate with hydrogen peroxide has been investigated. A significant improvement of the catalytic activity of PANI/FeZSM-5 composites compared to that of pure PANI and FeZSM-5 was observed, manifested by the almost one order of magnitude more efficient oxidative degradation of glyphosate with hydrogen peroxide. The maximum of oxidized/decomposed amount of glyphosate was achieved in the presence of PANI/FeZSM-5 composite synthesized using an initial aniline/FeZSM-5 = 1/5 wt ratio. It has been shown that the method of synthesis and interactions between PANI and zeolite in this complex composite system, leading to more efficient electron transfer and hydrogen peroxide decomposition, are crucial for the catalytic properties of tested PANI/FeZSM-5 materials. It is shown that new PANI/FeZSM-5 composites present advanced catalyst materials for enhanced green catalytic degradation of pesticide/herbicide pollutants in environmental remediation systems. © 2018 Elsevier Inc.

Janković, B.

Reliable method for determining the complete kinetic and thermodynamic information for thermal degradation of polymers in a multi-step process (2018) *Colloid and Polymer Science*, 296 (9), pp. 1459-1477.

<https://doi.org/10.1007/s00396-018-4366-z>

ABSTRACT: Proposed approach enables a reliable determination of kinetic and thermodynamic behaviors for thermal degradation of polymers. As a model polymer, poly(ethylene oxide) with average molecular weight $M_v \sim 100.000$ (PEO100) was used. Two-component continuous distribution kinetics best describes PEO100 thermal degradation, involving two main reactions with different values of reaction orders. Procedure enables the check of existence of true or real enthalpy-entropy compensation (EEC). It was established that in the case of random scission reaction step, the artificial EEC emerges. For second reaction step which involves β -scission reaction step ("slow" step), true (real) EEC emerges. It was found that this reaction step is responsible for occurrence of successive micro-phase transitions. These transitions are associated with significant reduction of PEO100 crystallinity through a hinder effect on polymer chains. It was concluded that these transitions are cyclic and reversible, related to the change of mechanical properties of the polymer. © 2018, Springer-Verlag GmbH Germany, part of Springer Nature.

Petrušić, I., Daković, M., Kačar, K., Mičić, O., Zidverc-Trajković, J. Migraine with aura and white matter tract changes (2018) *Acta Neurologica Belgica*, 118 (3), pp. 485-491.

<https://doi.org/10.1007/s13760-018-0984-y>

ABSTRACT: We aimed to explore whether a migraine with aura (MA) is associated with structural changes in tracts of a white matter and to compare parameters of diffusivity between subgroups in migraineurs. Forty-three MA and 20 healthy subjects (HS), balanced by sex and age, were selected for this study. Analysis of diffusion tensor parameters was used to identify differences between MA patients and HS, and then between MA subgroups. A diffusion tensor probabilistic tractography analysis showed that there is no difference between MA patients and HS. However, using more-liberal uncorrected statistical threshold, we noted a trend in MA patients toward lower diffusivity indices of selected white matter tracts located in the forceps minor and right anterior thalamic radiation (ATR), superior longitudinal fasciculus (temporal part) (SLFT), cingulum-cingulate tract, and left uncinate fasciculus. Migraineurs who experienced somatosensory and dysphasic aura, besides visual symptoms, had tendency toward lower diffusivity indices, relative to migraineurs who experienced only visual symptoms, in the right inferior longitudinal fasciculus, forceps minor, and right superior longitudinal fasciculus (parietal part), SLFT, and cingulum-angular bundle. Aura frequency were negatively correlated with axial diffusivity and mean diffusivity of the right ATR (partial correlation = - 0.474; p = 0.002; partial correlation = - 0.460; p = 0.002), respectively. There were no significant differences between MA patients and HS, neither between MA subgroups. Migraineurs with abundant symptoms during the aura possibly have more myelinated fibers relative to those who experience only visual symptoms. Lower diffusivity indices of the right ATR are linked to more frequent migraine with aura attacks. © 2018, Belgian Neurological Society.

Stanojević, A., Marković, V.M., Čupić, Ž., Kolar-Anić, L., Vukojević, V.

Advances in mathematical modelling of the hypothalamic-pituitary-adrenal (HPA) axis dynamics and the neuroendocrine response to stress (2018) Current Opinion in Chemical Engineering, 21, pp. 84-95.

<https://doi.org/10.1016/j.coche.2018.04.003>

ABSTRACT: Stress is a physiological reaction of an organism to a demand for change that is imposed by external factors or is coming from within by way of physiological strains or self-perceived mental and/or emotional threats (internal factors). It manifests itself through the sudden release of a flood of hormones, including corticosteroids, into the blood, which rouse the body for action. Normally, stress is beneficial, but when lasting or being very strong, it causes major damage to our mind and body. Despite intense research, we still do not understand fully how the stress response axis, whose main function is to respond to challenges while maintaining the normal physiological balance, loses under prolonged exposure to stressors its capacity to maintain homeostasis. Recent applications of mathematical modelling and dynamical systems theory have enabled us to emulate complex neurochemical transformations that underlie the stress response, and help us to acquire deeper understanding of this dynamical regulatory network. © 2018

Gutić, S.J., Jovanović, A.Z., Dobrota, A.S., Metarapi, D., Rafailović, L.D., Pašti, I.A., Mentus, S.V.

Simple routes for the improvement of hydrogen evolution activity of Ni-Mo catalysts: From sol-gel derived powder catalysts to graphene supported co-electrodeposits

(2018) International Journal of Hydrogen Energy, 43 (35), pp. 16846-16858.

<https://doi.org/10.1016/j.ijhydene.2017.11.131>

ABSTRACT: Development of noble metal-free catalysts for hydrogen production is one of the cores of the sustainable energy economy. Here we present results of systematic analysis of catalytic activity of Ni-Mo alloy powders in alkaline media towards hydrogen evolution reaction (HER). Catalysts were prepared in a wide concentration range (from Ni_{0.2}Mo_{0.8} to Ni_{0.9}Mo_{0.1}), and resulted with a volcano shaped activity-composition relationship, with maximum catalytic activity achieved for the powder with nominal composition Ni_{0.6}Mo_{0.4}. Improved HER activity is ascribed to reduced deactivation by hydride formation and adequate hydrogen-surface energetics on Ni-Mo catalysts. In the second part, we demonstrate a novel method for electrochemical formation of NiMo@rGO composites. Prepared composite electrodes show improved electrocatalytic activity compared to both pure Ni and Ni@rGO electrodes. Activity was observed to depend on the deposition time and is contributed by two factors: (i) formation of Ni-Mo system and (ii) formation of an interfacial region with rGO. We expect that the provided activity-composition relationship in combination with novel electrochemical NiMo-rGO composite formation procedure will provide a route for the development of new highly efficient noble metal-free HER electrocatalysts. © 2017 Hydrogen Energy Publications LLC

Stanisavljev, D.R., Stevanović, K.Z., Bujanja, I.N.M.

Outsized stochasticity of iodine oxidation with hydrogen peroxide and its implications on the reaction mechanism

(2018) Chemical Physics Letters, 706, pp. 120-126.

<https://doi.org/10.1016/j.cplett.2018.05.065>

ABSTRACT: We examined the most interesting subsystem of the Bray-Liebhafsky (BL) oscillator i.e. oxidation of iodine to iodate in acidic media with hydrogen peroxide. The reaction induction periods and formed iodate are characterized by potentiometric method and stopped-flow technique. Introduction of a very slow mixing, at 27 °C, increased standard deviation of results to 124 from 2.5 in experiments without mixing. It is confirmed at two lower temperatures. In such (initially) simple chemical system the stochasticity is related with random fluctuations forming critical oxygen cavities. Possible energetic coupling of the nucleation processes with chemical reactions is discussed in connection with previous results. © 2018 Elsevier B.V.

Stamenović, U., Gavrilov, N., Pašti, I.A., Otoničar, M., Ćirić-Marjanović, G., Škapin, S.D., Mitrić, M., Vodnik, V.

One-pot synthesis of novel silver-polyaniline-polyvinylpyrrolidone electrocatalysts for efficient oxygen reduction reaction

(2018) Electrochimica Acta, 281, pp. 549-561.

<https://doi.org/10.1016/j.electacta.2018.05.202>

ABSTRACT: A facile and fast aqueous phase-based strategy to synthesize silver-polyaniline-polyvinylpyrrolidone (Ag-PANI-PVP) nanocomposites, via chemical oxidative polymerization method is presented. In the presence of polyvinylpyrrolidone (PVP), which has an accelerating effect on the oxidation of aniline with silver nitrate, Ag nanoparticles (AgNPs) were in situ generated in aqueous solution during simultaneous formation of polyaniline (PANI), without any additional reducing agent or complicated treatment. We have demonstrated synthesis of three stable Ag-PANI-PVP nanocomposites with different content, size, and morphology of Ag nanoparticles by varying the experimental parameters, such as pH and PVP concentration. As a result, this led to different Ag nanostructures (spherical and polyhedral NPs), and, consequently, different morphology of formed nanocomposites (granular and nanosheets). The physicochemical properties of nanocomposites were examined by using different analytical techniques (UV-Vis, TEM, FESEM, FT-IR, XRD, and Raman). It is found that optical properties, electrical conductivity and the content of Ag in the composites vary depending on the synthetic conditions. The electrocatalytic behavior of Ag-PANI-PVP nanocomposites was examined towards the oxygen reduction reaction in acidic and alkaline media. All tested nanocomposites showed high electrocatalytic activity, while the most active catalyst is the one with the highest electrical conductivity ($\approx 0.6 \text{ S cm}^{-1}$) and the lowest Ag content (3.4 wt%), synthesized in the solution without added acid. The simplicity of synthesis and good electrocatalytic efficiency of prepared nanocomposites combined with large-scale availability make them attractive as Pt-free electrocatalysts. © 2018 Elsevier Ltd

Zhang, Y., Serrano-Luginbühl, S., Kissner, R., Milojević-Rakić, M., Bajuk-Bogdanović, D., Ćirić-Marjanović, G., Wang, Q., Walde, P. Enzymatic Synthesis of Highly Electroactive Oligoanilines from a p-Aminodiphenylamine/Aniline Mixture with Anionic Vesicles as Templates (2018) *Langmuir*, 34 (31), pp. 9153-9166.

<https://doi.org/10.1021/acs.langmuir.8b00953>

ABSTRACT: Oligoanilines with characteristic properties of the electrically conductive emeraldine salt form of polyaniline (PANI-ES) are promising molecules for various applications. A mixture of such oligoanilines can be obtained, for example, enzymatically under mild conditions from the linear aniline dimer p-aminodiphenylamine (PADPA) with hydrogen peroxide (H_2O_2) and low amounts of horseradish peroxidase (HRP) in an aqueous pH = 4.3 suspension of anionic vesicles formed from AOT, the sodium salt of bis(2-ethylhexyl)sulfosuccinate. However, the simultaneous formation of undesired side products containing phenazine-type units or oxygen atoms is unsatisfactory. We have found that this situation can be improved considerably by using a mixture of PADPA and aniline instead of PADPA only but otherwise nearly identical conditions. The PANI-ES-like oligoaniline products that are obtained from the PADPA and aniline mixture were not only found to have much lower contents of phenazine-type units and not contain oxygen atoms but also were shown to be more electroactive in cyclic voltammetry measurements than the PANI-ES-like products obtained from PADPA only. The AOT vesicle suspension remained stable without product precipitation during and after the entire reaction so that it could be analyzed by in situ UV/visible/near-infrared, in situ electron paramagnetic resonance, and in situ Raman spectroscopy measurements. These measurements were complemented with ex situ high-performance

liquid chromatography analyses of the deprotonated and reduced products formed from mixtures of PADPA and either fully or partially deuterated aniline. On the basis of the results obtained, a reaction mechanism is proposed for explaining this improved HRP-triggered, vesicle-assisted synthesis of electroactive PANI-ES-like products. The oligomeric products obtained can be further used, without additional special workup, for example, to coat electrodes for their possible application in biosensor devices. © 2018 American Chemical Society.

Čupić, Ž., Maćešić, S., Novakovic, K., Anić, S., Kolar-Anić, L.
Stoichiometric network analysis of a reaction system with conservation constraints
(2018) *Chaos*, 28 (8), art. no. 083114, .

<https://doi.org/10.1063/1.5026791>

ABSTRACT: Stoichiometric Network Analysis (SNA) is a powerful method that can be used to examine instabilities in modelling a broad range of reaction systems without knowing the explicit values of reaction rate constants. Due to a lack of understanding, SNA is rarely used and its full potential is not yet fulfilled. Using the oscillatory carbonylation of a polymeric substrate [poly(ethylene glycol)methyl ether acetylene] as a case study, in this work, we consider two mathematical methods for the application of SNA to the reaction models when conservation constraints between species have an important role. The first method takes conservation constraints into account and uses only independent intermediate species, while the second method applies to the full set of intermediate species, without the separation of independent and dependent variables. Both methods are used for examination of steady state stability by means of a characteristic polynomial and related Jacobian matrix. It was shown that both methods give the same results. Therefore, as the second method is simpler, we suggest it as a more straightforward method for the applications. © 2018 Author(s).

Mohaček-Grošev, V., Gebavi, H., Bonifacio, A., Sergio, V., Daković, M., Bajuk-Bogdanović, D.
Binding of p-mercaptobenzoic acid and adenine to gold-coated electroless etched silicon nanowires studied by surface-enhanced Raman scattering
(2018) *Spectrochimica Acta - Part A: Molecular and Biomolecular Spectroscopy*, 200, pp. 102-109.

<https://doi.org/10.1016/j.saa.2018.04.016>

ABSTRACT: Modern diagnostic tools ever aim to reduce the amount of analyte and the time needed for obtaining the result. Surface-enhanced Raman spectroscopy is a method that could satisfy both of these requirements, provided that for each analyte an adequate substrate is found. Here we demonstrate the ability of gold-sputtered silicon nanowires (SiNW) to bind p-mercaptobenzoic acid in 10^{-3} , 10^{-4} and 10^{-5} M and adenine in 30 and 100 μ M concentrations. Based on the normal mode analysis, presented here for the first time, the binding of p-mercaptobenzoic acid is deduced. The intensity enhancement of the 1106 cm^{-1} band is explained by involvement of the C-S stretching deformation, and the appearance of the broad 300 cm^{-1} band attributed to S-Au stretching mode. Adenine SERS spectra demonstrate the existence

of the 7H tautomer since the strongest band observed is at 736 cm⁻¹. The adenine binding is likely to occur in several ways, because the number of observed bands in the 1200-1600 cm⁻¹ interval exceeds the number of observed bands in the normal Raman spectrum of the free molecule. © 2018 Elsevier B.V.

Chanda, D., Dobrota, A.S., Hnát, J., Sofer, Z., Pašti, I.A., Skorodumova, N.V., Paidar, M., Bouzek, K.
Investigation of electrocatalytic activity on a N-doped reduced graphene oxide surface for the oxygen reduction reaction in an alkaline medium
(2018) International Journal of Hydrogen Energy, 43 (27), pp. 12129-12139.

<https://doi.org/10.1016/j.ijhydene.2018.05.012>

ABSTRACT: Today the search for new energy resources is a crucial topic for materials science. The development of new effective catalysts for the oxygen reduction reaction can significantly improve the performance of fuel cells as well as electrocatalytic hydrogen production. This study presents the scalable synthesis of nitrogen-doped graphene oxide for the oxygen reduction reaction. The combination of an ab initio theoretical investigation of the oxygen reduction reaction (ORR) mechanism and detailed electrochemical characterization allowed the identification of electrocatalytically active nitrogen functionalities. The dominant effect on electrocatalytic activity is the presence of graphitic and pyridinic nitrogen and also N-oxide functionalities. The overpotential of ORR for nitrogen-doped graphene oxide prepared by microwave-assisted synthesis outperformed the metal-doped graphene materials. © 2018 Hydrogen Energy Publications LLC

Miletić, J., Drakulić, D., Pejić, S., Petković, M., Ilić, T.V., Miljković, M., Stefanović, A., Prostran, M., Stojanov, M.
Prooxidant-antioxidant balance, advanced oxidation protein products and lipid peroxidation in Serbian patients with Parkinson's disease
(2018) International Journal of Neuroscience, 128 (7), pp. 600-607.

<https://doi.org/10.1080/00207454.2017.1403916>

ABSTRACT: Background: Biomarkers of oxidative stress are relevant in the evaluation of the disease status and prooxidant-antioxidant balance, advanced oxidation protein products and lipid peroxidation products (malondialdehyde and 4-hydroxynonenal) are being extensively evaluated regarding their relationship with clinical presentation and disease severity. Aim of the study: The aim of this study was to evaluate the levels of the above-mentioned parameters in plasma of 39 men and 17 women with Parkinson's disease, originated from the Republic of Serbia and their relation to clinicopathological characteristics (gender, age at examination, duration of the disease, and Hoehn and Yahr score) and oxidative status. Results: The incidence of disease was 2:1 towards males. The investigated oxidative parameters were gender and Hoehn and Yahr related. Significant association of higher Hoehn and Yahr scores was observed for malondialdehyde (p = 0.01) and prooxidant-antioxidant balance (p = 0.02). Relation between oxidant-antioxidant status was further supported by observed positive correlation between 4-hydroxynonenal (p = 0.04) and prooxidant-antioxidant balance (p = 0.03). Finally, the multivariate analysis indicated that prooxidant-

antioxidant balance and malondialdehyde were partially determined by gender (10.6% and 7.6%) and Hoehn and Yahr scores (13.6% and 18.8%), while Hoehn and Yahr scores contributed to the variance of advanced oxidation protein products with 13.2%. Conclusion: Our results indicate the higher level of oxidative stress (oxidant-antioxidant imbalance) and possible relation of several markers with gender and disease stage in patients with Parkinson's disease. The analyzed markers could be used to specify the severity of oxidative stress; however, their potential value should be analyzed in further studies. © 2017 Informa UK Limited, trading as Taylor & Francis Group.

Trtica, M.S., Radak, B., Milovanovic, D., Kuzmanovic, M., Savovic, J. Laser-based optical techniques for the detection of chemical agents* (2018) European Physical Journal Plus, 133 (7), art. no. 268, .

<https://doi.org/10.1140/epjp/i2018-12145-4>

ABSTRACT: Among numerous existing and developing techniques for the detection of air pollution, laser-based optical methods (LBM) are possibly the most promising ones. Unique sensing capabilities of LBM include high speed of analysis, high selectivity, sensitivity and accuracy, low detection limits, and remote detection. This paper gives a brief review of several laser-based systems for optical sensing of gas-phase chemical agents: laser intra-cavity, photoacoustic and laser-induced breakdown spectroscopy, and remote sensing based on differential absorption. For each method, a brief description of the principles of operation is given, and its analytical capabilities are outlined. © 2018, Società Italiana di Fisica and Springer-Verlag GmbH Germany, part of Springer Nature.

Jovanović, S., Holclajtner-Antunović, I., Uskoković-Marković, S., Bajuk-Bogdanović, D., Pavlović, V., Tošić, D., Milenković, M., Todorović Marković, B. Modification of graphene oxide surfaces with 12-molybdophosphoric acid: Structural and antibacterial study (2018) Materials Chemistry and Physics, 213, pp. 157-167.

<https://doi.org/10.1016/j.matchemphys.2018.04.011>

ABSTRACT: Antibacterial properties of graphene oxide (GO) have been studied extensively in the last few years, while for polyoxometalates there are just a few researches. Herein, we prepared nanocomposites of GO and different amounts of 12-molybdophosphoric acid (MoPA) and analyzed their antibacterial activity and both structural and morphological properties. In nanocomposites with higher amounts of MoPA, graphene sheets were significantly changed with disrupted flat, graphene-like morphology of GO. In the nanocomposites with low MoPA content, flat GO morphology was preserved. Additionally, structural analyses showed some changes in symmetry of the Keggin anion as a consequence of interactions between GO and MoPA, the increase in structural disorder and the lowering of electron density in GO structure due to interaction with MoPA. We have studied antibacterial properties on the gram-positive: *Staphylococcus aureus*, *Staphylococcus epidermidis*, *Bacillus subtilis*; and the gram-negative bacteria: *Escherichia coli*, *Klebsiella pneumoniae*, *Pseudomonas aeruginosa* and

Salmonella abony. Only a mild antibacterial effect of GO and nanocomposites with low amount of MoPA against *Bacillus subtilis* was observed, while the rest of analyzed materials did not show any antibacterial activity. © 2018

Janković, B., Dodevski, V.

The combustion performances and thermo-oxidative degradation kinetics of plane tree seeds (PTS) (*Platanus orientalis* L.) (2018) *Energy*, 154, pp. 308-318.

<https://doi.org/10.1016/j.energy.2018.04.149>

ABSTRACT: Combustion characteristics (reactivity and reactivity evaluation, ignition index (Di), burn-out index (Df), combustion performance index (S) and combustion stability index (RW)) and thermo-oxidative degradation kinetics of plane tree seeds (PTS) were investigated. Oxidation analysis shows that PTS exhibits stable and high combustion activity, where comparison of ignition and burn-out index values showed that a more developed pore structures of PTS particles exist, and higher volatile matter content is present. Results are also confirmed through derived experience constant value (ζ) and which were compared with other energy sources. It was established that different maximal reaction rate values at various heating rates point out the PTS complex nature, which is stimulated with carbon oxidation reactions and volatile matter release. Kinetic analysis has shown that process can be divided into two stages: devolatilization stage (280-380 °C) and char combustion stage (380-600 °C). In order to obtain a stable solid product, rich in carbon, the PTS shows good performance but with application of high-temperature processing conditions. © 2018 Elsevier Ltd

Hercigonja, R.V., Vranješ-Djurić, S.D., Mirković, M.D., Marković, B.M., Maksin, D.D., Marković, B.N., Nastasović, A.B.

Technetium removal from the aqueous solution using zeolites A and Y containing transition metal ions Co^{2+} and Zn^{2+} (2018) *Journal of Radioanalytical and Nuclear Chemistry*, 317 (1), pp. 215-225.

<https://doi.org/10.1007/s10967-018-5893-2>

ABSTRACT: The adsorption properties of two zeolite types, faujasite (NaY , ZnY , CoY) and LTA-4A zeolite (NaA , ZnA , CoA), towards technetium were studied in batch static experiments. The Si/Al ratio, acidity, dealumination, chargebalance cations of zeolite, contact time and temperature determined the adsorption efficiency. The maximum removal efficiency of 98.8% and K_d value ($2.06 \times 10^{-4} \text{ cm}^3 \text{ g}^{-1}$) was achieved using CoY (zeolite type Y). The kinetics of technetium adsorption followed the pseudo-second order model. The TcO_2 adsorption is mainly due to the hydrogen bonds between protons of the zeolitic structural OH groups (Bronsted acid center) and oxygen from the TcO_2 -. © 2018, Akadémiai Kiadó, Budapest, Hungary.

Janković, B., Dodevski, V., Stojmenović, M., Krstić, S., Popović, J.

Characterization analysis of raw and pyrolyzed plane tree seed (*Platanus orientalis* L.) samples for its application in carbon capture and storage (CCS) technology

(2018) Journal of Thermal Analysis and Calorimetry, 133 (1), pp. 465-480.

<https://doi.org/10.1007/s10973-018-7207-x>

ABSTRACT: Raw and pyrolyzed samples of the plane tree seeds (PTS) were tested by various advanced analytical techniques including simultaneous TG-DSC technique, FTIR analysis, X-ray diffraction (XRD) analysis, Raman spectroscopy analysis, GC-MS (gas chromatography-mass spectrometry) analysis and scanning electron microscope analysis, for its characterization procedure and the pre-treatments in possible application in CCS. Nondestructive analytical method (XRD) showed that raw material is typical for carbon-rich material, where was identified increase in interlayer spacing within graphite structure. The XRD results of pyrolyzed sample at 850 °C showed a sudden loss in interlayer spacing. Spectroscopic analyses of pyrolyzed sample demonstrated the presence of typical aromatic structures found in amorphous carbon. Results indicate the high levels of the growth in basal planes of graphite structure in pyrolyzed sample. It was established that integrated reaction model parameters for pyrolysis of untreated PTS sample realistically describe active temperature period required for charcoal forming, under non-isothermal conditions. It was found that mechanical treatment of material results in increase in the number of chemical compounds. Micrograph showed the presence of variety of shapes and structures, where after pyrolysis, some dissipated pores were detected. One of these pores was partially blocked in some places, depending on the size of surface area. The results showed that the resulting char has very good features for further activation process, while the PTS would represent a good candidate in its application in the CCS. © 2018, Akadémiai Kiadó, Budapest, Hungary.

Janković, B.Ž., Janković, M.M., Marinović-Cincović, M.M., Todorović, D.J., Sarap, N.B.

Thermal analysis testing and natural radioactivity characterization of kaolin as building material

(2018) Journal of Thermal Analysis and Calorimetry, 133 (1), pp. 481-487.

<https://doi.org/10.1007/s10973-018-7159-1>

ABSTRACT: Kaolins are used in a multiplicity of industries because of unique physical and chemical properties. Relationships between thermal and radioactivity properties are discussed in its application as a building material. Super-fine kaolin powder with particle sizes about 30 µm was analyzed. Simultaneous TGA/DTA analysis was performed on powder samples at various heating rates in an argon atmosphere. Based on investigated thermal properties, it was concluded that dehydroxylation process can vary depending on the characteristics of starting material. The maximum degree of the dehydroxylation (DT) was obtained at the lowest rate of heating (DT = 60.79% for 10 °C min⁻¹). With an increase in the heating rate, decline in DT value was observed. Based on comprehensive testing, it was identified that the degree of dehydroxylation does not drop below 50%. It was concluded that appointed experimental conditions seem sufficient admissible for obtaining degree of dehydroxylation (DT) higher than 50%. In order to safe use of kaolin as a building material from the standpoint of

radiological safety, content of natural radionuclides was determined by gamma spectrometry. © 2018, Akadémiai Kiadó, Budapest, Hungary.

Gajić-Kvaščev, M., Bikić, V., Wright, V.J., Radosavljević Evans, I., Damjanović-Vasilić, L.

Archaeometric study of 17th/18th century painted pottery from the Belgrade Fortress

(2018) *Journal of Cultural Heritage*, 32, pp. 9-21.

<https://doi.org/10.1016/j.culher.2018.01.018>

ABSTRACT: The chemical and mineralogical composition of ceramic bodies, glazes and pigments, as well as the firing temperatures of main groups of Austrian period painted pottery excavated at the Belgrade Fortress on the territory of Serbia, two groups of Malhornware and one group of Anabaptist faience, were determined by a combination of powder X-ray diffraction (PXRD), Fourier transform infrared (FTIR) spectroscopy, energy dispersive X-ray fluorescence (XRF) and micro-Raman spectroscopy. Investigated pottery was uncovered in the same archaeological context and dated the end of 17th/first decade of 18th century. The obtained mineralogical and chemical composition shows the similarities between the Malhornware groups that indicate a similar production technology. Use of calcareous clay fired at temperatures in the range 850–900°C indicates a different production technology for the Anabaptists faience. The compositional data treatment by multivariate statistical analysis reveals heterogeneity in the Anabaptist faience group of samples, suggesting potential interactions between the local potters and the Anabaptist communities. © 2018 Elsevier Masson SAS

Bober, P., Gavrilov, N., Kovalcik, A., Mičušík, M., Unterweger, C., Pašti, I.A., Šeděnková, I., Acharya, U., Pflieger, J., Filippov, S.K., Kuliček, J., Omastová, M., Breitenbach, S., Ćirić-Marjanović, G., Stejskal, J.

Electrochemical properties of lignin/polypyrrole composites and their carbonized analogues

(2018) *Materials Chemistry and Physics*, 213, pp. 352-361.

<https://doi.org/10.1016/j.matchemphys.2018.04.043>

ABSTRACT: Lignin/polypyrrole composites were prepared by single-step coating of water-insoluble kraft lignin with polypyrrole. The polymerization of pyrrole was performed with and without the presence of methyl orange, leading to the formation of polypyrrole films of two different morphologies, globular and nanotubular, respectively, on the lignin surface. Such composites were converted to double-carbon composites enriched in inert atoms by pyrolysis in nitrogen atmosphere at 650 °C. The carbonization process was followed by thermogravimetric analysis and confirmed by Raman spectroscopy. The properties of all composites were investigated by FTIR spectroscopy, XPS, EPR, SEM, specific surface area and electrical conductivity measurements. Electrochemical properties were analyzed in terms of their capacitive behavior mainly in acidic solutions, but also in neutral and alkaline media. © 2018 Elsevier B.V.

Krstić, S., Kragović, M., Pagnacco, M., Dodevski, V., Kaluđerović, B., Momčilović, M., Ristović, I., Stojmenović, M.

Hydrothermal synthesized and alkaline activated carbons prepared from glucose and fructose—detailed characterization and testing in heavy metals and methylene blue removal

(2018) *Minerals*, 8 (6), art. no. 246, .

<https://doi.org/10.3390/min8060246>

ABSTRACT: In the presented paper, activated carbons were prepared from fructose and glucose, and activating agents (KOH, NaOH, LiOH) by hydrothermal treatment (HTC) treatment. After preparation, samples were characterized in details. Different techniques were used: x-ray powder diffraction analysis, Raman spectral analysis, elemental analysis, and determination of textural and morphological properties. Obtained results showed dependence of investigated properties and the nature of precursors (glucose or fructose) as well as the type of hydroxides used as activating agents. After characterization, samples were tested as materials for heavy metals (Pb²⁺, Cd²⁺ and Zn²⁺) and methylene blue removal. Also, adsorption experiments were performed on wastewaters taken from tailings of the lead and zinc mine and kinetic of the methylene blue removal was studied. The factors which distinguished the KOH activated samples were high yield (~14%), content of organic carbon (63-74%), porosity and specific surface area (SBET ~700-1360 m²/g), a low degree of the crystal phase, indications that potassium ions may be included in heavy metals removal, good removal of the heavy metal ions (~47-59 mg/g for Pb²⁺, ~21-27 mg/g for Cd²⁺ and ~6-10 mg/g for Zn²⁺) and fast (~10-30 min) and good methylene blue (~60-200 mg/g) removal. © 2018 by the authors. Licensee MDPI, Basel, Switzerland.

Dimić, D., Milenković, D., Ilić, J., Šmit, B., Amić, A., Marković, Z., Dimitrić Marković, J.

Experimental and theoretical elucidation of structural and antioxidant properties of vanillylmandelic acid and its carboxylate anion

(2018) *Spectrochimica Acta - Part A: Molecular and Biomolecular Spectroscopy*, 198, pp. 61-70.

<https://doi.org/10.1016/j.saa.2018.02.063>

ABSTRACT: Vanillylmandelic acid (VMA), an important metabolite of catecholamines that is routinely screened as tumor marker, was investigated by the various spectroscopic techniques (IR, Raman, UV-Vis, antioxidant decolorization assay and NMR). Structures optimized by the employment of five common functionals (M05-2X, M06-2X, B3LYP, CAM-B3LYP, B3LYP-D3) were compared with the crystallographic data. The M05-2X functional reproduced the most reliable experimental bond lengths and angles (correlation coefficient >0.999). The importance of intramolecular hydrogen bonds for structural stability was discussed and quantified by the NBO analysis. The most prominent bands in vibrational spectrum were analyzed and compared to the experimental data. The positions of the carbon and hydrogen atoms in NMR spectra were well reproduced. The differences in UV-Vis spectrum were investigated by adding the explicit solvent and by performing NBO and QTAIM analyses. The discrepancy in the two spectra of about 50 nm could be explained by the solvent effect on carboxyl group. The most probable antioxidant activity mechanism was discussed for VMA and its carboxylate anion. The Molecular Docking study with the C - reactive

protein additionally proved that variety of functional groups present in VMA and its anion allowed strong hydrogen and hydrophobic interactions. © 2018 Elsevier B.V.

Zdravković, J.D., Radovanović, L., Poletić, D., Rogan, J.R., Vulić, P.J., Radovanović, Ž., Minić, D.M.

Mechanism and degradation kinetics of zinc complex containing isophthalato and 2,2'-dipyridylamine ligands under different atmospheres

(2018) Solid State Sciences, 80, pp. 123-131.

<https://doi.org/10.1016/j.solidstatesciences.2018.04.013>

ABSTRACT: The design of mixed-ligand complexes are of increasing interest from fundamental as well as technological and curative aspects. Having that in mind, we studied zinc complex containing 2,2'-dipyridylamine (dipya) and dianion of isophthalic acid (ipht), $[Zn(dipya)(ipht)]_n$, as promising precursor for synthesis of nanostructured metal oxide. In that sense, the mechanism and degradation kinetics of $[Zn(dipya)(ipht)]_n$ was analyzed under non-isothermal conditions in nitrogen and in air atmospheres. Peak deconvolution of the $[Zn(dipya)(ipht)]_n$ decomposition profile, in the form of a derivative thermogram (DTG), in nitrogen atmosphere, revealed the presence of three decomposition steps, while in air five single steps were isolated. In both cases ZnO is formed as residue at 530 °C: pure (in air) or in amorphous matrix (nitrogen). In air we obtained well crystallized ZnO nanospheres (~25 nm), by thermal treatment in temperature range 370-530 °C showing that this complex could be considered as good precursor for production of nanosized ZnO. © 2018 Elsevier Masson SAS

Rašljić, M., Obradov, M., Lazić, Ž., Vasiljević Radović, D., Čupić, Ž., Stanisavljev, D.

Metal layers with subwavelength texturing for broadband enhancement of photocatalytic processes in microreactors

(2018) Optical and Quantum Electronics, 50 (6), art. no. 237, .

<https://doi.org/10.1007/s11082-018-1507-z>

ABSTRACT: In this paper we joined plasmonics and microreactors for photocatalytic optofluidic devices. To this purpose we consider the use of subwavelength texturing of plasmonic films applied to microreactor channel bottom to ensure SPP localization and field enhancement. The small volume of the microchannel is ideal for the enhancement of photocatalytic processes using localized evanescent fields. A great advantage of our approach is that it is highly compatible with the standard chemical bulk micromachining techniques which are commonly used in fabrication of the microreactors i.e. standard photolithography can be used to define microchannels, and radiofrequent sputtering to deposit a gold film as a plasmonic material over the roughened surface. Subwavelength surface texturing can be obtained by varying etching techniques and parameters and the microreactor building materials. We show using ab initio FEM modeling that the stochastic surface profile ensures broadband coupling of visible light as well as enables us to merge plasmonic sensors and microreactors into a single device. © 2018, Springer Science+Business Media, LLC, part of Springer Nature.

Stanić, V.D., Adnadjević, B.K., Dimitrijević, S.I., Dimović, S.D., Mitrić, M.N., Zmejkovski, B.B., Smiljanić, S.
Synthesis of fluorapatite nanopowders by a surfactant-assisted microwave method under isothermal conditions
(2018) Nuclear Technology and Radiation Protection, 33 (2), pp. 180-187.

<https://doi.org/10.2298/NTRP1802180S>

ABSTRACT: Fluorapatite nanopowders with different amounts of fluoride ions were prepared using the surfactant-assisted microwave method under isothermal conditions. Microwave irradiation was applied for the rapid formation of crystals. A micellar solution of polyoxyethylene (23) lauryl ether was used as a regulator of nucleation and crystal growth. Characterization studies from X-ray diffraction, field-emission scanning electron microscopy and Fourier-transform infrared spectra showed that crystals have an apatite structure and particles of all samples are nano size, with an average length of 50 nm and about 15-25 nm in diameter. Antimicrobial studies have demonstrated that synthesized fluorapatite nanopowders exhibit activity against tested pathogens: Escherichia coli, Staphylococcus aureus and Candida albicans. Activity increased with the amount of fluoride ions. The synthesized fluorapatite nanomaterials are promising as materials in environmental protection and medicine for orthopedics and dental restorations. © 2018, Vinca Inst Nuclear Sci. All rights reserved.

Pecovska-Gjorgjevich, M., Stefov, V., Najdoski, M., Koleva, V., Mentus, S., Petruševski, G.
Mg₂KH(XO₄)₂·15H₂O (X = P, As) containing acidic dimer units: Electrochemical impedance spectroscopy, IR spectroscopy and DSC studies
(2018) Journal of Alloys and Compounds, 746, pp. 699-709.

<https://doi.org/10.1016/j.jallcom.2018.02.348>

ABSTRACT: The electrical properties of little known compounds of the type Mg₂KH(XO₄)₂·15H₂O (X = P, As), their dc and ac conductivity and complex impedances are studied for the first time by Electrochemical Impedance Spectroscopy in narrow temperature interval from room temperature until 76 °C. These compounds present interesting electrical behavior with change of the conductivity mechanism and sharp increase in conductivity to ~10⁻²S m⁻¹ when subjected to thermal treatment without structural changes. The complex impedance plots confirm the contribution of two relaxation mechanisms, through grains and grain boundaries, the later becoming dominant at higher temperatures. The ac conductivity obeys Jonscher's power law and is in good agreement with the correlated barrier hopping model. In order to explain their conductivity behavior, the salts are additionally studied by differential scanning calorimetry (DSC), infrared and attenuated total reflectance spectroscopy at higher temperatures. © 2018 Elsevier B.V.

Milovanović, B., Kojić, M., Petković, M., Etinski, M.
New Insight into Uracil Stacking in Water from ab Initio Molecular Dynamics

(2018) Journal of Chemical Theory and Computation, 14 (5), pp. 2621-2632.

<https://doi.org/10.1021/acs.jctc.8b00139>

ABSTRACT: Nucleobases spontaneously aggregate in water by forming stacked dimers and multimers. It is assumed that the main contributions to the aggregation stem from hydrophobic and base-base dispersion interactions. By studying the uracil monomer and dimer in bulk water with the first principle molecular dynamics, we discuss dimer structure and provide evidence that stacking increases the uracil-water hydrogen bonding strength and alters the hydration structure of uracil. These changes have a significant influence on the intensity and shift of the carbonyl stretching band as revealed by simulated infrared absorption spectra of the monomer and dimer and available experimental spectra. The contributions of dipole-dipole, dispersion, and water mediated forces to the stacking are discussed. The reported findings are valuable for understanding the microscopic mechanism of heteroaromatic association in water which is relevant to a large range of chemical and biological systems. © 2018 American Chemical Society.

Dimić, D.S., Milenković, D.A., Marković, J.M.D., Marković, Z.S.
Thermodynamic and kinetic analysis of the reaction between biological catecholamines and chlorinated methylperoxy radicals
(2018) Molecular Physics, 116 (9), pp. 1166-1178.

<https://doi.org/10.1080/00268976.2017.1414967>

ABSTRACT: The antiradical potency of catecholamines (dopamine, epinephrine, norepinephrine, L-DOPA), metabolites of dopamine (homovanillic acid, 3-methoxytyramine and 3,4-dihydroxyphenylacetic acid) and catechol towards substituted methylperoxy radicals is investigated. The thermodynamic parameters, together with the kinetic approach, are used to determine the most probable mechanism of action. The natural bond orbital and quantum theory of atoms in molecules are utilised to explain the highest reactivity of trichloromethylperoxy radical. The preferred mechanism is dependent both on the thermodynamic and kinetic parameters. The number of chlorine atoms on radical, the presence of intra-molecular hydrogen bond and number of hydroxy groups attached to the aromatic ring significantly influence the mechanism. The results suggest that sequential proton loss electron transfer (SPLET) is the most probable for reaction with methylperoxy and hydrogen atom transfer (HAT) for reaction with trichloromethylperoxy radicals, with a gradual transition between SPLET and HAT for other two radicals. Due to the significant deprotonation of molecules containing the carboxyl group, the respective anions are also investigated. The HAT and SPLET mechanisms are highly competitive in reaction with MP radical, while the dominant mechanism towards chlorinated radicals is HAT. The reactions in methanol and benzene are also discussed. © 2017 Informa UK Limited, trading as Taylor & Francis Group.

Janković, B., Marinović-Cincović, M., Janković, M.
A new data in the kinetic and thermodynamic analysis of non-isothermal decomposition of super-fine kaolin powder
(2018) Applied Clay Science, 156, pp. 160-168.

<https://doi.org/10.1016/j.clay.2018.02.008>

ABSTRACT: Kinetic and thermodynamic analysis of non-isothermal decomposition of super-fine kaolin powder was examined. It was established that the decomposition process proceeds through liberation of adsorbed water, the loss of the water of hydration and dehydroxylation process, which produces highly disordered metakaolin. By applying the distributed reactivity approaches, it was found that dehydroxylation can be described with simultaneous two-parallel reactions model. By applying the Exner-Linert statistical method on estimated Eyring plots, the true isokinetic temperature was confirmed. The appearance of entropy - enthalpy compensation (EEC) showed the direct cause-and-effect relationship between these thermodynamic observables resulting by physically real factors such as the steric factors. It was shown that the phenomenon of true compensation effect arises from conformational (geometrical) changes, which occur during metakaolin formation. © 2018 Elsevier B.V.

Pavićević, A., Lakočević, M., Popović, M., Popović-Bijelić, A., Daković, M., Mojović, M.

Changes of the peripheral blood mononuclear cells membrane fluidity from type 1 Gaucher disease patients: An electron paramagnetic resonance study

(2018) *Biological Chemistry*, 399 (5), pp. 447-452.

<https://doi.org/10.1515/hsz-2017-0241>

ABSTRACT: Gaucher disease (GD) is a lysosomal storage disorder, caused by an impaired function of β -glucocerebrosidase, which results in accumulation of glucocerebroside in cells, and altered membrane ordering. Using electron paramagnetic resonance spin labeling, a statistically significant difference in the order parameter between the peripheral blood mononuclear cell membranes of GD patients and healthy controls was observed. Moreover, the results show that the introduction of the enzyme replacement therapy leads to the restoration of the physiological membrane fluidity. Accordingly, this simple method could serve as a preliminary test for GD diagnosis and therapy efficiency. © 2018 Walter de Gruyter GmbH, Berlin/Boston 2018.

Amić, A., Marković, Z., Klein, E., Dimitrić Marković, J.M., Milenković, D.

Theoretical study of the thermodynamics of the mechanisms underlying antiradical activity of cinnamic acid derivatives

(2018) *Food Chemistry*, 246, pp. 481-489.

<https://doi.org/10.1016/j.foodchem.2017.11.100>

ABSTRACT: The role of antiradical moieties (catechol, guaiacyl and carboxyl group) and molecular conformation in antioxidative potency of dihydrocaffeic acid (DHCA) and dihydroferulic acid (DHFA) was investigated by density functional theory (DFT) method. The thermodynamic preference of different reaction paths of double ($2H^+/2e^-$) free radical scavenging mechanisms was estimated. Antiradical potency of DHCA and DHFA was compared with that exerted by their unsaturated analogs - caffeic acid (CA) and ferulic acid (FA). Cis/trans and anti-isomers of studied cinnamic acid derivatives may

scavenge free radicals via double processes by involvement of catechol or guaiacyl moiety. Carboxyl group of syn-isomers may also participate in the inactivation of free radicals. Gibbs free energies of reactions with various free radicals indicate that syn-DHCA and syn-DHFA, colon catabolites that could be present in systemic circulation in low μM concentrations, have a potential to contribute to health benefits by direct free radical scavenging. © 2017 Elsevier Ltd

Avdović, E.H., Milenković, D., Dimitrić Marković, J.M., Đorović, J., Vuković, N., Vukić, M.D., Jevtić, V.V., Trifunović, S.R., Potočňák, I., Marković, Z.

Synthesis, spectroscopic characterization (FT-IR, FT-Raman, and NMR), quantum chemical studies and molecular docking of 3-(1-(phenylamino)ethylidene)-chroman-2,4-dione (2018) *Spectrochimica Acta - Part A: Molecular and Biomolecular Spectroscopy*, 195, pp. 31-40.

<https://doi.org/10.1016/j.saa.2018.01.023>

ABSTRACT: The experimental and theoretical investigations of structure of the 3-(1-(phenylamino)ethylidene)-chroman-2,4-dione were performed. X-ray structure analysis and spectroscopic methods (FTIR and FT-Raman, ^1H and ^{13}C NMR), along with the density functional theory calculations (B3LYP functional with empirical dispersion corrections D3BJ in combination with the 6-311 + G(d,p) basis set), were used in order to characterize the molecular structure and spectroscopic behavior of the investigated coumarin derivative. Molecular docking analysis was carried out to identify the potency of inhibition of the title molecule against human's Ubiquinol-Cytochrome C Reductase Binding Protein (UQCRB) and Methylene-tetrahydrofolate reductase (MTHFR). The inhibition activity was obtained for ten conformations of ligand inside the proteins. © 2018 Elsevier B.V.

Oliveira, R.C.P., Vasić, M., Santos, D.M.F., Babić, B., Hercigonja, R., Sequeira, C.A.C., Šljukić, B.

Performance assessment of a direct borohydride-peroxide fuel cell with Pd-impregnated faujasite X zeolite as anode electrocatalyst (2018) *Electrochimica Acta*, 269, pp. 517-525.

<https://doi.org/10.1016/j.electacta.2018.03.021>

ABSTRACT: This work proposes a direct borohydride fuel cell (DBFC) with palladium (Pd)-impregnated faujasite X zeolite (PdX) as anodic electrocatalyst. The PdX was prepared by Pd ion exchange with Na ion within NaX zeolite and it was characterised by ICP-OES, FTIR, SEM-EDS, TEM and N_2 sorption analysis. PdX was subsequently tested as electrocatalyst for borohydride (BH_4^-) oxidation reaction (BOR) using linear scan voltammetry with and without electrode rotation. For this purpose, sodium borohydride (NaBH_4) solutions ranging between 0.01 and 0.06 M in alkaline medium were used. The reaction order for BH_4^- oxidation at PdX was determined to be close to 1. The PdX zeolite electrode showed high performance for BOR, as evidenced by 3-5 electrons exchanged, depending on NaBH_4 concentration. A laboratory direct borohydride-peroxide fuel cell was assembled using a PdX anode and tested in the 25-45 °C temperature range, reaching power densities between 214 and 263 mW cm^{-2} . © 2018 Elsevier Ltd

Stankovic, B., Jovanovic, J., Adnadjevic, B.
Application of the Suzuki-Fraser function in modelling the non-
isothermal dehydroxylation kinetics of fullerol
(2018) Reaction Kinetics, Mechanisms and Catalysis, 123 (2), pp. 421-
438.

<https://doi.org/10.1007/s11144-018-1380-6>

ABSTRACT: The possibility of fitting the non-isothermal kinetics of C₆₀(OH)₂₇ dehydroxylation by the Frazer-Suzuki equation has been investigated. Thermogravimetric curves of fullerol dehydroxylation have been recorded at different heating rates ranging from 5 to 25 K min⁻¹. The curves of fullerol dehydroxylation reaction rate were completely deconvoluted with the two Frazer-Suzuki functions at all heating rates and hence, it was concluded that mechanism of C₆₀(OH)₂₇ dehydroxylation consisted from two dehydroxylation reactions. Reaction components can be connected with the existence of two clusters on fullerene surface that are formed from OH groups. Using Vyazovkin's isoconversional method, it was found that, for both components, apparent activation energy changes with dehydroxylation degree, meaning that deconvolution using the Frazer-Suzuki function do not decomposes complex reaction of fullerol dehydroxylation on elementary steps. The dependence of activation energies on their dehydroxylation degree for each of the reaction components is the consequence of the existence of activation energy distribution in the form of a narrow peak, which can be further related with unique reaction model function for each dehydroxylation component. © 2018, Akadémiai Kiadó, Budapest, Hungary.

Jerosimić, S.V., Milovanović, M.Z.
Iron monocyanoide (FeCN): Spin-orbit and vibronic interactions in low-
lying electronic states
(2018) Journal of Molecular Spectroscopy, 346, pp. 32-43.

<https://doi.org/10.1016/j.jms.2018.01.005>

ABSTRACT: The spin-orbit eigenvalues of low-energy quartet and sextet spatially degenerate electronic states of FeCN are reported, together with the combined effect of vibronic and spin-orbit interaction in the lowest-lying 14 Δ and 16 Δ states of FeCN, by using perturbational and variational method. Spin-orbit constants (ASO) have been calculated in the basis of: (a) two components of each degenerate state, (b) four components of 14 Δ and 14 Π (16 Δ and 16 Π) states, and (c) ten components of 16 Δ 16 Π 16 Σ^+ , 14 Δ 14 Π and 14 Σ^+ states. The present calculations predict the values of ASO= -77 cm⁻¹ for 16 Δ and ASO= -108 cm⁻¹ for 14 Δ state in the lowest-energy spin-orbit manifolds of each state. The major perturbing state for the 14 Δ state is the 14 Π state (16 Π for the sextet 16 Δ). As expected, based on extremely small splitting and shallowness of the bending potential energy curves for the lowest-lying 4,6 Δ states, the present study indicate that the vibronic coupling does not create significant splitting of the bending levels, but the influence of anharmonicity in the bending mode is more pronounced. However, the spin-orbit fine structure dominantly influences the spectra of this species. © 2018 Elsevier Inc.

Zdolšek, N., Dimitrijević, A., Bendová, M., Krstić, J., Rocha, R.P., Figueiredo, J.L., Bajuk-Bogdanović, D., Trtić-Petrović, T., Šljukić, B. Electrocatalytic Activity of Ionic-Liquid-Derived Porous Carbon Materials for the Oxygen Reduction Reaction (2018) *ChemElectroChem*, 5 (7), pp. 1037-1046.

<https://doi.org/10.1002/celec.201701369>

ABSTRACT: Carbon materials, prepared by using different methods with ionic liquids, are compared as electrocatalysts for the oxygen reduction reaction (ORR). Materials were synthesized through the hydrothermal carbonization of glucose and by using the same method in the presence of 1-butyl-3-methylimidazolium methanesulfonate [bmim][MeSO₃] as an additive. Another two carbon-based materials were prepared by using ionic-liquid-based methods: ionothermal carbonization of glucose using [bmim][MeSO₃] as a recyclable medium for the carbonization reaction and by direct carbonization of the ionic liquid in a one-step method using [bmim][MeSO₃] as the precursor for N- and S-doped porous carbon (Carb-IL). Characterization results showed the possibility of morphology and porosity control by using [bmim][MeSO₃]. All materials were subsequently tested for the ORR in alkaline media. Carb-IL showed enhanced and stable electrocatalytic ORR activity, even in the presence of methanol, ethanol, and borohydride, opening the possibility for its application in fuel cells. © 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Jelić, D., Zeljković, S., Škundrić, B., Mentus, S. Thermogravimetric study of the reduction of CuO-WO₃ oxide mixtures in the entire range of molar ratios (2018) *Journal of Thermal Analysis and Calorimetry*, 132 (1), pp. 77-90.

<https://doi.org/10.1007/s10973-017-6921-0>

ABSTRACT: The oxide mixtures CuO-WO₃ of various compositions were synthesized by citrate-gel combustion process, starting with the aqueous solutions of copper nitrate, ammonium tungstate and citric acid. Cu-W nanocomposite powders were produced by reduction of oxide mixtures in hydrogen atmosphere under thermogravimetric control. Characterization of CuO-WO₃ mixtures and their reduction products was performed by SEM and XRD methods. The morphology of both oxide and metal particles displayed notable dependence on composition. Copper displayed promoting action during reduction of CuO-WO₃ mixtures. The mean reduction temperature shifted monotonously from that of CuO toward that of WO₃. The reduction proceeded in three steps, first of which was mainly reduction of CuO and the other two originated mainly of the two-step reduction of WO₃. The composition CuO-WO₃ at a molar ratio 1:1 was shown to form the compound CuWO₄. The reduction of this compound was subjected to a detailed thermokinetic study. For those purposes, model-free expanded Friedman, multiple heating rate Coats-Redfern and Kissinger methods and some model-fitting methods, incorporated in the software Kinetics2015, were used. Among model-fitting models, the nucleation and growth kinetic model enabled the best fit of experimental results for all three reduction stages. © 2017, Akadémiai Kiadó, Budapest, Hungary.

Pašti, I.A., Jovanović, A., Dobrota, A.S., Mentus, S.V., Johansson, B., Skorodumova, N.V.

Atomic adsorption on pristine graphene along the Periodic Table of Elements - From PBE to non-local functionals
(2018) Applied Surface Science, 436, pp. 433-440.

<https://doi.org/10.1016/j.apsusc.2017.12.046>

ABSTRACT: The understanding of atomic adsorption on graphene is of high importance for many advanced technologies. Here we present a complete database of the atomic adsorption energies for the elements of the Periodic Table up to the atomic number 86 (excluding lanthanides) on pristine graphene. The energies have been calculated using the projector augmented wave (PAW) method with PBE, long-range dispersion interaction corrected PBE (PBE+D2, PBE+D3) as well as non-local vdW-DF2 approach. The inclusion of dispersion interactions leads to an exothermic adsorption for all the investigated elements. Dispersion interactions are found to be of particular importance for the adsorption of low atomic weight earth alkaline metals, coinage and s-metals (11th and 12th groups), high atomic weight p-elements and noble gases. We discuss the observed adsorption trends along the groups and rows of the Periodic Table as well some computational aspects of modelling atomic adsorption on graphene. © 2017 Elsevier B.V.

Tankosić, L., Tančić, P., Sredić, S., Nedić, Z.
Comparative study of the mineral composition and its connection with some properties important for the sludge flocculation process-examples from omarska mine
(2018) Minerals, 8 (3), art. no. 119, .

<https://doi.org/10.3390/min8030119>

ABSTRACT: Studied sludge samples are composed of major goethite and quartz; less clay minerals; and minor magnetite, hematite, clinocllore and todorokite. They have quite similar qualitative, but different semi-quantitative compositions. There are similar particle size distributions between the samples, and the highest contents of ~50% belongs to the finest classes of <6 µm. Among size classes within the samples, almost identical iron contents are present; indicating their similar mineral compositions, which make these systems very complex for further separation processes. Sludge II has a higher natural settling rate, due to its higher density and mineral composition. With addition of the flocculant, settling rates increase significantly with the increase of the liquid component in both of the samples. The effect of flocculant on the settling rate is different between samples, and depends on their mineral composition. The time of settling does not play a role in selectivity, to the ratio of the mass of floating and sinking parts, and iron content does not change with time. The content of iron partially increases by flocculation; therefore, this method should be considered as an appropriate one. Zeta potential values for sludge are mostly between those for goethite and quartz, indicating their particle mixture and intricately association. © 2018 by the authors. Licensee MDPI, Basel, Switzerland.

Zivkovic, S., Savovic, J., Kuzmanovic, M., Petrovic, J., Momcilovic, M.
Alternative analytical method for direct determination of Mn and Ba in peppermint tea based on laser induced breakdown spectroscopy
(2018) Microchemical Journal, 137, pp. 410-417.

<https://doi.org/10.1016/j.microc.2017.11.020>

ABSTRACT: In this study, analytical capability of Laser Induced Breakdown Spectroscopy (LIBS) system based on Transversely Excited Atmospheric pressure (TEA) CO₂ laser for determination of elemental composition of tea samples was demonstrated. Analysis of LIBS spectra indicated emission lines attributed to the elements Fe, Mg, Cu, Ca, Al, Mn, Ba, P, K and Sr. For quantitative analysis of Mn and Ba, a standard addition method was employed. Linear calibration curves with regression coefficients exceeding 0.95 were obtained. The accuracy of LIBS results was confirmed by inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis. Calculated recoveries for Ba and Mn were 99.7 and 102.3%, respectively. The results presented confirm the suitability of the proposed LIBS setup for rapid quantitative analysis of tea, while at the same time simplifying the overall analytical procedure. This approach can be easily used as a helpful analytical tool for food quality and safety control. © 2017 Elsevier B.V.

Sarap, N.B., Senčanski, J.V., Pagnacco, M.C., Janković, M.M., Todorović, D.J., Majstorović, D.M.
Radioactivity level and concentration of metals in waters around power plants application of potential method for pollution assessment (2018) Nuclear Technology and Radiation Protection, 33 (1), pp. 117-124.

<https://doi.org/10.2298/NTRP1801117S>

ABSTRACT: Human activities may lead to increased levels of naturally occurring radioactive material and heavy metals in waters relative to undisturbed natural environment, consequently to reduced safety of environment. Therefore, evaluation of water quality from coal-fired power plants is essential to both environmental protection and protection of the human health. In this paper the concentrations of metals (K, Sr, and Pb) and corresponding radionuclides (⁴⁰K, ⁹⁰Sr, and ²¹⁰Pb) for 22 water samples in the vicinity of five coal-fired power plants in Serbia were determined. The total metal concentrations were measured using an atomic absorption spectrometer. The activities of radionuclides ⁴⁰K and ²¹⁰Pb were determined by gamma spectrometry using HPGe detector, while the activity of ⁹⁰Sr was determined by radiochemical analytical method and measured using low-level gas proportional counter. The water pollution status was assessed by the prospective method that is defined in this study. The preliminary results indicated that operation of the coal-fired power plants has no significant impact on the surrounding environment with regard to the radiological characteristics and content of metals of the investigated waters that can be used for suitable in future applications. © 2018, Vinca Inst Nuclear Sci. All rights reserved.

Jović Orsini, N., Babić-Stojić, B., Spasojević, V., Calatayud, M.P., Cvjetičanin, N., Goya, G.F.
Magnetic and power absorption measurements on iron oxide nanoparticles synthesized by thermal decomposition of Fe(acac)₃ (2018) Journal of Magnetism and Magnetic Materials, 449, pp. 286-296.

<https://doi.org/10.1016/j.jmmm.2017.10.053>

ABSTRACT: Iron oxide magnetic nanoparticles with diameters d , $7 \text{ nm} \leq d \leq 12 \text{ nm}$, were synthesized by thermal decomposition of $\text{Fe}(\text{acac})_3$. Different experimental conditions, keeping constant concentration of Fe ions in solvent, showed that the heating rates is the most important parameter determining the final particle size. Use of two different solvents, 1-eicosene and 1-octadecene, yielded similar nanoparticle sizes ($7.1 \text{ nm} \leq d \leq 7.5 \text{ nm}$), but different magnetic anisotropies. All samples were superparamagnetic at room temperature. Spin disordering was inferred in samples coated with trioctylphosphine oxide (TOPO) co-ligand in addition to oleic acid and oleyamine. The heating ability of $\sim 12 \text{ nm}$ -sized nanoparticles dispersed in hexane under alternating magnetic fields ($3.98 \text{ kA/m} \leq H_0 \leq 23.87 \text{ kA/m}$; $229.3 \text{ kHz} \leq f \leq 828 \text{ kHz}$) has been studied, finding a nearly quadratic dependence upon H_0 , as expected from the linear response theory. © 2017 Elsevier B.V.

Nilsson, J.O., Leetmaa, M., Wang, B., Žguncs, P.A., Pašti, I., Sandell, A., Skorodumova, N.V.
Modeling Kinetics of Water Adsorption on the Rutile TiO_2 (110) Surface: Influence of Exchange-Correlation Functional
(2018) *Physica Status Solidi (B) Basic Research*, 255 (3), art. no. 1700344, .

<https://doi.org/10.1002/pssb.201700344>

ABSTRACT: The accuracy of the theoretical description of materials properties in the framework of density functional theory (DFT) inherently depends on the exchange-correlation (XC) functional used in the calculations. Here we investigate the influence of the choice of a XC functional (PBE, RPBE, PW91, and PBE0) on the kinetics of the adsorption, diffusion and dissociation of water on the rutile $\text{TiO}_2(110)$ surface using a combined Kinetic Monte Carlo (KMC) - DFT approach, where the KMC simulations are based on the barriers for the aforementioned processes calculated with DFT. We also test how the adsorption energy of intact and dissociated water molecules changes when dispersion interactions are included into the calculations. We consider the beginning of the water layer formation varying coverage up to 0.2 monolayer (ML) at temperatures up to 180 K. We demonstrate that the dynamics of the simulated water-titania system is extremely sensitive to the choice of the XC functional. © 2017 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

Etinski, M., Ensing, B.
Puzzle of the intramolecular hydrogen bond of dibenzoylmethane resolved by molecular dynamics simulations
(2018) *Journal of Physical Chemistry A*, 122 (28), pp. 5945-5954.

<https://doi.org/10.1021/acs.jpca.8b01930>

ABSTRACT: The enol form of dibenzoylmethane has been the subject of many experimental and theoretical studies, yet the symmetry and the spectral response of the OHO intramolecular hydrogen bond remains mysterious due to conflicting assignments. In order to qualitatively

understand the complex proton dynamics, it is necessary to probe the neighborhood of stationary points on the potential energy landscape. Here, we employ density functional theory-based molecular dynamics (DFT-MD) simulations to sample the coupling between the intermolecular proton transfer and all other molecular modes. To account for the quantum nature of the proton motion, we employ the path integral formalism within the DFT-MD simulations. Our results reveal that the hydrogen-bonded proton is delocalized between two oxygen atoms with slightly higher probability to be observed in the asymmetric than the symmetric position. The simulated infrared spectrum is found to be in a reasonably good agreement with the experimental spectrum. The computed Voh band is remarkably broad and centered around 2640 cm⁻¹. The origin of the discrepancy between the simulated and experimental intensities of the Voh band is discussed. © 2018 American Chemical Society.

Nakarada, Đ., Petković, M.

Mechanistic insights on how hydroquinone disarms OH and OOH radicals (2018) *International Journal of Quantum Chemistry*, 118 (4), art. no. e25496, .

<https://doi.org/10.1002/qua.25496>

ABSTRACT: Phenol derivatives are distinguished as successful free radical scavengers. We present a detailed analysis of hydroxyl hydrogen abstraction from hydroquinone by hydroxyl and hydroperoxyl radical with emphasis on changes that take place in the vicinity of the transition state. Quantum theory of atoms in molecules is employed to elucidate the sequence of positive and negative charge transfer by studying selected properties of the three key atoms (the transferring hydrogen, the donor atom, and the acceptor atom) along intrinsic reaction path. The presented results imply that in both reactions, which are examples of proton coupled electron transfer, proton, and electron get simultaneously transferred to the radical oxygen atom. The fact that the hydrogen's charge and volume do not monotonously change in the vicinity of the transition state in the product valley results from the adjacency of the proton and the electron to the donor and the acceptor oxygen atoms. Obtaining a detailed understanding of mechanisms by which free radicals are disarmed is of paramount importance given the effects of those highly reactive species on biological systems. A comprehensive analysis of hydroxyl hydrogen abstraction from hydroquinone by hydroxyl and hydroperoxyl radicals, based on changes of selected electronic properties of the three most relevant atoms (hydrogen donor, hydrogen acceptor, and the hydrogen itself), along the reaction coordinate, can be obtained by first-principles calculations. © 2017 Wiley Periodicals, Inc.

Marić-Stojanović, M., Bajuk-Bogdanović, D., Uskoković-Marković, S., Holclajtner-Antunović, I.

Spectroscopic analysis of XIV century wall paintings from Patriarchate of Peć Monastery, Serbia (2018) *Spectrochimica Acta - Part A: Molecular and Biomolecular Spectroscopy*, 191, pp. 469-477.

<https://doi.org/10.1016/j.saa.2017.10.043>

ABSTRACT: The Church of the Holy Mother of God Hodegetria in Peć is decorated with wall paintings that date from the beginning of the 14th

century. In terms of style they correspond to Byzantine wall paintings from the epoch of Paleologos. The painting technique and pigment palette has been examined on micro fragments in thin cross-sections by means of optical microscopy (OM), scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS) and micro-Raman spectroscopy. Use of the fresco technique and two supporting plaster layers was noted on the majority of samples, while in large blue painted areas, a combination of fresco and secco techniques was used. The SEM-EDS results showed the presence of Ca as the main component of plaster besides the traces of Si and Mg. In some samples egg white as a binder was identified. The paint film is often multilayered. Twelve pigments were identified, mainly natural earth pigments such as red ochre, yellow ochre and green earth. A mixture of pigments was used for attaining desirable optical and aesthetical impressions. As decay product only weddelite was detected in many preparatory and painted samples. © 2017 Elsevier B.V.

Bubanja, I.N., Pagnacco, M.C., Maksimović, J.P., Stevanović, K., Stanisavljev, D.
Different influences of adrenaline on the Bray-Liebhafsky and Briggs-Rauscher iodate based oscillating reactions
(2018) *Reaction Kinetics, Mechanisms and Catalysis*, 123 (1), pp. 47-59.

<https://doi.org/10.1007/s11144-017-1305-9>

ABSTRACT: The influence of adrenaline on two iodate based oscillating chemical reactions, the Bray-Liebhafsky (BL) and Briggs-Rauscher (BR) reactions was investigated. It was observed that the addition of adrenaline has different effects on the examined systems. Its addition to the BR system significantly changes the dynamics, while in the BL system, the presence of adrenaline does not show any effect. In order to find out the cause of such a different response of two similar oscillators, UV/VIS spectroscopy was used. Results obtained from recorded UV/VIS spectra indicated that, from all investigated stable reaction species, adrenaline interacts only with potassium iodate and iodine, which are present in both oscillating reactions. Because of this, the different response of the oscillators cannot be ascribed to the reactions between adrenaline and common iodine (stable and unstable) components. As a result, the considerable response of the BR system to adrenaline may be related to the reactions between adrenaline (or its oxidation products) and non-common derivatives of malonic acid or manganese intermediate species. © 2017, Akadémiai Kiadó, Budapest, Hungary.

Pagnacco, M.C., Maksimović, J.P., Janković, B.Ž.
Analysis of transition from low to high iodide and iodine state in the Briggs-Rauscher oscillatory reaction containing malonic acid using Kolmogorov-Johnson-Mehl-Avrami (KJMA) theory
(2018) *Reaction Kinetics, Mechanisms and Catalysis*, 123 (1), pp. 61-80.

<https://doi.org/10.1007/s11144-017-1288-6>

ABSTRACT: The oscillatory behavior is not the only interesting nonlinear phenomena that appeared in the Briggs-Rauscher (BR) reaction. The BR reaction containing malonic acid may undergo a sudden transition from low (the state I) to high iodide and iodine (the state II) concentration states. This paper focuses on the mixture with an

immutable $[CH_2(COOH)_2]_0/[IO_3^-]_0 = 1.5$ value, where state I to state II transition occurs after a time delay and BR reaction ended with a solution abundant of solid iodine. The state I to the state II transition curves obtained at different temperatures were analyzed using the Kolmogorov-Johnson-Mehl-Avrami (KJMA) theory. The KJMA theory was applied for monitoring the crystallization process of isolated solid iodine product at various levels of operating temperatures. At $T < 33.5$ °C, we have one type of the process and iodine was formed by autocatalysis pathway. On the other hand, at $T \geq 33.5$ °C, two processes occur. With the rise in operating temperature, the emergence of inhomogeneous distribution of nuclei was identified and it was established the primary and secondary crystallization processes of iodine. At elevated temperatures, it was also found that the strong influence of impingement mechanism exists. Results obtained are the first step toward elucidation of the complex reaction mechanism of the state I \rightarrow state II transition. © 2017, Akadémiai Kiadó, Budapest, Hungary.

Milojević-Rakić, M., Dondur, V., Damjanović-Vasilić, L., Rac, V., Rakić, V.

The accessibility of sites active in the dissociative adsorption of aromatic hydrocarbons in FeZSM-5 zeolite (2018) *Reaction Kinetics, Mechanisms and Catalysis*, 123 (1), pp. 231-246.

<https://doi.org/10.1007/s11144-017-1275-y>

ABSTRACT: The competitive adsorption of aromatic hydrocarbons (benzene, methyl- and ethyl-benzene) and water on FeZSM-5 zeolites have been investigated by means of temperature-programmed desorption coupled with mass spectrometry (TPD/MS). The incorporation of iron in zeolite was done by aqueous ion exchange using dilute solutions of Fe complexes (ferric citrate and ferrous oxalate) and ferric nitrate. Diffuse reflectance UV-Vis spectroscopy and temperature-programmed reduction (TPR) were applied to characterize active sites on investigated zeolites. The existence of different iron species on FeZSM-5 zeolites was revealed. It has been demonstrated that the activity of the Fe exchanged zeolite depends on the iron salt used for ion exchange. The isolated, dispersed ions, which are often considered to be essential for adsorption and catalysis, were obtained with high yield only by ion exchange in the presence of ferrous oxalate. TPD/MS measurements show that aromatic hydrocarbons adsorb on specific, strong active sites in hydrated zeolites. The binding occurred when organic molecules replace water previously adsorbed at the same sites. Benzene showed non-dissociative adsorption/desorption, while new mass fragments were recorded during methyl-benzene and ethyl-benzene desorption implying their dissociative adsorption/desorption on active sites in hydrated zeolites. © 2017, Akadémiai Kiadó, Budapest, Hungary.

Anić, S.R., Čupić, Ž.D.

Dynamics and kinetics of complex reaction systems. Contributions of the Professor emeritus Ljiljana Kolar-Anić (2018) *Reaction Kinetics, Mechanisms and Catalysis*, 123 (1), .

<https://doi.org/10.1007/s11144-017-1290-z>

ABSTRACT: A brief review of Professor Ljiljana Kolar-Anić's research on the dynamics and kinetics of complex reaction systems is given, with a special emphasis on contributions in the research of the oscillatory processes of Bray, Belousov and Hypothalamic-pituitary-adrenal system. © 2017, Akadémiai Kiadó, Budapest, Hungary.

Adnadjevic, B., Gigov, M., Jovanovic, J.

The effects of external physical fields on the isothermal kinetics of fullerol formation

(2018) *Reaction Kinetics, Mechanisms and Catalysis*, 123 (1), pp. 269-286.

<https://doi.org/10.1007/s11144-017-1326-4>

ABSTRACT: The isothermal kinetics of fullerol formation under different heating modes: conventional (CH), ultrasonic (USH) and microwave (MWH) was investigated. The isothermal kinetic curves of fullerol formation at different temperatures (293, 298, 303, 308 and 313 K) were measured. The kinetic model of the reaction was determined on the basis of the shape of the dependencies of reaction rate on fullerene concentration and on method of initial rates. The values of isothermal rate constants under different heating conditions and temperatures and their kinetic parameters were calculated. The effect of heating mode on the values of the kinetic parameters was established. The possibility of an existence of overheating and hot spots on the rate of fullerol formation was evaluated and discussed. The model of impact of USH and MWH on the reaction kinetics that is based on the model of selective energy transfer is suggested. The established effects of USH and MWH on the reaction of fullerol formation are successfully explained by that model. © 2017, Akadémiai Kiadó, Budapest, Hungary.

Cervellati, R., Greco, E., Blagojević, S.M., Blagojević, S.N., Anić, S., Čupić, Ž.D.

Experimental and mechanistic study of the inhibitory effects by phenolics on the oscillations of the Orbàn-Epstein Reaction

(2018) *Reaction Kinetics, Mechanisms and Catalysis*, 123 (1), pp. 125-139.

<https://doi.org/10.1007/s11144-017-1306-8>

ABSTRACT: The system $\text{KSCN-H}_2\text{O}_2\text{-CuSO}_4\text{-NaOH}$, also known as the Orbàn-Epstein oscillatory reaction, is exposed to external perturbations by several phenolic compounds: catechol, resorcinol, hydroquinone, 2,5-dihydroxybenzoic acid, 2,6-dihydroxybenzoic acid, 2,3-dihydroxybenzoic acid, 2,4-dihydroxybenzoic acid, 3,4-dihydroxybenzoic acid, 3,5-dihydroxybenzoic acid, caffeic acid, and ferulic acid. As a result of the performed perturbation in most examined cases, oscillations have been inhibited for some characteristic time, and resumed afterwards. The evaluated inhibition time is typical for each substance and strongly dependent on its concentration. The chemical mechanism of the interaction between the Orbàn-Epstein system and phenolic compounds is briefly discussed. Numerical simulations are performed using the original Orbàn-Epstein model with 30 reactions, extended by three reactions describing the interaction with inhibitory substances. The rate constants of three added reactions are adjusted to fit experimental inhibition times, and compared among used compounds. The observed effects are discussed further in relation with the bond

dissociation enthalpy theory. Unlike other tested compounds, 2,5-dihydroxybenzoic acid remains off from predicted order of activity. © 2017, Akadémiai Kiadó, Budapest, Hungary.

Bubanja, I.N., Bánsági, T., Jr., Taylor, A.F.
Kinetics of the urea-urease clock reaction with urease immobilized in hydrogel beads
(2018) *Reaction Kinetics, Mechanisms and Catalysis*, 123 (1), pp. 177-185.

<https://doi.org/10.1007/s11144-017-1296-6>

ABSTRACT: Feedback driven by enzyme catalyzed reactions occurs widely in biology and has been well characterized in single celled organisms such as yeast. There are still few examples of robust enzyme oscillators in vitro that might be used to study nonlinear dynamical behavior. One of the simplest is the urea-urease reaction that displays autocatalysis driven by the increase in pH accompanying the production of ammonia. A clock reaction was obtained from low to high pH in batch reactor and bistability and oscillations were reported in a continuous flow reactor. However, the oscillations were found to be irreproducible and one contributing factor may be the lack of stability of the enzyme in solution at room temperature. Here, we investigated the effect of immobilizing urease in thiol-poly(ethylene glycol) acrylate (PEGDA) hydrogel beads, prepared using emulsion polymerization, on the urea-urease reaction. The resultant mm-sized beads were found to reproduce the pH clock and, under the conditions employed here, the stability of the enzyme was increased from hours to days. © 2017, The Author(s).

Bubanja, I.N., Bánsági, T., Jr., Taylor, A.F.
Correction to: Kinetics of the urea-urease clock reaction with urease immobilized in hydrogel beads (*Reaction Kinetics, Mechanisms and Catalysis*, (2018), 123, 1, (177-185), 10.1007/s11144-017-1296-6)
(2018) *Reaction Kinetics, Mechanisms and Catalysis*, 123 (1), p. 187.

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Carević, M.V., Abazović, N.D., Mitrić, M.N., Ćirić-Marjanović, G., Mojović, M.D., Ahrenkiel, S.P., Čomor, M.I.
Properties of Zirconia/Polyaniline hybrid nanocomposites and their application as photocatalysts for degradation of model pollutants
(2018) *Materials Chemistry and Physics*, 205, pp. 130-137.

<https://doi.org/10.1016/j.matchemphys.2017.11.016>

ABSTRACT: A serie of novel ZrO₂/Polyaniline (PANI) hybrid nanocomposite powders were successfully synthesized by the oxidative polymerization

of aniline with ammonium peroxydisulfate (APS) in water, in the presence of ZrO₂ nanoparticles. Syntheses were performed at initial ZrO₂/aniline mole ratios 50, 100 and 150 to produce ZP-50, ZP-100 and ZP-150. The morphological, structural, and optical properties of the synthesized nanocomposites were studied using Transmission electron microscopy (TEM), X-ray powder diffraction (XRD), Raman, UV-Vis and Electron-paramagnetic resonance (EPR) spectroscopies. EPR spectra of ZP-50 and ZP-100 nanocomposites showed the presence of intensive peak at the g-values comparable to that for free electrons (2.0023) indicating the presence of oligo/poly (semiquinone radical cations), i.e. polarons as charge carriers in PANI part; ZP-150 showed weak polaron peak of PANI, and peak that can be assigned to defects in zirconia matrix (Zr³⁺, oxygen vacancies). The monoclinic crystal structure of ZrO₂ nanoparticles in all nanocomposites was confirmed by XRD and by Raman spectroscopy. The photocatalytic activities of ZP nanocomposites were evaluated using the photocatalytic degradation of trichlorophenol (TCP) and Rhodamine B model compounds and compared with the activity of bare ZrO₂ nanoparticles. Enhanced degradation efficiencies of nanocomposites regarding TCP degradation were observed. © 2017 Elsevier B.V.

Maćešić, S., Čupić, Ž., Ivanović-Šašić, A., Anić, S., Radenković, M., Pejić, N., Kolar-Anić, L.
Bifurcation analysis: a tool for determining model parameters of the considered process
(2018) Reaction Kinetics, Mechanisms and Catalysis, 123 (1), pp. 31-45.

<https://doi.org/10.1007/s11144-017-1324-6>

ABSTRACT: In this paper, we intend to show the importance of the bifurcation analysis in understanding of an oscillatory process. Hence, we use the bifurcation diagram of the Bray-Liebafsky reaction performed in continuous well-stirred tank reactor under controlled temperature variations for the determination of the activation energies as well as rate constants of particular steps appearing in the kinetic model of oscillatory reaction mechanism. This approach has led us to the development of general procedure for treatment of experimentally obtained data and extracting kinetic parameters from them, which was very important considering that some rate constants of the already proposed model could not be determined experimentally and have to be fitted (or guessed). Also, the proposed approach has the potential to inspire the refinement of already proposed models and the development of a new one that will be able to reproduce experimentally obtained system's dynamical features more successfully. In particular, the dynamic states of the Bray-Liebafsky oscillatory reaction have been analyzed experimentally and numerically using already proposed model together with qualitative and quantitative analysis of bifurcation diagrams in both cases. © 2017, Akadémiai Kiadó, Budapest, Hungary.

Stanojević, A., Marković, V.M., Maćešić, S., Kolar-Anić, L., Vukojević, V.
Kinetic modelling of testosterone-related differences in the hypothalamic-pituitary-adrenal axis response to stress
(2018) Reaction Kinetics, Mechanisms and Catalysis, 123 (1), pp. 17-30.

<https://doi.org/10.1007/s11144-017-1315-7>

ABSTRACT: The sex hormone testosterone (TTS) and the hypothalamic-pituitary-adrenal (HPA) axis mutually control one another's activity, wherein TTS suppresses corticotrophin releasing hormone (CRH) stimulated HPA axis activity, whereas the activation of HPA axis has an inhibitory effect on TTS secretion. With an intention to explain these phenomena, a network reaction model is developed from the previously postulated stoichiometric models for HPA activity where main dynamic behaviors are controlled by two catalytic steps (one autocatalytic and one autoinhibitory) with respect to cortisol, both found experimentally. The capacity of the model to emulate TTS effects on HPA axis dynamics and its response to acute CRH-induced stress is examined using numerical simulations. Model predictions are compared with empirically obtained results reported in the literature. Thus, the reaction kinetic examinations of nonlinear biochemical transformations that constitute the HPA axis, including the negative feedback effect of TTS on HPA axis activity, recapitulates the well-established fact that TTS dampens HPA axis basal activity, decreasing both cortisol level and the amplitude of ultradian cortisol oscillations. The model also replicates TTS inhibitory action on the HPA axis response to acute environmental challenges, particularly CRH-induced stress. In addition, kinetic modelling revealed that TTS induced reduction in ultradian cortisol amplitude arises because the system moves towards a supercritical Hopf bifurcation as TTS is being increased. © 2017, The Author(s).

Novak, D., Mojovic, M., Pavicevic, A., Zatloukalova, M., Hernychova, L., Bartosik, M., Vacek, J.

Electrochemistry and electron paramagnetic resonance spectroscopy of cytochrome c and its heme-disrupted analogs
(2018) *Bioelectrochemistry*, 119, pp. 136-141.

<https://doi.org/10.1016/j.bioelechem.2017.09.011>

ABSTRACT: Cytochrome c (cyt c) is one of the most studied conjugated proteins due to its electron-transfer properties and ability to regulate the processes involved in homeostasis or apoptosis. Here we report an electrochemical strategy for investigating the electroactivity of cyt c and its analogs with a disrupted heme moiety, i.e. apocytochrome c (acytc) and porphyrin cytochrome c (pcyt c). The electrochemical data are supplemented with low-temperature and spin-probe electron paramagnetic resonance (EPR) spectroscopy. The main contribution of this report is a complex evaluation of cyt c reduction and oxidation at the level of surface-localized amino acid residues and the heme moiety in a single electrochemical scan. The electrochemical pattern of cyt c is substantially different to both analogs acyt c and pcyt c, which could be applicable in further studies on the redox properties and structural stability of cytochromes and other hemeproteins. © 2017 Elsevier B.V.

Nowakowska, S., Mazzola, F., Alberti, M.N., Song, F., Voigt, T., Nowakowski, J., Wäckerlin, A., Wäckerlin, C., Wiss, J., Schweizer, W.B., Broszio, M., Polley, C., Leandersson, M., Fatayer, S., Ivas, T., Baljovic, M., Mousavi, S.F., Ahsan, A., Nijs, T., Popova, O., Zhang,

J., Muntwiler, M., Thilgen, C., Stöhr, M., Pasti, I.A., Skorodumova, N.V., Diederich, F., Wells, J., Jung, T.A.
Adsorbate-Induced Modification of the Confining Barriers in a Quantum Box Array
(2018) ACS Nano, 12 (1), pp. 768-778.

<https://doi.org/10.1021/acsnano.7b07989>

ABSTRACT: Quantum devices depend on addressable elements, which can be modified separately and in their mutual interaction. Self-assembly at surfaces, for example, formation of a porous (metal-) organic network, provides an ideal way to manufacture arrays of identical quantum boxes, arising in this case from the confinement of the electronic (Shockley) surface state within the pores. We show that the electronic quantum box state as well as the interbox coupling can be modified locally to a varying extent by a selective choice of adsorbates, here C60, interacting with the barrier. In view of the wealth of differently acting adsorbates, this approach allows for engineering quantum states in on-surface network architectures. © 2017 American Chemical Society.

Pagnacco, M.C., Maksimović, J.P., Potkonjak, N.I., Božić, B.D., Horváth, A.K.
Transition from Low to High Iodide and Iodine Concentration States in the Briggs-Rauscher Reaction: Evidence on Crazy Clock Behavior
(2018) Journal of Physical Chemistry A, 122 (2), pp. 482-491.

<https://doi.org/10.1021/acs.jpca.7b11774>

ABSTRACT: The Briggs-Rauscher reaction containing malonic acid may undergo a sudden transition from low (state I) to high iodide and iodine (state II) concentration states after a well-defined and strongly reproducible oscillatory period. This study clearly shows that even though the time-dependent behavior of the oscillatory state is reproducible, the time lag necessary for the appearance of the state I to state II transition after the system leaves the oscillatory state becomes irreproducible for an individual kinetic run. This crazy clock behavior of the state I to state II transition is identified by repeated experiments in which stirring rate is taken as a control parameter and all other parameters such as initial conditions, temperature, vessel surface, and the age of solution were kept constant. Surprisingly, a better stirring condition does not make the transition reproducible; it simply does not allow the transition to happen at all. The proposed mechanism, additional explanations, and proposals for this irreproducibility of state I to state II transition have been presented. Considering the fact that the number of crazy clock reactions is only a few, this study may contribute to a better understanding of fundamentals of this phenomenon. © 2017 American Chemical Society.

Marinović, S.R., Ajduković, M.J., Jović-Jovičić, N.P., Mudrinić, T.M., Nedić-Vasiljević, B.N., Banković, P.T., Milutinović-Nikolić, A.D.
Discussion on the comments of Slobodan K. Milonjić on the article entitled "Adsorption of strontium on different sodium-enriched bentonites" by Sanja R. Marinović, Marija J. Ajduković, Nataša P. Jović-Jovičić, Tihana M. Mudrinić, Bojana N. Nedić-Vasiljević, Predrag T. Banković and Aleksandra D. Milutinović-Nikolić, published in the

Journal of the Serbian Chemical Society, vol. 82, issue 4, 2017, pp. 449-463

(2018) Journal of the Serbian Chemical Society, 83 (3), pp. 395-399.

<https://doi.org/10.2298/JSC180123026M>

ABSTRACT: A thorough discussion on the Comments on the article "Adsorption of strontium on different sodium-enriched bentonites", by Sanja R. Marinović, Marija J. Ajduković, Nataša P. Jović-Jovičić, Tihana M. Mudrinić, Bojana N. Nedić-Vasiljević, Predrag T. Banković and Aleksandra D. Milutinović-Nikolić published in the Journal of the Serbian Chemical Society, Volume 82, Issue 4, Pages: 449-463 (2017), given as Letter to the Editor by S. K. Milonjić, is provided in this letter. The authors of the commented paper have considered all the comments, and responded to each of them, point by point. © 2018 Serbian Chemical Society. All Rights Reserved.

Petković, S., Adnadević, B., Jovanović, J.

A novel advanced technology for removal of phenol from wastewaters in a ventury reactor

(2018) Thermal Science, 2018, 12 p.

<https://doi.org/10.2298/TSCI171219202P>

ABSTRACT: Phenol is a major pollutant in the waste waters coming from coal processing. Hydrodynamic cavitation presents a novel technology for phenol removal from waste waters. Hydrodynamic cavitation device with a cavitator of Ventury type for waste water purification was constructed. The hydraulic characteristic of the device were determined: the dependences of flow and cavitation number on inlet pressure. The effects of cavitation number, phenol concentration, pH, temperature, time and quantity of added H₂O₂ on the degree of phenol reduction in the waste water was investigated. The optimal technological parameters of the investigated cavitation purification process of waste waters from phenol were determined. © 2018 Serbian Society of Heat Transfer Engineers.

Tanić, M.N., Čujić, M.R., Gajić, B.A., Daković, M.Z., Dragović, S.D.

Content of the potentially harmful elements in soil around the major coal-fired power plant in Serbia: relation to soil characteristics, evaluation of spatial distribution and source apportionment

(2018) Environmental Earth Sciences, 77 (1), art. no. 28, .

<https://doi.org/10.1007/s12665-017-7214-4>

ABSTRACT: The concentrations and spatial distribution of nine potentially harmful elements (PHEs), namely Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn, and their relation to soil properties were investigated in thirty soil profiles (0-50 cm depth) sampled around the largest Serbian coal-fired power plant (CFPP) "Nikola Tesla A." Soil properties were determined following standard procedures, and total contents of PHEs were analyzed by atomic absorption spectrometer. Concentrations of Cd, Co, Fe, Mn, Pb and Zn were the highest in soil profiles sampled 1 km away from the CFPP, concentrations of Ni and Cu gradually increased up to 4 km, and the highest Cr concentrations were measured in samples taken 6 km away from the CFPP. The highest concentration of PHEs

analyzed, except Mn, corresponded with predominant wind directions. Depth did not show significant impact on distribution of any PHEs investigated. Among soil properties, the total organic carbon showed the closest relationship with the PHEs. Data were processed by a principal component analysis which enabled distinguishing anthropogenic from natural influences on soil properties and PHE contents. Although the impact of CFPP operations is obvious, assets of principal component analysis did not allow clear distinction of CFPP's contribution from parent material in enrichment of PHE contents in the soil in the study area. © 2018, Springer-Verlag GmbH Germany, part of Springer Nature.

Manić, N.G., Janković, B.Ž., Stojiljković, D.D., Jovanović, V.V., Radojević, M.B.

Tga-Dsc-MS analysis of pyrolysis process of various agricultural residues
(2018) Thermal Science, 2018, 15 p.

<https://doi.org/10.2298/TSCI180118182M>

ABSTRACT: Slow pyrolysis (gradual heating over a wide range of temperatures) characteristics of various biomasses (corn brakes (CB), wheat straw (WS) and hazelnut shell (HS)) were investigated by simultaneous thermal analysis (STA-TGA-DTG-DSC), coupled with mass spectrometry (MS). Thermal decomposition of these samples was divided into three stages corresponding to removal of water, devolatilization, and formation of bio-char. It was found that differences in thermal behavior of the samples are due to differences in their composition. MS results showed that H₂, CH₄, H₂O, CO₂ (C₃H₈), CO, and C₂H₆ were main gaseous products released during pyrolysis. Within the pyrolysis processes, it was found that CO₂ can be used on the large scale for production of CO-rich syngas. © 2018 Serbian Society of Heat Transfer Engineers.

Mitic, M., Milovanovic, M., Rankovic, R., Jerosimi, S., Peric, M.
Variational calculation of the vibronic spectrum in the X²Π_u electronic state of C₆ -
(2018) Journal of the Serbian Chemical Society, 83 (4), pp. 439-448.

<https://doi.org/10.2298/JSC171129001M>

ABSTRACT: A variational approach for ab initio handling of the Renner-Teller effect in six-atomic molecules with linear equilibrium geometry is elaborated. A very simple model Hamiltonian suitable for the description of small-amplitude bending vibrations in Π electronic states of arbitrary spin multiplicity was employed. The computer program developed within the framework of the present study was tested on the example of the X²Π_u state of C₆ -. The results are compared with those generated in corresponding perturbative calculations. © 2018 Serbian Chemical Society. All rights reserved.

Janković, B.

Kinetic and reactivity distribution behaviors during curing process of carbon/epoxy composite with thermoplastic interface coatings (T800/3900-2 prepreg) under the nonisothermal conditions
(2018) Polymer Composites, 39 (1), pp. 201-220.

<https://doi.org/10.1002/pc.23920>

ABSTRACT: In this work, the thermal stability, the non-isothermal cure kinetics and distributed reactivity model (DRM) for fiber reinforced resin matrix composite (T800H/3900-2 prepreg) have been systematically analyzed using combined phenomenological and partially fundamental approaches. It has been shown that the proposed actual kinetic model (expressed through the three-parameter Šesták-Berggren (SB) model including the diffusion effects) more accurately describes the curing process than the idealized kinetic model (which includes only the autocatalytic reaction). Presence of diffusion phenomena that occur at elevated temperatures and higher values of the extent of cures were demonstrated and explained in detail, through the use of modified Williams-Landel-Ferry (WLF) equation (based on the glass transition analysis) and the Avrami crystallization theory. The DRM was demonstrated that in autocatalytic stage, the reaction of primary amine with two epoxy groups plays an important role in the overall curing process. It has been shown that condensed phase effects can lower the apparent activation energy (E_a) value of the curing process. The lifetime analysis showed that the studied T800H/3900-2 prepreg possesses good thermal resistance, which is connected with the process including a ring-opening addition-type crosslinking reaction. POLYM. COMPOS., 39:201-220, 2018. © 2016 Society of Plastics Engineers. © 2018 Society of Plastics Engineers

Jerosimić, S.V., Gianturco, F.A., Wester, R.
Associative detachment (AD) paths for H and CN⁻ in the gas-phase:
Astrophysical implications
(2018) Physical Chemistry Chemical Physics, 20 (8), pp. 5490-5500.

<https://doi.org/10.1039/c7cp05573k>

ABSTRACT: The direct dynamical paths leading to Associative Detachment (AD) in the gas-phase, and specifically in the low-temperature regions of the Dark Molecular Clouds (DMC) in the ISM, or in cold trap laboratory experiments, are investigated with quantum chemical methods by using a high-level multi-reference Configuration Interaction (CI) approach that employs single and double excitations plus Davidson perturbative correction [MRSDCI(Q)] and the d-aug-cc-pV5Z basis set. The potential energy curves for H + CN⁻ are constructed for different directions of the H partner approaching the CN⁻ anion within the framework of the Born-Oppenheimer approximation. The present calculations found that the AD energetics at low temperature becomes favorable only along a selected range of approaching directions, thus showing that there is a preferred path of forming HCN at low temperatures, while that of forming its HNC isomer is found to be energetically forbidden. Given the existence in the ISM of different HCN/HNC ratios in different environments, we discuss the implications of our findings for selective formation of either isomer in the low-temperature conditions of the molecular cloud cores. © 2018 the Owner Societies.

Krstić, S.S., Kragović, M.M., Dodevski, V.M., Marinković, A.D., Kaluđerović, B.V., Žerjav, G., Pintar, A., Pagnacco, M.C., Stojmenović, M.D.

Influence of temperature and different hydroxides on properties of activated carbon prepared from saccharose. Characterization, thermal degradation kinetic and dyes removal from water solutions

(2018) Science of Sintering, 50 (2), pp. 255-273.

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ABSTRACT: In presented paper, influence of temperature, precursor concentration and different hydroxides on properties of activated carbon obtained from saccharose were investigated. The samples were prepared by hydrothermal treatment and activated using KOH, NaOH and LiOH. Two saccharose concentrations (0.5, 1.0 mol/dm³) and three temperatures (160, 200, 240 °C) were changed in hydrothermal treatment. Activation processes were performed at 750 °C under N₂ atmosphere. Samples were characterized by X-ray powder diffractometry, elemental analysis, N₂ adsorption-desorption measurements, Fourier-transform infrared spectrometry, scanning electron microscopy and thermal analysis. The obtained samples were tested for potential application in dyes removal from water solutions. © 2016 Authors. Published by the International Institute for the Science of Sintering.

Vasić, M., Čebela, M., Pašti, I., Amaral, L., Hercigonja, R., Santos, D.M.F., Šljukić, B.

Efficient hydrogen evolution electrocatalysis in alkaline medium using Pd-modified zeolite X

(2018) Electrochimica Acta, 259, pp. 882-892.

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ABSTRACT: Palladium ion-exchanged zeolite X (PdX) was prepared by zeolite impregnation with palladium acetylacetonate, followed by thermal degradation of the salt. PdX was characterised using SEM-EDS, ICP-OES and XRD. Analysis revealed presence of 7.78 wt.% of Pd in the form of PdO. Subsequently, PdX was tested for hydrogen evolution reaction (HER) in alkaline medium using linear scan voltammetry, chronoamperometry and electrochemical impedance spectroscopy measurements. The influence of addition of carbon black on the material's catalytic performance was also investigated. The HER kinetic parameters, including Tafel slope, exchange current density and activation energy, were determined. In order to provide atomic-level insights, experimental results were complemented by density functional theory calculations. It is suggested that favourable hydrogen adsorption energetics on PdO is responsible for efficient HER catalysis by this novel electrocatalyst. © 2017 Elsevier Ltd

Janićijević, J., Milić, J., Čalija, B., Micov, A., Stepanović-Petrović, R., Tomić, M., Daković, A., Dobričić, V., Nedić Vasiljević, B., Krajišnik, D.

Potential of the ibuprofen antihyperalgesic effect using inorganically functionalized diatomite

(2018) Journal of Materials Chemistry B, 6 (36), pp. 5812-5822.

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ABSTRACT: Refined diatomite from the Kolubara coal basin (Serbia) was inorganically functionalized through a simple, one-pot, non-time-consuming procedure. Model drug ibuprofen was adsorbed on the functionalized diatomite under optimized conditions providing high drug loading (~201 mg g⁻¹). Physicochemical characterization was performed

on the starting and modified diatomite before and after ibuprofen adsorption. Dissolution testing was conducted on composites containing the drug adsorbed on the modified diatomite (composite) and those containing a physical mixture of the drug with the modified diatomite. The antihyperalgesic and the antiedematous activity of ibuprofen from both composites and physical mixtures were evaluated in vivo employing an inflammatory pain model in rats. Functionalization and subsequent drug adsorption had no significant effect on the diatomite ordered porous structure. Two forms of ibuprofen most likely coexisted in the adsorbed state—the acidic form and a salt/complex with aluminium. Both composite types showed extended ibuprofen release in vitro, but no significant influence on the duration of the ibuprofen effect was observed upon in vivo application of the composite or physical mixture. However, both the composite and the physical mixture were more effective than equivalent doses of ibuprofen in pain suppression in rats. This potentiation of the ibuprofen antihyperalgesic effect may result from the formation of the drug complex with the carrier and can be of clinical relevance. © The Royal Society of Chemistry.

Elshaflu, H., Todorović, T.R., Nikolić, M., Lolić, A., Višnjevac, A., Hagenow, S., Padrón, J.M., García-Sosa, A.T., Djordjevic, I.S., Grubišić, S., Stark, H., Filipović, N.R.

Selenazolyl-hydrazones as novel selective MAO inhibitors with antiproliferative and antioxidant activities: Experimental and In-silico studies

(2018) *Frontiers in Chemistry*, 6 (JUL), art. no. 247, .

<https://doi.org/10.3389/fchem.2018.00247>

ABSTRACT: The novel approach in the treatment of complex multifactorial diseases, such as neurodegenerative disorders and cancer, requires a development of efficient multi-targeting oriented drugs. Since oxidative stress significantly contributes to the pathogenesis of cancer and neurodegenerative disorders, potential drug candidates should possess good antioxidant properties. Due to promising biological activities shown for structurally related (1,3-thiazol-2-yl)hydrazones, a focused library of 12 structurally related benzylidene-based (1,3-selenazol-2-yl)hydrazones was designed as potential multi-targeting compounds. Monoamine oxidases (MAO) A/B inhibition properties of this class of compounds have been investigated. Surprisingly, the p-nitrophenyl-substituted (1,3-selenazol-2-yl)hydrazone 4 showed MAO B inhibition in a nanomolar concentration range ($IC_{50} = 73$ nM). Excellent antioxidant properties were confirmed in a number of different in vitro assays. Antiproliferative activity screening on a panel of six human solid tumor cell lines showed that potencies of some of the investigated compounds was comparable or even better than that of the positive control 5-fluorouracil. In-silico calculations of ADME properties pointed to promising good pharmacokinetic profiles of investigated compounds. Docking studies suggest that some compounds, compared to positive controls, have the ability to strongly interact with targets relevant to cancer such as 5'-nucleotidase, and to neurodegenerative diseases such as the small conductance calcium-activated potassium channel protein 1, in addition to confirmation of inhibitory binding at MAO B. © 2018 Elshaflu, Todorović, Nikolić, Lolić, Višnjevac, Hagenow, Padrón, García-Sosa, Djordjevic, Grubišić, Stark and Filipović.

Lazarević-Pašti, T., Anićijević, V., Baljuzović, M., Anićijević, D.V., Gutić, S., Vasić, V., Skorodumova, N.V., Pašti, I.A.
The impact of the structure of graphene-based materials on the removal of organophosphorus pesticides from water
(2018) *Environmental Science: Nano*, 5 (6), pp. 1482-1494.

<https://doi.org/10.1039/c8en00171e>

ABSTRACT: The wide use of pesticides in modern agriculture and other areas results in an urgent need for their efficient removal from the environment. Adsorption of pesticides is one of the most commonly used strategies for this task. Here we analyze the adsorption of two organophosphorus pesticides, dimethoate (DMT) and chlorpyrifos (CPF), on graphene-based materials. The adsorption was found to be very sensitive to the structure of the adsorbents used. In particular, aliphatic DMT was found to prefer hydrophilic oxidized graphene surfaces. The CPF molecule, which contains an aromatic moiety, prefers adsorption on the surface of a graphene basal plane with high structural order and preserved π electron system. The toxicity of pesticide solutions is reduced after adsorption, suggesting that there is no oxidation of DMT and CPF to more toxic oxo forms. We emphasize that the combination of structural properties of adsorbents and adsorbates defines the adsorption of organophosphorus pesticides on graphene-based materials, while the specific surface area of adsorbents is not the major factor. © 2018 The Royal Society of Chemistry.

Kashima, K., Fujisaki, T., Serrano-Luginbühl, S., Khaydarov, A., Kissner, R., Ležaić, A.J., Bajuk-Bogdanović, D., Ćirić-Marjanović, G., Schuler, L.D., Walde, P.
How experimental details matter. The case of a laccase-catalysed oligomerisation reaction
(2018) *RSC Advances*, 8 (58), pp. 33229-33242.

<https://doi.org/10.1039/C8RA05731A>

ABSTRACT: The *Trametes versicolor* laccase (TvL)-catalysed oligomerisation of the aniline dimer p-aminodiphenylamine (PADPA) was investigated in an aqueous medium of pH = 3.5, containing 80-100 nm-sized anionic vesicles formed from AOT, the sodium salt of bis(2-ethylhexyl)sulfosuccinic acid. If run under optimal conditions, the reaction yields oligomeric products which resemble the emeraldine salt form of polyaniline (PANI-ES) in its polaron state, known to be the only oxidation state of linear PANI which is electrically conductive. The vesicles serve as "templates" for obtaining products with the desired PANI-ES-like features. For this complex, heterogeneous, vesicle-assisted, and enzyme-mediated reaction, in which dissolved dioxygen also takes part as a re-oxidant for TvL, small changes in the composition of the reaction mixture can have significant effects. Initial conditions may not only affect the kinetics of the reaction, but also the outcome, i.e., the product distribution once the reaction reaches its equilibrium state. While a change in the reaction temperature from $T \approx 25$ to 5 °C mainly influenced the rate of reaction, increase in enzyme concentration and the presence of millimolar concentrations of chloride ions were found to have significant undesired effects on the outcome of the reaction. Chloride ions, which

may originate from the preparation of the pH = 3.5 solution, inhibit TvL, such that higher TvL concentrations are required than without chloride to yield the same product distribution for the same reaction runtime as in the absence of chloride. With TvL concentrations much higher than the elaborated value, the products obtained clearly were different and over-oxidised. Thus, a change in the activity of the enzyme was found to have influence not only on kinetics but also led to a change in the final product distribution, molecular structure and electrical properties, which was a surprising find. The complementary analytical methods which we used in this work were in situ UV/vis/NIR, EPR, and Raman spectroscopy measurements, in combination with a detailed ex situ HPLC analysis and molecular dynamics simulations. With the results obtained, we would like to recall the often neglected or ignored fact that it is important to describe and pay attention to the experimental details, since this matters for being able to perform experiments in a reproducible way. © The Royal Society of Chemistry.

Lyskov, I., Etinski, M., Marian, C.M., Russo, S.P.
Exciton energy transfer in organic light emitting diodes with thermally activated delayed fluorescence dopants
(2018) Journal of Materials Chemistry C, 6 (25), pp. 6860-6868.

<https://doi.org/10.1039/c8tc01992d>

ABSTRACT: Molecular systems exhibiting thermally activated delayed fluorescence (TADF) are widely used as fluorescent dopants in organic light-emitting diodes (OLEDs) due to their capacity to harvest triplet excitons. The optoelectronic properties of a TADF-based OLED can be further improved by co-depositing a highly luminescent fluorophore into the emissive layer. In a double-dopant architecture, electrically generated excitons on the TADF molecules are transmitted to the fluorescent emitter for radiative recombination. In this theoretical study, we investigate the ability of singlet excitons on PXZ-TRZ to non-radiatively hop to Rubrene by varying the ambient temperature and solvent polarity. The non-zero probability of the exciton energy transfer is attributed to the vibronic interaction between the charge-transfer (CT) and optically bright high-lying states of the TADF monomer. We systematically extend the outcome of our calculations to a similar class of dimers and discuss how the preferential orientation of linear shaped TADF molecules and their complementary fluorophores can enhance the efficiency of energy transfer. © 2018 The Royal Society of Chemistry.

Gutić, S.J., Kozlica, D.K., Korać, F., Bajuk-Bogdanović, D., Mitrić, M., Mirsky, V.M., Mentus, S.V., Pašti, I.A.
Electrochemical tuning of capacitive response of graphene oxide
(2018) Physical Chemistry Chemical Physics, 20 (35), pp. 22698-22709.

<https://doi.org/10.1039/c8cp03631d>

ABSTRACT: The increasing energy demands of modern society require a deep understanding of the properties of energy storage materials, as well as the tuning of their performance. We show that the capacitance of graphene oxide (GO) can be precisely tuned using a simple electrochemical reduction route. In situ resistance measurements, in combination with cyclic voltammetry measurements and Raman

spectroscopy, have shown that upon reduction GO is irreversibly deoxygenated, which is further accompanied by structural ordering and an increase in electrical conductivity. The capacitance is maximized when the concentration of oxygen functional groups is properly balanced with the conductivity. Any further reduction and deoxygenation leads to a gradual loss of capacitance. The observed trend is independent of the preparation route and the exact chemical and structural properties of GO. It is proposed that an improvement in the capacitive properties of any GO can be achieved by optimization of its reduction conditions. © the Owner Societies.

Pašti, I.A., Johansson, B., Skorodumova, N.V.
Tunable reactivity of supported single metal atoms by impurity engineering of the MgO(001) support
(2018) *Physical Chemistry Chemical Physics*, 20 (9), pp. 6337-6346.

<https://doi.org/10.1039/c7cp08370j>

ABSTRACT: Development of novel materials may often require a rational use of high price components, like noble metals, in combination with the possibility to tune their properties in a desirable way. Here we present a theoretical DFT study of Au and Pd single atoms supported by doped MgO(001). By introducing B, C and N impurities into the MgO(001) surface, the interaction between the surface and the supported metal adatoms can be adjusted. Impurity atoms act as strong binding sites for Au and Pd adatoms and can help to produce highly dispersed metal particles. The reactivity of metal atoms supported by doped MgO(001), as probed by CO, is altered compared to their counterparts on pristine MgO(001). We find that Pd atoms on doped MgO(001) are less reactive than on perfect MgO(001). In contrast, Au adatoms bind CO much more strongly when placed on doped MgO(001). In the case of Au on N-doped MgO(001) we find that charge redistribution between the metal atom and impurity takes place even when not in direct contact, which enhances the interaction of Au with CO. The presented results suggest possible ways for optimizing the reactivity of oxide supported metal catalysts through impurity engineering. © 2018 the Owner Societies.

Milenković, D., Avdović, E.H., Dimić, D., Bajin, Z., Ristić, B., Vuković, N., Trifunović, S.R., Marković, Z.S.
Reactivity of the coumarine derivative towards cartilage proteins: combined NBO, QTAIM, and molecular docking study
(2018) *Monatshefte fur Chemie*, 149 (1), pp. 159-166.

<https://doi.org/10.1007/s00706-017-2051-4>

ABSTRACT: Abstract: The equilibrium geometries and chemical reactivities of the novel coumarine derivative, 3-[1-(3-hydroxypropylamino)ethylidene]chroman-2,4-dione, in water and benzene were investigated. The Fukui parameters, calculated by the Natural and Atoms in Molecules charges, were determined for all atoms in both phases. The most potent sites for the electrophilic, nucleophilic, and radical attack are discussed. Molecular docking analysis was carried out to identify the potency of inhibition of the title molecule against human cartilage proteins. The inhibition activity was obtained for ten

conformations of ligand inside protein. This study proved that the Fukui indices can be used as the reactivity descriptors for the novel substances with inhibitory activity. © 2017, Springer-Verlag GmbH Austria.

Ohui, K., Afanasenko, E., Bacher, F., Ting, R.L.X., Zafar, A., Blanco-Cabra, N., Torrents, E., Dömötör, O., May, N.V., Darvasiova, D., Enyedy, É.A., Popović-Bijelić, A., Reynisson, J., Rapta, P., Babak, M.V., Pastorin, G., Arion, V.B.

New Water-Soluble Copper(II) Complexes with Morpholine-Thiosemicarbazone Hybrids: Insights into the Anticancer and Antibacterial Mode of Action
(2018) Journal of Medicinal Chemistry, . Article in Press.

<https://doi.org/10.1021/acs.jmedchem.8b01031>

ABSTRACT: Six morpholine-(iso)thiosemicarbazone hybrids HL1-HL6 and their Cu(II) complexes with good-to-moderate solubility and stability in water were synthesized and characterized. Cu(II) complexes [Cu(L1-6)Cl] (1-6) formed weak dimeric associates in the solid state, which did not remain intact in solution as evidenced by ESI-MS. The lead proligands and Cu(II) complexes displayed higher antiproliferative activity in cancer cells than triapine. In addition, complexes 2-5 were found to specifically inhibit the growth of Gram-positive bacteria *Staphylococcus aureus* with MIC50 values at 2-5 µg/mL. Insights into the processes controlling intracellular accumulation and mechanism of action were investigated for 2 and 5, including the role of ribonucleotide reductase (RNR) inhibition, endoplasmic reticulum stress induction, and regulation of other cancer signaling pathways. Their ability to moderately inhibit R2 RNR protein in the presence of dithiothreitol is likely related to Fe chelating properties of the proligands liberated upon reduction. © Copyright 2018 American Chemical Society.

Fako, E., Dobrota, A.S., Pašti, I.A., López, N., Mentus, S.V., Skorodumova, N.V.

Lattice mismatch as the descriptor of segregation, stability and reactivity of supported thin catalyst films
(2018) Physical Chemistry Chemical Physics, 20 (3), pp. 1524-1530.

<https://doi.org/10.1039/c7cp07276g>

ABSTRACT: The increasing demand and high prices of advanced catalysts motivate a constant search for novel active materials with reduced contents of noble metals. The development of thin films and core-shell catalysts seems to be a promising strategy along this path. Using density functional theory we have analyzed a number of surface properties of supported bimetallic thin films with the composition A3B (where A = Pt and Pd, and B = Cu, Ag and Au). We focus on the surface segregation, dissolution stability and surface electronic structure. We also address the chemisorption properties of Pd3Au thin films supported by different substrates, by probing the surface reactivity with CO. We find a strong influence of the support in the case of mono-A and bilayers, while the surface strain seems to be the predominant factor in determining the surface properties of supported trilayers and thicker films. In particular, we show that the studied properties of the supported trilayers can be predicted from the lattice mismatch

between the overlayer and the support. Namely, if the strain dependence of the corresponding quantities for pure strained surfaces is known, the properties of strained supported trilayers can be reliably estimated. The obtained results can be used in the design of novel catalysts and predictions of the surface properties of supported ultrathin catalyst layers. © 2017 This journal is the Owner Societies.

Jovanović, A., Dobrota, A.S., Rafailović, L.D., Mentus, S.V., Pašti, I.A., Johansson, B., Skorodumova, N.V.
Structural and electronic properties of V2O5 and their tuning by doping with 3d elements-modelling using the DFT+ U method and dispersion correction
(2018) *Physical Chemistry Chemical Physics*, 20 (20), pp. 13934-13943.

<https://doi.org/10.1039/c8cp00992a>

ABSTRACT: New electrode materials for alkaline-ion batteries are a timely topic. Among many promising candidates, V2O5 is one of the most interesting cathode materials. While having very high theoretical capacity, in practice, its performance is hindered by its low stability and poor conductivity. As regards the theoretical descriptions of V2O5, common DFT-GGA calculations fail to reproduce both the electronic and crystal structures. While the band gap is underestimated, the interlayer spacing is overestimated as weak dispersion interactions are not properly described within GGA. Here we show that the combination of the DFT+U method and semi-empirical D2 correction can compensate for the drawbacks of the GGA when it comes to the modelling of V2O5. When compared to common PBE calculations, with a modest increase in the computational cost, PBE+U+D2 fully reproduced the experimental band gap of V2O5, while the errors in the lattice parameters are only a few percent. Using the proposed PBE+U+D2 methodology we studied the doping of V2O5 with 3d elements (from Sc to Zn). We show that both the structural and electronic parameters are affected by doping. Most importantly, a significant increase in conductivity is expected upon doping, which is of great importance for the application of V2O5 in metal-ion batteries. © 2018 the Owner Societies.

Pašti, I.A., Jovanović, A., Dobrota, A.S., Mentus, S.V., Johansson, B., Skorodumova, N.V.
Atomic adsorption on graphene with a single vacancy: Systematic DFT study through the periodic table of elements
(2018) *Physical Chemistry Chemical Physics*, 20 (2), pp. 858-865.

<https://doi.org/10.1039/c7cp07542a>

ABSTRACT: Vacancies in graphene present sites of altered chemical reactivity and open possibilities to tune graphene properties by defect engineering. The understanding of chemical reactivity of such defects is essential for successful implementation of carbon materials in advanced technologies. We report the results of a systematic DFT study of atomic adsorption on graphene with a single vacancy for the elements of rows 1-6 of the periodic table of elements (PTE), excluding lanthanides. The calculations have been performed using the PBE, long-range dispersion interaction-corrected PBE (PBE+D2 and PBE+D3) and non-local vdW-DF2 functionals. We find that most elements strongly bind to the vacancy, except for the elements of groups 11 and 12, and noble gases, for which the contribution of dispersion interaction to bonding

is most significant. The strength of the interaction with the vacancy correlates with the cohesive energy of the elements in their stable phases: the higher the cohesive energy is, the stronger bonding to the vacancy can be expected. As most atoms can be trapped at the SV site we have calculated the potentials of dissolution and found that in most cases the metals adsorbed at the vacancy are more "noble" than they are in their corresponding stable phases. © 2017 the Owner Societies.