Srpsko hemijsko društvo
Serbian Chemical Society

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2017
120 година
Српског хемијског друштва
120th anniversary of the Serbian Chemical Society

Klub Mladih hemičara Srbije
Serbian Young Chemists' Club

54. SAVETOVANJE SRPSKOG HEMIJSKOG DRUŠTVA

5. KONFERENCIJA MLADIH HEMIČARA SRBIJA

KRATKI IZVODI

i

KNJIGA RADOVA

54th MEETING OF THE SERBIAN CHEMICAL SOCIETY

5th Conference of Young Chemists of Serbia

Book of Abstracts

and

Prodeedings

Beograd 29. i 30. septembar 2017.
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KRATKI IZVODI I KNJIGA RADOVA

54th MEETING OF THE SERBIAN CHEMICAL SOCIETY and
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BOOK OF ABSTRACTS and PROCEEDINGS

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are at the end of the book.
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above titles of the Abstracts.

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KRATKI IZVODI
ABSTRACTS

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54th Meeting of the Serbian Chemical Society

Plenarna predavanja / Plenary Lectures

PP 1

Photo- and Electrochemical Molecular switching: mechanisms and the non-innocence of spectroscopic techniques

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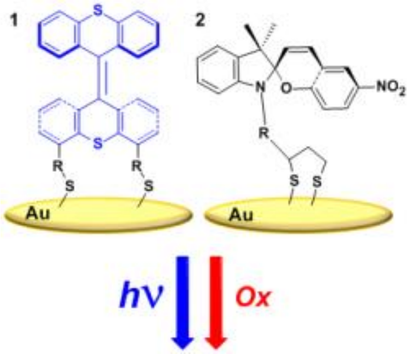
University of Groningen- Stratingh Institute for Chemistry

Responsive surfaces built on functional molecular systems open up a myriad of opportunities in the development of smart surfaces – enabling chemical fine tuning and often reversible control of surface properties such as wetting, adhesion, catalytic activity. A central question arises however in immobilising molecular systems on surfaces as to how their properties are influenced by confinement. In this lecture the functionality of several molecular switches, in particular spiropyrans, in solution, in self-assembled monolayers and in polymer films will be discussed. As an example of the effect of lateral interactions on conformational freedom in self-assembled monolayers (SAM), the bisthiaxanthylidene redox switch (**1**, Fig. 1) which shows excellent bistability, will be discussed.[1] In particular, the methods applicable to explore its photochromic, thermal and electrochemical properties. The main part of the lecture will focus on the well-known spiropyran motif, in which it will be demonstrated that the photo- and electrochemical properties are heavily influenced by both immobilisation and, critically, by the invasiveness of spectroscopic techniques used to characterise the functioning of the hybrid inorganic-organic devices formed.[2-5]



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PP 2

Proteomics in food, nutrition and environmental sciences

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Proteomics methods applied to food, nutrition and environmental sciences may provide answers to important biological questions: identification and quantification of proteins, characterization of processing induced modifications of food proteins, posttranslational modifications of proteins, degradation of proteins, bioactive peptides identification, etc…

An overview of high resolution MS analysis applications in molecular allergology will be given, such as quantification of allergens, identification of post-translational modifications of allergens and mining for novel causative allergenic molecules. An example of ragweed pollen allergens label-free quantification will be provided. An in-depth immunoproteomics of linden tree pollen proteins with the purposses of novel allergens identification, characterization and cloning for the purposes of improvement of molecular diagnostics of respiratory allergies will be presented. Finally, results of digestomics study of major allergenic foods (milk and peanut) will be presented.

Saopštenja / Contributions

Analitička hemija / Analytical Chemistry

AH S - PPP6

Neparametrijski pristup poređenju hromatografskih sistema (kolona)

Filip Andrić
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Odabir hromatografskih kolona (uslova) predstavlja prvi korak u razvoju i validaciji novih hromatografskih metoda. Tehnike za selekciju sličnih i ortogonalnih hromatografskih sistema su mnogobrojne i uglavnom su zasnovane na ograničenom broju test jedinjenja ili na kvantitativnim odnosima molekulske strukture i retencije.

U okviru ovog rada evaluiran je koncept Snajderovog hidrofobnog modela selektivnosti (HSM) koristeći nove neparametrijske tehnike rangiranja - metod sume razlike rangova (SRD) i generalizovani metod korelacije naporednih parova (GPCM), te klasične hemometrijske pristupe - analizu glavne komponente (PCA) i hijerarhijsku klastersku analizu (HCA). Koristeći retencione podatke 67 analita razdvojenih na 10 vrlo sličnih oktadecil-kolona identifikovani su hromatografski obrasci među kolonama i test-jedinjenjima. U poređenju prema konsenzusu izdvojene su optimalne mere sličnosti, a primenom kombinatorne optimizacije skup od 67 analita je efikasno redukovan na 7 test jedinjenja.

Ovo istraživanje je finansirano od strane Ministarstva obrazovanja, nauke i tehnološkog razvoja, Republike Srbije, br. 172017 i bilateralnog projekta između Srpske akademije nauka i umetnosti i Mađarske akademije nauka.

Nonparametric approach to comparison of chromatographic columns

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Selection of suitable chromatographic columns is the first step in development and validation of chromatographic methods. At present there are numerous techniques for selection of similar and orthogonal chromatographic columns. They are mostly based on limited sets of test solutes or quantitative retention relationships models (QSRR).

In the present work the Snyder's Hydrophobic Subtraction Model (HSM) was re-evaluated using non-parametric methods: the Sum of Ranking Differences (SRD) and the Generalized Pair-wise Correlation Method (GPCM), and classical chemometric approaches – Principal Component Analysis and Hierarchical Cluster Analysis. Based on the retention data of 67 solutes separated in 10 very similar octadecyl columns, patterns have been identified in chromatographic systems, as well as in the solute domain. Furthermore, the optimal similarity measures have been selected in a consensus driven comparison. Combinatorial optimization resulted in a reduced set of 7 test compounds.

This work is financed by the Ministry of Education, Science and Technological development of The Republic of Serbia, and by the bilateral cooperation project between Serbian Academy of Sciences and Ardts and Hungarina Academy of Sciences

AH 01

Toksikološki *skrining* sredstava zloupotrebe u kosi primenom LC-QTOF-MS

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***Univerzitet u Nišu - Prirodno-matematički fakultet, Niš, Srbija*

Analiza kose se smatra odličnim pristupom za istraživanje korišćenje droga u sudskoj toksikologiji, kliničkoj toksikologiji i kliničkoj hemiji, posebno kada je potrebno utvrditi unošenje droge nekoliko dana, meseci ili godina pre uzorkovanja. U ovom radu prikazana je primena metode tečne hromatografije sa TOF i masenom spektrometrijom (LC–QTOF-MS) za analizu uzoraka dlaka brade i kose. Nakon ispiranja, homogenizacije i inkubacije uzorci su su ekstrahovani etil-acetatom i centrifugirani. Supernatant je uparen do suvog ostatka u struji azota i rekonstituisani u 0,1 ml metanola. Sistem ESI-QTOF-MS je bio podešen u dva akviziciona moda MS i MS/MS za merenje celog masenog spektra i spektara nastalih fragmentacijom nakon kolizijom izazvane disocijacije (CID) na 10, 20, 30 i 40 eV u pozitivnom modu. U svim analiziranim uzorcima identifikovani su kokain i njegovi metaboliti. U jednom uzorku brade i kose identifikovan je i kokaetilen, marker istovremenog konzumiranja kokaina i alkohola, ali i paracetamol, kofein, sildenafil, levamizol, kvetiapin i lidokain. Primenjena procedura pripreme i analize uzorka kose LC–QTOF-MS metodom, pokazala se kao robusna i osetljiva za kvalitativnu toksikološku analizu velikog broja egzogenih supstanci u kosi.

Toxicological screening for drugs of abuse in hair using LC–QTOF-MS

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Analysis of hair is considered to be an excellent approach for investigation the drug-related history in forensic toxicology, clinical toxicology, and clinical chemistry, especially when it is necessary to determine whether the drug is injected for several days, months or years prior to sampling. This paper presents the application of the liquid chromatography hybrid quadrupole TOF mass spectrometry for the analysis of beard and hair samples. After washing, homogenization and incubation the samples were extracted with ethyl acetate and centrifuged. The supernatant was evaporated to a dry residue in the nitrogen stream and reconstituted in 0.1 ml of methanol. Sample extracts were analized by LC-QTOF MS. The ESI–QTOF-MS instrument was run in data dependent acquisition mode with switching between MS and MS/MS and measuring the full mass spectra and the collision induced dissociation (CID) at 10,20,30 and 40 eV in positive ion mode. Cocaine and its metabolites were identified in all the analyzed samples. Coca ethylene, a marker of the simultaneous consumption of cocaine and alcohol, were identified in one sample of beard and hair. Accurate mass full-spectrum data were processed for qualitative analysis. Proposed procedure of sample preparation and LC–QTOF-MS analysis proved to be a robust and sensitive enough for the routine qualitative screening of wide variety of toxic substances in hair.

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AH 02

Procena autentičnosti medljikovaca

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Medljika se dobija od sokova koje izlučuju biljne vaši na lišću i četinarima ili od sokova koje izlučuju same biljke. Pored veće nutritivne vrednosti u odnosu na cvetni med, ova specifična vrsta meda je malo istražena i manje poznata potrošačima. Cilj ovog rada je karakterizacija i definisanje botaničkog porekla medljikovaca na osnovu fizičko-hemijskih parametara i sadržaja polifenolnih jedinjenja. Sakupljeno je ukupno 80 autentičnih uzoraka medljikovaca sa različitih delova hrvatskog primorja. Pet fizičko-hemijskih parametara (sadržaj vlage, kiselost, električna provodljivost, pH, specifična rotacija) određeno je primenom Harmonizovanih metoda Internacionalne komisije za med, dok je sadržaj polifenola određen ultraefikasnom tečnom hromatografijom spregnutom sa masenom spektrometrijom visoke rezolucije. Utvrđeno je da je na osnovu sadržaja polifenola i fizičko-hemijskih parametara, uz primenu multivarijantne analize, moguće razlikovati medljikovce po botaničkom poreklu.

Zahvalnica: Ova istraživanja su podržana od strane Ministarstva prosvete, nauke i tehnološkog razvoja Republike Srbije (projekat br. 172017).

Authenticity assessment of honeydew honey

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Honeydew honey is mainly obtained from secretions of living parts of plants or excretions of plant-sucking insects on plants. Although of greater nutritional value compared to blossom honey, this specific variety of honey is still less studied and less known to consumers. The aim of the present study was to establish criteria based on physico-chemical parameters and phenolic content that are able to distinguish honeydew honeys of different botanical origin. Therefore, 80 authentic samples of honeydew honey of different botanical origin from several part of coastal area of Croatia were collected. Five physico-chemical parameters (moisture, acidity, electrical conductivity, pH, and specific optical rotation) were analyzed following the Harmonized Methods of the International Honey Commission and phenolic compounds were determined by ultra-high-performance liquid chromatography coupled with hybrid mass spectrometry, which combines the Linear Trap Quadrupole and OrbiTrap mass analyzer. Data on phenolic profile and physico-chemical parameters allowed the discrimination and classification of honeydew honeys in accordance to their botanical origin, using pattern recognition techniques.

Acknowledgment: This work has been supported by the Ministry of Education, Science and Technical Development of the Republic of Serbia, Grant No. 172017.

AH 03

Optimizacija uslova za degradaciju pesticida pomoću hlor dioksida

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S obzirom na sve veću upotrebu hlor dioksida u tretmanu vode, važno je ispitati njegovu reaktivnost sa uobičajenim organskim zagađivačima, kao što su pesticidi. Cilj ovog rada je bio da se pronađu optimalni uslovi za degradaciju pesticida, kao što su: petoksamid i metazahlor pomoću hlor dioksida u dejonizovanoj vodi. Degradacija pesticida je ispitivana sa različitim količinama hlor dioksida (5 i 10 ppm), nakon različitih vremena degradacije (30 min, 1 h, 2 h, 3 h, 6 h i 24 h), kao i pod uslovima svetla ili mraka. U svim eksperimentima polazna koncentracija pesticida je iznosila 10 ppm. Efikasnost degradacije (η) je praćena pomoću HPLC-DAD, dok su glavni degradacioni proizvodi identifikovani pomoću GC/MS analize. Bolja efikasnost degradacije postignuta je za petoksamid (η=100 %) tretiranjem sa 5 ppm hlor dioksida na svetlu, nakon 24 h od početnog tretmana u odnosu na metazahlor (η=47 %). Za proizvode degradacije nakon 24 h tretmana urađeni su testovi akutne toksičnosti koji su određivani na test organizmu *Daphnia magna*.

Optimization conditions for degradation of pesticides using chlorine dioxide

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In view of the increasing usage of chlorine dioxide in water treatment it is important to investigate its reactivity with common organic contaminants, such as pesticides. The aim of this study was to find optimal conditions for degradation of pesticides, such as pethoxamid and metazachlor with chlorine dioxide in deionized water. Degradation of pesticides was tested with different amounts of chlorine dioxide (5 and 10 ppm), after different time of degradation (30 min, 1 h, 2 h, 3 h, 6 h and 24 h), as well as under light or dark conditions. In all experiments the initial concentration of the pesticides was 10 ppm. The degradation efficiency (η) was monitored by HPLC-DAD, while the major degradation products were identified by GC/MS analysis. Better degradation efficiency was achieved for pethoxamid (η = 100 %) by treatment with 5 ppm of chlorine dioxide in the light, after 24 h of the initial treatment in comparison with metazachlor (η = 47 %). The tests of acute toxicity for degradation products were performed after 24 h of treatment, on the test organism *Daphnia magna*.

Acknowledgements. This work was financially supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia.

AH 04

Ispitivanje efikasnosti degradacije herbicida

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Predmet i cilj ovog rada su bili ispitivanje degradacije herbicida (dimetoata i klomazona) sa hlor-dioksidom u dejonizovanoj vodi, ispitivanje efikasnosti degradacije herbicida pomoću HPLC-DAD, određivanje proizvoda degradacije pomoću GC/MS analize i ispitivanje toksičnosti proizvoda degradacije herbicida posle tretmana sa hlor-dioksidom. U sistemu sa dejonizovanom vodom urađena je optimizacija sa različitim dozama hlor-dioksida, posle različitih vremenskih perioda degradacije i pri različitim pH vrednostima rastvora. Rezultati su pokazali da je hlor-dioksid efikasno sredstvo za degradaciju dimetoata. Najbolja efikasnost degradacije dimetoata postignuta je tretiranjem sa 10 ppm hlor-dioksida, nakon 24 h od početnog tretmana, pri pH 7, i iznosila je 97 %. U slučaju herbicida klomazona, najbolja efikasnost degradacije postignuta je tretiranjem sa 10 ppm hlor-dioksida, nakon 6 h od početnog tretmana, pri pH 3 i iznosila je 50 %. Toksikološka analiza je urađena za proizvode degradacije herbicida nakon tretmana hlor-dioksidom od 24 h.

Investigation of degradation efficiency of herbicides

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The objective and goal of this study was to investigate degradation of herbicides (dimethoate and clomazone) with chlorine dioxide in deionized water, investigate degradation efficiency of herbicides using HPLC-DAD, determine degradation products using GC/MS analysis, and examine toxicity of degradation product of herbicides after chlorine dioxide treatment. Optimization of chlorine dioxide dosage at different periods of degradation and at different pH values of solutions was performed in system with deionized water. The results showed that chlorine dioxide is an effective agent for degradation of dimethoate. The best degradation efficiency of dimethoate with yield of 97 % was achieved by treatment with 10 ppm of chlorine dioxide, after 24 h of initial treatment and at pH of 7. In the case of a clomazone herbicide, the best efficiency of degradation yielded 50 % and was achieved by treatment with 10 ppm of chlorine dioxide, after 6 h of initial treatment and at pH 3. Toxicological analysis was also performed for degradation products obtained after 24 h of treatment with chlorine dioxide.

Acknowledgements. This work was financially supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia.

AH 05

Hemijska analiza lišća jabuke tretirane sa metamitronom (BREVIS®)

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Proređivanje plodova predstavlja relevatnu praksu za dobijanje velikih, crvenih jabuka sa visokim parametrima kvaliteta ploda. U poslednje vreme akcenat se stavlja na privremenu inhibiciju fotosinteze prskanjem drveća odgovarajućim agensima. Preparat Brevis® sadrži kao aktivnu komponentu metanitron koji se pokazao kao veoma efikasan inhibitor fotosinteze kod jabuke. Cilj ovog rada bio je proučavanje promene polifenolnog i šećernog profila lišća jabuka kao odgovor na različite koncentracije ovog preparata. Sadržaj šećera u lišću jabuke analiziran je primenom visoko-efikasne jonske hromatografije sa pulsno amperometrijskom detekcijom, dok je polifenolni profil određen primenom ultra visoko efikasne tečne hromatografije kuplovane sa hibridnim masenim spektrometrom. Dobijeni rezultati pokazuju porast sadržaja šećernih alkohola i polisaharida sa porastom količine dodatog inhibitora.

Chemical analysis of apple leaves treated with metamitron (BREVIS®)

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Fruit thinning is relevant management practice to produce apples with high quality fruit size, red coloration, and high fruit quality parameters. Recently, thinning resulting from temporary photosynthetic inhibition, by spraying the trees with photosynthetic inhibitors has been done. Since inhibition of photosynthesis by the new fruit thinning agent Brevis® containing metamitron as active ingredient has been shown to be a very effective in apple. The aim of this study was to determine the polyphenolic and sugar profile in apple leaves treated with different concentration of this thinning agent. The sugar content was determined using high performance anion exchange chromatography with pulsed amperometric detection (HPAEC-PAD) whereas ultra high performance liquid chromatography (UHPLC) coupled with hybrid mass spectrometer was used to identify polyphenolics. The obtained results show an increase in the content of sugar alcohols and polysaccharides with the increase in the amount of added inhibitor.

AH 06

Sadržaj elemenata u semenu različitog gajenog i samoniklog voća

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Strukturna, funkcionalna i nutritivna svojstva voća su važna za definisanje njegovog kvaliteta. Zastupljenost i biodostupnost esencijalnih nutrijenata, kao što su elementi, određuju nutritivna svojstva voća. Uzimajući u obzir činjenicu da je seme voća bogato različitim bioaktivnim komponentama, njihova eksploatacija bi trebalo da bude veća što zahteva dodatne informacije o sastavu različitih sorti. Ukupno 70 različitih sorti samoniklog i gajenog voća iz Srbije je okarakterisano na osnovu sadržaja elemenata. Dvadeset elemenata je određeno primenom induktivno kuplovane plazme atomsko emisione spektrometrije i induktivno kuplovane plazme spregnute sa masenom spektrometrijom. Kalcijum i P su bili najzastupljeniji elementi, praćeni K i Na. Pored pomenutih makroelemenata, potvrđeno je da i mikroelementi i elementi u tragovima varijaju u zavisnosti od sorte. Sve primenjene statističke metode (jedno- i viševarijantne) potvrđuju jedinstveni set parametara koji bi se mogao koristiti kao fitohemijski biomarkeri za određivanje botaničkog porekla, tj. identifikovanje semena voća različitih sorti.

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Distribution of elements in seeds of some wild and cultivated fruits

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Compositional, functional and nutritional properties of fruits are important for defining its quality. The abundance and bioaccessibility of essential nutrients, such as elements, determines the nutritional properties of fruits. Regarding the fact that fruit seeds are also considered to be a good source of different bioactive components, their exploitation should be greater and, consequently more information of cultivars' seeds and their composition is required. A total of 70 different genuine Serbian wild and cultivated fruits species/cultivars were characterized by evaluation of their elements composition. Twenty elements were determined by inductively coupled plasma atomic emission spectrometry and inductively coupled plasma mass spectrometry. Calcium and P were the most abundant elements, followed by K and Na. Additionally to the mentioned macroelements, micro and trace elements were also verified that the bioavailability of essential nutrients varies among the samples. All employed statistical procedures (univariate and multivariate) confirm unique set of parameters that could be used as phytochemical biomarkers to differentiate fruit seeds samples belonging to different cultivars/genotypes according to their botanical origin.

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AH 07

Elektroanalitititičko određivanje bentazona na borom-dopovanoj dijamantskoj elektrodi

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Bentazon je selektivan kontaktni herbicid iz tiodiazinske hemijske grupe jedinjenja kod koga se sumnja da ima reproduktivan toksičan potencijal na ljude usled mogućeg zagađenja podzemnih i površinskih voda. Ovaj rad prezentuje jednostavno, brzo, osetljivo i tačno određivanje bentazona na nemodifikovanoj borom-dopovanoj dijamantskoj elektrodi, diferencijalnom pulsnom voltametrijom u Briton-Robinsonovom puferu (pH 4, oksidacioni pik na1,0 V). Pod optimalnim DPV uslovima dobijena je linearna kalibraciona kriva u opsegu od 2 to100 μM, sa granicom detekcije od 0,5 μM. Efekat mogućih ometajućih supstanci je neznatan, čime se potvrđuje selektivnost metoda. Metod je uspešno primenjen na određivanje bentazona u uzorcima rečnih voda. Elektrohemijsko određivanje bentazona predstavlja pogodnu alternativu drugim komplikovanim i skupim analitičkim tehnikama i procedurama koje se koriste.

Electroanalytical determination of bentazone at boron-doped diamond electrode

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Bentazone is selective contact-past herbicide from thiadiazine class of compounds with suspected reproductive toxicity potential for humans due to possible contamination of ground and surface waters. This work presents simple, rapid, sensitive and accurate determination of bentazone at unmodified boron-doped diamond electrode using differential pulse voltammetry in Britton-Robinson buffer (pH 4, oxidation peak on 1.0 V). Under optimized DPV conditions linear calibration curve was obtained for range of 2 to100 μM, with a detection limit of 0.5 μM. The effect of possible interfering agents is negligible, confirming good selectivity of the method. The method was successfully applied to determination of bentazone in spiked river water samples. This electrochemical determination of bentazone represents a favorable alternative to other used complicated and expensive analytical techniques and procedures.

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FH 01

Unapređenje elektrolita za litijum-jonske baterije

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Smeše jonskih tečnosti sa organskim rastvaračima elektrolita su ispitane u cilju optimizacije elektrolita za litijum-jonske baterije niske zapaljivosti, visoke termičke stabilnosti i visoke električne provodljivosti. Ispitana su fizičko-hemijska svojstva i zapaljivost elektrolita koji sadrži litijumovu so LiTFSI dodatu u binarnu smešu koju čine jonska tečnost (JT) 1-etil-3-metilimidazolijum *bis*(trifluorometilsulfonil)imid ([C_2mim][TFSI]) i γ-butirolakton (GBL). Optimizovani elektrolit LiTFSI/C_2mimTFSI/GBL je testiran na TiO_2 nanotubama kao anodnim materijalom. U cilju poboljšanja bezbedonosnih svojstava litijum-jonskih baterija, upoređena su elektrohemijska svojstva LiTFSI/C_2mimTFSI/GBL i elektrolita koji sadrži JT bez kiselog C(2)H atoma na imidazolovom katjonu, LiTFSI/C_2mmimTFSI/GBL. Ćelija sa LiTFSI/C_2mimTFSI/GBL elektrolitom u kombinaciji sa TiO_2 nanotubama pokazuje bolje elektrohemijske performanse posle 350 ciklusa punjenja-pražnjenja i nakon izlaganja na povišenoj temperaturi, T=328,15 K.

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Lithium-ion battery electrolytes with improved safety features

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Ionic liquid/organic solvent mixtures are investigated as potential optimal electrolytes for lithium-ion batteries (LIBs) that can combine low flammability, good thermal stability and high electrical conductivity. Here are investigated physicochemical properties and flammability of 1-ethyl-3-methylimidazolium *bis*(trifluoromethylsulfonyl)imide ([C_2mim][TFSI]) ionic liquid (IL) in γ-butyrolactone (GBL), C_2mimTFSI/GBL. The electrolyte LiTFSI/C_2mimTFSI/GBL was used for cycling TiO_2 nanotube arrays electrode as lithium-ion anode material. In an attempt to realize LIBs with enhanced safety, we report herein the comparatively investigated electrochemical properties of the LiTFSI/C_2mimTFSI/GBL and electrolyte containing IL without acidic C(2)H on imidazolium cation, LiTFSI/C_2mmimTFSI/GBL. There is shown that TiO_2 nanotube structures displayed a higher current efficiencies in LiTFSI/C_2mimTFSI/GBL electrolyte after 350 full (dis-)charge cycles and after cell exposure to T = 328.15 K.

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FH 02

Uticaj funkcionalizacije kiseonikom na fizičko-hemijska svojsva imidazolijumovih jonskih tečnosti

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U ovom radu, ispitana su fizičko-hemijska svojstva (gustina, viskoznost i provodljivost) jonske tečnosti funkcionalizovane kiseonikom. Primenom računarskih metoda u vidu DFT kalkulacija i MD simulacija, dobijeni su značajni podaci o interakcijama između jona. Takođe, razblaženi vodeni rastvori ovih jonskih tečnosti su ispitani merenjem gustina, viskoznosti i provodljivosti. Na osnovu dobijenih rezultata, dodatno potvrđenih računarskim simulacijama, utvrđena je da prisustvo hidroksilne grupe ne utiče u značajnoj meri na „structure making" osobine jonskih tečnosti. Ova pojava objašnjena je dodatnom interakcijom između OH grupe bočnog lanca katjona i vodonika sa imidazolovog prstena, koja je ujedno i glavni razlog tečnog agregatnog stanja ispitivanih jonskih tečnosti .

Influence of oxygen functionalization on physico-chemical properties of imidazolium based ionic liquids

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In this work physico-chemical properties (density, viscosity and conductivity) of oxygen functionalized ionic liquids were examined. Applying computational analysis based on DFT calculations and MD simulations, additional insight into the interactions between constituting ions was obtained in order to understand better the interactions in ILs responsible for liquid state. Additionally, diluted aqueous solutions of ionic liquids were also examined by measuring viscosity, density and electrical conductivity. Based on these results, it was noted that existence of hydroxyl group not promoted structure making properties in way as it expected, due to interactions between OH group and H2 from imidazolium cation. Concluding all results, interactions between functionalized side chain and imidazolium ring of cation was determined to be main reason for liquid state.

FH 03

Nove jonske tečnosti na bazi vitamina - fizičko-hemijske osobine, toksičnost i antibakterijska aktivnost

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Sintetisane su i okarakterisane tri nove jonske tečnosti, holinijum-nikotinat, holinijum-biotinat i holinijum-askorbinat. Na osnovu izmerenih fizičko-hemijskih parametara (gustina, viskoznost i provodljivost) ispitane su interakcije koje se javljaju u njima. Ispitana je toksikološka aktivnost prema zdravim ćelijama fetalnih fibroblasta pluća (MRC-5) i ćelijskoj liniji karcinoma jetre pacova (H-4-II-E). Antibakterijska aktivnost je ispitana prema gram-negativnim bakterijama: Pseudomonas aerugonosa i Escherichia coli, odnosno gram-pozitivnim bakterijama: Staphylococcus aureus i Listeria monocytogenes, disk-difuzionom metodom. Dobijeni rezultati su potvrdili netoksičnost sintetisanih jonskih tečnosti. Jednostavnim sintetičkim putem, zasnovanim na principima zelene hemije, moguća je sinteza jonskih tečnosti koje se sastoje od biološki aktivnih katjona i anjona. Na ovaj način prevazilaze se brojni problemi čvrstih formulacija, kao što su slaba rastvorljivost u vodi, niska biodostupnost, pojava polimorfizma, a kao novi dodaci ishrani omogućuju istovremenu dostupnost dve aktivne komponente u jednom jedinjenju.

Novel vitamin based ionic liquids - physicochemical properties, toxicity and antibacterial activity

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A three novel vitamin based ionic liquids, cholinium nicotinate, cholinium biotinate and cholinium ascorbate were synthesized and characterized. Physicochemical properties such as density, electrical conductivity and viscosity were measured and from the obtained experimental results nature of interactions was discussed.. Also, toxicity study of these ionic liquids has been performed using human non-tumor cell line (normal fetal lung fibroblasts, MRC-5) and rat liver hepatoma cell line (H-4-II-E). Antibacterial activity was determined by disc diffusion method on Gram negative bacteria Pseudomonas aerugonosa and Escherichia coli as well on Gram positive bacteria Staphylococcus aureus and Listeria monocytogenes. According to obtained results it was shown that these ILs can be considered as non-toxic. It can be concluded that using simple and green chemical route a non-toxic ionic liquids based on vitamins can be prepared, in which both cation and anion are biologically active components. Therefore, through their synthesis is completely neglected the problem of their low solubility in water, low absorbability, polymorphic forms and on the other side, reached the possibility to deliver two or more active ingredients at once as the novel food supplements.

FH 04

Simulacija molekulske dinamike i eksperimentalno proučavanje interakcija između molekula D-pantenola i vode

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D-pantenol je alkoholni analog pantotenske kiseline (vitamin B5), u koju se nakon apsorpcije u tkivima brzo metaboliše. U kozmetičkim preparatima pantotenska kiselina je nestabilna, pa se u kremama i mastima koristi stabilan alkohol D-pantenol kao hidratant koji vezuje i zadržava vodu, time održavajući mekoću i elastičnost kože. Mehanizam delovanja je do sada ostao nepoznat, ali se povezuje sa higroskopnim osobinama D-pantenola. Kako bi se ispitale interakcije između molekula D-pantenola i vode, u ovom radu određivane su volumetrijske i viskozimetrijske osobine smeša {D-pantenol + H_2O} u celom opsegu molskih udela komponenti i temperaturnom opsegu od T = (293.15 do 313.15) K. Na osnovu računarskih simulacija (molekulska dinamika (MD) i radijalne funkcije raspodele (RDF)) proučavana je priroda interakcija i strukturna organizacija vode u ispitivanom sistemu. Utvrđeno je da su hidroksilne grupe D-pantenola odgovorne za formiranje šupljina između molekula D-pantenola u koje se mogu ugraditi molekuli vode.

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Molecular dynamics simulation and experimental study of the interaction between D-panthenol and water molecules

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D-panthenol is a stable alcoholic analogue of pantothenic acid (vitamin B5). In tissues, including the skin after absorption, D-panthenol is rapidly and completely metabolized to pantothenic acid. Pantothenic acid is unstable in topical formulations and, therefore, the stable alcohol D-panthenol is used in creams and ointments where acts like a moisturizer, maintaining skin softness and elasticity. This activity may be based on the hygroscopic properties of D-panthenol. In this work volumetric and viscosimetric properties of {D-panthenol + H_2O} mixtures have been investigated over the whole composition range in the temperature range from T = (293.15 to 313.15) K, with a goal to understand interactions that occur in this system. From the theoretical aspects molecular dynamics (MD) simulations and radial distribution functions (RDFs) have been applied in order to understand the nature of interactions and water structuring in the studied system. It was found that hydroxyl groups of D-panthenol are responsible for forming cavities between D-panthenol molecules in which water molecules can be incorporated.

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EH S – PPP1

Elektrohemijski izvori električne energije na bazi polipirola i vodenih rastvora elektrolita

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Elektrode na bazi polipirola (PPY) dobijene su na grafitu galvanostatskom elektrohemijskom sintezom iz vodenih elektrolita. Formirani su sekundarni elektrohemijski izvori električne energije kombinovanjem elektroda na bazi PPY sa cinkom, olovo-oksidom i olovo-sulfatom, u hloridnom (Zn|PPY ćelija) i sulfatnom (PPY|PbO_2 i $PbSO_4$|PPY ćelija) elektrolitu. Na osnovu krivih punjenja i pražnjenja ovih sistema, određene su elektrohemijske i električne karakteristike ovih ćelija. Napon otvorenog kola Zn|PPY ćelije sa hloridnim elektrolitom je iznosio oko 1,3 V a specifični kapacitet pražnjenja 52 mAh g^{-1}. Napon otvorenog kola PPY|PbO_2 i $PbSO_4$|PPY ćelije sa elektrolitom na bazi sulfata je iznosio oko 1,5 V i 1,1 V respektivno, dok je specifični kapacitet pražnjenja bio 88 mAh g^{-1} i 50 mAh g^{-1}respektivno. Specifična energija ovih sistema iznosilila je 45 mWh g^{-1} za Zn|PPY ćeliju, 76 mWh g^{-1} za PPY|PbO_2 ćeliju i 37 mWh g^{-1} za $PbSO_4$|PPY ćeliju što odgovara klasičnim baterijskim sistemima. Vrednosti specifične snage ovih ćelija koje su iznosile: 326 mW g^{-1}, 584 mW g^{-1} i 574 mW g^{-1} respektivno daleko su veće od klasičnih baterijskih sistema, pa se one mogu sklasifikovati kao "superkapabaterijama".

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Electrochemical power sources based on polypyrrole and aqueous electrolytes

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Polypyrrole (PPY) electrodes were formed on graphite by galvanostatic electrochemical polymerization of pyrrole. PPY electrodes were combined to Zn, PbO_2 and $PbSO_4$ in order to form electrochemical cells with chloride (Zn|PPY cell) and sulfate (PPY|PbO_2 and $PbSO_4$|PPY cells) based aqueous electrolytes. Electrochemical and electrical characteristics of these cells were estimated from recorded charge/discharge curves. The open circuit potential of Zn|PPY cell in chloride electrolyte was 1.3 V, with specific discharge capacity of 52 mAh g^{-1}. The open circuit potentials of PPY|PbO_2 and $PbSO_4$|PPY cells in sulfate based electrolyte were 1.5 V and 1.1 V, with specific discharge capacity of 88 mAh g^{-1} and 50 mAh g^{-1} respectively. The specific discharge energy and specific power were estimated to 45 mWh g^{-1} and 326 mW g^{-1} for Zn|PPY cell; 76 mWh g^{-1} and 584 for PPY|PbO_2 cell, 37 mWh g^{-1} and 574 mWh g^{-1} for $PbSO_4$|PPY cell. The values of the specific discharge energy are similar to those expected for classical batteries, while the values of the specific power exceeded expected values for classical batteries; therefore, investigated cells can be classified as "supercapatteries"

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EH 01 – US3

Sinteza i karakterizacija $PtSnO_2/C$ katalizatora za reakciju oksidacije metanola

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Platinski katalizatori su najčešće ispitivani katalizatori za reakciju oksidacije metanola. Mnogobrojna istraživanja pokazuju ogroman napredak u sintezi bi metalnih katalizatora na bazi platine kao što su PtSn ili $PtSnO_2$. Međutim, promotivni efekat $PtSnO_2/C$ katalizatora, sa kalajem u nelegiranoj, oksidovanoj formi, još uvek nije dovoljno ispitan. U ovom radu $PtSnO_2/C$ katalizator je sintetizovan modifikovanim poliol postupkom sa mikrotalasnim zagrevanjem i ispitivan TGA, EDX, XRD i TEM analizom. Površina katalizatora je ispitivana oksidacijom adsorbovanog CO i cikličnom voltametrijom. Aktivnost $PtSnO_2/C$ katalizatora za reakciju oksidacije metanola je značajno poboljšana dodatkom kalaja, pokazan je pomeraj potencijala ka negativnim vrednostima za ~ 100 mV i ~ 2 puta veća aktivnost od Pt/C katalizatora.

Synthesis and characterization of $PtSnO_2/C$ catalyst for methanol oxidation reaction

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Platinum-based catalysts are the most common investigated catalysts for methanol oxidation reaction. There are numerus studies that show enormous progress in the synthesis of platinum based bi-metallic catalysts such as PtSn or $PtSnSnO_2$. However, insight to promoting effect of $PtSnO_2/C$ catalyst, with Sn in non-alloyed oxidized form, is still not completely clarified. In this work $PtSnO_2$ nanoparticles were prepared by the microwave-assisted polyol synthesis method and characterised by TGA, EDX, XRD and TEM analysis. Catalyst surface was investigated by CO stripping and cycling voltametry. Activity of $PtSnO_2/C$ catalyst for the methanol oxidation reaction was significantly improved by addition of Sn to Pt, showing the shift of onset potential for ~ 100 mV to more negative values and increasing the activity for ~ 2 times in comparison to Pt/C catalyst.

EH 02 – US4

Uticaj termičkog tretmana Pt elektroda na bazi tankih filmova na njihove katalitičke osobine

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Elektrode u obliku tankih filmova platine nanetih elektrodepozicijom ili spaterovanjem na nosač od staklastog ugljenika podvrgnute su različitim termičkim tretmanima pod kontrolisanim uslovima (temperatura i atmosfera). Ispitivan je uticaj ovih tretmana na strukturne promene elektroda, a samim tim i na njihovu katalitičku aktivnost za reakciju oksidacije HCOOH. Cilj je uspostavljanje veze izmedju aktivnosti dobijenih na dobro definisanim površinskim strukturama Pt (monokristali niskih i visokih Milerovih indeksa) i na nanočesticama sa preferencijalno orijentisanim dvodimenzionalnim domenima. Ovakve elektrode su idealni modeli za ispitivanje mehanizma elektrohemijskih reakcija, a mogu da posluže za razvoj nove generacije elektrokatalizatora tako što omogućavaju uspostavljanje veze izmedju balk elektroda, elektroda razvijenih površina i nanosistema.

The influence of thermal treatment of the Pt based thin films electrodes on their catalytic properties

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In order to investigate whether is it possible to control structural changes by using thermal treatment, the electrodes in the form of thin films, obtained by both electro-deposition and sputtering of Pt onto glassy carbon support, were investigated. Structural changes of deposited thin films obtained during different thermal treatments under controlled conditions (temperature and atmosphere) were followed in HCOOH oxidation reaction. The aim is to establish links between reactivity previously established for Pt electrodes with well defined surface structures (both single ctystal and stepped surfaces) and the reactivity of Pt nanoparticles with some preferential two dimensional surface domains. These films are ideal for mechanistic investigations of electrochemical processes, can serve as templates for development of electrocatalysts of next generation, and provide insight into the link between extended, bulk surfaces and nanoscale systems.

EH 03

Elektrohemijsko ispitivanje odabranih sukcinimida praćeno DFT analizom

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Sukcinimidi (ciklični imidi) su zbog potencijalne farmakološke aktivnosti predmet različitih istraživanja. Serija derivata sukcinimida je ispitivana cikličnom i voltametrijom pravougaonih impulsa. DFT analizom su određivani strukturni parametri koji utiču na uočenu elektrohemijsku aktivnost. Dobijeni rezultati u kombinaciji sa eksperimantalnim elektrohemijskim podacima su omogućili da se pretpostavi mehanizam oksidacije ispitivanih sukcinimida.

Zahvalnica: Ovaj rad je finansijski podržalo Ministarstvo obrazovanja, nauke i tehnološkog razvoja Republike Srbije (brojevi projekata 172013, 172035 i 172060)

Electrochemical examination of selected succinimides combined with DFT analysis

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Succinimides (cyclic imides) exhibit a great variety of biological activities and pharmaceutical uses. A series of succinimide derivatives were studied using the cyclic and square wave voltammetry. Density functional theory (DFT) was applied in order to determinate which of the structural parameters influence the electrochemical activity. The obtained data were combined with the experimental electrochemical data and used to propose the oxidation mechanism of the investigated succinimides.

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EH 04

Piting korozija AA6060 sa epoksidnom prevlakom dopiranom nanočesticama CeO_2 i ZrO_2

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U radu je ispitivan uticaj nanočestica CeO_2 i/ili ZrO_2 kao aktivnih ili barijernih pigmenata u epoksidnoj prevlaci. Epoksidne prevlake su taložene kataforetski na AA6060 iz epoksidne emulzije sa dodatkom solova cirkonije i cerije. Određivane su raspodela nanočestica i zeta (ζ) potencijal dobijenih suspenzija, kao i uticaj nanočestica na adheziju i korozionu stabilnost dobijenih zaštitinih sistema. Koroziona stabilnost je praćena standardnim elektrohemijskim metodama, spektroskopijom elektrohemijske impedancije i polarizacionim merenjima.

Pokazan je povoljan uticaj CeO_2 i ZrO_2 na stabilnost zaštitnih sistema, pri čemu su najbolji rezultati dobijeni u prisustvu obe vrste nanočestica. Piting aluminijuma se javlja kasnije kod sistema na bazi nanočestica. Ceria pokazuje efekat zalečenja, dok cirkonija ima barijerna svojstva.

Pitting corrosion of AA6060 with epoxy coating containing CeO_2 and ZrO_2 nanoparticles

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The effectiveness of CeO_2 and/or ZrO_2 nanoparticles as active or barrier dopants in epoxy coating was analyzed. The epoxy coatings were cataphoretically deposited on AA6060 from epoxy emulsion containing ceria and zirconia sols, or their combination. The particle size distribution and zeta (ζ) potential of epoxy suspension with and without addition of nanoparticles were determined and the effect of nanoparticles on adhesion strength and corrosion stability of protective systems was evaluated. The protective properties were followed by standard electrochemical methods, electrochemical impedance spectroscopy (EIS) and potentiodynamic measurements.

The beneficial effect of either CeO_2 or ZrO_2 nanoparticles on the corrosion stability of protective systems was shown, and the combination of both CeO_2 and ZrO_2 exhibited the best results. The pitting onset and propagation could be delayed in the presence of nanoparticles. The differences in pitting potential and protection potential were compared and it was shown that CeO_2 nanoparticles had self-healing ability, while ZrO_2 nanoparticles acted as barrier type dopants.

EH 05

Mikroemulziona sinteza i elektrohemijska karakterizacija PtAu/C nanokatalizatora

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Mikroemulziona sinteza korišćena je u prethodnim istraživanjima za sintezu nanočestica platine kontrolisanog oblika [1,2]. HCl je korišćena kao aditiv čija je uloga da utiče na oblik formiranih nanočestica, koji je variran od sfernog do kubnog. Ista metoda i isti uslovi sinteze korišćeni su za sintezu bimetalnih nanokatalizatora PtAu/C. Ispitan je uticaj aditiva na bimetalne nanočestice, kao i uticaj drugog elementa (Au) na njihovo elektrohemijsko ponašanje u osnovnom elektrolitu, i reakcijama od značaja za gorivne galvanske spregove. Redukcija prekursora je vrešena simultano, pomoću $NaBH_4$. Ispitivanja pokazuju poboljšano elektrohemijsko ponašanje u odnosu na Pt/C katalizatore sintetizovane na isti način.

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[1] *Appl Catal B: Environ* **196** (2016) 174-184
[2] *J Solid State Electrochem* **20** (2016) 3405-3414

Microemulsion synthesis and characterisation of PtAu/C nanocatalysts by electrochemical methods

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Water in oil microemulsion method was used in our previous publications to synthesize shape controlled Pt nanoparticles [1,2]. HCl was used as a capping agent to affect the particle shape that was varied from spherical to cubic. The same method and the same synthesis parameters were employed to prepare bimetallic PtAu/C nanocatalysts. The influence of the additive, and of the second element (Au) on their electrochemical behaviour in supporting electrolyte, and the reactions of interest for fuel cell applications, were investigated. The reduction of the precursors was applied simultaneously with $NaBH_4$. The investigations reveal improved electrochemical behaviour of bimetallic catalysts, in comparison to Pt/C catalysts synthesized the same way.

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[1] *Appl Catal B: Environ* **196** (2016) 174-184
[2] *J Solid State Electrochem* **20** (2016) 3405-3414

EH 06

Elektrohemijska oksidacija etanola na elektrodeponovanim AgPd legurama u alkalnom rastvoru

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Reakcija oksidacije etanola (ROE) je ispitivana na elektrodeponovanim prevlakama AgPd legura okarakterisanim skenirajućom elektronskom mikroskopijom i spektroskopskim tehnikama. U radu je pokazano da Ag poboljšava ROE na AgPd legurama u alkalnom rastvoru, dok gustine struje reakcije zavise od oksidacionog potencijala. Aktivnost ROE je povezana sa prisustvom neredukovanog Ag_2O i dobijene AgPd legure se moraju ciklizirati u oblasti potencijala gde se stvara i redukuje Ag_2O pre ispitivanja ROE kako bi se ostvarila katalitička aktivnost za ispitivanu reakciju. Najaktivnija i prema otrovima najtolerantnija je elektrodeponovana bimetalna prevlaka koja sadrži 76 at.% Ag i 24 at.% Pd.

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Electrochemical oxidation of ethanol on electrodeposited AgPd alloy coatings in alkaline solution

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Ethanol oxidation reaction (EOR) was investigated on electrodeposited AgPd alloy coatings characterized by scanning electron microscopy and spectroscopy techniques. This work shows that Ag improves ethanol oxidation on AgPd alloys in alkaline solution while the reaction current densities are depended on the oxidation potential. The activity for the EOR is closely related to the percentage of non-reduced Ag_2O and investigated AgPd alloy samples must be cycled in the potential region of Ag_2O formation and reduction before the investigation of the EOR, in order to provide their catalytic activity towards the EOR. The most active and the most poisoning tolerant coating contains 76 at.% Ag – 24 at.% Pd.

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EH 07

Removal of ammonia nitrogen from leachate by electrocoagulation process

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Landfill leachate contains various pollutants, and among the highest concentrations are nitrogen compounds such as ammonia. Ammonium nitrogen concentrations ($N\text{-}NH_4^+$) depend on many conditions. In this study, the leachate from the sanitary landfill "Ramići" Banja Luka, Bosnia and Herzegovina, was used. The electrocoagulation process with aluminum electrodes can significantly reduce their concentration. The effects of the current density and the time of electrolysis on the removal efficiency of ammonium nitrogen has been studied. In the laboratory electrochemical reactor at current density, j=25 mA/cm^2, in the presence of supporting electrolyte, γ_{NaCl}=5 g/L and constant stirring (400 rpm), the removal efficiency of $N\text{-}NH_4^+$ was 75.71% for 30 minutes of treatment.

Uklanjanje amonijačnog azota iz procjednih voda postupkom elektrokoagulacije

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Procjedne vode su opterećene raznim zagađivačima, a među najvećima su jedinjenja azota kao što je amonijak. Koncentracije amonijačnog azota ($N\text{-}NH_4^+$) zavise od mnogo uslova. Za ovo istraživanje korišćena je procjedna voda sa sanitarne deponije „Ramići" Banja Luka, Bosna i Hercegovina. Postupkom elektrokoagulacije sa aluminijskim elektrodama moguće je znatno smanjiti njihovu konentraciju. U radu je istraživan uticaj gustine struje i vremena elektrolize na efikasnost smanjenja amonijačnog azota. U laboratorijskom elektrohemijskom reaktoru pri gustini struje, j=25 mA/cm^2, uz prisustvo pomoćnog elektrolita, γ_{NaCl}=5 g/L i konstantno miješanje (400 obrtaja/min.) ostvarena je efikasnost uklanjanja $N\text{-}NH_4^+$ od 75,71 % za 30 minuta tretmana.

EH 08

Polivinil-alkohol/hitozan/grafen hidrogelovi sa nanočesticama srebra za primene u biomedicini

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U ovom radu su pripremljeni biokompatibilni polivinil-alkohol/hitozan/grafen (PVA/CHI/Gr) nanokompozitni hidrogelovi sa inkorporiranim nanočesticama srebra (Ag), za primenu u biomedicini kao antibakterijske obloge za rane. Nanočestice Ag su dobijene *in situ* elektrohemijskom sintezom u matrici nabubrelih hidrogelova PVA/CHI/Gr. Korišćene su dve koncentracije CHI (0,1 mas.% i 0,5 mas.%), u cilju ispitivanja uticaja sadržaja CHI na svojstva nanokompozitnih hidrogelova. Prisustvo nanočestica Ag je dokazano UV–vidljivom spektroskopijom, a takođe je pokazano da je veća količina nanočestica Ag dobijena u hidrogelovima sa 0,5 mas.% CHI, što je potvrđeno i metodom ciklične voltametrije. Ag/PVA/CHI/Gr nanokompoziti su karakterisani skenirajućom elektronskom mikroskopijom (SEM), Ramanskom spektroskopijom i spektroskopijom fotoelektrona izazvanih X-zračenjem (XPS), dok je termička stabilnost ispitivana metodom termogravimetrijske analize (TGA). Kinetika otpuštanja srebra u rastvoru fosfatnog pufera je praćena atomskom apsorpcionom spektroskopijom (AAS) tokom 28 dana. Antibakterijska aktivnost je potvrđena agar-difuzionim testom, dok je citotoksičnost ispitana direktnim testom odbacivanja boje sa tripan-plavim (DET).

Poly(vinyl alcohol)/chitosan/graphene hydrogels with silver nanoparticles for applications in biomedicine

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In this work, we prepared biocompatible poly(vinyl alcohol)/chitosan/graphene (PVA/CHI/Gr) nanocomposite hydrogels, loaded with silver nanoparticles (AgNPs), aimed for biomedical purposes as antibacterial wound dressings. AgNPs were produced by *in situ* electrochemical synthesis in the pre-swollen PVA/CHI/Gr hydrogel matrix. Two concentrations of CHI (0.1 wt% and 0.5 wt%) were used in order to investigate the influence of CHI content on the properties of nanocomposite hydrogels. The presence of AgNPs was proved by UV–visible spectroscopy. The concentration of AgNPs was found to be higher in the 0.5 wt% CHI hydrogel, which was also confirmed by cyclic voltammetry. The Ag/PVA/CHI/Gr nanocomposites were further characterized by scanning electron microscopy (SEM), Raman spectroscopy and X-ray photoelectron spectroscopy (XPS), while the thermal stability was examined using thermogravimetric analysis (TGA). Silver release was monitored in phosphate buffer solution during 28 days using atomic absorption spectroscopy (AAS). Antibacterial activity was confirmed by agar diffusion test, while the cytotoxicity was investigated using trypan blue dye-exclusion test (DET).

EH 09

Biokompatibilna prevlaka hidroksiapatit/hitozan/gentamicin dobijena postupkom elektroforetskog taloženja na titanu iz vodene suspenzije

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Elektroforetsko taloženje predstavlja efikasan postupak za dobijanje uniformnih keramičkih biokompatibilnih prevlaka kontrolisane debljine i morfologije. U ovom radu je ispitano elektroforetsko taloženje u jednom stupnju kompozitnih prevlaka na titanu iz trokomponentne vodene suspenzije hidroksiapatit/hitozan/gentamicin (HAP/CHI/Gent). Taloženje je izvedeno pri konstatnom naponu i uz prethodnu pripremu površine metala. Karakterizacija prevlaka je izvršena rendgenskom difrakcionom analizom (XRD), infracrvenom spektroskopijom sa Furijeovom transformacijom (FTIR), skenirajućom emisionom mikroskopijom (FE-SEM) i spektroskopijom fotoelektrona izazvanih X-zračenjem (XPS). Dobijeni rezultati potvrđuju formiranje nove kompozitne prevlake HAP/CHI/Gent koja pokazuje jaku antibakterijsku aktivnost i ima potencijal da se koristi kao ortopedski i dentalni implantat koštanog tkiva ili kao nosač lekova.

Biocompatible coating hydroxyapatite/chitosan/gentamicin obtained by electrophoretic deposition on titanium from aqueous suspension

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Electrophoretic deposition is an effective method for obtaining uniform coatings of precisely controlled thickness and morphology. In this research, a single step electophoretic deposition process for obtaining nanocomposite coating on titanium from a three-component aqueous hydroxyapatite/chitosan/ gentamicin (HAP/CHI/Gent) suspension was investigated. The deposition was carried out at a constant voltage, after the metal surface pretreatment. Characterization of the coating was performed by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), field emission scanning electron microscopy (FE-SEM) and X-ray photoelectron spectroscopy (XPS). Obtained results confirm the formation of a new composite coating HAP/CHI/Gent which exhibits strong antibacterial activity and has the potential to be used as an orthopedic and dental bone tissue implant or as a drug carrier.

EH 10

Influence of carbon nanotubes to the supercapacitive properties of the MnO_2
Uticaj ugljionikovih nanocevi na superkapacitivna svojstva MnO_2

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Manganese oxide is nowadays very attractive material for supercapacitive application. As the transition metal oxide with great number of oxidation states, MnO_2 has a lot of advantages when compared to other related oxides (RuO_2, V_2O_5, IrO_2 etc.). It has low toxicity, low cost, environmental friendliness and it is easy synthesised. Theoretical specific capacitance value of MnO_2 with one electron exchange is 1370 F/g [1], but such high value is not achievable in practice due to its intrinsically poor electronic conductivity and dense morphology which limits the penetration of ions into the bulk of the oxide layer [2]. The utilization of MnO_2 can be enhanced by preparation of composite electrode containing highly conductive materials such as conducting polymers or/and different carbon materials.

The aim of this work was to enhance the MnO_2 supercapacitive properties by the help of the multi-walled carbon nanotubes (CNT) which are very favourable due to high electric conductivity, high mechanical stability and a high surface area [3,4,5].

Manganese oxide was synthesised electrochemically from aqueous solution of 0.25 M $MnCl_2$ at constant potential of 0.9 V during 150 s, 300 s or 450 s. In order to examine the electrochemical behaviour, the MnO_2 was synthesised onto different supports such as Pt-quartz crystal electrode, CNT and oxidised CNT-EO. The CNTs were oxidised electrochemically by using cyclic voltammetry method in the potential range from -0.8 to 1.9 V during 3 cycles (CNT-EO1) or 6 cycles (CNT-EO2). Different degrees of oxidation introduce different amount of oxygen functionalities that are responsible for electron transfer activity, as well as for the CNT wettability and surface accessibility. The prepared electrodes were investigated in the 0.25 M $MnCl_2$, 0.5 M NaCl and 0.5 M LiCl in three-electrode cell containing saturated calomel electrode as reference electrode and Pt-foil as a counter electrode. The electrochemical behaviour of the electrodes was examined by the cyclic voltammetry and the method of electrochemical quartz crystal microgravimetry.

Results showed that CNT have favourable influence on the specific capacitance values of the MnO_2/CNT composite electrode compared to MnO_2 onto bare Pt electrode. The oxidation of the CNT resulted in increased specific capacitances of CNT-EO. Electrochemical quartz crystal microgravimetry clarified the reaction mechanism during charging/discharging process of MnO_2 electrodes.

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Hemijsko inženjerstvo / Chemical Engineering

HI 01

text rada / full text

Experimental determination of volumetric, ultrasonic, transport and refractive index properties of binary mixture (1-propanol + ethyl oleate) at atmospheric pressure

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The huge dependence of the world's industry and transport sector on the limited resources of fossil fuels is one of the biggest problems that modern society faces. The use of highly polluting fuels, such as diesel fuel, in addition to economy, also has a great impact on the environment. Because of that, researchers intensively work on finding less harmful fuels derived from renewable energy sources. One of the alternatives for diesel fuel is biodiesel which can be used in diesel engines pure or mixed with diesel and/or alcohol. However, the replacement of a diesel with biodiesel affects the injection system, as well as atomization and combustion processes of a fuel, due to their high thermodynamic properties which could be unsuitable for diesel engine.

The densities, speeds of sound, dynamic viscosities and refractive indices of pure 1-propanol and ethyl oleate and their binary mixtures at whole concentration range have been measured within a wide range of temperature at atmospheric pressure. The measurements were performed on DSA 5000 M density and sound velocity meter, Stabinger SVM3000 viscometer and RXA 156 refractometer, all produced by Anton Paar. The corresponding experimental data were used in calculation of the isentropic bulk modulus.

Eksperimentalno određivanje volumetrijskih, ultrazvučnih i transportnih svojstava i indeksa refrakcije binarnih smeša (1-propanol+etil oleat) na atmosferskom pritisku

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Ogromna zavisnost svetske industrije i sektora transporta od ograničenih izvora fosilnih goriva je jedan od najvećih problema sa kojima se moderno društvo susreće. Upotreba goriva koja dovode do velikih zagađenja, kao što je dizel gorivo, osim na ekonomiju, ima izuzetan uticaj i na životnu sredinu. Zbog toga istraživači intenzivno rade na pronalaženju manje štetnih goriva koja se mogu dobiti iz obnovljivih izvora energije. Jedna od zamena za dizel gorivo jeste biodizel koji se može koristiti kao gorivo u dizel motorima, bilo čist ili pomešan sa dizelom i /ili alkoholom. Međutim, zamena dizela biodizelom utiče na sistem za ubrizgavanje goriva, kao i procese atomizacije i paljenja goriva, zbog njegovih visokih termodinamičkih svojstava koja mogu biti neodgovarajuća za rad dizel motora.

Gustine, brzine zvuka, dinamičke viskoznosti i indeksi refrakcije čistih 1-propanola i etil oleata, kao i njihovih binarnih smeša u svim koncentracijama, su merene na širokom opsegu temperatura pri atmosferskom pritisku. Merenja su vršena na DSA 5000 M uređaju za merenje gustine i brzine zvuka, SVM3000 viskometru i RXA 156 refraktometru, proizvođača Anton Paar. Odgovarajući eksperimentalni podaci su omogućili računanje izentropskog modula stišljivosti.

HI 02

text rada / full text

Correlation of excess molar volume of binary mixtures diethyl tartrate + *n*-alcohol

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Density for three binary systems diethyl tartrate + *n*-alcohol have been measured in temperature range 288.15 - 323.15 K and at atmospheric pressure, using Anton Paar DMA 5000 densimeter. From these data, values for excess molar volume (V^E) were determined. Correlation of this property was done using equations of state (EOS). For quick evaluation, simple Peng-Robinson EOS and the van der Waals (vdW1-3) mixing rule were used, where unique interaction parameters were determined for the whole investigated temperature range. In addition, the V^E binary data were also correlated by the Peng–Robinson–Stryjek–Vera cubic equation of state (PRSV CEOS) combined with the van der Waals (vdW1) mixing rules or CEOS/G^E mixing rules introduced by Twu et al. (TCBT). With PRSV EOS correlation was performed on every temperature individually. The obtained results, analysed taking into account the applied approaches and equations, showed small percentage deviations, especially with PRSV equation and more complex mixing rules vdW1-3 and TCBT-3.

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Korelisanje dopunske molarne zapremine binarnih smeša dietil tartarat + *n*-alkohol

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Vrednosti gustine za tri binarna sistema dietil tartarat + *n*-alkohol izmerene su u temperaturnom opsegu 288.15 – 323.15 K i na atmosferskom pritisku, na digitalnom gustinomeru Anton Paar DMA 5000. Na osnovu ovih podataka, izračunate su vrednosti dopunske molarne zapremine (V^E). Korelisanje ove veličine urađeno je pomoću jednačina stanja (EOS). Za brzu procenu, korišćena je jednostavna Peng-Robinson jednačina stanja i van der Waals (vdW1-3) pravilo mešanja, pri čemu su određeni jedinstveni interakcioni parametri za ceo ispitivani temperaturni opseg. Dodatno, podaci za V^E korelisani su pomoću Peng–Robinson–Stryjek–Vera kubne jednačine stanja (PRSV CEOS) i van der Waals (vdW1) ili CEOS/G^E pravila mešanja razvijenih od strane Twu et al. (TCBT). Korelisanje pomoću PRSV CEOS urađeno je na svakoj temperaturi posebno. Dobijeni rezultati, analizirani imajući u vidu korišćene pristupe i jednačine, pokazali su mala procentualna odstupanja, posebno pri upotrebi PRSV jednačine i kompleksnijih pravila mešanja kao što su vdW1-3 and TCBT-3.

HI 03

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Eksperimentalna merenja termofizičkih karakterstika binarnog sistema cis-3-heksen-1-ol + heksan i FT-IR analiza

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Termofizičke karakteristike (gustina, viskoznost i brzina zvuka) merene su za binarni sisitem cis-3-heksen-1-ol i heksan. Cis-3-heksen-1-ol, poznat i kao alkohol lišća se najčešće koristi kao komponenta za miris i aromu u industrijskoj proizvodnji parfema i u prehrabrenoj industriji za voće i povrće.
Smeša cis-3-heksen-1-ol i heksan je ispitivana na sedam temperature u opsegu od 288.15 K do 318.15 K na atmosferskom pritisku. Eksperimentana merenja gusine i brzine zvuka su izvršena na digitalnom gustinomeru Anton Paar DMA 5000, dok je viskoznost merena na digitalnom viskozimetru Anton Paar SVM 3000.
Na osnovu ekperimentalnih podataka, izračunate su dopusnka zapremina (V^E), promena viskoznosti ($\Delta\eta$) i promena brzine zvuka (Δu) a pomoću Redlich-Kister jednačine su fitovani podaci. Dodatno, FT-IR spekti su analizirani radi boljeg razumevanja intermolekulskih interakija u ispitivanoj smeši. Po našem saznanju, ovo su prvi podaci o binarnom sistemu cis-3-heksen-1-ol + heksan.

Experimental measurements of thermophysical properties of the binary system cis-3-hexen-1-ol + hexane and FT-IR analysis

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Thermophysical properties (density, viscosity and speed of sound) were measured of the binary system of cis-3-hexen-1-ol and hexane. Cis-3-hexen-1-ol, also known as leaf alcohol, is one of the products used as a fragrance and an aroma compound in perfume industry and as fruits and vegetable flavors in food industry.
The mixture of cis-3-hexen-1-ol and hexane has been investigated at seven temperatures, in the range of 288.15 K to 318.15 K at atmospheric pressure. The measurements of density and speed of sound have been performed on Anton Paar DMA 5000 Density and Velocity Meter, while viscosity has been measured on Anton Paar SVM 3000 digital viscometer.
Based on the experimental data excess molar volumes (V^E), viscosity deviation ($\Delta\eta$) and speed of sound deviations (Δu) were calculated and Redlich-Kister equation has been used for fitting the calculated data. Additionally, FT-IR spectroscopy has been performed for discussing molecular interactions for this system. To the best of our knowledge, these are the first data on cis-3-hexen-1-ol + n-hexane system.

Tekstilo inženjerstvo / Textile Engineering

TI 01 – US5

text rada / full text

Fotokatalitička aktivnost PET tkanine modifikovane polipirolom i nanočesticama TiO_2

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U ovom radu je ispitana mogućnost dobijanja kompozitnog tekstilnog materijala na bazi PET tkanine, polipirola i nanočestica TiO_2 sa efikasnom fotokatalitičkom aktivnošću. Prisustvo PPy/TiO_2 kompozitnog sloja na površini vlakana je potvrđeno FE-SEM i EDS analizom. Fotokatailtička aktivnost PET tkanine obrađene polipirolom i nanočesticama TiO_2 kao i PET tkanine obrađene samo nanočesticama TiO_2 ispitana je u vodenom rastvoru boje *C.I. Acid Orange 7*. Rezultati ispitivanja fotokatalitičke aktivnosti su pokazali da uzorak modifikovan polipirolom i nanočesticama TiO_2 potpuno degradira boju za samo 120 minuta osvetljavanja lampom koja simulira sunčevo zračenje dok je uzorku modifikovanom nanočesticama TiO_2 za to potrebno 24 h. Takođe je utvrđeno da kompozitni uzorak PET/PPy/TiO_2 pokazuje odlična fotokatalitička svojstva u drugom i trećem ciklusu fotodegradacije. Bolja fotokatalitička aktivnost PET/PPy/TiO_2 uzorka je posledica prisustva polipirola.

Photocatalytic activity of PET fabric modified with polypyrrole and TiO_2 nanoparticles

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This study discusses the possibility of fabrication of composite textile material based on PET fabric, polypyrrole and TiO_2 nanoparticles (NPs) with efficient photocatalytic activity. The presence of PPy/TiO_2 layer on the PET surface was proved by FE-SEM and EDS analyses. Photocatalytic activity of PET fabric modified with polypyrrole and TiO_2 NPs and PET fabric loaded only with TiO_2 NPs was investigated in aqueous solution of dye C.I. Acid Orange 7. The results show that the sample modified with polypyrrole and TiO_2 NPs have obtained the complete photodegradation of dye within 120 min of illumination with a lamp simulating the sun light, while the PET sample modified with TiO_2 NPs for this needed 24 h. It was also proven that composite sample PET/PPy/TiO_2 ensured excellent photocatalytic properties during the second and the third photodegradation cycles. Better photocatalytic activity of the PET/PPy/TiO_2 sample is due to the presence of polypyrrole.

TI 02 – US6

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In situ sinteza Cu/Cu_2O nanočestica na TEMPO oksidovanoj pamučnoj tkanini

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In situ sinteza nanočestica Cu/Cu_2O na pamučnoj tkanini diskutovana u ovom radu bazirana je na adsorpciji Cu^{2+}-jona na karboksilnim grupama formiranim TEMPO oksidacijom celuloze i njihovoj redukciji natrijum-borhidridom. Hemijske promene nastale TEMPO oksidacijom su praćene titrimetrijski određivanjem sadržaja karboksilnih grupa u pamuku. Produžavanje vremena TEMPO oksidacije za rezultat je imalo povećanje sadržaja karboksilnih grupa na pamučnoj tkanini. Stoga su veće količine Cu^{2+}-jona mogle da se adsorbuju na supstratu. Ovo je dalje za posledicu imalo stvaranje većih količina nanočestica Cu/Cu_2O. Prisustvo nanočestica Cu/Cu_2O na pamučnoj tkanini potvrđeno je SEM i AAS analizama.Svi ispitivani tekstilni nankompoziti su obezbedili maksimum redukcije bakterija *E. coli* i *S. aureus*. Takođe je utvrđeno da pamučne tkanine sa inkorporiranim nanočesticama Cu/Cu_2O pružaju kontrolisano otpuštanje Cu^{2+}-jona u fiziološkom rastvoru što je imperativ za prevenciju infekcija.

In situ synthesis of Cu/Cu_2O nanoparticles on the TEMPO oxidized cotton fabric

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In situ synthesis of Cu/Cu_2O nanoparticles on the cotton fabric discussed in this study is based on the adsorption of Cu^{2+}-ions by carboxyl groups formed through the TEMPO-mediated oxidation of cellulose and their reduction by sodium borohydride. Chemical changes induced by TEMPO-mediated oxidation were evaluated by titrimetric determination of the amounts of carboxylic groups in cotton. The prolongation of TEMPO-mediated oxidation time resulted in an increase of carboxyl group content in the cotton fabric. Therefore, larger amounts of Cu^{2+}-ions were adsorbed on the substrate. This further led to a formation of larger amounts of Cu/Cu_2O nanoparticles. The presence of Cu/Cu_2O nanoparticles on the cotton fabric was proved by SEM and AAS analyses. All investigated textile nanocomposites ensured maximum reduction of *E. coli* and *S. aureus* bacteria colonies. It was also demonstrated that cotton fabrics with imbedded Cu/Cu_2O nanoparticles provided a controlled release of Cu^{2+}-ions in physiological saline solution which is an imperative for infection prevention.

MS 01 – OP6

Hibridni nanocompoziti sa izraženom enzimskom aktivnošću

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Imobilizacija različitih enzima na površinu nanočestica predstavlja adekvatan način za prevazilaženje problema gubitka aktivnosti enzima usled različitih spoljašnjih faktora (temperatura, pH, jonska jačina) ili za olakšan proces recikliranja. Biokompatibilan dvostruki slojeviti hidroksid (LDH), sačinjen od Mg^{2+} i Al^{3+} kao katjona i CO_3^{2-} kao anjona, je sintetisan ‘flash’ koprecipitacijom, a zatim korišćen kao podloga za proces imobilizacije. Adsorpcija superoksid dismutaze (SOD) je izvedena direktno na pozitivno naelektrisanu površinu LDH čestica, dok je imobilizacija peroksidaze rena (HRP) zahtevala prethodnu funcionalizaciju čestica negativno naelektrisanim polielektrolitom heparinom. Proces adsoprcije bio je praćen pomoću elektroforetske mobilnosti, dok je koloidna stabilnost LDH čestica i nanokompozita praćena merenjem rasipanja svetlosti (DLS). Infracrvena spektroskopija potvrdila je uspešnu sintezu hibridnog materijala, dok je kvantifikacija adsorpcije enzima izvršena Bredfordovim testom. Sa ciljem daljeg unapređenja koloidne stabilnosti i prevencije eventualnog curenja enzima, adsorbovani su dodatni slojevi polielektrolita. Ispitana je enzimatska aktivnost finalnih materijala sačinjenih od LDH, SOD i sloja heparina (LDH-SOD-HEP) u prvom slučaju, i LDH, sloja heparina, HRP i sloja poli-L-lizina ili protamina (LDH-HEP-HRP-PLL ili LDH-HEP-HRP-PROT) u drugom slučaju. Svi materijali pokazali su značajnu aktivnost, uporedivu sa nativnim formama enzima.

Hybrid nanocomposites with a strong enzymatic activity

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Immobilization of different enzymes at the surface of nanoparticles is a promising approach to overcome loss of enzyme activity due to operating conditions (temperature, pH, ionic strength) or improve their reusability. Biocompatible layered double hydroxide (LDH) nanoparticles, composed of Mg^{2+} and Al^{3+} cations and CO_3^{2-} as counterion, were synthesized by ‘flash’ coprecipitation and utilized as a solid support for enzyme immobilization. Superoxide dismutase (SOD) was adsorbed on the surface of positively charged LDH platelets, while immobilization of horseradish peroxidise (HRP) required prior functionalization of the platelets by negatively charged polyelectrolyte heparin. Adsorption process was followed by determining electrophoretic mobilities, while colloidal stability of the bare and functionalized particles was investigated by dynamic light scattering (DLS). IR spectroscopy proved successful synthesis of this hybrid material, while Bradford assay told us more regarding quantification of the enzyme immobilization. In order to further improve colloidal stability and prevent possible leakage, additional layers of polyelectrolyte were adsorbed. Final materials composed of LDH, SOD and heparin coating (LDH-SOD-HEP) in the first case, and LDH, heparin coating, HRP and poly-L-lysine or protamine coating (LDH-HEP-HRP-PLL or LDH-HEP-HRP-PROT) in the later case were tested for their enzymatic activities. All materials exhibited significant enzymatic activity that is comparable to bare enzymes.

MS 02

text rada / full text

Hidrotermalna sinteza RuO_2/redukovani grafen-oksid kompozita u mikrotalasnom reaktoru i njihova kapacitivna svojstva

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Superkapacitivni RuO_2/redukovani grafen-oksid kompoziti dobijeni su hidrotermalnom sintezom u mikrotalasnom reaktoru. Jednostepena simultana oksidacija $RuCl_3$ i redukcija grafen-oksida izvedena je pri različitim režimima temperature i pH vrednosti rastvora. Kapacitivne vrednosti kompozita su ispitivane cikličnom voltametrijom i spektroskopijom elektrohemijske impedancije na elektrohemijskoj kvarc-kristalnoj nanovagi u rastvorima H_2SO_4 i Na_2SO_4. Morfologija RuO_2/redukovani grafen-oksid kompozita, kao i sadržaj RuO_2 u njemu, određeni su metodom skenirajućeg elektronskog mikroskopa (SEM) kombinovanog sa spektroskopijom X-zraka sa disperzijom energije (EDS). Analiza dobijenih rezultata pokazuje zadovoljavajuća kapacitivna svojstva sintetisanih kompozita. Ova svojstva značajno zavise od primenjenog temperaturnog režima tokom sinteze, kao i od pH vrednosti početnog rastvora.

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Microwave assisted hydrothermal synthesis and capacitive properties of RuO_2/reduced graphene oxide composites

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Supercapacitive RuO_2/reduced graphene oxide composites were synthesized by microwave assisted single step synthesis at different temperatures. Syntheses were accomplished by single-step simultaneous oxidation of $RuCl_3$ and reduction of graphene oxide in solution with various pH. Capacitive responses of obtained samples were collected using combined electrochemical and quartz crystal nanobalance response. The cyclic voltammetry and electrochemical impedance spectroscopy have been performed in H_2SO_4 and Na_2SO_4 solutions. Morphological and elemental composition properties of synthesized RuO_2/reduced graphene oxide composites were investigated by SEM/EDX technique. The analysis of obtained results showed acceptable capacitive properties of synthesized composites. These capacitive properties strongly depend on the pH values of the precursor solution and temperature during synthesis.

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MS 03

Electrochemical synthesis and characterisation of composites based on conductive polymers and graphene oxide

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In this work an electrochemical approach for exfoliation of graphite and synthesis of composites based on conductive polymers and graphene oxide (GO) was studied. The overall procedure is simple and effective way of composite electrode formation that does not require any additional purification or isolation of products as it is expected for composites prepared by chemical method [1]. The experiments were conducted in two steps. In the first step, GO was prepared by electrochemical exfoliation of natural graphite flakes in sodium dodecyl sulphate (SDS) and sodium dodecyl benzene sulfonate (SDBS) aqueous solutions. Graphite electrode was alternately polarized at positive and negative potentials by using two-electrode system. During positive polarization, SDS and SDBS were intercalated within the structure of graphite, and oxygen evolution as well as carbon oxidation took place. By applying negative potential, cations were intercalated within graphite and also hydrogen evolution took place. The exfoliation process was followed by monitoring current transients. The obtained product was characterized by ultraviolet-visible spectrophotometry (UV/Vis), Raman spectroscopy and atomic force microscopy (AFM). In the second step, monomer (pyrrole or 3,4-ethylendioxythiophene) was dissolved in a solution obtained during first step and electrochemical synthesis of polypyrrole and poly(3,4-ethylendioxythiophene) was carried out. The obtained nanocomposites were characterized by means of scanning electron microscopy (SEM). The electrochemical measurements were performed by cyclic voltammetry (CV), and ion exchange behaviour of obtained composite material was studied by using the electrochemical quartz crystal nanobalance (EQCN).The obtained results has shown that GO was intercalated within the polypyrrole or poly(3,4-ethylendioxythiophene) layers and it has affected the properties of the obtained layers.

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NH 01

In vitro antiproliferativna aktivnost oktaazamakrocikličnih kompleksa Co(II) sa aromatičnim karboksilato koligandima

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Dinuklearni kompleksi Co(II) sa makrocikličnim tpmc ligandom (tpmc = $N,N^{'},N^{''},N^{'''}$-tetrakis(2-piridilmetil)-1,4,8,11-tetraazaciklotetradekan) i različitim aromatičnim karboksilato koligandima (benzoato, ftalato, izoftalato i tereftalato anjoni) sintetisani su po ranije opisanoj proceduri i testirani *in vitro* na tri odabrane ćelijske linije sa cisplatinom (*cis*-DDP) kao referentnom supstancom, tpmc ligandom, $Co(ClO_4)_2\cdot 6H_2O$, odgovarajućim kiselinama i DMSO rastvaračem (standardni MTT test). Kao ciljne ćelijske linije u našem radu korišćene su HeLa ćelije (ćelije humanog adenokarcinoma grlića materice), Fem-x ćelije (ćelije humanog malignog melanoma) kao i LS174 ćelije (ćelije humanog karcinoma kolona).
Ligandi tpmc i karboksilne kiseline, kao i $Co(ClO_4)_2\cdot 6H_2O$ i rastvarač DMSO nisu pokazali aktivnost. Poređenjem IC_{50} vrednosti testiranih kompleksa, liganada i *cis*-DDP zaključeno je da Co(II) kompleksi sa aromatičnim karboksilatima imaju znatan antiproliferativni efekat.

In vitro antiproliferative activity of Co(II) octaazamacrocyclic complexes with aromatic carboxylate coligands

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Dinuclear Co(II) complexes with macrocyclic tpmc ligand (tpmc = N,N',N'',N'''-tetrakis(2-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane) and various aromatic carboxylate coligands (benzoate, phthalate, isophthalate and terephthalate anions) were synthesized according to the described procedure and *in vitro* tested against three selected cell lines with cisplatin (*cis*-DDP) as a referent compound, together with the free ligand tpmc, $Co(ClO_4)_2\cdot 6H_2O$, appropriate acids and the solvent DMSO as a controls (standard MTT assay). As target cell lines, we used HeLa cells (human cervix adenocarcinoma cells), Fem-x cells (human melanoma cells), and LS174 cells (cells of human colon carcinoma).
Ligands tpmc and carboxylic acids, as well as $Co(ClO_4)_2\cdot 6H_2O$ and solvent DMSO, did not show activity. By comparing the IC_{50} values of the tested complexes, ligands and *cis*-DDP, it was concluded that Co(II) complexes with aromatic carboxylates have a significant antiproliferative effect.

NH 02

Hidroliza peptidne veze u dipeptidima koji sadrže L-metionin i L-histidin u prisustvu dinuklearnih paladijum(II) kompleksa

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Sintetizovana su dva nova dinuklearna paladijum(II) kompleksa, $[\{Pd(en)Cl\}_2(\mu\text{-}1,5\text{-nphe})](NO_3)_2$ i $[\{Pd(1,3\text{-pd})Cl\}_2(\mu\text{-}1,5\text{-nphe})](NO_3)_2$, i njihova struktura je potvrđena na osnovu rezultata elementarne mikroanalize, NMR (^{1}H i ^{13}C) i UV-Vis spektroskopije. Primenom ^{1}H NMR spektroskopije ispitivane su reakcije akva derivata dinuklearnih paladijum(II) kompleksa, $[\{Pd(en)(H_2O)\}_2(\mu\text{-}1,5\text{-nphe})]^{4+}$ and $[\{Pd(1,3\text{-pd})(H_2O)\}_2(\mu\text{-}1,5\text{-nphe})]^{4+}$, sa *N*-acetilovanim dipeptidima L-metionil-glicinom (Ac-L-Met-Gly) i L-histidil-glicinom (Ac-L-His–Gly). Sve reakcije su izučavane na 37 °C u pH oblasti $2.0 < pH < 2.5$ u D_2O kao rastvaraču. Nađeno je da u ispitivanim reakcijama dolazi do hidrolize Met-Gly i His-Gly peptidnih veza. Brzina hidrolize peptidne veze zavisi od sternog efekta bidentatno koordinovanog diaminskog liganda u dinuklearnim paladijum(II) kompleksima.

Hydrolysis of the amide bond in L-methionine- and L-histidine-containing dipeptides in the presence of dinuclear palladium(II) complexes

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Two new dinuclear palladium(II) complexes, $[\{Pd(en)Cl\}_2(\mu\text{-}1,5\text{-nphe})](NO_3)_2$ and $[\{Pd(1,3\text{-pd})Cl\}_2(\mu\text{-}1,5\text{-nphe})](NO_3)_2$, have been synthesized and characterized by elemental microanalysis, NMR (^{1}H and ^{13}C) and UV-Vis spectroscopy. These complexes were converted into the corresponding aqua derivatives, $[\{Pd(en)(H_2O)\}_2(\mu\text{-}1,5\text{-nphe})]^{4+}$ and $[\{Pd(1,3\text{-pd})(H_2O)\}_2(\mu\text{-}1,5\text{-nphe})]^{4+}$, and their reactions with Ac-L-Met-Gly and Ac-L-His-Gly were studied by ^{1}H NMR spectroscopy. All reactions were performed at $2.0 < pH < 2.5$ in D_2O and 37 °C. It was found that in both investigated reactions hydrolysis of the Met-Gly and His-Gly peptide bonds have been occured. Rate of hydrolyses strongly depends from the steric bulk of bidentate coordinated diamine ligand in the dinuclear palladium(II) complexes.

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NH 03

Kompleksi srebra(I) sa fenantrolinima: uticaj prirode liganda i srebro(I) soli na nuklearnost kompleksa

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Aromatična heterociklična jedinjenja koja sadrže donorski atom azota u prstenu predstavljaju veoma važnu grupu liganada u sintezi kompleksa srebra(I) kao potencijalnih terapeutskih agenasa [1]. U ovom radu, 1,7- i 4,7-fenantrolin su korišćeni kao ligandi za sintezu kompleksa srebra(I). Pored toga, različite AgX soli (X = $CF_3SO_3^-$, CF_3COO^-, ClO_4^-, SbF_6^-, BF_4^- i PF_6^-) su korišćene za sintezu srebro(I) kompleksa u cilju isptivanja uticaja kontra-anjona na nuklearnost kompleksa. Sintetisani kompleksi srebra(I) su okaraktersani primenom elementalne mikroanalize, NMR (^1H i ^{13}C), IR i UV-vis spektroskopije i ESI masene spektrometrije, dok su njihove kristalne strukture određene primenom rendgenske strukturne analize.

Silver(I) complexes with phenanthrolines: the influence of ligand and silver(I) salt on the complex nuclearity

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An attractive class of ligands for the synthesis of silver(I) complexes as potential therapeutic agents comprises aromatic nitrogen-containing heterocycles [1]. In the present study, 1,7- and 4,7-phenanthroline were used as ligands for the synthesis of silver(I) complexes. In order to investigate the influence of the counter-anion on the silver(I) complex nuclearity, different AgX salts (X = $CF_3SO_3^-$, CF_3COO^-, ClO_4^-, SbF_6^-, BF_4^- and PF_6^-) were also used as the starting reactants. The characterization of the obtained silver(I)-phenanthroline complexes was established on the basis of elemental analysis, NMR (^1H and ^{13}C), IR and UV-vis spectroscopy and ESI mass spectrometry, while their crystal structure was determined by single-crystal X-ray diffraction analysis.

Acknowledgements: This work was funded in part by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Project No. 172036) and the SupraMedChem@Balkans.Net SCOPES Institutional Partnership (Project No. IZ74Z0_160515).

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NH 42

Sinteza nanočestica srebra u prisustvu askorbinske kiseline i njihova antibakterijska aktivnost

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U ovom radu sintetisane su nanočestice srebra u vodenoj sredini redukcijom jona Ag^+ natrijum-borhidridom, pri čemu je askorbinska kiselina bila stabilizaciono sredstvo. Dobijene su dve koloidne disperzije: prva, uz prisustvo askorbinske kiseline (AgNPs) i druga, dodatno stabilisana želatinom nakon sinteze (AgNPs-g). Koloidne disperzije okarakterisane su primenom više fizičko-hemijskih metoda: UV-Vis spektroskopijom, mikroskopijom atomskih sila (AFM), metodom dinamičkog rasejanja svetlosti (DLS) kao i merenjem zeta potencijala. Veličina nanočestica srebra, određena AFM merenjima, iznosila je 10 nm za AgNPs i 15 nm za AgNPs-g. Antibakterijska aktivnost sintetisanih nanočestica ispitana je u odnosu na gram pozitivne i gram negativne bakterije. Nađeno je da sintetisane nanočestice Ag ispoljavaju antibakterijsku aktivnost prema svim ispitivanim bakterijama.

Preparation of silver nanoparticles in presence of ascorbic acid and their antibacterial properties

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In this study, we present a synthesis of silver nanoparticles (AgNPs) using ascorbic acid as stabilizing and sodium borohydride as reducing agents, respectively. Two colloidal dispersions were obtained, one of them additionally stabilized by gelatin (AgNPs-g). They were characterized by UV-Vis, AFM, DLS and zeta potential measurements. The size of both AgNPs and AgNPs-g, determined by AFM measurements, was 10 nm before, and 15 nm after stabilization with gelatin. Antibacterial activity of synthesized AgNPs was tested using series of gram positive and gram negative bacteria. It was found that AgNPs showed antibacterial activity in all cases.

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HŽS S – PPP5

Remedijacija sedimenta zagađenog perzistentnim organskim polutantima

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Perzistentni organski polutanti kao što su policiklični aromatični ugljovodonici i halogenovani ugljovodonici zbog svoje hidrofobnosti vezuju se za mineralnu i organsku materiju sedimenta. Ovakvi sedimenti, usled resuspenzije, postaju osnovni i stalan izvor ovih polutanata. Kao alat za procenu potrebe za remedijacijom ovakvih sedimenata, kao i kada je remedijacija završena, koriste se različite biološke i hemijske metode za procenu biodostupnosti polutanata prisutnih u sedimentu. Smatra se da samo frakcija koja je dostupna može da podlegne procesima bioakumulacije, biosorpcije i transformacije u prisustvu različitih organizama. Tehnike bioremedijacije su se pokazale veoma efikasnim za uklanjanje policikličnih aromatičnih ugljovodonika, kako u aerobnim tako i u anaerobnim uslovima. Međutim, kada su u pitanju organohalogeni polutanti, čija je biodegradabilnost mala, bioremedijacione tehnike su uglavnom neefikasne pri čemu je reduktivna dehlorinacija jedan od najčešćih načina njihove degradacije u životnoj sredini. Iz ovih razloga za remedijaciju sedimenta organohalogenim polutantima u poslednje vreme sve više na značaju dobijaju remedijacione tehnike stabilizacije ovih materija u sedimentu primenom ugljenikom-bogatih sorbenata.

Remediation of sediment contaminated with persistent organic pollutants

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Persistent organic pollutants, such as polycyclic aromatic hydrocarbons and halogenated hydrocarbons, due to their hydrophobic properties bind to the mineral and organic matter of the sediment. These sediments, as a result of resuspension, become the primary and permanent source of these pollutants. As a tool for assessing the need for the remediation of these sediments, as well as when the remediation is finished, various biological and chemical methods for assessing the bioavailability of pollutants present in the sediment are used. It is assumed that only the available fraction can undergo bioaccumulation, biosorption and transformation processes in the presence of various organisms. Techniques of bioremediation have proved to be very effective in removing polycyclic aromatic hydrocarbons, both in aerobic and anaerobic conditions. However, when it comes to organohalogen pollutants, which have low degradability, bioremediation techniques are mainly ineffective and therefore reductive dechlorination is one of the most common ways of their degradation in the environment. Because of this, remediation of sediment contaminated with organohalogen pollutants by stabilization of these substances in sediment using carbon-rich sorbents has recently become increasingly important.

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HŽS 01

Primena eksperimentalnog dizajna kod optimizacije modela zasnovanih na veštačkim neuronskim mrežama

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Ovaj rad opisuje primenu tehnike eksperimentalnog dizajna kod optimizacije veštačke neuronske mreže za predviđanje sadržaja rastvorenog kiseonika u reci Dunav u Srbiji. Skup podataka za modelovanje sastojao se od više od 30.000 pojedinačnih merenja ukupno 18 parametara kvaliteta voda koji su praćeni u periodu od 2002. do 2011. godine. Boks-Benken eksperimentalni dizajn sa tri faktora na tri nivoa primenjen je za simultanu prostornu optimizaciju (broj monitoring stanica), vremensku optimizaciju (broj istorijskih podataka - godina) i optimizaciju broja ulaznih promenljivih modela. Hi–kvadrat (χ^2) test i korelaciona analiza su korišćene za izbor najznačajnijih i međusobno nekorelisanih ulaza. Konturni dijagrami dobijeni korišćenjem RSM metodologije (*response surface methodology*) su omogućili izbor optimalnog seta faktora za kreiranje ANN modela sa poboljšanim performansama kod predviđanja rastvorenog kiseonika.

Application of experimental design for the optimization of artificial neural network models

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This study describes the application of experimental design technique for the optimization of Artificial Neural Network (ANN) for prediction of dissolved oxygen (DO) content in the Danube River in Serbia. Modelling dataset was comprised of more than 30,000 observations of total 18 water quality parameters monitored over the period from 2002 to 2011. Box-Behnken three-factor experimental design with three levels per factor was applied for simultaneous spatial (number of monitoring sites), temporal (number of historical monitoring data - years) and input variables (number of inputs) optimization of the ANN model. Chi-squared feature selection and correlation analysis were utilized to select the most significant and mutually uncorrelated inputs. Contour plots, obtained using response surface methodology, have allowed selection of optimal set of abovementioned factor for the creation of accurate DO prediction ANN models.

Zahvalnica: Istraživanja su realizovana u okviru naučnog projekta Ministarstva prosvete, nauke i tehnološkog razvoja Republike Srbije, broj 172007.

HŽSI 02

Razvoj GRNN modela za predviđanje godišnjih količina generisanog opasnog medicinskog otpada na nacionalnom nivou

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U ovom radu su za razvoj modela za predviđanje količina opasnog medicinskog otpada koji se godišnje generiše na nacionalnom nivou u 19 zemalja Evropske unije korišćene neuronske mreže sa opštom regresijom (GRNN) koje predstavljaju vrstu veštačkih neuronskih mreža (ANN). Da bi se dobio model koji će omogućiti precizna predviđanja, kao nezavisne ulazne promenjive su korišćeni lako dostupni ekonomski, demografski i medicinski indikatori. Podaci za period od 2004. do 2012. godine su korišćeni za obuku i validaciju mreže, dok su podaci iz 2014. upotrebljeni za testiranje modela. Optimalan set parametara je odabran korišćenjem korelacione analize i analize značajnosti. Vrednost koeficijenta determinacije (R^2) optimizovanog modela iznosi 0.975 i rezultati svih predviđanja imaju grešku manju od 25%. Razvijeni model se može koristiti za simulaciju različitih scenarija vezanih za nastajanje i tretman medicinskog otpada.

The development of a GRNN model for the prediction of the annual amount of generated hazardous medical waste at the national level

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General regression neural network (GRNN), a type of artificial neural network (ANN), was used for the prediction of the annual amount of hazardous medical waste at the national level in 19 EU countries. This is a one-pass supervised machine learning algorithm mainly used to solve nonlinear problems based on the estimation of a probability distribution function. In order to provide a model with accurate predictions, broadly available economic, demographic and medical indicators were used as independent input variables. The data from 2004 to 2012 was used for training and validation of network, whilst the data from 2014 was kept for testing the model. Optimal set of parameters were selected using correlation analysis and sensitivity analysis. The value of the coefficient of determination (R^2) of optimized model was 0.975 and there were no predictions with the error greater than 25%. The developed GRNN model can be applied for the simulation of various scenarios related to generation and treatment of medical waste.

Zahvalnica: Istraživanja su realizovana u okviru naučnog projekta Ministarstva prosvete, nauke i tehnološkog razvoja Republike Srbije, broj 172007.

HŽS 03

Fotorazgradnja tiakloprida iz Calypso® 480–SC komercijalne formulacije primenom novosintetisanih ZrO_2/Fe_3O_4 nanoprahova

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Koprecipitacionom metodom sintetisana su četiri ZrO_2/Fe_3O_4 nanopraha sa različitim masenim odnosom ZrO_2 prema Fe_3O_4 (0,5 %, 2 %, 7 % i 11 %). Ispitana je fotokatalitička efikasnost ovih nanoprahova u fotorazgradnji insekticida tiakloprida iz Calypso® 480–SC komercijalne formulacije u prisustvu simuliranog sunčevog zračenja (I_{UVA}=1,8×10^{-4} W/cm^2; I_{vis}=116,2×10^{-3} W/cm^2). Kinetika fotokatalitičke razgradnje tiakloprida je praćena primenom HPLC–DAD. Pre svega je određen optimalni maseni odnos ZrO_2 prema Fe_3O_4, a zatim je primenom ovog heterogenog sistema proučavana kinetika razgradnje tiakloprida u širokom opsegu koncentracija fotokatalizatora i vodonik-peroksida (heterogeni foto-Fenton), kao i pH. U prisustvu simuliranog sunčevog zračenja primenom heterogenog foto-Fentonskog sistema koji uključuje 7% $ZrO_2/Fe_3O_4/H_2O_2$ efikasnost razgradnje tiakloprida je bila 2,5 puta veća u poređenju sa sistemom Fe_3O_4/H_2O_2 koji nije modifikovan pomoću ZrO_2.

Photodegradation of thiacloprid **from Calypso® 480–SC commercial formulation** by applying the newly synthesized **ZrO_2/Fe_3O_4** nanopowders

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Four ZrO_2/Fe_3O_4 nanopowders with different mass ratio of ZrO_2 to Fe_3O_4 (0.5, 2, 7, and 11 %) were synthesized by co-precipitation method. The photocatalytic efficiency of these nanopowders in the photodegradation of thiacloprid insecticide from Calypso® 480–SC commercial formulation in the presence of simulated solar radiation (I_{UVA} = 1.8 × 10^{-4} W/cm^2; I_{vis} = 116.2 × 10^{-3} W/cm^2) was investigated. The kinetics of the photocatalytic degradation of thiacloprid was monitored by HPLC–DAD. Primarily the optimum mass ratio of ZrO_2 towards Fe_3O_4 was determined, and then, by the application of this heterogeneous system the kinetics of thiacloprid degradation was examined in a wide range of concentrations of the photocatalyst and hydrogen peroxide (heterogeneous photo-Fenton), as well as of pH. In the presence of simulated solar radiation by using heterogeneous photo-Fenton system that includes 7% $ZrO_2/Fe_3O_4/H_2O_2$ the degradation efficiency was 2.5 times greater compared to Fe_3O_4/H_2O_2 system unmodified with ZrO_2.

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HŽS 04

Uticaj fulerenola i elektron-akceptora na fotokatalitičku razgradnju mezotriona primenom TiO_2 Hombikat pod dejstvom simuliranog sunčevog zračenja

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Mezotrion {2-[4-(metilsulfonil)-2-nitrobenzoil]-1,3-cikloheksandion, M_r = 339,32, CAS No 104206-82-8, $C_{14}H_{13}NO_7S$} je selektivni herbicid iz grupe triketona koji se koristi za kontrolu širokog spektra korovskih vrsta prilikom uzgajanja kukuruza. Razvijen je od strane Zeneca kao jedan od novijih jedinjenja triketona, pri čemu je u Evropi registrovan 2000. godine, a u SAD 2001. godine. Efikasnost fotokatalitičke razgradnje mezotriona je ispitana primenom TiO_2 Hombikat bez/sa fulerenolom i elektron-akceptorima (H_2O_2 i $KBrO_3$) pod dejstvom simuliranog sunčevog zračenja. Dobijeni rezultati ukazuju na to da elektron-akceptori povećavaju efikasnost fotokatalitičke razgradnje. Naime, u slučaju $KBrO_3$ skraćeno je vreme ozračivanja sa 180 min na 60 min. Za najefikasnije sisteme u prisustvu TiO_2 Hombikat bez/sa fulerenolom i elektron-akceptorima (H_2O_2 i $KBrO_3$) su urađena i TOC merenja pri čemu su rezultati ukazali na to da je u prisustvu fulerenola veći stepen mineralizacije nego u njegovom odsustvu.

Influence of fullerenol and electron acceptors on the photocatalytic degradation of mesotrione using TiO_2 Hombikat under simulated sunlight

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Mesotrione {2-[4-(methylsulfonyl)-2-nitrobenzoyl]-1,3-cyclohexanedione, M_r = 339.32, CAS No 104206-82-8, $C_{14}H_{13}NO_7S$} is a selective herbicide from the group of triketone used to control a wide spectrum of weed species during maize cultivation. It was developed at Zeneca as one of a novel triketone compounds and registered in Europe in 2000 and in the U.S. in 2001. The efficiency of mesotrione photocatalytic degradation in the presence of TiO_2 Hombikat without/with fullerenol and electron acceptors (H_2O_2 and $KBrO_3$) under simulated sunlight was investigated. The obtained results indicate that electron acceptors increase the efficiency of mesotrione removal. Namely, in the case of $KBrO_3$ the irradiation time was reduced from 180 min to 60 min. For the most efficient systems in the presence of TiO_2 Hombikat without/with fullerenol and electron acceptors (H_2O_2 and $KBrO_3$) TOC measurements were carried out, wherein the results indicated that with fullerenol there was a higher degree of mineralization than without it.

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HŽS 04

Fotokatalitičko obezbojavanje safranina O primenom TiO_2, ZnO i zlatom modifikovanog ZnO

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Procesi za obezbojavanje i uklanjanje organskih boja iz industrijskih otpadnih voda daju značajan doprinos očuvanju životne sredine. U ovom radu su nemodifikovani i zlatom modifikovani poluprovodnički oksidi bili primenjeni za potpuno obezbojavanje nepuferisanih vodenih rastvora safranina O. Fotokatalitička aktivnost komercijalno dostupnog ZnO i TiO_2 (nanoprah anataze) je bila upoređena sa aktivnošću zlatom modifikovanog ZnO (Au/ZnO). Au/ZnO je napravljen od komercijalno dostupnog ZnO praha primenom tehnike naparavanja. Katalizatori na bazi ZnO su pokazali znatno veću snagu obezbojavanja u poređenju sa TiO_2. Au/ZnO je pokazao malo veću aktivnost nego nemodifikovani ZnO. Obezbojavanje safranina O pomoću Au/ZnO je bilo dodatno testirano u različitim tipovima mineralnih voda. Efikasnost obezbojavanja u mineralnim vodama je bila negativno korelisana sa sadržajem suve materije i u svim slučajevima je bila niža nego u destilovanoj vodi. Inhibirajući efekat hidrogenkarbonata je bio dodatno testiran.

Zahvalnica: Autor se zahvaljuje Ministarstvu prosvete, nauke i tehnološkog razvoja Republike Srbije na finansijskoj podršci (Projekat br. ON172059).

Photocatalytic Decolorization of Safranin O Using TiO_2, ZnO and Gold-Modified ZnO

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Processes for decolorization and removal of organic dyes from industrial wastewaters make an important contribution to environmental protection. In this work unmodified and gold-modified semiconductor oxides were used for the complete decolorization of non-buffered aqueous safranin O solutions. Photocatalytic activity of commercially available ZnO and TiO_2 (anatase nanopowder) was compared with this of gold-modified ZnO (Au/ZnO). Au/ZnO was prepared from commercially available ZnO powder by applying sputter coating technique. ZnO-based catalysts show significantly higher decolorization power in comparison with TiO_2. Au/ZnO show somewhat higher activity than unmodified ZnO. Decolorization of safranin O over Au/ZnO was additionally tested in different types of mineral water. The decolorization efficiency in mineral waters was negatively correlated with the dry residue content and in all cases was less than in distilled water. The inhibiting effect of hydrogen carbonate was additionally tested.

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HŽS 06

Mogućnost primene prirodnih koagulanata iz boba za obradu vode

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Iako je bob jedna od najstarijih gajenih biljaka, danas se malo proizvodi. S obzirom da se lako gaji, moguće ga je proizvesti u dovoljnoj količini i za druge potrebe, osim za ishranu ljudi i stoke. Ekstrakti semena leguminoza se već duže vreme ispituju kao potencijalni izvori prirodnih koagulanata koji bi zamenili štetne hemijske koagulante i flokulante u obradi vode i otpadnih voda. U radu je ispitano pet sorti boba koje su se međusobno razlikovale po sadržaju proteina, za koje se pretpostavlja da su važni nosioci koagulantnih svojstava u ekstraktima leguminoza. Razlike u sastavu dobijenih vodenih ekstrakata su za posledicu imale razlike u njihovoj koagulantnoj aktivnosti, u nekim slučajevima i za više od 50%. Ogledi su izvođeni na model vodi mutnoće 45 NTU, na pH 7. Najveća postignuta koagulaciona aktivnost je bila 65%. Ekstrakti su se takođe razlikovali i po promenama koagulantne aktivnosti do kojih dolazi prilikom povećanja primenjene doze. Može se zaključiti da se ekstrakti boba mogu uspešno koristiti kao prirodni koagulanti i da je prilikom njihove proizvodnje značajno odabrati odgovarajuću sortu.

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Possibility of using natural coagulants from fava bean for water treatment

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Although the fava bean is one of the oldest cultivated plants, it hasn`t been produced much nowadays. Since it is easily grown, it is possible to produce it in sufficient quantity for other purposes, except for human and livestock nutrition. Extracts of leguminoses seeds have been examined for a long time as potential sources of natural coagulants that could replace harmful chemical coagulants and flocculants in the water and wastewater treatment processes. In this paper five variety of fava beans were examined. They differed in content of proteins, which are presumed to be important carriers of coagulant properties in leguminoses extracts. Differences in the composition of the obtained water extracts resulted in differences in their coagulation activities, in some cases by more than 50%. The experiments were carried out in the model water with turbidity of 45 NTU, at pH 7. The highest achieved coagulation activity was 65%. The extracts also differed in the changes of coagulant activity, occurred when applied dose were increasing. It can be concluded that the extracts of fava beans could be successfully used as natural coagulants and that it is important to select the appropriate variety during their production.

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HŽS 07 text rada / full text

Volumetric and acoustic properties of binary mixture ethanol + d-limonene

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The aim of this study is investigation of the molecular structure for binary mixture containing widely used flavour & fragrance ingredient, such as d-limonene, and, on the other hand ethanol as a solvent permitted in food and cosmetics industry. In this study densities, refractive indices and ultrasonic velocities of binary system ethanol + d-limonene were measured at atmospheric pressure and in temperature range T = (288.15 to 323.15) K. Excess molar volumes, deviations in refractive indices and isentropic compressibility deviations were calculated from the experimental data. Based on the calculated thermodynamic properties, analysis of the molecular structure of the investigated binary system is given.

Volumetrijska i akustična svojstva binarne smeše etanol + d-limonen

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Cilj ovog rada jeste ispitivanje molekulske strukture binarne smeše koja sadrži široko upotrebljavani sastojak za davanje ukusa i mirisa, kao što je d-limonen, i s druge strane etanol kao rastvarač dozvoljen u prehrambenoj i kozmetičkoj industriji. Gustine, indeksi refrakcije i brzine zvuka binarnog sistema etanol + d-limonen izmereni su na atmosferskom pritisku i u temperaturnom opsegu T = (288.15 to 323.15) K. Dopunske molarne zapremine, devijacije indeksa refrakcije i devijacije izentropske kompresibilnosti izračunati su iz eksperimentalnih podataka. Na osnovu izračunatih termodinamičkih svojstava data je analiza molekulse strukture ispitivane binarne smeše.

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HŽS 08

Antimikrobna aktivnost amonijumove soli ditiokarbamata i njegovih kompleksa sa Cu(II) i Ni(II)

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Ditiokarbamati (dtc) imaju široku primjenu i interesantne biološke osobine zbog čega raste interesovanje za novim dtc-jedinjenijima. Ditiokarbamati i njihove metalne soli se dugo koriste u poljoprivredi (kao insekticidi, fungicidi), u liječenju alkoholizma, za izvlačenje viška platine iz organizma itd. U ovom radu mi smo ispitivali antimikrobnu aktivnost amonijumove soli N,N-diacetato-ditiokarbama i njegovih kompleksa sa Ni(II) i Cu(II) prema nekoliko mikroorganizama. Antimikrobni potencijal sintetisanih ditiokarbamata je bio procijenjen mikrodilucionom metodom kojom je određena MIC, MBC ili MFC. Rastvori supstanci su serijski razblaživani počev od 0,5 % do 0,004 %. Sedam bakterija (pet Gram pozitivnih i dvije Gam negativne) (pet od njih je iz ATCC, a dvije iz kolekcije Instituta za biologiju u Skoplju) i četiri gljivice (jedna iz ATCC) su korištene za ovo ispitivanje.

Dobijeni rezultati pokazuju da sve tri supstance imaju antimikrobnu aktivnost sa MIC 0,004 % za *Ascosphaera apis*, MBC od 0,015% za *Bacillus subtilis* ATCC 6633 i MFC od 0,008 % za *Ascosphaera apis*.

Antimicrobial activity of dithiocarbamate ammonium salt and its Cu(II) and Ni(II) complexes

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Dithiocarbamates (dtc) have wide application and interesting biological features, which is the reason for growing interest in new dtc compounds . Dithiocarbamates and their metal salts have long been used in agriculture (such as insecticides, fungicides), in the treatment of alcoholism, to extract excess platinum from the organism *etc*. In this paper, we investigated the antimicrobial activity of the ammonium salt of N, N- diacetato-dithiocarbamate and its complexes with Ni II) and Cu (II) ions, on several microorganisms.

The antimicrobial potential of synthesized dithiocarbamates has been evaluated using the micro-broth dilution method. which enables determination of MIC and MBC or MFC. The substances were subjected to serial dilutions in descending concentrations starting from a concentration of 0.5 % and finishing with a concentration of 0.004 %.

Seven bacteria (five Gram positive and two Gram negative) (five of them are from ATCC and two are from the collection of microorganisms held by Institute of Biology, "Ss. Cyril and Methodius" University, Skopje, Macedonia; four molds (one is ATCC) and one yeast (*C. albicans* ATCC 10231) were used.

Generally, substances were found to be active, with MIC ranging from 0.004 % for *Ascosphaera apis*, and with MBC ranging from 0.015 % for *Bacillus subtilis* ATCC 6633 and MFC ranging from 0.008 % for *Ascosphaera apis*.

BH S – PPP3

Biohemija / Biochemistry

Kombinovanje rastvaračem izazvanih promena hemijskih pomeranja, teorijskog predviđanja NMR parametara i potpune spinske analize pri strukturnoj analizi jedinjenja sa složenim ^{1}H NMR spektrima

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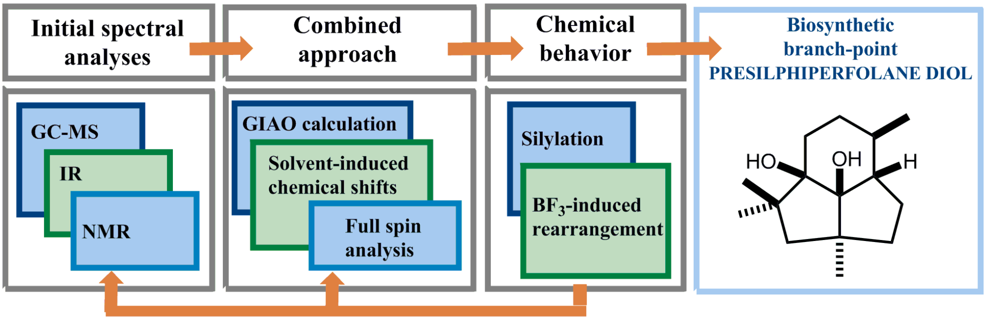
Kombinovanje rastvaračem izazvanih promena hemijskih pomeranja (uklanjanje slučajne izohronosti) i teorijskog (DFT-GIAO) predviđanja NMR parametara, uz potpunu spinsku analizu, može olakšati strukturnu analizu organskih molekula sa složenim ^{1}H NMR spektrima (preklopljeni signali, multipleti višeg reda). Ovaj tandemski pristup je razvijen i njegova korisnost ilustrovana na zahtevnom primeru novog trikvinanskog seskviterpena, presilfiperfolan-7α,8α-diola (**1a**), izolovanog iz biljne vrste *Pulicaria vulgaris* (Asteraceae). Pored podataka iz NMR eksperimenata (snimljenih u 10 različitih rastvarača), masenih i infracrvenih spektara, identitet jedinjenja **1a** je potvrđen i hemijskim transformacijama. Ovaj novi pristup smanjuje verovatnoću pogrešne identifikacije i omogućava rasvetljavanje stereohemije i potpunu interpretaciju (asignaciju) NMR podataka.



A combined approach of solvent-induced chemical shifts, GIAO calculation of NMR parameters and full spin analysis for the structural elucidation of compounds with difficult-to-interpret ^{1}H NMR spectra

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Combining solvent-induced removal of chemical shift degeneracy and theoretical (DFT-GIAO) prediction of NMR spectra with the analysis of ^{1}H NMR splitting patterns can facilitate structural elucidation of organic molecules with difficult-to-interpret NMR data (overlapping peaks, higher-order multiplets). The tandem approach was developed and its usefulness illustrated in the challenging case of a new triquinane sesquiterpene, presilphiperfolane-7α,8α-diol, **1a**, isolated from *Pulicaria vulgaris*; in addition to NMR (10 different solvents), MS and FTIR, the identity of **1a** was also confirmed by chemical transformations. The new approach decreased the probability of an erroneous identification, and allowed an unambiguous stereochemical elucidation and full NMR assignment.

BH 01 – OP1

Ispitivanje otpornosti na digestiju i alergeni potencijal alergena kikirikija u gastričnoj digestiji prema statičnom *in vitro* harmonizovanom modelu

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Glavni alergeni kikirija pokazuju rezistenciju ka gastričnoj digestiji, učestvujući u senzitizaciji preko gastrointestinalnog trakta. Veliki peptidni fragmenti su važni u ovom procesu senzitizacije, medjutim podaci za peptide malih masa nedostaju. Cilj ove studije je proučavanje stabilnosti tokom gastrične digestije kao i ispitivanje alergenosti malih i velikih peptdinih fragmenata alergena svežeg kikirikija, izvedene u in vitro uslovima koji simuliraju fiziološke. Proteini i njihovi peptidi malih i velikih molekulskih masa ekstrahovani su i analizirani putem 2D SDS-PAGE, tandemske masene spektrometrije, a alergenost ispitana na serumima alergičnih pacijenata pomoću ELISA, 2D imunoblota i ImmunoCAP. Proteinska frakcija iz digestije sugeriše da se procesi ekstakcije proteina iz matriksa hrane i njihova digestija dešavaju simultano. Pod ovim uslovima, svi glavni alergeni kikirikija ostaju uglavnom stabilni, tj manjim delom bivaju digestovani. Ova studija je delom izvedena sredstvima projekta OI172024, MPNTR Republike Srbije.

Digestion stability and allergenic potential assessment of peanut allergen gastric digesta fragmens in harmonized static *in vitro* digestion protocol

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Major peanut allergens show stability to gastric digestion, sensitizing individual *via* gastrointestinal tract. Large fragments are essential for sensitizing capacity, however data about sensitizing capacity of low molecular mass (LMM) peptides released by gastric digestion are missing. The aim of this study was to investigate digestion stability and allergenicity of large and LMM peptides released by pepsin digestion of whole peanut grains under standardized and physiologically relevant *in vitro* conditions. Proteins, high and LMM peptides, were extracted from the mixture and analysed by 2D SDS-PAGE, tandem mass spectrometry while allergenicity was assessed by western blot, ELISA and ImmunoCAP probed with allergic patients' sera. Digestion products of whole grains of raw peanut, point to simultaneous occurrence of protein extraction from the food matrix and enzymatic digestion processes. Under physiological-simulated conditions, major peanut allergens are mostly stable. This study was partially funded by a project 172024 of Ministry of Education, Science and Technological Development (MPNTR), Republic of Serbia.

BH 02 – OP2

Efekti aerozagađenja na post-translacione modifikacije (PTM) proteoma polena mačijeg repka (*Phleum pratense*) i njegov alergeni potencijal

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Zagađenje može da utiče na alergeni potencijal polena a time i na prevalencu alergija. Cilj ove studije je da se istraže efekti aero zagađenja na proteom, PTM profil i alergenost polena mačijeg repka poređenjem polena sakupljenog pored regionalnog puta za aerodrom u Kruševcu i sa obližnjih padina ekološki zaštićenog prostora. Procenat polenovih zrna koja otpuštaju sub-polenske partikule (SPP) je određen svetlosnom mikroskopijom. Pomoću nLC-MS/MS i PEAKS algoritama za „label-free" kvantifikaciju i kvantifikovano profilisanje PTM polena, 1D imunoblot i ELISA, ispitan je i upoređen alergeni potencijal dve grupe polena, zagađenog i ekološki očuvanog. Zagađeni polen pokazao je veći procenat otpuštanja SPP i malo veći alergeni potencijal. Ove osobine pripisane su kvalitativnim i kvantitativnim razlikama u ekspresionom obrascu proteoma, uključujući i znatno veći udeo oksidativnih PTM kod zagađenog polena, što sugeriše da aerozagađenje povećava alergenost polena mačijeg repka. Ova studija je delom izvedena sredstvima projekta OI172024, MPNTR Republike Srbije.

Air-traffic pollution effects on post-translational modifications of timothy grass (*Phleum pratense*) pollen proteome and its allergenic potential

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Pollutants may affect pollen allergenicity and thus the prevalence of allergies. The objective of this study was to evaluate the effect of traffic-related pollution on the proteome, PTM profiling and allergenicity of timothy grass pollen through a field-based experiment. Mature pollen grains were collected from timothy grass plants grown along main airport roadside of Krusevac city and in surroundings vegetated areas. The percentage of grains releasing sub-pollen particles (SPP) was evaluated by light microscopy. nLC-MS/MS with PEAKS algorithms for label free quantification (LFQ) and wide proteome PTM profiling were applied, including 1D immunoblot and ELISA to assess allergenicity of pollen samples. Pollen collected along airport-traffic road showed a higher SPP release and slightly higher allergenicity than pollen from vegetated areas. This was attributed to both quantitative and qualitative differences in proteome expression pattern and PTM profiling with increased extent of oxidative PTMs, suggesting that traffic-related pollution enhances timothy grass pollen allergenicity. This study was partially funded by a project 172024 of Ministry of Education, Science and Technological Development (MPNTR), Republic of Serbia.

BH 03 – US1

Biološki potencijal subkritičnih vodenih ektrakata kamilice: procena primenom elektrohemijskih DNK biosenzornih i spektrofotometrijskih metoda

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Sa ciljem povećanja funkcionalnosti biljnih proizvoda došlo je do razvoja novih ekstrakcionih tehnika. Jedna od tehnika koja privlači posebnu paznju jeste ekstrakcija vodom u subkritičnom stanju (SKV), koja omogućava dobijanje ekstrakata sa povećanom aktivnošću izbegavajući bilo kakvu toksičnost koja može biti povezana sa organiskim rastvaračima. SKV je u osnovi voda pod pritiskom u temperaturnom intervalu od 100 do 374 °C. U ovom radu ekstrakcija jezičastih cvetova kamilice je izvršena pomoću SKV. Uticaj temperature na biološki potencijal dobijenih ekstrakata bio je praćen u temperaturnom opsegu od 65 do 210 °C primenjujući pritisak od 45 bar. Antioksidativna aktivnost dobijenih ekstrakata je određena primenom DNK biosenzornih testova. Sposobnost ekstrakata da inhibiraju delovanje α-amilaze, α-glukozidaze i tirozinaze je takođe ispitana.

Biological potential of subcritical water extracts of chamomile: assessment using electrochemical DNA-based biosensor and spectrophotometric methods

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In order to increase the therapeutic functionality of plant extracts, there has been a huge upsurge for developing new extraction approaches. Among other, subcritical water (SCW) is the most promising one which is able to provide extracts with high activity while precluding any toxicity associated with organic solvent use. SCW is pressurized water between the usual boiling point (100 °C) and the critical temperature (374 °C). In this research chamomile ligulate flowers were extracted by SCW. Impact of temperature on the biological potential of chamomile extracts was determined at seven different temperatures in the range from 65 to 210 °C, and applying a pressure of 45 bar. Antioxidant activity of the obtained extracts was determined by means of DNA-based biosensor assays. Further, the ability of extracts to inhibit the activity of α-glucosidase, α-amylase and tyrosinase was investigated as well.

BH 04

Karakterizacija i efekti vezivanja atipičnih antipsihotika za katalazu iz goveđe jetre

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Oksidativni stres je nesumljivo pratilac psihijatrijskih bolesti, a plejotropni efekti atipičnih antipsihotika, lekova izbora u tretmanu psihoza, nisu razjašnjeni na molekulskom nivou. Katalaza je jedan od ključnih enzima primarnog sistema antioksidativne zaštite. U ovom radu je ispitano vezivanje pet antipsihotika druge generacije (klozapin, sertindol, ziprazidon, aripiprazol i kvetiapin) za komercijalni preparat katalaze iz goveđe jetre, pomoću uobičajenih spektroskopskih metoda. Rezultati ukazuju da se svi lekovi vezuju za protein ($K_a \sim 10^5$ M^{-1}), da mesto vezivanja nije u blizini aktivnog mesta, kao i da vezivanje nekih lekova (klozapin, sertindol i kvetiapin) utiče na strukturu i aktivnost enzima. Dobijeni nalazi bi mogli da objasne ranije uočene negativne uticaje nekih od ovih psihofarmaka na redoks status u shizofreniji.

Characterization and effects of binding of atypical antipsychotics to catalase from bovine liver

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Oxidative stress undoubtedly accompanies mental disorders, and the pleiotropic effects of atypical antipsychotics, recommended drugs in the treatment of psychosis, are not clarified at the molecular level. Catalase is one of the key enzymes of the primary antioxidant protection system. This paper studied the binding of five second-generation antipsychotics (clozapine, sertindole, ziprasidone, aripiprazole and quetiapine) to commercial bovine liver catalase, using conventional spectroscopic methods. The results suggest that all drugs bind to the protein ($K_a \sim 10^5$ M^{-1}), that the binding site is not near the active site, but that the drug binding (clozapine, sertindole and quetiapine) affects the structure and activity of the enzyme. These findings could explain the previously observed negative effects of some of these drugs on the redox status in schizophrenia.

BH 05

Kompleksi derivata isatina sa metalima i njihovo antimikrobno dejstvo

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Derivati isatina su se u novije vreme pokazali kao jedinjenja korisna u medicini i farmakologiji, jer ispoljavaju širok spektar dejstava kao što su antivirusna, antitumorna, antibakterijska, antituberkulozna, antigljivična i antikonvulzivna. Reč je o jedinjenjima koja nastaju reakcijom isatina i primarnih amina i spadaju u grupu Šifovih (*Schiff*) baza. Kao deo opsežnog istraživanja koje se bavi derivatima isatina, sintetisani su i njihovi kompleksi sa katjonima metala kao što su cink, kobalt i živa. Ispitana je njihova antimikrobna aktivnost, pomoću bujon - mikrodilucione metode, na kojoj se može zasnovati i mogućnost njihove primene. U ovom radu su poređeni kompleksi dva različita derivata isatina sa istim metalima.

Metal complexes of isatin derivatives and their antimicrobial activity

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Isatin derivatives have been recently shown to possess the potential to be applied in medicine and pharmacology due to their numerous activities such as antiviral, anticancer, antibacterial, antituberculosis, antifungal and anticonvulsive. These compounds belong to the group of Schiff bases and they are synthesized in the reaction of isatin and primary amines. As a part of the extensive investigation that deals with isatin derivatives, their complexes with metals such as zinc, cobalt and mercury were synthesized. Their antimicrobial activity was examined using the broth micro-dilution method, which could provide the grounds for the future application of these compounds. The complexes of two different isatin derivatives with the same metals were compared in this study.

BH 06

Sadržaj Ca, Mg i P u semenu odabranih cerealija/pseudocerealija i soje gajenih pod konvencionalnim i organskim uslovima proizvodnje

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Reakcijom na sve veću zagađenost životne sredine, nastalu kao posledica konvencionalne poljoprivredne proizvodnje, pojavljuje se sistem organske poljoprivrede, gde izuzetno važno mesto zauzima semenska proizvodnja. Žita odlikuje visok sadržaj mikro- i makroelemenata, neophodnih za zdravlje ljudi u svakodnevnoj ishrani. U tom cilju, ispitivan je sadržaj makroelemenata Ca, Mg i P u semenu kukuruza, pšenice spelte, soje i heljde, proizvedenih u organskom i konvencionalnom sistemu proizvodnje (tokom 2015. i 2016. godine). Za analizu koncentracije makroelemenata korišćena je metoda ICP-OES. Sadržaj Ca u organskom i konvencionalnom semenu ispitivanih vrsta, kretao se u rasponu od 0,23 do 1531,09 µg/g, sadržaj Mg od 420,22 do 1164,34 µg/g, dok je P bio zastupljen u najvećim količinama (od 1830,47 do 6046,98 µg/g). Najveća zastupljenost sva tri elementa detektovana je u semenu soje. Može se zaključiti da se sadržaj Ca, Mg i P razlikuje između kukuruza, spelte, soje i heljde, kako u različitim godinama proizvodnje, tako i u oba proizvodna sistema.

The content of Ca, Mg and P in seeds of selected organic and conventional grown cereals/pseudocereals and soybean

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The organic production system has been developed as a response to the increased environmental pollution caused by conventional agriculture. Crops possess good nutritional characteristics based on their high content of micro- and macroelements. In this work, the content of three macroelements (Ca, Mg and P) was determined in organically and conventionally produced maize, wheat, spelt, soybean and buckwheat collected during two seasons- 2015 and 2016. ICP-OES method was used to determine their concentrations. The content of Ca in the investigated organic and conventional grown seeds was in the range from 0.23 to 1531.09 µg/g, the content of Mg from 420.22 to 1164.34 µg/g, while phosphorus was the dominant mineral (1830.47 - 6046.98 µg/g). It was found that soybean seeds contain the highest concentration of all of three elements. It can be concluded that the content of Ca, Mg and P differs between maize, spelt, soybean and buckwheat in different years of production and in both production systems, as well.

Biotehnologija / Biotechnology

BT 01 – US2

Dissolution of chitin in eutectic solvents and quantitative analysis by using ATR-FTIR spectroscopy

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After cellulose, chitin is one of the most important and most widespread natural polymer. The poor solubility of chitin is a result of the close packing of chains and its strong inter- and intramolecular bonds among the hydroxyl and acetamide groups [1]. Chitosan is one of the most widely used derivative of chitin. It is well known for having common properties of polysaccharides such as biocompatibility, biodegradability, non-toxicity and antimicrobial characteristics. Chitosan has been involved practically in dietary supplements, water treatment, food preservation, agriculture, cosmetics, pulp, paper, and medical applications [2]. Deep eutectic solvents systems are formed from a eutectic mixture of Lewis and Brønsted acids and bases. They can comprise a variety of anionic and/or cationic species and have a large depression in melting point compared to the pure substances [3]. Deep eutectic solvents (DES) as the fourth generation of ionic liquids represents a known and recently widespread group of solvents. Due to ease of use and low prices, they tend to be relevant to replace traditional toxic organic solvents [4]. Four different deep eutectic solvents (DESs) prepared by the complexation of choline chloride with urea (1:2), choline chloride with glycerol (1:2), glycerol with betaine (1:1) and oxalic acid with choline chloride (1:1) were used as suitable eutectic mixtures to dissolve chitin. The aim of this study was to find a suitable mixture of solvents which would dissolve chitin in a short time. Then by exchanging DES with a solvent in which the polysaccharide is insoluble (ethanol, water), chitin could be obtained in its original form. For the analysis of chitin, we used ATR-FTIR and online FTIR (Si-Combi). For the dissolution of chitin in the deep eutectic solvent we tested temperature, speed of mixing of components, particle size of added chitin and mass of the sample. The optimal time to dissolve the chitin for all four-applied deep eutectic solvents was 4 h. Choline chloride-urea is a mixture that is obtained from vegetable raw materials, and in this paper the quantitative analysis on a FTIR spectrum showed the best dissolution of chitin at temperatures higher than 80˚C.

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BT 02

Antioksidativni potencijal ekstrakata brdena (*Asphodelus aestivus)*

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Brden *(Asphodelus aestivus,* syn. *A. microcarpus*) je samonikla, višegodišnja, zeljasta biljka, koja često pokriva velike površine. Brdena ima od deset do petnaest gomoljastih korijena i svaki je sposoban razviti novu biljku. Poslednjih godina intenzivirana su ispitivanja biljnih ekstrakata koji predstavljaju alternativu sintetskim antioksidansima.

U ovom radu ispitivan je antioksidativni potencijal ekstrakta gomoljastog korijena brdena sa područja Crne Gore. Korijen je samljeven i podvrgnut ultrazvučnoj ekstrakciji (40 Hz) i maceraciji etil-alkoholom kao rastvaračem, na sobnoj temperaturi i na temperaturi od 40°C. Antioksidativni potencijal dobijenih ekstrakata ispitani su DPPH metodom. Najjaču antioksidativnu aktivnost pokazao je ekstrakt brdena dobijen ultrazvučnom ekstrakcijom, na temperaturi 40°C (0.18 g/L ekv. vitamin C).

Dobijeni rezultati ukazuju da ekstrakti korijena brdena (*Asphodelus aestivus*), sa područja Crne Gore, imaju određeni antioksidativni potencijal, na koji utiče primjena ultrazvuka i povećana temperatura.

Antioxidative potential of summer asphodel (*Asphodelus aestivus*) extracts

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Summer asphodel (*Asphodelus aestivus, syn. A. microcarpus*) is wild-growing, perennial herb which can form vast stands that appear to dominate large areas. Summer asphodel has from ten to fiftheen bulbous roots, and each could develop new plant. In recent years investigation of herb extracts are intense due they present good alternative to synthetic antioxidants. In this work, the antioxidant potential of bulbous root of summer asphodel from Montenegro is investigated. Roots are milled and extracted by ethyl alcohol, by ultrasound extraction (40Hz) and maceration, at room temperature and 40°C. The antioxidant potential of obtained extracts is examined by DPPH method.

The highest antioxidant potential has summer asphodel extract obtained by ultrasound extraction at 40°C (0.18 g/L eqv. vit C).

Obtained results revealed that summer asphodel (*Asphodelus aestivus*) roots extracts, from Montenegro, have rather significant antioxidant potential which is influenced by ultrasound and temperature.

BT 03

Bioaktivni potencijal vinske komine (sorta Vranac)

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Vinova loza je najcjenjenija poljoprivredna kultura u svijetu. Vino je glavni proizvod prerade grožđa, mada se i zavidan procenat grožđa koristi u svježem stanju, kao sušene grožđice, za proizvodnju sokova i alkoholnih pića. Proizvodnja vina je biotehnološki proces u kome šećer iz bobice grožđa prelazi u etil-alkohol.Vino je poznato još iz antičkih vremena i bilo je važno u svim civilizacijama.

Obično, komina grožđa se definiše kao čvrsti otpad koji ostaje poslije proizvodnje vina ili soka. Komina se sastoji od pokožice i sjemenki, i rijetko peteljkovine.

U ovom radu vinska komina sorte Vranac (sa područja Crne Gore) vinarije Zenta, Podgorica sakupljena je u septembru 2016 i osušena liofilizacijom. Ispitivan je bioaktivni potencijal metanolskog ekstrakta DPPH metodom i disk difuzionom metodom na odabranim mikoorganizmima. Dobijeni rezultati ukazuju na bioaktivni potencijal ispitane vinske komine.

Bioactive potential of grape pomace (Vranac variety)

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Grapevine is the most appreciated horticultural crop in the world. Wine is main product from processing grape, but noteworthy percentages of the worldwide crop are used for fresh consumption, dried into raisins, production of non-alcoholic juice and distilled into spirits.

Wine making process is principally a biotechnological process that converts grape sugar into ethyl alcohol. Wine is an antique drink that has been an important part of human societies for thousands of years.

Commonly, grape pomace is defined as solid residue after juice or wine making processes. Grape pomace is a fibrous material that consists of processed skins, seeds and, seldom, stems.

In this work grape pomace was collected from Zenta Winery in Podgorica in September 2016 and dried by lyophilization. Bioactive potential of methanolic extract is examined by DPPH method and disc diffusion method on selected microorganisms. Gained results show that wine pomace has noteworty bioactive potential.

HTH 01 – OP3

Karakterizacija i efekti kovalentnog vezivanja fikocijanobilina za goveđi β-laktoglobulin

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Goveđi β-laktoglobulin (BLG) je glavni protein surutke, sa značajnim tehno-funkcionalnim svojstvima i velikim mogućnostima za primenu u industriji hrane. Fikocijanobilin (PCB), plava tetrapirolna hromofora sa izuzetnom antioksidativnom aktivnošću, je kovalentno vezana za ostatke cisteina (Cys) u C-fikocijaninu, glavnom proteinu cijanobakterija. U ovom radu je okarakterisano kovalentno vezivanje PCB-a za BLG, pod fiziološkim uslovima, uz pomoć spektroskopskih i elektroforetskih tehnika. Pokazano je da se PCB kao *P* konformer vezuje za ostatak Cys-121 u BLG-u, sa konstantom vezivanja od oko 10^5 M^{-1}. Kovalentno modifikovani protein ima izmenjenu tercijarnu strukturu, kao i sadržaj sekundarnih struktura u odnosu na slobodan BLG. Nakon zagrevanja, modifikovani protein je manje podložan oligomerizaciji i formiranju amiloida. Dalje, dobijeni BLG–PCB kovalentni adukt (plavi neo-hromoprotein) ima značajno veći aktioksidativni potencijal, kao i veću otpornost na digestiju pepsinom i pankreatinom u odnosu na nemodifikovani protein. Naši rezultati ukazuju da BLG–PCB kovalentni adukt ima poboljšane bioaktivne i tehno-funkcionalne karakteristike u odnosu na slobodan protein.

Characterization and effects of covalent binding of phycocyanobilin to bovine β-lactoglobulin

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Bovine β-lactoglobulin (BLG) is the major whey protein, with significant techno-functional properties and big potential for application in food industry. A blue tetrapyrrole chromophore with exceptional antioxidant activity, phycocyanobilin (PCB) is covalently bound to cysteine (Cys) residues of C-phycocyanin, major protein of cyanobacteria. This paper characterized covalent binding of PCB to BLG, under physiological conditions, using spectroscopic and electrophoretic techniques. It was shown that PCB is bound to Cys-121 residue of BLG as *P* conformer, with binding constant of 10^5 M^{-1}. In comparison to free BLG, the covalently modified protein has an altered tertiary structure, as well as the content of secondary structures. Upon heating, modified protein is less susceptible to oligomerization and the amyloid formation. Furthermore, obtained BLG–PCB covalent adduct (blue neo-chromoprotein) has increased antioxidant potential, as well as higher resistance to pepsin and pancreatin digestion than the unmodified protein. Our findings indicate that the covalent BLG–PCB adduct has improved bioactive and techno-functional properties in comparison to the free protein.

HTH 02

Antocijanski profil sortnih crvenih vina iz Srbije

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Antocijani su najznačajniji flavonoidi crvenih vina. U vinima se mogu se naći kao slobodni (antocijanidini) i kao vezani sa drugim flavonoidima, šećerima, i(ili) fenolnim kiselinama. Tokom vinifikacije i starenja vina, antocijani prolaze kroz složene hemijske promene koje rezultiraju stvaranjem čitavog niza antocijanskih pigmenata.

U okviru ovog rada okarakterisani su antocijani u sortnim crvenim vinima iz Srbije, sa ciljem da se bolje prouči njihov kvalitet i fitohemijski sastav. Korišćenjem *UHPLC-LTQ OrbiTrap* metode u dvanaest uzoraka crvenih vina identifikovano je četrdeset tri derivata antocijana (delfinidin 3-*O*-glukozid, malvidin 3-*O*-glukozid, malvidin 3,5-di-*O*-glukozid, cijanidin 3-*O*-glukozid i peonidin 3-*O*-glukozid su identifikovani u svim uzorcima, dok cijanidin 3-*O*-(2"-ksilosil)glukosid nije identifikovan samo u vinu *Game* poreklom iz Negotina). Takođe, identifikovan je i veliki broj piranoantocijana, koji nastaju starenjem vina. Od kvantifikovanih jedinjenja, najzastupljeniji je bio malvidin 3-*O*-glukozid (21,13 mg/L) u uzorku vina Prokupac iz Topličkog regiona. U pogledu identifikovanih derivata antocijana uočene su značajne razlike između ispitivanih vina.

Anthocyanin profile of monovarietal red wines from Serbia

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Anthocyanins are the most common flavonoids in red wines. They can exist in free form (as anthocyanidins), but also as related to other flavonoids, sugars, and phenolic acids. During winemaking and wine ageing anthocyanins undergo complex chemical changes which results in formation of a range of anthocyanin-derived pigments.

The aim of the present study was characterization of anthocyanins in Serbian monovarietal red wines, in order to better understand their quality and phytochemical composition. 43 anthocyanin derivatives were identified in 12 red wine samples using the UHPLC-LTQ OrbiTrap technique. Among them, delphinidin 3-*O*-glucoside, malvidin 3-*O*-glucoside, malvidin 3,5-di-*O*-glucoside, cyanidin 3-*O*-glucoside, and peonidin 3-*O*-glucoside were identified in all samples, whereas cyanidin 3-*O*-(2"-xylosyl)glucoside was not identified only in Game wine (Negotin). Also, a large number of piranoantocyanins, which are produced by aging of the wine, have been identified. Among quantified compounds, the most abundant was malvidin 3-*O*-glucoside (21,13 mg/L) in sample Prokupac wine sample from Toplica region. In respect to identified compounds, differences in the anthocyanin profiles of examined red wines have been found.

HTH 03

Ispitivanje polifenolnog sastava bobičastog voća voća primenom ciklične voltametrije

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U radu je ispitan polifenolni sastav uzoraka borovnica, kupina i malina primenom ciklične voltametrije (CV). Voltamogrami su snimljeni u opsegu potencijala od 0 mV do 800 mV, pri brzini skeniranja od 100 mV s^{-1}. Prvi anodni pik, koji se javlja između 0,310 V i 0,350 V, odgovara oksidaciji flavonola (kvercetina i njegovih glukozida) i kafene kiseline. Drugi i treći anodni pik, detektovani na potencijalima između 0,426 V i 0,444 V, kao i između 0,524 V i 0,540 V, odgovaraju antocijanima. Malvidin-3-*O*-glukozid pokazuje dva pika, na 0,428 V i 0,534 V. Cijanidin-3-*O*-glukozid učestvuje u dva oksidaciona procesa, na potencijalima oksidacije E_{pa} = 0,529 V i E_{pa} = 0,734 V. Ferulna i kumarna kiselina pokazuju pikove na 0,604 V i 0,759 V. Oksidacija –OH grupe na B prstenu kemferola rezultuje pojavom pika na 0,548 V. Dobijeni rezultati su u saglasnosti sa cikličnim voltamogramima standarda i sa rezultatima dobijenim primenom tečne hromatografije visokih preformansi (HPLC).

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Correlation of berry phenolic composition versus cyclic voltammetry response

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The aim of this study was identification of polyphenols in blueberries, blackberries and red raspberries using cyclic voltammetry (CV). CVs were taken in the potential range between 0 mV and 800 mV, with a scan rate of 100 mV s^{-1}. The first anodic peak appearing between 0.310 V and 0.350 V in the cyclic voltammograms could be attributed to the oxidation of flavonols (quercetin and its glucoside) and caffeic acid. The second and third anodic peak detected at potentials between 0.426 V and 0.444 V and 0.524 V and 0.540 V, respectively, may be ascribed to anthocyanins. Malvidin-3-*O*-glucoside presented two peaks at 0.428 V and 0.543 V. Cyanidin-3-*O*-glucoside displays two oxidation processes at E_{pa} = 0.529 V and E_{pa} = 0.734 V, respectively. Ferrulic and coumaric acids showed two peaks at 0.604 V and 0.759 V, respectively. Considering kaempferol, -OH group present on the B ring is responsible for the oxidation peak at 0.548 V. Obtained results are in good agreement with those obtained from CVs of standards and with results of high performance liquid chromatography (HPLC) for the samples.

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HTH 04

Određivanje odnosa stabilnih izotopa kiseonika i ugljenika u sortnim vinima iz Srbije

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Cilj ovog rad bio je određivanje odnosa stabilnih izotopa kiseonika $^{18}O/^{16}O$ iz vode iz vina i određivanje odnosa stabilnih izotopa ugljenika $^{13}C/^{12}C$ iz vinskog etanola. Merenje odnosa $^{18}O/^{16}O$ se primenjuje u određivanju geografskog porekla vina i kao metoda za detekciju dodatka vode. Analize određivanja odnosa $^{18}O/^{16}O$ su rađene direktno na Finnigan GasBench II periferalu povezanim sa Delta V Advantage masenim spektrometrom, bez prethodne pripreme uzorka. Odnos stabilnih izotopa ugljenika iz vinskog etanola se koristi za detekciju dodatka šećera u proizvodnji vina, kao i utvrđivanje botaničkog porekla šećera. Uzorak etanola je dobijen destilacijom vina, i sušenjem do čistoće min. 98 % (v/v). Analiza etanola je rađena na Flash HT Plus periferalu, povezanim sa Delta V Advantage masenim spektrometrom. Rezultati odnosa $^{18}O/^{16}O$ pokazuju razliku između različitih berbi, dok rezultati stabilnih odnosa $^{13}C/^{12}C$ ukazuju na razliku između sorti vina.

Determination of oxygen and carbon stable isotope ratio of monovarietal Serbian wines

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The aim of this study was to determine the stable isotope ratio of oxygen $^{18}O/^{16}O$ from wine water and to determine the stable isotope ratio of carbon $^{13}C/^{12}C$ from wine ethanol. Measurement of the $^{18}O/^{16}O$ ratio of water has application in determining the geographical origin of the wine, and is a method for detection of the addition of water in wine. Analysis of the stable isotope ratio of oxides was done directly on the Finnigan GasBench II peripheral, connected to the Delta V Advantage mass spectrometer, without the prior preparation of the sample. Stable isotope ratio of carbon from wine ethanol is used to detect the addition of sugar in the production of wine, as well as the determination of the botanical origin of sugar. The ethanol sample was obtained by distilling the wine, and drying to a purity of min. 98% (v/v). The ethanol analysis was performed on the Flash HT Plus peripheral, also connected to the Delta V Advantage mass spectrometer. The results of the stable isotope ratio of oxygen showed the difference between the various vintages. The ethanol analysis was performed on the Flash HT Plus peripheral, also connected to the Delta V Advantage mass spectrometer. The results of $^{18}O/^{16}O$ ratio shown difference between the various vintages, while $^{13}C/^{12}C$ ratio shown some differences between varieties of wine.

HTH 05

Kinetika ultrazvučne ekstrakcije polifenola iz semena korijandera

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Cilj ovog rada je bilo ispitivanje uticaja parametara ultrazvučne ekstrakcije na izolovanje polifenola iz semena korijandera (*Coriandrum sativum* L.). Eksperimenti su izvedeni korišćenjem pristupa promene jednog faktora, a ukupan prinos ekstrakcije (Y) i prinos ukupnih polifenola (TP) su ispitivani kao odzivi. Prvi korak je bilo određivanje optimalnog rastvarača. Prema tome, kao rastvarači su korišćeni umereno polarni organski rastvarači (aceton, metanol i etanol) i njihove smeše sa vodom (20-100%). Zaključeno je da 40% etanol obezbeđuje najveći Y i TP, pa je on korišćen u ostalim eksperimentima. Sledeći korak bilo je određivanje uticaja temperature na ekstrakciju polifenola u opsegu 20-80ºC. Rezultati su pokazali da Y i TP konstantno rastu sa povećanjem temperature, usled pozitivnog uticaja temperature na osobine rastvarača i biljnog materijala u prenosu mase. Uticaj vremena ekstrakcije na kinetiku procesa je određen nakon 5, 10, 20, 40, 60, 80 i 100 min. Za modelovanje ekstrakcionog procesa primenjeni su odgovarajući empirijski kinetički modeli kojima su uspešno fitovane kinetičke krive. Tako je određen eksperimentalni domen koji treba da bude primenjen na dalju optimizaciju ovog procesa.

Ultrasound-assisted extraction kinetics of polyphenols from coriander seeds

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The aim of this work was to investigate the influence of the ultrasound-assisted extraction (UAE) parameters on extraction of coriander (*Coriandrum sativum* L.) polyphenols. Experiments were performed using one-factor-at-a-time approach, where total extraction yield (Y) and total phenols yield (TP) were response variables. First step was determination of optimal extraction solvent. For this purpose, extractions were performed using moderately polar solvents (acetone, methanol and ethanol) and their mixtures with water (20-100%). It has been determined that 40% ethanol provided the highest Y and TP, therefore, it was used as solvent in further experiments. Next step was determination of temperature influence on polyphenols extraction in 20-80ºC range. Results showed that an increase of temperature provided constant increase of Y and TP, due to its impact on mass transfer properties. Influence of extraction time on extraction kinetics was determined after 5, 10, 20, 40, 60, 80 and 100 min. Commonly used empirical models were applied for modeling of extraction process, i.e., for successful fitting of kinetic curves. These experiments represented determination of experimental domain of extraction solvent, temperature and extraction time which would be used for optimization of this process using experimental design.

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HTM 01 – OP4

text rada / full text

Antifungalni filmovi na bazi polihidroksialkanoata

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Polihidroksialkanoati (PHA) su poliestri koje sintetišu Gram-pozitivne i Gram-negativne bakterije. Biodegradabilni su i biokompatibilni. Kako su kožne gljivične infekcije sve rasprostranjenije, neophodno je da se dejstvo tzv. „starih lekova", kao što su polieni, modifikuje i da se oni otpuštaju iz odgovarajućih sistema na kontrolisan način, što se može postići pomoću biokompatibilnih polimera koji imaju ulogu nosača lekova.

Predmet ovog rada je ispitivanje antifungalnih svojstava filmova PHA, dobijenih iz rastvora, u koje je inkorporiran nistatin. Prilikom izrade filmova varirana je masa polimera i nistatina. PHA/nistatin filmovi nisu sprečili rast gljiva *Aspergillus fumigatus*, *Microsporum gypseum* i *Trichophyton mentagrophytes,* ali su pokazali dobru antimikrobnu aktivnost prema gljivi *Candida albicans*. Zona inhibicije zavisi od masenog udela nistatina u filmovima. Minimalna inhibitorska koncentracija nistatina u PHA filmu iznosi 1,5 mas.%. UV/VIS spektroskopijom je utvrđeno da je 30,8% i 45,7% nistatina otpušteno na 30 °C i 37 °C, redom, što ukazuje da bi ovi filmovi mogli da se koriste u vidu obloga za lečenje obolele kože zahvaćene gljivičnom infekcijom.

Polyhydroxyalkanoates films with antifungal properties

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Polyhydroxyalkanoates (PHAs) are polyesters that are synthesized by Gram-positive and Gram-negative bacteria. They are biodegradable and biocompatible. As skin fungal infections are becoming more widespread, it is necessary to modify so-called "old drugs", such as polyenes, and release them from the appropriate systems in a controlled manner, which can be achieved by biocompatible biopolymers used as drug carriers.

The present paper reports on the investigation of the antimicrobial properties of the PHA films, loaded with nystatine, obtained by solvent-casting method. The film thickness was varied, as well as the mass of the nystatine. PHA/nystatin films did not prevent the growth of *Aspergillus fumigatus*, *Microsporum gypseum* and *Trichophyton mentagrophytes*, but showed good antimicrobial activity against *Candida albicans*. The inhibition zone depended on the concentration of nystatin. The minimum inhibitory concentration of nystatin in the PHA film is 1.5 wt.%. UV/VIS revealed that 30.8% and 45.7% of nystatin was released at 30 °C and 37 °C, respectively, which indicates that these films could be potentially used as a wound dressing for the treatment of skin affected by fungal infection.

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HTM 02 – OP5

Ispitivanje hidrofobnosti i mehaničkih svojstava filmova na bazi modifikovanog pektina

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Cilj ove studije bio je ispitivanje hidrofobnog karaktera i mehaničkih svojstava filmova na bazi modifikovanog pektina. Modifikovani pektin dobijen je u reakciji esterifikacije između hidroksilnih grupa pektina i di-acil hlorida (glutaroil i sebacoil hlorid). Filmovi su pripremani iz vodenih rastvora dobijenih derivata (2% w/v) metodom otparavanja rastvarača. Procena hidrofobnog karaktera dobijenih derivata data je na osnovu merenja vrednosti kontaktnog ugla vodene kapi na površini uzorka u formi filma (sessile drop method). Utvrđeno je da hidrofobnost i mehanička svojstva filmova zavise od stepena acilovanja kao i dužine umetnutog ugljeničnog lanca.

Investigation on hydrophobicity and mechanical performances of films based on modified pectin

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Present study reports the evaluation of hydrophobic character and mechanical performances of the films based on modified pectin. The pectin modifications were obtained in esterification reaction between hydroxyl groups from pectin and di-acyl chlorides (glutaryl and sebacoyl chloride). The films were prepared from water solutions of the resulted derivatives (2% w/v) using solvent casting method. The hydrophobicity of the obtained films was evaluated through the quantification of the contact angle (sessile drop method). It was found that the surface as well as mechanical properties were affected by acylation degree and length of the inserted carbon chains.

HTM 03

Sinteza superhidrofobnih blok-kopolimera na osnovu PLA

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Površinska svojstva materijala veoma su važna za njihovu krajnju primenu i polimeri, vrlo inertni materijali, odlični su za površinsku modifikaciju i funkcionalizaciju. Hidrofobnost, kao jedno od svojstava polimera, privlači dosta pažnje naučnika poslednjih godina. Postoji nekoliko načina za postizanje hidrofobnosti, kao što su modifikovanje površine i dodatak hidrofobnih agenasa, a takođe i kopolimerizacija kao metod za sintezu materijala sa ciljanim svojstvima. U ovom radu sintetisani su ABA-tip triblok kopolimeri koji sadrže segmente poli(dimetilsiloksana) i poli(laktida). Kao makroinicijator za polimerizaciju L-laktida korišćeni su hidroksil-hidroksil-funkcionalizovani poli(dimetilsiloksani). Sinteza je vođena u dihlormetanu u trajanju od 3 h na 35 °C, uz korišćenje trifluorometansulfonske kiseline kao katalizatora. Molekulske mase PLA blokova kontrolisane su odnosom L-laktida i dimetilsiloksana. FT-IR spektroskopija je korišćena za potvrdu mogućnosti kopolimerizacije laktida korišćenjem silikona. Diferencijalna skenirajuća kalorimetrija je korišćena za određivanje toplotnih svojstava kopolimera i potvrđen je uticaj dužine PLA blokova na toplotna svojstva kopolimera.

Synthesis of PLA based superhydrophilic block copolymer

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Surface properties of materials are very important for its end-application and polymers, as inert materials, are highly suitable for surface modification and functionalization. Hydrophobicity, as one of the characteristics of polymers, has been under huge interest recent years. There are few ways for achieving hydrophobicity, like surface modification and addition of hydrophobic agents, and also copolymerization as method for tailoring of materials properties. In this work ABA-type triblock copolymers consisting of poly(dimethylsiloxane) and poly(lactide) segments have been synthesized. The synthesis was carried out using hydroxyl end-functionalized poly(dimethylsiloxane)s, as a macroinitiators for the ring-opening polymerization (ROP) of L-lactide. Cationic ROP of L-lactide was performed in dichloromethane, with trifluoromethane sulfonic acid as catalyst, at 35 °C for 3 hours. The molecular weights of the poly(L-lactide) end-blocks were controlled by molar ratio of L-lactide/macroinitiator. FT-IR spectroscopy was used to confirm the possibility of L-lactide polymerization from silicone OH groups. Thermal properties of silicone based triblock copolymers were investigated by differential scanning calorimetry (DSC). The influence of the length of PLA block on thermal properties of the obtained materials was confirmed.

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HTM 04

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Spajanje metala pomoću adheziva na bazi prirodnih polimera

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Poslednjih godina sve više pažnje se posvećuje spajanju legura aluminijuma i drugih metalnih materijala lepljenjem pomoću odgovarajućih adheziva. Time se obezbeđuje spajanje metala u slučajevima kada uobičajeni postupci zavarivanja nisu mogući. Na tržištu postoji veliki broj različitih adheziva za čiju izradu se koriste komponente dobijene iz petrohemijskih izvora koje su štetne po zdravlje ljudi i životnu sredinu. Zbog toga je trend u industriji adheziva da se ove komponente delimično ili u potpunosti zamene netoksičnim materijalima dobijenim iz obnovljivih izvora, a da se pri tome zadrži efikasnost adheziva.

U radu je ispitana mogućnost izrade adheziva za spajanje metala u kome je komercijalna epoksidna smola potpuno ili delimično zamenjena sa prirodnim polimerima, hitozanom i/ili natrijum-alginatom. Oko 40 mas.% epoksidne smole je uspešno zamenjeno prirodnim polimerima pri čemu postignuta jačina adhezije odgovara željenoj vrednosti (4-5 MPa), a u pojedinim slučajevima je i veća u odnosu na komercijalnu epoksidnu smolu. Optimalni uslovi za postizanje ove vrednosti su 70 °C i 24 h. Uočeno je da je tretman površine neposredno pre lepljenja veoma bitan i da ima veliki uticaj na efikasnost lepljenja, kao i da prisustvo vode smanjuje jačinu adhezije. Pomoću adheziva kod kojih je 25 mas.% epoksi smole zamenjeno prirodnim polimerima uspešno su zalepljeni delovi trkačkog vozila koji su napravili članovi studentskog tima „Drumska Strela" za međunarodno takmičenje Formula student.

Metal-bonding by bio-based adhesives

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Adhesive bonding of metals is increasingly being used when welding of metals is not suitable due to metal structure and composition. It is mostly used for joining of certain aluminum alloys where conventional welding is practically impossible. That is why in the last decade researches focused on bonding of aluminum alloys, as well as other metal materials, by appropriate adhesives. There are a large number of commercial adhesives which consist of petrochemical components that could be harmful for human health and environment. Hence, there is a growing interest to develop environmental-friendly adhesives based on renewable resources.

The aim of this paper is to develop the adhesive for metal-bonding in which a commercial epoxy resin is replaced, partially or completely, by natural polymers, such as chitosan and/or sodium alginate. The epoxy resin was successfully replaced by natural polymers (up to 40 wt.%) keeping desired strength of adhesion (4-5 MPa), while in some cases even higher strength of adhesion was achieved compared to commercial epoxy resin. It was found that optimal conditions to obtain these values are 70 °C and 24 h. Furthermore, pretreatment of material surface has a great influence on the adhesion efficiency, while the presence of water decreases the adhesion strength. As a final point, members of the student team "Road Arrow" successfully bonded parts of intake system on the racing vehicle with adhesives where 25 wt.% of epoxy resin was replaced with natural polymers.

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HTM 05

Razgranati poli(ε-kaprolakton) sa različitim brojem grana: struktura, morfologija i reološka svojstva

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Poli(ε-kaprolakton), PCL, alifatski biodegradabilni poliestar je zahvaljujući svojoj biodegradabilnosti i biokompatibilnosti našao primenu u farmaciji, biomedicini i zaštiti životne sredine. Sintezom PCL razgranate molekulske strukture dobijaju se polimeri manje kristaliničnosti, čime se povećava njihova biodegradabilnost. Razgranati polimeri u obliku zvezde sa tri ili više grana koje izviru iz jezgra poseduju manju hidrodinamičku zapreminu, veću pokretljivost i ispoljavaju manje viskozitete rastopa i rastvora u odnosu na linearne polimere istih molarnih masa. Takođe se očekuje da razgranata struktura PCL utiče na njihovu morfologiju, mehanička i termička svojstva kao i na brzinu biodegradacije. Serija razgranatih PCL je sintetisana polimerizacijom otvaranja prstena, u prisustvu kalaj-oktoata, kao katalizatora. Različita multifunkcionalna jezgra (trimetilolpropan, ditrimetilolpropan, pentaeritritol i dipentaeritritol) su korišćeni za dobijanje PCL sa tri, četiri i šest grana. Strukutura i sastav sintetisanih poliestara su ispitani NMR i GPC analizom, dok su termička svojstva analizirana DSC i TG analizom. Morfologija filmova razgranatih poliestara dobijenih iz različitih rastvarača (hloroforma i etil-laktata) je ispitana AFM analizom. Uticaj broja grana na reološka svojstva PCL u rastopu je takođe testiran.

Star-shaped poly(ε-caprolacton) with different number of arms: structure, morphology and rheological behaviour

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Poly(ε-caprolactone), PCL, an aliphatic biodegradable polyester has been widely used for pharmacological, biomedical and environmental application due to its biodegradability and biocompatibility. Synthesis of PCL with branched structure leads to materials with reduced crystallinity which improves their biodegradability. The star-shaped polymers with three or more branches extending from a single core exhibit a smaller hydrodynamic volume, greater mobility and lower solution and melt viscosity compared to linear one. It is expected that star-shaped PCL structure affect their morphology, mechanical, thermal properties and biodegradation rate. A series of star-shaped PCL were synthesized by ring-opening polymerization using stannous octoate, as catalyst. Different multifunctional cores (trimethylolpropane, ditrimethylolpropane, penthaerytritol and dipentaerytritol) were used resulting in three, four and six armed PCL. The structure and composition of PCL were determined by NMR and GPC analysis, while their thermal properties were analized by DCS and TGA. Morfology of star-shaped polymer films casted from different solvents (chloroform and ethyl lactate) was investigated by AFM. The influence of number of arms on rheological properties of branched PCL in melt was also tested.

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HTM 06

Karakterizacija nezasićenih poliestarskih smola ojačanih česticama otpadnog PET-a

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Nezasićene poliestarske smole (NPS), u potpunosti na bazi prirodnih sirovina, sintetisane su polikondenzacijom u rastopu itakonske i ćilibarne kiseline sa 1,2-propandiolom. Kao reaktivni razređivač upotrebljen je dimetilitakonat. Dobijene smole su mešane sa česticama otpadnog PET-a (9 mas.%) čija je površina funkcionalizovana kalemljenjem itakonske kiseline. Smole su umrežavane slobodnom radikalskom polimerizacijom. Uticaj reakcionih parametara - način modifikovanja i sadržaj PET-a - na hemijska, mehanička i termička svojstva su ispitana DMA i TA analizom i merenjem zateznih svojstava. Zatezna čvrstoća (20-35 MPa), temperatura ostakljivanja (72-75 °C) i koeficijent termalnog širenja ($90\text{-}120 \cdot 10^{-6}$ °C^{-1}) umreženih smola su bili u željenom opsegu za nezasićene poliestarske smole.

Characterization of unsaturated polyester resins reinforced by waste PET particles

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Fully bio-based unsaturated polyesters resins (UPRs) were synthesized by melt polycondensation of itaconic acid and succinic acid with 1,2-propandiol and diluted by dimethyl itaconate. The obtained resins were then mixed with waste PET particles (0-9 wt.%) which surface were previously functionalized by grafting of itaconic acid. UPRs were cured by free radical polymerization. The impact of composition variables — PET content and grafting pathway — on the chemical, mechanical, and thermal properties of the thermosets was examined by DMA, TA and tensile measurements. The tensile strength (20-35 MPa), glass transition temperature (72-75 °C), and coefficient of thermal expansion ($90\text{-}120 \cdot 10^{-6}$ °C^{-1}) of the cured resins were in the desired range for UPRs.

MH S – PPP4

Uticaj N-terminalne aminokiseline i kontra-anjona na strukturu i biološku aktivnost kompleksa zlata(III) sa dipeptidima koji sadrže L-histidin

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U ovom radu su prikazani rezultati dobijeni u oblasti sinteze, strukturne karakterizacije i ispitivanja biološke aktivnosti kompleksa zlata(III) sa dipeptidima koji sadrže L-histidin, X-L-His (X = Gly, L-Ala, L-Val i L-Leu) [1]. U svim sintetisanim zlato(III)-dipeptid kompleksima, odgovarajući X-L-His dipeptid je tridentatno koordinovan za Au(III) jon preko N3 atoma azota imidazolovog prstena L-histidina, deprotonovanog atoma azota peptidne veze i atoma azota amino grupe N-terminalne aminokiseline. Međutim, N-terminalna aminokiselina i kontra-anjon u odgovarajućem kompleksu imaju značajan uticaj na strukturu i biološku aktivnost zlato(III)-dipeptid kompleksa.

Influence of N-terminal amino acid and counter anion in tuning the structure and biological activity of gold(III) complexes with L-histidine-containing dipeptides

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An overview of the results achieved in the field of synthesis, structural characterization and biological evaluation of gold(III) complexes with L-histidine-containing dipeptides X-L-His (X = Gly, L-Ala, L-Val and L-Leu) will be presented [1]. In all synthesized gold(III)-dipeptide complexes, the corresponding X-L-His dipeptide is tridentatedly coordinated to the Au(III) ion through the N3 imidazole nitrogen, the deprotonated nitrogen of the amide bond and to the nitrogen of the N-terminal amino group. However, the N-terminal amino acid and counter anion of the corresponding complex have great influence on the structural and biological properties of the gold(III)-dipeptide complexes.

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1. B. Warżajtis, B. Đ. Glišić, N. D. Savić, A. Pavic, S. Vojnovic, A. Veselinović, J. Nikodinovic-Runic, U. Rychlewska, M. I. Djuran, *Dalton Trans.* **46** (2017) 2594 and references therein.

MH 01

Antimikrobna i antitumorska aktivnost novih paladijum(II) kompleksa sa nekim aminokiselinskim derivatima

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In vitro antitumorska aktivnost novih enaminskih liganada i odgovarajućih paladijum(II) kompleksa određivana je MTT testom na dve ćelijske linije leukemije (JVM-13 i MOLT-4) i protiv primarnih leukemijskih ćelija izolovanih od pacijenata sa hroničnom limfocitnom leukemijom (CLL). Antimikrobna aktivnost testiranih jedinjenja je procenjena određivanjem MIK i MMK vrednosti za tri referentna bakterijska soja: *E. faecalis*, *P. aeruginosa*, *S. aureus* i jednog kliničkog izolata kvasca: *Candida spp.*

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Antimicrobial and antitumor reactivity of new palladium(II) complexes with some amino acid derivatives

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In vitro antitumor activity of the new enamines ligands and corresponding palladium(II) complexes was determined by MTT assay against two leukemia cell lines (JVM-13 and MOLT-4) and against primary leukemic cells isolated from chronic lymphocytic leukemia (CLL) patients. Antimicrobial activity of the tested compound was evaluated by determining the MIC and MMC against three reference bacterial strains: *E. faecalis*, *P. aeruginosa*, *S. aureus* and one clinical isolate of yeast: *Candida spp.*

Acknowledgements: The authors are grateful to the Ministry of Education, Science and Technological Development of the Republic of Serbia (Projects No. OI172016 and III41010) and biletaral project between Republic of Serbia and Republic of Montenegro for financial support.

MH 02

Izolovanje i identifikacija triterpenskih kiselina iz gljive *Piptoporus betulinus*

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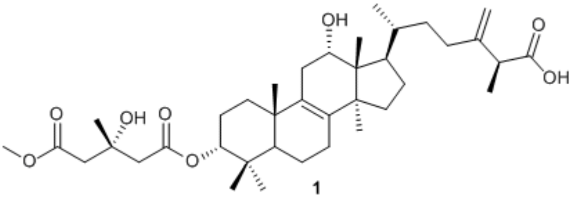
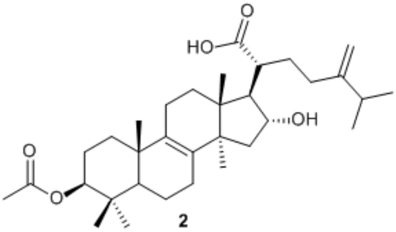
Triterpenske kiseline su biološki aktivna jedinjenja i predstavljaju važnu grupu sekundarnih metabolita gljiva.[1] U ovom radu opisan je postupak izolovanja i određivanja strukture triterpenskih kiselina iz gljive *Piptoporus betulinus* prikupljene u selu Oglađenovac u okolini Valjeva. Osušeni usitnjeni materijal je ekstrahovan smešom metilen-hlorida i metanola (2:1), a nakon re-ekstrakcije etil-acetatom dobijen je re-ekstrakt koji je frakcionisan i prečišćavan hromatografskim tehnikama. Izolovana jedinjenja su 12-hidroksi-3-(3'-hidroksi-4'-metoksikarbonil-3'-metilbutiriloksi)-24-metilen-lanosta-8,24(31)-dien-26-ska kiselina (**1**) i 3-acetoksi-16-hidroksi-24-metilen-lanosta-8-en-21-ska kiselina (**2**). Struktura jedinjenja određena je primenom NMR spektroskopskih metoda (^{1}H, ^{13}C, COSY, TOCSY, HSQC i HMBC). Jedinjenje **2** je prvi put izolovano iz ove vrste gljive.



1



2

Isolation and identification of the triterpenoid acids from fungus *Piptoporus betulinus*

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Triterpenoid acids are biologically active compounds and represent important group of secondary metabolites from fungi.[1] In this study, we reported isolation and characterisation of triterpenoid acids from fungus *Piptoporus betulinus* collected in village Oglađenovac near Valjevo. Air dried milled basidiocarp was extracted with mixture od methylene chloride and methanol (2:1) and than re-extracted with ethyl acetate. Final extract was fractioned and purified by chromatografic techniques. Isolated compounds are 12-hydroxy-3-(3'-hydroxy-4'-methoxycarbonyl-3'-methylbutyryloxy)-24--methylenelanosta-8,24-(31)-dien-26-oic acid (**1**) and 3-acetoxy-16-hydroxy-24-methylene-lanost-8-en-21-oic acid (**2**). The structures of compounds were determined using NMR, including 1D (^{1}H, ^{13}C, COSY, TOCSY, HSQC and HMBC). Compound **2** was isolated for the first time from this fungus.

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1. Alresly Z. et al. *Rec. Nat. Prod.*, **10** (2016) 103-108

MH 03

Antidijabetska aktivnost alkoholnih ekstrakata *Aronia melanocarpa* L. sa teritorije Rasinskog okruga, Srbija

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Dijabetes melitus je hronična bolest uzrokovana nasleđenim i/ili stečenim nedostatkom proizvodnje insulina od strane pankreasa ili neefikasnošću proizvedenog insulina [1]. Aroniju karakteriše visok sadržaj fenolnih jedinjenja [2] koja se razlikuju po svojoj strukturi, i često ih predstavljaju fenolne kiseline, tanini i flavanoidi kao što su antocijanini i flavanoli. Ove bioaktivne kompenente aronije mogu imati ulogu u smanjenju nivoa glukoze u krvi inhibicijom enzima α-glukozidaze čime sprečavaju početak dijabetesa kontrolisanjem hiperglikemije [1].

Naše istraživanje obuhvatilo je ispitivanje inhibitorsog dejstva alkoholnih ekstrakata (metanol zakišljen 0,1 % HCl, **1**; 80 % metanol, **2**; i 50 % etanol, **3**) sveže Aronije na enzimsku aktivnost α-glukozidaze. Rezultati pokazuju da ekstrakti **2** i **3** imaju snažnu antidijabetsku aktivnost sa IC_{50} vrednostima od 10,81±0,38 i 10,15±0,20 mg/mL, redom, što je ~30 puta veća aktivnost u odnosu na akarbozu koja je korišćena kao referentni lek. Sa druge strane, uzorak **1** je pokazao manju aktivnosti u odnosu na **2** i **3** (IC_{50} = 109,38±1,17 mg/mL) ali i pored toga ova aktivnost je ~3 puta veća od aktivnosti koju pokazuje akarboza.

Antidiabetic activity of alcohol extracts of *Aronia melanocarpa* L. collected from the Rasina District, Serbia

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Diabetes mellitus is a chronic disease caused by inherited and/or acquired deficiency in the production of insulin by the pancreas, or by the ineffectiveness of the insulin produced [1]. Aronia is characterized by a high content and wide diversity of phenolic compounds [2]. They differ in their structure and are frequently represented by phenolic acids, tannins, and flavonoids such as anthocyanidins, and flavanols. These bioactive compounds of Aronia can have beneficial effects in reducing blood glucose levels due to inhibition of α-glucosidase and thus preventing the onset of diabetes by controlling post-prandial hyperglycemia [1].

In our investigation, the inhibitory activity of alcohol extracts (acidified methanol (0.1 % HCl), **1**; 80% methanol, **2**; and 50% ethanol, **3**) of fresh Aronia against mentioned enzyme was carried out. Results have shown that samples **2** and **3** demonstrate strong antidiabetic activity (IC_{50} = 10.81±0.38 and 10.15±0.20 mg/mL, respectively) which is ~30 times greater action in comparison to acarbose used as reference drug. On the other hand, sample **1** exhibited lower activity than **2** and **3** (IC_{50} = 109.38±1.17 mg/mL) but nevertheless, that is ~3 times greater than the action shown by acarbose.

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MH 04

Novi azotni mimetici goniofufurona: sinteza i antiproliferativna aktivnost

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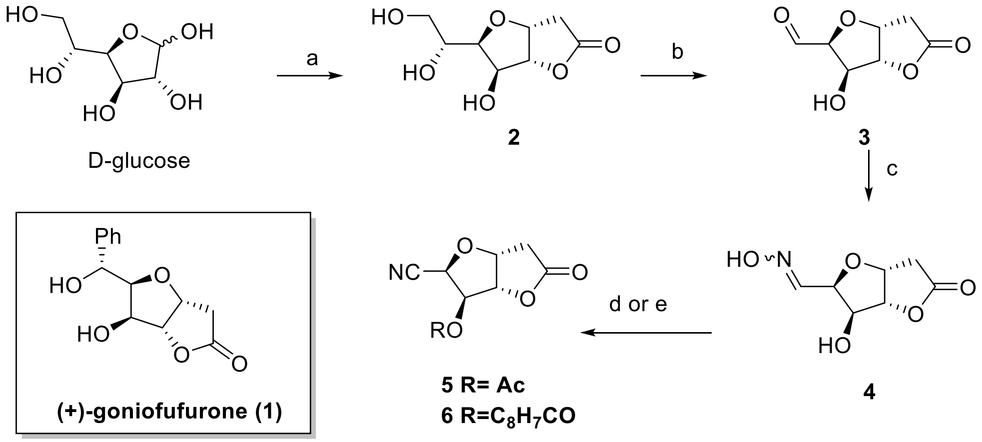
Ostvarene su višefazne sinteze tri nova mimetika goniofufurona sa oksimino ili nitrilnom funkcijom u položaju C-7, primenom višefazne sintetske sekvence prikazane na reakcionoj shemi. Ispitana je *in vitro* citotoksična aktivnost novosintetizovanih mimetika prema odabranim tumorskim ćelijskim linijama, kao i prema jednoj normalnoj ćelijskoj liniji (fetalni fibroblasti pluća, MRC-5).



Scheme 1. *Reagents and conditions: (a) Meldrum's acid, DMF, Et_3N, 46−48 °C; (b) $NaIO_4$, CH_3OH+H_2O (2:1), rt; (c) $NH_2OH \times HCl$, CH_3COONa, EtOH, rt; (d) AcCl, Py, rt; (e) cinnamoyl-chloride, DMAP, CH_2Cl_2, 0 °C→rt.*

New nitrogen goniofufurone mimics: synthesis and antiproliferative activity

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Synthesis of three new goniofufurone mimics with oximino or nitrile function at the C-7 position was completed by using a multi-step sequence, which is shown in the reaction scheme. *In vitro* cytotoxic activity of synthetized mimics was evaluated toward selected human tumour cells, as well as a normal cell line (fetal lung fibroblasts, MRC-5).

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MH 05

Uticaj kompleksa rutenijuma(II) sa N-alkilfenotiazinima na oksido-redukcione procese u K562 ćelijama humane leukemije

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Kompleksi rutenijuma privlače veliku pažnju kao lekovi bazirani na metalima u medicini zbog svoje antioksidativne aktivnosti i citotoksičnosti. Uticaj tri kompleksa Ru(II), opšte formule L[RuCl$_3$(DMSO)$_3$] **(1-3)**, gde je L protonovani hlorpromazin (CP.H), trifluoperazin (TF.2H) ili tioridazin (TR.H), u koncentraciji 15 μM ispitan je na oksido-redukcione procese u K562 ćelijama humane leukemije (sadržaj karbonilnih (CO) grupa proteina i malondialdehida (MDA)) i aktivnost enzima antioksidativne odbrane (superoksidne-dismutaze (SOD), katalaze (CAT) i laktat-dehidrogenaze (LDH)). Primenom svih kompleksa zabeležena je povećana aktivnost SOD, a smanjena aktivnost CAT. Kompleks **1** povećava aktivnost SOD za 48% u odnosu na kontronu grupu, a izaziva i najveće oštećenje proteina praćenjem sadržaja CO grupa. Povećan sadržaj MDA primenom svih kompleksa posledica je visokog procenta lipidne peroksidacije. Inhibicija totalne aktivnosti LDH primenom kompleksa **2** u K562 ćelijama u odnosu na ostala dva kompleksa, rezultat je povećanja reaktivnih kiseoničnih vrsta i oksidativnog stresa, što dovodi do nekroze i apoptoze.

The effect of ruthenium(II) complexes with N-alkylphenothiazines on the oxidation-reduction processes in K562 human leukemic cells

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Ruthenium complexes have a great attention as metal-based therapeutic agents in medicine because of their antioxidant activity and cytotoxicity. The effect of three Ru(II) complexes of the general formulae L[RuCl$_3$(DMSO)$_3$] **(1-3)** where L is protonated chlorpromazine (CP.H), trifluoperazine (TF.2H) or thioridazine (TR.H), applied in concentration of 15 μM are investigated on the oxidation-reduction processes in K562 human leukemic cells (carbonyl (CO) group of proteins, malondyaldehyde content (MDA)) and activities of enzymes antioxidative defenses (superoxide dismutase (SOD), catalase (CAT) and lactate-dehydrogenase (LDH)). The highest value of SOD and the lowest value of CAT activity are observed using the complexes. The complex **1** increased 48% of the SOD activity in compared to the control group as well as this complex shows high damage on CO groups of proteins. All complexes increased MDA content and showed a great degree of lipid's peroxidation. Inhibition of total LDH activity by the complex **2** in K562 cells compared to the other two complexes is the result of an increase in reactive oxygen species and oxidative stress, which leads to necrosis and apoptosis.

MH 06 text rada / full text

Health risk assessment of potentially toxic elements in vegetables from green market

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Food quality and safety are a main concern of the modern world. The contents of Al, As, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sb, Zn and Mo were determined in twelve vegetable species taken at the Čačak green market (Central Serbia) using Inductively Coupled Plasma–Optical Emission Spectrometry (ICP–OES) analysis. In order to assess the safety of consumption of studied vegetables regarding the content of Al, Cr, Cu, Mn, Ni, Pb and Zn, estimated weekly intake (EVI) was calculated. The average hazard quotient (HQ) of toxic elements through vegetable consumption in the study area was found to be in the order of Pb>Ni>Cr>Zn>Al>Cu. Human health risk assessment indicated high risk probability (HQ>1) for chromium, nickel and lead. The average long-term hazard quotient of studied elements was in the order of Pb>Cr>Mn>Ni>Cu>Zn>Al, whilst the high risk was indicated regarding to content of chromium, manganese and lead (HQ>1).

Procena zdravstvenog rizika potencijalno toksičnih elemenata u povrc u sa zelene pijace

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Kvalitet i zdravstvena bezbednost hrane glavna su briga savremenog sveta. Sadržaj Al, As, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sb, Zn i Mo određen je u dvanaest vrsta povrća sa gradske zelene pijace (Čačak–Centralna Srbija). Za određivanje sadržaja elemenata korišćena je analitička tehnika induktivno kuplovana plazma sa optičkom emisionom spektrometrijom (*eng*. Inductively coupled plasma – optic emission spectrometry, ICP–OES). Da bi se procenila zdravstvena bezbednost svežeg povrća u odnosu na sadržaj Al, Cr, Cu, Mn, Ni, Pb and Zn izračunat je procenjeni nedeljni unos (PNU, *eng*. EWI). Prosečan koeficijent rizika (KR, *eng*. HQ) toksičnih elemenata po ljudsko zdravlje kroz potrošnju povrća na području istraživanja je u nizu Pb>Ni>Cr> Zn>Al>Cu. Visok koeficijent rizika po ljudsko zdravlje (KR>1) procenjen je za hrom, nikl i olovo. Prosečan dugoročni rizik ispitivanih elemenata je u nizu Pb>Cr>Mn>Ni>Cu>Zn>Al, pri čemu je visok rizik indikovan u odnosu na sadržaj hroma, mangana i olova (KR>1).

MH 07

Novi konformaciono kruti mimetik goniofufurona i njegova *in vitro* antitumorska aktivnost

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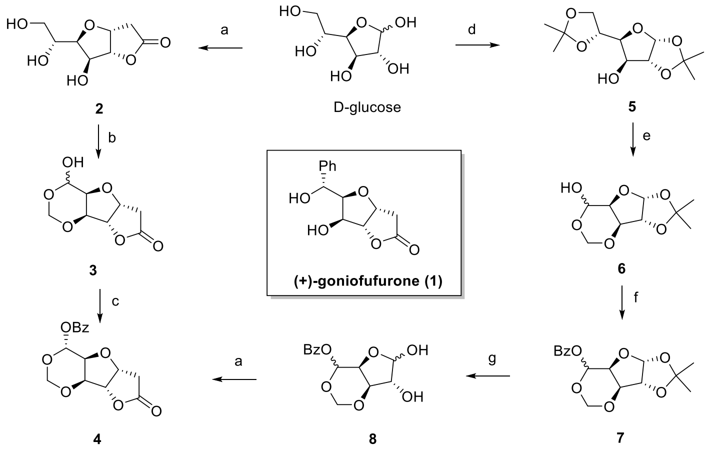
Ostvarena je sinteza novog konformaciono krutog mimetika goniofufurona sa 5,7-*O*-metilidenskom i 7-benzoiloksi funkcijom (jedinjenje **4**), primenom dva nezavisna puta, prikazana na reakcionoj shemi. Ispitana je antiproliferativna aktivnost novosintetizovanog jedinjenja prema jedanaest ćelijskih linija humanih tumora i prema jednoj zdravoj ćelijskoj liniji (MRC-5).



Scheme 2. *Reagents and conditions: (a) Meldrum's acid, DMF, Et_3N, 46−48 °C; (b) $NaIO_4$, CH_3CN, rt; (c) BzCl, Py, 0 °C→rt; (d) conc. H_2SO_4, Me_2CO, rt; (e) H_5IO_6, EtOAc, rt; (f) BzCN, DMSO, rt; (g) 90% aq TFA, 0 °C.*

A novel conformationally constrained goniofufurone mimic and its *in vitro* antitumour activity

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Synthesis of a conformationally constrained goniofufurone mimic, with 5,7-*O*-methylidene and 7-benzoyloxy functions (compound **4**) was completed by using two independent multi-step sequences, as shown in the reaction scheme. *In vitro* cytotoxicity of newly synthetized analogue was evaluated against eleven human tumour cell lines and a single normal cell line (MRC-5).

The work was supported by the Ministry of Education, Science and Technological Development (Project 172006).

MH 08

In vitro testing of bioactive compounds from natural sources
In vitro testiranje bioaktivnih spojeva iz tradicionalnih

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Natural products such as fruits, vegetables and herbs contain different bioactive substances which vary widely in chemical structure and function. Beneficial effects of isolated bioactive compounds on human health are associated with anti-tumor, anti-allergic, antibiotic, antioxidant and other properties. Protective effects of bioactive compounds toward different types of tumors are of huge importance since the cancer is one of the leading causes of morbidity and mortality worldwide. Therefore, biologically active substances from plants are being investigated as a potential source of new drugs, wherein *in vitro* assays using different cell lines are frequently used. Cell lines represent a useful alternative approach in toxicological studies, from general toxicity to ecotoxicity. In addition, human cell lines (normal and tumor) are often used in testing of bioactive compounds from different plant sources. In this study, we will present results of biological activity of subcritical water extracts from different plants toward tumor cell lines (HeLa, HepG2 and MCF-7) assessed by commercial CellTiter 96® Cell Proliferation Assay (Promega, USA). Obtained results gained by *in vitro* tests could serve as guidelines for further *in vivo* studies of tested samples.

MH 09

Nanočestice na bazi silicijuma za primenu u zaštiti kože od sunčevog ultraljubičastog zračenja

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Sinteza i karakterizacija novih nanomaterijala na bazi silicijuma (mezoporozne nanočestice silicijum-dioksida (MSN) i periodične mezoporozne organosilikatne nanočestice (PMONP)) su ispitivane za primenu u zaštiti kože od sunčevog ultraljubičastog zračenja. Nanomaterijali su sintetisani u vodenom rastvoru, u prisustvu surfaktanta kao templata za mezopore, hidrolizom i kondenzacijom tetraetil ortosilikata u slučaju MSN, odnosno 1,4-bis(trietoxisilil)benzena u slučaju PMO nanočestica, u baznoj sredini. Takođe, ispitivana je sposobnost nanomaterijala kao nanonosača za avobenzon, molekula koji je često upotrebljavan u preparatima za zaštitu kože. Novi istraživački rezultati ukazuju da avobenzon, titan-dioksid i drugi sastojci preparata za zaštitu kože od UV zračenja izazivaju štetne posledice na koži tokom produženog izlaganju sunčevim zracima, što je i dodatna motivacija za ovo istraživanje, tj. ublažavanje štetnih efekata ovakvih preparata, uz poboljšanje njihove efikasnosti. Dobijeni rezultati ukazuju da MSN i PMO nanočestice uspešno blokiraju ultraljubičaste zrake usled disperzije svetlosti, kao i da je MSN efikasan nosač za avobenzon.

Silicon-based Nanoparticles for Applications in Skin Protection from UVA/UVB Sun Irradiation

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Synthesis and characterization of novel silicon-based nanomaterials (mesoporous silica nanoparticles (MSN) and periodic mesoporous organosilica nanoparticles (PMONP)) is presented for application in protection of skin from UVA/UVB sun irradiation. The nanomaterials are synthesized in aqueous environment, in the presence of a surfactant as a mesopore template, through hydrolysis and condensation of tetraethyl orthosilicate in case of MSN, and 1,4-Bis(triethoxysilyl)benzene in case of PMONP, in basic environment. Furthermore, we test the capability of these nanomaterials to carry avobenzone, which is a known sun-absorbing agent. Recent research revealed that avobenzone, as well as titanium dioxide and other ingredients of sunscreen products cause harmful effects on the skin upon prolonged exposure to UV irradiation, which are additional factors that motivated this research, i.e. to alleviate these harmful effects of sunscreening products, in addition to improving their efficacy. The obtained results reveal that MSN and PMO effectively block UV light through the light dispersion from nanoparticles, as well as that MSN is effective as avobenzon carrier.

Organska hemija / Organic Chemistry

OH S – PPP2

NMR spektroskopija u analizi novih nedozvoljenih supstanci na srpskom tržištu

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Zloupotreba supstanci predstavlja globalni problem na koji nije imuno ni srpsko tržište. Uslužna proizvodnja, koja najčešće potiče iz azijskih zemalja, u kombinaciji sa kupovinom preko interneta olakšavaju stavljanje takvih proizvoda u promet. Najčešći načini zloupotrebe supstanci su korišćenje sintetskih lekova u proizvodima koji se deklarišu kao sto posto prirodni i neškodljivi proizvodi utemeljeni na narodnoj medicini. Takođe se pribegava i upotrebi novih nelegalnih supstanci, koje su neznatno hemijski izmenjene u cilju izbegavanja standardnih ciljanih analiza na poznate nelegalne supstance.

Ovo predavanje će se fokusirati na ulozi NMR spektroskopije u sprečavanju prevara na domaćem tržištu, kroz skorašnje primere iz prakse Laboratorije za instrumentalnu analizu Hemijskog fakulteta i Centra za hemiju IHTM-a Univerziteta u Beogradu. Pored lažnih prirodnih preparata za povećanje potencije, gde su pronađene aktivne komponente vijagra i cialis i sredstava za mršavljenje kod kojih je pronađen sibutramin, najviše reči biće o dva najskorija slučaja zloupotrebe supstanci. Prvi je otkriven tokom priprema za Letnju školu hromatografije za Istraživačku stanicu Petnica, gde se u osveživaču prostora nalazio novi sintetski kanabinol pod nazivom AB-FUBINACA, dok je najsvežiji primer iz avgusta 2017. godine, kada je u dijeteskim proizvodima za mršavljenje pronađen antidepresiv fluoksetin (Prozac, Flunirin, Flunisan...). Takođe biće reči i o prednostima NMR-a u odnosu na druge instrumentalne tehnike.

NMR spectroscopy in the identification of new substances of abuse on the Serbian market

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Substances of abuse (SOA) are continuously emerging global problem and there are some examples on Serbian market too. Contract manufacturing service and private label fabrication in combination with internet shopping help these fake products to appear on the market. The examples of SOA were mainly usage of synthetic drugs in, so call all natural formula for treatment of different health problems, and usage of new SOA with slightly altered chemical structure compared with an original illegal drug.

This presentation will focus on the purpose of NMR spectroscopy in identification of novel SOA on the Serbian market by Laboratory of Instrumental Analysis (Faculty of Chemistry and Center for Chemistry ICTM, both University of Belgrade). Except the fake natural capsules for the treatment of erectile dysfunction with Viagra and Cialis as active components, and green coffee for slimming with sibutramine, two most recent case of study will be explained. First was synthetic cannabinol AB-FUBINACA from air-freshner, and the last one it was antidepressant fluoxetine (Prozac) fined in dietary supplement for weigh loss. A development of fast method for identification and structural characterization of newly emerging SOA is crucial, and NMR spectroscopy is method of choice.

Acknowledgments: The financial support by Ministry of education, science and technological development (Grant No. 172053) is highly appreciated.

Sadržaj : : Contents Štampaj : : Print

OH 01

Sinteza polifunkcionalnih konjugovanih diena na silika-gelu bez rastvarača

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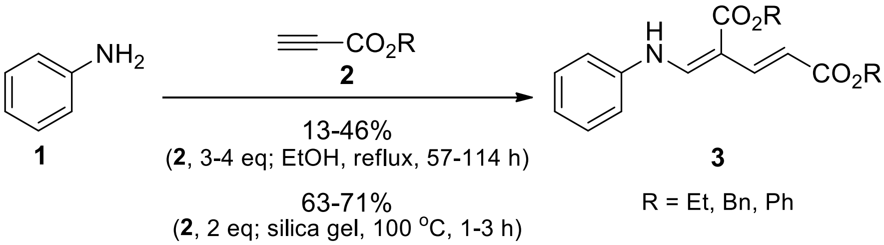
Slabo nukleofilni aromatični amini, kao, na primer, anilin (**1**) slabo reaguju sa estrima propiolne kiseline **2** dajući konjugovane diene **3**, pod standardnim uslovima sinteze u rastvaraču. Mi predstavljamo efikasniji metod koji se zasniva na reakciji na silika-gelu, bez rastvarača. Pod ovim uslovima poboljšava se prinos proizvoda, smanjuje se reakciono vreme i poboljšava se hemoselektivnost u odnosu na izolovani enamino estarski intermedijer ili 1,2- i 1,4-dihidropiridinske sporedne proizvode.

Zahvalnica: Autori se zahvaljuju Ministarstvu prosvete, nauke i tehnološkog razvoja Republike Srbije za finansijsku podršku (Projekat br. 172020).



Solvent-free silica gel-promoted synthesis of polyfunctionalized conjugated dienes

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Weakly nucleophilic aromatic amines, represented by aniline (**1**), hardly react with propiolic esters **2** to give conjugated dienes **3**, under classical solution-phase conditions. We present a more efficient, solvent-free, silica gel-promoted method that enhances product yields, reduces reaction times and improves chemoselectivity with respect to isolated enamino ester intermediate or 1,2- and 1,4-dihydropyridine by-products.

Acknowledgement: Financial support from the Ministry of education, science and technological development of the Republic of Serbia is acknowledged (Project No. 172020).

OH 02

Organokatalizovana funkcionalizacija indola “u jednom balonu” (one pot): Majklova adicija i oksidativna β-funkcionalizacija indola katalizovana sekundarnim aminima

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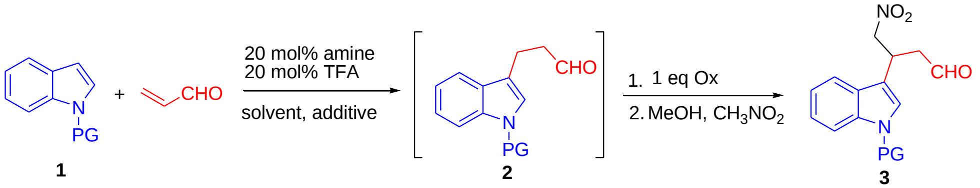
Polazeći od jednostavnih indola **1** u jednofaznoj **(one-pot)** proceduri dobijeni su funkcionalizovani indoli na C-3 poziciji. Reakcija uključuje organokatalizovanu adiciju indola **1** na akrolein pri cemu se dobija funkcionalizovani indol **2.** Dodatak oksidacionog agensa poput DDQ ili IBXa u isti balon dovodi do oksidacije aldehida (preko enamina) do α,β- nezasićenog aldehida. Nakon završetka ove reakcije u reakcioni balon se dodaje protični solvent i nitrometan koji podleže reakciji Majklove adicije na α,β-nezasiceni aldehid pri čemu se dobija finalni proizvod **3.** Ovo formalno kuplovanje aldehida i nitrometana predstavlja jedan od retkih primera formalne β-funkcionalizacije aldehida. Reakcija je takodje katalizovana i hiralnim diaril prolinol katalizatorima sto otvara mogućnost za enantioselektivnu sintezu indola **3.**



Scheme 1. *Organocatalyzed C-3 functionalization of indole*

One –pot organocatalyzed C-3 functionalization of indoles: Michael addition and oxidative β-functionalization of aldehydes catalyzed by secondary amine catalyst

Zdravko Džambaski, Bojan P. Bondžić
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Starting from simple indoles **1** it was possible in a one-pot procedure to obtain highly functionalized indoles alkylated at C-3 position. Reaction involves organocatalyzed addition of indoles **1** to acroleine to give C-3 functionalized indole **2**. Addition of oxidating agents such as DDQ and/or IBX to the same reaction flask leads to the organocatalyzed oxidation (via enamine species) of saturated aldehyde to the α,β-unsaturated aldehyde. Upon completion of reaction to a reaction mixture is added protic solvent and nitrometane which adds to α,β unsaturated moiety giving final adduct **3.** Reaction is shown to proceed with enantiopure diarylprolinol catalysts as well. This gives potential for enantioselective synthesis of final indole compounds.

This work was supported by the Ministry of Education and Science of the Republic of Serbia (project No. 172020)

OH 03

Solvatohromna svojstva 5-(4-supstituisanih fenilazo)-3-amido-6-hidroksi-4-metil-2-piridona

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U okviru rada izvršena je sintetiza devet azo boja iz 3-amido-6-hidroksi-4-metil-2-piridona i odgovarajućih anilina. Dobijena jedinjenja su okarakterisana temperaturom topljenja, FTIR, ^{1}H NMR i ^{13}C NMR spektroskopijom. Solvatohromna svojstva sintetisanih 5-(4-supstituisanih fenilazo)-3-amido-6-hidroksi-4-metil-2-piridona, ispitana su snimanjem UV-Vis i emisionih spektara sintetisanih azo boja u petnaest rastvarača različitih svojstava u opsegu od 200-700 nm (UV-Vis), odnosno 400-700 nm (emisioni spektri). Interakcije između rastvorka i rastvarača analizirani su korišćenjem metode linearne korelacije solvatacionih energija predložene od strane Kamleta i Tafta. Uticaj supstituenata na apsorpcione i emisione spektre ispitivan je Hametovom jednačinom.

Solvatochromic properties of 5-(4-substituted phenylazo)-3-amido-6-hydroxy-4-methyl-2-pyridones

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In this work, nine dyes have been obtained from 3-amido-6-hydroxy-4-methyl-2-pyridone and corresponding amines. All synthesized compounds were characterized by melting point, FTIR, ^{1}H and ^{13}C NMR spectroscopy. Solvatochromic properties of obtained 5-(4-substituted phenylazo)-3--amido-6-hydroxy-4-methyl-2-pyridones, have been investigated in fifteen solvents of different polarity. UV-Vis and emission spectra of the studied dyes were recorded in the range from 200 to 700 nm and from 400 to 700 nm, respectively. The solute–solvent interactions have been analyzed on the basis of linear solvation energy relationships concept proposed by Kamlet and Taft. The effects of substituents on the absorption and emission spectra have been evaluated using Hammett equation.

Acknowledgment. Authors are grateful to the Ministry of Education, Science and Technological Development of the Republic of Serbia (Project 172013) for the financial support of this work.

OH 04

Atropoizomerizam kod 1-aril-4-ferocenil-3-feniltetrahidropirimidin-2(1*H*)-ona

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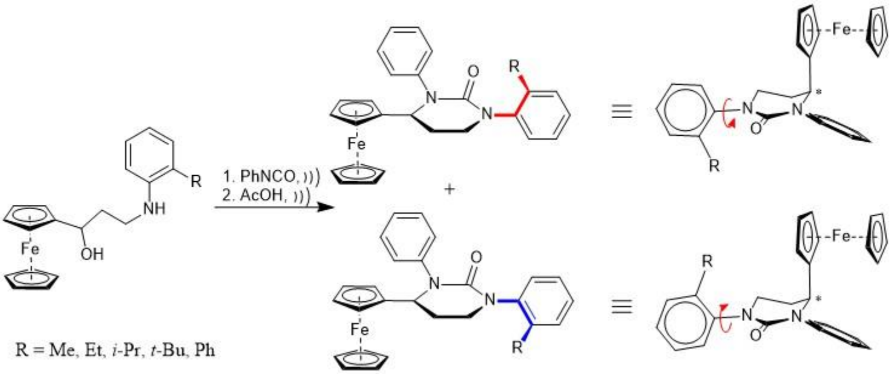
Atropoizomerizam je stereohemijski fenomen uzrokovan sprečenom rotacijom oko veza u neplanarnim molekulima [1]. Tokom našeg pređašnjeg istraživanja uočen je ovaj vid izomerije kod 1-aril-4-ferocenil-3-feniltetrahidropirimidin-2 (1*H*)-ona dobijenih iz orto supstituisanih 3-(arilamino)-1-ferocenilpropan-1-ola [2]. Kako bi se detaljno opisala ova pojava sintetisana je serija ovakvih orto supsttituisanih derivata koja je predstavljena u okviru ovog rada. Detaljno će biti diskutovane spektralne karakteristike, a za reprezentativne primere i rezultati X-ray analize.



Atropoisomerism in novel 1-aryl-4-ferrocenyl-3-phenyltetrahydropyrimidin-2(1H)-ones

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The stereochemical phenomenon that arises from hindered rotation around bonds in nonplanar molecules is termed atropoisomerism [1]. During our previous work we noted the presence of this kind of isomerism in 1-aryl-4-ferrocenyl-3-phenyltetrahydropyrimidin-2(1*H*)-ones obtained from ortho-substituted 3-(arylamino)-1-ferrocenylpropan-1-ols [2]. In order to give the detailed description of this feature we synthesized series of such ortho-substituted derivatives and appropriate synthesis will be presented in the framework of this report. The spectral characteristics will be discussed. Additionally, for representatives, the results of X-ray single crystal analysis will be presented.

Acknowledgement: This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Project 172034)

[1] a) R. Adams *et al.*, *Chem. Rev.* **1933**, *12*, 261 b) G.Bringmann, *et al.*, *Chem. Rev.* **2011**, *111*, 563.
[2] A. Minić *et al.*, *RSC Adv.* **2015**, *5*, 24915.

OH 05

Ekperimentalno i teorijsko proučavanje UV-Vis spektara 3-(4-supstituisanihanilino)izobenzofuran-1(3*H*)-ona

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Ftalidi (3*H*-izobenzofuran-1-oni) predstavljaju rasprostranjenu grupu sekundarnih metabolita biljaka i poseduju široki spektar biološke aktivnosti. Karakteriše ih biciklično jezgro nastalo spajanjem γ-laktona sa benzenom i smatra se da predstavljaju unutrašnje estre odgovarajućih γ-hidroksi karboksilnih kiselina. Geometrija 10 različitih sintetisanih ftalida u ovom radu je u potpunosti optimizovana pomoću DFT metoda i rezultati potvrđuju veću stabilnost laktonske u odnosu na otvorenu strukturu. Mehanizam pobuđivanja elektrona i promene raspodele elektronske gustine i u osnovnom i u pobuđenom stanju ispitivanih jedinjenja proučavano je izračunavanjem HOMO/LUMO energija i njihovih razlika (Egap) u gasnoj fazi. Elektronski prelazi izračunati su TD-DFT metodom u metanolu kao rastvaraču. Eksperimentalna i teorijska proučavanja utvrdila su da su fizičko-hemijska svojstva proučavanih ftalida posledica različite geometrije molekula usled prenošenja elektronskih efekata supstituenata kroz π-konjugovani sistem molekula.

Experimental and theorethical study of UV-Vis spectra of 3-(4-substitutedanilino)isobenzofuran-1(3*H*)-ones

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Saša Ž. Drmanić**, Aleksandar D. Marinković**
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***Faculty of Technology and Metallurgy, University of Belgrade, Serbia*

Phthalides or 3*H*-isobenzofuran-1-ones represent a widespread group of plants secondary metabolites with diverse biological activities. They are characterized by a bicyclic core, derived from the fusion of a γ-lactone with benzene and are considered internal esters of the corresponding γ-hydroxy carboxylic acids. The geometry of ten synthesized phtalides was fully optimized by DFT method. The results confirmed that the lactone product is more stable compared to open imine structure. Mechanism of electronic excitations and the changes in the electron density distribution in both ground and excited states of the investigated molecules were studied by calculation of HOMO/LUMO energies and energy gap (Egap) values in gas phase. Electronic transitions are calculated by TD-DFT method in methanol as a solvent. The experimental and theoretical study indicate that physico-chemical properties of studied phthalides are the consequence of the overall effect of the molecule geometry, influenced by the electronic substituent effects transmitted through π-conjugated systems.

Acknowledgement: Authors are grateful to the Ministry of Education, Science and Technological Development of the Republic of Serbia (Project No. 172013).

OH 06

Novi azini sa kumarinskim jezgrom u molekulu – sinteza i spektralna karakterizacija

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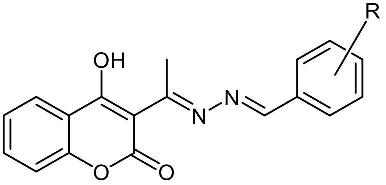
Kumarinski derivati i azini privlače veliku pažnju organskih sintetičara zahvaljujući širokom spektru njihovog biološkog/terapeutskog delovanja. U ovom radu pripremljeni su mešoviti azini 3-acetil-4-hidroksikumarina i različitih aromatičnih aldehida. Prvi korak u našoj sintezi bio je dobijanje 3-acetil-4-hidroksikumarina iz 4-hidroksikumarina ($CH_3COOH/POCl_3$). Odgovarajući hidrazon je dobijen u reakciji sa hidrazinom u metanolu, a koji je potom u reakciji sa različito supstituisanim aromatičnim aldehidima, u apsolutnom etanolu, dao seriju novih azina u vrlo dobrim prinosima. Strukture sintetisanih jedinjenja potvrđene su masenom spektrometrijom visoke rezolucije (HRMS-EI), IR, 1D (^{1}H- i ^{13}C-NMR) i 2D (^{1}H-^{1}H COSY, NOESY, HSQC, HMBC) NMR spektroskopijom.



New azines containing a coumarin moiety – synthesis and spectral characterization

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Coumarin derivatives and azines attract attention of synthetic chemists due to a wide range of their biological/therapeutic activities. In this work we prepared a series of mixed azines of 3-acetyl-4-hydroxycoumarin and different aromatic aldehydes. The first step in our synthesis was the acetylation of 4-hydroxycoumarin ($CH_3COOH/POCl_3$) to yield 3-acetyl-4-hydroxycoumarin. The corresponding hydrazone was obtained in the reaction of 3-acetyl-4-hydroxycoumarin and hydrazine in methanol, that was afterwards converted, with a very good yield, into a series of azines in the reaction with differently substituted aromatic aldehydes in absolute ethanol. The structures of the synthesized compounds were confirmed by HRMS-EI, IR, 1D (^{1}H and ^{13}C NMR) and 2D (^{1}H-^{1}H COSY, NOESY, HSQC, HMBC) NMR spectroscopy.

Acknowledgement: This work was funded by the Ministry of Education, Science and Technological Development of Serbia (Project No. 172061 and 45022).

OH 07

Sekvencijalne reakcije organometala u sintezi kondenzovanih derivata pirola

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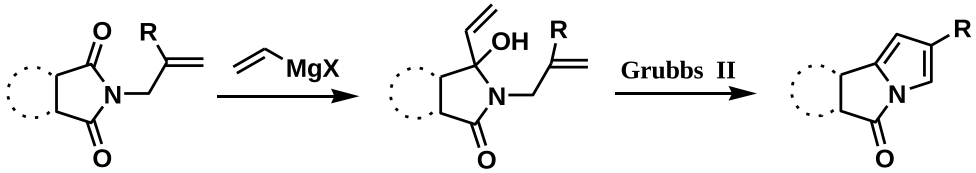
Kondenzovani piroli ulaze u sastav mnogih prirodnih proizvoda i biološki aktivnih jedinjenja.[1,2] U ovoj studiji prikazana je reakciona sekvenca koja omogućuje dobijanje različitih pirolizinona, kondenzovanih derivata pirola i ciklopentanona, primenom hemije organometala. Adicijom vinilmagnezijum bromida na *N*-alilovane imide, zatvaranjem prstena olefinskom metatezom koje je praćeno dehidratacijom i aromatizacijom moguće je dobiti različite pirolizinone u dobrom prinosu (Shema 1).



Shema 1.

Sequential reaction of organometallics in synthesis of fused pyrrole derivatives

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Pyrrole based fused heterocyclic compounds are widespread in various natural products and bioactive compounds. In this report we describe the reaction sequence for synthesis of various pyrrolizinone derivatives, utilising the chemistry of organometallic compounds. Addition of vinylmagnesium bromide to *N*-allyl imides, followed by RCM reaction, dehydration and aromatisation, pyrrolizinones were obtained in good yields.

Acknowledgements: This research was supported by the Ministry of Education, Science, and Technological development of Serbia (Grant 172009)

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Štampaj : : Print

OH 08

Sinteza derivata imidazolona promovisana pomoću 1,8-diazabiciklo[5.4.0]undec-7-ena (DBU)

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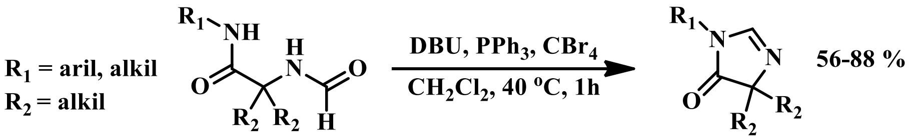
Imidazoloni **2** pokazuju različita zanimljiva svojstva u biologiji, farmakologiji i fotohemiji.[1,2] Razvijena je blaga i efikasna intramolekulska ciklizacija diamidnih jedinjenja **1**, dobijenih Ugi-jevom reakcijom, koja dovodi do nastanka derivata imidazolona. Ovom transformacijom se dobijaju proizvodi u dobrim prinosima u kratkom reakcionom vremenu.



1 **2**

Shema 1.

Imidazolone derivatives synthesis promoted by 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)

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Imidazolones **2** exhibit a variety of interesting properties in biology, pharmacology and photochemistry.[1,2] Mild and efficient intramolecular cyclization of diamide compounds, obtained by the Ugi reaction, leading to imidazolone derivatives has been developed. The transformation affords the products in good yields in a short reaction time.

Acknowledgements: This research was supported by the Ministry of Education, Science, and Technological development of Serbia (Grant 172009)

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5. KONFERENCIJA MLADIH HEMIČARA SRBIJE

5th Conference of Young Chemists of Serbia

Radionica / Workshop

POSTER PRESENTATION - Tips, tricks & tools

Alice Soldà, chair@eycn.eu
European Young Chemists' Network

Posters are widely used in the academic community, and most conferences include poster presentations in their program. Scientific posters concisely and attractively summarize information or a research project to help publicize it and generate discussion. A poster is an opportunity to effectively share research results and engage in scientific dialog with colleagues and the feedback can help you in refining your research and preparing it for publication.

Posters should be considered a snapshot of your work intended to engage colleagues in a dialog about the work, or, if you are not present, to be a summary that will encourage the reader to want to learn more. Many a lifelong collaboration has begun in front of a poster board. A poster can be even better than giving a talk!

It takes intelligence, even brilliance, to condense and focus information into a clear and simple poster, that will be read and remembered! 8 SIMPLE RULES will be given in order to design a great POSTER PRESENTATION and for maximizing the return on the time-consuming process of preparing and presenting an effective poster.

KMH S1 – PPP(M)2

text rada / full text

Рецензирање, кључни елемент процеса евалуације научног сазнања: Како то добро урадити?

Александар Декански, Ивана Дрвеница*, Олгица Недић**
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***Институт за примену нуклеарне енергије (ИНЕП), Универзитет у Београду, Србија*

Рецензирање представља незаобилазни део поступка публиковања резултата научног истраживања. Може се рећи да је оно срж тог процеса, јер обезбеђује поуздано и тачно презентовање, за јавност корисног, оригиналног научног сазнања. Свакако постоје многи недостаци тог поступка, иако су промене којима је током историје подвргаван тежиле да га унапреде. Последњих година су напори да се рецензирање учини поузданијим, објективнијим и без предрасуда већи него икада. У оквиру тих напора, једна од најзначајнијих активности је образовање, пре свега младих научника, за обављање тог веома одговорног и важног задатка. Овај текст је допринос тим напорима, имајући у виду да у Србији не постоји ниједан институционализовани облик таквог образовања. Поред описа процеса рецензирања, текст се бави етичким принципима добре праксе рецензирања, а након тога покушава да нађе одговор на питање: **Како коректно, објективно и непристрасно рецензирати научни рад?** На крају, садржи и сугестије за писање коректног рецензентског извештаја.

Peer review, a key element in the process of evaluation of the scientific knowledge: How to perform it properly?

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Peer review is a key element in the process of publication of scientific results, as it provides a reliable and accurate presentation of original scientific knowledge, useful for the entire society. Despite of many shortages which this evaluation has, it is still an indispensable part of the process of scientific publishing. In recent years, efforts have been made to improve peer review to become more reliable, objective and with less prejudices than before. To achieve this goal, one of the most important activities is education, primarily of the young scientists, to perform this responsible and important task. This text is a contribution to these efforts, taking into consideration that there is no systematic and institutionalized education for performing such task. After description of the review process itself, the text deals with ethical principles of good reviewing practice, and tries to offer an answer to the question: **How to review a scientific work correctly, objectively and impartially?** At the end, it also contains suggestions for writing a correct review report.

KMH S2 - PPP(M)1

Kardiobutanolid i njegovi analozi kao potencijalni antitumorski agensi: sinteza, SAR i mehanizam delovanja

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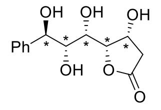
(+)-Kardiobutanolid je stiril-lakton izolovan 2003. godine iz drveta *Goniothalamus cardiopetalus*.[1] Zbog strukturne kompleksnosti koja se ogleda u pet uzastopnih stereocentara i potencijalne farmakološke aktivnost privukao je pažnju organskih sintetičara. Iako je publikovano deset sinteza kardiobutanolida, njegova biološka aktivnost nije ispitana sve dok nedavno nije izolovan iz kore *Goniothalamus elegants* nakon čega su uradjeni testovi citotoksičnosti prema tri tumorske ćelijske linije.[1] Ovom prilikom biće prezentovana nova sinteza kardiobutanolida i analoga, kao i rezultati ispitivanja antiproliferativne aktivnosti prema odabranim tumorskih ćelijskim linijama, glavne strukturne karakteristike odgovorne za aktivnost ustanovljene primenom SAR analize i pretpostavljeni mehanizam antitumorskog delovanja.



(+)-Cardiobutanolide

Cardiobutanolide and its analogues as potential antitumour agents: synthesis, SAR and mechanism of action

Ivana M. Kovačević
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(+)-Cardiobutanolide, a styryllactone, was isolated from *Goniothalamus cardiopetalus* trees in 2003 by Hisham et al.[1] It attracted the attention of synthetic community because of the structural complexity of having five contiguous stereocenters and potential pharmacological activity. Although there have been reported ten syntheses of cardiobutanolide, its pharmacological potential was not investigated until recently after its isolation from the bark of *Goniothalamus elegants* when its cytotoxicity assay was performed against three cancer cell lines.[2] Herein, we will present a novel synthesis of cardiobutanolide and its analogues, along with the evaluation of their antiproliferative activity against selected human tumour cell lines, main structural features responsible for their antitumour potency revealed by means of SAR analysis and insight into the mechanism underlying their antiproliferative effects.

Acknowledgement: The work was supported by a grant from the Ministry of Education, Science and Technological Development (Project 172006).

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KMH 01 – OP(Y)4

Ipitivanje konformacionih promena sirtuina 2 primenom simulacija molekulske dinamike

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Sirtuin 2 (Sirt2) se poslednjih godina sve više povezuje sa patogenezom kancera, neurodegeneracijom i inflamacijom zbog čega predstavlja atraktivan target za razvoj novih lekova. Većina do danas okarakterisanih inhibitora Sirt2 ne poseduje odgovarajuću aktivnost i/ili selektivnost. Kristalografske strukture objavljene u poslednjih par godina obezbedile su određeni pomak u razvoju novih inhibitora, međutim i dalje postoje nedoumice u vezi sa mehanizmom inhibicije koje su posledica visoke konformacone fleksibilnosti Sirt2 enzima. U cilju sticanja detaljnijeg uvida u konformacionu fleksibilnost Sirt2, izvedeno je sedamnaest simulacija molekulske dinamike u trajanju od po 100ns. Rezultati ove studije ukazali su na neke od ključnih rezidua neophodnih za stabilizaciju kompleksa Sirt2/inhibitor. Takođe, opisane konformacije daju jasniji uvid u katalitički ciklus deacilovanja. Opisan je i značaj konformacije kofaktorske petlje na konformaciju vezivnog mesta inhibitora. Rezultati ove studije će omogućiti racionalniji pristup dizajnu selektivnijih i potentnijih inhibitora sirtuina2.

Exploring conformational changes of sirtuin 2- molecular dynamic approach

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Maija Lahtela-Kakkonen*
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Sirtuin 2 (Sirt2) has been implicated in pathogenesis of cancer, inflammation and neurodegeneration, which makes Sirt2 attractive target for development of novel therapeutics. A number of small molecule Sirt2 inhibitors have been reported, but most of them lack selectivity and/or high potency. Very recently published X-ray structures of selective ligand/Sirt2 complexes have revealed more details about mechanism of action of inhibitors, but some information still missing. Here, we will try to answer on questions regarding the conformational changes during enzyme catalysis, based on our recent molecular dynamic study of Sirt2. Total of seventeen 100 ns simulations have been performed on five different crystal structures. Results of this study have suggested one of key residues responsible for conformational stability of cofactor-binding loop and significant interaction with novel inhibitors. Further, “closing” of Sirt2 induced by presence of substrate has been described as major factor responsible for conformational changes in substrate-binding site. In conclusion, this study provides dynamic information on Sirt2 and may facilitate the rational design on novel, more potent and selective inhibitors.

KMH 02 – OP(Y)2

3-Supstituisani anilido-piperidini: sinteza i antinociceptivna aktivnost

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U cilju proučavanja antinociceptivne (analgetičke) aktivnosti novih analoga fentanila sintetisani su metil (1-fenetil-4-(*N*-fenilpropionamido)piperidin-3-il)karbamati *cis* **2** i *trans* **2**, i *N*-(3-cijano-1-fenetilpiperidin-4-il)-*N*-fenilpropionamidi *cis* **3** i *trans* **3**. Karbamati **2** dobijeni su diastereoselektivno i u visokim prinosima, modifikovanim Hofmann-ovim premeštanjem *cis* i *trans* 1-fenetil-4-(*N*-fenilpropionamido)piperidin-3-karboksamida **1**, uz pomoć *N*-bromacetamida i $LiOH{\cdot}H_2O$ u MeOH, na 60 °C, u toku 5 minuta. Nitrili **3** su nova jedinjenja a dobijeni su , u visokim prinosima diastereoselktivnom dehidratacijom *cis* i *trans* amida **1** uz pomoc $SOCl_2$ u *N,N*-dimetilformamidu, u toku 3 h na 25 °C. *In vivo* ispitivanje interakcije jedinjenja **2** i **3** sa μ-opioidnim receptorima, odgovornim za antinociceptivnu aktivnost opioida, vršeno je na mužjacima Wistar pacova, pomocu testa potapanja repa u toplu vodu. Kao referentna proba korišćen je fentanil. Jedinjenja *cis* **2**, *trans* **2** i *trans* **3** pokazala su slabiju analgetičku aktivnost uz brže i kraće dejstvo u odnosu na fentanil. *Cis* **3** nije pokazao analgetičku aktivnost u relevantnim dozama u ovom eksperimentu. Dalja ispitivinja su u toku.

3-Supstitued Anilidopiperidines: Synthesis and Antinociceptive Activity

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In order to determine antinociceptive (analgesic) activity of novel analogs of fentanyl, methyl (1-phenethyl-4-(*N*-phenylpropionamido)piperidin-3-yl)carbamates *cis* **2** and *trans* **2,** and *N*-(3-cyano-1-phenethylpiperidin-4-yl)-*N*-phenylpropionamides *cis* **3** and *trans* **3** were synthesized. Carbamates **2** were synthesized diastereoselective and in high yields, by modified Hofmann rearrangement of *cis* and *trans* 1-phenethyl-4-(*N*-phenylpropionamido)piperidine-3-carboxamide **1**, utilizing *N*-bromoacetamide and $LiOH{\cdot}H_2O$ in MeOH at 60 °C, during 5 minutes. Nitriles **3** are novel compounds synthesized in high yields, by diastereoselective dehydration of *cis* and *trans* amides **1** by $SOCl_2$ in *N,N*-dimetilformamide at 25 °C, during 3 h . *In vivo* examinations of interaction of compounds **2** and **3** with μ-opioid receptors, responsible for antinociceptive activity was performed on male Wistar rats, using the rat tail-withdrawal test. Fentanyl was used as a referent probe. Compounds *cis* **2**, *trans* **2** and *trans* **3** showed weaker analgesic activity yet earlier onset and shorter duration of action compared to fentanyl. *Cis* **3** did not showed analgesic activity in any of relevant doses in this experiment. Further examinations are in progress.

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KMH 03 - – OP(Y)1

Derivati aminohinolina pokazuju aktivnost protiv lajšmanija parazita u *in vivo* uslovima

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Lajšmanija je tropska bolest izazvana parazitom iz roda *Leishmania*. Prenosi se ubodom zaražene ženke insekta roda *Phlebotomus*. U našoj laboratoriji sintetisani su različiti derivati aminohinolina kojima je prvobitno ispitana *in vitro* aktivnost na parazite u formi *L. infantum* i *L. tropica* promastigota. Najaktivniji derivati su zatim testirani na formu *L. infantum* amastigota i pokazali inhibiciju do 82% pri koncentraciji 0,5 μM. U cilju ispitivanja mehanizma delovanja, izvršeni su testovi u kojima se ispituje uticaj ovih jedinjenja na proizvodnju azot-monoksida i citokina od strane makrofaga. Dva derivata aminohinolina koja ne iskazuju toksičnost u modelu miša pri dozi 300 mg/kg, odabrana su za ispitivanje aktivnosti u *in vivo* uslovima. Pokazali su izvrsnu redukciju parazitemije u jetri miševa, kao i zavisnost aktivnosti od primenjene doze.

Aminoquinoline derivatives with activity against Leishmania parasites *in vivo*

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Leishmaniasis is a tropical disease caused by infection with *Leishmania* parasites. It is transmitted to humans by the bite of infected female sandflies genus *Phlebotomus*. Diverse aminoquinoline derivatives synthesized in our laboratory were investigated for their *in vitro* activity against *L. infantum* and *L. tropica* promastigotes. The most active derivatives were evaluated for the activity against *L. infantum* amastigotes and showed up to 82% inhibition at 0.5 μM concentration. In order to explore the mechanism of action, we examined the influence of these compounds on nitric oxide and cytokine production by macrophages. Two derivatives which proved to be non-toxic in mouse model at 300 mg/kg dose were selected for evaluation in *in vivo* Leishmania model. They showed excellent reduction of liver parasitemia in dose-dependent manner.

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KMH 04 – OP(Y)3

Višestruki efekti bis-guanilhidrazona na *C. albicans*

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Jedinjenja koja sadrže dve funkcionalne grupe guanilhidrazona (iminoguanidina) pokazala su različite biološke aktivnosti. Sintetisani su novi bis-guanilhidrazoni i ispitana je njihova antibakterijska i antifungalna aktivnost. Vrednosti minimalnih inhibitornih koncentracija su pokazale selektivnost prema različitim sojevima gljiva, pa smo želeli da rasvetlimo mehanizam njihovog antifungalnog dejstva. Interakcije između hromozomske DNK iz *C. albicans* ATCC 10231 i bis-guanilhidrazona ukazale su da je njihova meta molekul DNK. Najaktivnije jedinjenje BG3 testirano je prema celim ćelijama *C. albicans*. Metabolička održivost je ispitana FUN1 bojenjem ćelija koje su pretretirane sa BG3 i ustanovljen je fungistatski efekat. Studija fluorescentne citometrije (FACS) pokazala je pro-apoptotski efekat jedinjenja BG3 i prisustvo reaktivnih kiseoničnih vrsta (ROS). Na osnovu ovih rezultata može se zaključiti da najaktivnije jedinjenje BG3 interaguje sa DNK, što kao posledicu može imati onemogućenu replikaciju i može voditi u programiranu ćelijsku smrt. Bis-guanilhidrazoni su dobra osnova za razvoj novih antifungalnih jedinjenja i treba ih detaljnije izučavati.

Multiple effects of bis-guanylhydraznes on *C. albicans*

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Compounds containing two guanylhydrazone (iminoguanidine) functional groups have shown various biological activities. Novel bis-guanylhydrazones were synthesized and their antibacterial and antifungal properties were examined. Minimal inhibitory concentration (MIC) values showed selectivity against a panel of fungal strains, so we wanted to shed light on the mechanism of their antifungal action. Interaction of chromosomal DNA from *C. albicans* ATCC 10231 with bis-guanylhydrazones indicated that DNA is their target. The most active compound BG3 was tested further for its effect on *C. albicans* whole-cells. Cell viability was assessed with FUN1 staining of cells pretreated with BG3 and showed its fungistatic effect. Fluorescence activated cell sorting (FACS) cytometry studies of *C. albicans* whole-cells showed pro-apoptotic effect of BG3 and the generation of reactive oxygen species (ROS). Based on these results, the conclusion is that the most promising compound BG3 interracts with DNA, which may prevent replication and lead to programmed cell death. Bis-guanylhydrazones are a good base for novel antifungals and should be further examined.

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KMH 05 – OP(Y)5

Pokušaj sinteze lipozomskog in vivo inhibitora virusa ebole

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Virus ebole opasan je patogen koji uzrokuje smrtonosnu hemoragijsku groznicu kod ljudi i primata. Trenutno ne postoji odobren lek niti vakcina protiv ove bolesti. U svojim prethodnim radovima razvili smo klasu malih molekula, derivata diazahrizena, koji leče miševe zaražene virusom.[1] Koristeći činjenicu da su makrofage jedna od lokacija ranog umnožavanja virusa u zaraženom organizmu, kao i njihovu osobinu da vrše fagocitozu lipidnih čestica, odlučili smo da naša jedinjenja ciljano unesemo u makrofage lipozomima. Standardnom metodom tankog filma, i višestrukim ceđenjem kroz filtere (0,2 μm prečnik pora), pripremljen je koloidni rastvor lipozoma u vodi (137 mM NaCl, 2,7 mM KCl, 10 mM fosfatni pufer, pH 7,4). Količina enkapsuliranog jedinjenja određena je pomoću UV spektrofotometrije, a lokalizacija jedinjenja unutar membrane lipozoma dokazana je pomoću NMR spektroskopije. Vizuelizacija i određivanje veličine i morfologije čestica izvršeno je pomoću krio transmisione elektronske mikroskopije (cryo-TEM). Na kraju, in vivo evaluacija lipozoma u BALB/C miševima, uz intraperiotonealnu administraciju, pokazala je da ovakva formulacija ima značajno slabiju aktivnost od neenkapsuliranog jedinjenja, što pokušavamo objasniti daljim ispitivanjima mehanizma dejstva jedinjenja. Lipozomska formulacija jedinjenja nije uticala negativno na zdravlje miševa kada je primenjena na zdrave jedinke.

An attempt to produce a liposome-carried in vivo Ebola inhibitor

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The Ebola virus is a dangerous pathogen that causes a deadly hemorrhagic fever in humans and non-human primates. There is currently no approved vaccine or drug to counter this disease. During our previous work we developed a class of small molecules, diazachrysene derivatives, that cure Ebola infected mice.[1] Utilizing the fact that macrophages host the early stages of viral replication and their role in taking up lipid particles, we decided to deliver our compounds directly to the macrophages via liposomal carriers. We prepared a colloidal solution of liposomes in water (137 mM NaCl, 2.7 mM KCl, 10 mM phosphate buffer, pH 7.4) using the standard thin film approach followed by filtration through 0.2 μm pore filters. The amount of encapsulated compound was determined by UV spectroscopy, and the localization of the compound within the liposomal membrane was proven via NMR spectrometry. Cryo transmission electron microscopy was used to visualize and characterize the size and morphology of the liposomes. Finally, in vivo evaluation of the activity of the liposomal formulation using BALB/C mice (intraperitoneal administration) showed that liposomes display a significantly lower potency than the non-encapsulated compound. We are trying to explain this by looking into the compounds' mechanism of action. When administered to healthy mice, the liposomal formulation had no negative effect on their well-being.

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KMH 06

Disregulacija esencijalnih i toksičnih tragova elemenata u hipotiroidizmu

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Hipotiroidizam je vodeći poremećaj štitaste žlezde u Srbiji sa neispitanom disregulacijom metala i metaloida. Induktivno spregnuta plazma sa masenom spektrometrijom (ICP-MS) je korišćena za određivanje devet tragova elemenata u serumu pacijenata sa hipotiroidizmom ($n = 23$) i zdravih ispitanika ($n = 70$). Istovremeno su kvantifikovani sledeći elementi: Cr, Mn, Co, Ni, Cu, Zn, As, Se, Cd. Cilj ovog istraživanja je bio postavljanje eksperimentalnih uslova za tačno kreiranje jedinstvenog profila esencijalnih i toksičnih elemenata u lečenom hipotireoidizmu (eutiroidnom stanju). Metoda je optimizovana i validirana sa standardnim referentnim materijalom seruma. Dobra linearnost ($R^2 > 0.99$) i niske granica detekcije su dobijene za ^{52}Cr, ^{66}Zn, ^{75}As, ^{112}Cd u kolizionom (helijumovom) modu i ^{55}Mn, ^{59}Co, ^{60}Ni, ^{65}Cu, ^{78}Se u standardnom modu. Tretman uzoraka seruma sa vodenim rastvorom koji sadrži azotnu kiselinu, Triton X-100 i 1-butanol dao je najbolje rezultate. PCA i PLS-DA metode hemometrije su uposlene da razdvoje hipotiroidnu (HP) od kontrolne grupe. Utvrđeno je da su koncentracije elemenata u HP grupi značajno više u poređenju sa kontrolnom grupom i da svih devet elemenata diskriminišu HP grupu sa gotovo istom diskriminacionom snagom. Statistički značajna korelacija ($p < 0.01$) je zabeležena između nekoliko elemenata: Cu-Zn i Cu-Se kod obe grupe i dodatne tri korelacije u HP grupi (Mn-Co, Ni-Se i As-Se). Rezultati ukazuju na jasnu razliku u elementarnom profilu hipotiroidítične i kontrolne grupe i mogu se smatrati jedinstvenim profilom eutiroidnog stanja.

Dysregulation of essential and toxic trace elements in hypothyroidism

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Hipothyroidism is the leading disorder of the thyroid gland in Serbia with unexplored dis-regulation of metals and metalloids. Inductively coupled plasma mass spectrometry (ICP-MS) was used to determine nine trace elements in serum of patients with hypothyroidism ($n = 23$) and healthy respondents ($n = 70$). Simultaneously, the following elements were quantified: Cr, Mn, Co, Ni, Cu, Zn, As, Se and Cd. The aim of this research was to set the experimental conditions for accurate determination of a unique profile of essential and toxic trace elements in treated hypothyroidism (euthyroid state). The method was optimized and validated with standard reference material of blood serum. Good linearity ($R^2 > 0.99$) and the lowest detection limits were obtained for ^{52}Cr, ^{66}Zn, ^{75}As, ^{112}Cd in collision (helium) mode and ^{55}Mn, ^{59}Co, ^{60}Ni, ^{65}Cu, ^{78}Se in standard mode. Treatment of serum samples with diluent containing nitric acid, Triton X-100 and 1-butanol gave the best results. PCA and PLS-DA methods of hemometry were employed to separate the hypothyroid (HP) from the control group. It was found that the concentrations of all elements were higher in HP group when compared with control; all nine elements discriminated hypothyroid group of samples with almost the same discriminating power. Statistically significant correlation ($p < 0.01$) was observed between several elements: Cu-Zn and Cu-Se in both groups and additional three correltion in the HP group (Mn-Co, Ni-Se, As-Se). Results suggested clear differences in element profile between HP and control group, and could be used as a unique profile of euthyroid state.

KMH 07 – PPP(M)3

Medicinska hemija-primer dobre prakse

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Medicinska hemija, po definiciji, obuhvata različite oblasti hemije, čiji rezultati istraživanja mogu da doprinesu razvoju terapeutika. Organska hemija se smatra najznačajnijom, međutim, hemija kompleksa sve više dobija na značaju. Fizičko-hemijske, biohemijske, biološke i farmaceutske nauke su od izuzetnog značaja za karakterizaciju i merenje efikasnosti sintetisanih ili izolovanih jedinjenja, a sve u saradnji sa stručnjacima iz oblasti medicine. Racionalni dizajn lekova u velikoj meri oslanja se na kompjuterske tehnike i simulacije. Saradnjom stručnjaka iz različitih oblasti hemije i nauke uopšte krajnji cilj Medicinskje hemije postaje dostupniji. Tako su dizajn, sinteza, karakterizacija novih steroidnih jedinjenja i ispitivanje njihove farmakološke aktivnosti od velikog značaja za razvoj preparata za lečenje obolelih od steroid-zavisnih bolesti. Neki modifikovani steroidi menjaju aktivnost enzima, neki kompetituju sa receptorima, a neki indukuju morfološke promene ili smrt ćelija kancera.

Medicinal chemistry - an example of good practice

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Medicinal chemistry, by definition, covers various areas of chemistry, the results of which research can contribute to the development of therapeutics. Organic chemistry is considered to be the most important, however, chemistry of the complexes becomes more and more important. Physico-chemical, biochemical, biological and pharmaceutical sciences are of exceptional importance for the characterization and measurement of the efficacy of synthesized or isolated compounds, in cooperation with experts in the field of medicine. Rational drug design relies heavily on computer techniques and simulations. Through the cooperation of experts from various fields of chemistry and science, the ultimate goal of Medicinal chemistry becomes more accessible. Thus, the design, synthesis, characterization of new steroid compounds and the testing of their pharmacological activity are of great importance for the development of the new drugs for the treatment of patients with steroid-dependent diseases. Some modified steroids change enzyme activity, some compete with receptors, and some induce morphological changes or death of cancer cells.

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KMH 08

Glassy carbon electrode modified with graphene oxide and gold nanoparticles for ascorbic acid detection

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Glassy carbon electrodes modified with graphene oxide (GO), gold nanoparticles (AuNP) and methylene blue (MB were produced by using the drop casting method for ascorbic acid (AA) determination. Nafion was used as a polymeric immobilizing matrix.
The GCE/GO-AuNP-MB-Nafion and GCE/GO-AuNP-Nafion electrodes were characterized by using cyclic voltammetry and electrochemical impedance spectroscopy to investigate their electrocatalytic efficiency, stability and reproductibility. After optimization, the analytical parameters of the electrode with the best electrochemical characteristics were determined by chronoamperometry. The limit of detection for ascorbic acid was determined to be 7 µM, while the linear domain was up to 100 µM.
The electrodes showed significant electrocatalytic effect with good stability and reproductibility.

OTKAZANO
CANCELLED

KMH 09

Elektrohemisjka ispitivanja anodnih Ti-13Nb-13Zr nanotuba u simuliranoj telesnoj tečnosti

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U radu su ispitivane legure titana Ti-13Nb-13Zr (u polaznom stanju, CG, i nakon HPT obrade, eng. high pressure torsion, UFG), kao potencijalnih biomaterijala. Legure su modifikovane formiranjem nanotubularnih oksidnih slojeva u rastvoru 1M H_3PO_4 + 0.5 wt% NaF, na sobnoj temperaturi tokom različitog vremena anodizacije. Cilj rada je određivanje uticaja modifikacije površine Ti legura na korozionu stabilnost, ispitivanu u simuliranoj telesnoj tečnosti. Ipitivanja su vršena standardnim elektrohemijskim metodama.

Morfologija modifikovanih površina Ti legura je analizirana skenirajućom elektronskom mikroskopijom i pokazano je da se anodizacijom dobijaju visoko orijentisani slojevi nanotuba, sa najravnomernijom raspodelom nanotuba na UFG TNZ leguri. Na osnovu polarizacionih krivih pokazane su manje gustine struje korozije na anodiziranim uzorcima, koje pored postojanja dve pseudo-pasivacione oblasti, ukazuju na njihovu veću korozionu stabilnost. Povoljan uticaj procesa anodizacije je potvrđen i EIS merenjima.

Electrochemical behaviour of anodic Ti-13Nb-13Zr oxide nanotubes in simulated body fluid

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In order to enhance corrosion stability of Ti-13Nb-13Zr alloy (coarse-grained, CG, and ultrafine-grained, UFG, obtained by high pressure torsion) as potential biomedical material, the alloy surface was modified by self-organized nanotubular oxide layers, formed in 1M H_3PO_4 + 0.5 wt % NaF electrolyte, at room temperature during different times. The aim of the work was determining the influence of surface modification on the corrosion behaviour of alloy nanotubes in SBF by utilization of standard electrochemical tests (Electrochemical impedance spectroscopy, EIS, and potentiodynamic polarization measurements).

The modified alloy surface morphology was evaluated by scanning electron microscopy and it was shown that highly ordered nanotubular layers were obtained by anodization. The most uniformly arranged nanotubes were formed on UFG alloy. The smaller corrosion curent density and the presence of two pseudo-passive regions in polarization curves for anodized samples indicate their increased corrosion stability. The beneficial effect of anodization was confirmed by EIS measurements.

KMH 10

Procena zdravstvenog rizika usled prisustva toksičnih metala u uzorcima semena organski i konvencionalno gajenih cerealija/pseudocerealija i soje

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Poslednjih godina organska proizvodnja hrane zauzima sve veću pažnju, usled brojnih benefita po ljudsko zdravlje. Žita, usled sadržaja neophodnih nutritijenata, zauzimaju značajno mesto u svakodnevnoj ishrani ljudi. Međutim, osim korisnih sastojaka, u žitima se mogu naći i toksični metali, čiji prekoračeni unos dovodi do nastanka brojnih akutnih i hroničnih bolesti. U tom cilju, ispitivan je sadržaj toksičnih metala Al, Cd, Ni i Sr u organskom i konvencionalno proizvedenom semenu kukuruza, pšenice spelte, soje i heljde (tokom 2015 i 2016. godine), izračunat njihov nedeljni unos (PNI), na osnovu koga je procenjen zdravstveni rizik unosa ovih metala izražen kao akutni (KR_A) i dugoročni (KR) koeficijent rizika [1]. Smatra se da je pri $KR_A>1$ i $KR>0{,}01$ prisutan značajan zdravstveni rizik. Na osnovu sadržaja ovih metala, određenih ICP-OES metodom, utvrđeni su najviši KR_A i KR za Ni kod semena heljde (KR_A: 2,97, KR: 0,78) i organskog semena soje (KR_A: 1,41, KR: 0,35), dok kod ostalih vrsta semena rizik je bio umeren ili zanemarljiv.

Toxic metal health risk assessment in organic and conventional grown cereals/pseudocereals and soybean seed samples

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During the last years a lot of attention has been paid over the organic food production because of numerous benefits on human health. The crops take significant place in human nutrition because of presence of several essential nutrients. Beside the useful components, presence of toxic metals and its intake, through crops as food, can lead to development of some of the acute and/or chronic diseases. Thus, the content of toxic metals (Al, Cd, Ni and Sr) in organically and conventionally produced maize, spelt, soybean and buckwheat seeds was determined in samples collected in 2015 and 2016. Their estimated weekly intake (EWI) has been calculated and, based on given data, the health risk assessment has been expressed as acute (HQ_A) and long term (HQ) hazard quotient [1]. It is considered that if $HQ_A>1$ and $HQ>0.01$ then the significant health risk is presented. According to the content of these metals, determined by ICP-OES method, the highest HQ_A and HQ have been found for Ni in the buckwheat seed (HQ_A: 2.97, HQ: 0.78) and the organic soybean seed (HQ_A: 1.41, HQ: 0.35), while for the other seeds moderate or insignificant risk has been determined.

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KMH 11

Uticaj strukture na antiproliferativnu aktivnost derivata cikloalkanspiro-5-hidantoina

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U okviru proučavanja uticaja strukture na biološku aktivnost derivata cikloalkanspiro-5-hidantoina, u radu je testirana citotoksičnost novih serija jedinjenja: 3-(4-supstituisanih benzil)-1,3-diazaspiro[4.5]dekan-2,4-diona i 3-(4-supstituisanih benzil)-1,3-diazaspiro[4.6] undekan-2,4-diona. Citotoksična aktivnost određena je MTT testom prema ćelijskoj liniji humanog karcinoma dojke (MDA-MB-231). Strukturne karakteristike jedinjenja su određene rendgenskom strukturnom analizom kao i odgovarajućim spektroskopskim metodama. Testirana jedinjenja su pokazala statistički značajnu antiproliferativnu aktivnost prema ćelijskoj liniji MDA-MB-231 u proučavanom opsegu koncentracija. Naročito su se istakli derivati koji u okviru svoje strukture sadrže kao supstituente atome halogena i nitro-grupu. Rezultati su upoređeni sa prethodno određenom antiproliferativnom aktivnošću za 3-(4-supstituisane benzil)-5,5-difenilhidantoine. Diskutovan je uticaj strukture na antiproliferativnu aktivnost proučavanih jedinjenja.

The influence of the structure on the antiproliferative activity of the cycloalkanespiro-5-hydantoin derivatives

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In order to investigate the influence of the structure on the antiproliferative activity of the cycloalkanespiro-5-hydantoine derivatives, the cytotoxity of the new series of compounds: 3-(4-substituted benzyl)-1,3-diazaspiro[4.5]decane-2,4-dione and 3-(4-substituted benzyl)-1,3-diazaspiro[4.6]undecane-2,4-dione has been tested. Cytotoxic activity was determined by the MTT assay againist the cell line of human breast cancer (MDA-MB-231). The structural characteristics of the compounds are determined by X-ray structural analysis, as well as by appropriate spectroscopic methods. The tested compounds showed statistically significant antiproliferative activity to the MDA-MB-231 cell line in the studied concentration range. Among the most active are derivatives containing as substituents halogen atoms and a nitro group. The results were compared with a predetermined antiproliferative activity for 3-(4-substituted benzyl)-5,5-diphenylhydantoines. The influence of structure on the antiproliferative activity of the studied compounds is also discussed.

KMH 12

Sinteza, karakterizacija i anticancer aktivnost asimetričnog tiokarbohidrazona na humanim ćelijama karcinoma dojke (MCF-7)

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Savremeni ciljevi dizajna novog leka podrazumevaju kreiranje molekula koji mogu efikasno da zaustave širenje tumora na drugi način u odnosu na citotoksičnu aktivnost. U ovom radu ispitivana je antikancer aktivnost 1-[(8-hidroksi-2-hinolil)metilen]-5-[(2-hidroksifenil)metilen] tiokarbohidrazona (**1**) na ćelijama karcinoma dojke (MCF-7) pomoću fluorescentne trojne metode bojenja (kalcein AM / propidium jodid / Hoechst 33342) nakon inkubacije od 24 h. Koncentracijski-zavisnim načinom ispitivanja dobijeni su rezultati koji ukazuju na dvostruki režim aktivnosti **1**. U MCF-7 uzorcima tretiranim sa **1** na 30 i 50 mM, apoptoza je jedina forma ćelijske smrti koja smanjuje broj preživelih ćelija na 44,6% (30 mM) i 42,1% (50 mM) u poređenju sa kontrolom. U MCF-7 ćelijama koje su podvrgnute **1** na 75 i 100 mM apoptotički događaji bili su retki bez istovremenog zapažanja nekroze. Međutim, u oba uzorka procenti preživelih ćelija u odnosu na kontrolu bili su 43,2% i 42% za 75 i 100 mM respektivno. Prema tome, antitumorska aktivnost jedinjenja **1** može se menjati od proapoptotske do antiproliferativne pažljivom menjanjem njegove koncentracije, što pokazuje da molekul **1** zaslužuje dalja biološka ispitivanja.

Synthesis, characterization and anticancer activity of asymmetrical thiocarbohydrazone against human breast cancer cells (MCF-7)

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Contemporary goals of a new drug design imply creation of molecules which can effectively stop tumor spreading by other way than exerting cytotoxic activity. Here, we investigated antitumor activity of 1-[(8-hydroxi-2-quinolil)methylen]-5-[(2-hydroxiphenyl) methylen] thiocarbohydrazone (**1**) against human breast cancer cells (MCF-7) by means of fluorescent triple staining method (calcein AM/propidium iodide/Hoechst 33342) after 24 h incubation. Acquired results revealed that **1** displayed dual mode of activity in a concentration-dependent manner. In the MCF-7 samples treated with **1** at 30 and 50 μM, apoptosis was the exclusive form of cell death reducing the number of viable cells to 44.6 % (30 μM) and 42.1 % (50 μM) compared to control. In MCF-7 cells subjected to **1** at 75 and 100 μM apoptotic events were rare with no concomitantly observed necrosis. However, in both of those samples percentages of viable cells in respect to control were 43.2% and 42 % for 75 and 100 μM respectively. Therefore, antitumor activity of **1** can be modulated from proapoptotic toward antiproliferative by attentive titration of its concentration. This valuable feature indicates **1** is the molecule that deserves further biological testing.

KMH 13

Eksperimentalna, biološka i kvantnohemijska proučavanja N-aril-2,2-disupstituisanih sukcinimida

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U radu je sintetisana nova serija N-aril-2,2-disupstituisanih sukcinimida. Hemijska struktura i čistoća jedinjenja, potvrđene su ^{1}H i ^{13}C NMR, FT-IR i UV-Vis spektroskopskim metodama. Uticaj supstituenata na apsorpcione spektre sukcinimida, u različitim rastvaračima, proučavan je primenom Hametove jednačine. Korišćenjem Kamlet-Taftovih parametara analiziran je efekat polarnosti i polarizabilnosti rastvarača na pomeranje UV-Vis apsorpcionih maksimuma. Eksperimentalni rezultati su pokazali zadovoljavajuću saglasnost sa rezultatima kvantnohemijskih proračuna dobijenih primenom DFT metode. Pokazano je da supstituenti značajno utiču na intramolekulski transfer naelektrisanja (ICT) kao i na antifungalnu aktivnost proučavanih jedinjenja.

Experimental, biological and quantum-chemical studies of N-aryl-2,2-disubstituted succinimide

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In this work a new series of N-aryl-2,2-disubstituted succinimide was synthesized. The chemical structure and purity of the compounds were confirmed by ^{1}H and ^{13}C NMR, FT-IR and UV-Vis spectroscopic methods. The effect of substituents on the absorption spectra of succinimide in different solvents, was studied by Hammett equation. The effects of solvent polarity and polarizability on the UV-Vis absorption maximum were analyzed using Kamlet-Taft solvent parameters. The experimental results showed a satisfactory agreement with quantum chemical calculations obtained using DFT method. It has been shown that the substituents significantly influence the intramolecular charge transfer (ICT) as well as the antifungal activity of the studied compounds.

RADOVI
PROCEEDINGS

54. SAVETOVANJE SRPSKOG HEMIJSKOG DRUŠTVA

54th Meeting of the Serbian Chemical Society

HI 01

Experimental determination of volumetric, ultrasonic, transport and refractive index properties of the binary mixture (1-propanol + ethyl oleate) at atmospheric pressure

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Abstract

The huge dependence of the world's industry and transport sector on the limited resources of fossil fuels is one of the largest problems that modern society faces. The use of highly polluting fuels, such as diesel fuel, in addition to economy, has a great impact also on the environment. Because of that, researchers intensively work on finding less harmful fuels derived from renewable energy sources. One of the alternatives for diesel fuel is biodiesel, which can be used in diesel engines pure or mixed with diesel and/or alcohol.

Densities, speeds of sound, dynamic viscosities and refractive indices of pure 1-propanol and ethyl oleate as well as their binary mixtures at the whole concentration range have been measured at a wide range of temperatures at atmospheric pressure. The measurements were performed using DSA 5000 M density and sound velocity meter, Stabinger SVM3000 viscometer and RXA 156 refractometer, all produced by Anton Paar. The corresponding experimental data were used in calculations of the isentropic bulk modulus.

Introduction

The policy of reducing fuel consumption, together with the increasing awareness of environmental concerns, have prompted extensive research worldwide on alternative fuel development and improvement in the performance of existing engines. In this quest, biodiesel has gained much attention in recent years as alternative, ecological and economically viable fuel.[1-3] However, replacement of diesel with biodiesel still affects the injection system, atomization and combustion processes of the fuel, due to thermodynamic properties which could be unsuitable for diesel engine.[4] Density is an important parameter for diesel engine performance since fuel injection equipment operates on a volume metering system. Biodiesel is denser than diesel fuel[5] which leads to a slightly greater mass of used biodiesel as compared to diesel. The speed of sound also affects the engine operation, namely, the higher speed of sound and the bulk modulus result in a quicker fuel pressure rise from the fuel pump towards the injectors and, consequently, in higher NO_x emission.[6,7] Viscosity is a measure of fluid resistance to flow, which is closely related to the operation of fuel injection system and it is, also higher for biodiesel than for diesel fuel.[5] One of the methods used to overcome these disadvantages is to blend biodiesel with diesel or other additives like alcohols. Differences in physicochemical properties of diesel, biodiesel and alcohols, associated with their chemical structures, cause the obtained blends to behave differently comparing to pure diesel fuel, affecting engine performance and emission characteristics of diesel engine.[8,9] These properties are directly influenced by the temperature and pressure of engine operating conditions, as well as by the composition of the blends. For this reason, the major requirement when dealing with fuel mixtures is the knowledge of fundamental thermodynamic properties and their dependences on composition and temperature. The purpose of this work is to report densities, speeds of sound, viscosities and refractive indices for pure components 1-propanol and ethyl oleate and their mixtures at atmospheric pressure along isotherms ranging from 293.15 to 343.15 K, at the whole concentration range. Based on the corresponding experimental data, isentropic bulk modulus was calculated. To the best of authors' knowledge, there is no data about mentioned properties in literature for the studied mixtures.

Experimental Section

Chemicals. Ethyl oleate (Ph.EUR) was supplied by Sigma Aldrich, whereas 1-propanol (99 mas %) was purchased from Merck. Chemicals were kept in dark bottles in an inert atmosphere, degassed just before a sample preparation and used without further purification. The purity of components was ascertained by comparison of the experimental density, speed of sound and viscosity values at four temperatures with those reported in literature (Table I). The agreement of measured data with literature[10-14] was very good with a maximum percentage deviations for 1-propanol of 0.07% (0.59 $kg\cdot m^{-3}$) for density, 0.07% (0.80 $m\cdot s^{-1}$) for speed of sound and 1.01% (0.02 mPa·s) for viscosity, while the mentioned deviations for ethyl oleate were 0.001% (0.01 $kg\cdot m^{-3}$), 0.16% (2.24 $m\cdot s^{-1}$) and 7.53% (0.32 mPa·s), respectively.

Experimental. Densities (ρ) and speeds of sound (u) of the investigated binary mixtures and pure components were measured on Anton Paar DSA 5000 M Density and Sound Velocity Meter. Measurements of dynamic viscosities (η) were conducted using the Anton Paar Stabinger SVM 3000/G2 viscometer, while refractive indices (n_D) were measured using an automatic Anton Paar RXA 156 refractometer.[15]

Table I. Comparison of measured density, viscosity and speed of sound with literature data at atmospheric pressure

Substance	Temperature, K	Density, $kg\cdot m^{-3}$		Speed of sound, $m\cdot s^{-1}$		Viscosity, mPa·s	
		Exp.	Lit.	Exp.	Lit.	Exp.	Lit.
1-Propanol	303.15	795.9	795.3[10]	1188.64	1188.77[11]	1.716	1.734[10]
	308.15	791.8	791.3[10]	1171.64	1172.37[11]	1.533	1.545[10]
	313.15	787.7	787.3[10]	1154.73	1155.53[11]	1.379	1.384[10]
	318.15	783.6	783.3[10]	1137.89	1137.48[12]	1.234	1.241[10]
Ethyl oleate	303.15	861.6	861.62[13]	1358.43	1360.67[14]	4.9859	5.3094[13]
	308.15	858.0	858[13]	1340.81	1342.98[14]	4.4244	4.7156[13]
	313.15	854.4	854.39[13]	1323.34	1325.49[14]	3.9185	4.2137[13]
	318.15	850.8	850.77[13]	1306.04	1308.17[14]	3.5541	3.7876[13]

The combined expanded uncertainties of the density, speed of sound, viscosity, and refractive index measurements with a coverage factor $k = 2$ (confidence level of 95%) were estimated to be 0.08 $kg\cdot m^{-3}$, 0.2 $m\ s^{-1}$, 0.003 mPa·s and $5\cdot 10^{-5}$, respectively. The corresponding binary mixtures were prepared by means of a Mettler AG 204 balance with a precision 1×10^{-7} kg. The standard uncertainty of the mole fraction calculation was less than $\pm 1\times 10^{-4}$.

The isentropic bulk modulus (β), can be calculated using the equation (1):

$$\beta = \rho u^2 \qquad (1)$$

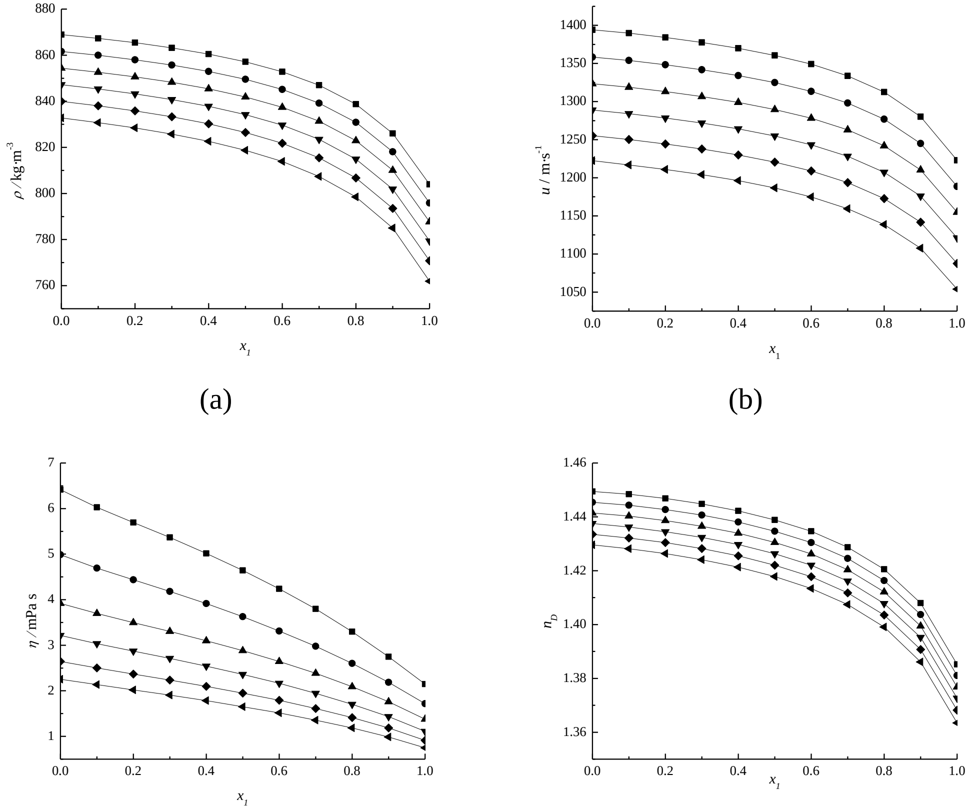
where u is the speed of sound and ρ refers to the density of a sample.

Results and discussion

The experimentally determined values for density, speed of sound, viscosity, and refractive index in the temperature range 293.15-343.15 K for pure 1- propanol and ethyl oleate and their mixtures are presented in Fig. 1.

The densities, speeds of sound, viscosities and refractive indices obtained for the pure ethyl oleate are greater than those of 1-propanol. As expected, the measured values of the examined properties decrease when temperature increases at atmospheric pressure, as well as with the increase of ethyl oleate concentration in the mixtures.

As can be seen in Fig. 1, dependences of density, speed of sound and refractive index on the share of 1-propanol in the mixture have an interesting shape. The mentioned properties are significantly higher for pure ethyl oleate than for pure 1-propanol and they decrease linearly when the portion of 1-propanol increases up to equimolar mixture. The isotherms slopes are quite small meaning that the influence of the 1-propanol on the behaviour of its mixtures with ethyl oleate is quite low at its shares up to 0.5. However, when the mole fraction of 1-propanol is increased over 0.5 the decrease of ρ, u and n_D is exponential *i.e.* their values fall significantly with addition of 1-propanol to the mixture. Fig. 1 also shows that density, speed of sound and refractive index of the examined binary mixtures depend linearly on temperature in the studied temperature range.



(a) (b)

(c) (d)

Figure 1. Experimental data of (a) density, (b) speed of sound, (c) viscosity and (d) refractive index for the binary system (1-propanol (1) + ethyl oleate (2)) at atmospheric pressure and (■) 293.15 K, (●) 303.15 K, (▲) 313.15 K, (▼) 323.15 K, (◆) 333.15 K and (◀) 343.15 K.

On the other hand, viscosity of ethyl oleate is also higher than that of 1-propanol, but it decreases almost linearly when the share of 1-propanol in mixture is increased (Fig. 1). The influence of mole fraction of 1-propanol on mixture’s viscosity is more noticeable at lower temperatures because differences between viscosities of pure compounds are much higher at the lowest than at the highest temperature from the examined interval. As expected, viscosity depends exponentially on temperature meaning that the deviations of viscosities measured at lower temperatures are higher than those measured at higher temperatures.

Fig. 2 presents the dependence of the isentropic bulk modulus on share of 1-propanol in mixtures with ethyl oleate. As it can be seen, similar to density and speed of sound, 1-propanol has a weaker effect on isentropic bulk modulus of the mixture when it is present at molar fractions lower than 0.5. However, when the portion of 1-propanol is increased over 0.5, the values of β decrease more noticeably. The isentropic bulk modulus decreases linearly with the increase in temperature in the studied temperature range.

The isentropic bulk modulus is the reciprocal value of the isentropic compressibility and consequently it is related to the intermolecular free length. Since pure ethyl oleate has higher β than 1-propanol, it has lower isentropic compressibility and lesser free space between its molecules as compared to pure 1-propanol, which could be result of stronger intermolecular bonds within ethyl oleate.

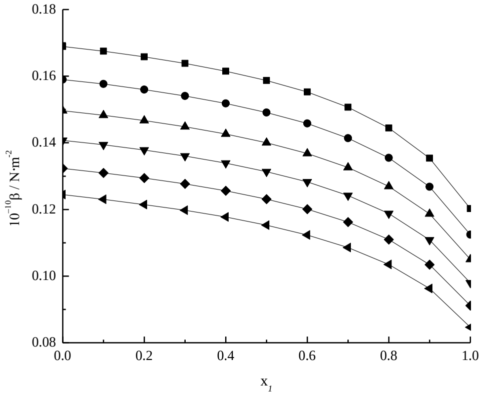


Figure 2. Isentropic bulk modulus for the binary system (1-propanol (1) + ethyl oleate (2)) at atmospheric pressure and (■) 293.15 K, (●) 303.15 K, (▲) 313.15 K, (▼) 323.15 K, (◆) 333.15 K and (◀) 343.15 K.

Conclusion

Density, speed of sound, viscosity and refractive index of pure 1-propanol and ethyl oleate and their binary mixtures at the whole concentration range were measured at temperatures 293.15-343.15 K and atmospheric pressure. The knowledge of density and speed of sound data enabled calculation of the isentropic bulk modulus in the same temperature interval.

All the studied properties have higher values for ethyl oleate than for 1-propanol. Density, speed of sound, refractive index and the isentropic bulk modulus of the examined mixtures slightly decrease as the molar fraction of 1-propanol rises up to 0.5 while in the mixtures richer with 1-propanol the decrease is more noticeable. The mentioned properties decrease linearly with the increase in temperature within the studied temperature range.

Viscosity of pure ethyl oleate is also higher than that of 1-propanol. However, viscosities of the mixtures almost linearly decreased when the portion of 1-propanol is increased. The influence of 1-propanol share on mixture’s viscosity is more obvious at lower temperatures than at higher temperatures in the studied range. The change of viscosity as a response to temperature change is exponential in the studied temperature range.

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Експериментално одређивање волуметријских, ултразвучних и транспортних својстава и индекса рефракције бинарних смеша (1-пропанол + етил олеат) на атмосферском притиску

Огромна зависност светске индустрије и сектора транспорта од ограничених залиха фосилних горива је један од највећих проблема са којим се модерно друштво суочава. Употреба горива која доводе до великих загађења, као што је дизел гориво, осим на економију, има огроман утицај и на животну средину. Због свега тога, истраживачи интензивно раде на проналажењу мање штетних горива која се могу добити из обновљивих извора енергије. Једна од замена за дизел гориво јесте и биоидзел који се у дизел моторима може користити чист или помешан са дизел горивом и / или алкохолом.
Густине, брзине звука, вискозности и индекси рефракције чистих 1-пропанола и етил олеата, као и њихових бинарних смеша у читавом опсегу концентрација, су мерене на широком опсегу температура на атмосферском притиску. Мерења су извршена на „DSA5000 M" уређају за мерење густине и брзине звука, „Stabinger SVM3000" вискометру и „RXA 156" рефрактометру, произвођача „Anton Paar". Одговарајући експериментални подаци су искоришћени за израчунавање изентропског модула стишљивости који је, такође, представљен у раду.

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HI 02

Correlation of excess molar volume of binary mixtures diethyl tartrate + *n*-alcohol

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Abstract

Density for three binary systems diethyl tartrate + n-alcohol have been measured in the temperature range 288.15 - 323.15 K and at atmospheric pressure, using Anton Paar DMA 5000 densimeter. From these data, values for excess molar volume (V^E) were determined. This property was correlated using equations of state (EOS). For quick evaluation, simple Peng-Robinson EOS and the van der Waals (vdW1-3) mixing rule were used, where unique interaction parameters were determined for the whole investigated temperature range. In addition, the V^E binary data were also correlated by the Peng–Robinson–Stryjek–Vera cubic equation of state (PRSV CEOS) combined with the van der Waals (vdW1) mixing rules or CEOS/G^E mixing rules introduced by Twu et al. (TCBT). Using the PRSV EOS, correlation was performed for every temperature individually. The obtained results, analysed taking into account the applied approaches and equations, showed small percentage deviations, especially with PRSV equation and more complex mixing rules vdW1-3 and TCBT-3.

Introduction

All processes in chemical engineering, numerical calculations, as well as equipment design, require accurate and reliable data of the chemical, physical and transport properties of pure solvents and their binary mixtures with other substances. Density is one of the most important properties used in numerous correlations for fluid flow analysis and mass and heat transfer calculations. These calculations should be based on reliable experimental data for a particular mixture, at temperatures, pressures and compositions depending on the needs. However, these data are often not available, so it is necessary to use various models to calculate density. Based on experimental data for density and excess molar volume, it is possible to test correlation using different equations of state.

In this study, excess molar volumes of three binary mixtures of diethyl tartrate and *n*-alcohol are correlated using different equations of state. Beside the simple Peng-Robinson equation of state[1] and van der Waals 1-3 mixing rule[2], V^E modelling was performed by the PRSV CEOS[3] coupled with two types of mixing rules: (i) the composition dependent van der Waals one-fluid (vdW1) mixing rule[2] and (ii) the modern mixing rule, which incorporates the excess free energy model G^E developed by Twu and co-workers (TCBT)[4]. More details about the models used in this work can be found in our previous papers[5,6].

Results and discussion

Previously measured densities of the mixtures ρ for three binary systems (diethyl tartrate + 1-propanol, diethyl tartrate + 1-butanol, diethyl tartrate + 1-hexanol), at eight temperatures (T=288.15, 293.15, 298.15, 303.15, 308.15, 313.15, 318.15 and 323.15 K) and atmospheric pressure, and for pure components ρ_i, were used to calculate the excess molar volumes V^E using the equation:

$$V^{\mathrm{E}} = \sum_{i=1}^{2} x_i M_i \left[\left(\frac{1}{\rho} \right) - \left(\frac{1}{\rho_i} \right) \right] \qquad (1)$$

in which M_i is the molecular weight of the component *i* and x_i is its mole fraction.

In this work, modelling was performed for determination of the excess molar volume from which it is very easy to calculate density.

All interaction parameters were obtained using the Marquard technique[7] for minimization of the objective function given by the equation:

$$OF = \frac{1}{m}\sum_{i=1}^{m}\left(\frac{V_{\mathrm{exp}}^{E} - V_{cal}^{E}}{V_{\mathrm{exp}}^{E}}\right)^{2} \rightarrow \min \qquad (2)$$

where V^E_{exp} and V^E_{cal} stand for experimental and calculated values of excess molar volume, respectively. The quality of models was evaluated by the percentage deviations (PD_{max}) between the experimental and the calculated values of V^E:

$$PD_{\max}(V^{E}) = \frac{100}{m}\sum_{i=1}^{m}\left|\frac{V_{\mathrm{exp}}^{E} - V_{cal}^{E}}{V_{\mathrm{exp,max}}^{E}}\right|_{i} \qquad (3)$$

where $V^E_{exp,max}$ denotes the maximum of m experimental V^E values.

The values of PD_{max} for every mixture for excess molar volume correlation can be found in Table 1. For PR EOS the modeling and determination of interaction parameters were performed in the whole temperature range, while for the PRSV EOS it was done for every temperature individually.

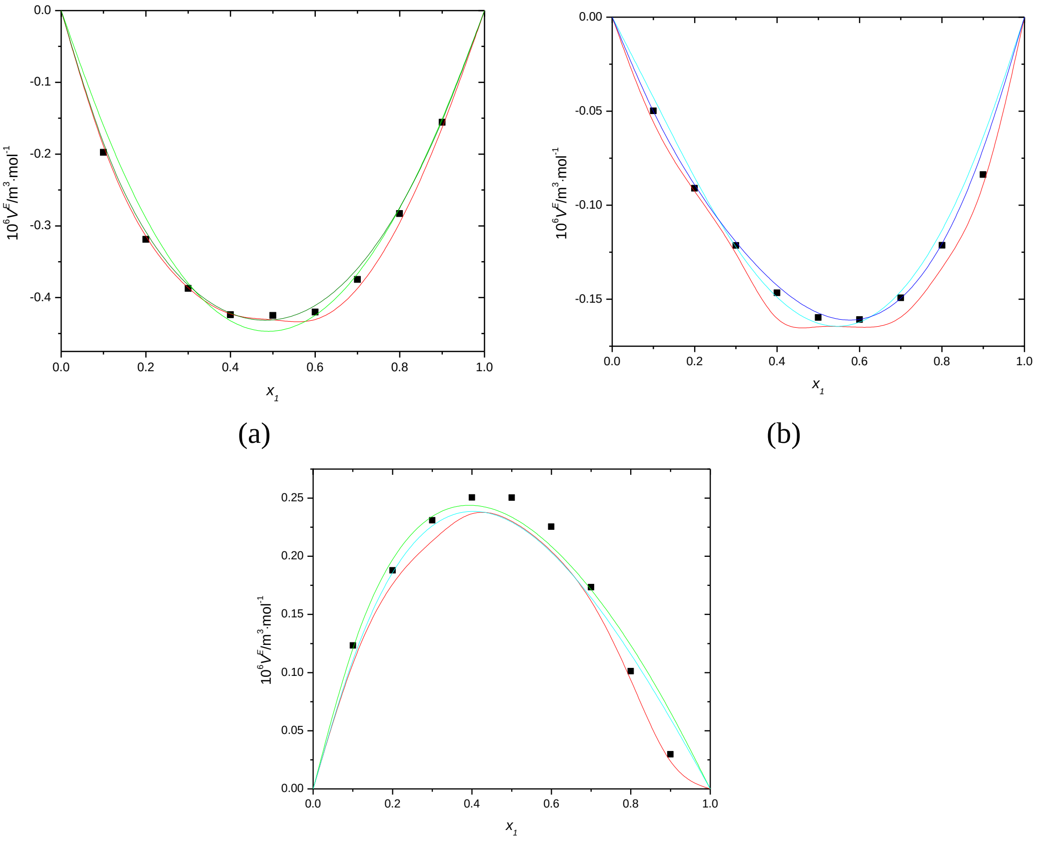
Table 1. Results of excess molar volume correlation for investigated mixtures diethyl tartrate + n-alcohol by PR and PRSV EOS and different mixing rules at T = (288.15 to 323.15) K and atmospheric pressure.

***T* / K**	***PD*max / %**				
	PR EOS[a]	PRSV EOS[b]			
	vdW1-3	vdW1-2	vdW1-3	TCBT-2	TCBT-3
diethyl tartrate (1) + 1-propanol (2)					
288.15	2.16	1.59	0.87	2.85	0.86
293.15	2.77	1.70	0.98	2.90	1.00
298.15	2.38	1.75	0.95	2.96	0.98
303.15	2.16	1.66	0.98	3.07	0.95
308.15	2.08	1.62	1.03	3.12	1.00
313.15	2.29	1.57	1.07	3.24	0.99
318.15	2.29	1.63	1.08	3.29	1.04
323.15	2.54	1.68	1.11	3.32	1.03
diethyl tartrate (1) + 1-butanol (2)					
288.15	6.22	1.78	0.57	1.18	0.52
293.15	5.82	2.77	0.87	2.01	0.90
298.15	5.27	3.59	1.69	3.90	1.43
303.15	7.29	3.93	1.55	4.04	1.50
308.15	6.45	4.05	1.71	4.19	1.36
313.15	5.35	4.67	1.89	4.36	1.76
318.15	4.88	5.25	2.18	4.48	2.01
323.15	6.87	5.81	2.24	4.37	2.04
diethyl tartrate (1) + 1-hexanol (2)					
288.15	3.73	5.37	3.82	4.94	3.85
293.15	3.83	5.42	3.79	4.46	3.81
298.15	3.21	5.58	3.80	4.93	3.81
303.15	2.19	4.88	3.40	4.21	3.55
308.15	2.16	4.51	3.20	3.93	3.15
313.15	3.67	4.12	2.93	3.39	3.03
318.15	2.91	3.93	2.77	3.37	2.74
323.15	4.95	3.72	2.62	3.10	2.76

[a] unique set of parameters for the whole temperature range

[b] interaction parameters determined for every temperature individualy

Results for excess molar volume correlation and differences between used equations and mixing rules are also presented graficaly in Figure 1 for every investigated system at 298.15 K.
From Table 1 it can be noticed that results for correlation of V^E using PR EOS are satisfactory, except for the system diethyl tartrate + 1-butanol, where somewhat higher values of PD_{max} are obtained. The situation with PRSV EOS is slightly different; the obtained values of percentage deviations are lower, which was expected since the modified Peng-Robinson equation was used and modeling was performed for each temperature individually. The smallest difference between two equations is for system with positive V^E values, diethyl tartrate + 1-hexanol. For other two systems noticeably better results are obtained using the PRSV equation. Bearing in mind the number of parameters in used mixing rules, the best results are obtained for three parameter vdW1-3 and TCBT-3 mixing rules with almost no difference between them regarding the quality of the obtained results.
Same conclusions can be made by analysis of Figure 1. Small differences between different mixing rules and PRSV eqauation are noticeable, but deviation of the curve representing PR EOS and vdW1-3 mixing rule is much more visible, due to the fact that correlation was made for all experimental data together, *i.e.* for the whole temperatire range investigated.



(a) (b)

(c)

Figure 1. Results of excess molar volume correlation at 298.15 K for the systems (a) diethyl tartrate (1) + 1-propanol (2), (b) diethyl tartrate (1) + 1-butanol (2), (c) diethyl tartrate (1) + 1-hexanol (2): (■) experimental data, (—) PR EOS + vdW1-3, (—) PRSV EOS + vdW1-2, (—) PRSV EOS + vdW1-3, (—) PRSV EOS + TCBT-2, (—) PRSV EOS + TCBT-3.

Conclusions

Correlation of excess molar volume for investigated binary mixtures diethyl tartrate + *n*-alcohol showed very good results. Peng-Robinson equation of state, applied on the whole investigated temperature range, together with the van der Waals 1-3 mixing rule, resulted in percentage deviations between 2 and 7 %. It was expected that also tested Peng-Robinson-Stryjek–Vera equation of state produces better results because of the used more complex modified equation and the fact that correlation was done for every temperature individually. For calculation of V^E this equation was used coupled with vdW and TCBT mixing rules. Smaller values of PD_{max} are obtained for mixing rules with larger number of optimized parameters (vdW1-3 and TCBT-3). The best results are obtained applying PRSV EOS and TCBT-3 mixing rule; at some temperatures values of PD_{max} are even smaller than 1 %.

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Korelisanje dopunske molarne zapremine binarnih smeša dietil tartarat + *n*-alkohol

Vrednosti gustine za tri binarna sistema dietil tartarat + n-alkohol izmerene su u temperaturnom opsegu 288.15 - 323.15 K i na atmosferskom pritisku, na digitalnom gustinomeru Anton Paar DMA 5000. Na osnovu ovih podataka, izračunate su vrednosti dopunske molarne zapremine (V^E*). Korelisanje ove veličine urađeno je pomoću jednačina stanja (EOS). Za brzu procenu, korišćena je jednostavna Peng-Robinson jednačina stanja i van der Valsovo (van der Waals, vdW1-3) pravilo mešanja, pri čemu su određeni jedinstveni interakcioni parametri za ceo ispitivani temperaturni opseg. Dodatno, podaci za* V^E *korelisani su pomoću Peng-Robinson-Strijek-Vera (Peng–Robinson–Stryjek–Vera) kubne jednačine stanja (PRSV CEOS) i van der Valsovog (vdW1) ili CEOS/*G^E *pravila mešanja razvijenih u literaturi (TCBT). Korelisanje pomoću PRSV CEOS urađeno je na svakoj temperaturi posebno. Dobijeni rezultati, analizirani imajući u vidu korišćene pristupe i jednačine, pokazali su mala procentualna odstupanja, posebno pri upotrebi PRSV jednačine i kompleksnijih pravila mešanja kao što su vdW1-3 and TCBT-3.*

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HI 03

Experimental measurements of thermophysical properties of the binary system cis-3-hexen-1-ol + hexane and FT-IR analysis

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Abstract

Density, viscosity and speed of sound were measured of the binary system of cis-3-hexen-1-ol and hexane at seven temperatures, in the range of 288.15 K to 318.15 K at atmospheric pressure. The measurements of density and speed of sound have been performed on Anton Paar DMA 5000 Density and Velocity Meter, while viscosity has been measured on Anton Paar SVM 3000 digital viscometer. Based on the experimental data excess molar volumes (V^E), viscosity deviation ($\Delta\eta$) and speed of sound deviations (Δu) were calculated and Redlich-Kister equation has been used for fitting the calculated data. FT-IR spectroscopy has been performed for discussing molecular interactions in the mixture.

Introduction

The study of thermophysical properties of alcohols has been of great interest since it plays an important role in explaining alcohol nature and the behavior in mixtures. Alcohols have a wide range of applications from alcoholic beverage industry, medical and perfumery, to flavoring industrial branch. The substance cis-3-hexen-1-ol, also known as leaf alcohol, is one of the products used as a fragrance and an aroma compound in perfume industry and as fruits and vegetable flavors in food industry[1]. This substance is one of the natural components occurring in odiferous leaves and plants, and its natural odor is intense of freshly cut green grass and leaves. As one of essential oils found in plants, cis-3-hexen-1-ol is present in a very small amount and can be obtained through extraction from plants[2]. Moreno-Marrodan et al. published synthetic procedures for synthesis of 3-hexen-1-ol that can be used commercially[3]. Cis-3-hexen-1-ol is also identified as a pheromone for various insects and some mammals. It affects behaviors of attraction, so it acts like an attractant to many predatory insects[4]. The yearly production of cis-3-hexen-1-ol is about 30 tones.

To the best of our knowledge, there has been only one paper published measuring the thermophysical properties of cis-3-hexen-1-ol[5]. Since, there has not been study reported on the cis-3-hexen-1-ol in mixtures, we performed the measurement of termophysical properties (density, viscosity and speed of sound) of the binary mixture of cis-3-hexen-1-ol and n-hexane. We used n-hexane as one of commonly used alkanes that is considered a good reference because its properties are well known. Also, n-hexane is used in catalyzing the transesterfication of cis-3-hexen-1-ol for lipase synthesis of (Z)-3-hexen-1-yl acetate[6]. The measurements have been done at the temperature range from 288.15 K to 318.15 K (at seven points) at atmospheric pressure. This work provides information about thermodynamic and transport properties and molecular interactions of investigated liquid substances and their mixtures. It also expands the database of properties of cis-3-hexen-1-ol and its mixtures. To the best of our knowledge, these are the first data on cis-3-hexen-1-ol + n-hexane system, hence results measured and discussed in this work cannot be compared with literature data.

For more detailed analysis Fourier-transform infrared (FT-IR) spectroscopy studies of the pure compounds and their mixtures were performed. FT-IR spectroscopy is recognized as a good technique for analyzing more detailed insight into inter- and intramolecular interactions. It measures the association properties of alcohol by analyzing band shifts and changes of the band shape [7].

Experimental section

Chemicals. Cis-3-hexen-1-ol was supplied by Sigma Aldrich with high mass purity of 99%, while n-hexane was supplied by Merck with mass purity of 99%. The substances were stored over molecular sieves (Sigma, type 0.4 nm) and degassed prior to their measurement and the purity of the substances were compared with the literature data.

Measurements. Densities and speeds of sound of the pure substances and their binary mixture were measured using the Anton Paar DSA 5000 M Density and Velocity Meter with a stated accuracy $\pm 5\times 10^{-3}$ kgm^{-3} for density and ±0.1 ms^{-1} for the speed of sound. The temperature in the cell was measured by means of two integrated Pt 100 platinum thermometers with the stability better than ±0.002 K. Temperature in the cell was regulated ±0.001 K by a built-in solid-state thermostat.

Viscosities of the pure substances and their binary mixture were measured using the digital Anton Paar Stabinger SVM 3000/G2 viscometer with a stated accuracy of ±0.1% of the measured value. Temperature in the cell was regulated by a solid-state thermostat that is placed in the instrument with the uncertainty of ±0.01 K.

The experimental uncertainties in the density, viscosity and speed of sound measurements were about $\pm 1\times 10^{-2}$ kgm^{-3}, < 1.5% and 0.1 ms^{-1}, respectively.

Mettler AG 204 balance with a precision of 1×10^{-4} was used for preparing all mixtures by measuring weights of pure substances. The uncertainty of the mole fraction calculation was less than $\pm 1\times 10^{-7}$.

The Fourier-transform infrared (FT-IR) spectra were analyzed using the BOMEM (Hartmann & Braun) spectrometer. The spectra were collected for pure substances and their mixture at 298.15 K in the range of 4000 cm^{-1} - 500 cm^{-1} with the resolution of 4 cm^{-1}

Results and discussion

The thermophysical properties (*i.e*. density (ρ), viscosity (η) and speed of sound (u)) were measured for the binary system of cis-3-hexen-1-ol + n-hexane at seven temperatures (T=288.15 K, 293.15 K, 298.15 K, 303.15 K, 308.15 K, 313.15 K and 318.15 K) at atmospheric pressure.

Using measured data of densities for pure components and its mixtures, the excess molar volumes (V^E) were calculated by the equation:

$$V^E = \sum_{i=1}^{N} x_i M_i \left[\left(1/\rho\right) - \left(1/\rho_i\right) \right] \tag{1}$$

where N is the number of components; x_i and M_i are the mole fraction and molecular mass of component i in the mixture; ρ and ρ_i are the measured densities of the mixture and the pure component i, respectively.

Viscosity deviations, $\Delta\eta$, were calculated by the equation:

$$\Delta\eta = \eta - \sum_{i=1}^{N} x_i \eta_i \tag{2}$$

where η and η_i are the measured viscosities of the mixture and the pure component i, respectively.

The speed of sound deviations, Δu, were calculated using the equation:

$$\Delta u = u - \sum_{i=1}^{N} x_i u_i \tag{3}$$

where u and u_i are the measured speeds of sound of the mixture and the pure component i, respectively.

The results of excess molar volume V^E, viscosity deviations ($\Delta\eta$) and speed of sound deviations (Δu) for the binary mixture were correlated using the Redlich-Kister (RK) polynomial equation[8]:

$$Y^E(\Delta Y) = x_i x_j \sum_{p=0}^{k} A_p \left(2x_i - 1\right)^p \tag{4}$$

where $Y^E(\Delta Y)$ denotes $V^E/10^{-6}\text{m}^3\text{mol}^{-1}$, $\Delta\eta$ / mPas, or Δu /ms^{-1}; A_p, stands for the adjustable parameters of the related property, and the degree of adjustable parameters (k + 1) determined applying the F-test.

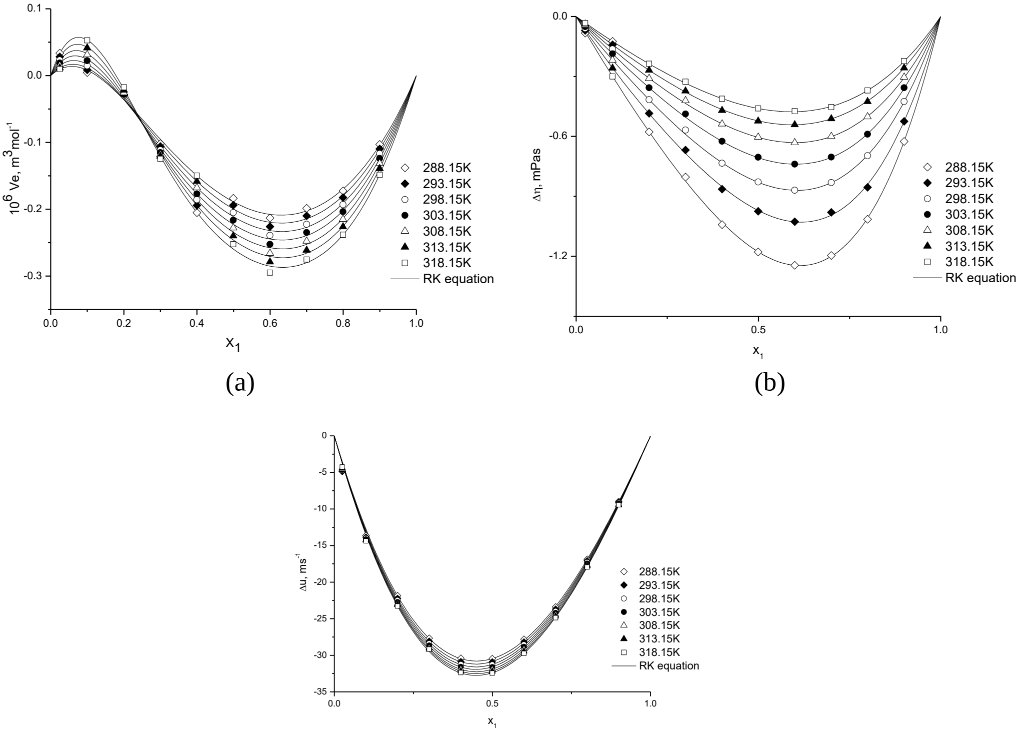
The root-mean-square deviation (rmsd) of the correlation for the V^E, Δn_D and $\Delta\eta$ is defined by the equation:

$$\sigma = \left(\sum_{i=1}^{m} \left(Y^E_{\exp,i} - Y^E_{cal,i} \right)^2 \Big/ m \right)^{1/2} \tag{5}$$

where m is the number of experimental data points.

Figure 1 represents (a) excess molar volume V^E, (b) viscosity deviations ($\Delta\eta$) and (c) speed of sound deviations (Δu) and fitted data using the RK polynomial equation for the binary mixture of cis-3-hexen-1-ol + n-hexane.

It can be seen that values of excess molar volumes exhibit the characteristic „S“-shape curve, with negative values for almost over the whole range of mixture compositions except for a very small region where the values are positive (Fig. 1a). This effect can be explained by disruption of alkanol self-association interactions. The 1-alkanol molecules are characteristic for their -OH group that makes them polar and self-associated through hydrogen bonding in pure state[9].



(a) (b)

(c)

Figure 1. *Experimental data of (a) excess molar volume (V^E), (b) viscosity deviations ($\Delta\eta$) and (c) speed of sound (Δu) for the binary system cis-3-hexen-1-ol (1) + n-hexane(2) at (◊) 288.15 K, (♦) 293.15 K, (○) 298.15 K, (●) 303.15 K, (Δ) 308.15 K, (▲) 313.15 K, (□) 318.15 K, (■) 323.15K, (—) RK equation at atmospheric pressure. Symbols refer to experimental data points. Solid lines present the RK results calculated by eq (4).*

Viscosity deviations are represented in Figure 1(b) and they are negative over the whole composition range. Values of the viscosity deviations become less negative as temperature increases. The viscosity curves are asymmetric and this can be explained by comparing viscosities of pure components at room temperature, where values differ in one order of magnitude.

As shown in Figure 1(c) the speeds of sound deviations are negative and slightly asymmetric, shifted toward lower cis-3-hexen-1-ol concentration, while the change of temperature had a small impact on the curves.

Figure 2 represents FT-IR spectra for pure substances, cis-3-hexen-1-ol and n-hexane, and for the investigated system (1) cis-3-hexen-1-ol + (2) n-hexane, at the minimum of $V^E - x_1$ curve (Fig. 1a), which corresponds to x_1=0.6. FT-IR analysis plays an important role in terms of discussing intermolecular interactions and is very useful for recognition of hydrogen bonds interactions.

The most characteristic influence of the mixture is on the –OH band. The -OH stretching vibration is shifted to lower wavenumber, from 3650 cm^{-1}, for the pure substance of cis-3-hexen-1-ol to 3333 cm^{-1} in the mixture. Intermolecular hydrogen bonds give broad bands while intramolecular hydrogen bonds are sharp bands. Data in Figure 2 shows that at 3650 cm^{-1} there is a sharp band for pure cis-3-hexen-1-ol, while in the mixture this band is shifted and there is a clear broadening band to the lower wavenumber region, around 3333 cm^{-1}. This indicates the existence of somewhat weaker H-bond interactions in the mixture.

Band area from 665 cm^{-1} to 730 cm^{-1} corresponds to bending δ (RCH=CHR') group in *cis*-conformation with the maximum at 728 cm^{-1} for pure cis-3-hexen-1-ol. For pure cis-3-hexen-1-ol, stretching ν (C-OH) is at 1050 cm^{-1}, while in the mixture it is at 1049 cm^{-1}. Stretching of ν (C-C-H) (sp^3 stretching) is at 2970 cm^{-1}, for the pure substance and at 2964.3 cm^{-1} in the mixture, the stretching ν (C=C-H) (sp^2 stretching) is at 3010 cm^{-1}, for the pure substance, and at 3008.7 cm^{-1} in the mixture. Bands in the areas resulting from stretching vibrations of alkyl groups remain unchanged.

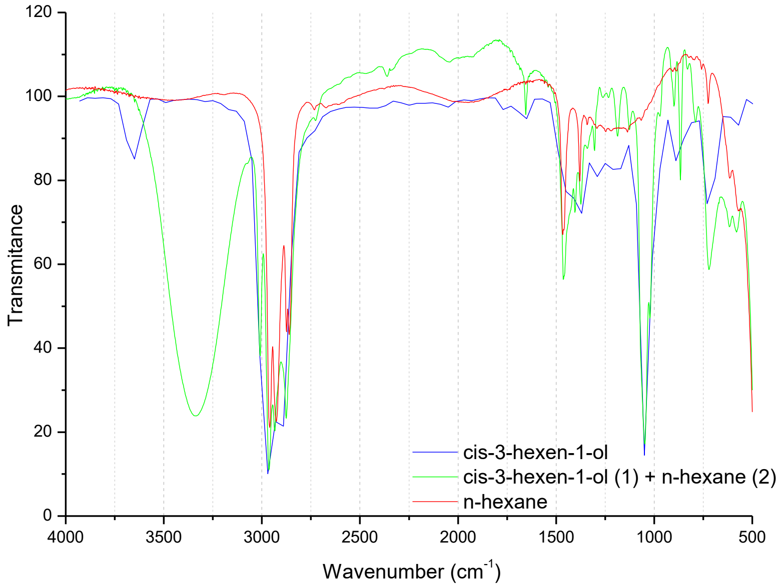


Figure 2. *Infrared spectra of pure cis-3-hexen-1-ol (1), pure n-hexane (2), and their mixture for molar fraction of cis-3-hexen-1-ol of x_1=0.6*

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The FT-IR analysis in combination with excess and deviation properties provide better understanding of behavior, namely a detail insight in molecular interactions in the mixtures is obtained. As mentioned before, alcohols are characteristic for their –OH group, hence cis-3-hexen-1-ol is self-associated, which is also shown on the $V^E - x_1$ curve (Fig. 1a) as a positive contribution. From the FT-IR spectra, -OH stretching band has shifted, from higher to lower frequencies, indicating weaker interactions of molecules in the mixture.

Eksperimentalna merenja termofizičkih karakterstika binarnog sistema cis-3-heksen-1-ol + heksan i FT-IR analiza

Gustina, viskoznost i brzina zvuka merene su za binarni sisitem cis-3-heksen-1-ol i heksan na sedam temperatura, u opsegu od 288.15 K do 318.15K na atmosferskom pritisku. Ekperimentalna merenja gusine i brzine zvuka su izvršena na digitalnom gustinomeru Anton Paar DMA 5000, dok je viskoznost merena na digitalnom viskozimetru Anton Paar SVM 3000. Na osnovu ekperimentalnih podataka, izračunate su dopusnka zapremina (V^E), promena viskoznosti ($\Delta\eta$) i promena brzine zvuka (Δu), a pomoću Redlih-Kisterove (Redlich-Kister) jednačine su podaci modelovani. Dodatno, FT-IR spekti su analizirani radi boljeg razumevanja intermolekulskih interakija u ispitivanoj smeši.

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TI 01

Photocatalytic activity of PET fabric modified with polypyrrole and TiO_2 nanoparticles

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Introduction

Nanoscale titanium dioxide (TiO_2) has been widely exploited as a photocatalyst due to its nontoxicity, good stability, low cost, simple preparation method and high photoactivity [1-3]. However, TiO_2 nanoparticles (TiO_2 NPs) have a wide band gap (3.2 eV) indicating that they are photoactive only under the UV light. Taking into account that the UV light makes up only about 4-6% of the sunlight it could be concluded that TiO_2 NPs cannot be efficiently activated only by sunlight [2]. The high recombination rate of photogenerated electrons and holes in TiO_2 NPs additionally decreases its photocatalytic activity[2]. In order to overcome these drawbacks many methods have been developed to enhance the TiO_2 NPs photoactivity under sunlight. It was reported that the doping of TiO_2 NPs with noble metals, transition metal ions and rare earth metal ions have positive affect on TiO_2 photoactivity under the sunlight[1-4]. On the other hand, the photosensitization with organic dyes and conductive polymers seems to be a promising method for TiO_2 modification in order to improve the visible light utilization[1-4]. Conductive polymers with extended π-conjugates electron systems (e.g. polyanilne, polypyrrole, polythiophene etc.) have remarkable electronic, optical and magnetic properties[5]. Owing to their high absorption coefficients in the visible region, efficient electron donating, high mobility of charge carriers and excellent stability conductive polymers are increasingly used as a photosensitizers for modification of inorganic semiconductors with a wide band gap such as TiO_2[2,5].

Simple preparation method and excellent conductivity have been the main reasons for the selection of polypyrrole (PPy) as a photosensitizer for TiO_2 NPs in this study. *In situ* synthesis of PPy and TiO_2 NPs on polyethylene terephthalate (PET) fabric was performed. The photocatalytic activity of this nanocomposite was compared with the PET fabric loaded with TiO_2 NPs by testing it in aqueous solution of the dye C.I. Acid Orange 7 in three repeated photodegradation cycles.

Experimental

All chemicals used in the synthesis were of analytical grade and used as received without any further purification. Milli-Q deionized water was used as a solvent. Colloidal TiO_2 NPs were synthesized by acidic hydrolysis of $TiCl_4$ [6]. The solution of $TiCl_4$ (Fluka) cooled down to -20 °C was added drop-wise to cooled water (at 4 °C) under vigorous stirring and kept at this temperature in the next 30 min. The pH of the solution ranged between 0 and 1, depending on the concentration of $TiCl_4$. Slow growth of the particles was achieved by dialysis against water at 4 °C until the pH of the solution reached 3.5. The concentration of TiO_2 colloid was determined from the concentration of the peroxide complex obtained after dissolving the particles in concentrated H_2SO_4[7]. In order to improve the crystallinity and overall photocatalytic efficiency of generated TiO_2 NPs, the colloid was thermally treated in reflux at 60 °C for 16 h[8]. Mostly single crystalline, irregularly shaped TiO_2 NPs with average dimensions of 6 nm were observed by HREM[8]. The electron diffraction pattern and Raman spectroscopy measurements confirmed the formation of anatase crystal structure[9]. Obtained TiO_2 NPs were used for synthesis of PPy/TiO_2 coating on PET fabric.

PPy coated PET fabrics were fabricated by in situ polymerization of Py (Acros Organic) in the presence of colloidal TiO_2 NPs with APS in acidic (HCl) medium, at room temperature. An initial mole ratio of [APS] and [Py] was 1.25. 1.00 g of PET fabric was immersed in 80mL of 0.1M TiO_2 colloid and stirred for 10 min. Afterwards, 10mL of 1.2 M HCl solution containing Py (6 μL) was poured into TiO_2 colloidal solution and stirred for further 10 min. Finally, 10 mL of 1.2 M HCl solution containing APS drop by drop was added into reaction mixture. The PPy/TiO_2 nanocomposite prepared at initial [TiO_2]/[Py]=100:1 mole ratio was labeled as PET+PPy/TiO_2. The reaction mixture was stirred for 3 days. In order to remove residual monomer, oxidant and low-molecular weight fractions, the samples were rinsed in 0.01 M HCl. Finally, the nanocomposites were dried at room temperature until the constant mass was reached.

As a reference sample, TiO_2 treated PET fabric was used. PET sample was immersed in TiO_2 NPs colloidal solution (0.1 M) for 10 min at liquor-to-fabric ratio of 25:1, squeezed out through laboratory pad (2 kg/cm^2) and dried at room temperature. After 5 min long curing at 100 ºC the sample was rinsed twice (5 min) with deionized water and dried at room temperature. This sample was marked as PET+TiO_2 in the following text.

The photocatalytic activity of TiO_2 NPs deposited on PET samples was examined in aqueous solution of acid dye C.I. Acid Orange 7 (AO7, Cassella). The chemical structure of AO7 is shown in Fig. 1.

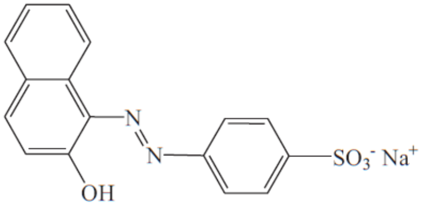

Figure1. *Chemical structure of dye AO7*

The morphology of the fibers was analyzed by field emission scanning electron microscopy (FESEM, Tescan

Mira3 FEG). The samples were coated with a thin layer of Au prior to analysis. Energy-dispersive X-Ray spectroscopy (EDS) of the fibers was performed using a JEOL JSM 5800 SEM with a SiLi X-Ray detector (Oxford Link Isis series 300, UK).

Photocatalytic degradation experiments were performed in accordance with a following procedure: 0.50 g of PET+TiO_2 and PET+PPy/TiO_2 samples were put into 25 mL of AO7 solution (10 mg/L). The beaker with a sample was placed in the water bath (with shaking) and it was illuminated by ULTRA-VITALUX lamp (300 W, Osram). The applied lamp provides sun-like irradiation. The distance between the lamp and the sample was set to 35 cm. Optical power was measured using R-752 Universal Radiometer Readout with sensor model PH-30, DIGIRAD and it was 30 mW·cm^2. The concentration of AO7 solution after 30, 60, 90, 120, 180, 240, 300 and 1440 min of illumination was determined by measuring absorption intensity of AO7 dye at λ_{max}=484 nm using an UV-VIS spectrophotometer Cary 100 Scan (Varian). The percentage of dye removal was calculated according to the following expression:

$$\text{Dye removal, \%} = \frac{(C_0 - C)}{C_0} \times 100 \qquad (1)$$

where: C_0 is the initial concentration of dye solution and C is the concentration of dye solution at investigated time.

In order to evaluate a possible reusability of samples impregnated with TiO_2 and PPy/TiO_2 described procedure was repeated two more times.

Results and Discussion

The morphology of the surface of PET and PET+PPy/TiO_2 fibers was evaluated by FE-SEM analysis (Fig. 2). Fig 2a revealed the smooth surface of PET fiber. Unevenly distributed PPy/TiO_2 layers are visible on the surface of PET+PPy/TiO_2 fiber (Fig 2b). The formation of similar PPy layers after coating of cotton fiber with PPy can be found in [10,.11].

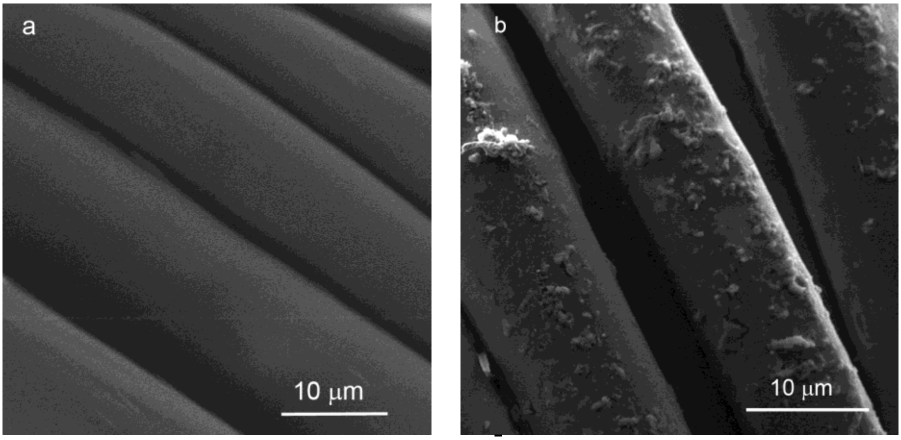

Figure 2. *FE-SEM images of the (a) untreated PET fiber, (b) PET+PPy/TiO_2 fiber*

In addition, EDS was applied for the elemental composition analysis. EDS spectrum (Fig 3) revealed the presence of titanium and nitrogen on the PET+PPy/TiO_2 surface originating from TiO_2 NPs and PPy, respectively.

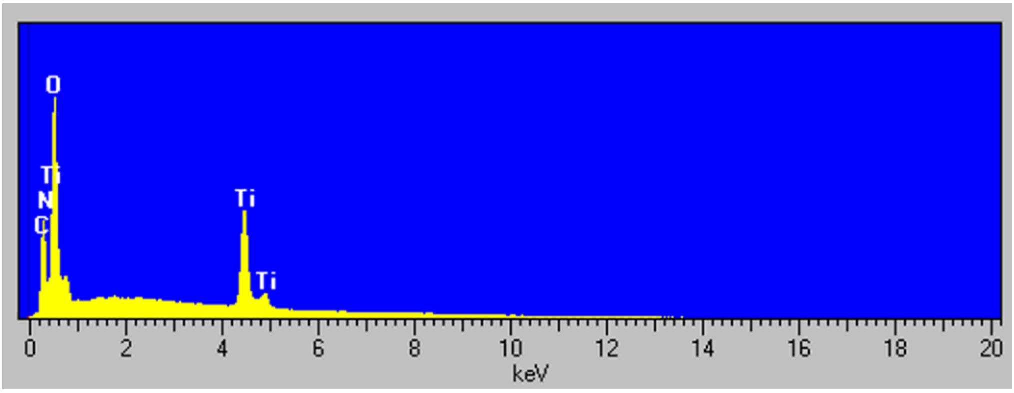

Figure 3*. EDS spectrum of the PET+PPy/TiO_2 sample*

The photocatalytic activity of the PET+TiO_2 and PET+PPy/TiO_2 samples was assessed by following the degradation of AO7 in aqueous solution under sun-like illumination. In order to exclude the contribution of possible photolysis of dye AO7 the dye solution was exposed to sun-like illumination for 24 h. It was shown that this dye was not prone to photolysis as the change in dye concentration could not be detected.

The dependence of percent of dye removal versus time of sun-like illumination is presented in Fig 4. Fig 4a shows that the PET+TiO_2 sample provided complete dye removal from the solution after 24 h of illumination. Fig 4a also revealed that complete dye removal from the solution in the presence of the PET+TiO_2 sample was obtained in repeated photodegradation cycles. It should be noticed that the rate of dye degradation was significantly slower during the third photodegradation cycle compared to the first and the second cycle. However, the overall photodegradation efficiency after 24 h was still comparable with the first and the second cycle. Observed decrease in photodegradation rate was probably due to some desorption of TiO_2 NPs from the surface of the PET+TiO_2 fabrics during the repeated photodegradation cycles. Fig 4b shows that the PET+PPy/TiO_2 sample ensured complete removal of dye from the solution already after 120 min of sun-like illumination. It is also clear that excellent photodegradation efficiency was preserved during the second and the third photodegradation cycle. Slight drop of photodegradation rate can be observed during the third photodegradation cycle.

(a) (b)

Figure 4. *The percent of AO7 dye removal during repeated photodegradation processes in presence of the: (a) PET+TiO_2 and (b) PET+PPy/TiO_2 samples*

The results presented in Fig 4 pointed out that the PET+PPy/TiO_2 sample exhibited significantly higher photocatalytic activity than the PET+TiO_2 sample. When PET+PPy/TiO_2 sample is illuminated with sunlight, the electrons in PPy (e^-) are excited from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) (Fig 5)[1, 4-5]. The excited electrons are injected in the conduction band of the TiO_2 leading to a creation of positive holes (h^+) in the HOMO of PPy.

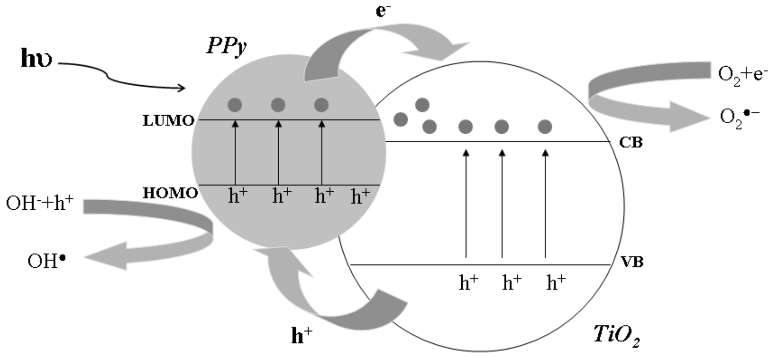

Figure 5. *Schematic illustration of the processes that occur on PPy/TiO_2 composites under sunlight*

At the same time TiO_2 absorbs the light (UV part of the sunlight), electron-hole pairs are produced and excited electrons in TiO_2 migrate from the valence band to the conduction band. The excited electrons from the PPy molecules can be injected into the conduction band of TiO_2 and finally react with oxygen at the surface. This results in the formation of highly reactive particles such as superoxide radical ion $O_2^{\bullet -}$ and consequently the hydroxyl radical $OH^{\bullet}$. The latter is responsible for the degradation of organic compounds[12]. In this case PPy also have photosensitizing function. The photogenerated holes in the HOMO-orbital of PPy can migrate to the interface and react with water to yield hydroxyl radicals. Moreover, photoproduced holes from valence band of TiO_2 can migrate to HOMO-orbital of PPy and additionally contribute to efficient photocatalytic process. Therefore, the higher photocatalytic activity of this system compared to bare TiO_2 NPs is due to rapid charge separation and slow charge recombination[12].

Fig 6 shows the photographs of the samples after repeated photodegradation cycles. It should be noted that the PET+TiO_2 sample remained white after repeated photodegradation cycles. In addition, pale gray color of native PET+PPy/TiO_2 sample was kept after each photodegradation cycle implying that dye was removed from both the solution and the samples.

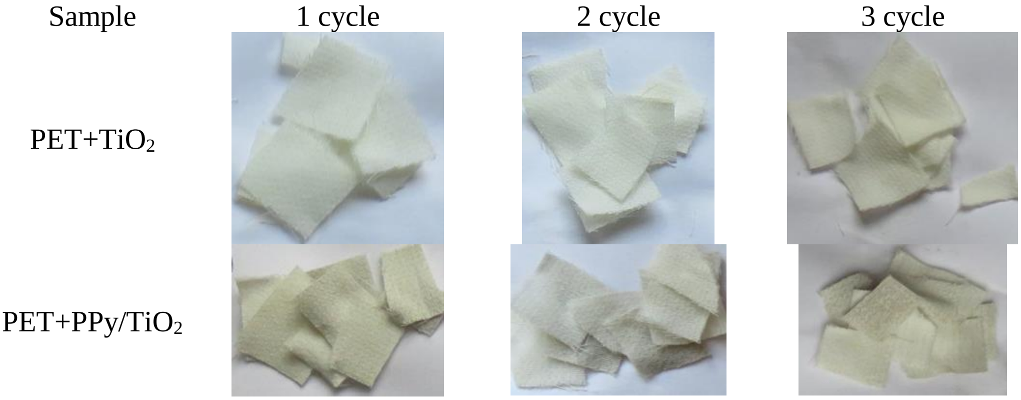

Figure 6. *The photographs of the samples after repeated photodegradation cycles*

Conclusions

Composite textile material based on PET fabric, PPy and TiO_2 NPs was successfully prepared by *in situ* synthesis. FE-SEM analysis confirmed the presence of unevenly distributed PPy/TiO_2 layer on the PET fiber. The results of photocatalytic activity of the PET+TiO_2 sample as a referent sample showed that complete photodegradation of dye AO7 was achieved after 24 h long exposure to sun-like illumination. The PET+PPy/TiO_2 sample provided complete photodegradation of dye already after 120 min of sun-like illumination. It is assumed that the presence of PPy on the PET+PPy/TiO_2 samples enhanced the photocatalytic activity of TiO_2 NPs by reducing the recombination rate of electrons and holes in TiO_2 NPs. It was also shown that the photocatalytic efficiency was preserved after three repeated cycles.

Acknowledgement: The financial support for this study was provided by the Ministry of Education, Science and Technological Development of Republic of Serbia (projects no. 172056 and 45020).

Fotokatalitička aktivnost PET tkanine modifikovane polipirolom i nanočesticama TiO_2

U ovom radu je ispitana mogućnost dobijanja kompozitnog tekstilnog materijala na bazi PET tkanine, polipirola i nanočestica TiO_2 sa efikasnom fotokatalitičkom aktivnošću. Prisustvo PPy/TiO_2 kompozitnog sloja na površini vlakana je potvrđeno FE-SEM i EDS analizom. Fotokatalitička aktivnost PET tkanine obrađene polipirolom i nanočesticama TiO_2 kao i PET tkanine obrađene samo nanočesticama TiO_2 ispitana je u vodenom rastvoru boje C.I. Acid Orange 7. Rezultati ispitivanja fotokatalitičke aktivnosti su pokazali da uzorak modifikovan polipirolom i nanočesticama

TiO_2 potpuno degradira boju za samo 120 minuta osvetljavanja lampom koja simulira sunčevo zračenje dok je uzorku modifikovanom nanočesticama TiO_2 za to potrebno 24 h. Takođe je utvrđeno da kompozitni uzorak PET+PPy/TiO_2 pokazuje odlična fotokatalitička svojstva u drugom i trećem ciklusu fotodegradacije. Znatno bolja fotokatalitička aktivnost kompozitnog uzorka u odnosu na PET tkaninu modifikovanu nanočesticama TiO_2 je upravo posledica prisustva polipirola.

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TI 02

In situ synthesis of Cu/Cu_2O nanoparticles on the TEMPO oxidized cotton fabric

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Introduction

Recent breakthrough in nanotechnologies had large impact on research in the field of medical textiles. So far many efforts have been made to fabricate antimicrobial textile materials with incorporated metal (Ag, Cu) and metal oxide (TiO_2, ZnO, CuO, Cu_2O) nanoparticles (NPs) and to learn more about the mechanism of their action[1-3]. The possible application of Cu, CuO and Cu_2O NPs for antibacterial protection of cotton fabrics became the focus of many research groups since the copper in different forms (ionic, copper oxides, copper complexes) is very active against various bacterial strains and precursor salts of copper are much cheaper than those of silver.

Unlike in the case of Ag NPs where the dip-coating from Ag NPs suspensions/colloids was mostly applied for nano-finishing of cotton fabrics, *in situ* synthesis of Cu, CuO and Cu_2O NPs seems to be the method of choice in published studies until now[4,5]. Namely, the dominant approach relies on the introduction of carboxyl groups to cotton fibers by coating them with appropriate polymer or chemical modification of cellulose, adsorption of Cu^{2+}-ions and their reduction. In our study we applied the TEMPO/NaClO/$NaClO_2$ system under neutral conditions for selective oxidation of cellulose in order to enhance its ability to bind Cu^{2+}-ions. We focused our study on much shorter oxidation times since the aim was to preserve the structure of cellulose fibers i.e. their mechanical strength. Therefore, the main goal of our study was to discuss the influence of the functional groups generated by TEMPO-mediated oxidation of cotton fabric at different reaction times on the amount, activity and stability of *in situ* synthetized Cu/Cu_2O NPs using sodium borohydride as a reducing agent at room temperature.

Experimental

Desized and bleached cotton (Co) woven fabric (117.5 g/m^2, 52 picks/cm, 27 ends/cm, thickness of 0.26 mm) was used as a substrate. Co fabrics were cleaned in the bath containing 0.1% nonionic washing agent Felosan RG-N (Bezema) at liquor-to-fabric ratio of 50:1. After 15 min of washing at 50 ^oC, the fabrics were rinsed first with warm water (50 ^oC) and then thoroughly with cold water. The samples were dried at room temperature.

The TEMPO-mediated oxidation was carried under neutral condition (pH 7) according to the method described previously[5,6]. Co fabric (10 g) was soaked in 0.05 M sodium phosphate buffer solution at pH 7 (50 mL phosphate buffer solution/g Co fabric), containing TEMPO (20 mg TEMPO/g Co fabric). Sodium chlorite (50 mg $NaClO_2$ /g Co fabric) and sodium hypochlorite solution (5 mmol NaClO/g Co fabric) were added to the flask and stirred at 200 rpm and 60°C for fixed periods of time: 15 and 45 min. After stirring for a designed time, the oxidation was quenched by adding ethanol (ca. 5 mL). The oxidized Co fabric was thoroughly washed with water by filtration, subsequently with ethanol, and dried at room temperature. Depending on the duration of oxidation, TEMPO oxidized Co fabrics are marked as Co15 and Co45 in the following text.

To obtain oxidized Co fabric containing only carboxyl groups, the aldehyde groups were selectively oxidized to carboxyl groups with $NaClO_2$ at pH 4–5. Oxidation was carried out by stirring the mixture comprising of distilled water (50 mL), 5 M CH_3COOH (10 mL), $NaClO_2$ (0.905 g) and Co fabric (1 g) at room temperature for 48 h, followed by washing thoroughly with water by filtration.

Determination of carboxyl content in oxidized Co fabric was based on the calcium acetate method described by Kumar and Yang and modified by Praskalo et al.[7,8].

A procedure for the *in situ* synthesis of Cu-based NPs was adopted from Errokh et al.[5], though several changes have been made including the introduction of sodium borohydride as a reducing agent instead of hydrazine and hydroxylamine. Briefly, 0.50 g of TEMPO oxidized Co fabric was soaked in 25 mL of 10 mM solution of $CuSO_4$ for 2 h. In order to eliminate the excessive Cu^{2+}-ions, the samples were rinsed for three times (1 min) in deionized water. 0.050 g of sodium borohydride ($NaBH_4$) was dissolved in 25 mL of 0.1 mM NaOH solution and the samples were immediately dipped into the solution where the reduction process took place in the following 30 min at room temperature. The samples were thoroughly rinsed with deionized water and left to dry at room temperature. These samples are marked as Co15+Cu/Cu_2O and Co45+Cu/Cu_2O.

The amounts of adsorbed Cu^{2+}-ions on the TEMPO oxidized Co fabrics from $CuSO_4$ solution were calculated on the basis of the concentration of residual Cu^{2+}-ions in the solution which was measured using a Spectra AA 55 B (Varian) atomic absorption spectrometer (AAS). AAS was also utilized for determination of total Cu content in the Co fabrics after reduction process. Dry impregnated Co fabrics were dissolved in the 1:1 HNO_3 solution. Additionaly, AAS was used for the evaluation of Cu^{2+}-ions release from the sample in physiological saline solution.

The morphology of Co fibers impregnated with Cu/Cu_2O NPs was assessed by field emission scanning electron microscopy (FESEM, Mira3 Tescan). The samples were coated with a thin layer of Au prior to analysis.

The antibacterial activity of Co fabrics was tested against Gram-negative bacteria *E. coli* ATCC 25922 and Gram-positive bacteria *S. aureus* ATCC 25923 using a standard test method for the determining the antimicrobial activity of immobilized antimicrobial agents under dynamic contact conditions ASTM E 2149-01 (2001). The percentage of bacterial reduction (R / %) was calculated by the following equation:

$$R = \frac{C_0 - C}{C_0} \cdot 100 \qquad (1)$$

where C_0 (CFU – colony forming units) is the number of bacteria colonies on the control fabric and C (CFU) is the number of bacteria colonies on the fabric with NPs.

Cu^{2+}-ions release was tested by immersing the sample of impregnated fabric in physiological saline solution (9 g/L NaCl) at 37 ºC in static conditions. The concentration of released Cu^{2+}-ions was measured after 1, 3, 6 and 24 hours by Spectra AA 55 B (Varian) atomic absorption spectrometer.

Results and discussion

The duration of TEMPO-mediated oxidation can be used as an efficient parameter for tailoring the carboxyl group contents in oxidized Co fabrics. Table 1 shows the relation between oxidation time and carboxylic group content in the oxidized Co fabrics. The longer the oxidation time the larger the amounts of carboxylic groups. Generated carboxylic groups were the potential sites for adsorption of Cu^{2+}-ions from aqueous $CuSO_4$ solution. The values of Cu^{2+}-ions uptake after 2 hours long adsorption are also given in Table 1. Evidently, an increase in carboxylic group content brought about an increase in Cu^{2+}-ions uptake.

A change in the Cu^{2+}-ions uptake can be also visually evaluated by change of the color of fabrics from white to different shades of blue. The photographs of samples after adsorption of Cu^{2+}-ions are presented in Fig. 1. Obviously, the larger the Cu^{2+}-ions uptake the bluer the samples.

Table 1 *COOH groups content in TEMPO oxidized Co fabrics under different conditions, Cu^{2+}-ions content after adsorption and total Cu content after reduction of Cu^{2+}-ions*

Sample	COOH content, μmol/g	Cu^{2+}-ions uptake, μmol/g	Total content of Cu after reduction, μmol/g
Co15	631.9 ± 23.9	142±1.13	134±8.76
Co45	792.9 ± 18.5	148±10.1	146±9.61

Cu^{2+}-ions adsorbed on the TEMPO oxidized Co fabrics were in the next step reduced with sodium borohydride in alkaline conditions at room temperature. Both samples immediately changed the color from pale blue to dark brown as can be seen in Fig.1. It is supposed that the brown color appeared due to reduction of Cu^{2+}-ions and formation of Cu NPs. This color change was confined only to the fabrics. In other words, it could not be visually detected in the solution containing reducing agent. These results are practically confirmed by the values of Cu content that are summarized in Table 1. It is obvious particularly in the case of Co45 sample that the whole amount of Cu^{2+}-ions was converted into Cu/Cu_2O NPs.

However, obtained brown color gradually changed during the drying of samples at room temperature. The samples became green (Fig. 1). Again, the color yield depended on the Cu content in the samples. The larger the Cu content the greener the sample. The instability of metallic Cu NPs in the air, particularly when borohydride is used as a reducing agent is well known feature. As our samples were dried and stored in the air, it is very likely that oxidation process took place in these phases. Cady et. al. observed the same behavior[4]. They suggested that the reduction of Cu^{2+}-ions initially resulted in the formation of Cu NPs and then the drying in the air caused a partial oxidation to Cu_2O. These authors also assumed that the core/shell form of NPs (Cu core/Cu_2O shell) was obtained, but we do not have strong proof for such assumption.

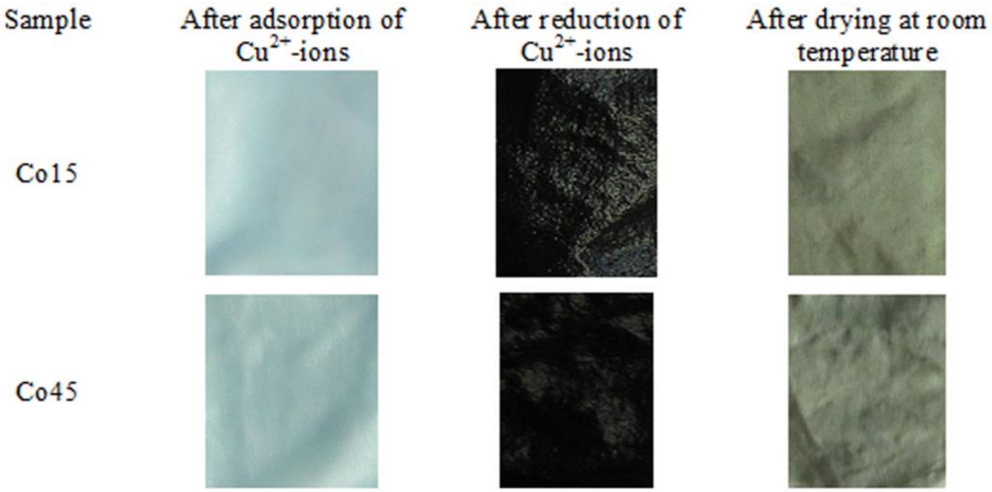

Figure 1. *The photographs of the fabrics with adsorbed Cu^{2+}-ions, the fabrics immediately after Cu^{2+}-ions reduction and the fabrics after drying in air at room temperature*

The morphology of fibers surface was evaluated by SEM analysis. SEM images of the control fiber and the TEMPO oxidized fibers impregnated with Cu/Cu_2O NPs are shown in Fig. 2. Presented images confirmed the presence of unevenly distributed Cu/Cu_2O NPs with an average dimension around 50 nm. It is also evident that NPs agglomerated on the fiber surface.

Antibacterial activity of Cu/Cu_2O NPs immobilized on the TEMPO oxidized Co fabrics was tested against Gram-negative bacteria *E. Coli* and Gram-positive bacteria *S. aureus*. The results from Table 3 indicate that both investigated samples provided maximum bacterial reduction (99.9 %) for both bacteria strains. It is generally accepted that the larger the amount of Cu-based NPs, the stronger the antibacterial activity[5]. In our study such tendency was not observed likely due to sufficiently large amounts of NPs that could impart desired antibacterial activity to Co fabrics.

Taking into account the key role of Cu^{2+}-ions in bacteria cell inactivation, it was necessary to study their release from fabricated samples. In order to simulate the body fluids physiological saline solution was applied as a release medium. Since both investigated samples provided equivalent antibacterial activity, the sample $Co15+Cu/Cu_2O$ was chosen for release experiments due to shorter TEMPO oxidation time. Cumulative release of Cu^{2+}-ions in the physiological saline solution is presented in Fig. 3. Keeping in mind that the potential application of such textile nanocomposite would be for the production of wound dressings, a controlled leaching of Cu^{2+}-ions during short time interval (less than 24 h) would be preferable for infection prevention. It is evident from Fig. 3 that fabricated sample meets this important demand.

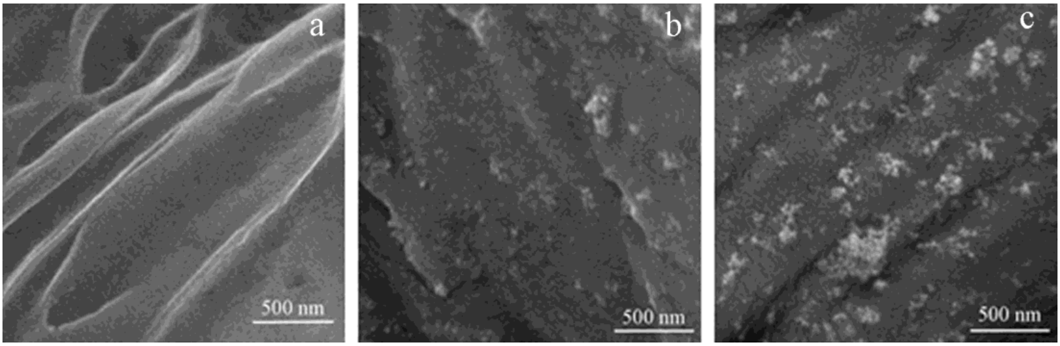

Figure 2. *SEM images of the (a) untreated Co fiber, (b) $Co15+Cu/Cu_2O$ fiber and (c) $Co45+Cu/Cu_2O$ fiber*

Table 2 *Antimicrobial activity of Co fabrics impregnated with Cu/Cu_2O NPs*

Sample	Number of bacterial colonies (CFU)	R, %	Number of bacterial colonies (CFU)	R, %
	E. coli		*S. aureus*	
Control Co	2×10^5		3×10^4	
$Co15+Cu/Cu_2O$	<10	99.9	<10	99.9
$Co45+Cu/Cu_2O$	<10	99.9	<10	99.9

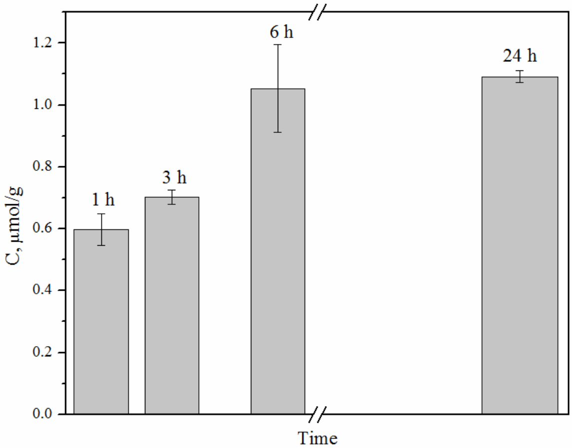

Figure 3. *Release of Cu^{2+}-ions from the $Co15+Cu/Cu_2O$ fabric into physiological solution*

Conclusions

Cu/Cu_2O nanoparticles were successfully *in situ* synthetized on the surface of TEMPO-oxidized cotton fabrics. TEMPO-mediated oxidation of cellulose enhanced the adsorption of Cu^{2+}-ions due to formation of carboxyl groups. The larger the amounts of carboxyl groups the larger the Cu^{2+}-ions adsorption. Reduction of Cu^{2+}-ions with sodium borohydride resulted in the formation of Cu/Cu_2O nanoparticles. SEM analysis revealed uneven distribution of agglomerates of nanoparticles with an average dimension of approximately 50 nm.

Obtained textile nanocomposites provided maximum bacterial reduction of 99.9 % against Gram-negative *E. coli* and Gram-positive *S. aureus*. Controlled release of Cu^{2+}-ions from the samples into physiological solution was achieved, making them viable candidates for medical applications.

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In situ sinteza Cu/Cu_2O nanočestica na TEMPO oksidovanoj pamučnoj tkanini

In situ sinteza nanočestica Cu/Cu_2O na pamučnoj tkanini diskutovana u ovom radu bazirana je na adsorpciji Cu^{2+}-jona na karboksilnim grupama formiranim TEMPO oksidacijom celuloze i njihovoj redukciji natrijum-borhidridom. Hemijske promene nastale TEMPO oksidacijom su praćene titrimetrijski određivanjem sadržaja karboksilnih grupa u pamuku. Prisustvo nanočestica Cu/Cu_2O na pamučnoj tkanini potvrđeno je SEM i AAS analizama. Promene obojenja tkanina su određene refleksionom spektrofotometrijom. Antibakterijska aktivnost generisanih nanočestica Cu/Cu_2O je testirana prema Gram-negativnoj bakteriji E. coli i Gram-pozitivnoj bakteriji S. aureus.

Produžavanje vremena TEMPO oksidacije za rezultat je imalo povećanje sadržaja karboksilnih grupa na pamučnoj tkanini. Stoga su veće količine Cu^{2+}-jona mogle da se adsorbuju na supstratu. Ovo je dalje za posledicu imalo stvaranje većih količina nanočestica Cu/Cu_2O. Svi ispitivani tekstilni nankompoziti su obezbedili maksimum redukcije bakterija E. coli i S. aureus. Takođe je utvrđeno da pamučne tkanine sa inkorporiranim nanočesticama Cu/Cu_2O pružaju kontrolisano otpuštanje Cu^{2+}-jona u fiziološkom rastvoru što je imperativ za prevenciju infekcija.

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MS 02

Microwave assisted hydrothermal synthesis and capacitive properties of RuO_2/reduced graphene oxide composites

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Abstract

Supercapacitive RuO_2/reduced graphene oxide composites were synthesized by hydrothermal microwave-assisted single-step method at different temperatures. Syntheses were accomplished by simultaneous oxidation of Ru from $RuCl_3$ and reduction of graphene oxide in solution of various pH. Capacitive responses of obtained samples were analyzed using combined electrochemical and quartz crystal nanobalance techniques. The cyclic voltammetry and electrochemical impedance spectroscopy have been performed in H_2SO_4 and Na_2SO_4 solutions. The analysis of obtained results showed that synthesized composites are of acceptable capacitive properties. The capacitive properties of composite synthesized at neutral pH showed weakly depandance on synthesis temperature, with moderate increase of the capaticance with increasing temperature. On the other hand, composite synthesized in alkaline conditions had the higest capacitive properties at average temperature in the examined range of temperatures.

Introduction

Supercapacitors are devices capable of storing and releasing very high amounts of charge which, with good chemical and mechanical stability, offer new opportunity to satisfy specific energy demands. Nowadays, the focus of investigation is onto various materials such as metal oxides or hydroxides (MnO_2 [1,2], SnO_2 [3], RuO_2 [4-6], IrO_2 [7], Ni oxides[8-10]), conductive polymers (PANI, PEDOT, PPy)[11-12] or carbon materials (graphene, carbon foam)[13-14], which were proven to have the promising capacitive or pseudocapacitive properties suitable for supercapacitors electrodesCapacitive properties of graphene can be improved by combinig graphene with transition metal oxide. Namely, graphene has tendency to agglomeration, which decreases its overall electroactive surface and thus electrochemical properties. This impairment of graphene can be overcome by synergistic effect between graphene and transition metal oxide. In this system, graphene serves as a conducting network[13] that supports redox reaction of a transtion metal oxide and enables better disperison of metal oxide as well. The aim of this work was to synthesize *in situ* reduced graphene oxide (rGO)-supported RuO_2 composites from graphene oxide and Ru^{3+}, and to examine the influence of synthesis conditions on the capacitive properties of a composite. $RuO_2 \cdot xH_2O$ is one of the best candidates with extremely high achievable capacitance of 1580 F/g as published by Hu *et al*.[15]. Extremely high specific capacitances of $RuO_2 \cdot xH_2O$ were achieved when small quantities of the oxide have been mixed with materials of high electronic conductivity. In such cases, high utilization of $RuO_2 \cdot xH_2O$ was result of good proton diffusion along with good electron conductivity. As a result, microwave-assisted hydrothermal synthesis of RuO_2/rGO can lead to better electrochemical performance, mechanical stability, good control of particle size distribution and morphology of obtained materials.

Experimental

RuO_2/reduced graphene oxide (RuO_2/rGO) synthesis

RuO_2/rGO composites were synthesized at different pH and different temperatures by a simple hydrothermal microwave (MW)-assisted single-step method, starting from aqueous $RuCl_3$ solution mixed with graphene oxide aqueous solution prepared by Hummers method[16]. pH was adjusted by adding few drops of NaOH solution into the reaction mixture. The reaction mixture (6 mL) was continuously stirred at 600 rpm inside a closed reactor (10 mL) and MW irradiated isothermally to 120, 160 and 200 °C in an MW oven (Monowave 300, Anton Paar, Ashland, VA, USA). The temperature was maintained for 5 min. Afterwards the reaction mixture was cooled spontaneously to ambient temperature. The obtained composites, denoted as c-7-120, c-7-180, c-7-200, were synthesized at pH 7 at 120, 160 and 200°C, whereas c-10-120, c-10-160, c-10-200 were synthesized at pH 10 at mentioned temperatures. After MW irradiation treatment, initially brown precursor mixture of GO and $RuCl_3$ turned black suggesting successful reduction of GO and oxidation of $RuCl_3$ to RuO_2.Upon keeping, the mixture separated into colorless supernatant solution and visible sponge-like agglomerates of RuO_2/rGO composite.

Electrochemical measurements

Electrode preparation

The Pt EQCM electrode (1.22 cm^2) was washed with ethanol, acetone and bi-distilled water and afterwards electrochemically cycled in 0.1 M $HClO_4$ in potential range from -200 – 1300 mV (vs. SCE) at 100 mV s^{-1} until a stable CV scan was achieved. Aqueous homogenous suspensions of obtained composites were applied onto Pt EQCM electrode by drop casting and allowed to dry at room temperature to form Pt/RuO_2/rGO electrodes. Electrodes were tested by cyclic voltammetry in 1 M H_2SO_4 and 0.5 M Na_2SO_4 from -100 – 1000 mV at scan rate of 50 mV s^{-1}. The usual three-electrode setup was used with EQCM Pt electrode as working electrode, Pt foil (1 cm^2) as counter electrode and saturated calomel electrode (SCE) as the reference electrode. Potentiostat used for analysis was EG&G Princeton Applied Research, model 263A, and for EIS measurements phase sensitive detector EG&G Princeton Applied Research, model 5210, at DC potential that corresponds to open circle potential of 370 mV *vs.* SCE, with the amplitude of 5 mV of sinusoidal potential in the frequency range from 100 kHz to 10 mHz, was used. For the EQCM measurements, the frequency of the quartz crystal coated with Pt was monitored by a Stanford Research System QCM 200 quartz crystal micro-balance connected to the potentiostat. The fundamental frequency was 5 MHz and the integral sensitivity was 4.85×10^{-7} Hz cm^2 g^{-1}. The area of the working electrode was 1.22 cm^2 and piezoelectrically active area was 0.427 cm^2.

Results and discussion

Cyclic voltammetry (CV)

Cyclic voltammograms of different composites synthesized at pH 7 and 10, and at different temperatures, are shown in Fig. 1. The CV responses indicate that, for composites synthesized at neutral pH, temperature increase gives rise to the registered currents. Broad and well pronounced redox peaks around 0.5 V are commonly observed in CV for hydrous $RuO_2 \cdot xH_2O$[17] due to reversible redox process accompanied with sorption of hydrated protons according the equation:

$$RuO_x(OH)_y + ze^- + zH^+ \Leftrightarrow RuO_{x-z}(OH)_{y+z} \qquad (1)$$

Different trend was registered for composites synthesized in alkaline solution (pH 10), for which significant current rise was registered for sample c-10-160 synthesized at 160°C probably due to optimal reduction degree of graphene oxide in combination with beneficial crystallinity and water content for RuO_2 which ensure higher transport rate for protons and electrons. The obtained layer showed best capacitive properties and it was tested in both 1M H_2SO_4 and 0.5 M Na_2SO_4 solutions with simultaneous quartz crystal resonant frequency change (Fig. 2). Obtained capaciance in H2SO4 at 50 mV/s was 100 F/g.

Significant difference during polarization of a c-10-160 layer was evident in different electrolytes, accompanied with lower currents and diminishing current peaks in 0.5M Na_2SO_4 in comparison to the CV registered in 1M H_2SO_4. During anodic polarization in acidic electrolyte, frequency decreases with potential up to 360 mV suggesting incorporation of H_3O^+ into metal oxide lattice

(Fig. 2b). Afterwards, frequency increases suggesting ejection of H_3O^+ at the potentials up to 1000 mV. During cathodic polarization, continuous mass gain was obtained down to 0 mV *vs*. SCE. The obtained result indicates mass change similar to the one obtained in previous investigations that are in accordance with redox reaction (1).

The impedance data of RuO_2/rGO (c-10-160) registered in 1 M H_2SO_4 at open circuit potential (370 mV) are presented in *Figure 3*. The dependences in all types of presented EIS plots indicate the transmission line response with finely distributed relaxation times[18] as follows.

a) **b)**

Figure 1. *Cyclic voltammograms of different composites synthesized at: a) pH 7 and b) pH 10 in 1M H_2SO_4 at scan rate 50 mV/s*

a) **b)**

Figure 2. *Cyclic voltammograms of composite synthesized at pH 10, 160 °C in a) 1M H_2SO_4 and 0.5 M Na_2SO_4, b) in 1M H_2SO_4 with with corresponding EQCM frequency change at scan rate 50 mV/s*

The double declined linear dependence of capacitive-like response is seen in complex plane plot (*Figure 3a*) with the knee frequency positioned at quite low value (500 mHz). The declination at high frequencies (above 500 mHz) corresponds to theoretical value of 1 (0.96 is obtained with r^2 accuracy of 0.992). At frequencies below 500 mHz, typical capacitive-like response of a straight line at constant real impedance is distorted and considerably declined toward real axis. Well-resolved capacitance loops can also be hardly observed in capacitance complex plane plot (*Figure 3b*), with real capacitance ($Y_r\omega^{-1}$) not approaching $Y_i\omega^{-1}$ axis at lowest frequencies (down to 10 mHz), but a constant value between 25 and 30 mS rad^{-1} s. Bode plots (*Figure 3c*) also indicate that capacitive-like response is not reached down to 10 mHz. Constant phase shift close to –90° is not reached, while the log|*Z*|–log*f* slope below 100 mHz is –0.7 ($r^2 = 0.9994$), and reflects much the response related to diffusion limitations (–0.5 slope) than the capacitive-related one (the slope of –1). All of these findings indicate that capacitive response relates to highly distributed RCs originating from the intrinsic material morphology of hardly accessible responding surfaces and/or their pronounced inhomogeneity and fractal dimensionality[19].

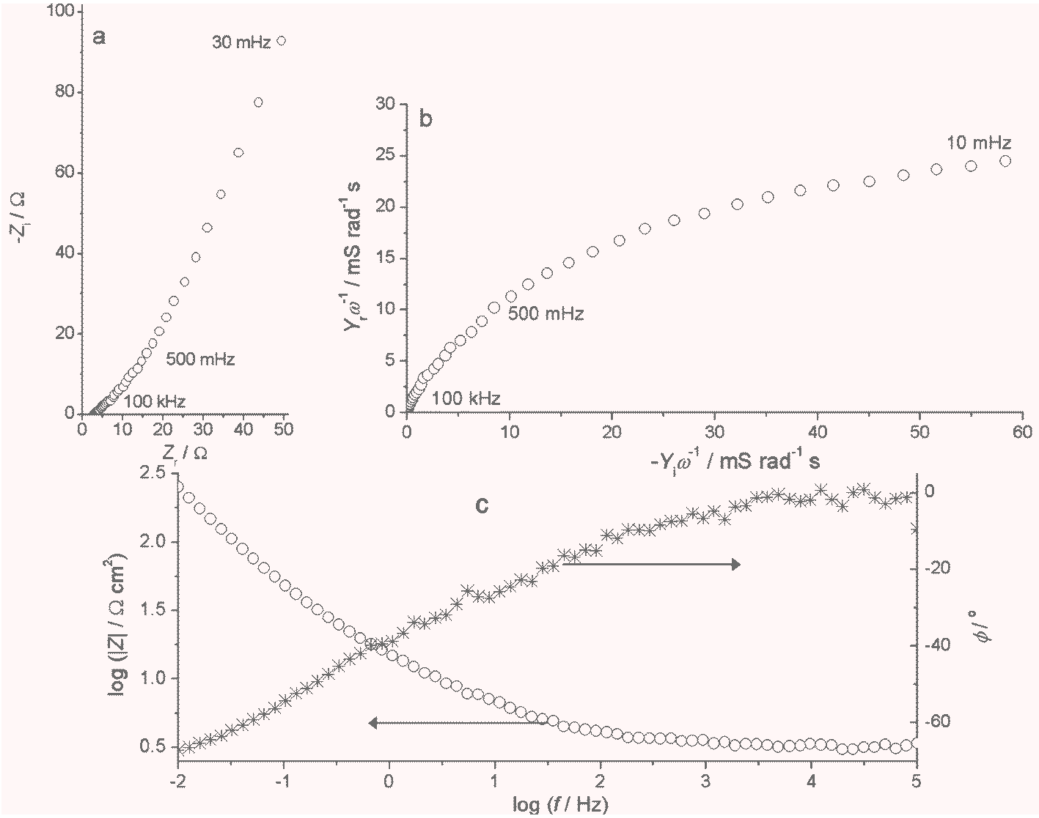

Figure 3. *The impedance and capacitance complex plane (a and b) and Bode (c) plots for the RuO_2/rGO registered in 1 M H_2SO_4 at open circuit potential.*

This morphology can be recognized as unique for rGO-based composites because of defined rGO structure of exfoliated graphite planes available for decoration by active component, *e.g.*, RuO_2, during simultaneous GO reduction/Ru oxidation as in the case of SnO_2/rGO[20]. Registered highly-pronounced transmission line response differs considerably from the responses of carbon black-supported RuO_2[21] and RuO_2 itself[22]. This suggests that considerable amount of hardly accessible RuO_2 in RuO_2/rGO could originate from tightly stacked finely decorated rGO planes.

The difficult accessibility of loose surfaces of synthesized RuO_2/rGO composite is indicated also by the appearance to diffusion limitations-related features of Bode plots (*Figure 3c*). Besides distorted capacitive-related phase shift and modulus dependences at lowest frequencies related to transmission line distribution, ϕ–log*f* and log|*Z*|–log*f* reaches the features typical for EIS of diffusion-controlled processes at in 0.1–1 Hz frequency range. In addition, the shape of complex plate plot (*Figure 3a*) and the position of a knee frequency indicate the capacitive response accompanied by finite diffusion with reflective mass transport boundary conditions[23]. Related psudocapacitive processes apparently require considerable mass to be exchanged as found by EQCM measurements (*Figure 2b*). The largest mass gain/loss is registered around open circuit potential, which also corresponds to the position of redox processes in cyclic voltammetry response (*Figures 1 and 2*). The diffusion model with reflective mass transport boundary conditions announces the Nerst diffusion thickness much larger than that usual for finite diffusion through porous materials, which is indicated by the position of a knee frequency at quite low frequencies (*Figure 3a*). This could suggest that electrolyte species participating in redox transition processes should diffuse through the narrow gaps between tightly stacked, quite long, rGO planes decorated by RuO_2 in order to reach the most hidden inner surfaces of RuO_2/rGO. This model supposes that diffusion layer thickness should then be of the order of rGO plane length, which can explain the observed EIS features related to finite diffusion with reflective mass transport boundary conditions.

Hidrotermalna sinteza RuO_2-redukovani grafen oksid kompozita u mikrotalasnom reaktoru i njihova kapacitivna svojstva

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Superkapacitivni RuO_2-redukovani grafen oksid kompoziti dobijeni su hidrotermalnom sintezom u mikrotalasnom reaktoru. Jednostepena istovremena oksidacija hidratisanog Ru^{3+} do oksida i redukcija oksida grafena izvedena jena različitim temperaturama i pH vrednostima. Kapacitivna svojstva kompozita ispitivana su cikličnom voltametrijom na elektrohemijskoj kvarc-kristalnoj nanovagi i spektroskopijom elektrohemijske impedancije u rastvorima H_2SO_4 i Na_2SO_4. Analiza dobijenih rezultata pokazuje zadovoljavajuća kapacitivna svojstva sintetisanih kompozita. Uzorak sintetisan u neutralnoj sredini pokazuje blag rast kapacitivnosti sa rastom temperature sinteze, dok je za uzorak sintetisan u baznoj kiselini najveća kapacitivnost zabeležena pri srednjoj temperaturi sinteze u primenjenom temperaturnom režimu.

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HTM 01

Antifungalni filmovi na bazi polihidroksialkanoata

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Gljivična oboljenja ljudi su veoma rasprostranjena i relativno česta u savremenom svetu. Najčešće su zarazna i zahtevaju dugotrajno lečenje. Spoljašnja se uglavnom javljaju na naborima i zatvorenim delovima kože kao što su stopala ili područje pazuha, ali mogu da zahvate i kožu trupa, kosu, nokte nogu i ruku. Poslednjih godina značajno raste broj osoba obolelih od gljivičnih infekcija, a za njihovo lečenje se koriste antimikrobni agensi u koje se ubrajaju antibiotici, antivirusni lekovi, antimikotici, antiparazitni.[1] Veoma je važno voditi računa o pravilnom doziranju i vremenu primene antifungalnih lekova da bi se izbegli neželjeni i/ili toksični efekti. Sve veću opasnost po zdravlje ljudi predstavlja i antimikrobna rezistencija, koja se poslednjih godina javlja i kod gljiva i zbog koje standardni tretmani više nisu efikasni, infekcije je sve teže kontrolisati pa je kod obolelih povećan rizik od smrtnog ishoda.[2]

Poslednjih godina sve više istraživanja je usmereno na pronalaženje načina kako da se prevaziđu ovi problemi. Jedno od rešenja je inkorporacija aktivne supstance u nosač koji se dobija od prirodnog polimera čime bi se omogućilo kontrolisano otpuštanje na mestu primene u toku dužeg vremenskog perioda.[3] Prirodni polimeri koji privlače sve više pažnje su prirodni poliestri, a među njima polihidroksialkanoati (PHA) koji su veoma interesantni zbog svoje biokompatibilnosti, biodegradabilnosti i permeabilnosti. Uglavnom se dobijaju iz Gram-pozitivnih i Gram-negativnih bakterija kod kojih se akumuliraju najčešće u vidu granula. Bakterije proizvode PHA granule tokom stacionarne faze rasta, kada su izložene uslovima nutritivnog stresa, sa više dostupnog ugljenika i ograničenim količinama azota, kiseonika, sumpora, magnezijuma i/ili fosfora.[4]

Tema ovog rada je ispitivanje antifungalnih svojstava filmova polihidroksialkanoata sa nistatinom, koji su dobijeni metodom izlivanja iz rastvora i otparavanjem rastvarača.[5] Prilikom izrade filmova variran je sadržaj PHA i masa inkorporiranog nistatina. Antimikrobna svojstva pripremljenih filmova su ispitana *in vitro* na gljivama *Candida albicans* ATCC 10231, i kliničkim izolatima *Aspergillus fumigatus*, *Microsporum gypseum* i *Trichophyton mentagrophytes* metodom zasejavanja na čvrstoj podlozi koja se zasniva na standardnom disk-difuzionom eseju. Otpuštanje nistatina iz pripremljenih filmova praćeno je u veštačkom znoju pomoću UV/VIS spektrofotometra.

Eksperimentalni deo

Materijali: polihidroksialkanoat (PHA, kopolimer 3-hidroksioktanske kiseline (95%) i 3-hidroksidekanske kiseline) srednje dužine lanca, dobijen od *Pseudomonas putida* KT2440 koji je rastao na glukozi i oktanskoj kiselini; hloroform (Centrohem); nistatin (NYS, Fisher); veštački znoj (sastav dat u tabeli 1).[6] Reaktanti su korišćeni bez prečišćavanja.

Tabela 1. *Sastav veštačkog znoja*

Soli	Proizvođač	Masa, g
NaCl	Lach:Ner	5,49
$CaCl_2$	Sigma	3,32
$MgSO_4$	Lach:Ner	0,24
KH_2PO_4	Acros	1,36
pH		4,9

Priprema filmova sa nistatinom: Filmovi PHA, sa i bez nistatina, dobijeni su metodom izlivanja iz rastvora i otparavanjem rastvarača. PHA i nistatin su rastvoreni u odgovarajućoj zapremini hloroforma na 25 °C uz mešanje na magnetnoj mešalici, a tokom pripreme je varirana masa PHA i nistatina u filmu (tabela 2). Rastvori su zatim izliveni u Petri šolje i ostavljeni da se suše na vazduhu. Radi poređenja, napravljeni su i kontrolni filmovi PHA bez nistatina. U nazivu uzorka je naznačena masa PHA i maseni udeo nistatina računat prema masi polimera.

Tabela 2. *Sastav PHA/nistatin filmova*

Film	PHA, g	Nistatin, mas.%
PHA0,5/NYS1	0,5	1
PHA0,5/NYS2		2
PHA1/NYS1,5	1,0	1,5
PHA1/NYS20		20
PHA2/NYS10	2,0	10
PHA2/NYS15		15

Ispitivanje antimikrobne aktivnosti filmova polihidroksialkanoata:
Antimikrobna aktivnost pripremljenih PHA filmova je ispitana na sojevima gljiva *Candida albicans* ATCC 10231, *Aspergillus fumigatus*, *Microsporum gypseum* i *Trichophyton mentagrophytes* metodom zasejavanja na čvrstoj podlozi koja se zasniva na standardnom disk-difuzionom eseju ispitivanja antimikrobnih svojstava različitih jedinjenja. Ćelije gljiva su zasejane na ploče sa Saboroud dekstroznim agarom (HiMedia Laboratories, Indija), a filmovi su naneti na površinu podloge. Ploče su inkubirane na 30 °C i 37 °C nakon čega su merene zone inhibicije. Film bez nistatina je korišćen kao kontrolni uzorak.

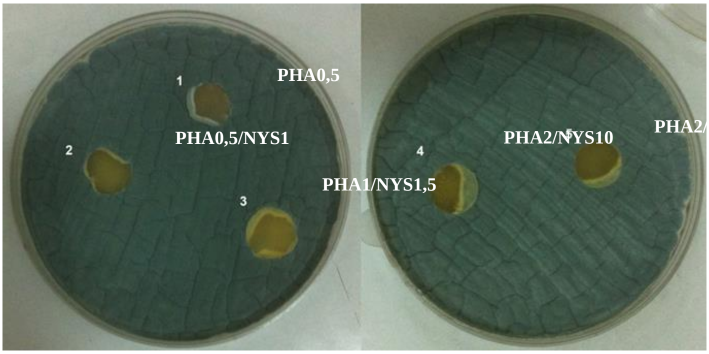
***In vitro* otpuštanje nistatina iz pripremljenih filmova:** Otpuštanje nistatina iz pripremljenih filmova *in vitro* praćeno je u veštačkom znoju (tabela 1) na dve temperature 30 ºC i 37 ºC u vodenom kupatilu sa mehaničkim mešanjem (WND14 Memert, Nemačka). Od svakog filma su isečena po tri uzorka (3,5×1 cm) i potopljena u 10 ml veštačkog znoja. Otpuštanje nistatina sa vremenom iz filmova praćeno je pomoću UV/VIS spektrofotometra (Shimatzu 1800, Japan).

Rezultati i diskusija

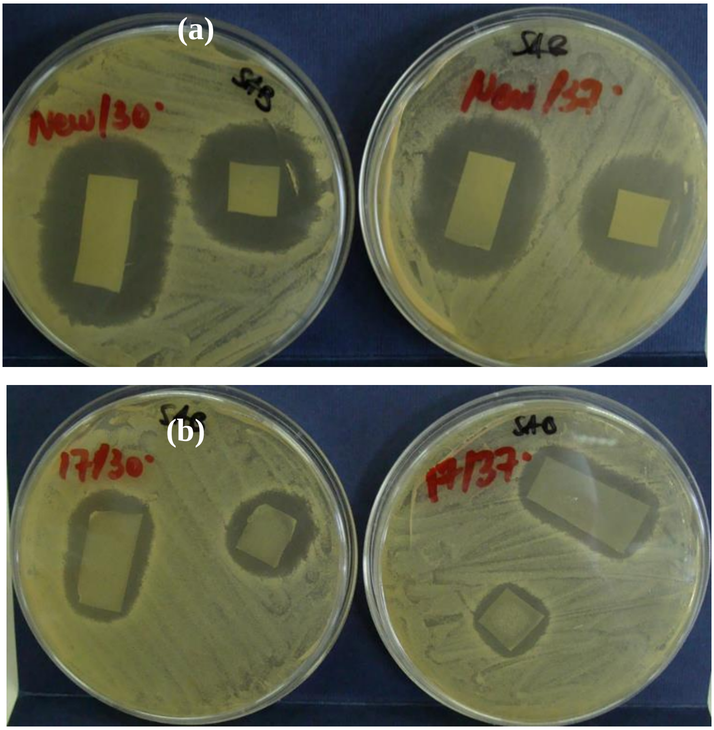
Antimikrobna aktivnost PHA filmova: Tokom pripreme PHA filmova sa nistatinom varirana je masa PHA, kao i masa inkorporiranog nistatina. Prosečna debljina dobijenih filmova je iznosila oko 0,5 mm.

Da bi se ispitala antimikrobna aktivnost, od pripremljenih filmova su isečena po 4 diska prečnika 12 mm koji su postavljeni na površinu podloge zasejane odgovarajućom gljivom (na 37 °C). Na slici 1 su prikazani uzorci na podlozi na kojoj je zasejana gljiva *Aspergillus fumigates*. Kod svih filmova (kontrolni film i filmovi sa nistatinom) utvrđeno je da nema zone inhibicije, odnosno ne dolazi do sprečavanja rasta gljive *Aspergillus fumigatus*, bez obzira na koncentraciju nistatina u filmovima. Isti rezultat je dobijen i za ostale gljive (*Candida albicans* ATCC 10231, *Microsporum gypseum* i *Trichophyton mentagrophytes*).

Razlog antimikrobne neaktivnosti verovatno je nedovoljan udeo nistatina u filmovima i u nehomogenoj raspodeli nistatina u filmovima. Zbog toga je za naredni eksperiment izabran uzorak sa najvećim udelom nistatina PHA1/NYS20 i uzorak PHA1/NYS1,5 radi utvrđivanja minimalne inhibitorne koncentracije (MIC), odnosno najmanje koncentracije nistatina koja sprečava rast ispitivanog mikroorganizma. Uzorci su bili u obliku kvadrata i pravougaonika. Antimikrobna aktivnost je testirana na *Candida albicans* na 30 °C i 37 °C, koja je pokazala najveću osetljivost na dejstvo nistatina od svih ispitanih gljiva (slika 2).



Slika 1. *PHA/NYS filmovi na podlozi zasejanoj gljivom Aspergillus fumigatus*



Slika 2*. Antimikrobna aktivnost filmova (a) PHA1/NYS20 i (b) PHA1/NYS1,5 na Candida albicans, na 30 °C i 37 °C.*

Sa slike 2a se vidi da je za uzorak PHA1/NYS20 u značajnoj meri razvijena zona inhibicije na obe temperature čime je sprečen rast gljive *Candida albicans*. Film PHA1/NYS1,5 takođe pokazuje antimikrobnu aktivnost (prisustna je zona inhibicije oko uzorka) (slika 2b). Dobijeni rezultat ukazuje da i značajno manja koncentracija nistatina pokazuje antimikrobnu aktivnost prema gljivi *Candida albicans*.

U tabeli 3 date su dimenzije isečenih uzoraka i zona inhibicije. Zona inhibicije (32x22 mm) u slučaju filma PHA1/NYS20 je značajno veća u odnosu na dimenzije isečenog uzorka (18x8 mm). Poređenjem veličina zona inhibicije prikazanih filmova na 30 °C i 37 °C primećeno je da je antimikrobna aktivnost PHA1/NYS20 filma veća u odnosu na PHA1/NYS1,5, što je očekivano zbog većeg masenog udela nistatina u filmu.

***Tabela 3**: Dimenzije uzoraka PHA1/NYS20 i PHA1/NYS1,5 filma i odgovarajuće zone inhibicije*

***T* / °C**	**PHA1/NYS20**	**Dimenzije uzorka, mm**	**Zona inhibicije, mm**	**PHA1/NYS1,5**	**Dimenzije uzorka, mm**	**Zona inhibicije, mm**
30	Pravougaonik	18×8	32x22	Pravougaonik	19×10	28×17
	Kvadrat	8×8	22x22	Kvadrat	10×9	19×17
37	Pravougaonik	15×8	28x21	Pravougaonik	23×10	28×16
	Kvadrat	8×8	21x19	Kvadrat	9×9	14×14

***In vitro* otpuštanje nistatina:** Nakon što je potvrđeno da pripremljeni filmovi imaju antimikrobnu aktivnost, ispitana je brzina otpuštanja nistatina na podlogu zasejanu gljivama *Candida albicans*. Za preliminarna ispitivanja otpuštanja korišćen je uzorak PHA1/NYS20. S obzirom da bi ovi filmovi mogli da se primene u vidu obloga za lečenje kože zahvaćene gljivičnom infekcijom, otpuštanje nistatina je praćeno u veštačkom znoju. Rezultati su pokazali da je tokom tri sata otpušteno 30,8 % nistatina na 30 °C, odnosno 45,7 % na 37 °C. Imajući u vidu da se tokom tri sata otpušta značajna količina nistatina i razvija zadovoljavajuća zona inhibicije, dobijeni rezultati ukazuju da bi ovi filmovi mogli da skrate dužinu tretmana obolele kože.

Zaključak

Predmet ovog rada bio je priprema filmova na bazi polihidroksialkanoata u koje je inkorporiran nistatin. Filmovi su pripremljeni metodom izlivanja iz rastvora i otparavanjem rastvarača. U slučaju kliničkih izolata gljiva *Aspergillus fumigatus*, *Microsporum gypseum* i *Trichophyton mentagrophytes* nije razvijena zona inhibicije, odnosno ne dolazi do sprečavanja rasta gljiva bez obzira na koncentraciju nistatina u filmovima. Sa druge strane, utvrđeno je da PHA filmovi sa nistatinom pokazuju zadovoljavajuću antimikrobnu aktivnost prema gljivi *Candida albicans*, nezavisno od temperature na kojoj su izvedena ispitivanja. Takođe je određena minimalna koncentracija nistatina u PHA filmu koja pokazuje antimikrobnu aktivnost. Zona inhibicije zavisi od koncentracije nistatina u filmovima, pa sa povećanjem koncentracije raste i zona inhibicije. Ispitano je otpuštanja nistatina iz filmova u veštačkom znoju i utvrđeno da se tokom tri sata otpusti 30,8 % na 30 °C i 45,7% nistatina na 37 °C. Imajući u vidu zadovoljavajuće rezultate otpuštanja i dobru antimikrobnu aktivnost, može se pretpostaviti da bi ovi filmovi mogli da se koriste u vidu obloga za lečenje obolele kože zahvaćene gljivičnom infekcijom.

Zahvalnica

Autori se zahvaljuju Ministarstvu za prosvetu, nauku i tehnološki razvoj Republike Srbije za finansijsku podršku ovom radu u okviru projekta br. 172062, " Sinteza i karakterizacija novih funkcionalnih polimera i polimernih nanokompozita" i projekta br. ESCMID 2015 nosioca Jasmine Nikodinović-Runić.

Polyhydroxyalkanoates films with antifungal properties

Polyhydroxyalkanoates (PHAs) are polyesters that are synthesized by Gram-positive and Gram-negative bacteria. They are biodegradable and biocompatible. As skin fungal infections are becoming more widespread, it is necessary to modify so-called "old drugs", such as polyenes, and release them from the appropriate systems in a controlled manner, which can be achieved by biocompatible biopolymers used as drug carriers.

The present paper reports on the investigation of the antimicrobial properties of the PHA films, loaded with nystatine, obtained by solvent-casting method. The film thickness was varied, as well as the mass of the nystatine. PHA/nystatin films did not prevent the growth of Aspergillus fumigatus, Microsporum gypseum *and* Trichophyton mentagrophytes, *but showed good antimicrobial activity against* Candida albicans. *The inhibition zone depended on the concentration of nystatin. The minimum inhibitory concentration of nystatin in the PHA film is 1.5 wt.%. UV/VIS revealed that 30.8 %*

and 45.7 % of nystatin was released at 30 and 37 °C, respectively, which indicates that these films could be potentially used as a wound dressing for the treatment of skin affected by fungal infection.

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HTM 04

Spajanje metala pomoću adheziva na bazi prirodnih polimera

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Uvod

Aluminijum i njegove legure (Al-legure) su veoma atraktivni za industriju zahvaljujući maloj gustini, dobroj otpornosti na koroziju, odličnoj električnoj i toplotnoj provodljivosti i mehaničkim svojstvima. Za mnoge primene potrebno je spojiti legure aluminijuma što se može izvesti na više načina: mehaničkim spajanjem, zavarivanjem, lemljenjem ili lepljenjem. Najčešće se za spajanje Al-legura koristi mehaničko spajanje i zavarivanje, s tim da se bolja mehanička svojstva spoja dobijaju zavarivanjem.[1] Iako ima niz prednosti, spajanje Al-legura zavarivanjem je praćeno nizom teškoća, među kojima su najznačajnije: 1) prisustvo teško topivog oksidnog sloja Al_2O_3 koji ima znatno višu temperaturu topljenja od aluminijuma, pa mora biti uklonjen ili odvojen pre početka zavarivanja uz istovremeno sprečavanje ponovnog formiranja u toku procesa zavarivanja, 2) greške u materijalu, 3) omekšavanje materijala u zoni uticaja toplote i dr. Takođe, zbog strukture i sastava pojedinih Al-legura zavarivanje je praktično nemoguće. Zbog svega toga sve više pažnje se posvećuje spajanju Al-legura lepljenjem pomoću odgovarajućih adheziva. Imajući u vidu da se lepljenje može primeniti za spajanje svih legura aluminijuma i metalnih materijala uopšte, očekuje se da će se ovaj način spajanja primenjivati u industriji gde god je to moguće. Pored spajanja metalnih materijala, sve češće se javlja potreba za spajanjem raznorodnih materijala, npr. metal/plastika ili kompoziti, gde se lepljenje takođe nameće kao poželjan vid spajanja. Spajanje materijala lepljenjem ima nekoliko prednosti: 1) jednostavniji postupak predtretmana uzorka; 2) kada se oksidni sloj jednom ukloni nema potrebe za sprečavanjem formiranja novog; 3) postupak samog spajanja materijala je jednostavniji i povoljniji i ne zahteva prisustvo stručnog lica; 4) debljina materijala ne utiče značajno na postupak spajanja; 5) moguće je spajanje različitih geometrijskih oblika i nije potreban naknadni tretman kako bi se poboljšale karakteristike lepljenog spoja.[2]

Na tržištu postoji veliki broj različitih komercijalnih adheziva, od kojih se za spajanje metalnih i kompozitnih materijala najviše koriste adhezivi na bazi epoksidnih smola, poliuretana, cijanoakrilata i dr.[3] Iako su se ovi adhezivi pokazali kao vrlo efikasni, za izradu se koriste komponente dobijene iz petrohemijskih izvora koje su štetne po zdravlje ljudi i životnu sredinu. Zbog toga je trend u industriji adheziva da se ove komponente delimično ili u potpunosti zamene netoksičnim komponentama dobijenim iz obnovljivih izvora, a da se pri tome zadrži efikasnost adheziva. U tu svrhu su do sada dosta korišćeni celuloza, skrob i njihovi derivati, a poslednjih godina više pažnje se posvećuje drugim polisaharidima, kao što je hitozan i/ili natrijum-alginat.

Cilj ovog rada bio je da se pripremi adheziv u kome bi epoksidna smola delimično ili u potpunosti bila zamenjena hitozanom i/ili natrijum-alginatom i da se tako pripremljenim adhezivom ispita mogućnost spajanja različitih materijala. Napravljeno je više različitih adheziva u kojima je variran sadržaj epoksidne smole, hitozana i natrijum-alginata, a zatim je ispitana jačina adhezije za tri različita materijala: komercijalna aluminijumska legura, pocinkovani lim i karbon. Nakon toga je ispitana mogućnost lepljenja delova trkačkog vozila koji su napravili članovi studentskog tima „Drumska Strela” za učestvovanje na međunarodnom takmičenju Formula student.

Eksperimentalni deo

Materijali: Hitozan (Ch, Sigma-Aldrich; viskoznost <200 mPa·s, molarna masa 653 kg/mol; natrijum-alginat (A, Sigma-Aldrich, molarna masa 216,7 kg/mol); sirćetna kiselina (Zorka); natrijum-hidroksid (Lech:ner); komercijalna epoksidna smola i umreživač na bazi amina (ES, Epoxy resin L 385, Hardener 386, redom, R&G Faserverbundwerkstoffe GmbH); komercijalna aluminijumska legura, pocinkovani lim i karbon.

Priprema adheziva: neposredno pre izrade adheziva napravljeni su rastvori hitozana (4 mas.% u 2 mas.% sirćetnoj kiselini) i natrijum-alginata u vodi (1 mas.%). Pri izradi adheziva variran je udeo epoksidne smole, hitozana i/ili natrijum-alginata (tabela 1), a pojedinim formulacijama su dodata i staklena vlakna (SV), 20 mas.% računato na epoksidnu smolu.

Aktiviranje površine za lepljenje: za lepljenje su korišćene ploče (150×30×2 mm) izrađene od komercijalne Al-legure, pocinkovanog lima i karbona. Neposredno pre nanošenja adheziva, površina ispitivanih materijala je očišćena i aktivirana mehanički (brušenjem) pomoću brusnog papira 240 i/ili hemijski pomoću rastvora natrijum-hidroksida (4M NaOH).

Nanošenje adheziva: površina lepljenog spoja u svim slučajevima bila je 30×30 mm; adheziv je nanet u tankom sloju vodeći računa da kompletna površina bude ravnomerno pokrivena adhezivom, a zatim je dodat umreživač (kod svih uzoraka odnos adheziv: umreživač bio je 3:1). Da bi se utvrdila efikasnost i jačina pripremljenih adheziva, napravljeni su i referentni uzorci za čije lepljenje je korišćena isključivo komercijalna epoksidna smola i umreživač u odnosu 3:1. Nakon nanošenja adheziva, lepljeni spojevi su fiksirani i ostavljeni u sušnici na 70 °C 24 h, a zatim su ohlađeni do sobne temperature.

Tabela 1. *Formulacije adheziva*

Uzorak	ES, g	Ch, g	A, g	SV
A1	100	-	-	-
A2	100	-	-	✓
A3	75,0	25,0	-	✓
A4	75,0	17,0	8,00	-
A5	60,0	40,0	-	-
A6	60,0	27,0	13,0	-
A7	50,0	50,0	-	-
A8	0,00	100	-	-
A9	0,00	-	100	-

Karakterizacija: jačina adhezije zalepljenih uzoraka ispitana je jednoosnim zatezanjem, primenom opterećenja na smicanje na kidalici (Instron AG – X plus); merenjem maksimalne sile (pri brzini od 1 mm/min) pri kojoj dolazi do pucanja lepljenog spoja. Na osnovu maksimalne sile izračunat je maksimalni napon prema jednačini:

$$\tau = F / A \qquad (1)$$

gde je τ maksimalni tangencijalni napon (MPa), F maksimalna sila (kN), A površina lepljenog spoja koja je kod svih uzoraka bila konstantna (900 mm^2). Prikazani rezultati predstavljaju srednju vrednost pet nezavisnih merenja.

Rezultati i diskusija

Pripremljeno je devet formulacija adheziva u kojima je variran sadržaj epoksidne smole, hitozana i/ili natrijum-alginata. Preliminarna ispitivanja su pokazala da je tretman materijala, odnosno aktiviranje površine, pre nanošenja adheziva veoma važno i da utiče na efikasnost lepljenja. U pojedinim slučajevima spajanje materijala je moguće i bez aktiviranja površine, s tim da je jača adhezija postignuta nakon aktiviranja površine. Nasuprot tome, lepljenje pocinkovanog lima je bilo moguće tek nakon aktiviranja površine za lepljenje.

Spajanje ispitivanih materijala pomoću komercijalnog umreživača i adheziva napravljenim isključivo od hitozana ili natrijum-alginata nije uspelo iako je površina bila aktivirana pre nanošenja adheziva. Zbog toga su dalja ispitivanja izvedena sa adhezivima u kojima je jedna od komponenti bila komercijalna epoksidna smola. Mogućnost spajanje Al-legure, pocinkovanog lima i karbona je ispitana sa uzorcima A1-A7. U tabelama 2 i 3 su prikazani dobijeni rezultati za uzorke kod kojih je spajanje lepljenjem bilo uspešno.

Tabela 2. *Jačina adhezije zalepljenih pločica (pocinkovani lim i Al-legura); željena jačina adhezije 4-5 MPa*

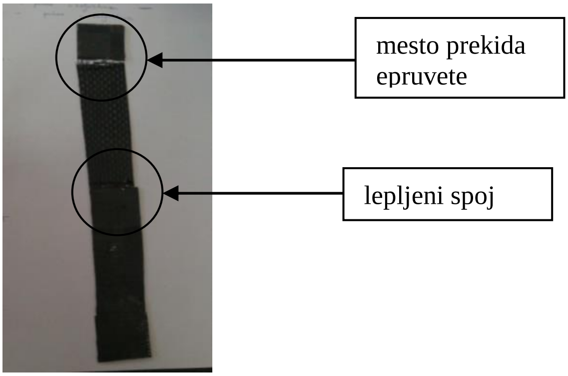
Uzorak	ES/Ch/A	Pocinkovani lim		Al-legura	
		Maksimalna sila, N	**Maksimalan napon, MPa**	**Maksimalna sila, N**	**Maksimalan napon, MPa**
A1	100/0/0	3951	4,39	6147	6,83
A2	100/0/0 + SV	4149	4,61	2808	3,12
A3	75/25/0 + SV	4527	5,03	5103	5,67
A4	75/17/8	4509	5,01	4410	4,90
A7	50/50/0	-	-	2304	2,56

Na osnovu prikazanih rezultata uočeno je da smanjivanjem udela epoksidne smole i dodatkom hitozana i/ili natrijum-alginata u adheziv, jačina adhezije na pocinkovanom limu odgovara željenoj vrednosti i raste u odnosu na referentni uzorak, komercijalnu epoksidnu smolu. S druge strane, u slučaju Al-legure jačina adhezije opada sa porastom udela prirodnih polimera u formulaciji, a kod uzorka A7 je znatno niža od željene vrednosti. Dodatak staklenih vlakana u pojedinim slučajevima može poboljšati jačinu adhezije (uzorak A3).

Tabela 3. *Jačina adhezije zalepljenih pločica od karbona; željena jačina adhezije 4-5 MPa*

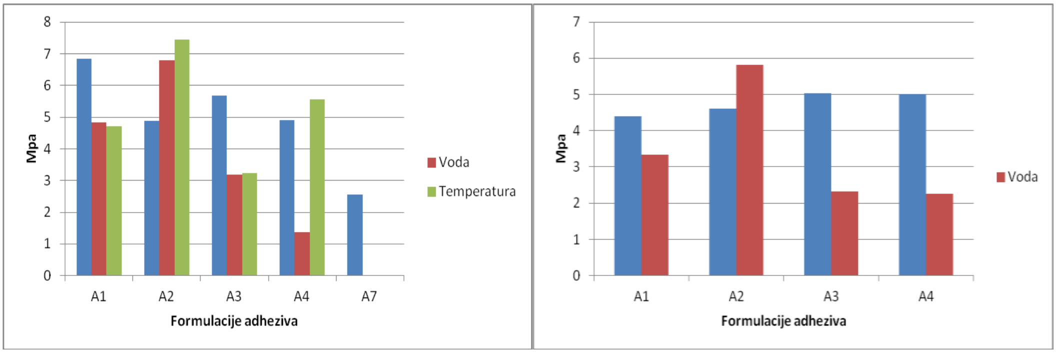
Uzorak	Sastav ES/Ch/A	Karbon	
		Maksimalna sila, N	**Maksimalan napon, MPa**
A1	100/0/0	5472	6,08
A2	100/0/0 + SV	/	/
A3	75/25/0 + SV	7938	8,82
A5	60/40/0	8460	9,40
A6	60/27/13	7956	8,84

U slučaju karbona jačina adhezije je bila veća od željene za 35 %. Može se uočiti da se bolja adhezija, odnosno veća jačina adhezije, postiže sa uzorcima A1 i A3 na karbonu u odnosu na pocinkovani lim i Al-leguru. Za razliku od pocinkovanog lima i Al-legure, smanjivanjem udela epoksidne smole u adhezivu dolazi do povećanja jačine adhezije. Kada se u komercijalni lepak dodaju staklena vlakna, jačina adhezije je toliko velika da pri primenjenim opterećenjima pre dolazi do pucanja materijala nego do razdvajanja lepljenog spoja (slika 1).



Slika 1: Izgled uzorka karbona nakon pucanja; spajanje je izvedeno pomoću adheziva A2

Nakon toga je ispitan uticaj vode (potapanjem zalepljenih pločica u vodu 24 h na 25 °C) i temperature umrežavanja (25 °C, 70 °C i 100 °C tokom 24 h) na jačinu adhezije pripremljenih adheziva. Dobijeni rezultati za Al-leguru i pocinkovani lim su prikazani na slici 2.



(a) (b)

Slika 2: Uticaj temperature i vode na jačinu adhezije za Al-leguru (a) i pocinkovani lim (b)

Prisustvo vode dovodi do smanjenja jačine adhezije kod svih uzoraka, osim za uzorak A2 u koji su dodata staklena vlakna. Takođe je ispitan i uticaj temperature umrežavanja adheziva na jačinu adhezije. Najmanja jačina adhezije dobijena je na 25 °C (rezultati nisu prikazani), dok sa porastom temperature do 70 °C jačina adhezije raste. Međutim, daljim porastom temperature do 100 °C jačina adhezije opada za sve uzorke (slika 2a), osim za uzorak A2 što je posledica prisustva staklenih vlakana. Isti trend je uočen i za jačinu adhezije na karbonu.
Na kraju je ispitana mogućnost lepljenja delova trkačkog vozila, koji su napravili članovi studentskog tima „Drumska Strela" za učestvovanje na međunarodnom takmičenju Formula student, pomoću pripremljenih adheziva. Najbolji rezultati su postignuti sa adhezivima A3 i A4 pomoću kojih je zalepljen restriktor koji je sastavni deo usisnog voda na bolidu.

Zaključak

U radu je ispitana mogućnost izrade adheziva u kome je komercijalna epoksidna smola potpuno ili delimično zamenjena sa prirodnim polimerima, hitozanom i/ili natrijum-alginatom. Oko 50 mas.% epoksidne smole je uspešno zamenjeno prirodnim polimerima pri čemu postignuta jačina adhezije odgovara željenoj vrednosti (4-5 MPa), a u pojedinim slučajevima je i veća u odnosu na komercijalnu epoksidnu smolu. Optimalni uslovi za postizanje ove vrednosti su 70 °C i 24 h. Uočeno je da je tretman površine neposredno pre lepljenja veoma bitan i da ima veliki uticaj na efikasnost lepljenja, kao i da prisustvo vode smanjuje jačinu adhezije. Pomoću adheziva kod kojih je 25 mas.% epoksi smole zamenjeno prirodnim polimerima uspešno su zalepljeni delovi trkačkog vozila koji su napravili članovi studentskog tima „Drumska Strela" za učestvovanje na međunarodnom takmičenju Formula student.

Zahvalnica: *Autori se zahvaljuju Ministarstvu za prosvetu, nauku i tehnološki razvoj Republike Srbije za finansijsku podršku ovom radu u okviru projekta br. 172062 " Sinteza i karakterizacija novih funkcionalnih polimera i polimernih nanokompozita".*

Metal-bonding by bio-based adhesives

Adhesive bonding of metals is increasingly being used when welding of metals is not suitable due to metal structure and composition or when an oxidized layer is placed on the surface of the metal. It is mostly used for joining of certain aluminum alloys where conventional welding is practically impossible. That is why in the last decade researches focused on bonding of aluminum alloys, as well as other metal materials, by appropriate adhesives. There are a large number of commercial adhesives which consist of petrochemical components that could be harmful for human health and *environment. Hence, there is a growing interest to develop environmental-friendly adhesives based on renewable resources.*

The aim of this paper is to develop the adhesive in which a commercial epoxy resin is replaced, partially or completely, by natural polymers, such as chitosan and/or sodium alginate. The epoxy resin was successfully replaced by natural polymers (up to 50 wt.%) keeping desired strength of adhesion (4-5 MPa), while in some cases even higher strength of adhesion was achieved compared to commercial epoxy resin. It was found that optimal conditions to obtain these values are 70 ℃ and 24 h. Furthermore, pretreatment of material surface has a great influence on the adhesion efficiency, while the presence of water decreases the adhesion strength. As a final point, members of the student team "Road Arrow" successfully bonded parts of intake system on the racing vehicle with adhesives where 25 wt.% of epoxy resin was replaced with natural polymers.

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HŽS 07

Volumetric and acoustic properties of binary mixture ethanol + d-limonene

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Abstract

The aim of this study is investigation of the molecular structure for binary mixture containing widely used flavour & fragrance ingredient, such as d-limonene, and, on the other hand ethanol as a solvent permitted in food and cosmetics industry. In this study densities, refractive indices and ultrasonic velocities of binary system ethanol + d-limonene were measured at atmospheric pressure and in temperature range T = (288.15 to 323.15) K. Excess molar volumes, deviations in refractive indices and isentropic compressibility deviations were calculated from the experimental data. Based on the calculated thermodynamic properties, analysis of the molecular structure of the investigated binary system is given.

Introduction

Flavourings are substances used to impart taste and/or smell to food. Flavourings have a long history of safe use in a wide variety of foods, from confectionery and soft drinks to cereals, cakes and yoghurts (definition by the European Commission). Limonene is used in food manufacturing and in cosmetics as a flavor & fragrance substance, giving fresh orange aroma. Limonene is also the main constituent of natural citrus essential oils[1]. It is a colorless liquid hydrocarbon classified as a cyclic terpene. The more common is d-isomer, which possesses a strong smell of oranges. One of the largest users of ethyl alcohol is the personal care products industry. Additionally, according to Directive 2009/32/EC ethanol is a permitted solvent in food industry.

Following the aforementioned attractiveness of limonene as food & cosmetics ingredient, the aim of this work was performing the detailed analysis of thermophysical properties for the binary mixture ethanol + d-limonene. To the best of our knowledge there are no literature data with the thermodynamic analysis of the mentioned binary mixture. Densities, refractive indices and ultrasonic velocities have been measured for the investigated binary system, at temperatures between 288.15 and 323.15 K with a step of 5 K and at atmospheric pressure. From these experimental data, excess molar volumes, deviations in refractive index and isentropic compressibility deviations were calculated. Based on the calculated properties and molecular nature of individual components, the interpretation of molecular effects in the mixture is established in this work.

Experimental Section

Chemicals. Ethanol was supplied by Merck with high mass purity of 99.9%, and d-limonene was purchased from Sigma with the assay claimed to be >97% and optical purity >98%.

Measurements. The experimental measurements of density ρ, refractive index n_D and ultrasonic velocity u were performed on Anton Paar devices; DSA 5000 M digital vibrating U-tube densimeter and automatic Anton Paar RXA 156 refractometer. Detailed description of the apparatus can be found in our previous work[2].

All the mixtures were prepared gravimetrically using a Mettler AG 204 balance with a precision $1 \cdot 10^{-7}$ kg. The uncertainty of the mole fraction calculation was less than $\pm 1 \cdot 10^{-4}$. Density and refractive index measurements were performed with the experimental uncertainty of $\pm 4 \cdot 10^{-2}$ kg·m^{-3} and ± 0.00005 units, respectively. The uncertainty of ultrasonic velocity is ± 0.5 m·s^{-1}.

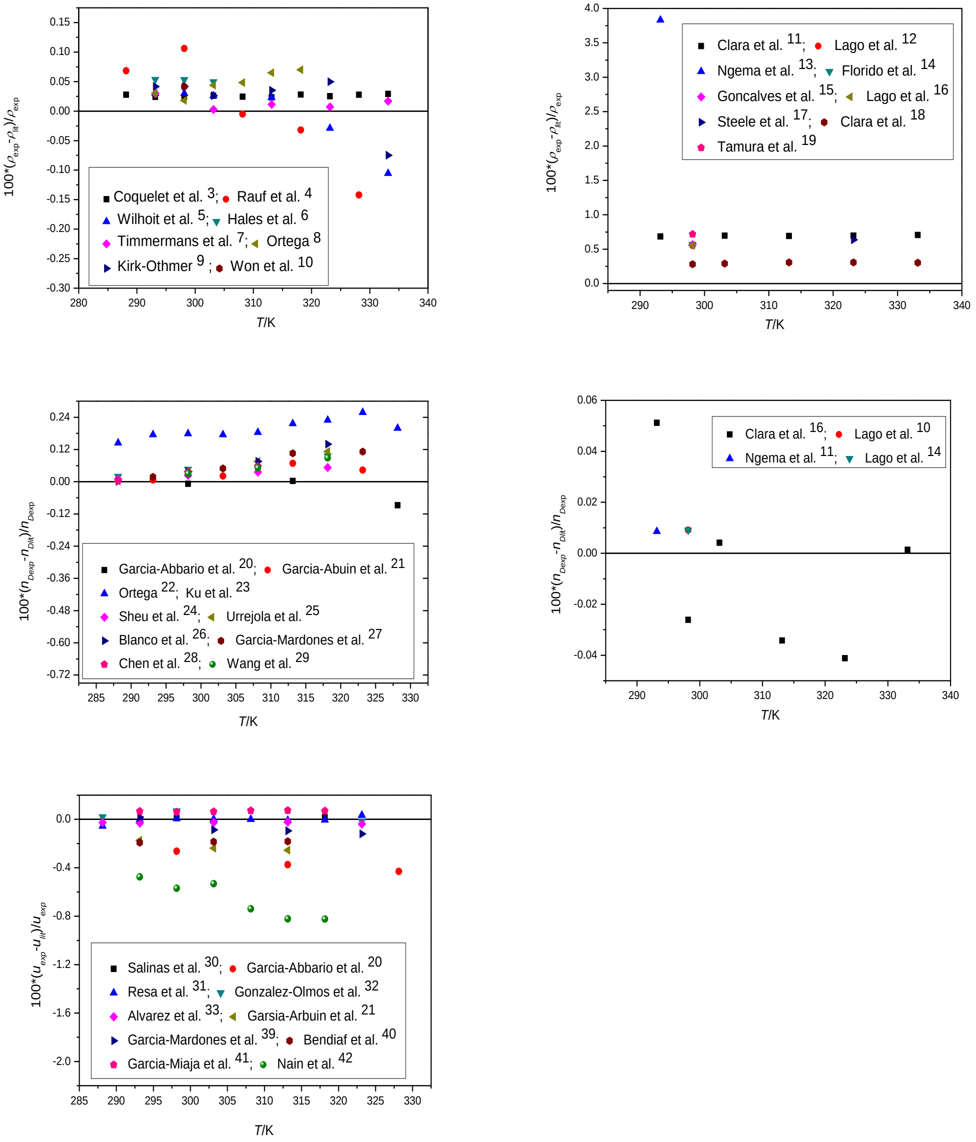
Results and discussion

The experimental values of densities ρ, refractive indices n_D and ultrasonic velocities u for the system ethanol + d-limonene were measured in a temperature range T = (288.15 to 323.15) K and at atmospheric pressure. All experimental data show satisfactorily agreement with literature (Figure 1).

The excess molar volumes V^E were calculated using the experimental densities ρ of binary mixtures and the pure components ρ_i from the equation:

$$V^E = \sum_{i=1}^{N} x_i M_i \left[\left(\frac{1}{\rho} \right) - \left(\frac{1}{\rho_i} \right) \right] \tag{1}$$

where N is the number of components, x_i is the mole fraction of component i in a mixture and M_i is the molecular weight of a component i.



(a) *(b)*

Figure 1. *Relative deviations vs. temperature obtained from comparison of experimental data with literature for (a) ethanol and (b) d-limonene*

The refractive index deviations Δn_D were obtained using the equation:

$$\Delta n_D = n_D - \sum_{i=1}^{N} x_i n_{Di} \tag{2}$$

Isentropic compressibility deviations k_S^E are calculated using the following equation:

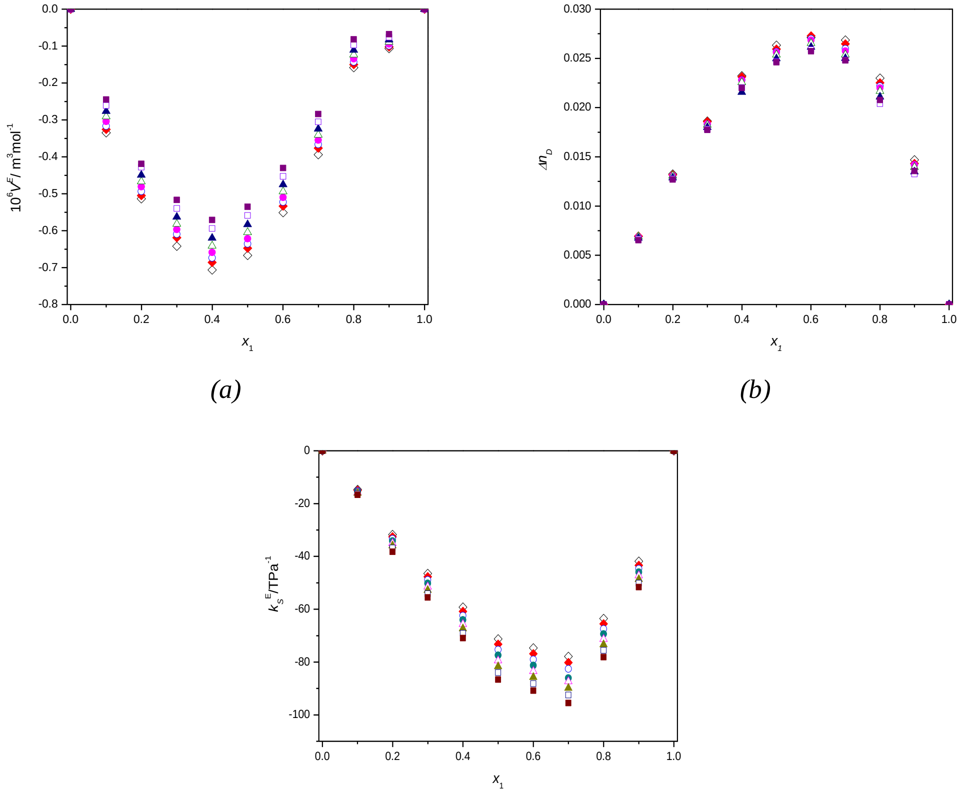
$$k_S^E = k_S - \sum_{i=1}^{n} x_i k_{Si} \tag{3}$$

where isentropic compressibility k_S can be obtained from experimental density ρ and ultrasonic velocity u data using the following equation:

$$k_s = \frac{1}{\rho u^2} \tag{4}$$

where k_S and k_{Si} refer to the isentropic compressibility of a mixture and a pure component i, respectively.

All calculated properties, V^E, Δn_D and k_S^E, for the investigated binary system ethanol + d-limonene are presented in Figure 2.



(a) *(b)*

(c)

Figure 2. *Experimental data of (a) excess molar volume (V^E); (b) refractive index deviation (Δn_D); and isentropic compressibility deviation (k_S^E) as a function of mole fraction x_1, for the binary system ethanol (1) + d-limonene (2) at following temperatures: (◊)288.15 K, (♦) 293.15 K, (○) 298.15 K, (●) 303.15 K, (Δ) 308.15 K, (▲) 313.15 K, (□) 318.15 K, (■) 323.15 K and at atmospheric pressure*

The system ethanol + d-limonene exhibits negative trend in V^E curve, where absolute V^E values decrease with temperature increase. The minimum of the curve is at x_1=0.4 (Figure 1(a)). Experimental refractive index deviations are plotted vs. x_1 (Figure 1(b)). System exhibits positive Δn_D values with maximum at x_1=0.6 and Δn_D values decrease with increasing temperature from 288.15 K to 323.15 K. Isentropic compressibility deviations are plotted vs. x_1 (Figure 1(c)). k_S^E curve has negative trend with minimum of the curve at x_1=0.7. Absolute k_S^E values increase with temperature increase. For all three properties temperature influence is not so pronounced, specially for the refractive index deviations.

Negative excess molar volumes could be the consequence of formation of some kind of heterogeneous complex of components molecules. It could also be the result of structural effects that can lead to closer geometrical packing of unlike molecules[2,38]. Positive refractive index deviations follow a general rule, e.g. the better the molecules are packed, the less the speed of light and therefore higher the refractive indices[39]. This conclusion corresponds with negative excess molar volume data. Strong specific interactions between the component molecules are leading to negative value of k_S^E, but also due to interstitial accommodation of molecules and changes in free volume k_S^E exhibits negative trend[40].

Ethanol is a polar molecule, capable for hydrogen bonding and dipole-dipole interactions. D-limonene is a non-polar molecule capable of forming dispersion forces with polar compound. According to molecular nature of individual components it can be concluded that negative V^E values are mainly caused by efficient geometrical packing of ethanol molecules (V_m=58.66 cm$^3\cdot$mol^{-1}) into the interstitial space of d-limonene molecules (V_m=161.54 cm$^3\cdot$mol^{-1}).

Conclusion

In this paper density, refractive index and ultrasonic velocity data of binary mixture ethanol + d-limonene were measured at atmospheric pressure and at temperatures ranging from 288.15 K to 323.15 K with a step of 5 K. Excess molar volumes, deviations of refractive index and isentropic compressibility were calculated from the experimental data. These properties are discussed on the basis of the molecular interactions between like and unlike molecules existing in the studied mixtures. Generally, negative excess molar volumes and deviations in isentropic compressibility, and positive deviations in refractive index indicate the domination of geometrical effects on deviation of the mixture's behavior from ideal behavior. Efficient packing of smaller ethanol molecules into the interstitial space of cyclic d-limonene molecules leads to contraction of molar volume of the mixture. This is in accordance with the trend of calculated excess properties.

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Volumetrijska i akustična svojstva binarne smeše etanol + d-limonen

Cilj ovog rada jeste ispitivanje molekulske strukture binarne smeše koja sadrži široko upotrebljavani sastojak za davanje ukusa i mirisa, kao što je d-limonen, i s druge strane etanol kao rastvarač dozvoljen u prehrambenoj i kozmetičkoj industriji. Gustine, indeksi refrakcije i brzine zvuka binarnog sistema etanol + d-limonen izmereni su na atmosferskom pritisku i u temperaturnom opsegu T = (288.15 to 323.15) K. Dopunske molarne zapremine, devijacije indeksa refrakcije i devijacije izentropske kompresibilnosti izračunati su iz eksperimentalnih podataka. Na osnovu izračunatih termodinamičkih svojstava data je analiza molekulse strukture ispitivane binarne smeše.

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MH 06

Health risk assessment of potentially toxic elements in vegetables from green market

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Introduction

Vegetables play an important role in human nutrition. They are one of the main sources of nutrients in many parts of the world, because of their low costs and wide availability. The chemical composition of vegetables determines their importance in diet. [1] Numerous studies indicate the high degree of contamination of soil and plants produced in certain agro-ecological conditions, especially near urban and industrial areas where there is a high concentration of heavy metals in the soil.[2-4] Contamination of agricultural soil and crops (fruits, vegetables and grains) with toxic metals such as cadmium, chromium, copper, manganese and nickel poses a serious environmental problem due to their non-biodegradable and persistent nature. The presence of toxic metals in vegetables is of growing concerns since some soils and irrigation waters are polluted.[5-7] Due to the high-level of toxicity and carcinogenicity, arsenic, cadmium, chromium, lead, and mercury have high priority when the public health is considered. Even low levels of exposure to these elements may cause damage to different organs. According to the United States Environmental Protection Agency (U.S. EPA), and the International Agency for Research on Cancer (IARC), these metals are also classified as either ″known″ or ″probable″ human carcinogens based on epidemiological and experimental studies showing an association between exposure and cancer incidence in humans and animals.[8] Iron, copper and zinc are considered as important life elements. Nevertheless, both deficiency and excessive intake of life essential elements can lead to adverse health effects (various acute and chronic disorders).[9]

At each agricultural production site, local production around big cities is very important because city population mostly depends on the supply of vegetables produced in their vicinity. Therefore, markets are mostly supplied by fresh products from production areas (villages) which are closest to the town. Vegetables make an important part of everyday diet in Serbia, and Central Serbia records the highest average consumption when compared to other parts of the national territory.[10] However, the available data on microminerals and toxic metals content in vegetables in Serbia are limited.[11] Given the public concern about food safety, it has become necessary to monitor the quality of different types of food to ensure the benefits from its consumption.

The the main goal of this study was to analyze the content of both the various essential (Co, Cu, Mn, Mo and Zn) and toxic (Al, As, Cd, Cr, Ni, Pb and Sb) elements in vegetables from the largest city market in Čačak, as well as to evaluate the potential health risks for the consumers (in adult population).

Experimental

Vegetable samples (**1**–**12**) of selected species including: **1**–celery root (*Apium graveolens* L.), **2**–onion (*Allium cepa* L. *syn. var. cepa*), **3**–pumpkin (*Cucurbita maxima Duch*.), **4**–carrot (*Daucus carota* L. *ssp. sativus Hoffm*.), **5**–sweet red pepper (*Capsicum annuum* L.), **6**–potato (*Solanum tuberosum* L.), **7**–beet (*Beta vulgaris* L. *ssp. esculenta Salisb*.), **8**–cauliflower (*Brassica* *oleracea* L. *var. botrytis*), **9**–cabbage (*Brassica oleracea* L. *var. capitata*), **10**–zucchini (*Cucurbita pepo* L.), **11**–tomato (*Lycopersicon esculentum Mill.*) and **12**–eggplant (*Solanum melongena* L.) were collected during October 2016 from the central green market in Čačak (Moravica district, Central Serbia), Figure 1.

Studied vegetables were exclusively from producers from the study area. Contents of twelve elements (Al, As, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sb, Zn and Mo) were determined by mean of inductively coupled plasma–optical emission spectrometry (ICP–OES) (ICP–OES Spectroblue, SPECTRO Analytical Instruments GmbH, Germany) using US EPA Method 200.7.[12]

Principal Component Analysis was carried out by PLS ToolBox, v.6.2.1, for MATLAB 7.12.0 (R2011a) as an exploratory data analysis by using a singular value decomposition algorithm and a 0.95 confidence level for Q and T2 Hotelling limits for outliers. All data were autoscaled prior to multivariate analysis.

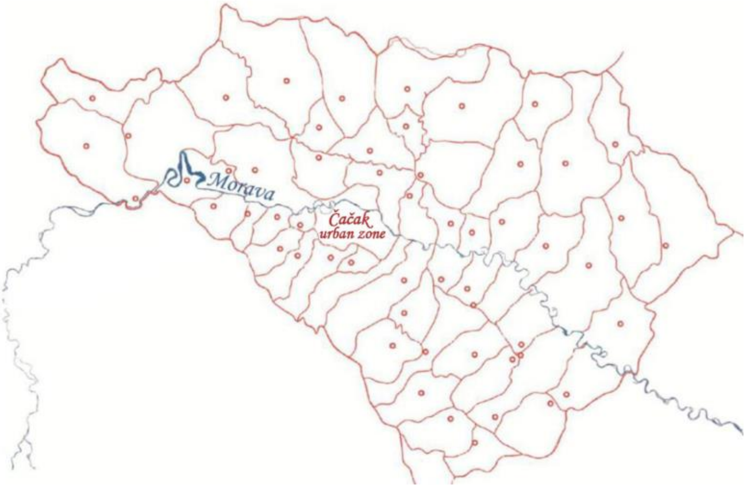

Figure 1. *Study area*

Risk assessment of elements exposure through vegetable consumption was performed and expressed as hazard quotient (HQ) for both acute and long–term risk using equations 1–3, respectively:

$$\mathrm{HQ} = \mathrm{EWI}/\mathrm{PTWI} \qquad (1)$$

where EWI is estimated weekly intake of toxic elements in mg kg^{-1} of body weight (bw) and PTWI is provisional tolerable weekly intake in mg kg^{-1} of body weight, set by Joint FAO/WHO Expert Committee on Food Additives (JECFA).[13,14]

The long-term carcinogenic risk caused by consuming studied vegetables, was determined according to equations 2 and 3.[15]

$$\mathrm{Intake}_{\mathrm{oral}} = (c \times \mathrm{IR} \times \mathrm{EF} \times \mathrm{ED})/(\mathrm{BW} \times \mathrm{AT}) \qquad (2)$$

where c is concentration of the studied metals (mg kg^{-1}); IR is average vegetable consumption–0.345 kg or 0.100 kg per day [8]; EF is exposure frequency, i.e. the duration of the year (365 days); ED is average exposure duration (30 years); BW is average body weight of adult person in Serbia (man–84.3 kg and women–65.0 kg, respectively)[16] and AT is average time of exposure of carcinogenic effect (in this case 10.950 days). HQ$_{\mathrm{oral}}$ represents hazard quotient of carcinogenic risk by oral intake and RfD$_{\mathrm{oral}}$,[17] and was calculated as the ratio between oral intake of toxic metals and RfD (eq. 3).

$$\mathrm{HQ}_{\mathrm{oral}} = \mathrm{Intake}_{\mathrm{oral}}/RfD_{\mathrm{oral}} \qquad (3).$$

Results and discussion

In the area of sampling there is a long tradition of cultivation and consumption of vegetables, and agriculture is one of the primary branches of economy. Urban population is oriented to the supply of vegetables from the city green market. At the beginning of the autumn, the studied plant species from green market are mostly purchased for fresh use, as well as for the preparation of homemade processed food for winter. Recent literature data indicate that the most frequently consumed vegetables in Central Serbia are potatoes, cabbage, sweet peppers and root vegetables (carrots, beet and celery).[8]

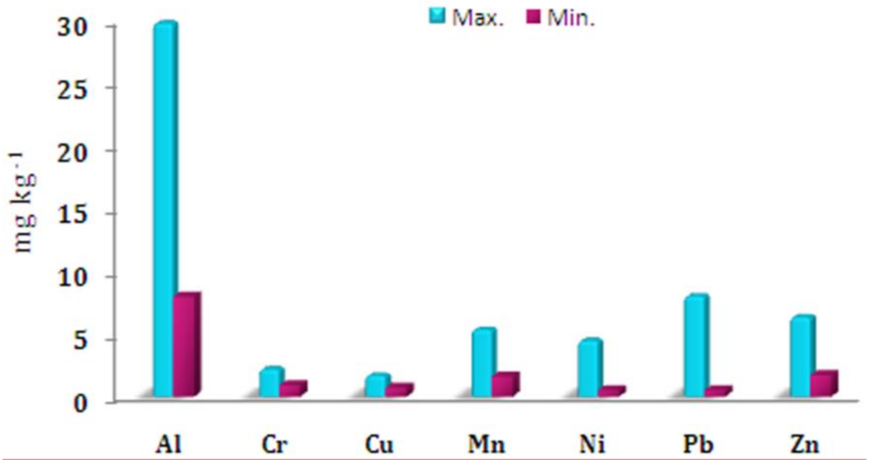

Figure 2. *Maximum and minimum concentrations of detected elements (mg kg^{-1})*

Maximum and minimum concentrations (mg kg^{-1}) of detected elements Al, Cr, Cu, Mn, Ni, Pb and Zn, in studied vegetables are presented in Figure 2. Concentrations of As, Cd, Co, Sb and Mo were below the limit of detection (LOD). Toxic metals accumulated in vegetables, especially in their edible parts, and consumed by humans could cause a range of health problem.[18,19] The humans′ body mechanism cannot detoxify toxic metals, instead they tend to accumulate in different tissues and threaten the health of humans.[20]

Based on the content of toxic elements in the vegetable samples, Principal Component Analysis (PCA) was conducted in order to get a detailed insight into the data structure and identify similarities and specificities of object groupings. PCA resulted in a two-component model, explaining 70.33 % of total variance in the data. The results obtained through PCA, based on the content of aluminium, chromium, copper, manganese, nickel, lead and zinc in the vegetable samples are shown in Figure 3.

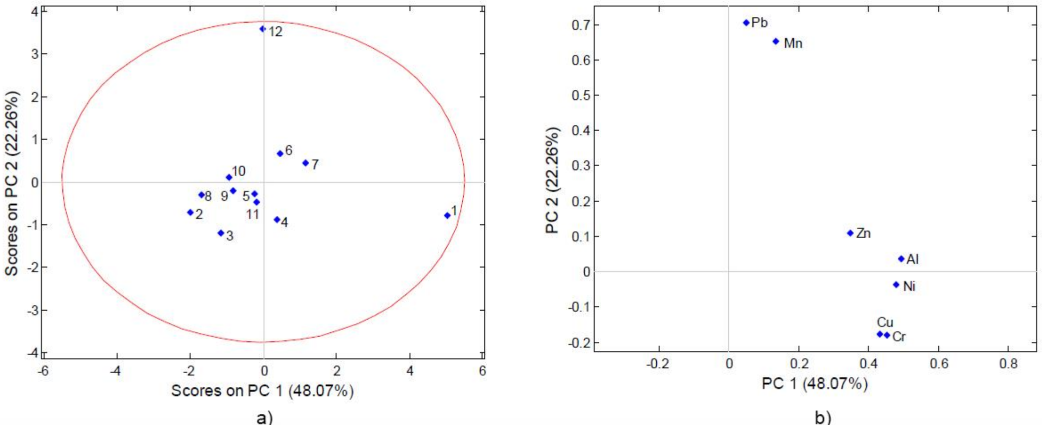

Figure 3. *PCA, score plot a) and loading plot b)*

Three groups of objects stood out in the score plot (Figure 3a). Celery root (sample **1**) was separated from the remaining samples and formed a separate group (group I). The second group consists of onion, pumpkin, carrot, sweet red pepper, potato, beet, cauliflower, cabbage, zucchini and tomato (samples **2**–**11**, Figure 3a), and within this group of objects additional two sub-groups can be separated. The first subgroup (IIa) consists of samples of onion, cauliflower, cabbage, carrot, sweet peppers, zucchini, tomato and pumpkin, while the second one (IIb) consists of potato and beet samples. Eggplant (sample **12**) stood out as a separate object (group III, Figure 3a). The separation of the first group of objects, i.e. the separation of the celery sample from the rest, was positively most strongly influenced along the PC1 axis by aluminum, but also nickel, chromium, copper and zinc, which was in accordance to the fact that the concentration of these elements is the highest in this sample (Figure 3b). The separation of the second group of objects was positively influenced by nickel, manganese and zinc, which, along with copper, also contributed to the separation of the second group into two subgroups – IIa and IIb (Figure 3a). Subgroups were separated based on the nickel, manganese and zinc contents, the concentration of which is higher in samples of the IIb subgroup, but also based on the concentration of copper, which was measured in samples of the IIb subgroup, while in the most of samples of the IIa subgroup being under the detection limit (Figure 3). The third group of objects (eggplant sample) was positively most strongly influenced along the PC2 axis by lead and manganese, which was in accordance with the fact that concentrations of these elements were the highest in this sample. The separation was negatively influenced along the PC2 axis by copper and chromium, which corresponded to the fact that these elements were below detection limits in this sample (Figure 3b).

Exposure of population in study area to toxic elements and essential elements with potential toxic effects was estimated according to the average vegetable consumption for adults, and estimated weekly intake (EWI) of analyzed elements was calculated. The average EWIs for aluminum, chromium, copper, manganese, nickel, lead, and zinc were 0.392, 0.010, 0.015, 0.096, 0.019, 0.038 and 0.124 mg kg^{-1}, respectively. The potential human health risk assessment was done by considering estimated weekly intake of Al, Cr, Cu, Ni, Pb and Zn from consuming studied vegetables, and values of provisional tolerable weekly intake (PTWI),[14] and expressed as hazard quotient (HQ), Table 1.

According to Leung et al. HQ<1 is safe for the exposed population; HQ>1 denotes the probability of negative health impacts, while HQ>10 is considered that high chronic risk occur.[21] The average HQ of toxic elements through vegetable consumption in the study area was found in order of Pb>Ni>Cr>Zn>Al>Cu.

Table 1. Hazard quotient (HQ) for Al, Cr, Cu, Ni, Pb and Zn in vegetables

No.		***HQ***					
		Al	*Cr*	*Cu*	*Ni*	*Pb*	*Zn*
1	Celery root	0.14	0.88	0.03	1.20	0.56	0.14
2	Onion	0.04	0	0	0.16	0.18	0.04
3	Pumpkin	0.18	0	0.05	0.82	0.89	0.15
4	Carrot	0.22	1.37	0.05	0.83	0.77	0.36
5	Red sweet pepper	0.27	0	0	0.74	0	0.48
6	Potato	0.22	0	0.07	1.01	0.77	0.39
7	Beet	0.21	1.64	0.09	0.46	0.77	0.40
8	Cauliflower	0.13	0	0	0	0.78	0.31
9	Cabbage	0.26	1.24	0	0	1.16	0.14
10	Zucchini	0.22	0	0	0	1.27	0.39
11	Tomato	0.24	0	0.06	0	0.64	0.42
12	Eggplant	0.26	0	0	1.10	10.38	0.39
	HQ$_{\mathbf{average}}$	**0.20**	**0.43**	**0.03**	**0.53**	**1.51**	**0.30**

Hazard quotient for Al, Cu and Zn was in range of 0.04–0.27, 0.03–0.09 and 0.04–0.48, respectively. Regarding these elements, no obvious health risk could be considered, and studied vegetables are assumed to be quite safe. On the basis of estimated weekly intakes of toxic elements, it can be concluded that HQ exceeded the limit of health safety in case of chromium, nickel and lead for some vegetable species. According to the results obtained for HQ, it can be noted that values obtained for chromium (1.24, 1.37 and 1.64), nickel (1.01, 1.10 and 1.20), and lead (1.16 and 1.27), indicate a high risk probability for human health (HQ>1), especially for people who consume celery, carrot, potato, beet, cabbage, zucchini and eggplant on daily basis. High acute risk could be considered in case of lead in eggplant, with HQ=10.38, Table 1.

In addition to acute (weekly) potential health risk long-term health risk was also calculated, and results expressed through HQ are presented in Table 2.

Table 2. Long-term hazard quotient (HQ) with RfD$_{oral}$ values for Al, Cr, Cu, Mn, Ni, Pb and Zn in vegetables

		Al	Cr	Cu	Mn	Ni	Pb	Zn
No.	**RfD**, mg kg^{-1}	**1**	**0.003**	**0.027**	**0.024**	**0.02**	**0.0035**	**0.3**
					HQ			
1	Celery root	0.04	0.98	0.08	0.16	0.30	0.57	0.03
2	Onion	0.01	0	0	0.13	0.04	0.19	0.01
3	Pumpkin	0.05	0	0.12	0.31	0.21	0.91	0.03
4	Carrot	0.06	1.52	0.14	0.46	0.21	0.79	0.07
5	Sweet red pepper	0.09	0	0	0.44	0.18	0.44	0.07
6	Potato	0.05	0	0.19	0.76	0.24	1.57	0.08
7	Beet	0.06	1.82	0.24	1.01	0.11	0.79	0.08
8	Cauliflower	0.04	0	0	0.52	0	0.79	0.06
9	Cabbage	0.05	0.70	0	0.56	0	0.59	0.03
10	Zucchini	0.06	0	0	0.59	0	1.30	0.08
11	Tomato	0.07	0	0.15	0.51	0	0.65	0.08
12	Eggplant	0.07	0	0	1.03	0.27	10.60	0.07
	HQ$_{average}$	**0.05**	**1.25**	**0.15**	**0.54**	**0.20**	**1.60**	**0.06**

The average long-term hazard quotient (HQ) of toxic elements was in the order of Pb>Cr>Mn>Ni>>Cu>Zn>Al. In case of most toxic elements, it can be observed that there is a significant or high long-term health risk for people who consume studied vegetables. Consummation of carrot and beet could present a great risk due to the chromium content, since HQ was higher than 1, and close to this value in case of celery. Similar results were in case of manganese for people who consume beet (HQ=1.01) and eggplant (HQ=1.03). The use of potatos (HQ=1.57) and zucchini (HQ=1.3) from this green market contaminated with lead carries a greater risk for the development of malignancies, whereas in case of eggplant (HQ =10.60) health risk can be characterized as extremely high.

In some cases it may be noted that a high risk is associated with the use of the above-ground and in some vegetables with the use of an underground part of the plant, i.e. tuber. It can be assumed that there were two possible contamination pathways; in case of underground parts of plants, toxic metals probably reached from the ground naturally abundant with these minerals or was contaminated. On the other hand, for the above-ground parts of vegetables, contamination was likely anthropogenic (due to nearby industrial zone or roads). Generally, in case of all studied vegetables long-term health risk is significant (if someone consumes more than the calculated average intake of vegetables) since there is a possibility of more than eight people (in a thousand) to suffer from cancer.[22]

Conclusions

The average estimated weekly intakes for Cr, Ni and Pb in some vegetables were considerably higher than the safe limits set by FAO/WHO. Results obtained for HQ in the human health risk assessment indicated high risk probability (HQ >1) for chromium, nickel and lead, especially for people who consume celery, carrot, beet, potato, cabbage, zucchini and eggplant on daily basis. For population which consumes carrot, beet, potato, zucchini and eggplant long-term risk was indicated regarding to content of chromium, manganese and lead (HQ>1). Both, acute (HQ=10.38) and long-term (HQ =10.60) health risk can be characterized as extremely high in case of eggplant. Given the fact that vegetable is important part of everyday diet for Serbian people, the evaluation of exposure to toxic elements through vegetable consumption is advisable.

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Рецензирање, кључни елемент процеса евалуације научног сазнања: Како то добро урадити?

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Извод: *Рецензирање представља незаобилазни део поступка публиковања резултата научног истраживања. Може се рећи да је оно срж тог процеса, јер обезбеђује поуздано и тачно презентовање, за јавност корисног, оригиналног научног сазнања. Свакако постоје многи недостаци тог поступка, иако су промене којима је током историје подвргаван тежиле да га унапреде. Последњих година су напори да се рецензирање учини поузданијим, објективнијим и без предрасуда већи него икада. У оквиру тих напора, једна од најзначајнијих активности је образовање, пре свега младих научника, за обављање тог веома одговорног и важног задатка. Овај текст је допринос тим напорима, имајући у виду да у Србији не постоји ниједан институционализовани облик таквог образовања. Поред описа процеса рецензирања, текст се бави етичким принципима добре праксе рецензирања, а након тога покушава да нађе одговор на питање:* ***Како коректно, објективно и непристрасно рецензирати научни рад?*** *На крају, садржи и сугестије за писање коректног рецензентског извештаја.*

Увод

Научни резултати практично „не постоје“ све док се у писаној форми не објаве у научном часопису и тако презентују научној заједници и јавности. Да би био објављен, резултат мора бити стручно оцењен од стране експерата - рецензената (енглески „Reviewer“ или „Referee“). Зато сумње и коментари изражени од стране рецензената заузимају важно место у целокупном научном процесу[1]. Од рецензената се очекује компетентност, да поседују довољно знања и искуства да процене да ли су у описаном истраживању коришћене прикладне методе и/или експерименти, да ли су добијени резултати тачни и поуздани, а интерпретација резултата смислена и у складу са постојећим знањима.

Са друге стране, за ауторе публиковање резултата представља верификацију ваљаности и корисности спроведених истраживања, а тиме је од пресудног значаја за њихов реноме, каријеру, па и материјални статус. Зато је рецензирање веома одговоран и друштвено значајан задатак и рецензент га мора извршити професионално и стручно уз поштовање моралних и етичких принципа.,.

Проналажење довољно компетентног рецензента, спремног и вољног да квалитетно и на време оцени рад поднет у часопис је велики изазов за уреднике. Они морају узети у обзир квалификације потенцијалног рецензента, његов научни опус, избегавајући да буде изложен сукобу интереса, али и мотивисати га да прихвати да рецензира рад.

Последњих година, уредници се све чешће обраћају млађим научницима, претпостављајући да они имају више времена и мотива да на време ураде квалитетну рецензију. Поред тога, експерти често прихватају захтеве за рецензирање препуштајући их млађим сарадницима чији су ментори, уз различите нивое увида и супервизије њихових извештаја. Млађим научницима, пред којима је тек каријера, атрактивна је могућност да својим знањем, коментарима и оценама могу утицати на развој одређене научне дисциплине и/или правца.

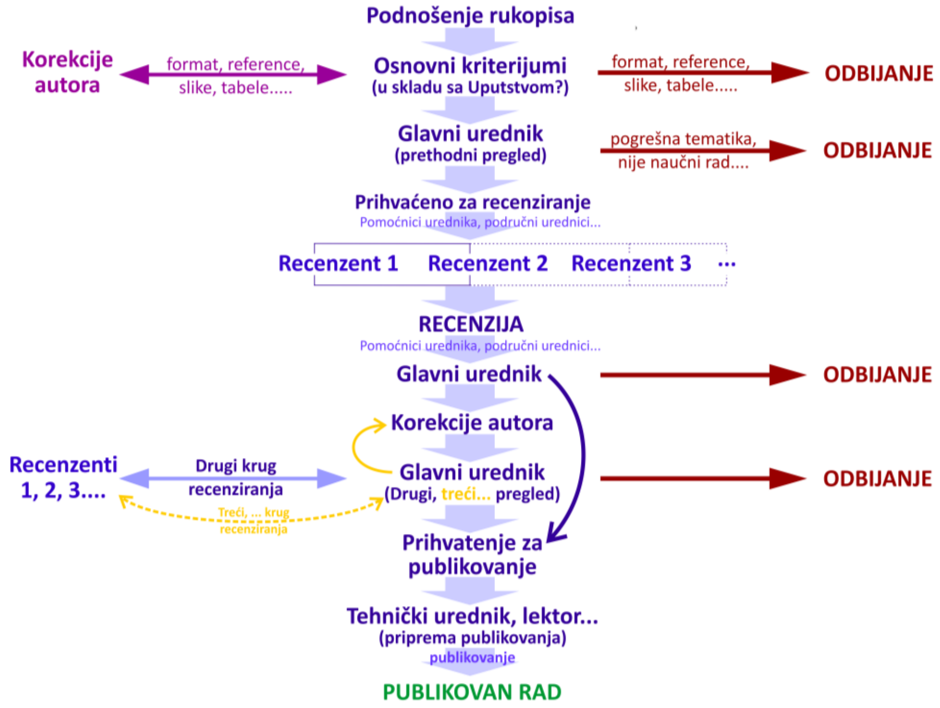
Како ни у свету, а поготово у Србији, не постоји систематско образовање за рецензирање, млади се уче од својих ментора (који су исто учили од својих), размењујући искуства са колегама или једноставно путем покушаја и грешака. Уредницима су, пак, потребне рецензије које задовољавају извесна правила, у форми која се може лако тумачити. Да би се то обезбедило, издавачи и/или уредници све чешће креирају упутстава за рецензирање, часописи објављују препоруке, па и кратке електронске курсеве како сачинити добру рецензију[2-4].

Овај текст, заснован на прегледу литературе и искуству аутора, је основни приручник како рецензирати научни рад, поштујући принципе писања квалитетне рецензије.

Врсте рецензирања и стандардни поступак

Процес рецензирања (Слика 1) се развијао кроз историју, од првих, унутрашњих рецензија (у оквиру уске групе експерата блиске издавачу), које је почело да практикује Краљевско друштво из Единбурга, 1731[5], до данашње три врсте рецензирања:

- **Једноструко слепо** („Single Blind“) - Рецензенти знају идентитет аутора, али аутори не знају идентитет рецензената, данас најчешће коришћени облик рецензирања.
- **Двоструко слепо** („Double Blind“) - Рецензенти и аутори међусобно не знају идентитете.
- **Отворено** („Open Review“) - Цео поступак је отворен, сви идентитет су познати свима.



***Слика 1**. Основне фазе процеса публиковања и рецензирања научног рада*

Свака од ових врста може имати и додатне елементе:

- *Трансфер рецензије* („Transferable Review“)[6] – Рецензије могу да се пренесу у други часопис, по предлогу уредника и уз сагласност аутора.
- *Колаборативна рецензија* („Collaborative Review“)[7] – два или више рецензената заједнички процењују рад и сачињавају један, заједнички извештај и предлог, или два или више рецензената сарађују са ауторима у модификовању рада док се не достигне квалитет погодан за публиковање.

- *Рецензије након публиковања* („Post Publication Review“)[8] - поступак рецензирања се одвија након публиковања, у облику коментара, дискусионих форума или слично, доступан је свима, па је битно знати ко је њихов аутор (колико су „рецензент“ и његово мишљење поуздани).

Без обзир на врсту рецензије, поступак публиковања и рецензије рада је, уз могуће незнатне варијације, у складу са схемом на Слици 1. (детаљнији опис је доступан у нашем публикованом раду[9])

Етика рецензирања

Добијен позив да рецензирање рада значи да сте публиковали неколико радова (или бар један) у области којој припада и рад за који сте позив добили. И не само то, већ и да вас препознају као експерта у области, да поседујете знање довољно да оцените други рад. Квалитет радова које сте објавили су потврдили рецензенти који су уложили значајан труд и потрошили доста времена да би оценили рад и сугерисали вам правац у ком га треба поправити пре прихватања (обично су дораде потребне). Без њих не бисте имали углед стручњака и стекли компетентност који су вас препоручили за рецензента. Сада се од вас очекује исто, да компетентно, коректно и брзо оцените рад неког другог истраживача, као и да му помогнете да рад учини још бољим. Позив за рецензирање је стога част, признање али и научна, професионална и морална обавеза. Чак ни то што у данашњој науци рецензирање није довољно признато и вредновано не сме бити мотив да се позив одбије без ваљаних и оправданих разлога. Напротив! Наводимо основне етичке вредности које се морају имати у виду при рецензирању научног рада.

Непристрасност и предрасуде

Без обзира на врсту рецензије, без обзира из којег часописа је стигао позив за рецензију рада, без обзира на идентитет и порекло аутора, рецензија МОРА БИТИ ИСТОВЕТНА - КВАЛИТЕТНА. Другим речима, на садржај рецензије не сме утицати ни реноме часописа ни реноме аутора, ништа осим презентованог истраживања, резултата и начина како су тумачени и објашњени. Циљ сваког рецензирања је добити објективну процену рада. Рецензенту је често немогуће да занемари идентитет аутора или институције, порекло, пол или националност аутора, што може ограничити објективност рецензента. Етички је да рецензент обавести уредника ако постоје елементи који би могли субјективно утицати на процену рада, и у таквим ситуацијама је препоручљиво одбити позив за рецензију.

Компетентност: Рецензент мора проценити да ли је заиста довољно компетентан да оцени рад, да ли тема рада заиста одговара његовој стручности и да ли поседује довољан ниво знања о њој. Некада су само делови рада изван компетентности рецензента и ако се прихвати рецензирање таквог рада, јасно се морају назначити делови за чију процену треба тражити мишљење других, компетентнијих. Догађа се да рецензент сам пронађе колегу који може урадити процену ових делова, те је у тим случајевима коректно у извештају навести ко је све учествовао у рецензирању и тиме обезбедити да и други добију признање за свој рад (и вољу да то ураде поново).

Због питања компетентности, неки часописи при позиву за рецензирање дају три опције одговора: прихватам да рецензирам, одбијам да рецензирам и нисам компетентан за област (или слично).

Сукоб интереса: Постоје научне области које су врло уске, са малим бројем истраживача и часописа који се баве одређеним темама, па је врло тешко ангажовати компетентног рецензента који није (макар некада) био сарадник или опонент некоме од аутора. Данас се доста истражује на тему мрежа које се формирају између истраживачких група и последица њиховог постојања на објављивање, цитираност и утицајност у тој научној области. Очекује се да рецензент који је у било каквом сукобу интереса, са бар једним аутором, одбије позив да рецензира рад.

Време: Истраживања су показала да је препоручљиво бар два пута прочитати рад (једном површније, а други пут детаљно), да је за квалитетно рецензирање потребно више сати, некад и више дана.[10] Пре прихватања позива мора се добро проценити да ли се располаже довољним временом да се рецензија уради квалитетно и у року. Брзе, површне и непотпуне рецензије чине штету и ауторима, и часопису и рецензенту.

Уколико морате одбити позив за рецензирање, из било ког разлога, колегијално је и професионално, а уредник то и очекује, предложити бар једног колегу који би могао оценити рад. Најгора варијанта, која се често догађа, је да рецензент не прихвати да уради рецензију, а ни не обавести уредника о томе. Тиме се непотребно продужава време за преглед рада. Ако не можете да рецензирате, обавестите уредника.

Ауторитативност и анонимност: Објективно рецензирање не би требало да узима у обзир никакве ауторитете, академску или било какву другу хијерархију. Рецензент би требало да буде неприкосновени ауторитет, чак и за нобеловца чији рад рецензира. Нажалост, у пракси то није увек случај, посебно у отвореном типу рецензирања. Млађи рецензенти, уколико њихова каријера и напредовање зависе од старијих чије радове процењују, испољавају већу уздржаност да нешто оцене негативно.[11] Ако је рецензија једноструко слепа, рецензент остаје аноniman, и то му даје већу слободу да буде објективан.

Поверење: Позивом за рецензирање уредник рецензенту указује поверење и рецензент треба да га поштује. Разговори о раду са другим особама, поготово са ауторима рада, за рецензента су недопустиви. То не искључује консултације и/или прибављање мишљења других (колега, сарадника) о коришћеним методама и резултатима приказаним у раду, али без откривања идентитета аутора. Једина особа са којом рецензент слободно комуницира у вези са радом је уредник. Поред тога, рецензент не сме да користи информације и податке из рада ког рецензира пре него што се рад публикује.

Критичка, објективна и добра рецензија

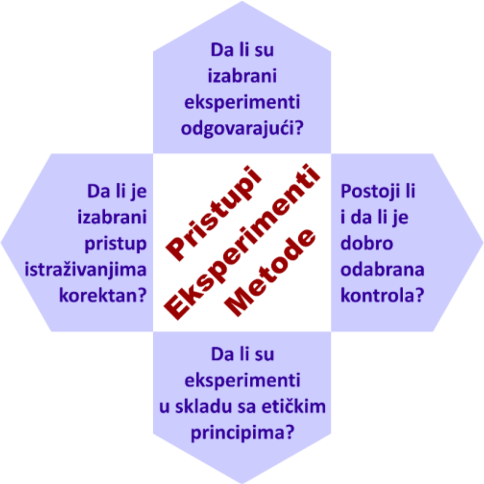
Основа рецензирања је у пажљивом и „правилном“ читању рукописа (што важи када год се чита научни рад). Читање научног рада је потпуно другачији процес од читања чланка о науци у блогу или новинама. Треба правити белешке, рад прочитати више пута, а најчешће прегледати и друге публикације, да би се разјаснили детаљи и/или стекла знања која ће помоћи у разумевању текста. Читање научног рада захтева много времена, али стрпљивим стицањем искуства тај процес се може убрзати.[12]

Предуслов за позитивну рецензију је добро написан рад, а препоруке како то учинити садрже раније публиковани радови.[8,13]. Како се сваки научни рад састоји из више стандардних делова: Увод – Експериментални део/Методе, Резултати и дискусија, Закључак; и рецензија рада треба да оцени сваку од ових целина.

Увод: Рецензент треба да оцени да ли је описано истраживање оригинално и актуелно, или су презентовани резултати већ доступни. Неоригинално, неинтересантно и небитно истраживање не занима читаоце (па ни часопис). Презентовани материјал треба да је допринос науци, мора постојати оправдана потреба за сазнањем које се стиче из резултата истраживања, и циљ истраживања мора бити јасно дефинисан (Слика 2). Питање које рецензент може себи поставити (а могао би и сам аутор) јесте – да ли је и зашто важно да колеге и друштво сазнају о резултатима тог истраживања? Том циљу треба да помогне преглед литературе и публикованих резултата сличних истраживања, који мора бити свеобухватан и релевантан. На основу увода треба, такође, оценити да ли тематика истраживања одговара тематици часописа.

Експерименти, методи, приступи: Изабрани експерименти/методе/технике морају бити одговарајући, а приступ истраживањима коректан. Ако је потребна контрола у експериментима, она мора бити добро изабрана (Слика 3). Уколико истраживања обухватају експерименте на људима, животињама или узорцима добијеним од њих, морају бити поштовани одговарајући, дефинисани, етички принципи (већина часописа од аутора захтева при предаји рада потврду придржавања тих принципа). Увек је добро консултовати литературу, колеге или сараднике (поверљиво), ако рецензент недовољно познаје коришћене методе или технике, или уколико му нису блиска правила етичких ограничења. Уколико се процени да је неопходно, од аутора се може тражити и дорада, другачији приступ, извођење другачијих експеримената.

Слика 2



Слика 3

Слика 4

Слика 5

Резултати, интерпретација, дискусија: Ово је суштина рада и она захтева најдетаљнији преглед и оцену. Резултати морају бити јасно и логично приказани, праћење једноставно, интерпретација убедљива и поткрепљена доказима, а дискусија смислена, у складу са полазном хипотезом и циљем. Слике и табеле треба да су прикладне за разумевање поруке аутора, без непотребних детаља, али довољно детаљне да би се резултат разумео (Слика 4). Сматра се да је људском оку и уму најлакше да прати резултате приказане сликом, па табеларно треба приказати само податке који се не могу ваљано представити графички. На рецензенту је да процени могу ли се резултати приказати боље него што је учињено.

Закључци: Као део рада који сумира истраживање и његове резултате, који извлачи „вишу вредност“ из података, закључци морају бити јасно саопштени, директно повезани са постављеним циљем, логично проистицати из резултата, поткрепљени подацима и бити у складу са постојећим знањима (Слика 5). Извод и закључци морају дати читаоцу јасну слику зашто и како су истраживања извршена и који је допринос тих истраживања науци.

Изглед рецензије

Већина часописа рецензентима на располагање ставља *Рецензентски лист* са дефинисаним питањима, на која треба одговорити избором једне од понуђених опција, које уреднику помажу у доношењу коначне одлуке, а ауторима у евентуалним исправкама рада. По правилу, рецензентски лист садржи и простор за унос текста у слободној форми, један намењен ауторима (и уреднику) и други само за уредника (поверљива комуникација). Пожељно је да рецензент и ауторима и уреднику кроз те текстове образложи одговоре и укаже им како треба кориговати рукопис, да што детаљније опише сваку своју примедбу, сугестију, запажање. Ни аутор, ни уредник не треба да остану у недоумици, морају тачно знати шта рецензент сматра да је (ако је) потребно учинити како би рад, по његовом мишљењу, био бољи и прихватљив за публиковање. Није неуобичајено да се примедбе и сугестије унесу и у сам текст рукописа (уз праћење корекција - „Track changes“).

Препознавање значаја и друштвено вредновање рецензентског рада

Вредновање и валоризација рада рецензената недовољни су и несразмерни значају који рецензирање има. Последњих година се свест о томе мења, а важност рецензирања добија нову димензију у светлу растућег броја препознатих плагијата, фалсификата и измишљених резултата. Срећом, појавили су се различити видови вредновања и друштвених признања тог рада, који истовремено повећавају мотивисаност за прихватање овог захтевног посла. Велики издавачи, али и независни сервиси развијају подстицајне програме и посебне weб платформе намењене одавању признања рецензентим[14], а ми ћемо овде само кратко набројати неке најзначајније: **BioMed Central** (BMC) и **Springer**[15]; **Publons** (https://publons.com/about/mission/); **ReviewerCredits** (http://reviewercredits.com/); **Elsevier** (https://www.reviewerrecognition.elsevier.com/); **ScienceOpen** (https://www.scienceopen.com/). За детаље погледајте наш публикован рад[13] и/или посетите наведене Интернет странице.

На крају, желимо да упутимо поруку свим постојећим и новим рецензентима: Рецензирајте имајући у виду какву рецензију ви лично никако не бисте волели да добијете!

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Peer review, a key element in the process of evaluation of the scientific knowledge: How to perform it properly?

Peer review is a key element in the process of publication of scientific results, as it provides a reliable and accurate presentation of original scientific knowledge, useful for the entire society. Despite of many shortages which this evaluation has, it is still an indispensable part of the process of scientific publishing. In recent years, efforts have been made to improve peer review to become more reliable, objective and with less prejudices than before. To achieve this goal, one of the most important activities is education, primarily of the young scientists, to perform this responsible and important task. This text is a contribution to these efforts, taking into consideration that there is no systematic and institutionalized education for performing such task. After description of the review process itself, the text deals with ethical principles of good reviewing practice, and tries to offer an answer to the question: ***How to review a scientific work correctly, objectively and impartially****? At the end, it also contains suggestions for writing a correct review report.*