

# Influence of corrosive media on elution of titanium alloy metal ions

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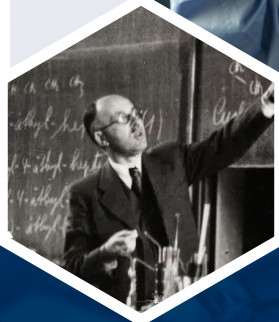


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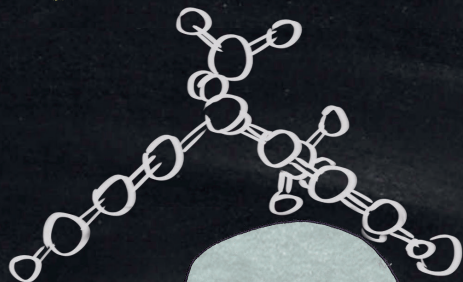
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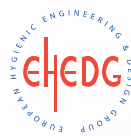
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**Plenarna predavanja/*Plenary lectures***

## **DE NOVO MECHANISTIC DESIGN OF CATALYSTS, WITH A HISTORICAL TWIST**

Peter Chen

Laboratory of Organic Chemistry, ETH Zurich, Vladimir-Prelog-Weg 1-5/10, 8093 Zurich,  
Switzerland

The lecture covers the story of several novel homogeneous catalysts for the electrophilic cyclopropanation of olefins, as a case study of mechanistic design as a guiding principle. We show how a combination of physical and chemical techniques can bring us close enough that we can discover new reactivity, even if the designs are never perfect. Nevertheless, of the gold, nickel, and palladium systems, all function at least well enough for further development, and one, the palladium catalyst, is competitive with the previous best reactions used in industrial production. Lastly, the story includes a very human element from which we can learn much about creativity and innovation.

## N-BENZIMIDAZOLE AND IMIDAZO[4,5-*b*]PYRIDINE DERIVED TUBULINE POLYMERIZATION INHIBITORS

Marijana Hranjec

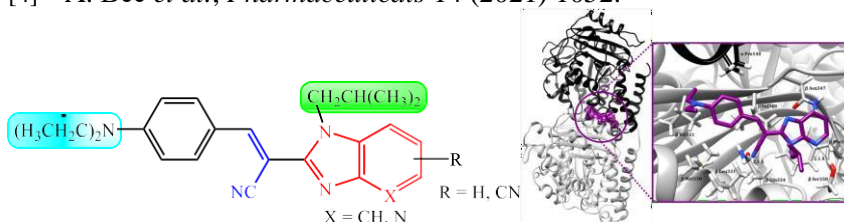
Department of Organic Chemistry, Faculty of Chemical Engineering and Technology,  
University of Zagreb, Marulićev trg 19, 10 000 Zagreb, Croatia

Nitrogen heterocycles, due to their widespread applications and interesting chemical, biological and pharmacological features, are nowadays still contributing extensively in the current organic and medicinal chemistry in the rational design of novel biologically active molecules [1]. Benzazole scaffold has become a fundamental building block widely incorporated in the structure of numerous natural, and synthetic molecules displaying versatile biological activities [2]. The structural similarity of benzimidazole and imidazo[4,5-*b*]pyridine nuclei with natural purines, allowed their optimization to obtain more efficient and selective molecules which could play a crucial role in the function of many biologically important molecules, being thus of particular interest in pharmaceutical industry.

Within this lecture, I will present the design, synthesis, and antiproliferative activity *in vitro* of novel *N*-benzimidazole and imidazo[4,5-*b*]pyridine derived acrylonitriles [3, 4]. The chosen lead compounds were tested *in vitro* for tubulin polymerization inhibition as a possible mechanism of biological action. Immunofluorescence staining and tubulin polymerization assays confirmed tubulin as the main target which was also supported by the computational analysis. In addition, some compounds have proven to be very selective, non-cytotoxic and thus, a very promising antitumoral agents for further investigation.

**Keywords:** antitumor activity, benzimidazoles, imidazo[4,5-*b*]pyridines, tubulines

- [1] W. Akhtar *et al.*, *Eur. J. Med. Chem.* 126 (2017) 157.
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## NONPOLAR COMPOUNDS OF MACROALGAE

Igor Jerković

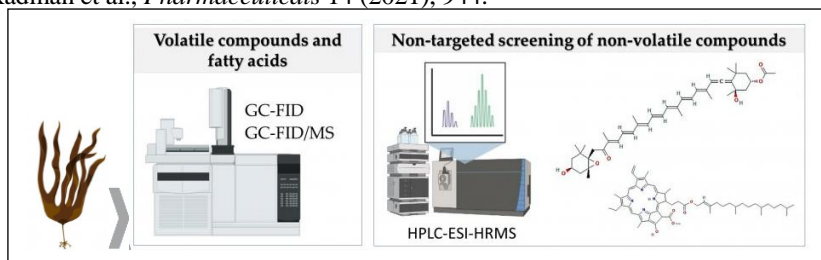
Zavod za organsku kemiju, Kemijsko-tehnološki fakultet, Sveučilište u Splitu,  
Ruđera Boškovića 35, 21000 Split, Croatia

The main aims of the research [1,2] were to: a) identify and compare volatile organic compounds (VOCs) of fresh (Fr) and air dried (Dr) macroalgae obtained by headspace solid-phase microextraction (HS-SPME) and hydrodistillation (HD) analyzed by gas chromatography and mass spectrometry (GC-MS); b) determine fatty acids (FAs) composition of freeze-dried macroalgae (Fd) by gas chromatography with flame ionization detector (GC-FID) after derivatization as methyl esters; c) determine the composition of less polar fractions of Fd samples by high-performance liquid chromatography–high-resolution mass spectrometry with electrospray ionization (UHPLC-ESI-HRMS). The major VOCs, depending on the macroalgal species, were: mono- and sesquiterpenes, alkanes and other aliphatic compounds (including C<sub>11</sub>-hydrocarbons), C<sub>13</sub>-norisoprenoids, others. Significant changes of VOCs were found after drying strongly depending on the macroalgal species. These changes could influence the chemotaxonomy markers. In general, ω6 FAs were present in higher content than ω3 FAs pointing macroalgae as a good source of dietary polyunsaturated FAs. After fractionation by solid-phase extraction (SPE), two nonpolar fractions were obtained. The major compounds determined by UHPLC-ESI-HRMS in the fractions were: chlorophyll derivatives (pheophytin *a*), fatty acid glycerides and related compounds, terpenes, steroids and carotenoids (fucoxanthin). The antioxidant activity of the fractions was investigated by *in vivo* and *in vitro* assays indicating macroalgae as the potent source of natural antioxidants [1,2]. The research was funded by the Croatian Government and the European Union through the project Bioprospecting of the Adriatic Sea (K.K.01.1.1.01.001) granted to The Scientific Centre of Excellence for Marine Bioprospecting-BioProCro.

*Ključne riječi:* marine macroalgae, volatiles, fatty acids, pigments

[1] I. Jerković et al., *Mar. Drugs* 19 (2021), 235.

[2] S. Radman et al., *Pharmaceuticals* 14 (2021), 944.



## OLEAGINOUS YEASTS FOR BIOCHEMICALS, FEED AND FOOD FROM LOW VALUE RESIDUES

Volkmar Passoth, Jule Brandenburg, Mikołaj Chmielarz, Giselle Martín-Hernandez, Yashaswini Nagaraj, Bettina Müller, Johanna Blomqvist  
Department of Molecular Sciences, Swedish University of Agricultural Sciences, Box 7015,  
SE-75007 Uppsala, Sweden

Yeast lipids produced from lignocellulose and crude glycerol can serve as sustainable alternatives to vegetable oils, which production is frequently accompanied with monocultures, land use changes, or rain forest clearings. We aim to understand the physiology of lipid production by oleaginous yeasts, optimise the production and establish novel applications of microbial lipid compounds.

We have established methods for fermentation and intracellular lipid quantification [1,2]. Following the kinetics of lipid accumulation in different strains, we found high variability in lipid formation even between very closely related oleaginous yeast strains on both, wheat straw hydrolysate and crude glycerol. For example, on complete wheat straw hydrolysate we saw that one *Rhodotorula glutinis* strain, when starting assimilating xylose also assimilated the accumulated lipids, while a *Rhodotorula babjevae* strain could accumulate lipids on xylose [3]. We also found that the presence of hemicellulose hydrolysate stimulated glycerol assimilation in both strains [4].

Apart from microbial oil, *R. toruloides* also produces carotenoids. First attempts of extraction using the classical acetone- based method showed that  $\beta$ -carotene is the major carotenoid [5]. However, there are indications that there are also substantial amounts of torulene and torularhodine, which have a very high potential as antioxidants.

To enable a deeper understanding of their physiology, we sequenced a variety of genomes of *Rhodotorula* species. By a combination of long- and short read sequences, we could reconstruct most of the yeast chromosomes [6,7]. We identified 18-21 chromosomes and several circular structures. In general, a high diversity was found and some strains of the same species showed a phylogenetic distance to each other as to those of other species.

1. Chmielarz et al. 2019 Biotechnol Biofuels, 12:169. 2. Shapaval et al. 2019, Biotechnol Biofuels, 12: 140. 3. Brandenburg et al. 2021 Biotechnol Biofuels, 14: 124. 4. Chmielarz et al. 2021 Biotechnol Biofuels, 14: 6. 5. Nagaraj et al. 2022 Fermentation 8: 300. 6. Martín-Hernandez et al. 2022, J Fungi 8: 323. 7. Martín-Hernandez et al. 2021, Genomics 113: 4022-4026



## **APPLIED RESEARCH IN THE FIELD OF POLYMER MORPHOLOGY: FROM TOTAL JOINT REPLACEMENTS TO NOVEL MICROSCOPIC METHODS**

Miroslav Šlouf

Institute of Macromolecular Chemistry CAS, Heyrovsky sq. 2, 16206 Prague, Czech  
Republic

The motto of 19<sup>th</sup> Ružička days conference reads: *Today science – tomorrow industry*. This contribution will introduce key results of two research projects, pursued at the Department of Polymer Morphology, which were successfully transferred to real-life applications.

The first project was focused on monitoring and minimization of UHMWPE wear. UHMWPE (ultra-high molecular weight polyethylene) is a key component of total joint replacements (TJR). UHMWPE wear (micro/nanoparticles released during mutual motion TJR components) is one of the main reasons of TJR failures. A careful optimization of the UHMWPE structure resulted in a material with the improved wear and oxidation resistance that has been employed in the production of TJR's since 2007.

The second project has been connected with recently introduced 2D-array scanning-transmission electron detectors (pixelated STEM) for SEM microscopes. The pixelated STEM detectors yield a 2D-image for each point of 2D-scanning array, which is called 4D-STEM microscopy. Thanks to a long-lasting collaboration with electron microscope manufactures, we managed to develop a method called 4D-STEM/PNBD, which reduces a huge and complex 4D-STEM dataset to a single, standard and easy-to-process 2D-diffraction pattern. This converts modern SEM microscopes to user-friendly powder electron diffractometers and opens quite new possibilities in microscale chemical analysis.

Acknowledgement: TACR TN01000008.

**Pozvana predavanja/*Invited lectures***

**PRIMJENA 3D-TISKANJA U PROIZVODNJI FUNKCIONALNIH  
PROIZVODA NA BAZI MAGINJE (*Arbutus unedo* L.)  
THE USE OF 3D-PRINTING IN THE PRODUCTION OF  
FUNCTIONAL PRODUCTS BASED  
ON STRAWBERRY TREE FRUIT (*Arbutus unedo* L.)**

Anica Bebek Markovinović<sup>1</sup>, Karlo Jurica<sup>2</sup>, Irena Brčić Karačonji<sup>3,4</sup>, Dario Lasić<sup>5</sup>,  
Predrag Putnik<sup>6</sup>, Dora Brdar<sup>1</sup>, **Danijela Bursać Kovačević<sup>1</sup>**

<sup>1</sup>Faculty of Food Technology and Biotechnology, University of Zagreb, Pierottijeva 6, 10000 Zagreb, Croatia

<sup>2</sup>Ministry of the Interior of the Republic of Croatia, Ulica grada Vukovara 33, 10000 Zagreb, Croatia

<sup>3</sup>Institute for Medical Research and Occupational Health, Ksaverska cesta 2, 10000 Zagreb, Croatia

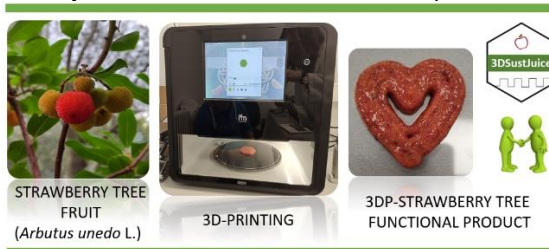
<sup>4</sup>University of Rijeka, Faculty of Health Studies, Viktora Cara Emina 5, 51000 Rijeka, Croatia

<sup>5</sup>Teaching Institute of Public Health Andrija Štampar, Mirogojska 16, 10000 Zagreb, Croatia

<sup>6</sup>University North, Trg Dr. Žarka Dolinara 1, 48000 Koprivnica, Croatia

The Republic of Croatia has a long tradition of fruit growing due to its geographical position, climatic conditions and high quality of fruit crops. Autochthonous fruit varieties are characterized by good morphological/pomological properties, but their nutritional and biological potential has been underestimated, as well as their ability to be processed into functional foods, which are in great demand on the market. The fruit of the strawberry tree (*Arbutus unedo* L.) is an underestimated fruit species in Croatia, and its cultivation and consumption potential has not yet been sufficiently exploited. This fruit is a rich source of health-promoting components such as vitamins, minerals, easily digestible sugars, fiber, and various bioactive compounds with functional value. Therefore, it can be considered as an excellent raw material for the production of functional foods, which are increasingly demanded by consumers. Functional nutrition has largely become the main direction for a healthy lifestyle and is therefore attracting great interest from consumers as well as the food industry, with the aim of improving human health and creating economic wealth in a sustainable way. The existing combination of information and communication solutions is likely to usher in the fourth industrial revolution in the near future, with a focus on additive manufacturing led by 3D printing technology (3DP) in the food industry. 3DP is an emerging digitized technology for producing three-dimensional objects from digital files created layer by layer. Recent advances have led to the ability to create more complex and multi-ingredient food products using 3DP with customized color, shape, flavor, texture, and nutritional content. Since 3DP of food products has great potential to improve the quality and utility of food products, the objective of this work was to investigate the effect of two printing programs with different printing speed, ingredient flow speed, first layer nozzle height and line thickness on the printability of a strawberry tree fruit-based formulation developed by adding different proportions (4, 6, and 8%) of wheat starch (WS) and corn starch (CS). In this study, an extruder-type 3D food printer (Natural Machines Foodini) was used to develop and investigate the applicability of 3DP for functional food production. All samples were analyzed for total phenols, hydroxycinnamic acids, flavonols, flavonoids, anthocyanins, condensed tannins, chlorophylls, and carotenoids, as well as antioxidant capacity (DPPH and FRAP). The type of starch and also the different amounts added played a crucial role in the stability of the bioactive compounds and the antioxidant capacity of the 3DP products. This study suggests that strawberry tree may be a valuable nutrient for the production of novel functional 3DP foods.

**Keywords:** 3D-printing, strawberry tree fruit, functional food, bioactive compounds, antioxidant capacity



## PHOTOCATALYTIC WATER TREATMENT OF CONTAMINANTS OF EMERGING CONCERN USING SOLAR ACTIVE MATERIALS

**Hrvoje Kušić**

Faculty of Chemical Engineering and Technology, University of Zagreb, Marulicev trg 19,  
10000 Zagreb, Croatia

Clean water is nowadays among the highest priorities sustaining economic growth and societal wellbeing. Protection of water resources, of fresh and salt water ecosystems and of the water we drink and bathe in is recognized as one of the cornerstones of environmental protection in Europe. However, (waste)water treatment ((W)WT) technologies are facing increasing requirements and challenges for the removal of recalcitrant organic pollutants present in influents. One of main challenges for common (W)WT plants, based on primary (mechanical) and secondary (biological) treatment, present the contaminants of emerging concern (CEC); chemical, physical or biological compounds that have no regulatory standards (“emerging”), but can cause deleterious effects (“concern”). Moreover, WWTPs are marked as black-spots for spreading various CECs and their upgrade by advanced treatment methods is highly demanded. The potential tertiary treatment methods include advanced physical processes or advanced oxidation/reduction processes. However, the interdependency of energy and water treatment has to be strongly considered; e.g. (waste)water processes should be low energy consumption technologies employing efficient materials, and if possible, renewable energy has to be harvested and/or implemented within.

Accordingly, the application of photocatalytic treatment for CECs remediation employing nano-sized materials active under Solar irradiation seems as the promising solution. Although TiO<sub>2</sub> is the most studied semiconducting material, possessing photocatalytic activity under UV irradiation and chemical and thermal stability, and attractive mechanical properties, the current research focus is on the materials which can effectively harvest broader spectrum of Solar irradiation because TiO<sub>2</sub> band gap of 3.0 – 3.2 eV restrains its excitation by visible and IR portion within Solar spectrum. The recombination rate of photogenerated charges (electron / hole ( $e^-$ )/( $h^+$ ) pairs), causing the decrease in photocatalytic activity, has to be also considered during tailoring effective solar-active catalyst. Strategies for improving these two deficiencies, not only in the case of TiO<sub>2</sub>, but other semiconducting materials as well, include: doping with non-metals, incorporation/deposition of noble metals (ions), and material engineered solutions based on composites formation with transition metals, carbon-based materials (e.g. nanotubes, (reduced) graphene (oxide) – (r)G(O), quantum dots - CQD), dye sensitizers, conductive polymers, and/or other semiconducting materials, presenting viable, attractive and energy efficient options for the utilization of the vast abundance of outdoor Solar irradiation for catalyst activation for water purification, thus leading to the significant decrease of operational costs.

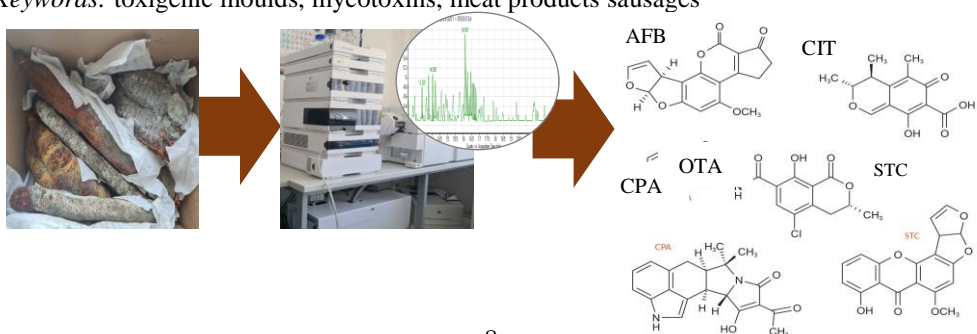
# UVJETI KOJI UTJEČU NA KONTAMINACIJU HRVATSKIH TRADICIONALNIH MESNIH PROIZVODA MIKOTOKSINIMA CONDITIONS INFLUENCING MYCOTOXIN CONTAMINATION OF CROATIAN TRADITIONAL MEAT PRODUCTS

**Jelka Pleadin**, Tina Lešić

Croatian Veterinary Institute, Savska Cesta 143, 10000 Zagreb, Croatia

Mycotoxins are secondary fungal metabolites produced during mould growth, which contaminate a variety of foodstuffs worldwide. They represent a heterogeneous group of substances with diverse and strong pharmacological and toxic effects on humans and animals, including carcinogenicity, teratogenicity, immune toxicity, neurotoxicity, hepatotoxicity, nephrotoxicity, reproductive & developmental toxicity, and so forth. Traditional meat products (TMPs) are consumed worldwide, consumers thereby increasingly demanding their higher-level quality and safety. However, documented cases of mycotoxin occurrence in meat products call for further research into potential contamination sources. TMPs can be contaminated with mycotoxins through three pathways: carry-over effect from farm animals exposed to contaminated feed, contaminated spices and other raw materials used in the production, and mycotoxin-producing moulds present on the surface of dry-cured meat products. In order to establish the contamination source and route more precisely, concentrations of all mycotoxins of relevance for this type of products should be determined. In this study, aflatoxin B<sub>1</sub> (AFB<sub>1</sub>), ochratoxin A (OTA), sterigmatocystin (STC), citrinin (CIT), and cyclopiazonic acid (CPA) were investigated using LC-MS/MS (liquid chromatography-tandem mass spectrometry). Mycotoxins were detected in 27% of 250 analysed meat product samples, with the highest occurrence and concentrations of CPA (13% of samples in concentrations of up to 335.5 µg/kg), followed by OTA (10% of samples) and STC (4% of samples). No contamination with AFB<sub>1</sub> and CIT was observed. The study revealed a rather high percentage of positive dry-fermented sausages in comparison with dry-cured meat products, indicating a possible contamination of spices added to the sausages. Meat products' contamination strongly depends on household hygienic conditions and regional weather, which influence the growth of toxicogenic moulds on the products' surfaces and result in mycotoxin contamination of TMPs.

**Keywords:** toxigenic moulds, mycotoxins, meat products sausages



## SAMOOBNAVLJANJE ORGANOGELOVA BILJNIH ULJA I W/O EMULZIJA SELF-HEALING ORGANOGELATORS OF VEGETABLE OIL AND W/O EMULSIONS

**Nataša Šijaković Vujičić**, Ivanka Jerić, Josipa Suć Sajko, Petra Radošević,  
Lidija Brkljačić and Ivona Kurečić

Division of Organic Chemistry, Ruđer Bošković Institute, Bijenička 54, 10000 Zagreb,  
Croatia

The powerful applicability of oil gelators is envisaged in food, cosmetics, pharmaceutical industry, paints, coatings, and agrochemicals. Concerning regulations requiring the elimination of saturated fats, rising concerns among consumers health and ecological damage caused by palm oil production motivated us to design small organic molecules capable to efficiently transform liquid oil to solid state.

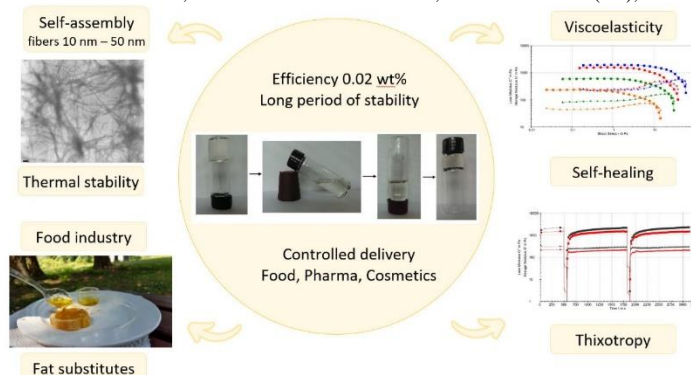
Patent protected Low molecular weight organic gelators show remarkable gelation efficiency in vegetable oils and emulsions, a thermal and mechanical stability, self-healing properties, a long period of stability and controlled delivery of hydro and liposoluble compounds [1, 2].

The gelators of the present invention showed thermoreversible and thixotropic properties in vegetable oil and emulsions with a minimum gelation concentration of 0.025 wt%. Oil gels subjected to rheological measurements showed moderate to strong gelation ability examined at low concentrations from 0.5 to 0.05 wt%. Storage modulus ( $G'$ ) values of the gels from 0.1 to 0.5 wt% were in the range from 1 to 100 kPa, and yield point values from 10 Pa to 100 Pa, respectively. The Proof of concept is explored in preparation of new margarine, spreads, and confectionary products in collaboration with various food companies.

**Keywords:** oil, gelator, self-assembly, self-healing, rheology, fat substitutes

[1] Nataša Šijaković Vujičić, LOW MOLECULAR WEIGHT ORGANIC GELATORS OF VEGETABLE OIL, Patent PCT/HR2016/000016; WO2017194980A1, RU2716588 (C1).

[2] N. Šijaković Vujičić, I. Jerić, J. Suć Sajko, P. Radošević, COMPOSITION COMPRISING OXALAMIDE GELATORS AND VEGETABLE OIL, Patent PCT/EP2018/085216, WO2020125926 (A1), EP3897560 (B1).



**Usmena priopćenja/*Oral presentations***

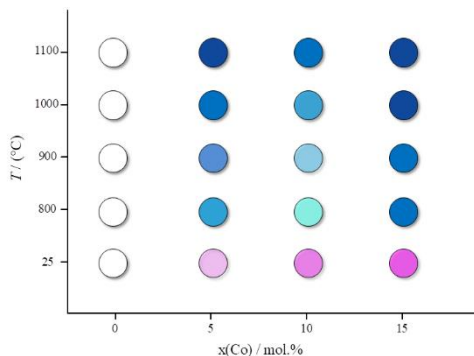
## SINTEZA KOBALTOM DOPIRANOG VILEMITA COBALT DOPED WILLEMITE SYNTHESIS

Filip Brleković, Andrej Terzin, Stanislav Kurajica

University of Zagreb, Faculty of Chemical Engineering and Technology, Marulićev trg 20,  
10000 Zagreb, Croatia

Cobalt blue alongside prussian blue is one of the world's most famous blue pigments. While the latter has no significant consequences for human health, cobalt blue is toxic when inhaled or ingested. A safer and environmentally preferable way of obtaining cobalt blue like pigments is doping of different nontoxic and natural minerals with small amounts of cobalt. In this work doping of zinc silicate mineral, willemite  $Zn_2SiO_4$ , with 5, 10 and 15 mol.% of Co with the aim of obtaining  $Zn_{2-x}Co_xSiO_4$  was carried out. Thermal properties of sol-gel derived samples were examined with simultaneous differential thermal and thermogravimetric analysis (DTA/TGA), which showed standard effects and mass loss for this type of synthesis, and crystallization effect at 800 °C for willemite. X-ray powder diffraction analysis (XRD) showed amorphous and crystalline nature of raw samples, as well as the formation of willemite phase at 800 °C with accompanying ZnO phase and change of willemite crystallinity with increase of annealing temperature from 800 to 1000 °C, while samples doped with 15 mol.% Co show the presence of  $ZnCoO_2$  phase. Fourier transform infrared spectroscopy (FTIR) shows characteristic bands for present oxides and their bonds with adsorbed water and carbon dioxide. Coloration of prepared samples changes with annealing temperature whereas higher Co concentrations and temperatures accentuate the intense blue colour. Diffuse reflectance spectroscopy (DRS) shows higher absorbance with annealing temperature and specific bands as a result of different Co coordination present in the samples.

**Keywords:** Willemite, doping, cobalt blue





**UČINAK OBOGAĆIVANJA MEDA PROPOLISOM NA  
ANTIOKSIDACIJSKI KAPACITET I SADRŽAJ  
POLIFENOLA  
THE EFFECT OF ENRICHMENT HONEY WITH  
PROPOLIS ON ANTIOXIDANT CAPACITY AND  
POLYPHENOL CONTENT**

Stipe Čelan<sup>1</sup>, Aldina Kesić<sup>2</sup>, Orjana Semren<sup>3</sup>, Zora Pilić<sup>4</sup>,  
Nadira Ibrišimović Mehmedinović<sup>2</sup>

<sup>1</sup>Zavod za hranu i veterinarstvo Hercegbosanske županije, Obtnička b.b., Livno 80101, BiH

<sup>2</sup>Prirodno-matematički fakultet Tuzla, Univerzitetska 4, Tuzla 75 000, BiH

<sup>3</sup>Uprava za inspeksijske poslove Hercegbosanske županije, Župana Želimira 16, Livno  
80101, BiH

<sup>4</sup>Fakultet prirodoslovno-matematičkih i odgojnih znanosti Mostar,  
Ulica Matice hrvatske b.b., Mostar 88 000, BiH

Pčelinji proizvodi, posebno propolis, vrijedan su izvor biološki aktivnih tvari. Čini se da je najprirodniji način uvođenja propolisa u prehranu njegov dodatak medu. Cilj ovog rada bio je utvrditi učinak dodatka alkoholnog ekstrakta propolisa medu, u količini od 1 %, na sadržaj i profil polifenola, a time i na antioksidacijsku aktivnost meda. Ispitano je ukupno 20 uzoraka meda i 8 uzoraka propolisa i alkoholnog ekstrakta propolisa, te njihove smjese. Uzorci su prikupljeni u periodu od rujna 2020. do rujna 2021. godine, na području Federacije Bosne i Hercegovine. Većina analiza provedena je u Laboratoriju za analitičku kemiju i ispitivanje rezidua Zavoda za hranu i veterinarstvo Hercegbosanske županije u Livnu, osim profila polifenola u uzorcima, koji je analiziran na Kemijskom fakultetu Univerziteta u Beogradu. Prema dobivenim rezultatima, a koji se odnose na parametre kvalitete definirane Pravilnikom o medu i pčelinjim proizvodima (Anonim, 2009a, 2011), dodatak propolisa medu, u količini od 1 %, ne narušava senzorska svojstva (boju, okus i miris), kao ni fizikalno-kemijska svojstva meda (električnu provodljivost, udio vode, slobodnu kiselost i sadržaj hidroksimetilfurfurala (HMF), ali s druge strane značajno utječe na obogaćivanje meda polifenolnim spojevima i povećava njegov antioksidacijski kapacitet. Naime, analizom uzoraka meda utvrđena je prosječna vrijednost antioksidacijske aktivnosti od 423,021  $\mu\text{mol Fe(II)/L}$ , a nakon dodatka alkoholnog ekstrakta propolisa ova vrijednost porasla je na 762,060  $\mu\text{mol Fe(II)/L}$ , odnosno za 80,14 %, dok je prosječna vrijednost ukupnog sadržaja polifenola u uzorcima porasla za 31,09 %.

*Ključne riječi:* propolis, med, senzorski i fizikalno-kemijski parametri, antioksidacijska aktivnost, profil polifenola

*Objavlivanje rada financirano je od strane Federalnog ministarstva obrazovanja i nauke BiH.*

## UTJECAJ KOROZIVNOG MEDIJA NA ELUCIJU METALNIH IONA TITANSKE LEGURE INFLUENCE OF CORROSIVE MEDIA ON ELUTION OF TITANIUM ALLOY METAL IONS

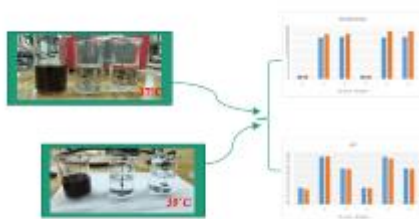
Magdalena Jajčinović<sup>1</sup>, Ljerka Slokar Benić<sup>1</sup>,  
Anita Štrkalj<sup>1</sup>, Andreja Carek<sup>2</sup>

<sup>1</sup>University of Zagreb Faculty of Metallurgy, Aleja narodnih heroja, 3, 44000 Sisak, Croatia

<sup>2</sup>University of Zagreb School of Dental Medicine, Gundulićeva, 5, 10000 Zagreb, Croatia

The superior mechanical properties of titanium alloys have singled out this type of alloy as an essential material for various applications, especially in the field of biomedicine. Due to the growing demand for permanent implants, it has become necessary to accelerate the growing development research of biomaterials, and thus titanium alloys. In this research, influence of corrosive media on elution of titanium-chromium-niobium alloy of new chemical composition, Ti-10Cr-10Nb, was investigated. It was produced by melting and casting in an electric arc furnace in argon atmosphere. The alloy was tested in three different media (saline, saliva and sweet carbonated beverage) at two temperatures (37 °C and 39 °C), in the same time interval. The polished surface of the samples was observed by a light microscope and Vickers hardness was measured as well. Conductivity and pH of corrosive media were measured before and after the elution. Concentrations of eluted metal ions were determined by inductively coupled plasma spectroscopy. The obtained results showed dependence of chromium ions elution on temperature as well as on type of corrosive media.

*Keywords:* titanium alloys, biomedical materials, elution, properties, microstructure



## **UTJECAJ DODATAKA NA OKUS TJESTENINE EFFECTS OF ADDITION ON PASTA TASTE**

Amina Kolić, Amela Kusur, Martina Tanović, Amel Selimović,  
Dijana Miličević, Gordan Avdić  
Univerzitet u Tuzli, Tehnološki fakultet, Urfeta Vejzagića 8,  
75 000 Tuzla, Bosna i Hercegovina

Tjestenina je trajni proizvod napravljen od pšenične krupice miješanjem, oblikovanjem i sušenjem. Tarana spada u grupu sitne tjestenine koja se nekad pravi i od ostataka nakon proizvodnje tjestenine oblikovanjem ili valjanjem. Može se svrstati i u kiselu tjesteninu jer se najčešće pravi sa dodatkom rajčice. Obično služi kao tjestenina za juhu.

U ovom istraživanju je napravljeno nekoliko vrsta tjestenine različitih okusa (rajčica, piletina i špinat) i vršena je njihova usporedba. Urađena je i potpuna analiza sirovine (kemijska i mikrobiološka). Gotova tjestenina je senzorski ocijenjena, napravljen je test kuhanja i određeni su osnovni parametri kvalitete (količina suhe tvari, pepela, stupanj kiselosti).

Rezultati su pokazali da dodaci utječu na kiselost, odnosno stupanj kiselosti, kao i na kvalitetu tjestenine.

*Ključne riječi:* tjestenina, okus, rajčica, piletina, špinat

# MEHANOKEMIJSKA SINTEZA HIBRIDNIH HALIDNIH PEROVSKITA: PROBIR, KARAKTERIZACIJA I PRIMJENA

## MECHANOCHEMICAL SYNTHESIS OF HYBRID HALIDE PEROVSKITES: SCREENING, CHARACTERIZATION AND APPLICATION

Suzana Kralj<sup>1</sup>, Tatiana Soto Montero<sup>1</sup>, Monica Morales-Masis<sup>1</sup>  
University of Twente, Drienerlolaan 5, 7522 NB Enschede, The Netherlands

Hybrid halide perovskites (HP) have emerged as a prospective candidates for a broad range of optoelectronic applications, most notably for photovoltaics (PV) [1]. So far, common techniques for their preparation are solvent-based [2]. However, with rising concerns of using toxic solvents in conventional chemical synthesis, cleaner and up scalable alternatives are needed [3].

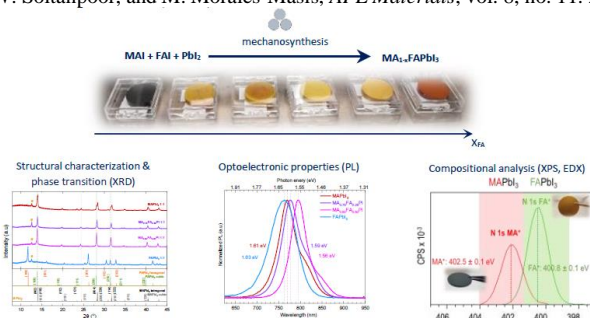
Herein, we suggest a completely solvent-free hybrid halide perovskite fabrication approach. We applied mechanochemical synthesis principles with the aim of fabrication of HP pellets and their production process optimization. In the first stage of research, the pellets were employed to study fundamental material properties. Complete study on their structural, compositional and optoelectronic characterization will be discussed. In the second stage of the research, HP pellets were used as a material source for pulsed laser deposition (PLD) of thin- films. Finally, we implemented PLD fabricated films in perovskite solar cells (PSCs). The first proof of concept devices gives efficiencies up to 14%.

**Keywords:** solvent-free synthesis, mechanochemistry, hybrid halide perovskites (HP), thin-films, pulsed laser deposition (PLD)

[1] M. R. Filip, G. Volonakis, F. Giustino, Hybrid Halide Perovskites: Fundamental Theory and Materials Design. In: W. Andreoni, S. Yip (eds) *Handbook of Materials Modeling*, Springer, 2018

[2] V. M. Kiyek *et al.*, *Adv. Mater. Interfaces*, vol. 7, no. 11, pp. 5–9, 2020

[3] T. Soto-Montero, W. Soltanpoor, and M. Morales-Masis, *APL Materials*, vol. 8, no. 11. 2020



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## DOPIRANI CERIJ (IV) OKSIDNI NANOKATALIZATORI DOPED CERIA NANO CATALYSTS

Stanislav Kurajica<sup>1</sup>, Katarina Mužina<sup>1</sup>, Goran Dražić<sup>2</sup>, Ivana Katarina Ivković<sup>1</sup>, Marina Duplančić<sup>1</sup>, Gordana Matijašić<sup>1</sup>, Vilko Mandić<sup>1</sup>, Patrick Guggenberger<sup>3</sup>, Martina Župančić<sup>4</sup>, Filip Brleković<sup>1</sup>, Ivana Panžić<sup>1</sup>, Iva Minga<sup>1</sup>, Juraj Šipušić<sup>1</sup>, Vesna Tomašić<sup>1</sup>, Sabina Kesser<sup>5</sup>, Ivan Simčić<sup>6</sup>, Dražan Jozić<sup>7</sup>, Vasył Shvalya<sup>8</sup>, Uroš Cvelbar<sup>8</sup>, Fabio Faraguna<sup>1</sup>, Arijeta Bafti<sup>1</sup>, Leo Bauer<sup>1</sup>, Luka Pavić<sup>9</sup>, Monika Mihaljević<sup>1</sup>, Jakov-Stjepan Pavelić<sup>1</sup>, Lucija Volf<sup>1</sup>, Helena Bach-Rojecky<sup>1</sup>, Tea Grbešić<sup>1</sup>, Emina Ema Alić<sup>1</sup>

<sup>1</sup>University of Zagreb, Faculty of Chemical Engineering and Technology,  
Marulićev trg 19, 10000 Zagreb, Croatia

<sup>2</sup>G. Dražić, National Institute of Chemistry, Hajdrihova 19, 1001 Ljubljana, Slovenia

<sup>3</sup>Department of Inorganic Chemistry - Functional Materials, Faculty of Chemistry, University of Vienna, Währinger Straße 42, 1090 Vienna, Austria

<sup>4</sup>Leibniz-Institut für Kristallzüchtung, Max-Born-Straße 2, 12489 Berlin, Germany

<sup>5</sup>University of Zagreb, Faculty of Pharmacy and Biochemistry, A. Kovačića 1,  
10000 Zagreb, Croatia

<sup>6</sup>Pliva Croatia Ltd., Prilaz baruna Filipovića 25, HR-10000 Zagreb, Croatia

<sup>7</sup>Faculty of Chemistry and Technology, University of Split, Ruđera Boškovića 35,  
21000 Split, Croatia

<sup>8</sup>Jožef Stefan Institute, Jamova 39, SI-1000 Ljubljana, Slovenia

<sup>9</sup>Ruđer Bošković Institute, Bijenička Cesta 54, 10000 Zagreb, Croatia

A recent investigation of doped ceria catalyst, as well as advanced synthesis methods of ceria catalyst support will be presented. First, the optimization of the hydrothermal synthesis process in order to obtain as small crystallites as possible, as well as testing of the catalytic activity of the prepared nanocatalysts will be described. Then, the properties of ceria doped with various transition metal ions will be presented, after which the focus will be on ceria doped with manganese and copper, which have proven to be the most effective catalysts. Particularly, crystal phases and distribution of manganese, grain growth kinetics, properties and catalytic activity of manganese doped hydrothermally derived ceria, as well as doping levels, thermal stability, properties and catalytic activity of copper doped hydrothermally derived ceria will be presented. Other synthesis procedures such as sol-gel and mechanochemical synthesis will be also presented, as well as the use of doped ceria for other purposes such as UV filter, with focus on cell toxicity, and humidity sensing thin films. Finally, several possible directions of research in the field of synthesis, utilization and properties of ceria and doped ceria nanomaterials will be proposed.

*Keywords:* nanocatalyst, doped ceria, hydrothermal synthesis

This work has been fully supported by Croatian Science Foundation under the project IP-01-2018-2963.

## PRINCIPI ZELENE KEMIJE U ANALITICI TENZIDA U DETERGENTSKOJ INDUSTRIJI PRINCIPLES OF GREEN CHEMISTRY IN SURFACTANT ANALYSIS IN DETERGENT INDUSTRY

Dubravka Madunić-Čačić<sup>1</sup>, Nikola Sakač<sup>2</sup>, Blaženka Čiško-Anić<sup>1</sup>,  
Marija Jozanović<sup>3</sup>

<sup>1</sup>Saponia, Chemical, Pharmaceutical and Foodstuff Industry, M. Gupca 2,  
31000 Osijek, Croatia

<sup>2</sup>Faculty of Geotechnical Engineering, University of Zagreb, Hallerova 7,  
42000 Varaždin, Croatia

Department of Chemistry, J. J. Strossmayer University of Osijek, Cara Hadrijana 8,  
31000 Osijek, Croatia

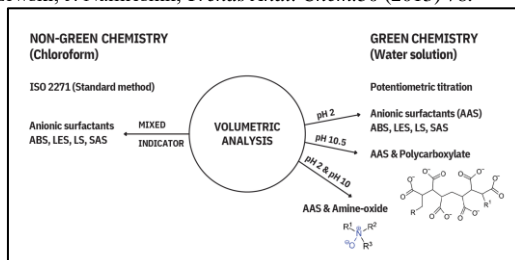
Green chemistry is design of chemical products and processes that reduce or eliminate use or generation of hazardous substances [1]. Respecting the general principles of green chemistry [2,3], they should be also applied in laboratories whenever possible. Even though that standard methods for ionic surfactants determination suffer from numerous matrix interferences and uses chloroform, they are still most used all over the world. Following the *Green chemistry* principles that it is better to prevent the generation of waste, and to avoid the use of harmful solvents, in the case of surfactant analysis we prefer potentiometric titrations. They are performed directly in water solution on highly-automated instrument. In the presence of interferences accuracy can be achieved simply by adjusting the conditions according to the nature of the matrix. In the last twenty years, we have worked in our laboratories on the development of new methods and our own surfactant-sensitive ion-selective electrodes. We paid special attention to complex matrixes, and developed methods, for example, for the determination of anionic surfactants in products that also contain amphoteric surfactants, polycarboxylates, etc. In these studies, we presented the results of surfactant analysis in complex matrix products from the detergent market, containing interferences like amphoteric, polycarboxylates etc. We used new sensor developed, characterized and tested on model and real samples. Results were compared with self-made sensor previously used in commercial samples analysis and confirmed a high degree of agreement.

**Keywords:** Green chemistry, surfactant analysis, potentiometric titrations

[1] <https://www.epa.gov/greenchemistry/basics-green-chemistry#definition>

[2] P.T. Anastas, J.C. Warner, *Green Chemistry: Theory and Practice*, Oxford University, Press: New York, 1998, pg.30.

[3] A. Gałuszka, Z. Migaszewski, J. Namieśnik, *Trends Anal. Chem.* 50 (2013) 78.



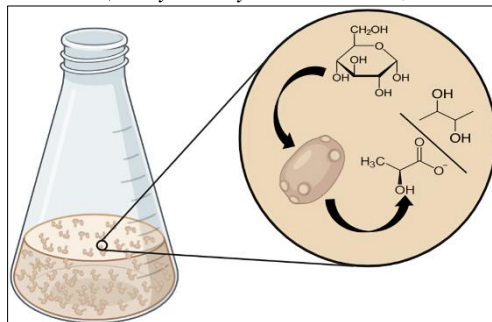
**Proizvodnja L-laktata i 2,3-butandiola pomoću genetički modificiranog kvasca *Kluyveromyces marxianus***  
**Production of L-lactate and 2,3-butanediol using genetically modified yeast *Kluyveromyces marxianus***

Angela Matanović, Marina Svetec Miklenić, Anamarija Štafa,  
Božidar Šantek, Ivan Krešimir Svetec

University of Zagreb, Faculty of Food Technology and Biotechnology, Pierottijeva 6,  
10000 Zagreb, Croatia

L-lactate and 2,3-butanediol are important chemicals used in many industries. Lactate is industrially produced by lactic acid bacteria, while *Klebsiella* bacteria are considered for the production of 2,3-butanediol. However, these bioprocesses have certain disadvantages such as reliance on raw materials that could be used for human consumption or the use of potentially pathogenic bacteria. These disadvantages can be avoided by using a suitable microorganism and therefore the possibility of using the yeast *Kluyveromyces marxianus* for the production of L-lactate and 2,3-butanediol was investigated in this study. *K. marxianus* is a non-conventional yeast that has some industrially important characteristics such as rapid growth rates, thermotolerance, ability to grow on xylose, and due to its GRAS status, it is also suitable for use in the food industry. To examine the potential of *K. marxianus* yeast for L-lactate production, a strain containing optimized genes encoding L-lactate dehydrogenase (*ldhL*) isolated from *Lactobacillus gasseri* was constructed. To study the production of 2,3-butanediol, optimized genes encoding  $\alpha$ -acetolactate synthase (*alsS*) and  $\alpha$ -acetolactate decarboxylase (*alsD*) isolated from *Bacillus subtilis* were expressed in *K. marxianus*, and the effect of overexpression of native gene encoding 2,3-butanediol dehydrogenase (*BDHI*) was examined. Wild-type yeast *K. marxianus* produces neither L-lactate nor 2,3-butanediol when grown on glucose, while genetically modified strains produce up to 2,5 g/L of L-lactate and about 4 g/L of 2,3-butanediol.

**Keywords:** genetic modifications, *Kluyveromyces marxianus*, L-lactate, 2,3-butanediol



This research is funded by the Croatian Science Foundation (projects IP-2018-01-9717 and DOK-2018-09-7667).

## POSTAVLJANJE STUDIJE UZORKOVANJA PROIZVODA OD INDUSTRIJSKE KONOPLJE U TRGOVINI NA MALO U REPUBLICI HRVATSKOJ SETTING UP A STUDY ON SAMPLING OF INDUSTRIAL HEMP PRODUCTS IN RETAILS IN REPUBLIC OF CROATIA

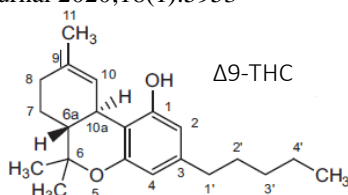
Sanja Miloš, Martina Jurković, Dražen Knežević

Croatian Agency for Agriculture and Food, Centre for Food Safety, Ivana Gundulića 36b,  
31000 Osijek, Croatia

In the last few years a large number of different food products containing hemp mainly produced from seeds, flowers and leaves have been available on the Croatian market, such as oils, bakery products, beer, chocolate, tea, etc. Hemp have acknowledged nutritional properties, a high content in essential fatty acids and proteins, but concern for public health could be the content of  $\Delta^9$ -tetrahydrocannabinol ( $\Delta^9$ -THC) because of its potential psychotropic effects. The acute reference dose (ARfD) is 1  $\mu\text{g}$   $\Delta^9$ -THC/kg body weight [1]. Croatian Agency for Agriculture and Food has recognised a need for systematic data collection and consumer exposure to THC and other cannabinoids in foods and have in plan to collect and analysed representative number of samples of different food products. As a first step a screening of retails and available hemp products was performed. Products was categorised according to EFSA classification and description system FoodEx2. The sampling plan was created according to analytical results provided from EU Member states and worldwide to EFSA from 2008 till 2020. The data were purified and for each food category a sample size necessary to achieve the desired effects of bilateral t-test on the amount of share expectations of  $\Delta^9$ -THC in retails is determined by use of R statistical software. A total of 202 statistically justified samples need to be sampled. Total sample number is divided differently, by eight food categories and random sampling method in retails is predicted whit respecting a different lot numbers. The aim of this paper is to present the results of screening hemp products in retails and design of a sampling plan.

**Keywords:** THC, cannabinoids, hemp products, sampling plan

[1] D. Arcella et al., EFSA Journal 2020;18(1):5953





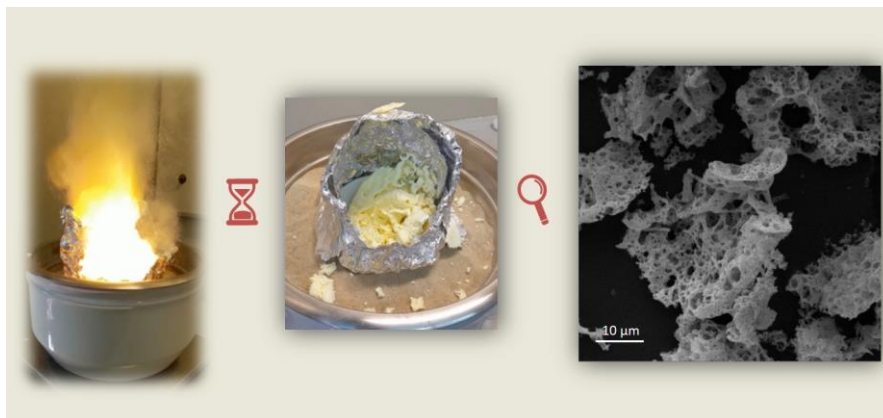
## PRIPRAVA CeO<sub>2</sub> DOPIRANOG CIRKONIJEM SINTEZOM SAGORIJEVANJEM COMBUSTION SYNTHESIS OF ZIRCONIUM DOPED CeO<sub>2</sub>

Katarina Mužina, Helena Bach-Rojecky, Marina Duplančić,  
Stanislav Kurajica

University of Zagreb, Faculty of Chemical Engineering and Technology, Marulićev trg 19,  
10000 Zagreb, Croatia

Zirconium doped ceria is a promising catalytic material extensively researched and used in three-way catalytic converters, oxidation of volatile organic compounds (VOCs), solid oxide fuel cells, etc., owing to its high oxygen storage and release capacity, high reduction properties and thermal stability. In this work, pure and zirconium doped ceria nanoparticles (Ce<sub>1-x</sub>Zr<sub>x</sub>O<sub>2</sub>, where x = 0, 0.1, 0.2 and 0.3) were prepared by combustion synthesis using glycine as fuel and cerium and zirconium nitrate as oxidants. The obtained powders were characterized using X-ray powder diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), differential thermal and thermogravimetric analysis (DTA-TGA) and UV-Vis diffuse reflectance spectroscopy (UV-Vis DRS). The catalytic activity of the prepared nanocatalysts was tested in the VOCs oxidation process. The combustion temperature increased with the increase of zirconium content in the samples, while the XRD patterns show solely ceria diffraction peaks. The crystallite sizes are in the range from 25.2 to 11.7 nm, and they do not change significantly after thermal treatment at 500 °C for 2 hours, indicating good thermal stability of the prepared samples. SEM analysis showed that the obtained samples are very porous. The ceria sample with 10 mol. % of zirconium exhibited the best catalytic activity in the VOCs oxidation process.

*Keywords:* ceria, zirconium, combustion synthesis, catalysis



## FLORISTIČKE ZNAČAJKE KOPAČKOG RITA I DELTE DUNAVA FLORISTIC CHARACTERISTICS OF KOPAČKI RIT AND DANUBE DELTA

Siniša Ozimec<sup>1</sup>, Denise Deže<sup>2</sup>, Dragan Prlić<sup>3</sup>

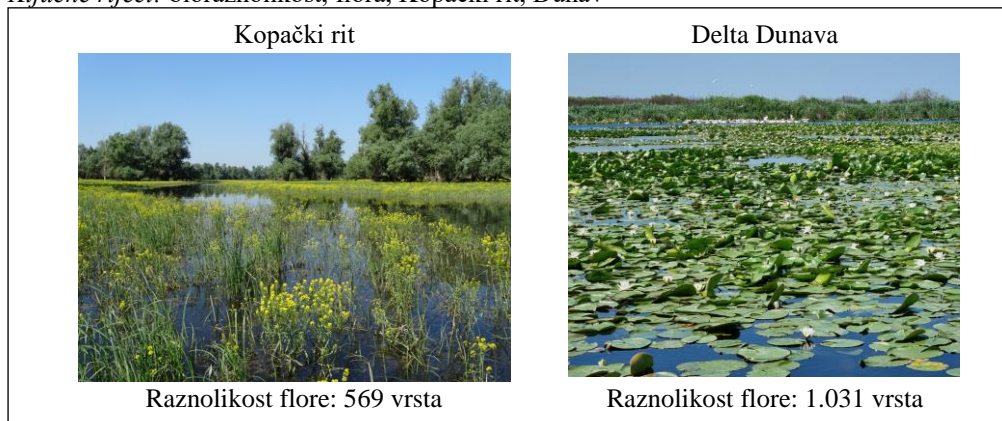
<sup>1</sup>Sveučilište Josipa Jurja Strossmayera u Osijeku, Fakultet agrobiotehničkih znanosti Osijek,  
Vladimira Preloga 1, 31000 Osijek, Hrvatska

<sup>2</sup>Sveučilište Josipa Jurja Strossmayera u Osijeku, Poslijediplomski interdisciplinarni  
sveučilišni studij Zaštita prirode i okoliša (student), Trg Svetog Trojstva 3, 31000 Osijek,  
Hrvatska

<sup>3</sup>Donji Meljani 92c, 33520 Slatina, Hrvatska

Dva najpoznatija močvarna područja u slivu rijeke Dunava su: Kopački rit, smješten u srednjem dijelu toka i delta Dunava u području ušća u Crno more. Zbog iznimno vrijednih bioloških i ekoloških obilježja ova su područja zaštićena na nacionalnoj razini kao Park prirode "Kopački rit" u Hrvatskoj i Rezervat biosfere "Delta Dunava" u Rumunjskoj. Također su uvrštena među Ramsarska područja, UNESCO-vu Svjetsku mrežu rezervata biosfere, te ekološku mrežu EU Natura 2000. Istražena je i analizirana raznolikost vaskularne flore Kopačkog rita i delte Dunava. Raznolikost flore Kopačkog rita čini 97 porodica, 311 rodova i 569 vrsta (11 % flore Hrvatske); floru delte Dunava čini 113 porodica, 435 rodova i 1.031 vrsta (27 % flore Rumunjske). Spektar životnih oblika pokazuje najveći udio hemikriptofita (39 %) za Kopački rit, odnosno terofita (39 %) za deltu Dunava. Razlike u florističkim obilježjima uvjetovane su biogeografskim položajem. Delta Dunava nalazi se u području utjecaja četiriju biogeografskih regija Europe: Crnomorske, Stepske, Kontinentalne i Mediteranske, a Kopački rit u području utjecaja dviju biogeografskih regija: Kontinentalne i Panonske.

*Ključne riječi:* bioraznolikost, flora, Kopački rit, Dunav



## RASPODJELA MIKROPLASTIKE U VODOVODNOJ VODI ZAGREBA ANALIZIRANA RAMANOVOM SPEKTROSKOPIJOM MICROPLASTICS DISTRIBUTION IN ZAGREB TAP WATER ANALYSED BY RAMAN SPECTROSCOPY

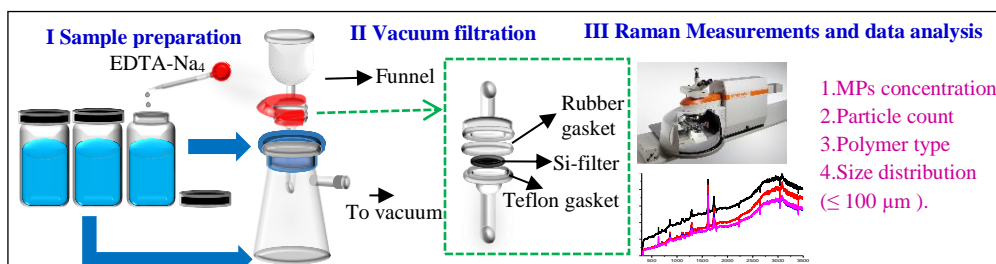
TamilSelvi Selvam, Ana Tolić, Vlasta Mohaček Grošev, Mile Ivanda  
Ruđer Bošković Institute, Bijenička cesta 54, 10000 Zagreb, Croatia

Microplastics (MPs) are omnipresent in our environment, from soils and oceans, and in food chains – thus leading to their accumulation in our day-to-day consumable products<sup>1</sup>. Drinking water is one of the primary sources of human exposure to microplastics. Currently we are investigating the presence of the MPs in tap-water collected from pipelines across city of Zagreb. The collected samples were filtered through Si-filters or TEM grids and the deposited particles were systematically analysed by Raman spectroscopy. Water samples were treated with EDTA-Na<sub>4</sub> solution<sup>2</sup> by facilitating the formation of the soluble EDTA-M<sup>2+</sup>chelates when relatively large quantities of the inorganic particles particularly alkaline carbonates (M<sup>2+</sup>CO<sub>3</sub>) were present. In this way one achieves the deposition of larger MPs to inorganic particles ratio on the filter which increases the efficiency of detection of the MPs. Raman micro-spectroscopy was used as primary tool for the analysis of MPs deposited on the filters. Findings related to microplastic concentrations, particle count, polymer types and particle size distribution (particularly ≤ 100 μm) are reported.

*Keywords:* Microplastics, drinking water, Raman spectroscopy

[1] V.C. Shruti , Fermín P´erez-Guevara, Priyadarsi D. Roy, Gurusamy Kutralam-Muniasamy, Journal of Hazardous Materials, 2022, 423, 127171.

[2] Barbara E. Oßmann, George Sarau, Heinrich Holtmannspötter, Monika Pischetsrieder, Silke H. Christiansen, Wilhelm Dicke, Water research, 2018, 141, 307-316.



## KVALITETA BOSNASKO-HERCEGOVAČKOG MEDA U SVJETLU PROPISA O MEDU THE QUALITY OF BOSNIAN-HERZEGOVINIAN HONEY IN THE LIGHT OF HONEY REGULATIONS

Orjana Semren<sup>1</sup>, Aldina Kesić<sup>2</sup>, Stipe Čelan<sup>3</sup>, Zora Pilić<sup>4</sup>,  
Nadira Ibrišimović Mehmedinović<sup>2</sup>

<sup>1</sup>Uprava za inspeksijske poslove Hercegbosanske županije, Župana Želimira 16,  
Livno 80101, BiH

<sup>2</sup>Prirodno-matematički fakultet Tuzla, Univerzitetska 4, Tuzla 75000, BiH

<sup>3</sup>Zavod za hranu i veterinarstvo Hercegbosanske županije, Obtnička b.b., Livno 80101, BiH

<sup>4</sup>Fakultet prirodoslovno-matematičkih i odgojnih znanosti Mostar,  
Ulica Matice hrvatske b.b., Mostar 88 000, BiH

Med je po definiciji namirnica kojoj se ništa ne smije dodavati niti oduzimati kako bi zadržala svoja izvorna karakteristična svojstva. Specifičnog je kemijskog i nutritivnog sastava, koji mu daju status visoko-vrijedne hrane. Cilj ovog rada bio je utvrditi vrijednosti fizikalno-kemijskih parametara meda bosnasko-hercegovačkog podrijetla, te ih usporediti s propisanim zahtjevima kvalitete. Analiza je provedena na 20 uzoraka meda, prikupljenih u vremenskom periodu od rujna 2020. do rujna 2021. godine, na području Federacije Bosne i Hercegovine, a analiziran je poliflorni, livadski i planinski med. Sve analize provedene su u Laboratoriju za analitičku kemiju i ispitivanje rezidua Zavoda za hranu i veterinarstvo Hercegbosanske županije u Livnu, a istima su obuhvaćeni slijedeći senzorski i fizikalno-kemijski parametri: boja, udio vode, električna provodljivost, slobodna kiselost i sadržaj hidroksimetilfurfurala (HMF), te ukupna antioksidacijska aktivnost. Analizom je utvrđeno da svi uzorci udovoljavaju kriterijima propisanim Pravilnikom o medu i drugim pčelinjim proizvodima (Anonim, 2009a, 2011) za analizirane parametre, osim pet uzoraka za sadržaj HMF-a (u rasponu od 42,368 do 67,488 mg/kg). Nakon dužeg skladištenja (1 godina/18 – 22 °C) udio HMF-a u uzorcima meda porastao je u prosjeku za 59,241 %, pri čemu je u samo tri uzorka ostao u dozvoljenim granicama. Dobivene vrijednosti antioksidacijske aktivnosti uzoraka (u rasponu od 199,375 do 1.064,375  $\mu\text{mol Fe(II)/L}$ ) jasan su pokazatelj da je med bogat izvor antioksidanasa u prehrani, što ukazuje da bi antioksidacijska aktivnost meda mogla biti jedan od parametara ocjene njegove kvalitete.

*Ključne riječi:* med, senzorski i fizikalno-kemijski parametri, hidroksimetilfurfural (HMF), antioksidacijska aktivnost

## MJERENJE KONCENTRACIJE LUTEINA U SERUMU KOD MLADIH ZDRAVIH ISPITANIKA MEASUREMENT OF LUTEIN CONCENTRATION IN SERUM OF YOUNG HEALTHY SUBJECT

Petar Šušnjara<sup>1,2</sup>, Olivera Galović<sup>2</sup>, Nikolina Kolobarić<sup>1,2</sup>, Zrinka Mihaljević<sup>1,2</sup>,  
Ines Drenjancević<sup>1,2</sup>

<sup>1</sup>Institute and Department of Physiology and Immunology, Faculty of Medicine,  
Josip Juraj Strossmayer University of Osijek, J. Hottlera 4, 31000 Osijek, Croatia

<sup>2</sup>Scientific Center of Excellence for Personalized Health Care, Josip Juraj Strossmayer University of  
Osijek, Trg Svetog Trojstva 3, 31000 Osijek, Croatia

<sup>3</sup>Department of Chemistry, Josip Juraj Strossmayer University of Osijek, Ul. cara Hadrijana 8a,  
31000 Osijek, Croatia

**Introduction:** Recent scientific evidence confirms the hypothesis that certain foods or their ingredients have a positive physiological effects on an individual's health. [1,2]. Functional food is a food that contains components with beneficial effects on one or more body functions, beyond their nutritive values, and improves general condition and health of person or significantly reduces the risk of disease [3]. **Materials and Methods:** Randomized, double-blind, controlled, interventional study was conducted in healthy young subjects (N=34) who consumed 3 hen eggs per day for 3 weeks. Nutri4 group consumed enriched hen eggs: consumed approximately 3.29 mg of vitamin E, 1.85 mg of lutein, 0.06 mg of selenium and 1026 mg of n-3 PUFAs daily, and control subjects consumed ordinary (approximately 1.785 mg of vitamin E, 0.330 mg of lutein, 0.054 mg of selenium and 438 mg of n-3 PUFAs daily) hen eggs, from the same farm. Serum lutein concentration was determined according the method of Tzeng MS, et al., by HPLC [4]. **Results and Discussion:** Consumption of Nutri4 eggs caused a significant increase in serum lutein concentration (before 0.153±0.073 µmol/L; after 0.232±0.078 µmol/L\*), while no significant difference was found in the control group (before 0.199±0.104 µmol/L; after 0.199±0.202 µmol/L) or between groups. Increased intake of essential carotenoid such as lutein can have various beneficial effects on the body, due to increased serum concentration. **Conclusions:** Consumption of Nutri4 enriched eggs affects the serum levels of lutein in healthy young people.

**Keywords:** Lutein, health, serum, functional food

[1] Rebello C, Greenway FL, Dhurandhar NV. Functional foods to promote weight loss and satiety. *Curr Opin Clin Nutr Metab Care*. 2014; 6:596-604.

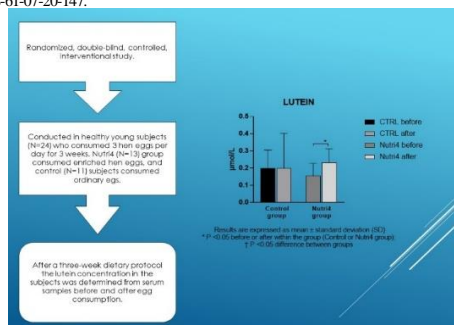
[2] Kralik G, Kralik Z, Grčević M, Škrtić Z. Obogaćivanje peradarskih proizvoda funkcionalnim sastojcima. *Poljoprivreda*. 2012; 18(1):52-59.

[3] Walter P. 10 years of Functional Foods in Europe. *Int J Vitam Nutr Res*. 2008; 78(6):253-60.

[4] Tzeng M.-S, Yang F.-L, Wang-Hsu G.-S, Chen B.-H. Determination of major carotenoids in human serum by liquid chromatography. *J Food Drug Anal*. 2004; 12(1), Article 13.

**Funding and financial support:** This study was supported by European Structural and Investment Funds, grant for the Croatian National Scientific Center of Excellence for Personalized Health Care, University Josip Juraj Strossmayer Osijek #KK.01.1.1.01.0010.

**Ethical Committee Approval:** The study was approved by the Ethics Committee of the University of J.J. Strossmayer in Osijek, Faculty of Medicine in Osijek CLASS: 602-04/20-08/07.REGISTRATION.NUMBER:2158-61-07-20-147.



**Posterska priopćenja/*Poster presentations***

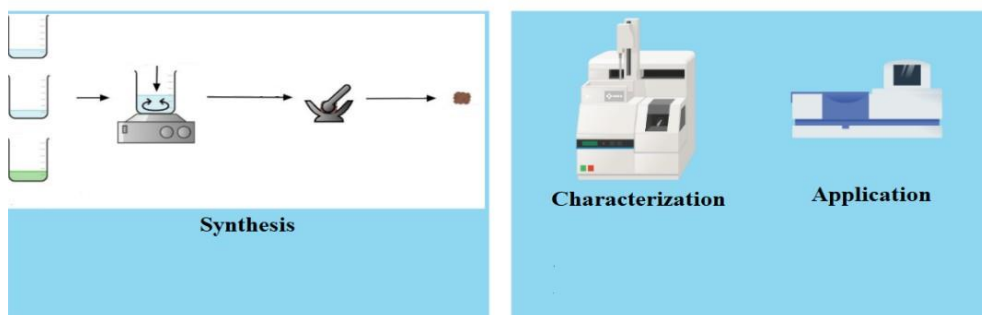
## **AKTIVNOST RAZGRADNJE AZO-BOJA KOD MATERIJALA SA PEROVSKITNOM STRUKTUROM AZO DYE DEGRADATION ACTIVITY OF PEROVSKITE- TYPE MATERIALS**

Roberto Basara, Ana Ivanković, Dalibor Tatar,  
Jelena Kojčinović and Igor Djerdj  
Department of Chemistry, Josip Juraj Strossmayer University of Osijek,  
Ulica cara Hadrijana 8/A, 31000 Osijek, Croatia

In this work, we have prepared single-perovskite-type materials. This research deals with the photocatalytic degradation of synthetic organic dyes: Methylene blue (MB), Naphthol Green B (NG), and Rhodamine B (RDB). Materials used for these experiments are simple nanocrystalline oxide-based perovskites comprising transition metals and lanthanides which were synthesized via the modified citrate sol-gel method. Single perovskite  $\text{CeNiO}_3$  was used as a parent compound, and we further increased the configurational entropy by adding different lanthanide cations on the Ce position and transition metal cations on the Ni position. All the materials used for photocatalytic degradation were characterized by powder X-ray diffraction, thermogravimetric analysis, and Brunauer-Emmet-Teller surface area analysis. The photocatalytic activity was monitored during irradiation at the wavelength of maximum absorbance for each dye (663 nm for MB, 734 nm for NG, and 554 nm for RDB) using UV/Vis spectroscopy. The results indicate a reduction in maximum absorbance of tested dyes in the given time frame which confirms the efficiency of synthesized photocatalysts.

*Keywords:* photocatalysis, single perovskite, nanocrystalline, citrate sol-gel, organic dyes

### **International Conference 19th Ružička days**



## OPTIMIZACIJA SONOKEMIJSKE SINTEZE NANOČESTICA ZrO<sub>2</sub> OPTIMIZATION OF SONOCHEMICAL SYNTHESIS OF ZrO<sub>2</sub> NANOPARTICLES

Ivan Ćorić, Jelena Kojčinović, Dalibor Tatar, Elvira Kovač-Andrić  
Department of Chemistry, Josip Juraj Strossmayer University of Osijek, Ulica cara Hadrijana  
8a, 31000 Osijek, Croatia

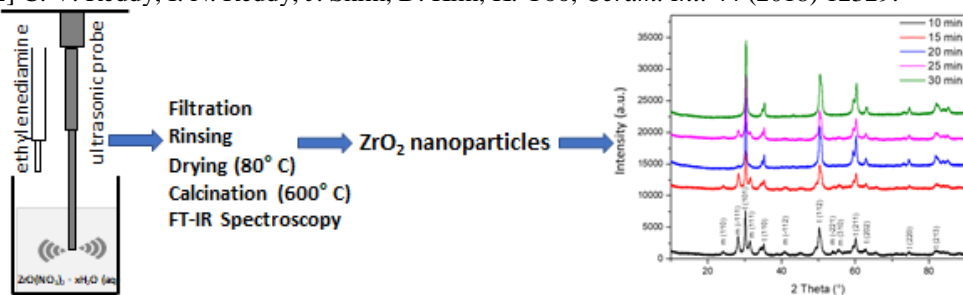
The dimensions and properties of nanoparticles enable their wide application. Today, various syntheses are being developed to obtain nanoparticles. Sonochemical synthesis resulting from ultrasonic cavitation [1, 2] is one of the effective methods.

The aim of this work is to determine the influence of the duration of synthesis, amplitude and pulse duration of ultrasound assisted synthesis on the final phase ratio and crystallite size of ZrO<sub>2</sub> nanoparticles. For the synthesis, ZrO(NO<sub>3</sub>)<sub>2</sub> · xH<sub>2</sub>O and ethylenediamine were used in aqueous media. IR analysis showed that the qualitative composition of the precursor is the same and does not depend on the synthesis parameters. The synthesis and pulse duration have the greatest effect on the composition after calcination. The experiment showed that the time of precursor synthesis has a significant effect on the proportions of phases in the product. Quantitative PXRD analysis revealed a presence of monoclinic and tetragonal ZrO<sub>2</sub> phases in the samples after calcination. An increased proportion of the monoclinic phase was detected in samples sonicated for up to 15 min and in samples sonicated with ultrasound pulse for 1 and 2 s. The pure tetragonal phase is present only in a sample sonicated for 30 min.

**Keywords:** nanoparticles, sonochemical synthesis, ultrasonic cavitation

[1] J. Clark, D. Macquarrie, Handbook of Green Chemistry & Technology, Wiley – Blackwell, Hoboken, New Jersey, 2002.

[2] C. V. Reddy, I. N. Reddy, J. Shim, D. Kim, K. Yoo, *Ceram. Int.* 44 (2018) 12329.





## UTJECAJ SELENIJA NA PROFIL GLUKOZINOLATA U KLICAMA RIKULE INFLUENCE OF SELENIUM ON GLUCOSINOLATE PROFILE IN ROCKET SPROUTS

Azra Đulović, Luana Grmuša, Ivica Blažević

Faculty of Chemistry and Technology, University of Split, Ruđera Boškovića 35,  
21000 Split, Croatia

Glucosinolates ( $\beta$ -thioglucoside-*N*-hydroxysulfates) are a large group of specialised metabolites that give a characteristic bitter and pungent taste mostly due to isothiocyanates, their degradation products, which are known for their biological activity [1]. Rocket sprouts are nutritionally rich, and their advantage is very easy cultivation. Additionally, they are rich in vitamins, essential fatty acids and fibres. Plants generally do not tolerate selenium concentrations higher than 10-100  $\mu\text{g/g}$  dry weight in tissues, but species belonging to the *Brassicaceae* family can accumulate selenium in tissues and tolerate concentrations up to 1000  $\mu\text{g/g}$  dry weight [2]. In this way, plants can produce various selenium metabolites that can play a role in preventing cancer. Studies have shown that a selenium atom can be incorporated into the side chain of glucosinolates instead of sulfur.

In this study, rocket sprouts were grown hydroponically in selenium solutions of different concentrations (1; 2.5; 5; 7.5; 10 ppm). The development of the plants was monitored for 7 days, and only at the highest concentration of selenium the plant did not grow. After collection, glucosinolates were isolated by extraction with 70% methanol and qualitatively and quantitatively analysed by UHPLC-DAD-MS/MS. Four glucosinolates were identified: glucoraphanin, glucoerucin, glucosativin dimer and 4-methoxyglucobrassicin. The amount of glucoerucin was significantly higher in sprouts treated with selenium concentrations than the amount of other identified glucosinolates.

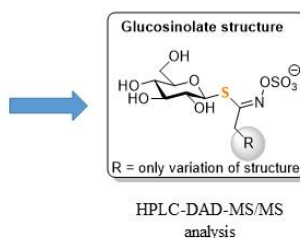
*Ključne riječi:* glucosinolates, selenium, HPLC-DAD-MS/MS

[1] I. Blažević, *et al.*, *Phytochemistry* 169 (2020) 112100

[2] A.J. Matich, *et al.*, *Phytochemistry* 75 (2012) 140–152



Rocket sprouts (*Eruca vesicaria* (L.) Cav.)



## **UTJECAJ VELIČINE ČESTICA I OMJERA SUHE TVARI I EKSTRAKCIJSKE SMJESE NA EKSTRAKCIJU LUTEINA IZ HRANE ZA NESILICE**

### **INFLUENCE OF PARTICLE SIZE AND SAMPLE- EXTRACTION MIXTURE RATIO ON EXTRACTION OF LUTEIN FROM LAYING HENSE FEED MIXTURE**

Olivera Galović<sup>1,4</sup>, Doris Prokopec<sup>1</sup>, Zlata Kralik<sup>2,4</sup>, Manuela Košević<sup>2,4</sup>,  
Gordana Kralik<sup>3,4</sup>

<sup>1</sup>Department of Chemistry, Josip Juraja Strossmayer University of Osijek, Ulica cara  
Hadrijana 8a, 31000 Osijek, Croatia

<sup>2</sup>Faculty of Agrobiotechnical Sciences Osijek, Josip Juraj Strossmayer University of Osijek,  
Vladimira Preloga 1, 31000 Osijek, Croatia

<sup>3</sup>Nutricin j.d.o.o. Darda, HR-31326 Darda

<sup>4</sup>Scientific Center of Excellence for Personalized Health Care, Josip Juraj Strossmayer  
University of Osijek, Trg sv. Trojstva 3, 31000 Osijek, Croatia

The role of lutein in human and animal health has already been investigated. Due to its importance, it is of great interest to determine its content in the food we consume or is consumed by animals whose products we use in our diet. In this study, the influence of particle size and dry matter (sample): extraction mixture ration on determination of lutein content in laying hens feed was investigated. Mixture of methanol and acetone, 0.2% BHT solution and 40% KOH solution was used as extraction mixture. All extractions were performed on the same samples and assisted by an ultrasonic probe. The lutein content of the samples was determined by means of HPLC with a UV-VIS detector at 450 nm. In ground samples, the determined content of lutein in mg / kg of sample is 52% better compared to ungrinded samples. Comparing the results obtained by the same method but with saponification, 3% more lutein was determined with saponification and the RSD value was significantly reduced (from 1.498% to 0.420%). The ratios of dry matter: extraction mixture: 1: 5, 1:10, 1:20 and 1:40 were investigated, and the obtained results (3,152; 3,956; 5,148 and 2,015 mg / kg of sample) indicate that the best ratio is 1:20.

**Keywords:** lutein, particle size, ultrasound assisted extraction



## UTJECAJ NEIONSkih TENZIDA NA ODZIVNA SVOJSTVA TENZIDNOG SENZORA NA BAZI 2-METIL-1,3-DIOKTADECIL-1H-BENZO[d]IMIDAZOLA INFLUENCE OF NONIONIC SURFACTANTS ON RESPONSE PROPERTIES OF 2-METHYL-1,3-DIOCTADECYL-1H-BENZO[d]IMIDAZOL-3-IUM – BASED SURFACTANT SENSOR

Nada Glumac<sup>1</sup>, Marija Jozanović<sup>2</sup>, Dubravka Madunić-Čačić<sup>3</sup>,  
Dean Marković<sup>4</sup>, Tajana Koščak<sup>5</sup>, Nikola Sakač<sup>5</sup>

<sup>1</sup>Medimurske Vode d.o.o., Ulica Matice hrvatske 10, 40000 Čakovec, Croatia

<sup>2</sup>Department of Chemistry, J.J. Strossmayer University of Osijek, Ulica cara Hadrijana 8A, 31000 Osijek, Croatia

<sup>3</sup>Saponia, Inc., Ulica Matije Gupca 2, 31000 Osijek, Croatia

<sup>4</sup>Department of Biotechnology, University of Rijeka, Ulica Radmile Matejčić 2, 51000 Rijeka, Croatia

<sup>5</sup>Faculty of Geotechnical Engineering, University of Zagreb, Hallerova 7, 42000 Varaždin, Croatia

Surfactants, lower the surface tension. There are four main types: anionic (AS), cationic (CS), amphoteric and nonionic (NS). All surfactants consists of a hydrophilic part and hydrophobic part. In commercial cleaning agent formulations, AS are used in combination with NS to enhance the cleaning properties by removing the grease, reducing the foaming and providing the resistance to hard water. The use of NS in combination with AS has a negative impact on detection of AS by potentiometric surfactant sensor based on 2-methyl-1,3-dioctadecyl-1H-benzo[d]imidazol-3-ium. The AS dodecyl sulfate ( $4 \times 10^{-3}$  M) was mixed with i) ethoxylated nonionic surfactants (EONSs) with different number of EO groups at fixed concentration; ii) with EONS containing 10 EO groups at various concentrations; and titrated with CS cetylpyridinium ( $4 \times 10^{-3}$  M). Increased number of EO groups and increased concentration of EONS resulted in negative changes in shape, inflexion and signal change of the potentiometric titration curves, making the AS quantification less reliable or even impossible.

**Keywords:** Nonionic surfactants, anionic surfactants, sensor, potentiometry



## **Hrvatske tradicionalne sorte jabuka kao izvor bioaktivnih spojeva Croatian traditional apple varieties as a source of bioactive compounds**

Ana-Marija Gotal Skoko<sup>1</sup>, Maria Celeiro<sup>2</sup>, Aly Castillo<sup>2</sup>, Marta Lores<sup>2</sup>,  
Martina Skendrović Babojelić<sup>3</sup>, Leonardo Vinković<sup>1</sup>,  
Tihomir Kovač<sup>1</sup>, Ante Lončarić<sup>1</sup>

<sup>1</sup>J. J. Strossmayer University of Osijek, Faculty of Food Technology Osijek, Franje Kuhača  
18, 31000 Osijek, Croatia

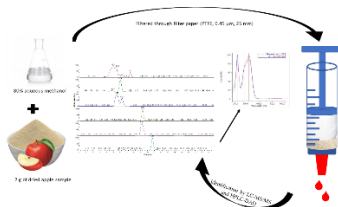
<sup>2</sup>Department of Analytical Chemistry, Universidad de Santiago de Compostela, E-15782  
Santiago de Compostela, Spain

<sup>3</sup>Department of Pomology, Faculty of Agriculture, University of Zagreb, Svetošimunska 25,  
10000 Zagreb, Croatia

Features that make traditional apple varieties interesting for researchers are their polyphenol content, especially phenolic acids, anthocyanins, dihydrochalcones, flavonols and flavan-3-ols [1]. Twenty-three Croatian traditional apple varieties were extracted from dried fruit using 80% aqueous methanol and analysed by HPLC-DAD and LC-MS/MS. Total polyphenol content (TPC) was measured by an optimized Folin-Ciocalteu assay and antioxidant activity was determined by the DPPH method. The TPC content varied from 326.49 mg/100 g to 378.15 mg/100 g dw depending on the varieties. The sum of polyphenols in apple samples ranged from 9.6 mg/kg to 1243.8 mg/kg dw. LC-MS/MS allowed the identification and quantification of eight compounds, namely procyanidin B1, procyanidin B2, catechin, epicatechin, quercetin-3- $\beta$ -glucoside, quercetin-3-rutinoside, astragalín and chlorogenic acid. The main polyphenol in all apple samples was chlorogenic acid with content ranging from 1.3 mg/kg dw to 455.9 mg/kg dw, the highest content of chlorogenic acid had “Princeza”. This work was supported by the project UIP-2020-02-8461 (The Croatian Science Foundation).

**Keywords:** traditional apple varieties, bioactive compounds, polyphenols, chlorogenic acid

[1] Lončarić, Ante; Matanović, Katarina; Ferrer, Perla; Kovač, Tihomir; Šarkanj, Bojan; Skendrović Babojelić, Martina; Lores, Marta (2020). *Peel of Traditional Apple Varieties as a Great Source of Bioactive Compounds: Extraction by Micro-Matrix Solid-Phase Dispersion*. *Foods*, 9(1), 80–. doi:10.3390/foods9010080



## ISPITIVANJE UTJECAJA REAKCIJSKIH PARAMETARA NA SINTEZU HEKSILNIH ESTERA MASNIH KISELINA THE INFLUENCE OF THE REACTION PARAMETERS ON THE SYNTHESIS OF FATTY ACID HEXYL ESTERS

Mia Gotovuša, Matija Krvavica, Fabio Faraguna

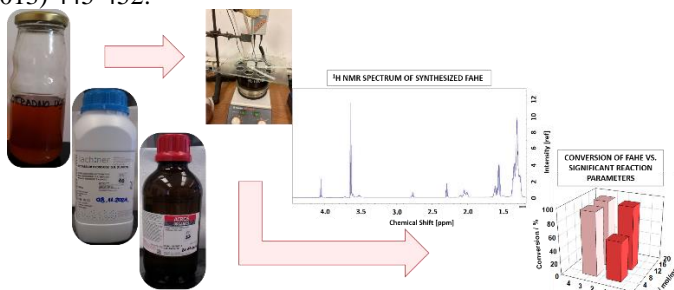
University of Zagreb, Faculty of Chemical Engineering and Technology, Marulićev trg 19,  
10000 Zagreb, Croatia

Hexan-1-ol as a longer chain alcohol is used in biodiesel synthesis due to its potential to improve fuel's application properties, e.g. cetane number [1]. On the other hand, to further contribute to the sustainability of the process, waste feedstock, e.g. waste cooking oil, is also used in the transesterification reactions [2]. Fatty acid hexyl esters (FAHE) were synthesized from alcohol hexan-1-ol and waste cooking oil, in the presence of potassium hydroxide (dried in a vacuum dryer prior to the synthesis, to eliminate the presence of water, purity 89.5%), as a catalyst. Transesterification reactions were conducted isothermally, with temperature values varying from 40 to 80 °C. Samples of the reaction mixture were taken after 2, 5, 15, 30 and 60 minutes. Molar ratio of hexan-1-ol to oil was either 5:1 or 12:1, while mass fraction of the catalyst was 1 or 3 %. Reaction conversion in each experiment was determined through nuclear magnetic resonance analysis (NMR). The highest reaction conversion of 100 % was obtained at the temperature of 60 °C, after 30 minutes, with the molar ratio of the reactants being 12:1 and mass fraction of the catalyst of 3%. The increase of the molar ratio of the reactants and the mass fraction of the catalyst leads to the increase in the reaction conversion. Furthermore, the transesterification reactions achieved higher conversions at lower temperatures of 40 and 60 °C than at 80 °C, whereas the influence of time on the conversion was little to none, since the maximum conversion values were, in some cases, achieved after only 5 minutes.

**Keywords:** biodiesel, transesterification, hexan-1-ol, waste cooking oil, potassium hydroxide

[1] G. Knothe, *Fuel Process. Technol.* (2005) 1059-1070.

[2] C. D. M. de Araújo, C. C. de Andrade, E. de Souza e Silva, F. A. Dupas, *Renew. Sust. Energ. Rev.* (2013) 445-452.



## UTJECAJ ZAŠTINE SKUPINE NA KONFORMACIJU FEROCENSKOG KONJUGATA S VALINOM THE INFLUENCE OF THE PROTECTING GROUP ON THE CONFORMATIONAL PROPERTIES OF FERROCENE CONJUGATES WITH VALINE

Monika Kovačević<sup>1</sup>, Emili Vidan<sup>1</sup>, Klara Širić<sup>1</sup>, Ivan Kodrin<sup>2</sup>, Sunčica Roca<sup>3</sup>,  
Krešimir Molčanov<sup>3</sup>, Valentina Milašinović<sup>3</sup> and Lidija Barišić<sup>1</sup>

<sup>1</sup>Faculty of Food Technology and Biotechnology, University of Zagreb, Pierottijeva 6,  
10 000 Zagreb, Croatia

<sup>2</sup>Department of Chemistry, Faculty of Science, University of Zagreb, Horvatovac 102a,  
10000 Zagreb, Croatia

<sup>3</sup>Rudjer Bošković Institute, Bijenička 54, 10 000 Zagreb, Croatia

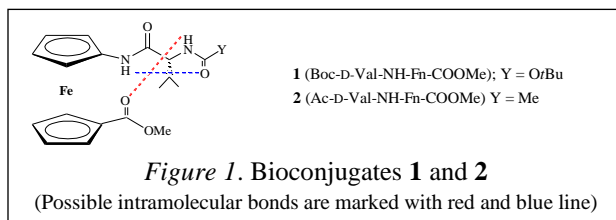
The biochemical properties of D-amino acids, as well as peptides containing D-amino acids, are of great interests because of their toxic, protective, or signalling effect. [1] To date, very few ferrocene peptides based on D-amino acids have been studied. [2, 3] Here, we synthesized the bioconjugates Boc-D-Val-NH-Fn-COOMe (**1**) and Ac-D-Val-NH-Fn-COOMe (**2**) (Ac = acetyl, Boc = *tert*-butoxycarbonyl). To determine whether the branched isopropyl side chain of valine and the protecting groups affect the intramolecular hydrogen bonding (Figure 1), i.e., their conformational behaviour, we performed a detailed spectroscopic analysis (IR, NMR and CD), followed by a crystallographic and DFT study.

**Keywords:** D-amino acid, D-valine, ferrocene, conformational analysis

[1] M. Abdulbagi, L. Wang, O. Siddig, B. Di, B. Li, *Biomolecules* 11 (2021) 1716.

[2] T. Moriuchi, T. Hirao, *J. Inc. Phenom. Macrocycl. Chem.* 74 (2012) 23.

[3] M. Kovačević, I. Kordin, S. Roca, K. Molčanov, Y. Shen, B. Adhikari, H-B. Kraatz, L. Barišić, *Chem. Eur. J.* 23 (2017) 10372.



**Acknowledgements:** This work has been fully supported by Croatian Science Foundation under the project IP-2020-02-9162.

## BIORAZGRADNJA AMOKSICILINA BIODEGRADATION OF AMOXICILLIN

S. Kovačić<sup>1</sup>, V. Lovrinčević<sup>2</sup>, D. Vuk<sup>2</sup>, M. Vuković Domanovac<sup>3</sup>

<sup>1</sup>Pliva Croatia Ltd., Prilaz baruna Filipovića 25, 10000 Zagreb, Croatia

<sup>2</sup>Department of Organic Chemistry, Faculty of Chemical Engineering and Technology,  
University of Zagreb, Marulićev trg 20, 10000 Zagreb, Croatia

<sup>3</sup>Department of Industrial Ecology, Faculty of Chemical Engineering and Technology,  
University of Zagreb, Marulićev trg 19, 10000 Zagreb, Croatia

The antibiotic residue in the environment is a huge problem nowadays, since they represent one of the main discoveries in a medicinal field. Therefore, the usage of antibiotics is increasing rapidly but it is getting out of control also. Sometimes unnecessary and improper consumption has increased the levels of residual antibiotics in ecosystems and some bacterial communities, which results with antibiotics losing their primary activity, bacterial function changing and finally bad effects on human health.

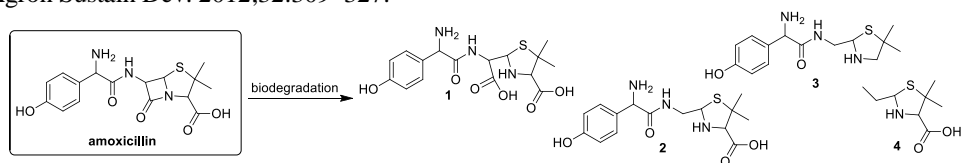
Environmental antibiotic contamination should be diminished by regulating the causes of occurrence and antibiotic discharge by detection and quantification of the antibiotics and the characterization of their behavior in the environment, which should all be summarized in risk assessments.<sup>1</sup> Meanwhile, the removal of the antibiotic residues from the nature is also very important. The accumulation with the highest concentration of the residues in the environment is in the places where the antibiotics are most commonly used and thus are the greatest source of pollution. Such places are livestock farms, hospitals and pharmaceutical factories. Antibiotics eventually end in the ground, soil and aquatic environment through the waste water, sludge and manure used in agriculture, and finally in the food we are eating.<sup>2</sup>

In this work, the process of biodegradation of amoxicillin was studied under batch conditions using pure environmental bacterial cultures of *Pseudomonas aeruginosa* (Gramm-negative) and *Bacillus subtilis* (Gramm-positive). The focus was on amoxicillin, as it is an antibiotic that is commonly used nowadays to treat diseases and is therefore not uncommonly found in the environment as a residual antibiotic. Biodegradation was monitored by UHPLC method with gradient elution and reversed phase column. Identification of degradation products was also performed by the method LC-MS, focusing on scanning the masses of the main peaks that grow and change the most during the sampling period.

**Keywords:** antibiotic residues, environment contamination, amoxicillin, biodegradation.

[1] Svetlana Iuliana Polianciuc, Anca Elena Gurzău, Bela Kiss, Maria Georgia Ștefan, Felicia Loghin; Antibiotics in the environment: causes and consequences, Medicine and Pharmacy reports Vol.93, No.3, 2020: 231-240.

[2] Du L, Liu W. Occurrence, fate, and ecotoxicity of antibiotics in agro-ecosystems. A review. Agron Sustain Dev. 2012;32:309–327.



## BIOKONJUGATI FEROCENA I DERIVATA 2-TIOURACILA: SINTEZA, SPEKTRALNA KARAKTERIZACIJA I BIOLOŠKA AKTIVNOST BIOCONJUGATES OF FERROCENE AND 2-THIOURACIL DERIVATIVES: SYNTHESIS, SPECTRAL CHARACTERIZATION AND BIOLOGICAL ACTIVITY

Jasmina Lapić, Rebeka Perčić, Iva Logarušić, Martina Bagović,  
Kristina Radošević, Senka Djaković  
Prehrambeno-biotehnološki fakultet Sveučilišta u Zagrebu, Pierottijeva 6,  
10000 Zagreb, Hrvatska

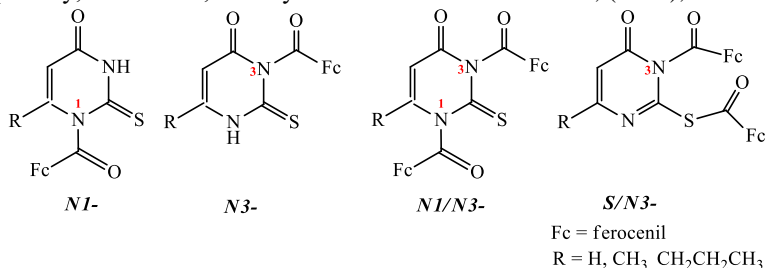
Organometalni nukleozidi čine važnu skupinu spojeva koja pokazuju antikancerogeno i antivirusno djelovanje, a također mogu poslužiti kao elektrokemijski biosenzori, radioaktivne, IR i luminiscentne sonde te reaktivni međuprodukti u sintetskoj kemiji. [1] U našim prethodnim istraživanjima, ispitano je nekoliko postupka za pripremu *N*-ferocenoiliranih derivata uracila, pri čemu karbonilna skupina povezuje organometalni i heterociklički dio, a ovisno o uvjetima reakcije nastaju N1 i N1/N3 konjugati. [2] 2-Tiouracil, 6-metil-2-tiouracil i 2-tiocitozin sasatavni su dio *t*-RNA, dok njihovi S-, N-, ili S, N-disupstituirani derivati pokazuju terapijska svojstva. [3] Slijedom toga ovdje ćemo se fokusirati na sintezu ferocenoil-tiouracil konjugata koja se temelji na reakciji aciliranja baze s ferocenoil-kloridom. Posebna pozornost će biti usmjerena ka praćenju steričkog efekta supstituenta u položaju C6 baze i uvjeta reakcije na iskorištenje i regioselektivnost reakcije. Novo sintetizirani spojevi biti će karakterizirani FT-IR, <sup>1</sup>H i <sup>13</sup>C NMR spektroskopijom te će biti ispitana njihova biološka aktivnost *in vitro* primjenom kulture stanica.

**Ključne riječi:** organometalni nukleozidi, tiouracil, ferocen

[1] M.K. Ismail, K. A. Armstrong, S. L. Hodder, S. L. Horswell, L. Male, H. V. Nguyen, E. A. Wilkinson, N. Hodges, J. Tucker, *Dalton Trans.* 49, (2020), 1181-1190.

[2] J. Lapić, V. Havaić, D. Šakić, K. Sanković, S. Djaković, V. Vrčec, *Eur. J. Org. Chem.* 24 (2015) 5424-5431.

[3] T. Pospieszny; I. Małecka; Z. Paryzek. *Tetrahedron Letters* 51, (2010), 4166-4169.





## EKOLOŠKI PRIHVATLJIVA SINTEZA DERIVATA TRIAZOLA S KUMARINSKOM JEZGROM AN ECO-FRIENDLY ROUTE FOR THE SYNTHESIS OF COUMARIN BASED TRIAZOLE DERIVATIVES

Mirjana Lončar<sup>1</sup>, Maja Molnar<sup>1</sup>, Marco Blangetti<sup>2</sup>, Davide Arnodo<sup>2</sup>,  
Federica de Nardi<sup>2</sup>

<sup>1</sup>J. J. Strossmayer University of Osijek, Faculty of Food Technology Osijek,  
Franje Kuhača 18, 31000 Osijek, Croatia

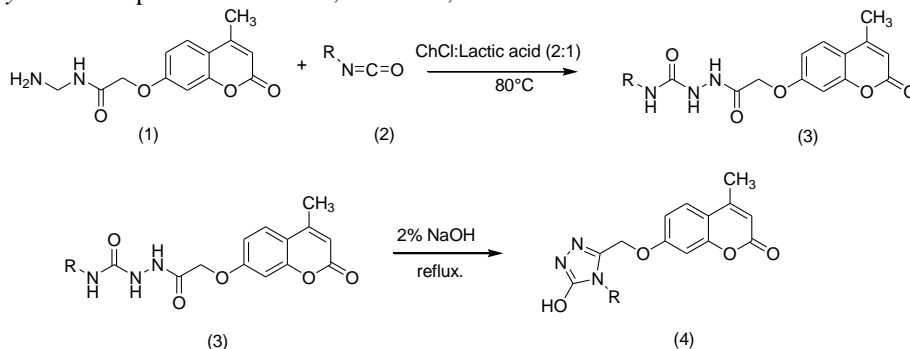
<sup>2</sup>University of Turin, Department of Chemistry, Via P. Giuria 7, I-10125 Torino (TO), Italy

Coumarins and their derivatives have attracted considerable attention due to their extensively biological, pharmacological, biochemical and therapeutic activities. Some authors have shown that the combination of coumarin moiety and some nitrogen-containing heterocycles, such as triazoles, contribute to better biological activity in comparison with initial material [1].

Deep eutectic solvents (DESs) are novel generation of "green solvents" that have proven to be a convenient media for many synthetic pathways. They are often described as environmentally friendly and sustainable mixtures of nontoxic and cheap components, whose properties can be adjusted for various applications [2, 3].

Prompted by the above mentioned facts and in continuation of our on-going interest in the development of new green synthetic approaches, the aim of this study was to synthesize coumarin triazole derivatives from 2-[(4-methyl-2-oxo-2*H*-chromen-7yl)oxy]acetohydrazide (1) and different isocyanates (2) utilizing ChCl-based DES as a reaction media. In first step, we obtained semicarbazides (3), which were subjected to cyclization in 2% sodium hydroxide solution under reflux to obtain final product (4). Our method is more convenient than conventional ones, providing high product yields and cleaner reaction paths.

**Keywords:** deep eutectic solvents, coumarin, triazole



[1] Y. Shi, C.-H. Zhou, *Bioorg. Med. Chem. Lett.* 21 (2011) 956–960.

[2] J. García-Álvarez, *Eur. J. Inorg. Chem.* 31 (2015), 5147–5157.

[3] G. García, S. Aparicio, R. Ullah, M. Atilhan, *Energy Fuels*, 29(4) (2015), 2616-2644.

**PRIMJENA NAFTNIH BIOMARKERA ZA  
KARAKTERIZACIJU I ODREĐIVANJE  
PORIJEKLA NAFTE  
APPLICATION OF PETROLEUM BIOMARKERS FOR  
CHARACTERIZATION AND SOURCE  
IDENTIFICATION OF CRUDE OIL**

Slavica Marinović

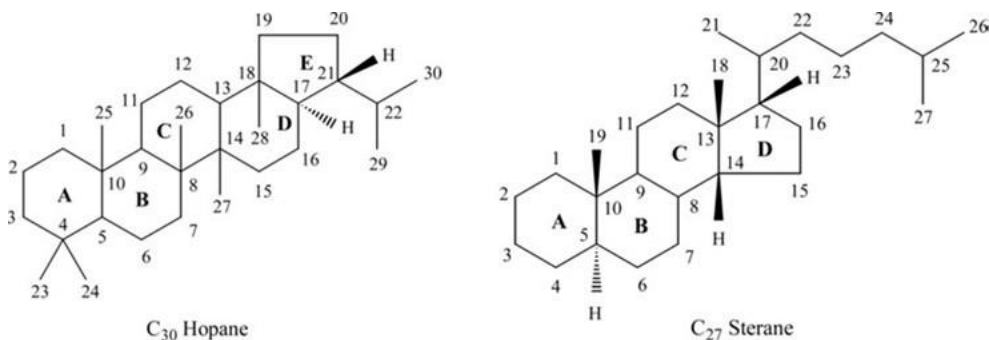
INA Industrija nafte d.d., Exploration & Production, Exploration & Production Laboratory,  
Lovinčićeva 4, 10 000 Zagreb, Croatia

The formation of crude oil occurred many millions of years ago from decaying plants and animals. Sediment and rock covered the organic material creating an anaerobic environment that eventually, under temperature and pressure conditions, formed crude oil. Crude oils from various regions differ in the plant and animal source materials, as well as the time, temperature, and pressure conditions that occurred during formation. Therefore, each crude oil has a unique fingerprint that can potentially be determined using biomarkers.

Biomarkers are one of the most important hydrocarbon groups in petroleum for chemical fingerprinting, they are complex molecules derived from formerly living organisms. The biomarkers found in crude oils, rocks, and sediments are stable and show little or no changes in structures from their parent organic molecules, biogenic precursors (e.g., bacteriohopanetrol, sterols), in living organisms, and thus carry information about the nature, source, type, geological conditions, and thermal history of these organisms.

Biomarkers can be detected in low quantities (ppm and subppm level) in the presence of a wide variety of other types of petroleum hydrocarbons using the gas chromatography/mass spectrometry (GC/MS). Relative to other hydrocarbon groups such as alkanes and most aromatic compounds, biomarkers, hopanes and steranes are also more biodegradation-resistant hydrocarbon compounds.

*Keywords:* crude oil, petroleum biomarkers, hopanes, steranes



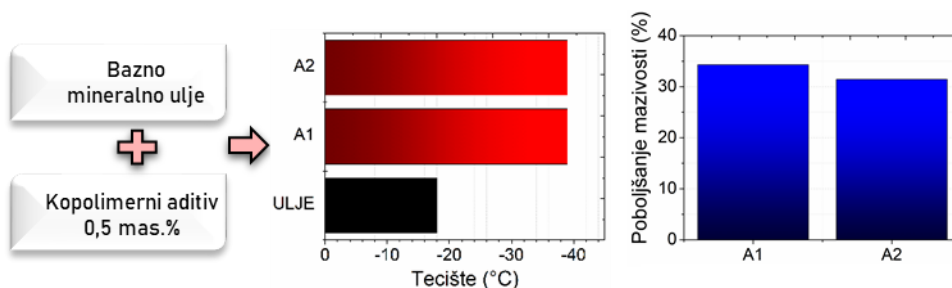
## POBOLJŠANJE TECIŠTA I MAZIVOSTI MINERALNOG YUBASE 4 ULJA UZ POMOĆ POLIMERNIH ADITIVA NA OSNOVI HIDROKSIPROPIL I BENZIL METAKRILATA POUR POINT AND LUBRICITY IMPROVEMENT OF MINERAL YUBASE 4 OIL WITH HYDROXYPROYL AND BENZYL METHACRYLATE POLYMER ADDITIVES

Mihovil Medić, Lucija Rebrović, Fabio Faraguna, Elvira Vidović, Ante Jukić  
Fakultet kemijskog inženjerstva i tehnologije, Sveučilište u Zagrebu, Marulićev trg 19,  
10000 Zagreb, Hrvatska

Maziva ulja se u današnje vrijeme koriste u raznim sustavima poput motora s unutarnjim izgaranjem, vozila, mjenjača i kompresora. U formulaciju mazivih ulja ulaze mineralna ili sintetska bazna ulja koja ne mogu zadovoljiti sve zahtjeve visokih performansi bez dodatka aditiva. Iz tog razloga se dodaju polimerni aditivi koji za cilj imaju poboljšati svojstva poput tečišta i mazivosti. To omogućava primjenu ulja pri širem rasponu temperaturnih uvjeta i dulji životni vijek opreme sukladno smanjenju trenja i trošenja.

U svrhu poboljšanja svojstva mineralnog ulja, provedena je sinteza kopolimera na osnovi metil metakrilata (MMA), dodecil metakrilata (DDMA), oktadecil metakrilata (ODMA) i hidroksipropil metakrilata (HPMA) ili benzil metakrilata (BZMA) uz pomoć peroksidnog inicijatora pri 95 °C. Dodatkom 0,5 mas.% kopolimera u mineralno bazno ulje, ispitan je utjecaj aditiva na maglište i tečište ulja prema normama ASTM D5771 i ASTM D5950. Uz to, ispitan je i utjecaj na mazivost prema normi HRN EN ISO 12156-1. Dodatkom aditiva došlo je do sniženja maglišta za 3 °C, a tečišta za 21 °C. Također, mazivost se poboljšala za 34,3 i 31,4 %.

*Ključne riječi:* polimerni aditivi, mazivost, tečište, mineralno ulje





## **IN VITRO KARAKTERIZACIJA GENERIČKOG PEPTIDNOG LIJEKA: PRIMJER AGONISTA GLP-1R/ IN VITRO CHARACTERIZATION OF THE GENERIC PEPTIDE THERAPEUTIC: THE GLP-1R AGONIST CASESTUDY**

Mia Mrčela, Dubravka Gembarovski, Nina Krpan, Sandro Makarić,  
Anamarija Skenderović, Vladimir Radić

Teva Pharmaceuticals, Global R&D, Prilaz baruna Filipovića 25, 10 000 Zagreb, Croatia

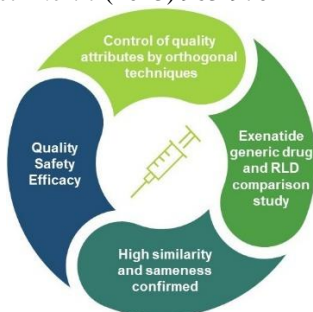
Newer generation of antidiabetics such as glucagon-like peptide-1 receptor agonists (GLP-1RA) have shown to be an efficient adjunctive therapy in patients with diabetes type 2 who failed to respond to oral antihyperglycemic agents [1, 2]. Generic version of GLP-1RA would decrease drug price vastly and would make newer diabetes medications widely accessible. In order to meet the regulatory requirements, a comprehensive analytical characterization needs to be performed and an equivalency of the generic Exenatide injection to the innovator drug must be demonstrated.

In this work, the extensive comparability study, which was aimed to ensure quality, safety and efficacy of the generic peptide product similar to the Byetta<sup>®</sup> Reference Listed Drug (RLD), is described. *In vitro* characterization of the generic drug included various analyses of physicochemical properties such as identity, structure, self-association and aggregation studies, purity and peptide content determination, whereby different orthogonal analytical techniques were employed. Most of the analytical methods were developed and optimized in-house. The comparison study was performed on different batches of the Exenatide injection, the RLD and the Exenatide drug substance. It is demonstrated that the generic Exenatide injection drug shows highly similar quality attributes related to safety and efficacy and meets the same standards as the innovator drug.

**Keywords:** antidiabetics, Exenatide, analytical characterization

[1] Cvetkovic R.S. and Plosker G.L., *Drugs* 67 (2007) 935-954

[2] Cai Y et al., *Drug Des Devel Ther.* 7 (2013) 963-970



## Sinteza i strukturna karakterizacija novih 1,2,3-triazolnih derivata benzo[d]oksazol-2-tiola

### Synthesis and structural characterization of novel 1,2,3-triazole derivatives of benzo[d]oxazole-2-thiol

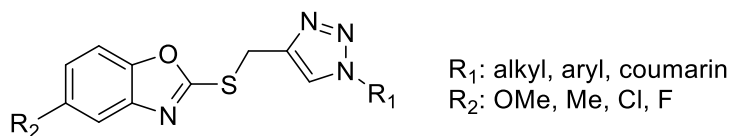
Robert Ostrički<sup>1</sup>, Tatjana Gazivoda Kraljević<sup>2</sup>

<sup>1</sup>Pliva Hrvatska d.o.o., Prilaz baruna Filipovića 25, 10000 Zagreb, Croatia

<sup>2</sup>Department of Organic Chemistry, Faculty of Chemical Engineering and Technology  
University of Zagreb, Marulićev trg 19, 10000 Zagreb, Croatia

Treatment of malignant diseases is among the most demanding challenges in modern medicine. Despite significant progress in diagnosing and treating of malignant diseases in the last few decades, there is still a lot of space for improvement. Modern chemotherapy is mostly not selective and attention is focused on the development of new, potent and selective antitumor agents. Benzoxazoles represent an important class of heterocyclic compounds that exhibit remarkable pharmacological activities such as anticancer, antiviral, antibacterial and antifungal. Furthermore, some benzoxazole derivatives are used as fluorescent bleaching agents and functional materials.[1-2]

In order to evaluate their antitumor activity, novel derivatives of benzo[d]oxazole-2-thiol containing 1,2,3-triazole ring as a linker were synthesized. Propargylated 2-thiobenzoxazole was prepared by cyclization reaction of 2-aminophenol using carbon disulfide, followed by *N*-alkylation reaction with propargyl bromide as an alkylating reagent. 1,2,3-triazole derivatives of benzo[d]oxazole-2-thiol were prepared by utilizing the copper-catalyzed azide-alkyne cycloaddition reaction (CuAAC) of 2-propargylated benzoxazoles with corresponding azides. Structures of synthesized 1,2,3-triazolyl derivatives of benzo[d]oxazole-2-thiol were confirmed by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy and mass spectrometry as well.



[1] C. P. Kaushik, M. Chahal, *J. Chem. Sci.*, 2020, 132, 142

[2] R. Sattar, R. Mukhtar, M. Atif, M. Hasnain, A. Irfan, *J. Het. Chem.*, 2020, 57, 2079-2107

# MEHANOKEMIJSKA SINTEZA I ANTITUMORSKA ISPITIVANJA NOVIH OKSIM-ETERSKIH I ESTERSKIH HETEROCIKLIČKIH DERIVATA FEROCENA ESTER AND OXIME-ETHER LINKED HETEROCYCLIC DERIVATIVES OF FERROCENE: MECHANOCHEMICAL SYNTHESIS AND ANTIPROLIFERATIVE EVALUATION

Martina Piškori<sup>1</sup>, Silvija Maračić<sup>1</sup>, Sandra Kraljević Pavelić<sup>2</sup>, Krešimir Pavelić<sup>2</sup>, Silvana Raić-Malić<sup>1</sup>

<sup>1</sup>Department of Organic Chemistry, Faculty of Chemical Engineering and Technology,  
University of Zagreb, 10000 Zagreb, Croatia

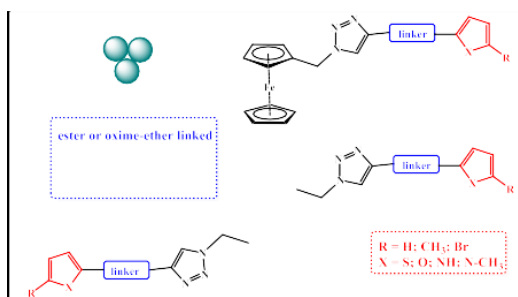
<sup>2</sup>Faculty of Medicine, Juraj Dobrila University of Pula, 52100 Pula, Croatia

Cancer is one of the deadliest threats to human health worldwide. To overcome the current clinical problems associated with drug resistance, there is an urgent need to identify and test new promising molecular structures that represent potential drug candidates. Organometallic compounds, especially ferrocene derivatives, possess remarkable structural and mechanical diversity, low toxicity, low cost, making them promising drug candidates for therapy cancer. [1, 2] Ester and oxime-ether linked heterocyclic derivatives of ferrocene were synthesized using regioselective copper(I)-catalyzed 1,3-dipolar cycloaddition under solvent-free mechanochemical conditions. The antitumor effects of all compounds were evaluated.

**Keywords:** ferrocene, oxime ethers, esters, heterocyclic derivatives, green synthesis

[1] H. Skoupilova, M. Bartosik, L. Sommerova, J. Pinkas, T. Vaculovic, V. Kanicky, J. Karban, R. Hrstka, *Eur. J. Pharmacol.* 867 (2020) 172825.

[2] S. Jakopc, J. N. Pantalon A. Brozovic, D. Jadreško, B. Perić, S. I. Kirin, S. Raić-Malić, *Appl Organomet Chem.* 36 (2022) 6575.



**SINTEZA DERIVATA KINAZOLINONA PRIMJENOM  
ODABRANIH ZELENIH METODA I NJIHOVA  
POTENCIJALNA ANTIBAKTERIJSKA AKTIVNOST  
SYNTHESIS OF QUINAZOLINONE DERIVATIVES USING  
SELECTED GREEN METHODS AND THEIR POTENTIAL  
ANTIBACTERIAL ACTIVITY**

Fran Prašnikar<sup>1</sup>, Mario Komar<sup>2</sup>, Valentina Pavić<sup>1</sup> and Maja Molnar<sup>2</sup>

<sup>1</sup>Josip Juraj Strossmayer University of Osijek, Department of Biology, Ulica cara Hadrijana 8/A, 31000 Osijek, Croatia

<sup>2</sup>Josip Juraj Strossmayer University of Osijek, Faculty of Food Technology Osijek, Franje Kuhača 18, 31000 Osijek, Croatia

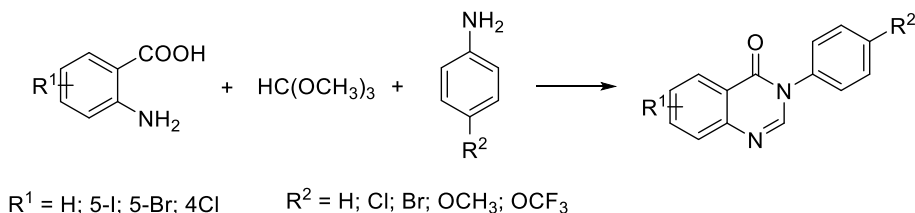
One of the main advantages of green chemistry is the tendency to develop procedures and techniques with low environmental impact. Deep eutectic solvents (DESs) have become an important part of the organic synthesis due to their properties [1]. Different quinazolinones were synthesized in choline-chloride : urea (1 : 2) DES using microwave-assisted and ultrasound-assisted synthesis. First, optimization was performed to find the appropriate DES, time of reaction and temperature. Starting compounds for the quinazolinone synthesis were differently substituted anthranilic acids, anilines and trimethyl orthoformate. The most appropriate method for synthesis was microwave-assisted synthesis using ethanol as a solvent. Antibacterial activity of quinazolinone derivatives was studied by minimal inhibitory concentration. All derivatives have shown antibacterial activity.

**Keywords:** Green chemistry; Quinazolinone derivatives; Deep eutectic solvents, Antibacterial activity

[1] B. B. Hansen *et al.* *Chem. Rev.* 121 (2021) 1232.

**Acknowledgments**

This work has been supported in part by Croatian Science Foundation under the project *Green Technologies in Synthesis of Heterocyclic Compounds* (UIP-2017-05-6593). The biological activity has been supported by research ID: 3105-12.





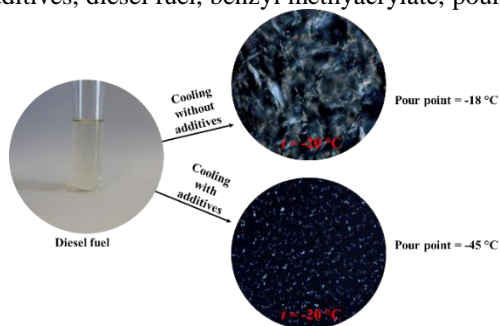
## **SINTEZA METAKRILATNIH POLIMERNIH ADITIVA S RAZLIČITIM UDJELIMA BENZIL METAKRILATA KAO ADITIVA ZA SNIŽENJE TECIŠTA DIZELSKOG GORIVA SYNTHESIS OF METHACRYLIC POLYMER ADDITIVES WITH DIFFERENT AMOUNTS OF BENZYL METHACRYLATE AS POUR POINT DEPRESSANTS FOR DIESEL FUEL**

Ivan Pucko, Rafael Anelić, Fabio Faraguna, Marko Racar

Fakultet kemijskog inženjerstva i tehnologije Sveučilišta u Zagrebu, Marulićev trg 19, 10000  
Zagreb, Croatia

To reduce the impact on climate change, stricter regulations on the composition of diesel fuel have been enacted in recent decades to reduce emissions. This has reduced the amount of sulphur, aromatics, and olefins in the fuel, resulting in an increase in *n*-paraffin content. This improves combustion properties but has the disadvantage of worsening low-temperature properties. Our research is focused on synthesizing polymer additives that improve these properties, with an emphasis on additives that improve flowability. The synthesized additives are based on benzyl methacrylate (BMA) with octadecyl methacrylate (ODMA), dodecyl methacrylate (DDMA) and 2-(*tert*-butylamino)ethyl methacrylate (TBAEMA) with different molar ratios of the comonomers. The additives were synthesized by radical polymerization in toluene solution with a radical initiator at 96 °C. The thermal properties of the additive formulations with non-additivated diesel fuel were investigated by differential scanning calorimetry (DSC). The influence of the additive on the crystal morphology and crystallization behavior was studied by optical microscopy with polarization, and the pour point (PP) was investigated according to ASTM D5950. The results obtained with the synthesized additives showed a significant improvement in the low-temperature properties of diesel, with a decrease in the PP temperature by up to 27 °C.

**Keywords:** polymer additives, diesel fuel, benzyl methacrylate, pour point depressant



## RAZVOJ NOVE CJENOVNO PRIHVATLJIVE MIKROFLUIDIČKE METODE ZA ODREĐIVANJE KARNOZINA U DODATACIMA PREHRANI DEVELOPMENT OF NEW COST-EFFECTIVE MICROFLUIDICS METHOD FOR CARNOSINE DETERMINATION IN DIETARY SUPPLEMENTS

Iva Pukleš<sup>1,2</sup>, Nikola Sakač<sup>3</sup>, Brunislav Matasović<sup>1</sup>, Bojan Šarkanj<sup>4</sup>,  
Ana Vesigner<sup>5</sup>, Marija Jozanović<sup>1,2</sup>

<sup>1</sup>Department of Chemistry, Josip Juraj Strossmayer University of Osijek,  
Ulica cara Hadrijana 8, 31000 Osijek, Croatia

<sup>2</sup>Doctoral School of Chemistry, University of Pécs, Ifjúság útja, 7624 Pécs, Hungary

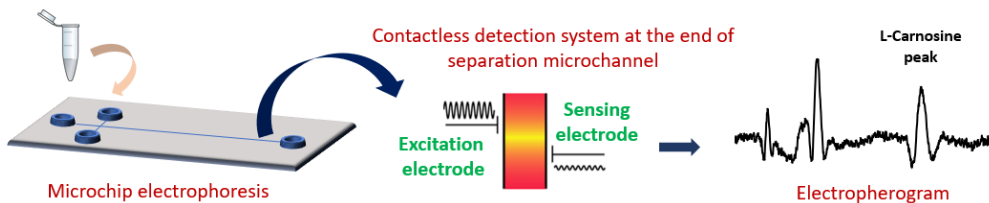
<sup>3</sup>Faculty of Geotechnical Engineering, University of Zagreb, Hallerova 7,  
42000 Varaždin, Croatia

<sup>4</sup>Department of Food Technology, University North, Trg dr. Žarka Dolinara 1, 48000  
Koprivnica, Croatia

<sup>5</sup>Döhler, Riedstraße D-64295, Darmstadt, Germany

Dipeptide L-carnosine is used in dietary supplements formulations to improve endurance during intense exercise. This report describes the new microchip electrophoresis (MCE) method to determine L-carnosine in dietary supplements samples. Capacitively coupled contactless conductivity detection (C<sup>4</sup>D) was employed as an alternative to expensive, time-consuming, and complex detection methods commonly used for peptides detection. Detector response showed high linearity in the tested range of 2.5 – 25 μmol/L. The separation was rapid, owing to 73 s migration time of L-carnosine. The proposed microfluidic method showed great potential for further analysis of L-carnosine in dietary supplement samples.

*Ključne riječi:* Carnosine, C<sup>4</sup>D detector, dietary supplements, microchip capillary electrophoresis



## PALADIJEM KATALIZIRANA SINTEZA I STRUKTURNA KARAKTERIZACIJA NOVIH DERIVATA 2- ARILBENZOKSAZOLA PALLADIUM CATALYZED SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF NOVEL 2- ARLYBENZOXAZOLE DERIVATIVES

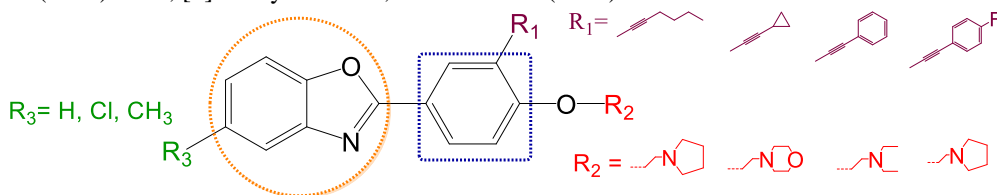
Anja Rakas<sup>1</sup>, Kristina Olujić, Jurja Vukovinski, Tatjana Gazivoda Kraljević  
Department of Organic Chemistry, Faculty of Chemical Engineering and Technology,  
University of Zagreb, Marulićev trg 20, 10000 Zagreb, Croatia

Benzoxazole scaffold is a core structure in many synthetic compounds having different biological activities such as anti-inflammatory, anticancer and antimicrobial [1]. In the search for more efficient drugs, transition metal-catalyzed cross-coupling reactions that enable carbon-carbon bond construction, such as Sonogashira reaction, emerged as an attractive solution to synthesizing challenges, which has found widespread use in the synthesis of benzoxazole derivatives substituted with alkynyl fragments.[2] From the viewpoint of green chemistry, DESs (Deep eutectic solvents) are attractive since some of them have proven to be biodegradable and compatible with enzymes further increasing their interest [3].

In this work we present synthesis of 2-(3-alkynyl-4-*O*-alkylphenyl)benzoxazoles by Sonogashira reaction. 4-*O*-alkylated benzaldehyde derivatives for the synthesis of target benzoxazole derivatives were prepared by alkylation reaction of 4-hydroxybenzaldehyde in DES (ChCl/glycerol) which were then converted in Schiff bases by mechanochemical reaction with 2-aminophenole. Microwave assisted cyclization of Schiff bases gave 2-arylbenzoxazoles. Introduction of alkynyl substituents at position 3 of phenyl ring was performed by Pd-catalyzed Sonogashira cross-coupling reaction. Structures of all newly prepared 2-(3-alkynyl-4-*O*-alkylphenyl)benzoxazoles were confirmed by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy.

**Keywords:** benzoxazole, deep eutectic solvent, microwave reaction, Sonogashira reaction

[1] D. Osmaniye *et al.*, *Eur. J. Med. Chem.* 131 (2021) 92, [2] A. Paun *et al.*, *Tetrahedron Lett.* 56 (2015) 5349, [3] R. Ayoub *et al.*, *Molecules* 27 (2022) 23.



## RAZVOJ ELEKTRODE S UGLJIKOVOM PASTOM ZA POTENCIOMETRIJSKO ODREĐIVANJE ACEBUTOLOLA DEVELOPMENT OF CARBON PASTE ELECTRODE FOR THE POTENTIOMETRIC DETERMINATION OF ACEBUTOLOL

Josip Radić, Marija Bralić, Anđela Radan, Lana Škutin, Marija Vučetić  
Department of Environmental Chemistry, Faculty of Chemistry and Technology, University  
of Split, R. Boškovića 35, 21000 Split, Croatia

Electrodes based on carbon paste are often used in electrochemical measurements due to their good physical and chemical properties.[1] In this work carbon paste electrodes (CPEs) for the potentiometric determination of the acebutolol hydrochloride, cardiovascular drug from the family of beta blockers, were prepared. The design and manufacture of the working electrode body was previously reported.[2] Some of the most frequently tested binders in the last ten years, such as: dibutyl phthalate, bis(2-ethylhexyl)phthalate, paraffin oil, tris(2-ethylhexyl)phosphate, 2-nitrophenyl-octyl-ether and bis(2-ethylhexyl) adipate were used. In order to improve the sensitivity, the CPE were modified by the addition of previously precipitated ion association complexes (IAC) and various ion additives.

All measurements were performed in the concentration range of working solutions of acebutolol from  $3.16 \times 10^{-6}$  M to  $3.16 \times 10^{-3}$  M in an acetate buffer with a pH value of 5.0.

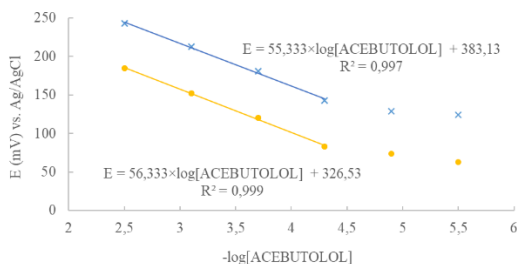
Although this research gave promising results, prepared CPEs showed worse preliminary response characteristics than CPE for acebutolol determination previously reported.[3] In further research, emphasis is going to be placed on the incorporation of different nanomaterials into the paste, especially those made of carbon materials.

**Keywords:** carbon paste electrodes, potentiometry, acebutolol

[1] I. Švancara, K. Vytřas, K. Kalcher, A. Walcarius, J. Wang, *Electroanalysis* 21 (2009) 7.

[2] J. Radić, M. Buljac, B. Genorio, E. Gričar, M. Kolar, *Sensors* 21 (2021) 2955.

[3] N. A. Alarfaj, M. F. El-Tohamy, *J. Chinese Chem. Soc.* 61 (2014) 910.



**Figure 1.** Potentiometric responses of various prepared CPEs for acebutolol determination

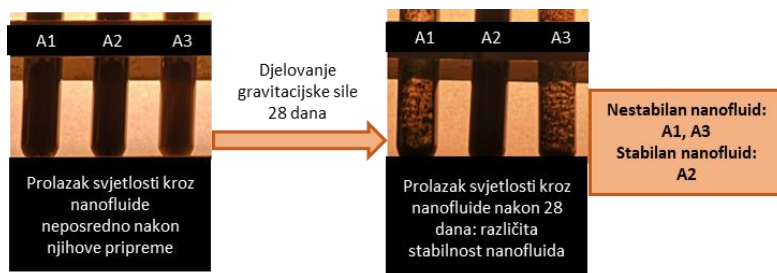
## UTJECAJ POLIMERNIH POVRŠINSKI AKTIVNIH TVARI NA STABILNOST NANOFLUIDA NA OSNOVI UGLJIKOVIH NANOCIJEVI I SINTETSKOG MAZIVOG ULJA EFFECT OF POLYMERIC SURFACTANTS ON STABILITY OF CARBON NANOTUBES AND SYNTETIC OIL-BASED NANOFLUIDS

Lucija Rebrović, Mihovil Medić, Fabio Faraguna, Elvira Vidović, Ante Jukić  
Fakultet kemijskog inženjerstva i tehnologije Sveučilišta u Zagrebu, Marulićev trg 19,  
10000 Zagreb, Hrvatska

Dugoročna stabilnost nanofluida jedan je osnovnih zahtjeva koji mora biti zadovoljen da bi se omogućio prijenos topline u rashladnim sustavima. Zbog tendencije nanočestica aglomeraciji uslijed djelovanja Van der Waalsovih sila, dolazi do ubrzane sedimentacije pod utjecajem gravitacijske sile. Uslijed sedimentacije nanočestica pogoršavaju se svojstva nanofluida poput toplinske vodljivosti i mazivosti. Stabilnost je uvjetovana načinom pripreme nanofluida pri čemu se za raspršenje nanočestica i razbijanje aglomerata, osim fizikalnih metoda poput ultrazvučne homogenizacije, mogu koristiti kemijske metode poput dodatka površinski aktivnih tvari. Na navedene načine može se osigurati dugoročna postojanost svojstava nanofluida koja bi omogućila primjenu u industrijske svrhe.

U ovome radu ispitana je stabilnost nanofluida pod djelovanjem gravitacijske sile, a i djelovanjem centrifugalne sile u svrhu simuliranja uvjeta dugoročnije gravitacijske stabilnosti. Ispitan je učinak 0,1 mas. % kopolimera metakrilatne osnove kao površinski aktivnih tvari na stabilnost nanofluida na osnovi višestjenčanih ugljikovih nanocijevi (MWCNT, 0,01 mas. %) u sintetskom polialfaolefinskom baznom ulju niske viskoznosti. Kao najdjelotvornija površinski aktivna tvar pokazao se kopolimer s funkcionalnom amino skupinom (A2) osiguravajući 99,5% početne raspršenosti MWCNT nakon 28 dana i 99,0% raspršenosti nakon izloženosti 45-minutnoj prisilnoj sedimentaciji.

*Ključne riječi:* nanofluidi, MWCNT, gravitacijska stabilnost, prisilna sedimentacija



## SINTEZA, BOJADISARSKA SVOJSTVA I BIOLOŠKA AKTIVNOST NOVIH BENZOTIAZOLNIH AZO BOJILA SYNTHESIS, DYEING PROPERTIES AND BIOLOGICAL ACTIVITY OF NEW BENZOTHIAZOLE AZO DYES

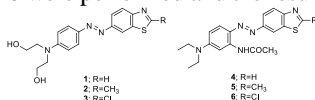
Magda Relić<sup>1</sup>, Mario Herceg<sup>1</sup>, Ana Sutlović<sup>1</sup>, Mihailo Banjanac<sup>2</sup>, Vedrana Radovanović<sup>2</sup>, Leentje Persoons<sup>3</sup>, Dirk Daelemans<sup>3</sup>, Livio Racané<sup>1</sup>

<sup>1</sup>Sveučilište u Zagrebu Tekstilno-tehnološki fakultet, Prilaz baruna Filipovića 28a, 10000 Zagreb, Croatia

<sup>2</sup>Pharmacology *in vitro*, Selvita Ltd. Prilaz baruna Filipovića 29, 10000 Zagreb, Croatia

<sup>3</sup>KU Leuven, Department of Microbiology, Immunology and Transplantation, Rega Institute, 3000 Leuven, Belgium

Aromatic and heteroaromatic azo compounds represent the most numerous and diverse group of synthetic dyes, used not only as textile dyes, but also in many other different industry fields: for dyeing various substrates, biological-medical research, in the field of nonlinear optics and optical data storage. Aromatic diazo components, in the synthesis of azo dyes, are increasingly being replaced by heteroaromatic diazo components because the prepared heterocyclic azo dyes show better dyeing properties such as color tone and brightness, and better light fastness compared to the corresponding carbocyclic azo dyes. In this work, an efficient method for the synthesis of a small library of 6-azo-substituted benzothiazole molecules by diazotization reactions of three 6-amino-substituted benzothiazole derivatives and by copulation of the corresponding diazonium salts to two *N,N*-disubstituted aniline derivatives have been presented. The obtained dyes have been tested as disperse dyes for polyester (PES) and polyamide (PA) textile material. All six tested dyes have good application properties for dyeing PA textile materials, while dyes 4-6 proved to be good for PES. In order to determinate biological activity of presented new azo dyes *in vitro* antiproliferative and antibacterial evaluations of dyes 1-6 were performed and the results have been presented.



**Keywords:** azo-benzothiazole, disperse dyes, synthesis, dyeing, biological activity  
Polyester (PES) and polyamide (PA) fabrics coloured with azo dyes 1–6

	1	2	3	4	5	6
PES						
PA						

## DIZAJN I SINTEZA MANOZILIRANIH FEROCENSKIH DERIVATA DESMURAMIL-PEPTIDA DESIGN AND SYNTHESIS OF MANNOSYLATED FERROCENE DERIVATIVES OF DESMURAMYL PEPTIDES

R. Ribić<sup>1</sup>, V. Petrović Peroković<sup>2</sup>, Ž. Car,<sup>2</sup> M. Kovačević<sup>3</sup>, L. Barišić<sup>3</sup>

<sup>1</sup>University North, University Center Varaždin, Jurja Križanića 31b,  
42000 Varaždin, Croatia

<sup>2</sup>Department of Chemistry, Faculty of Science, University of Zagreb, Horvatovac 102a,  
10000 Zagreb, Croatia

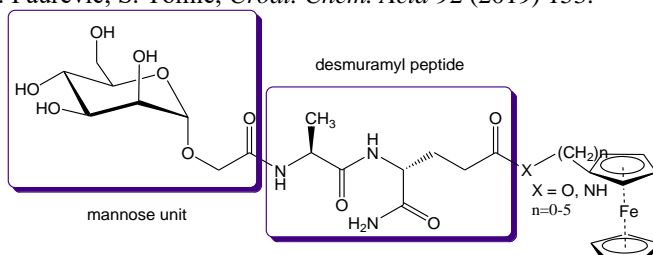
<sup>3</sup>Faculty of Food Technology and Biotechnology, University of Zagreb, Pierottijeva 6,  
10000 Zagreb, Croatia

Muramyl dipeptide (MDP, *N*-acetylmuramyl-L-alanyl-D-isoglutamine) is the smallest peptidoglycan fragment capable to trigger the immune response. MDP acts as a pathogen-associated molecular pattern and activates the NOD2 receptor [1]. The main parameter for the improvement of NOD2 agonistic properties is increased lipophilicity. Mannose receptors presented on immunocompetent cells are pattern-recognition receptors, as well as NOD2, and consequently they can affect the immune reactions [2]. Therefore, we present the design and synthesis of mannosylated desmuramyl peptides containing ferrocene lipophilic substituents attached at D-isoglutamine of dipeptide pharmacophore through ester or amide bond. Alkyl spacers of different lengths are inserted between peptide and ferrocene unit to further increase lipophilicity of the synthesized compounds.

**Keywords:** desmuramyl peptide, ferrocene, mannose, immunomodulation

[1] A. Maršavelski, M. Paurević, R. Ribić, *Org. Biomol. Chem.* 19(32) (2021) 7001.

[2] R. Ribić, M. Paurević, S. Tomić, *Croat. Chem. Acta* 92 (2019) 153.





## EKSTRAKCIJA METALA I METALOIDA IZ UZORAKA TLA VODENIM OTOPINAMA AMONIJEVIH SOLI EXTRACTION OF METALS AND METALLOIDS FROM SOIL SAMPLES BY AQUEOUS SOLUTIONS OF AMMONIUM SALTS

Vibor Roje, Ivor Košutić

<sup>1</sup>University of Zagreb – Faculty of Forestry and Wood Technology, Svetošimunska cesta 23,  
10002 Zagreb, Hrvatska

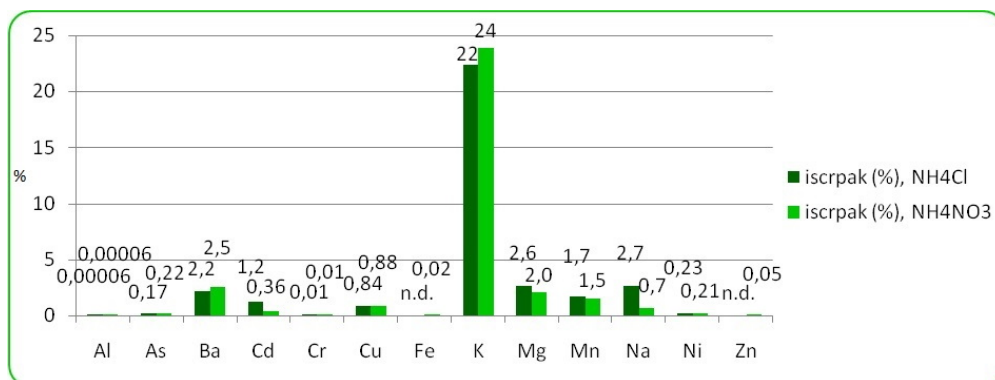
U znanstvenoj i stručnoj praksi poznate su brojne metode određivanja metala i metaloida u uzorcima tla. Odabir metode ponajprije ovisi o ciljevima istraživanja. Tako se, primjerice, za cjelovitu elementnu karakterizaciju tla ne primjenjuju se metodologije iste onima kakvima se pribjegava u svrhu procjene bioraspoloživosti tzv. 'teških metala' u tlima [1,2].

U ovom radu istraživana je ekstrakcijska moć vodenih otopina amonijevih soli jednakih koncentracija ( $\text{NH}_4\text{Cl}$  odnosno  $\text{NH}_4\text{NO}_3$ ,  $0,1 \text{ mol dm}^{-3}$ ). Kvantifikacija analitâ u ekstraktima provedena je tehnikom ICP-AES. Kao modelni uzorak korišten je certificirani referentni materijal za tlo Metranal-33.

*Ključne riječi:* tlo, teški metali, ekstrakcija, ICP-AES

[1] H.M. (Skip) Kingston & S.J. Haswell (Eds.), Microwave-enhanced chemistry – fundamentals, sample preparation, and applications, American Chemical Society, Washington DC, 1997, str. 223-349.

[2] A. Sahuquillo, A. Rigol, G. Rauret, Overview of the use of leaching/extraction tests for risk assessment of trace metals in contaminated soils and sediments, Trends Anal. Chem. 22 (2003) 152.





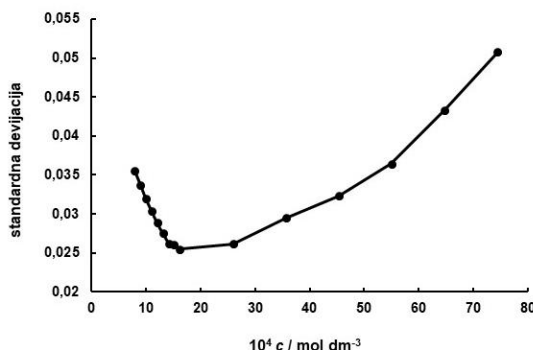
## ODREĐIVANJE GRANICE STVARANJA TROSTRUKIH IONA U OTOPINAMA KBr I 90 % BUTAN-2-OLA DETERMINATION OF THE LIMITING CONCENTRATION OF TRIPLE ION FORMATION IN SOLUTIONS OF KBr AND 90 % BUTAN-2-OL

Vesna Sokol, Ante Radoš, Boris-Marko Kukovec

Kemijsko-tehnološki fakultet, Sveučilište u Splitu, R. Boškovića 35, 21000 Split, Hrvatska

U ovom radu mjerena je vodljivost otopina kalijevog bromida u 90 %-tnom butan-2-olu u temperaturnom području od 15 do 35 °C. U otapalima niske relativne električne permitivnosti pri nižim koncentracijama elektrolita dolazi do reakcije ionske asocijacije  $K^+$  i  $Br^-$  iona i stvaranja neutralnih ionskih parova ( $K^+Br^-$ ), a kod većih koncentracija dolazi do reakcije asocijacije ionskog para s drugim  $K^+$  i  $Br^-$  ionima te nastaju trostruki kationi ( $K^+Br^-K^+$ ), odnosno anioni ( $Br^-K^+Br^-$ ). Trostruki ioni su nabijene čestice, pa povećanjem koncentracije elektrolita raste provodnost otopine. Za obradu podataka korišten je kemijski model provodnosti utemeljen na jednadžbi Fuoss-Hsia (model FHFP). Na temelju dobivenih rezultata procijenjena je granična koncentracija nastajanja trostrukih iona (Slika 1). Iz koncentracijske ovisnosti vodljivosti razrijeđenih otopina izračunate su granična molarna provodnost elektrolita i termodinamička konstanta ravnoteže za ionsku asocijaciju pri svim temperaturama, te su izvedene termodinamičke veličine za reakciju asocijacije. Reakcija stvaranja trostrukih iona istražena je uz pretpostavku da su ravnotežne konstante trostrukih kationa i aniona jednake  $K_T^+ = K_T^- = K_T$ . Određene su vrijednosti granične molarne provodnosti trostrukih iona i termodinamička konstanta ravnoteže za reakciju nastajanja trostrukih iona te su izračunate termodinamičke veličine za reakciju nastajanja trostrukih iona.

*Ključne riječi:* ionska asocijacija, trostruki ioni, molarna provodnost



**Slika 1.** Granična koncentracija nastajanja trostrukih iona ( $K^+Br^-K^+$ ) i ( $Br^-K^+Br^-$ ) prema modelu FHFP pri 25 °C

## UPOTREBA BILJNIH EKSTRAKTA U ZELENOJ SINTEZI NANOČESTICA ŽELJEZA USAGE OF PLANT EXTRACTS IN GREEN SYNTHESIS OF IRON NANOPARTICLES

Martina Sušjenka<sup>1</sup>, Martina Jakovljević Kovač<sup>2</sup>,  
Mislav Mustapić<sup>3</sup>, Maja Molnar<sup>2</sup>

<sup>1</sup>Department of Biology, Josip Juraj Strossmayer University of Osijek, Ulica cara Hadrijana 8/A, 31000 Osijek, Croatia

<sup>2</sup>Faculty of Food Technology Osijek, Josip Juraj Strossmayer University of Osijek, Franje Kuhača 18, 31000 Osijek, Croatia

<sup>3</sup>Department of Physics, Josip Juraj Strossmayer University of Osijek, Trg Ljudevita Gaja 6, 31000 Osijek, Croatia

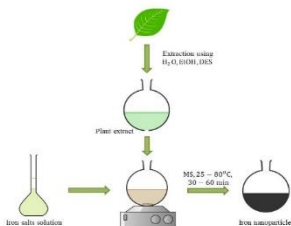
In last 20 years, iron-based nanoparticles have gained attention due their specific properties such as special magnetic properties, availability, versatility, multivalent oxidation states. The most common iron nanoparticles in nature are magnetite ( $\text{Fe}_3\text{O}_4$ ), maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ) and hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ). Conventional methods have been shown as a successful in synthesis of magnetic nanoparticles but they are expensive, complex, take a lot of time and create a lot of side products. In order to prevent that, scientists try novel green synthesis models which are rapid, eco-friendly with less waste products and more simple [1]. The aim of this research was to synthesize iron oxide nanoparticles, mainly magnetite, using plant extracts obtained by GRAS (*generally recognized as safe*) solvents and deep eutectic solvents (DESs). Total phenolic content and antiradical activity using DPPH method was measured for prepared extracts. Nanoparticles were synthesized from different iron salts and afterwards characterized by application of appropriate techniques.

**Keywords:** green synthesis, iron nanoparticles, plants, extracts

[1] O.P. Bolade, et al. *Environ. Nanotechnol. Monit. Manag.* 13(2020) 100279

### Acknowledgments

This work has been supported in part by Croatian Science Foundation under the project Green Technologies in Synthesis of Heterocyclic Compounds (UIP-2017-05-6593).



## HLAPLJIVI SPOJEVI RAKIJE TRAVARICE VOLATILE COMPOUNDS OF BRANDY TRAVARICA

Mladenka Šarolić<sup>1</sup>, Željana Pavlović<sup>1</sup>, Zvonimir Marijanović<sup>1</sup>,  
Ani Radonić<sup>1</sup>, Žana Delić<sup>2</sup>

<sup>1</sup>Kemijsko-tehnološki fakultet, Sveučilište u Splitu, Ruđera Boškovića 35,  
21 000 Split, Hrvatska

<sup>2</sup>Veleučilište „Marko Marulić“ u Kninu, Petra Krešimira IV 30, 22 300 Knin, Hrvatska

Travarica je jako alkoholno piće koje u Hrvatskoj ima dugu tradiciju proizvodnje, posebice na području Dalmacije, Istre i otoka. Pripada skupini specijalnih rakija te se proizvodi aromatiziranjem vinskog destilata, komovice, lozovače ili voćnih rakija odabranim aromatičnim biljem ili njihovim maceratima [1]. U ovom radu analiziran je aromatični profil rakija travarica kupljenih na domaćem tržištu. Hlapljivi spojevi izolirani su pomoću mikroekstrakcije vršnih para na krutoj fazi (HS-SPME) korištenjem CAR/PDMS i DVB/CAR/PDMS vlakana, te analizirani vezanim sustavom plinska kromatografija-masena spektrometrija (GC-MS). Identificirani hlapljivi spojevi pripadaju sljedećim kemijskim skupinama: esteri, alkoholi, ketoni, ugljikovodici, acetali i cikloeteri (oksidi). Među hlapljivim spojevima dominantni su bili esteri, a najzastupljeniji spoj u svim uzorcima bio je etil-dekanoat koji je karakteriziran voćnim aromama [2]. Dobiveni rezultati ukazali su na postojanje razlika u aromatičnom profilu rakija travarica, što je bilo i očekivano obzirom da svaki proizvođač ima svoju recepturu i specifičnost u tehnološkom procesu proizvodnje.

*Gljučne riječi:* hlapljivi spojevi, rakija, travarica, HS-SPME/GC-MS

[1] M. Mihaljević Žulj, *Gospodarski list* 8 (2019). <https://gospodarski.hr/rubrike/vocarstvo-rubrike/aromaticne-rakije-travarice/>

[2] D. Raičević, T. Popović, D. Jančić, D. Šuković, R. Pajović-Šćepanović, *Molecules* 27 (2022) 2974.



## PRIPRAVA NANOKRISTALNIH METALO-ORGANSKIH MREŽA NA BAZI LANTANOIDA I NJIHOVIH DERIVATA PREPARATION OF NANOCRYSTALLINE LANTHANIDE- BASED METAL-ORGANIC FRAMEWORKS AND THEIR DERIVATIVES

Tomislav Šilješ<sup>1</sup>, Sara Goman<sup>1</sup>, Jelena Kojčinović<sup>1</sup>, Dalibor Tatar<sup>1</sup>,  
Srijita Nundy<sup>2</sup>, Igor Djerdj<sup>1</sup>

<sup>1</sup>Department of Chemistry, Josip Juraj Strossmayer University of Osijek, Ulica cara  
Hadrijana 8/A, 31000 Osijek, Croatia

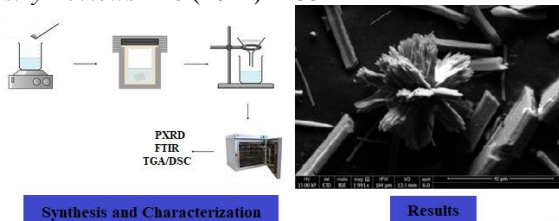
<sup>2</sup>Environment and Sustainability Institute, University of Exeter, Penryn TR10 9FE, UK

Metal-organic frameworks (MOFs) are a type of porous materials built from metal cations coordinated by organic ligands, the so-called linkers, in the form of one-, two- or three-dimensional structures. Due to the large specific surface area of MOFs and the ability to easily release and accept electrons from lanthanide metals, they have potential applications in electrocatalysis, photocatalysis [1], and gas storage [2]. In this research, nanocrystalline succinate MOFs based on lanthanides La, Ce, and Pr were synthesized. The synthesis was carried out via the solvothermal method, in which a mixture of DMF and water was used. The structure of the obtained crystals was characterized using Fourier transform infrared spectroscopy (FTIR), powder X-ray diffraction (PXRD), and thermogravimetric analysis (TGA) coupled with differential scanning calorimetry (DSC). Morphology was determined using scanning electron microscopy (SEM). Pyrolysis of the obtained MOFs in the oxidative and inert atmosphere was monitored *in situ* by TGA/DSC, and residues were characterized by PXRD. Performed analyses revealed nanocrystalline rod-like nanostructures which could be used directly in catalysis or as storage materials. Synthesized MOFs are also suitable for application as precursors for the synthesis of shape-controlled lanthanide oxides and lanthanide-doped carbon nanostructures.

**Keywords:** metal-organic framework, lanthanides, nanorods, photocatalysis

[1] H. Yang, L. Ji, Z. Zhang, B. Xu, Z. Liu, Q. Zhang, Y. Cao, Z. Nan, M. Zhang, T. Ohno, *Journal of Catalysis*, **405** (2022) 74-83

[2] U. Ryu, S. Jee, P. Chandra Rao, J. Shin, C. Ko, M. Yoon, K. Sung Park, K. Min Choi, *Coordination Chemistry Reviews* **426** (2021) 213544



## STABILNOST METIMAZOLA U DIKLORMETANU STABILITY OF METHIMAZOLE IN DICHLOROMETHANE

Leo Štefan,<sup>1</sup> Ivica Đilović,<sup>2</sup> Ana Čikoš,<sup>3</sup> Miljenko Dumić<sup>4</sup>

<sup>1</sup> JADRAN-GALENSKI LABORATORIJ d.d., Svilno 20, 51000 Rijeka, Hrvatska

<sup>2</sup> Sveučilište u Zagrebu, Prirodoslovno-matematički fakultet, Kemijski odsjek,  
Horvatovac 102a, 10000 Zagreb, Hrvatska

<sup>3</sup> Institut Ruđer Bošković, Centar za NMR, Bijenička cesta 54, 10000 Zagreb, Hrvatska

<sup>4</sup> Sveučilište u Rijeci, Odjel za biotehnologiju, Radmile Matejčić 2, 51000 Rijeka, Hrvatska

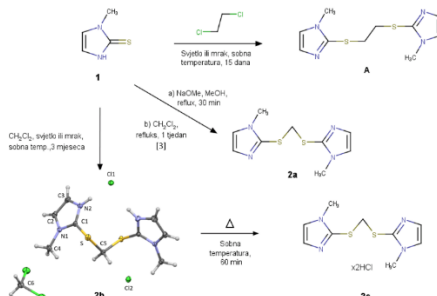
U okviru istraživanja stabiliteta tireostatika metimazola (1-metil-2,3-dihidro-1*H*-imidazola, **1**) nedavno je opisan kemizam njegove spontane *S*-alkilacije s 1,2-dikloretnom u 1,2-bis[(1-metil-1*H*-imidazol-2-il)tio]etnan (**A**) [1] te neke čvrste forme bis derivata **A** [2]. U nastavku istraživanja utvrdili smo i spontanu *S*-alkilaciju **1** s diklormetanom pri sobnoj temperaturi, na svjetlu ili u mraku, pri čemu je, nakon 3 mjeseca s iskorištenjem od 41,0 % izoliran diklormetanski solvat 1,1-bis[(1-metil-1*H*-imidazol-2-il)tio]metan dihidroklorida (**2b**). Osnovna supstancija, 1,1-bis[(1-metil-1*H*-imidazol-2-il)tio]metan (**2a**) je krutina,  $t_f = 51\text{--}52\text{ }^\circ\text{C}$ , poznata iz literature kao produkt alkilacije **1** u vrijućem diklormetanu u prisutnosti jakih baza [3]. Solvat **2b** [(C<sub>9</sub>H<sub>14</sub>N<sub>4</sub>S<sub>2</sub>)Cl<sub>2</sub>·CH<sub>2</sub>Cl<sub>2</sub>], (*Mr* 398,19) kristalizira kao hidrokloridna sol u monoklinskom sustavu ( $P2_1/c$ ,  $a = 6,7755(3)\text{ \AA}$ ,  $b = 11,0081(5)\text{ \AA}$ ,  $c = 23,4971(11)\text{ \AA}$ ,  $\beta = 94,657(5)^\circ$ ,  $V = 1746,75(14)\text{ \AA}^3$ ,  $Z = 8$ ,  $R = 0,0359$ ,  $R_w = 0,0945$ ,  $S = 0,933$ ). Solvat **2b** je nestabilan i tijekom izolacije već pri sobnoj temperaturi dolazi do brze desolvatacije pri čemu je dobiven amorfni 1,2-bis[(1-metil-1*H*-imidazol-2-il)tio]metan dihidroklorid (**2c**),  $t_f$  DSC onset 131 °C.

*Ključne riječi:* metimazol, 1,1-bis[(1-metil-1*H*-imidazol-2-il)tio]metan, desolvatacija

[1] L. Štefan, A. Čikoš, R. Vianello, I. Đilović, D. Matković-Čalogović, M. Dumić, *Molecules*, **26** (2021) 7032.

[2] L. Štefan, D. Matković-Čalogović, D. Filić, M. Dumić, *Crystals*, **10** (2020) 667.

[3] R. M. Silva, M. D. Smith, J. R. Gardinier, *J. Org. Chem.*, **70** (2005) 8755–8763.



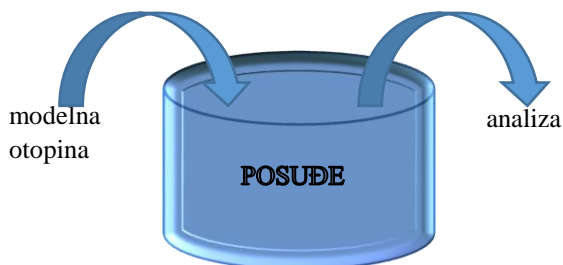
## **ANALIZA POSUĐA OD NEHRĐAJUĆEG ČELIKA STAINLESS STEEL COOKWARE ANALYSIS**

Anita Štrkalj, Zoran Glavaš, Martina Marić

Sveučilište u Zagrebu, Metalurški fakultet, Aleja narodnih heroja 3, 44000 Sisak, Hrvatska

Od prapovijesnih dana pa sve do danas posuđe je korišteno za pripremu, čuvanje i posluživanje hrane. Nekada se izrađivalo od materijala koji su pronađeni u prirodi. Danas nove tehnologije omogućavaju izradu posuđa od sofisticiranih materijala koji su otporni na visoke temperature, oštećenja, osiguravaju neprianjanje hrane prilikom termičke obrade i sl. Sve navedeno ujedno donosi i određene opasnosti koje se odnose na migraciju elemenata iz posuđa u hranu. U ovom radu istraživana je migracija iona As, Cd, Cr, Ni, Pb i Zn iz posuđa od nehrđajućeg čelika u ovisnosti o vremenu, a uslijed kontakta posuđa s hranom. Dobiveni rezultati su pokazali da dolazi do migracije pojedinih elemenata što je vezano uz vrijeme kontakta posuđa s hranom, ali i o starosti posuđa.

*Ključne riječi:* teški metali, posuđe, hrana, migracija



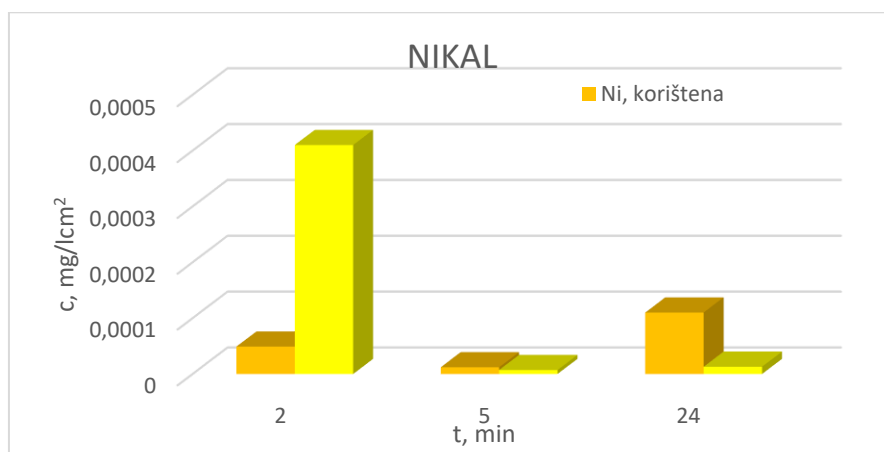
## MIGRACIJA NIKLA IZ NAKITA OD ČELIKA MIGRATION OF NICKEL FROM STEEL JEWELRY

Anita Štrkalj, Zoran Glavaš, Uršula Apalović

Sveučilište u Zagrebu, Metalurški fakultet, Aleja narodnih heroja 3, 44000 Sisak, Hrvatska

Uloga nakita u životu čovjeka vrlo malo se mijenjala kroz povijest. Uglavnom se nakit koristi za ukrašavanje ljudskog tijela, ali i kao statusni simbol ili za izražavanje pripadnosti određenim grupama ili kulturama. Međutim, procesi proizvodnje nakita značajno su napredovali. Istraživanja vezana uz utjecaj pojedinih komponenti iz nakita na zdravlje čovjeka također su značajno napredovala. Poznato je da tijekom nošenja dolazi do interakcije nakita s kožom. Znoj koji se oslobađa na koži utječe na migraciju teških metala. Ova pojava je posebno izražena kod nakita koji je napravljen od neplemenitih metala (npr. od ugljičnog čelika i sl.). U ovom radu istraživana je migracija iona nikla iz nakita napravljenog od različitih vrsta čelika koji je bio u kontaktu s modelnom otopinom znoja. Dobiveni rezultati su pokazali da dolazi do migracije navedenih iona. Koncentracija iona koja migrira uslijed kontakta nakita i modelne otopine znoja ovisi o vremenu kontakta.

*Ključne riječi:* nakit, nikal, znoj, migracija



## RAZVOJ METODE ZA DETEKCIJU MIKROPLASTIKE u PITKOJ VODI PRIMJENOM MIKRO-RAMANOVE SPEKTROSKOPIJE DEVELOPMENT OF METHOD FOR MICROPLASTICS DETECTION IN DRINKING WATER BY MICRO-RAMAN SPECTROSCOPY

Ana Tolić, Tamilselvi Selvam, Vlasta Mohaček Grošev,  
Lara Mikac, Mile Ivanda

Laboratorij za molekulsku fiziku i sinteze novih materijala, Institut Ruđer Bošković,  
Bijenička 54, 10000 Zagreb, Hrvatska

Mikroplastika nekontrolirano ulazi u okoliš, ili degradacijom makroplastike ili kao namjerno proizvedene plastične čestice mikro- veličina. Dosadašnja istraživanja su pokazala prisutnost mikroplastike u različitim izvorima pitke vode. Nedostatak standardiziranih metoda identifikacije i kvantifikacije mikroplastike u pitkoj vodi umanjuje obnovljivost rezultata i usporedbu rezultata iz različitih istraživanja. Stoga, naš fokus je razvoj i optimizacija metode za određivanje kvalitativne i kvantitativne analize mikroplastike u pitkoj vodi primjenom mikro-Raman spektroskopije. Koraci u analizi mikroplastike su: uzorkovanje, priprema uzorka, filtracija, analiza uzorka mikro-Ramanovom spektroskopijom i obrada podataka. Prikladnost i učinkovitost metode je ispitana koristeći referentne materijale odnosno dodavanjem dvije vrste mikroplastike različitih veličina u ultračistu vodu. Kako je analiza cijele površine filtera zahtjevna i može trajati više od 24 h, primjenjuje se model poduzorkovanja kojim se uzima statistički značajan dio filtera koji se analizira. Dobiveni rezultati se ekstrapoliraju na cijelu površinu. Osim toga, kako bi se smanjilo ukupno vrijeme analize, povećava se udio plastičnih čestica u odnosu na neplastične čestice primjenom metode za uklanjanje anorganskih nečistoća iz pitke vode. Ovom metodom je ustanovljena prisutnost mikroplastike u realnim uzorcima pitke vode, a najčešći tip mikroplastike u pitkoj vodi su polietilen tereftalat (PET) i polietilen (PE).

*Ključne riječi:* mikroplastika, pitka voda, mikro-Raman spektroskopija, razvoj metode





**VOLUMETRIJSKA SVOJSTVA OTOPINA  
1-METILIMIDAZOLIJEVOG ACETATA U *N,N*-  
DIMETILACETAMIDU, *N,N*-DIMETILFORMAMIDU I  
DIMETIL SULFOKSIDU  
VOLUMETRIC PROPERTIES OF SOLUTIONS OF  
1-METHYLIMIDAZOLIUM ACETATE IN *N,N*-  
DIMETHYLACETAMIDE, *N,N*-DIMETHYLFORMAMIDE  
AND DIMETHYL SULFOXIDE**

Renato Tomaš<sup>a</sup>, Ivan Pehar<sup>a</sup>, Snežana Papović<sup>b</sup>, Zdzisław Kinart<sup>c</sup>, Teona  
Teodora Borović<sup>b</sup>, Milan Vraneš<sup>b</sup>

<sup>a</sup>Faculty of Chemistry and Technology, University of Split, Ruđera Boškovića 35,  
21000 Split, Croatia

<sup>b</sup>Faculty of Sciences, University of Novi Sad, Trg Dositeja Obradovića 3, 21000 Novi Sad, Serbia

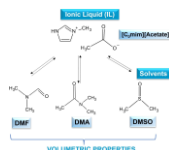
<sup>c</sup>Faculty of Chemistry, University of Lodz, 90-236 Lodz, Pomorska 163/165, Poland

Volumetric properties (apparent molar volume, standard partial molar volumes, apparent molar volume at infinite dilution, limiting apparent molar expansibilities and Heppler's coefficient) of 1-methylimidazolium acetate, [C<sub>0</sub>mim][Ac] ionic liquid binary mixtures with two polar aprotic amides: *N,N*-dimethylacetamide (DMA), and *N,N*-dimethylformamide (DMF), and one polar aprotic organosulfur and environmentally-friendly solvent: dimethyl sulfoxide (DMSO), are calculated from the experimental densities and reported in the temperature range from (278.15 to 313.15) K in DMA and DMF or (293.15 to 318.15) K in DMSO at atmospheric pressure (0.1 MPa) and in the molality range from (0.0050 to 0.1000) mol kg<sup>-1</sup>, respectively. The validity of Masson's equation [1] was checked and applied to describe the apparent molar volume dependence on molarity. The apparent molar volume at infinite dilution and interaction coefficient were obtained from this dependence at each temperature. Finally, structure-maker or structure-breaker properties of investigated ionic liquid in various solvents are discussed [2].

**Keywords:** 1-methylimidazolium acetate, DMA, DMF, DMSO, volumetric properties

[1] D. O. Masson, *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science*, 8 (1929) 218.

[2] R. Tomaš, Z. Kinart, A. Tot, S. Papović, T. T. Borović, M. Vraneš, *J. Mol. Liq.* 345 (2022) 118178.



## Zelena sinteza nanočestica srebra upotrebom vodenog ekstrakta gljive *Fomes fomentarius* (L.)

### Green synthesis of silver nanoparticles using the aqueous extract of *Fomes fomentarius* (L.)

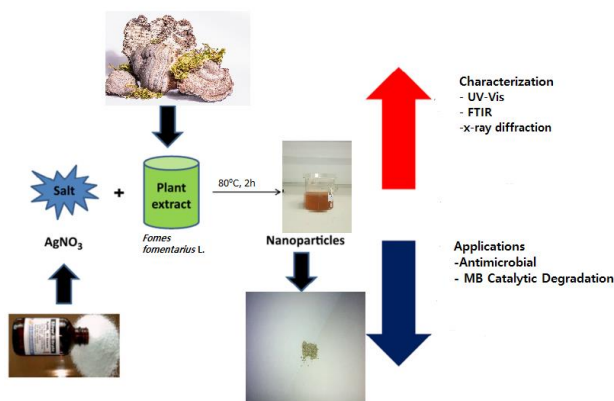
Vanesa Viljevac<sup>1</sup>, Ivan Čorić<sup>1</sup>, Elvira Kovač-Andrić<sup>1</sup>, Valentina Pavić<sup>2</sup>,  
Vlatka Gvozdić<sup>1</sup>

<sup>1</sup>Department of Chemistry, Josip Juraj Strossmayer University of Osijek, Ulica cara Hadrijana 8/A, 31000 Osijek, Croatia

<sup>2</sup>Department of Biology, Josip Juraj Strossmayer University of Osijek, Ulica cara Hadrijana 8/A, 31000 Osijek, Croatia

In the present study, for the first time, we report a suitable green procedure for the synthesis of silver nanoparticles using an aqueous extract of *Fomes fomentarius* (L.) as a reducing and capping agent. The results of the characterisation indicate the successful synthesis using *Fomes fomentarius* extract as a reducing agent, with UV-Vis absorption peak at 420 nm. The investigation showed good catalytic activity of silver nanoparticles on the degradation of methylene blue dye, with methylene blue degraded after a few hours. The extract was found to be the potent agent against human pathogens *E. coli*, *P. aeruginosa*, *B. subtilis* and *S. aureus*.

**Keywords:** *Fomes fomentarius*, silver nanoparticles, antibacterial activity



## CO<sub>2</sub> KAO POČETNI MATERIJAL U KATALITIČKOJ SINTEZI KARBONATA I KARBAMATA CO<sub>2</sub> AS A STARTING MATERIAL IN THE CATALYTIC SYNTHESIS OF CARBONATES AND CARBAMATES

Filip Vranješević<sup>a</sup>, Maria Kolympadi-Markovic<sup>b</sup>, Davor Šakić<sup>c</sup>,  
Valerije Vrčec<sup>c</sup>, Dean Marković<sup>a</sup>

<sup>a</sup>Department of Biotechnology, University of Rijeka, Radmile Matejčić 2, 51000 Rijeka, Croatia

<sup>b</sup>Department of Physics, University of Rijeka, Radmile Matejčić 2, 51000 Rijeka, Croatia

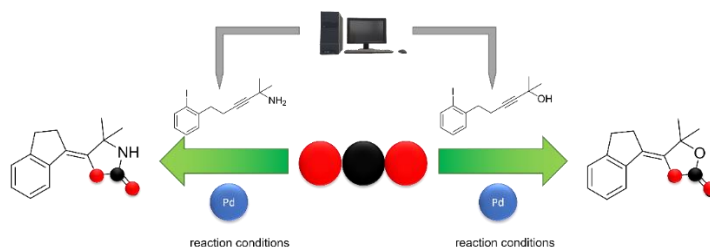
<sup>c</sup>Faculty of Pharmacy and Biochemistry, University of Zagreb, Ante Kovačića 2, 10000 Zagreb, Croatia

*In silico* substrate design represents a novel attempt at a rational approach to organic synthesis. Likewise, CO<sub>2</sub> has been increasingly interesting to synthetic chemists as a green, cheap and readily available carbon source. In this project, we have modelled the ability of certain unsaturated alcohols and amines to undergo a double cyclisation reaction with carbon dioxide using transition metal-based catalysts. Several substrates have been selected and synthesized. Their CO<sub>2</sub>-absorbing abilities are currently being investigated under a range of conditions and with different transition-metal based catalysts. While cyclic carbonate and carbamate formation using CO<sub>2</sub> is a well-established synthetic procedure, the carboxylation-aromatic substitution double cyclisation is proving more challenging. The scope of this reaction will also be probed.

Intermolecular reactions employing such substrates and aryl or vinyl halides are also being investigated. The compounds obtained by this process – bicyclic carbonates and carbamates – may prove to be biologically active compounds and will be tested for potential anti-bacterial and anti-cancer activity. Finally, the mechanism of this reaction will be examined both using *in silico* and experimental methods, such as NMR. Preliminary mechanistic studies indicate the possible formation of an epoxide intermediate in the catalytic cycle. Further mechanistic study will help to further refine catalysts for such processes.

**Keywords:** catalysis, carbon dioxide, green chemistry

[1] P. García-Domínguez, L. Fehr, G. Rusconi, C. Nevado, *Chem. Sci.* 7 (2016) 3914–3918.



## EKSTRAKCIJA METALNIH KATIONA S POROZNIM OKSA-AZA MAKROCIKLIČKIM SPOJEVIMA EXTRACTION OF METAL CATIONS WITH POROUS OXO-AZA MACROCYCLIC COMPOUNDS

Hana Zajkić, Milenko Korica, Tomislav Balić

Department of Chemistry, Josip Juraj Strossmayer University of Osijek, Ulica cara Hadrijana  
8/A, 31000 Osijek, Croatia

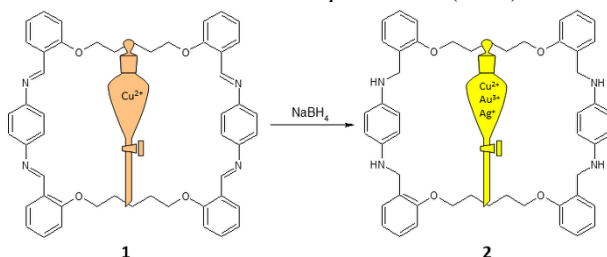
Removal of highly toxic air, water and soil pollutants from the environment is a major scientific topic. Macrocycles are organic compounds that can bind toxic species and be designed for extraction of specific metal cations [1, 2]. Macrocycles containing oxygen and nitrogen donor atoms in the inner macrocyclic ring (*oxa-aza* macrocycles) have been studied for that purpose [1]. The affinity of an *oxa-aza* macrocycle towards specific cations can be designed by changing several factors: ring size (cavity size), HSAB principle, donor atom properties, planarity of the system (puckering) and orientation of donor atoms (*exodentate* or *endodentate*) [1, 2]. In this work we have synthesized a novel N<sub>4</sub>O<sub>4</sub>-donor macrocycle (**2**) by reduction of previously prepared [2] porous macrocyclic Schiff base (**1**). Compounds were characterized by elemental and thermal analysis, FT-IR and NMR spectroscopy. Picrate extraction studies were performed following modified Pedersen's procedure [3] for Ni<sup>2+</sup>, Cd<sup>2+</sup>, Zn<sup>2+</sup>, Ag<sup>+</sup>, Co<sup>2+</sup>, Hg<sup>2+</sup>, Cu<sup>2+</sup>, Fe<sup>3+</sup>, Mn<sup>3+</sup>, Au<sup>3+</sup> and Cr<sup>3+</sup>. The composition of extracted species and extraction constant ( $K_{ex}$ ) were calculated using dependence of the distribution ratio ( $D$ ) on macrocycle concentration ( $\log D$ - $\log L$  plot) for Cu<sup>2+</sup>, Au<sup>3+</sup> and Ag<sup>+</sup>. Metal extraction experiments indicate that highest extraction is achieved for Cu<sup>2+</sup> (87%) in the case of compound **1** and for Au<sup>3+</sup> (100%), Cu<sup>2+</sup> (100%) and Fe<sup>3+</sup> (100%) in the case of compound **2**. The composition of extracted species in case of **1** and Cu<sup>2+</sup> is 1:1 (ligand:metal ratio,  $K_{ex} = 11.062$ ), and 1:1 ratio for **2** and Ag<sup>+</sup> and Au<sup>3+</sup> ( $K_{ex} = 8.7107$  and  $17.667$ , respectively).

**Keywords:** *oxa-aza* macrocycles, metal extraction

[1] T. Balić et al., *J. Incl. Phenom. Macrocycl. Chem.* 85 (2016) 17–26.

[2] T. Balić et al., *Microporous and Mesoporous Materials* 2016;226:53–60.

[3] J. J. Pedersen, *J. Fed. Proc. Fed. Am. Soc. Exp. Biol.* 27 (1968) 1305-1309.



## HLAPLJIVI SPOJEVI IZVERUGANE RUMENICE I JADRANSKE RUMENICE VOLATILE COMPOUNDS FROM *AURINIA SINUATA* AND *AURINIA LEUCADEA*

Ljilja Žilić, Lidija Pirija, Ani Radonić

Zavod za organsku kemiju, Kemijsko-tehnološki fakultet Sveučilišta u Splitu, R. Boškovića  
35, 21000 Split, Hrvatska

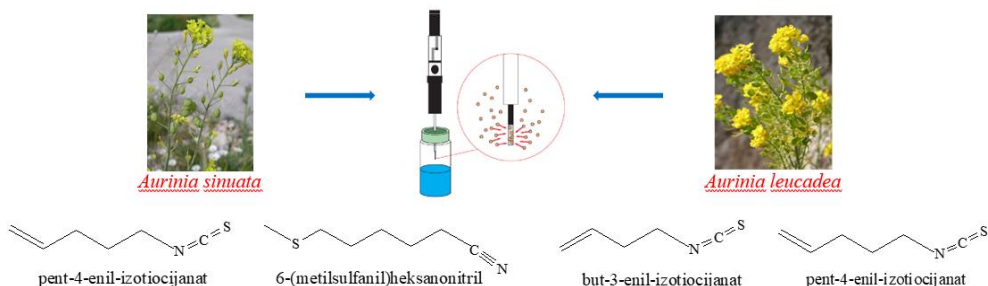
Ovaj rad je nastavak istraživanja hlapljivih spojeva dviju samoniklih biljaka roda *Aurinia* (Brassicaceae): izverugane rumenice, *Aurinia sinuata* (L.) Griseb. i jadranske rumenice, *Aurinia leucadea* (Guss.) K. Koch [1], [2], [3]. Za razliku od dosadašnjih istraživanja, u ovom radu primijenjena je HS-SPME/GC-MS metoda. *A. sinuata* i *A. leucadea* su endemske biljne vrste rasprostranjene u mediteranskom dijelu Hrvatske, a rastu po stijenama, liticama, kamenim zidovima te nasipima uz cestu. Spojevi karakteristični za biljke porodice Brassicaceae su glukozinolati. Glukozinolati su nehlapljivi tioglikozidi čijom razgradnjom nastaju hlapljivi spojevi. U ovom radu razgradnja glukozinolata provedena je pomoću endogenog enzima mirozinaze, oslobođeni hlapljivi spojevi izolirani su mikroekstrakcijom vršnih para na krutoj fazi (HS-SPME) i analizirani plinskom kromatografijom-masenom spektrometrijom (GC-MS). Glavni spojevi vršnih para *A. leucadeae* su but-3-enil-izotiocijanat i pent-4-enil-izotiocijanat, razgradni produkti glukonapina i glukobrasikanapina. Glavni spojevi vršnih para *A. sinuatae* su razgradni produkti glukobrasikanapina, pent-4-enil-izotiocijanat i heks-5-enonitril, i glukoberteroina, 6-(metilsulfanil)heksanonitril i 5-(metilsulfanil)pentil-izotiocijanat.

**Cljučne riječi:** *A. sinuata*, *A. leucadea*, HS-SPME/GC-MS

[1] I. Blažević, A. Radonić, J. Mastelić, M. Zekić, M. Skočibušić, A. Maravić, *Food Chem.* 121 (2010) 1020.

[2] I. Blažević, A. Radonić, M. Skočibušić, G. R. De Nicola, S. Montaut, R. Iori, P. Rollin, J. Mastelić, M. Zekić, A. Maravić, *Chem. Biodivers.* 8 (2011) 2310.

[3] I. Blažević, G. R. De Nicola, S. Montaut, P. Rollin, *Nat. Prod. Commun.* 8 (2013) 1463.



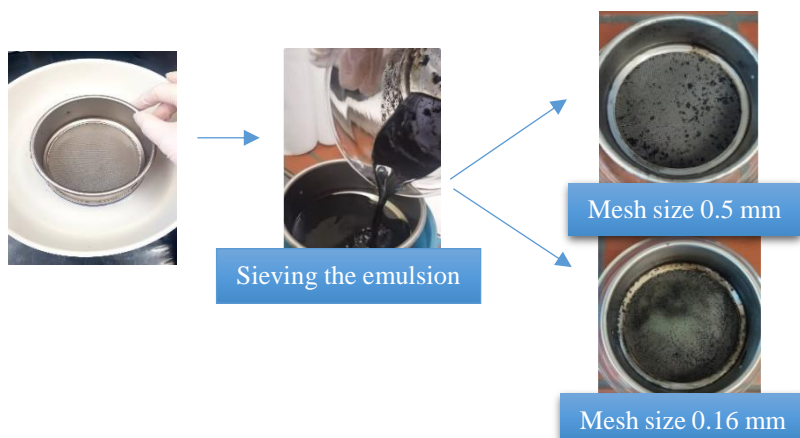
## **ODREĐIVANJE OSTATKA PRI PROSIJAVANJU HOMOGENIZIRANE OTPADNE EMULZIJE DETERMINATION OF RESIDUE ON SIEVING OF HOMOGENOUS WASTE EMULSION**

Marko Babić, Petra Ačkar, Elvira Vidović, Ante Jukić

Faculty of Chemical Engineering and Technology, University of Zagreb, Marulićev trg 19,  
10000 Zagreb, Croatia

There are several methods by which emulsions can be characterized. Differential scanning calorimetry can be used to determine the water content of a particular emulsion. The thermal stability of the emulsion can be determined by thermogravimetric analysis. The viscosity of the emulsion can be determined by rheological measurements. Optical microscopy monitors the particle size and homogeneity of the emulsion. However, the two most important methods of emulsion analysis are the adhesion of the emulsion to the substrate or stone and the sieve test. Sieving is a very simple method that allows determining the homogeneity of emulsions. In this work, the sieve residue of the homogenized waste emulsion is analyzed. The known mass of the homogenized waste emulsion is filtered through a sieve with a mesh size of 0.5 mm and 0.16 mm. The weight percentage of the residual particles is important to avoid clogging of the equipment used to spray the emulsion when paving the asphalt layer. The amount of binder retained on the sieves is weighed after washing and drying. The weight percentage of the remaining particles of homogenized waste emulsion that passed through a sieve with a mesh size of 0.5 mm was 1.80% and through a sieve with a mesh size of 0.16 mm was 2.34%.

*Keywords:* waste emulsion, sieving, mesh size, residue



## NAKNADNO OTKRIVENI KRISTALNI POLIMORFI U FARMACEUTSKOJ INDUSTRIJI LATE APPEARING CRYSTAL POLYMORPHS IN PHARMACEUTICAL INDUSTRY

Aleksandar Bajrović, Petra Gurović, Damir Šahnić

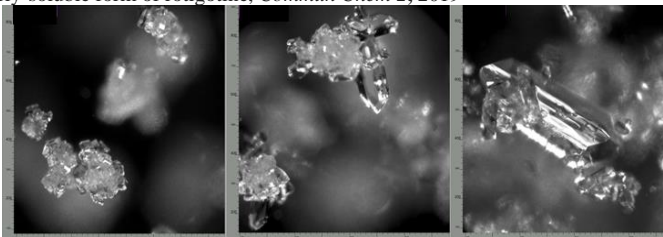
PLIVA Hrvatska d.o.o., Prilaz baruna Filipovića 25, 10000 Zagreb, Hrvatska

Tijekom razvoja i proizvodnje aktivnih farmaceutskih supstanci (API) ključan je postupak kristalizacije prilikom kojeg se dobiva API odgovarajuće kvalitete i željenih fizikalnih svojstava. Osim kemijske čistoće, bitna je i kristalna forma API-ja, odnosno izolira li se odgovarajući polimorf. U kristalografiji, pojam polimorfije odnosi se na sposobnost molekula jednakog kemijskog sastava da tvore više različitih kristalnih tvorevina, ovisno o preslagivanju molekularnih veza.[1] Tijekom razvoja procesa cilj je pripremiti i okarakterizirati različite polimorfne forme (solvati, hidrati, anhidro forme) API-ja što će ovisiti o različitim kinetičkim i termodinamičkim uvjetima. Obzirom da se patentna odobrenja odnose na točno određenu formu te da različite forme imaju različita fizikalna, a nekad i kemijska svojstva (npr. biodostupnost), bitno je moći konzistentno dobivati kristal točno određene polimorfne forme i čistoće. Povremeno i neočekivano, u kasnijim fazama razvoja (u nekim primjerima već i u proizvodnji)[2] naknadno se može pojaviti nova, termodinamički stabilnija forma. Ovakva naknadna pojava polimorfa može poremetiti dosadašnje razvojne napretke; prijašnja kristalna struktura odjednom se priprema uz velike poteškoće ili se uopće više ne može pripremiti. Tevin razvojni tim radio je na izolaciji sulfonatne soli API-ja određene forme A. Prilikom uvećavanja procesa dobivanja API forme A pojavljuje se nova, stabilnija forma u obliku hidrata, forma B. Nakon laboratorijske šarže kod koje je prvi put izolirana takva neočekivana forma, svi eksperimenti po standardnom postupku, neovisno o proizvodnoj lokaciji ili polaznim materijalima, rezultiraju formom B. Kako bi se sintetizirala prethodna forma, istraženi su različiti kristalizacijski sustavi: ispitane su topljivosti forme A i B u smjesama otapala različitog omjera vode i metanola, acetonitrila, 2-propanola, acetona, etanola i pri različitoj koncentraciji aktivne supstance. Pri niti jednim uvjetima nije sintetizirana čista forma A, već različite forme B, C, D i njihove smjese sa određenim udjelom forme A. Zaključeno je da dotične forme prelaze jedna u drugu ovisno o procesnim uvjetima. Forma A, različitih fizikalnih svojstava od prvotno dobivene forme A, dobivena je naposljetku desolvatacijom forme B u acetonu pri povišenoj temperaturi.

**Ključne riječi:** kristalizacija, polimorfija, farmaceutski aktivna supstanca

[1] Thakuria, R., Thakur, T.S., Crystal Polymorphism in Pharmaceutical Science, *Comprehensive Supramolecular Chemistry II*, 2017, str. 283-309.

[2] Mortazavi, M., Hoja, J., Aerts, L., Quere, L., van de Streek, J., Computational polymorph screening reveals late-appearing and poorly-soluble form of rotigotine, *Commun Chem* 2, 2019



**Slika 1.** Polimorfni prijelaz API-ja forme A u formu B snimljen procesnim mikroskopom *Blaze 900*



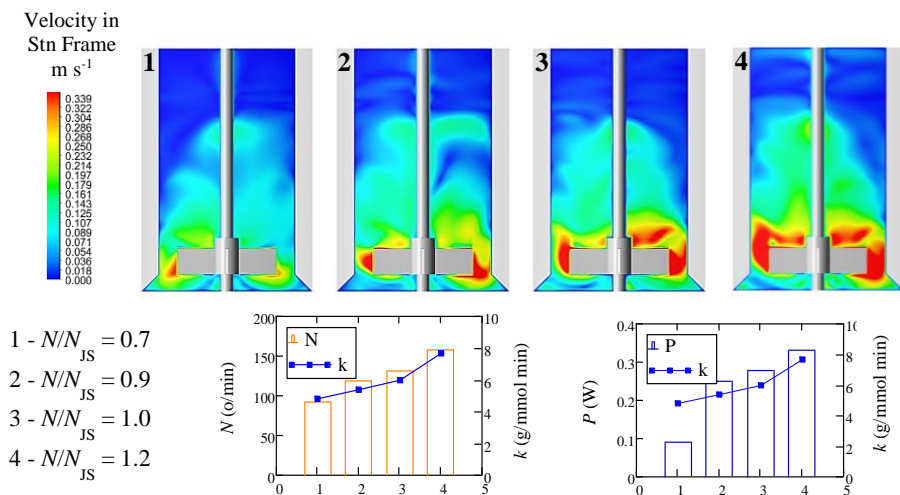
## UTJECAJ BRZINE VRTNJE SBT MIJEŠALA NA SORPCIJU BAKRA NA ZEOLITU IMPACT OF SBT IMPELLER SPEED ON COPPER SORPTION ON ZEOLITE

Anita Bašić, Ana Herceg, Sandra Svilović, Nenad Kuzmanić  
Faculty of Chemistry and Technology, University of Split, Ruđera Boškovića 35,  
21000 Split, Croatia

The sorption of copper ions on zeolite NaX is a heterogeneous process, and as such dependent on hydrodynamics in a batch reactor. Therefore, this work aimed to study the effect of mixing speed ( $N/N_{JS}$  ratio values, i.e. impeller speed/minimum impeller speed for complete suspension) on the kinetics and power consumption of the process examined.

The experiments were carried out in a glass batch reactor of nonstandard configuration ( $D/d_T = 0.6$ ,  $C/H = 0.1$ ), equipped with baffles and the SBT impeller. A transient multiphase computational fluid dynamics model was developed to gain valuable insight into complex flow kinetics. The Blanchard model, Mixed surface reaction and diffusion-controlled sorption kinetic model, and Weber-Morris model were used for the kinetic analysis of the experimental kinetic data. According to  $\tau$  and RMSE values, the reaction is kinetic controlled in all experiments performed.

**Keywords:** SBT impeller, NaX zeolite, kinetics, CFD





# EKSPERIMENTALNO I NUMERIČKO ODREĐIVANJE PARAMETARA MIJEŠANJA U SUSTAVU S DVAMA MIJEŠALIMA EXPERIMENTAL AND NUMERICAL DETERMINATION OF MIXING PARAMETERS IN DUAL-IMPELLER SYSTEM

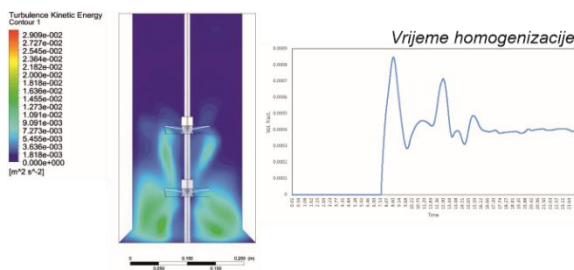
Antonija Čelan<sup>1</sup>, Željko Penga<sup>2</sup>, Marija Ćosić<sup>1</sup>, Nenad Kuzmanić<sup>1</sup>

<sup>1</sup>Sveučilište u Splitu, Kemijsko-tehnološki fakultet, Zavod za kemijsko inženjerstvo, R. Boškovića 35, 21000 Split, Hrvatska

<sup>2</sup>Sveučilište u Splitu, Fakultet elektrotehnike, strojarstva i brodogradnje, Zavod za strojarstvo i brodogradnju, R. Boškovića 32, 21000 Split, Hrvatska

Mehaničko miješanje se primjenjuje u čitavom nizu proizvodnih procesa. Potpuno razumijevanje ove operacije počiva na poznavanju hidrodinamičkih uvjeta koji vladaju u miješalici temeljem kojih je moguće provedbu miješanja i optimirati. Ukoliko se miješanje provodi dvama miješalima, hidrodinamika u promatranom sustavu postaje znatno kompleksnija u odnosu na sustave s jednim miješalom. Cilj ovog rada je bio sagledati utjecaj udaljenosti dvaju miješala od dna posude ( $C/D$ ) na karakteristične parametre miješanja u miješalici volumena 14.15 dm<sup>3</sup>. Miješanje se provodilo korištenjem dvaju turbinskih miješala s lopaticama nagnutim pod kutom od 45° (PBT) čija je međusobna udaljenost ( $S/D$ ) zadržana konstantnom. U radu je eksperimentalno određeno vrijeme homogenizacije,  $N_{tm}$ , mjerenjem vremena do ustaljenja potencijala otopine nakon injektiranja trasera. Pri odabranim brzinama vrtnje miješala mjeren je i zakretni moment na osovini miješala kako bi se odredio utrošak snage. Numerički model je razvijen u računalnom programu ANSYS<sup>TM</sup> Fluent v17.2. Isti je korišten za prikaz specifičnih tokova fluida, kao i kontura rasipanja privedene energije unutar miješalice. Ovakav kvantitativan i kvalitativan opis miješanja omogućava potpuniju analizu utjecaja miješanja na pojedine stupnjeve provedbe separacijskih procesa, prije svega šaržne kristalizacije za koju je i razvijen.

**Ključne riječi:** miješanje, sustav s dvama miješalima, vrijeme homogenizacije, utrošak snage miješanja



## **UTJECAJ OTPADA TALOGA KAVE NA SVOJSTVA I BIORAZGRADIVOST BIKOMPOZITA NA BAZI POLILAKTIDA EFFECT OF SPENT COFFE GROUNDS ON THE PROPERTIES AND BIODEGRABILITY OF BIOCOMPOSITE BASED ON POLYLACTIDE**

Ema Čemerika, Dora Milički, Martina Miloloža, Dajana Kučić Grgić,  
Vesna Ocelić Bulatović

Fakultet kemijskog inženjerstva i tehnologije Sveučilišta u Zagrebu,  
Marulićev trg 19, 10 000 Zagreb, Hrvatska

Kava je jedan od najpopularnijih napitaka diljem svijeta te druga roba, nakon nafte, kojom se najviše trguje. Radi sve većeg širenja tržišta kave, industrija kave nosi veliku odgovornost prema nekontroliranoj proizvodnji otpada među kojima se ističe istrošeni otpad talog kave (OTK) koji čini i do 95 % otpad nakon konzumacije kave. Stoga bi razvoj tehnologija za ponovnu upotrebu otpada taloga kave u funkcionalne svrhe pomogao pretvoriti ovu veliku količinu otpada u nove resurse.

U ovom radu ispitana su svojstva biokompozita na bazi polilaktida (PLA) i različitog udjela otpada taloga kave (OTK) kao punila. Svojstva biokompozita PLA/otpad taloga kave praćena su primjenom diferencijalne pretražne kalorimetrije (DSC) i termogravimetrijske analize (TG). Ispitana je i veličina čestica te raspodjela veličina čestica metodom laserske difrakcije, te apsorpcija vode. Ispitana je biorazgradivost biokompozita PLA/otpad taloga kave procesom kompostiranja. Proces kompostiranja proveden je u 6 adijabatskih reaktora radnih volumena,  $V_r = 1$  L, tijekom 19 dana. Biorazgradivost biokompozita PLA/otpad taloga kave pratila se gubitkom mase i praćenjem promjena morfološke strukture svjetlosnim mikroskopom prije i nakon procesa kompostiranja.

*Ključne riječi:* biokompoziti, otpad taloga kave, PLA, biorazgradnja



## ODREĐIVANJE SASTAVA KATALIZATORA USPOREDBOM S TEORIJSKIM RAMAN SPEKTRIMA/ CATALYST COMPOSITION FROM THEORETICAL MODEL OF RAMAN SPECTRA

Vjeran Gomzi<sup>a</sup>, Filip Car<sup>b</sup>, Vesna Tomašić<sup>b</sup>

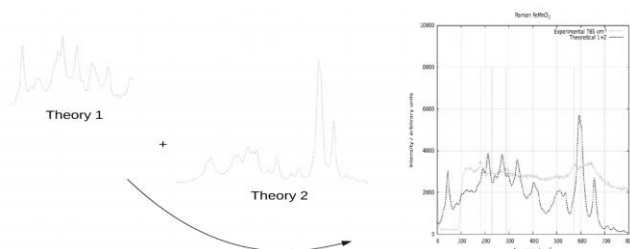
<sup>a</sup>University of Zagreb, Faculty of Electrical Engineering and Computing, Unska 3,  
10000 Zagreb, Croatia

<sup>b</sup>Faculty of Chemical Engineering and Technology, University of Zagreb, Marulićev trg 19,  
10000 Zagreb, Croatia

Raman spectroscopy is optical resonance technique sensitive to atomic bonding. As such it is often used for catalyst characterization and for the investigation of the bulk and surface chemistry during catalyst use. Method is of considerable interest in situations when catalyst is not single-phase material, but consists of a mixture of crystal phases. Ideally, in such cases, Raman spectra in comparison with theoretical model would be indispensable tool for description of physicochemical properties of these complex structures including phase contacts. Modeling the Raman spectra, however, even at the level of density-functional theory proves to be rather computationally demanding. In the attempt to elucidate catalyst composition, and complement experimental findings (XRD, XPS, Raman spectroscopy) in our research of MnMO<sub>x</sub> catalysts, we begin by modeling separate crystal phases expected to be present in the multi-phase catalyst samples [1]. To some extent, the interfacial effects are accounted for by the finite size of the theoretically studied structures representing crystallites. Based on comparison of weighted superposed theoretical spectra of several crystal phases and experimental Raman spectra of the catalyst, we comment on the possibility to use such approach for determination of multi-phase catalyst composition and investigation of its properties.

*Cljučne riječi:* DFT, Raman spectra, multi-phase catalyst

[1] F. Car, V. Gomzi, V. Tomašić, D. Vrsaljko: Development of novel monolithic catalysts for catalytic oxidation of BTEX compounds using 3D-printing technology, *submitted*.



## STRUKTURA I TOPLINSKA SVOJSTVA PEO/25A/LiBOB NANOKOMPOZITNIH POLIMERNIH ELEKTROLITA STRUCTURE AND THERMAL PROPERTIES OF PEO/25A/LiBOB NANOCOMPOSITE POLYMER ELECTROLYTES

Irena Krešić, Matko Erceg, Petra Skorić

Faculty of Chemistry and Technology, University of Split, Ruđera Boškovića 35,  
21 000 Split, Croatia

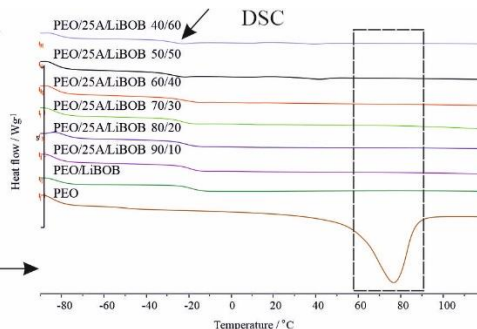
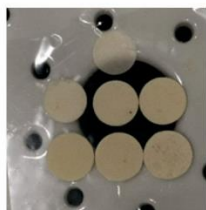
Nanocomposite polymer electrolytes based on poly(ethylene oxide)/Cloisite 25A were prepared by melt intercalation method. Samples were made with different weight ratios of poly(ethylene oxide) (PEO) to Cloisite 25A (25A) while the ratio of cation of lithium bis(oxalato)borate (LiBOB) to ether-oxygen was kept constant at EO : Li = 8. By comparing the obtained PEO/25A/LiBOB samples the effect of Cloisite 25A nanofiller and LiBOB salt on the structure and thermal properties was determined.

FTIR analysis revealed the interaction between polymer and salt. The addition of Cloisite 25A additionally affected the crystal structure of PEO in PEO/25A/LiBOB samples.

The thermal transitions and degree of crystallinity of PEO in PEO/25A/LiBOB samples were investigated using differential scanning calorimetry (DSC). It was found that the crystal structure of PEO completely disappeared on the addition of both Cloisite 25A and LiBOB. This was accompanied by an increase in the glass transition temperatures which is related to the stiffening effect of lithium salt on PEO chains. Thermogravimetric analysis (TGA) showed lower thermal stability and more complex thermal degradation process of nanocomposite polymer electrolytes compared to PEO.

**Keywords:** nanocomposite polymer electrolyte, polymer nanocomposite, poly(ethylene oxide), thermal properties, structure

NANOCOMPOSITE POLYMER  
ELECTROLYTES



## UTJECAJ SREBRA NA LEGURE S EFEKTOM PRISJETLJIVOSTI OBLIKA NA BAZI BAKRA EFFECT OF SILVER ADDITION ON Cu-BASED SHAPE MEMORY ALLOYS

Lovro Liverić<sup>1</sup>, Tamara Holjevac Grgurić<sup>2</sup>, Emi Govorčin Bajsić<sup>3</sup>,  
Vilko Mandić<sup>3</sup>, Vedrana Špada<sup>4</sup>, Wojciech Sitek<sup>5</sup>, Przemysław Snopiński<sup>5</sup>,  
Sunčana Smokvina Hanza<sup>1</sup>

<sup>1</sup>Faculty of Engineering, University of Rijeka, Vukovarska 58, 51 000 Rijeka, Croatia

<sup>2</sup>School of Medicine, Catholic University of Croatia, Ilica 242, 10 000 Zagreb, Croatia

<sup>3</sup>Faculty of Chemical Engineering and Technology, University of Zagreb, Marulićev trg 19,  
10 000 Zagreb, Croatia

<sup>4</sup>Juraj Dobrila University in Pula, Zagrebačka 30, 52100 Pula, Croatia

<sup>5</sup>Faculty of Mechanical Engineering, Silesian University of Technology, ul. Konarskiego  
18a, Gliwice 44-100, Poland

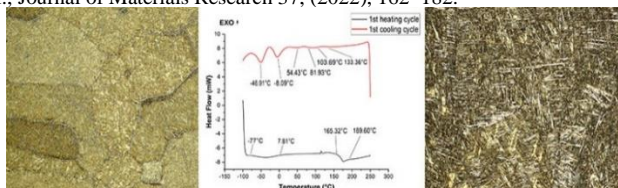
Shape memory alloys are a special type of materials that, when deformed below a certain temperature, can return to their original shape before deformation simply by heating. Alloys with this atypical property are used as functional materials in temperature sensors, actuators and clamping devices. SMA materials also have a property called superelasticity. It is rubber like property, but when bent or stretched, it returns to its original shape when the deforming force is removed. This property is used in everyday products such as electrical and electronic equipment, as well as in the medical and optical fields. [1, 2, 3] The Cu-Al-Ag alloy Cu based with 10 wt% Al and 1 wt% Ag was prepared in the electric arc furnace. The alloy was remelted 4 times for better homogenization and cast into a cylindrical mould with dimensions of 8 mm x 12 mm. Heat treatment was performed at 900°C for 30 minutes, followed by quenching in water. The microstructure of the characteristic states of the studied alloy was observed using an optical microscope (OM) and a scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectroscopy detector (EDS). The martensitic and austenitic transformation temperatures were determined using the Differential Scanning Calorimeter (MDSC). Hardness was determined using the Future Tech FM-ARS -F 9000 with FM-700 microhardness tester. The results showed fully formed martensite structure, with different types of martensite, in quenched Cu-10Al-1Ag samples.

**Keywords:** Cu-based alloys, Cu-Al-Ag alloys, Microstructure, Phase transformations

[1] D. Manasijević et al., *Kovove Mater* 58, (2020), 293–299.

[2] T. Holjevac Grgurić et al., *Journal of alloys and compounds* 765, (2018), 664–676.

[3] E.M. Mazzer et al., *Journal of Materials Research* 37, (2022), 162–182.



## Mehanokemijska sinteza $\text{Ti}_3\text{C}_2$ bez upotrebe fluorida Mechanochemical synthesis of fluoride-free $\text{Ti}_3\text{C}_2$

Gabrijela Ljubek<sup>1</sup>, Magdalena Kralj<sup>2</sup>, Marijana Kraljić Roković<sup>3</sup>,  
Marko Racar<sup>3</sup>

<sup>1</sup>Faculty of mining, geology and petroleum engineering, University of Zagreb, Pierottijeva 6,  
10 000 Zagreb, Croatia

<sup>2</sup>Institut Ruđer Bošković, Bijenička cesta 54, 10 000 Zagreb, Croatia

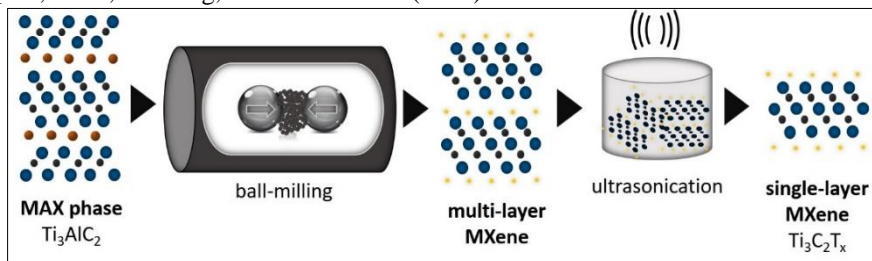
<sup>3</sup>Faculty of Chemical Engineering and Technology, University of Zagreb, Marulićev trg 19,  
10 000 Zagreb, Croatia

MXenes, a family of two-dimensional (2D) layered early transition metal carbides and carbonitrides, have rapidly drawn intensive research attention due to their high metallic conductivity, large theoretical specific surface area, excellent mechanical properties, and high hydrophilicity. Their general chemical formula is  $\text{M}_{n+1}\text{X}_n\text{T}_x$  ( $n=2-4$ ), where M represents a transition metal, X is carbon and/or nitrogen, and T stands for surface termination groups ( $-\text{OH}$ ,  $-\text{F}$ ,  $-\text{O}$ ) [1].  $\text{Ti}_3\text{C}_2\text{T}_x$  was the first MXene reported in 2011, and more than 25 different MXene compositions have been synthesised since then. To date, most MXenes have been prepared through the wet chemical etching methods where A-element atomic layers (e.g., aluminum) are etched from the  $\text{M}_{n+1}\text{AX}_n$  phase (e.g.,  $\text{Ti}_3\text{AlC}_2$ ) using highly hazardous HF or LiF/HCl solutions [2]. Therefore, there is an urgent need to explore safe, reliable, and fluoride-free synthetic methods to prepare MXene. In this work, we describe several different fluoride-free mechanochemical routes for the preparation of the  $\text{Ti}_3\text{C}_2$  MXene from the  $\text{Ti}_3\text{AlC}_2$  MAX phase. It consists of a ball-milling of the MAX phase with LiCl or  $\text{ZnCl}_2$ , followed by washing and ultrasonication in order to completely exfoliate the MXene sheets. The prepared  $\text{Ti}_3\text{C}_2$  was studied by powder X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier-transform infrared spectroscopy (FTIR), ultraviolet-visible (UV/Vis) spectrophotometry and dynamic light scattering (DLS). The results reported here pave the way for new preparation methods for various fluoride-free MXenes as ideal candidates for many functional applications such as energy storage, catalysis, electronics, and sensors.

**Keywords:** 2D materials, ball-milling, mechanochemistry, solid state

[1] M. Hu, H. Zhang, T. Hu, B. Fan, X. Wang, Z. Li, *Chem. Soc. Rev.* 49 (2020) 6666-6693.

[2] Q. Li, Y. Li, W. Zeng, *Chemosensors* 9 (2021) 225.



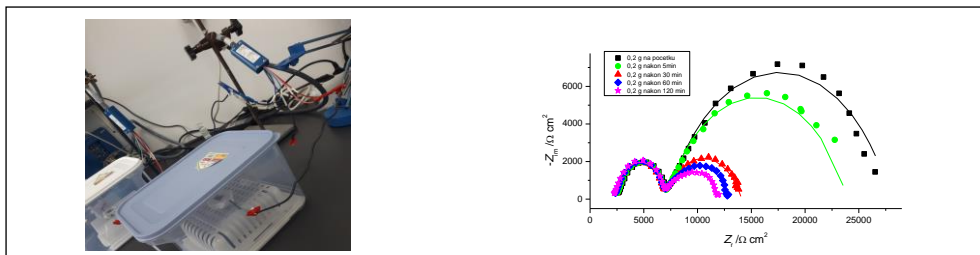
## UTJECAJ TEMPERATURE I DULJINE HLAPLJENJA INHIBITORA NA DJELOTVORNOST KOROZIJSKE ZAŠTITE THE INFLUENCE OF TEMPERATURE AND INHIBITOR VOLATILIZATION DURATION OF ON CORROSION PROTECTION

Antonio Pelesk, Helena Otmačić Ćurković

Fakultet kemijskog inženjerstva i tehnologije Sveučilišta u Zagrebu, Savska cesta 16,  
10000 Zagreb, Hrvatska

U zaštiti od atmosfere korozije često se koriste hlapivi inhibitori korozije, koji hlapljenjem zasićuju prostor u kojem se nalazi metal, a potom se adsorbiraju na njegovu površinu stvarajući tanki zaštitni film. Da bi se postigla zadovoljavajuća zaštita, nužno je da se na površini metala adsorbira dovoljno inhibitora. Cilj ovog istraživanja je istražiti kako temperatura i vrijeme hlapljenja inhibitora utječu na površinsku koncentraciju adsorbiranog inhibitora, odnosno na postignutu korozijsku zaštitu. U ovom istraživanju korištena su dva inhibitora mase 0,2 g koji su hlapili zasebno 20 sati, 7 dana i 14 dana u zatvorenim komorama na sobnoj temperaturi, odnosno 30 min, 1 i 20 sati na povišenoj temperaturi. Unutar komore postavljena je disk pločica koja se sastoji od dvije čelične elektrode veličine (1x1) cm<sup>2</sup> međusobno odvojenih ne više od 1 mm. Na takvu pločicu na koju se vezao inhibitor hlapljenjem nakon prethodno navedenog vremena dodalo se 230 μL otopine kiselice pH=6.5 koja je simulirala korozivne uvjete. Nakon navedenog vremena u komore se dodaje i 0,3 L destilirane vode kako bi se osiguralo da ne dođe do hlapljenja elektrolita. Metodom elektrokemijske impedancijske spektroskopije određivala se otpornost prema koroziji u vremenskom intervalu od dodavanja otopine kiselice: odmah, nakon 5 min, 30 min, 1 sata i 2 sata. Usporedno su provedena mjerenja kod kojih se umjesto hlapljenjem, inhibitor vezao na površinu iz otopine poznate koncentracije. Sumiranjem dobivenih podataka zaključeno je o djelovanju inhibitora na površini disk pločice čelika i njegovom inhibirajućem svojstvu pri sobnoj i povišenoj temperaturi.

*Ključne riječi:* tanki film elektrolita, inhibitor, hlapljenje, temperatura



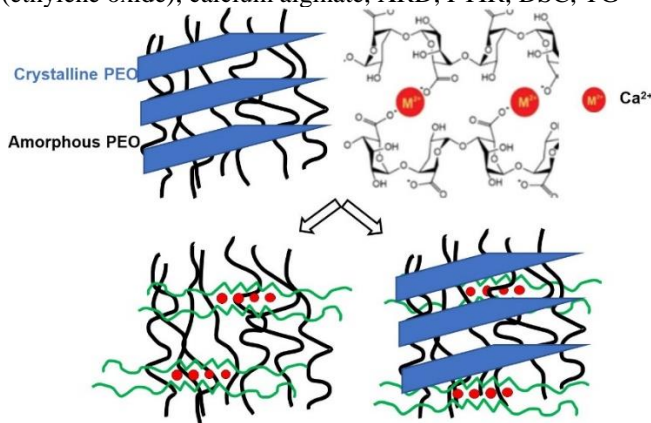


## STRUKTURNA I TOPLINSKA ANALIZA MJEŠAVINA NA BAZI POLI(ETILEN-OKSIDA) S KALCIJEVIM ALGINATOM STRUCTURAL AND THERMAL CHARACTERISATION OF POLY(ETHYLENE OXIDE) BLENDS WITH CALCIUM ALGINATE

Sanja Perinović Jozić, Lucija Karaman, Dražan Jozić, Miće Jakić  
Faculty of Chemistry and Technology, University of Split, Ruđera Boškovića 35,  
21000 Split, Croatia

Modification of poly(ethylene oxide) (PEO) was carried out by adding calcium alginate (CaAlg), as a natural polymer, to prepare new polymer blends that can be potentially used as polymer electrolyte in Ca batteries. The samples were prepared by extrusion in twin-screw extruder that has circulation channel, so the homogeneity of materials as well as defined composition was achieved. Structural features, in terms of crystalline structure and interaction between components of the blends, have been investigated using X-ray diffraction (XRD) and Fourier transform infrared microscopy (FTIR), respectively. It is interesting that alginate didn't change crystalline structure of PEO even though it interacts with PEO through the hydrogen bond. Thermal properties and thermal stability were investigated by using differential scanning calorimetry (DSC) and thermogravimetry (TG). The addition of CaAlg in PEO has the most pronounced influence on the crystallisation from the melt. It postpones it, and as the content of alginate increases, it is more pronounced. However, the degree of crystallinity remained high and in the range from 59 to 73%, too high for desired purpose. PEO/CaAlg degrades in three degradation stages with a slight shift of PEO degradation stage to a lower temperature than pure PEO.

*Keywords:* poly(ethylene oxide), calcium alginate, XRD, FTIR, DSC, TG





## METODOLOGIJA RAZVOJA SIGURNOG PROCESA HIDROGENACIJE METHODOLOGY OF SAFETY DEVELOPMENT FOR HYDROGENATION PROCESS

Domagoj Prlić, Igor Kultan, Ivan Vrban, Ozren Wittine, Eugen Marcelić  
PLIVA Hrvatska d.o.o., Prilaz baruna Filipovića 25, 10000 Zagreb, Croatia

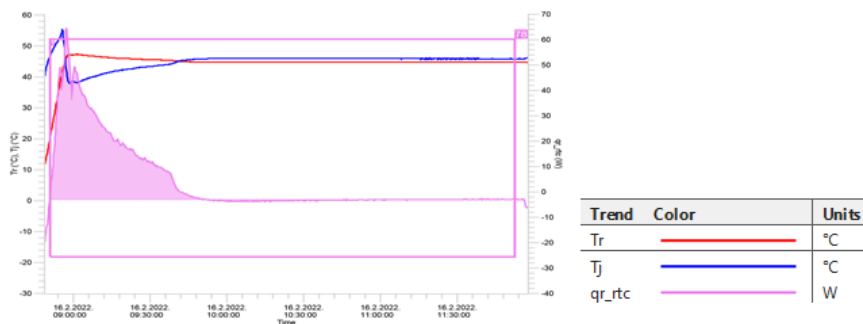
Reaction calorimetry measures the heat released from a chemical reaction or physical process and provides the fundamentals of the thermochemistry and kinetics of a reaction. The information obtained is essential to describe the heat release of a chemical reaction over time, which can uncover unexpected behavior and make any scalability issues visible and quantifiable. Measured data are used to characterize, optimize and understand process parameters in a controlled, accurate and reproducible environment, and to enable safe scale-up and transfer into manufacturing.

Hydrogenation process is usually used to reduce or saturate organic compounds. Catalysts are needed for the reaction to be usable; noncatalytic hydrogenation takes place only at very high temperatures.

During experimental work RC1 and ARSST were used to determine the reaction enthalpy generated by a chemical reaction. Compound X is prepared by reduction of nitro compound Y. The reduction is performed as catalytic hydrogenation in MeOH as solvent and with 5% Pd/C as catalyst. Reaction temperature is 45 °C and pressure of hydrogen is 5 bar.

Based on calorimetric and thermodynamic data which are measured, criticality classes are determined and due to MTSR (Maximum temperature of synthesis reaction – 128 °C) being higher than MTT (Maximum temperature of synthesis reaction – 65 °C) reaction belongs to criticality class 3. According to the DSC (Differential scanning calorimetry) data, material is thermally sensitive because of low onset temperature (95 °C), but with very low decomposition energy. Because of these data, Yoshida's correlation is used and results for SS (Shock sensitivity) and EP (Explosion propagation) are negative. The reaction enthalpy generated by the chemical reaction is 78.041 kJ.

**Keywords:** calorimetry, hydrogenation, RC1, safety development



## *Phanerochaete chrysosporium* glyoxal oxidase reactivation by coper ion loadings

### Reaktivacija *Phanerochaete chrysosporium* glioksal oksidaze dodatkom iona bakra

Tonči Rezić<sup>1</sup>, Matea Zrilić<sup>1</sup>, Roland Ludwig<sup>2</sup>

<sup>1</sup>Department of Biochemical Engineering, Faculty of Food Technology and Biotechnology,  
University of Zagreb, Pierottijeva 6, 10000 Zagreb, Croatia

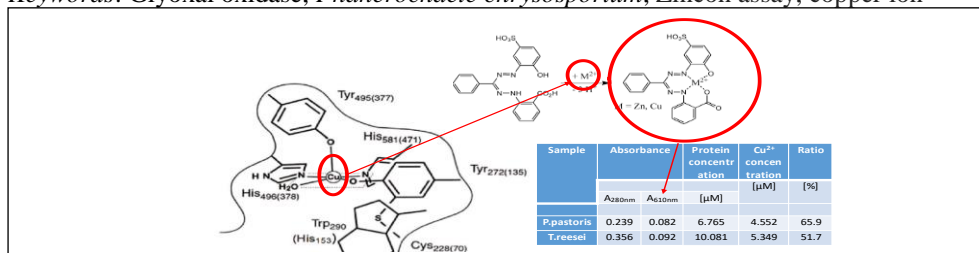
<sup>2</sup>Biocatalysis and Biosensing Research Group, Department of Food Science and Technology,  
BOKU-University of Natural Resources and Life Sciences, Muthgasse 18,  
Vienna A-1190, Austria

Glyoxal oxidase (GLOX) is an extracellular H<sub>2</sub>O<sub>2</sub>-generating metalloenzyme produced by various wood-degrading fungi, one of them being *Phanerochaete chrysosporium*, a white-rot fungus with the ability to completely degrade lignin. Because of the presence of one copper ion in its active site, GLOX is classified as radical copper oxidase, forming the AA5 family in the CAZymes system.

In order to determine copper in metalloproteins, a method known as Zincon assay was used. The method is based on the use of metal chelator Zincon, a colorimetric indicator used for spectrophotometric determination of zinc, copper and mercury. Initially, the proteins were denatured with guanidine hydrochloride whereby copper is released from the active site into solution. The released copper then binds to zincon and forms a metal-zincon complex whose formation is detected spectrophotometrically.

In the GLOX samples from both expression hosts, only 52-66% of the enzymes were found to contain a copper ion required for fully activity in their active site. An attempt to reactivate the enzyme, loading it with copper and thus increasing the percentage of active enzyme, unfortunately failed.

**Keywords:** Glyoxal oxidase, *Phanerochaete chrysosporium*, Zincon assay, copper ion



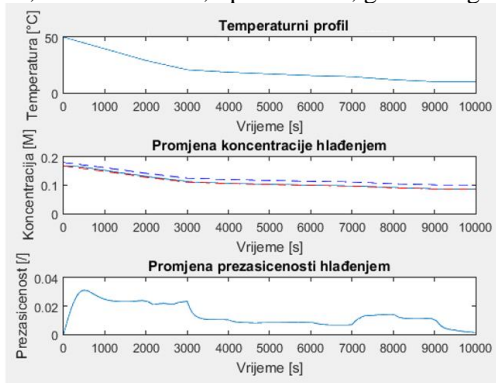
## PRORAČUN OPTIMALNOG TEMPERATURNOG PROFILA ŠARŽNOG KRISTALIZATORA DETERMINATION OF OPTIMAL COOLING PROFILE OF BATCH COOLING CRYSTALLIZER

Josip Sacher, Marko Sejdić, Matea Gavran, Nenad Bolf,  
Željka Ujević Andrijić, Nikola Rimac, Srećko Herceg

Faculty of Chemical Engineering and Technology, University of Zagreb, Marulićev trg 19,  
10000 Zagreb, Croatia

The batch cooling crystallization is widely used unit operation for separation and purification of a compound in a single step. It is widely applied in pharmaceutical, fine chemicals and food industry among the others. In pharmaceutical industry a large number of products (or intermediates) requires crystallization in at least one step of the process. A number of problems can occur due to excessive formation of fine crystals during the process (long filtering times, clogging of the equipment, cake compression) and because of that crystals generated by nucleation are considered undesirable. In this work we developed a program in Matlab using moment transformation of population balance as the process model. Crystallization kinetics for potassium sulphate was taken from literature because of good quality data and certain kinetics. An optimization problem was formulated to minimize ratio of the third moment of nucleation generated crystals to third moment of seed grown crystal. In addition, constraints were added in order to limit the duration of the process and ensure that appropriate yield is achieved at the end of the process. Optimization was performed first with genetic algorithm in order to find a solution which is near to the optimal solution. Afterwards, a sequential quadratic programming algorithm was applied to further improve the profile obtained by genetic algorithm. The solution obtained by sequential use of algorithms proves to be stable and satisfies conditions set by constraints. Therefore, the developed program can be used for calculation of the optimal temperature profile of batch crystallizer if the kinetics of the crystallizing compound is known.

*Keywords:* crystallization, moment model, optimization, genetic algorithm



## **EKSTRAKCIJA PIPERINA IZ PAPRA** **EXTRACTION OF PIPERINE FROM PEPPER**

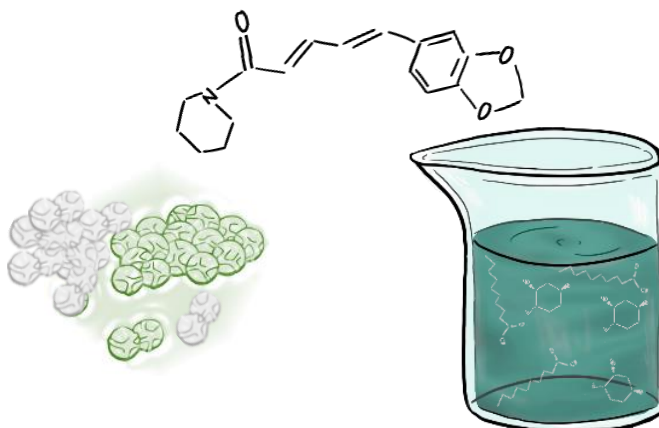
Aleksandra Sander<sup>1</sup>, Andrea Opačak<sup>1</sup>, Ana Petračić<sup>1</sup>, Dajana Kučić Grgić<sup>1</sup>,  
Martina Miloloža<sup>1</sup>, Marko Rogošić<sup>1</sup>, Mia Radović<sup>2</sup>

<sup>1</sup>Fakultet kemijskog inženjerstva i tehnologije Sveučilišta u Zagrebu, Trg Marka Marulića  
20, 10 000 Zagreb, Hrvatska

<sup>2</sup>Prehrambeno-biotehnološki fakultet Sveučilišta u Zagrebu, Pierottijeva ul. 6,  
10 000 Zagreb, Hrvatska

U ovom radu istražena je djelotvornost hidrofobnih niskotemperaturnih eutektičkih otapala pri ekstrakciji piperina iz zelenog i bijelog papra. Obje vrste papra dobivaju se iz plodova biljke *Piper nigrum* iz navedene porodice a razlikuju se u vremenu berbe i prerade. Na temelju procjene topljivosti piperina modelom COSMO-RS odabrana su i pripravljena tri otapala: timol : 1-oktanol (DES1); mentol : dekanska kiselina, 1:1 (DES2) i mentol : dekanska kiselina, 2:1 (DES3). Otapalima su eksperimentalno određena fizikalna svojstva (gustoća, površinska napetost i viskoznost) a najmanjoj veličinskoj frakciji papra raspodjela veličina čestica. Koncentracija piperina u ekstraktima određena je UV/Vis spektroskopijom. Istražen je utjecaj veličina čestica i vrste papra na efikasnost ekstrakcije piperina uz stalan maseni omjer papra i otapala. Najučinkovitije otapalo za ekstrakciju piperina iz papra je otapalo DES1. Učinkovitost ekstrakcije raste sa smanjenjem veličina čestica papra. Eksperimentalno je određena toksičnost otapala i antimikrobna aktivnost ekstrakata. Ekstrakti oba papra u otapalu DES1 najučinkovitije inhibiraju rast bakterija, dok su se svi ekstrakti pokazali učinkovitima u inhibiciji rasta kvasca.

*Ključne riječi:* ekstrakcija, niskotemperaturna eutektička otapala, papar, piperin



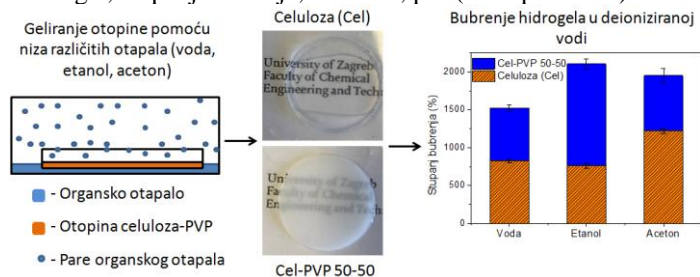
# FIZIKALNO UMREŽENI HIDROGELOVI NA OSNOVI CELULOZE MODIFICIRANE S POLI(VINIL-PIROLIDONOM) PHYSICALLY CROSSLINKED CELLULOSE-BASED HYDROGELS MODIFIED WITH POLY(VINYLPYRROLIDONE)

Jakov Sinti, Roko Blažić, Elvira Vidović

Fakultet kemijskog inženjerstva i tehnologije Sveučilišta u Zagrebu, Marulićev trg 19,  
10000 Zagreb, Hrvatska

Celuloza, biorazgradiv i biokompatibilan polisaharid, ima tendenciju stvaranja fizikalno umreženog hidrogela stvaranjem vodikovih veza između mnogobrojnih OH skupina u molekuli. Celulozni hidrogelovi različitih vrijednosti stupnja bubrenja te određenih mehaničkih svojstva pripremaju se kontrolom procesa regeneracije (geliranja) celuloze iz otopine kroz odabir pogodnog organskog otapala za regeneraciju, optimiranjem vremena geliranja te sastava otopine celuloze. Modifikacijom celuloznih hidrogelova s različitim funkcionalnim polimerima moguće je pripremiti materijale koji zbog specifičnih svojstava nalaze svoju primjenu u različitim procesima, poput adsorbensa u porocesima pročišćavanja voda od teških metala, materijala za primjenu u tkivnom inženjerstvu te materijala za primjenu u nosivoj elektronici. Poli(vinil-pirolidon) (PVP) biokompatibilan je i vodotopljiv sintetski polimer koji zbog svoje strukture ima tendenciju stvaranja vodikovih veza s organskim molekulama te mogućnost koordinacije s metalnim ionima. U ovom radu ispitan je utjecaj deionizirane vode te organskih otapala (etanol, aceton) na regeneraciju celuloze iz otopine dimetilacetamid (DMAc)/LiCl ili otopine celuloze i PVP u istom otapalu. Također, provedeno je grafitiranje PVP na celulozu pomoću ionizirajućeg zračenja dozom od 200 kGy te je potom istraženo geliranje tako modificirane celuloze s PVP. Gravimetrijski je određen stupanj bubrenja za pripremljene hidrogelove. Nadalje, sastav pripremljenih hidrogelova karakteriziran je infracrvenom spektroskopijom, a mehanička svojstva određena su dinamičko mehaničkom analizom. Najviši stupanj bubrenja za celulozni hidrogel (1200 %) postignut je prilikom regeneracije s parama acetona, dok je za hidrogel celuloza/PVP najviši stupanj bubrenja (2000 %) zabilježen regeneracijom u parama etanola.

**Ključne riječi:** hidrogel, stupanj bubrenja, celuloza, poli(vinil-pirolidon)



## SINTEZA METAKRILATNOG POLIMERA RADIKALSKOM POLIMERIZACIJOM U ZELENOM OTAPALU

### SYNTHESIS OF METHACRYLATE POLYMER BY RADICAL POLYMERIZATION IN GREEN SOLVENT

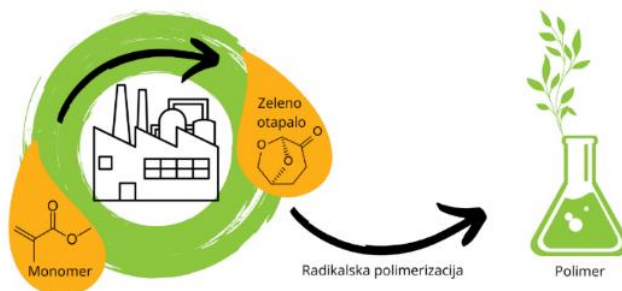
Kristina Sušac, Elvira Vidović, Ante Jukić

Fakultet kemijskog inženjerstva i tehnologije Sveučilišta u Zagrebu Trg Marka Marulića 19,  
10000 Zagreb, Hrvatska

Održivost (engl. *sustainability*) temeljni je izazov u 21. stoljeću za proizvodne industrije, od kojih se traži da primjenjuju kružno gospodarstvo te provedu tranziciju prema biogospodarstvu oslanjajući se na biosirovine. Otkrićem i razvojem zelenih otapala, koja mogu zamijeniti široko korištena organska toksična otapala petrokemijske industrije, postupno će se sve više proizvoditi u skladu s temeljnim načelima zelene kemije. Na taj način utjecat će se na ublažavanje klimatskih promjena kojima svjedočimo zbog rastuće potrebe za energijom i kemikalijama.

U ovom radu, kao zeleno netoksično otapalo korišten je dihidrolevoglukozenon koji se sintetizira iz obnovljivog celuloznog otpada proizvodnim procesom koji je energetski izuzetno prihvatljiv, a kao nusprodukt u sintezi nastaje voda. Radikalnom polimerizacijom u dihidrolevoglukozenonu sintetiziran je metakrilatni polimer, poli(metil-metakrilat) (PMMA). Osim što je u sintezi korišteno zeleno otapalo, dodatni pozitivan učinak je sedam puta skraćeno vrijeme polimerizacije pri čemu se prema GPC analizi molekulska masa polimera povećala u odnosu na sintezu u standardnim organskim otapalima, a da je pri tome poboljšana i polidisperznost polimernih makromolekula. NMR analizom utvrđeno je iskorištenje reakcije i struktura PMMA polimera, dok je FTIR analizom potvrđeno da nema zaostalog otapala. DSC analizom pratili su se temperaturni prijelazi, dok se TGA analiza koristila s ciljem određivanja temperature degradacije PMMA dobivenog u standardnom organskom otapalu i u zelenom otapalu.

*Ključne riječi:* zeleno otapalo, radikalna polimerizacija, PMMA



## **POROZNE KOAKSIJALNE DVOSTRUKE ELEKTRODE ZA UČINKOVITU BIOELEKTROANALIZU POROUS COAXIAL TWIN-ELECTRODES FOR EFFICIENT BIOELECTROANALYSIS**

Tatjana Šafarik<sup>1,2</sup>, Aleksandar Karajić<sup>3</sup>, Stéphane Reculusa<sup>2</sup>,  
Nicolas Mano<sup>1</sup>, Alexander Kuhn<sup>2</sup>

<sup>1</sup>CNRS, Univ. Bordeaux, CRPP, Pessac, France

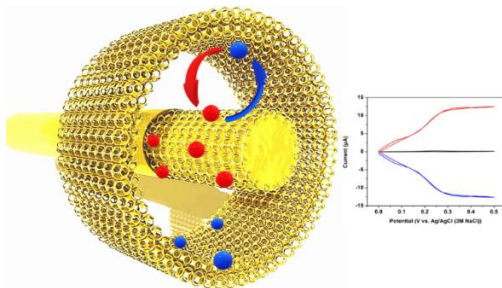
<sup>2</sup>Univ. Bordeaux, CNRS, Bordeaux INP, ISM, Pessac, France

<sup>3</sup>Novel Device Lab, University of Cincinnati, Cincinnati, OH 45221, USA

Velika potražnja za bioelektrokemijskim uređajima usmjerila je njihov razvoj prema poboljšanju elektrokemijskih svojstava kroz odgovarajući izbor materijala, površinske kemije te dizajna. Trodimenzionalna, koaksijalna, makroporozna, dvostruka elektroda je razvijena *bottom-up* tehnikom. Mikro uređaj se sastoji od dvije cilindrične porozne zlatne mikroelektrode s razmakom koji se može mijenjati. Zbog mikrometerske udaljenosti između dvije elektrode te zatvorene strukture, molekule analita umjesto jednom izmjenjuju elektrone višestruko, što rezultira pojačavanjem signala odnosno ukupne struje.

Nadalje, mala kompaktna biogoriva ćelija se formira ukoliko se površine elektroda modificiraju s dva različita enzima. S obzirom na minijaturizaciju, jednostavnost sinteze, pojačavanje signala i biokompatibilnost, ovakva se struktura može implementirati u brojne bioanalitičke svrhe, osobito u području implantabilnih uređaja.

*Ključne riječi:* porozna zlatna elektroda, *bottom-up* tehnika, mikrometerski uređaj, bioelektroanaliza, biogorivna ćelija





## UTJECAJ ŽELJEZOVIH NANOČESTICA NA TiO<sub>2</sub> ILI SiO<sub>2</sub> NOSAČU NA PRIMJENSKA SVOJSTVA PLA KOMPOZITA INFLUENCE OF TiO<sub>2</sub> AND SiO<sub>2</sub> AS CARRIERS FOR IRON NANOPARTICLES ON APPLICATION PROPERTIES OF PLA COMPOSITES

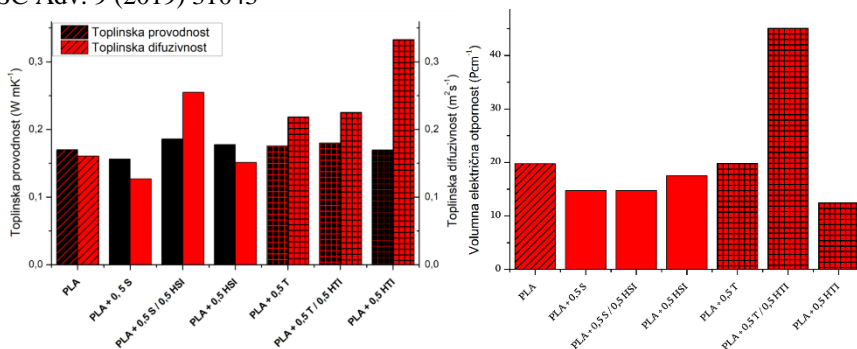
Andrea Špoljarić, Ante Jukić, Elvira Vidović

Fakultet kemijskog inženjerstva i tehnologije Sveučilišta u Zagrebu, Marulićev trg 19,  
10 000 Zagreb, Hrvatska

Ispitan je utjecaj različitih oksidnih nosača željezovih nanočestica na krajnja svojstva kompozitnog materijala sa polilaktidnom matricom (PLA). Nanočestice željeza sintetizirane su prema literaturi [1] te su modificirana koristeći SiO<sub>2</sub> ili TiO<sub>2</sub> kao njihove nosače. Različite kombinacije punila korištene su za pripremu PLA kompozita. Prvo su pripremljeni kompoziti sa 0,5 % mas punila čistih oksida. Naknadno, u takvu početnu smjesu dodavano je 0,5 % mas hibridnih punila (punila: silicijev oksid/željezove nanočestice -HSI, titanov oksid/željezove nanočestice -HTI). Također, priređeni su kompoziti samo sa 0,5 % mas hibridnog punila. Pripremljenim kompozitnim materijalima ispitana su različita primjenska svojstva. Toplinska stabilnost praćena je uz pomoć termogravimetrijske analize (TGA), toplinska provodnost ispitana je metodom „vrućeg mosta“, a volumna električna otpornost pomoću uređaja konstruiranog prema ASTM D257 normi. Također je provjeren utjecaj pripremljenih čestica i na mehanička svojstva kompozitnog materijala mehaničkim vlačnim ispitivanjem. Rezultati pokazuju kako korištenje druge vrste nosača za željezove nanočestice može imati različit utjecaj na primjenska svojstva; primjerice dodatak TiO<sub>2</sub> kao nosača uvelike narušava mehanička svojstva kompozita za razliku od SiO<sub>2</sub>, odnosno SiO<sub>2</sub> povećava toplinsku provodnost, a dodatak TiO<sub>2</sub> nema značajan utjecaj na nju.

*Ključne riječi:* kompozitni materijali, silicijev dioksid, titanov dioksid, željezove nanočestice

[1] S. Rončević, Nemet I., Zubin Ferri T., Matković-Čalogović D., *Pure Appl. Chem.* 64 (1992) 42. RSC Adv. 9 (2019) 31043





## MEHANIČKA I TOPLINSKA SVOJSTVA BIOKOMPOZITA NA BAZI PLUTA I PLA MATRICE

### MECHANICAL AND THERMAL PROPERTIES OF BIOCOMPOSITES BASED ON CORK AND PLA MATRIX

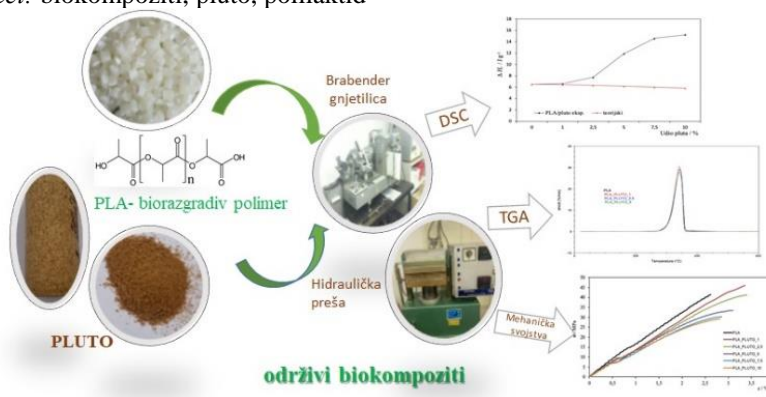
Sara Šušak, Vesna Ocelić Bulatović, Mirela Leskovic  
Fakultet kemijskog inženjerstva i tehnologije Sveučilišta u Zagrebu,  
Marulićev trg 19, 10 000 Zagreb, Hrvatska

Današnja sve veća svijest o očuvanju okoliša te nepovoljni utjecaj plastičnog otpada na onečišćenje okoliša, stavlja veliki naglasak na istraživanja biokompozita koji kao matricu imaju biorazgradive polimere te kao ojačavala prirodna punila. Kao alternativni materijal za upotrebu u polimernim kompozitima nameće se pluto. Pluto, osim što je obnovljiv i biorazgradiv izvor, relevantan je za ugradnju u kompozite zbog niske gustoće, niske propusnosti za tekućine i plinove, dobre elastičnosti, ima nizak koeficijent toplinske vodljivosti, otporan je na mehaničko trošenje, koroziju i gorenje.

U ovom radu istraženi su biokompoziti na bazi pluta i polilaktidne (PLA) matrice. Toplinska svojstva ispitana su diferencijalnom pretražnom kalorimetrijom (DSC), termogravimetrijskom analizom (TGA) i mjerenjem toplinske vodljivosti dok su rastezna svojstva određena testom jednoosnog naprezanja. Analiza površinskih svojstava određena je primjenom kontaktnog kuta te su na osnovi proračuna parametara adhezije procijenjene interakcije na međupovršini PLA/pluto.

Proračun parametara adhezije ukazuje na prisutnost slabijih interakcija na međupovršini PLA/pluto. Iz DSC rezultata vidljiv je znatan porast entalpije kristalizacije, s porastom udjela pluta u PLA/pluto biokompozitima što upućuje da prisutnost pluta znatno potiče kristalizaciju PLA u ciklusu hlađenja. Pluto ne utječe na poboljšanje toplinske stabilnosti biokompozita. Smanjenje toplinske vodljivosti PLA/pluto biokompozita ukazuje na izvrsna izolacijska svojstva.

*Ključne riječi:* biokompoziti, pluto, polilaktid



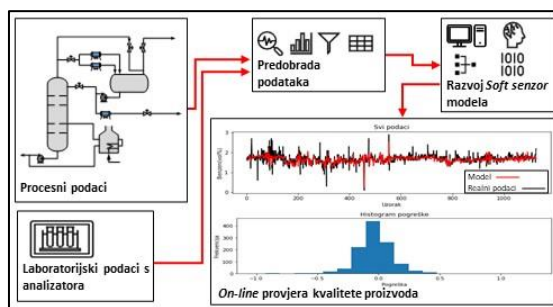
## RAZVOJ SOFTVERSKIH SENZORA PRIMJENOM METODA STROJNOG UČENJA DEVELOPMENT OF SOFT SENSORS USING MACHINE LEARNING METHODS

Željka Ujević Andrijić, Nikola Rimac, Ines Martić

Fakultet kemijskog inženjerstva i tehnologije Sveučilišta u Zagrebu, Savska cesta 16/5A,  
10000 Zagreb, Hrvatska

U procesu katalitičkog reforminga u rafineriji nafte Rijeka kontinuirano mjerenje količine benzena u produktu procesa katalitičkog reforminga vrlo je važno zbog ekoloških i tehničkih zahtjeva. Primjena softverskog senzora za on-line provjeru kvalitete proizvoda, uvelike bi olakšala i poboljšala vođenje procesa budući da su trenutne analize pomoću procesnog analizatora u laboratoriju dosta rijetke. U ovome radu prikazan je razvoj modela softverskih senzora za kontinuirano praćenje sadržaja benzena u rafinerijskom procesu frakcionacije reformata. Cilj rada bio je izraditi modele softverskih senzora metodama strojnog učenja na temelju kontinuirano mjerenih veličina, kao što su temperature, tlakovi i protoci. Dobiveni podaci iz rafinerije predobrađeni su različitim metodama te su u programskom jeziku *Python* izrađeni modeli softverskih senzora primjenom umjetnih neuronskih mreža i metodom potpornih vektora. Rezultati modela statistički su validirani na neovisnom skupu podataka. Najboljim modelima, od obje vrste modela softverskih senzora, dobivene su slične vrijednosti koeficijenta korelacije i pogreške te se mogu primijeniti u rafinerijskom informacijskom sustavu. Na temelju primjene razvijenih softverskih senzora moguće je očekivati poboljšanje vođenja procesa i konačne kvalitete proizvoda, a time i značajne uštede u proizvodnji, kao i zadovoljenje strogih propisa zaštite okoliša.

*Ključne riječi:* softverski senzor, neuronske mreže, benzen, reformat, metoda potpornih vektora



## PROCJENA KLJUČNIH PROCESNIH VELIČINA NA TEMELJU PODATAKA IZ INDUSTRIJSKIH PROCESA DATA-DRIVEN ESTIMATION OF CRITICAL QUALITY ATTRIBUTES ON INDUSTRIAL PROCESSES

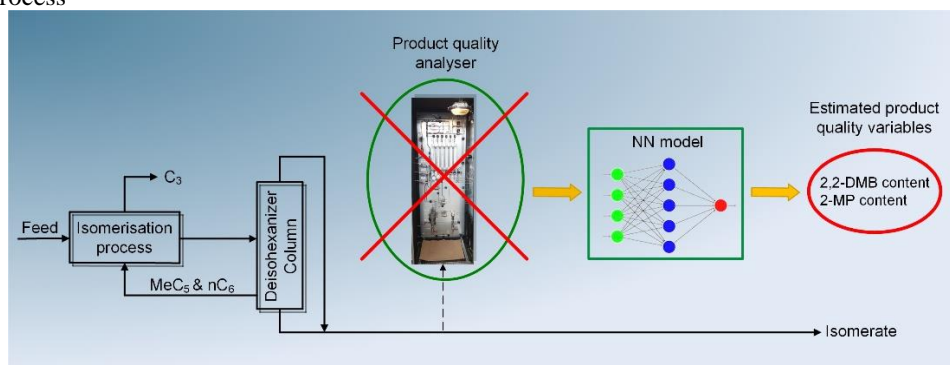
Željka Ujević-Andrijić, Srećko Herceg, Nenad Bolf

Faculty of Chemical Engineering and Technology, University of Zagreb, Savska c. 16/5a,  
10 000 Zagreb, Croatia

Large data sets created and stored by continuous monitoring of process variables in process plants enable the development of data-driven mathematical models of a process. Such models, although they do not provide detailed insight into the process, enable a feasible description of complex process dynamics characterized by nonlinearity. These models are often used to estimate key process attributes in real time.

This paper presents an industrial case study of data-driven models based on multilayer perceptron (MLP) neural networks for refinery light naphtha isomerisation process. The models for the estimation of critical quality attributes of the product were developed. Significant attention was paid to the selection and analysis of data sets for different periods with the aim of capturing enhanced process dynamics. Optimal models were obtained by changing the types of learning function and transfer function, as well as the number of neurons in the hidden layer. Models based on MLP neural networks have shown better generalization abilities in comparison with earlier developed polynomial linear and non-linear models for isomerisation process. This makes the developed MLP neural network models desirable for application to such a process, especially in the field of advanced process control.

**Keywords:** data-driven model, process monitoring, MLP neural network, isomerisation process

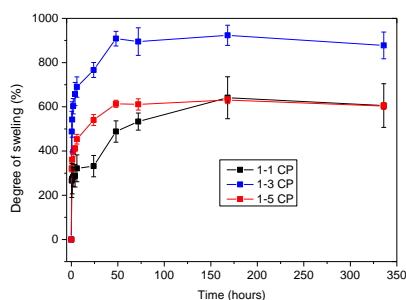


## SWELLING PROPERTIES OF CELLULOSE-*g*-PDMAEMA HYDROGELS STUDIJA BUBRENJA CELULOZA-*g*-PDMAEMA HIDROGELOVA

Elvira Vidović, Roko Blažić, Domagoj Rebernjak, Katarina Marušić  
Faculty of Chemical Engineering and Technology, University of Zagreb, Marulićev trg 19,  
10 000 Zagreb, Croatia

Hydrogels possess unique properties in terms of porosity, swelling, mechanics, even biological responses that make them relevant to a broad range of potential applications. In order to prepare hydrogel abundant natural material cellulose, rich in hydroxyl groups, was modified by graft copolymerization with poly(2-dimethylaminoethyl methacrylate) (PDMAEMA)[1]. Hydrogels are prepared from cellulose:DMAEMA in the ratios 1:1, 1:3 or 1:5 and crosslinked with *N,N*-methylenebis(acrylamide) *i*) via chemical synthesis or *ii*) by additional irradiation (10, 30 or 100 kGy) [2]. The hydrogel spheres have been prepared and their swelling kinetics was studied in deionized water at 20 °C for 14 days. The swelling study of hydrogels prepared by chemical synthesis showed large equilibrium swelling (600 to 900 %). Samples 1-3\_CP and 1-5\_CP reached the maximum swelling degree in two days, while sample 1-1\_CP reached it in seven days, suggesting that PDMAEMA contributes to the faster swelling. Selected samples were structurally characterized by scanning electron microscopy and recorded micrographics revealed structural differences related to the content of PDMAEMA.

**Keywords:** hydrogels, cellulose, poly(2-dimethylamino ethyl methacrylate), equilibrium swelling



**Figure 1.** Comparison of equilibrium swelling kinetic for hydrogel samples with different molar ratio of cellulose and DMAEMA

[1] R. Blažić, K. Lenac, E. Vidović, *KUI* **69**(2020) 269.

[2] R. Blažić, K. Marušić, E. Vidović, *J. Appl. Polym. Sci.* (in press.)

## KINETIKA BIOREMEDIJACIJE SIMULIRANE PROCJEDNE VODE IZ BIOOTPADA BIOREMEDIATION KINETICS OF SIMULATED LEACHATE FROM BIOWASTE

Marija Vuković Domanovac<sup>1</sup>, Ivana Stojmilović<sup>1</sup>, Martina Trtinjak<sup>1</sup>,  
Tomislav Domanovac<sup>2</sup>, Monika Šabić Runjavec<sup>1</sup>

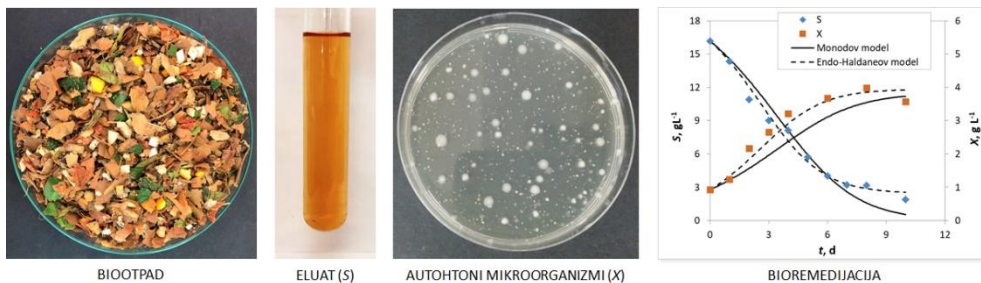
<sup>1</sup>Fakultet kemijskog inženjerstva i tehnologije Sveučilišta u Zagrebu, Zavod za industrijsku ekologiju, Marulićev trg 19, 10000 Zagreb, Hrvatska

<sup>2</sup>IPZ UNIPROJEKT TERRA, Voćarska cesta 68, 10000 Zagreb, Hrvatska

Tijekom posljednjih nekoliko desetljeća, rizici povezani s onečišćenjem procjednim vodama postali su sve očigledniji, kako za okoliš, tako i za zdravlje ljudi. Procjedne vode se mogu kategorizirati kao specifična vrsta otpadnih voda na koju utječe varijabilnost u sastavu otpada i njegovih fizikalnih, kemijskih i bioloških promjena. Kontrola onečišćenja procjednim vodama je globalna briga i veliki izazov u smanjenju izvora i uklanjanju onečišćujućih tvari. Biološka obrada predstavlja potencijalno prihvatljivo rješenje za pročišćavanje procjednih voda s okolišnog i ekonomskog stajališta zahvaljujući djelovanju mikroorganizama. Autohtoni mikroorganizmi su dragocjen resurs za bioremedijaciju procjedne vode, jer su tolerantni na visoko opterećenje i mogu sudjelovati u razgradnji onečišćenja.

U ovom radu istraživana je kinetika procesa bioremedijacije pri uklanjanju organskih onečišćujućih tvari iz simulirane procjedne vode iz biootpada u šaržnim uvjetima. Proces je opisan Monodovim i Endo-Haldaneovim modelom. Na temelju procijenjenih vrijednosti kinetičkih parametara i ocjene prihvatljivosti predloženih modela, Endo-Haldaneov model bolje opisuje proces bioremedijacije procjedne vode iz biootpada.

*Ključne riječi:* procjedna voda, biootpad, bioremedijacija, kinetika



## UTJECAJ SUSTAVA OTAPALA NA KRISTALNU STRUKTURU DJELATNE TVARI INFLUENCE OF SOLVENT SYSTEM ON THE CRYSTAL STRUCTURE OF API

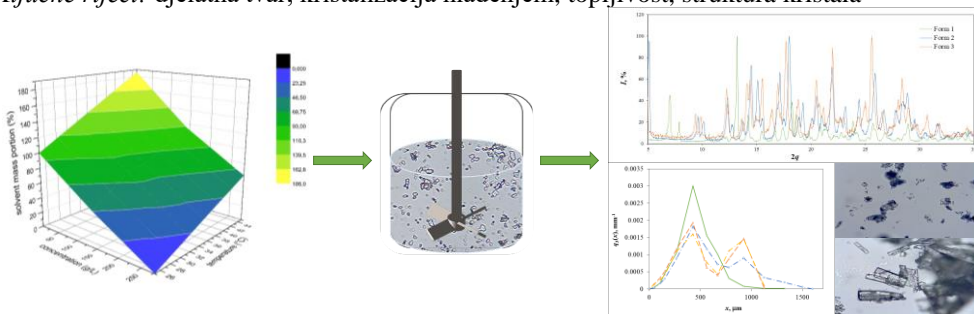
Iva Zokić, Ana Krajina, Luka Dornjak, Jasna Prlić Kardum  
Fakultet kemijskog inženjerstva i tehnologije Sveučilišta u Zagrebu, Marulićev trg 19,  
10000 Zagreb, Hrvatska

Problemi niske topljivosti i slabe bioraspoloživosti prisutni su kod više od 80 % molekula lijekova, što dovodi do poteškoća u kasnim fazama formulacije lijeka i pretkliničkim studijama. Iz tog razloga znanstvenici i farmaceutske tvrtke istražuju primjenu procesa kristalizacije za kontrolu i podešavanje fizikalno-kemijskih svojstava djelatnih tvari (engl. *active pharmaceutical ingredient*, API), kao što su granulometrijska svojstva, topljivost, stabilnost te brzina oslobađanja.

Topljivost djelatne tvari određena je pri temperaturi 25 °C u čistim otapalima (etanol, metanol, aceton, izopropanol i voda) i u smjesama otapala (etanol-voda, izopropanol-voda i aceton-voda) pri različitim volumnim omjerima. Djelatna tvar je istaložena iz otopine podešavanjem pH dodatkom 10 %-tne natrijeve lužine te je određeno iskorištenje procesa. Na temelju izračunatih topljivosti i iskorištenja za daljnji su rad odabrani sustavi etanol-voda i aceton-voda u omjeru 3:1. U navedenim je sustavima, pri temperaturama 35 °C i 45 °C, provedena kristalizacija hlađenjem uz prethodno podešavanje pH dodatkom 10 %-tne natrijeve lužine. Unutarnja struktura nastalih kristala određena je rendgenskom difrakcijom na prahu i Ramanovom spektroskopijom.

Rezultati su pokazali kako su provođenjem kristalizacije u sustavima etanol-voda i aceton-voda nastale različite kristalne forme djelatne tvari, što znači da izbor otapala i antiotapala u kojima se provodi kristalizacija uvelike utječe na kristalnu strukturu. Vanjska struktura kristala određena je svjetlosnom mikroskopijom, koja je pokazala kako su kristali nastali iz sustava aceton-voda puno krupniji od onih nastalih u sustavu etanol-voda, zbog čega su pogodniji za daljnji rad.

**Ključne riječi:** djelatna tvar, kristalizacija hlađenjem, topljivost, struktura kristala





## FOTOREDUKCIJA GRAFEN OKSIDA INTENZIVNOM PULSIRAJUĆOM SVJETLOŠĆU PHOTOREDUCTION OF GRAPHENE OXIDE BY INTENSE PULSED LIGHT

Marko Zubak, Juraj Vuić, Petar Kassal

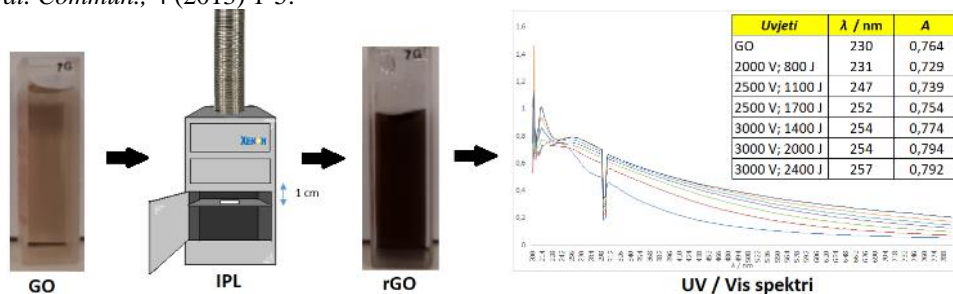
Fakultet kemijskog inženjerstva i tehnologije Sveučilišta u Zagrebu, Marulićev trg 19,  
10000 Zagreb, Hrvatska

Zbog izvrsnih električnih i mehaničkih svojstava grafen je materijal koji izaziva veliku pažnju znanstvene zajednice te su razvijene različite metode njegovog dobivanja. Kemijska redukcija grafen oksida zahtijeva korištenje reducensa koji imaju nepovoljan učinak na zdravlje i okoliš, dok termalna redukcija iziskuje utrošak velike količine energije i vremena. Metoda koja pruža izvrsnu alternativu prethodno spomenutim postupcima je fotoredukcija. Uzevši u obzir ekonomičnost, brzinu postupka i kvalitetu krajnjeg produkta za fotoredukciju se najčešće koriste UV i halogene lampe, laseri te intenzivna pulsirajuća svjetlost (eng. *Intense Pulsed Light*, IPL) [1]. IPL je tehnika koja se temelji na ultrabrzom emitiranju svjetlosti (190 – 1100 nm) koja je uzrokovana stvaranjem električnog luka između volframovih elektroda pod visokim naponom (>1000 V). U ovom radu je po prvi put korištena intenzivna pulsirajuća svjetlost za redukciju dispergiriranog grafen oksida u različitim kapljevitim sustavima (voda, etanol, citratni pufer pH = 10, N,N-dimetilacetamid). Cilj eksperimenta je bio utvrditi utjecaj disperznog sredstva na fotoredukciju te utvrditi optimalne parametre IPL sustava koji u konačnici daju zadovoljavajući proizvod. Spektrofotometrijski je utvrđen visok stupanj redukcije, a vrijeme trajanja procesa je < 30 s.

*Cljučne riječi:* grafen, grafen oksid, intenzivna pulsirajuća svjetlost, fotoredukcija

Ovaj rad financirala je Hrvatska zaklada za znanost projektima UIP-2020-02-9139 i DOK-2021-02-2362

[1] Regis Y.N. Gengler, D. S. Badali, D. Zhang, K. Dimos, K. Spyrou, D. Gournis, R.J. Dwayne Miller, Revealing the ultrafast process behind the photoreduction of graphene oxide, *Nat. Commun.*, 4 (2013) 1-5.



## **VOĆNI ŽELE I SNACK PROIZVODI FRUIT JELLY AND SNACK PRODUCTS**

Ajla Avdić, Amela Kusur, Martina Tanović, Amel Selimović,  
Dijana Miličević, Gordan Avdić  
Univerzitet u Tuzli, Tehnološki fakultet, Urfeta Vejzagića 8,  
75 000 Tuzla, Bosna i Hercegovina

Snack proizvodi su jako rašireni u cijelom svijetu, bilo da se radi o slatkim ili slanim proizvodima. I jedni i drugi su u početku trebali biti hrana za grickanje, u malim pakiranjima, koja se konzumira odmah. Međutim, danas se većina snack proizvoda pakira u velika pakiranja, a postoje i kategorije ovih proizvoda kojima je potrebna neka termička obrada prije konzumiranja. Osim toga, većina sadrži velike količine soli, šećera i masnoća, prije svega ulja, što ih svrstava u proizvode koji nisu baš najbolji za ljudsko zdravlje.

Cilj ovog rada je bio napraviti žele i snack proizvode od voća, s vrlo malo dodataka i blagom termičkom obradom. Napravljen je žele od soka naranče, uz dodatak šećera. Pulpa naranče je iskorištena za proizvodnju dehidriranih snack proizvoda, sušenih na 70 °C, uz dodatak kombinacije škroba, šećera, smeđeg šećera, gelan gume, itd.

Rezultati su pokazali da se mogu proizvoditi ovakvi proizvodi, ali treba voditi računa o dodacima, te o teksturi proizvoda.

*Ključne riječi:* naranča, žele, snack proizvodi, gelan guma



**UTJECAJ METODA SUŠENJA NA ISKORIŠTENJE I  
FIZIKALNA SVOJSTVA SUHIH EKSTRAKATA KORE  
MANDARINE Citrus unishu  
INFLUENCE OF DRYING TECHNIQUES ON THE  
PRODUCT YIELD AND PHYSICAL PROPERTIES OF  
Citrus unishu PEEL DRY EXTRACTS**

Marija Banožić, Krunoslav Aladić, Stela Jokić

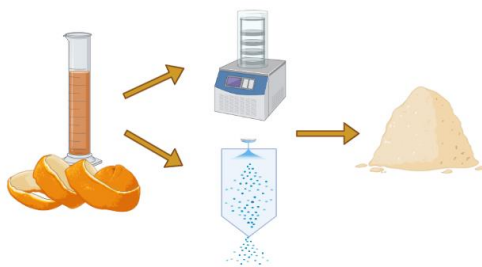
Josip Juraj Strossmayer University of Osijek, Faculty of Food Technology Osijek, Franje  
Kuhača 18, 31000 Osijek, Croatia

The product yield and physical properties of citrus peel dry extract, developed by two drying techniques: freeze drying and spray drying were investigated. Maltodextrin and Arabic gum were tested for their ability to serve as carriers for citrus peel extract. Obtained powders were evaluated for their moisture content, flow, solubility and color properties. Freeze drying gave almost 100% process yield, while spray drying yield was significantly lower (around 50%). On the other hand, the moisture content of dry extracts obtained with spray drying was lower than those obtained with freeze-drying. Both drying techniques significantly improved the flow and solubility properties of citrus peel dry extracts, while color changes were lower when freeze drying was used. Obtained results also showed that maltodextrin is a better carrier choice when spray drying is used, while for freeze drying Arabic gum is more suitable. Above all, those results could be used as guidance on the practical production of functional food powders delivered from by-products like selecting a suitable drying approach and carrier choice.

*Keywords:* spray drying, freeze drying, citrus peel

**Acknowledgments**

This work has been supported by Croatian Science Foundation under the project “Application of innovative techniques of the extraction of bioactive components from by-products of plant origin” (UIP-2017-05-9909).

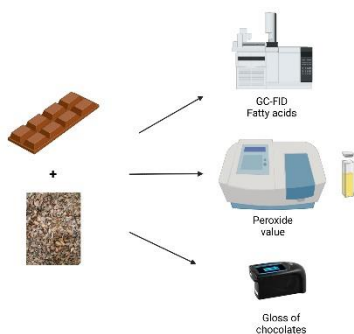


## **STABILNOST MASTI ČOKOLADA S DODANOM KAKAOVOM LJUSKOM FAT STABILITY OF CHOCOLATES WITH ADDED COCOA SHELL**

Veronika Barišić, Ivana Flanjak, Antun Jozinović, Jurislav Babić,  
Drago Šubarić, Borislav Miličević, Đurđica Ačkar  
Josip Juraj Strossmayer University of Osijek, Faculty of Food Technology Osijek, Franje  
Kuhača 18, 31000 Osijek, Croatia

Chocolates are one of the most favourite confectionery products that have a long shelf life, commonly one to two years. Cocoa bean shell is one of the by-products generated in the cocoa industry that has a high content of dietary fibres and bioactive components. Since this by-product is generated in large quantities, it presents a growing environmental problem. The aim of this study was to implement cocoa shell in chocolate production and analyse the stability of such chocolates. Production was performed in a ball mill. Dark and milk chocolate without added cocoa shell were produced, and the cocoa shell was used in share of 15% for the production of dark chocolate and 5% for the production of milk chocolate. After refining and conching, chocolates were tempered and cooled. All analyses were performed after the production, and after 3, 6, 9 and 12 months of storage in the dark, at ambient temperature. The stability of chocolates was determined by analysing fatty acid composition, peroxide value and gloss of chocolates. Fatty acids were determined by GC-FID and peroxide value was determined by the spectrophotometric method. The gloss of chocolates was measured with a gloss meter. Results showed that chocolates had the highest content of palmitic, oleic and stearic acid. In addition, all analysed fatty acids were stable during tested period. The peroxide value of chocolates after the production was similar for all chocolates, while after one year chocolates with added cocoa shell had a slightly higher peroxide value but it was still in acceptable range. The gloss of all dark chocolates decreased after 3 months and for milk chocolates after 6 months of storage.

*Ključne riječi:* cocoa shell, fatty acids, peroxide value, chocolate, gloss



## TRANSFORMACIJA TALOGA KAVE U VISOKOVRIJEDNE PRODUKTE TRANSFORMATION OF SPENT COFFEE GROUNDS TO HIGH-VALUE ADDED PRODUCTS

Mirna Brekalo<sup>1</sup>, Krunoslav Aladić<sup>1</sup>, Lidija Jakobek Barron<sup>1</sup>, Blanka Bilić Rajs<sup>1</sup>, Jovana Stanojev<sup>2</sup>, Nikola Maravić<sup>3</sup>, Sandra Budžaki<sup>1</sup>, Ivica Strelec<sup>1</sup>

<sup>1</sup>Josip Juraj Strossmayer University of Osijek, Faculty of Food Technology Osijek, Franje Kuhača 18, 31000 Osijek, Croatia

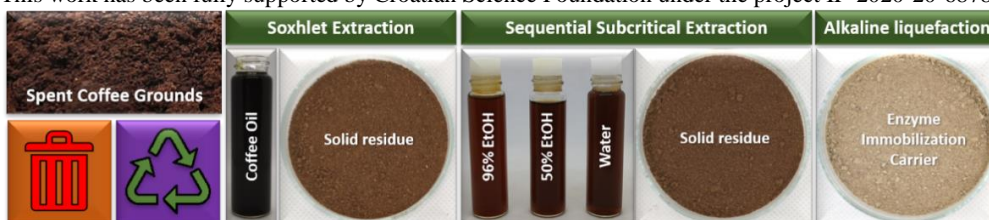
<sup>2</sup>BioSense Institute, University of Novi Sad, Dr Zorana Đinđića 1, 21000 Novi Sad, Serbia

<sup>3</sup>Faculty of Technology Novi Sad, University of Novi Sad, Bulevar Cara Lazara 1, 21000 Novi Sad, Serbia

Development of innovative transformation techniques of waste generated by agri-food industry into high-value added products, is one of pillars of circular economy oriented toward “zero-waste” approach. In this respect, we have examined the possibility of complete utilization of spent coffee grounds using sequential extraction by several solvents, followed by alkaline liquefaction of solid residue. Soxhlet extraction of spent coffee grounds with *n*-hexane has been used for the production of coffee oil, while continuous sequential subcritical extraction of defatted residue by 96% and 50% ethanol, and water for the production of targeted bioactive compounds. The solid residue remained after sequential subcritical extraction was subjected to alkaline liquefaction in order to produce possible carrier for enzyme immobilization. The complete utilization of 100 g of spent coffee ground containing 95% of dry matter resulted with the production of ~10.5 g of coffee oil rich in linoleic and palmitic acid, ~330 mg of caffeine and ~120 mg of chlorogenic acid, and with ~20 g of chemically inert cellulose carrier for the enzyme immobilization. Based on the current evidence, it can be safely concluded that spent coffee grounds represent the valuable raw-material for the production of high value-added products, instead being discarded on landfills.

*Ključne riječi:* spent coffee grounds, transformation, coffee oil, caffeine, enzyme immobilization carriers

This work has been fully supported by Croatian Science Foundation under the project IP-2020-20-6878.



## **KOMPLEKSIRANJE PREHRAMBENIH VLAKANA S POLIFENOLIMA CVIJETA BAZGE (*Sambucus nigra*) COMPLEXATION OF DIETARY FIBERS WITH ELDERFLOWER (*Sambucus nigra*) POLYPHENOLS**

Ivana Buljeta<sup>1</sup>, Anita Pichler<sup>1</sup>, Josip Šimunović<sup>2</sup>, Mirela Kopjar<sup>1</sup>

<sup>1</sup>Faculty of Food Technology Osijek, Josip Juraj Strossmayer University, F. Kuhača 18,  
31000 Osijek, Croatia

<sup>2</sup>Department of Food, Bioprocessing and Nutrition Sciences, North Carolina State  
University, Raleigh, NC 27695, USA

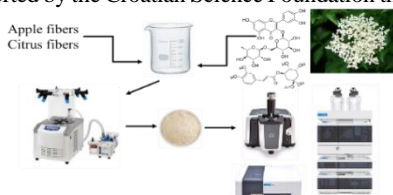
Wild plants have recently attracted attention due to the rich content of bioactive components and the potential positive effect on human health [1]. Among them, elderflower is recognizable for its intense and attractive flavor but also due to its rich phenolic acids and flavonoid content. [1]. Dietary fibers, besides health benefits, have the ability to interact with polyphenols. The aim of the present study was to prepare bioactive complexes based on apple or citrus fibers with elderflower polyphenols. Elderflower extract (water:ethanol 1:1) was mixed with 4% of apple or citrus fibers and then freeze-dried. Obtained powders were evaluated spectrophotometrically for total polyphenols content and antioxidant activity (FRAP, CUPRAC, ABTS and DPPH assays) as well as for individual polyphenols content by HPLC analysis. IR spectra were recorded to confirm complexation. Obtained results showed that bioactive complex with apple fibers possessed higher total polyphenols content (5.41 g/kg) than complex with citrus fibers (3.48 g/kg). Chlorogenic acid and rutin are polyphenols usually present in elderflower extracts and also identified and quantified in these complexes. The results of antioxidant activity followed the same trend as for total polyphenol content. These bioactive complexes can be applied for the enrichment of different food products with antioxidants.

*Keywords:* elderflower, polyphenols, apple fibers, citrus fibers, antioxidant activity

[1] T. Uzlasir, P. Kadiroglu, S. Selli, H. Kelebek, *J. Food Process. Preserv.* 45 (2020) 14478.

### **Acknowledgment**

This study was financially supported by the Croatian Science Foundation through grant PZS-2019-02-1595.



## INKAPSULACIJA ETERIČNOG ULJA KOMORAČA PRIMJENOM SUŠENJA RASPRŠIVANJEM ENCAPSULATION OF FENNEL ESSENTIAL OIL BY SPRAY DRYING

Ena Cegledi, Maja Repajić, Nina Marčac, Ivona Elez Garofulić,  
Marta Balun, Erika Dobrosravić, Verica Dragović-Uzelac  
Prehrambena-biotehnoški fakultet Sveučilišta u Zagrebu, Pierottijeva 6,  
10000 Zagreb, Hrvatska

Komorač (*Foeniculum vulgare* Mill.) je višegodišnja, ljekovita i aromatična biljka koja pripada obitelji štitarki (lat. *Apiaceae*). Od davnina se koristi u narodnoj medicini i kulinarstvu, a danas se sve više koristi u farmaceutskoj, kozmetičkoj i prehrambenoj industriji. Sjemenke komorača obiluju eteričnim uljem (5-6 %) koje karakterizira bogata aroma te je značajno zbog svojih antimikrobnih i antioksidativnih svojstava [1]. Međutim, visoka hlapljivost eteričnog ulja i podložnost oksidaciji u prisutnosti svjetlosti, zraka i vlage te nestabilnost tijekom prerade ograničava njegovu upotrebu u industriji. Slijedom navedenog, inkapsulacija sušenjem raspršivanjem predstavlja pogodnu metodu za produljenje stabilnosti eteričnih ulja i zadržavanje njihovih funkcionalnih svojstava tijekom manipulacije, obrade i skladištenja. Stoga je cilj ovog rada bio ispitati utjecaj omjera dvokomponentne kombinacije nosača maltodekstrina i arapske gume (1:1, 1:3 i 3:1) te temperature sušenja (120, 160 i 200 °C) na iskorištenje procesa, zadržavanje ulja i učinkovitost inkapsulacije. Porastom udjela arapske gume dolazi do povećanja vrijednosti sva tri promatrana parametra, dok porast temperature do 160 °C dovodi do povećanja zadržavanja i učinkovitosti. Daljnjim porastom temperature dolazi do povećanja iskorištenja. Optimalni uvjeti za učinkovitu inkapsulaciju eteričnog ulja iz sjemenki komorača su omjer maltodekstrina i arapske gume 1:3 te temperatura sušenja 160 °C.

**Ključne riječi:** komorač, eterično ulje, sušenje raspršivanjem, inkapsulacija

[1] Badgular, Shamkant B., Vainav V. Patel, and Atmaram H. Bandivdekar. "Foeniculum vulgare Mill: a review of its botany, phytochemistry, pharmacology, contemporary application, and toxicology." *BioMed research international* 2014 (2014).



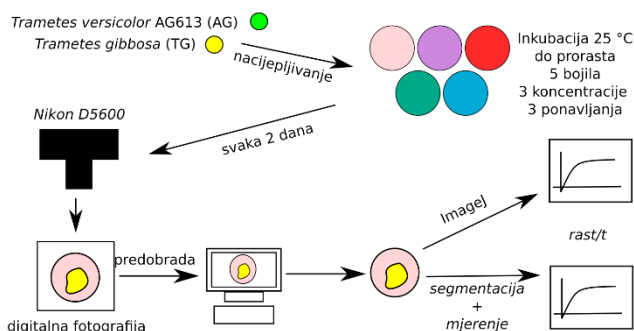
## PRAĆENJE RASTA GLJIVA PRIMJENOM STROJNOG VIDA MACHINE VISION FOR FUNGI GROW MONITORING

Frane Čačić Kenjerić, Anamarija Brkić, Natalija Velić,  
Darko Velić, Hrvoje Pavlović

Sveučilište Josipa Jurja Strossmayera u Osijeku, Prehrambeno-tehnološki fakultet Osijek,  
Franje Kuhača 18, 31000 Osijek, Hrvatska

Cilj rada je primjenom računalne analize slike, odnosno strojnog vida, pratiti rast odabranih viših gljiva na krutim hranjivim podlogama s dodatkom sintetskih bojila. Uklanjanje bojila iz obojenih otpadnih voda u kojima završavaju nakon proizvodnih procesa, od iznimmog je značaja prije ispuštanja otpadnih voda u okoliš, stoga što su, često, kemijski jako stabilna, a toksična za žive organizme (mutageni, karcinogeni, inhibitori rasta, iritanti i dr.). Nakon dodatka bojila (fuksin, kristal violet, kongo crvenilo, malahitno zelenilo, metilensko modriilo) u tri koncentracije ( $10 \text{ mg L}^{-1}$ ,  $50 \text{ mg L}^{-1}$  i  $100 \text{ mg L}^{-1}$ ) u krumpirov glukozni agar (PDA), podloge su nacijepljene diskom poraslih gljiva *Trametes gibbosa*, i *T. versicolor* AG613. Porast gljiva praćen je tijekom inkubacije pri  $25 \text{ }^{\circ}\text{C}$ , a gornji dio Petrijeve zdjelice s bojiлом i gljivom fotografiran je pomoću digitalnog fotoaparata Nikon D5600, svaka dva dana, do potpunog prorasta gljive. Fotografijama je uklonjena pozadina i obrezane su na veličinu Petrijeve zdjelice. Nakon predobrade, pomoću aplikacije ImageJ, izmjeren je rast/inhibicija gljiva, što zahtjeva rad analitičara (poluautomatsko). Potpuna automatizacija postupka moguća je dodatnom obradom fotografija primjenom tehnika strojnog vida, odnosno algoritama za segmentaciju slika (detekcija linija, metoda praga, tekstura). U radu je primijenjeno nekoliko različitih algoritama segmentacije slika, te su uspoređeni rezultati s ciljem pronalaska optimalnog algoritma segmentacije za automatizaciju mjerenja rasta/inhibicije gljiva.

*Ključne riječi:* praćenje rasta gljiva, strojni vid, segmentacija slika



## INKAPSULACIJA VANILINA U HIDROGELOVE NA BAZI ALGINATA I KITOZANA ENCAPSULATION OF VANILLIN IN ALGINATE/CHITOSAN HYDROGEL BEADS

Ina Ćorković<sup>1</sup>, Mirta Škraba<sup>1</sup>, Anita Pichler<sup>1</sup>, Josip Šimunović<sup>2</sup>,  
Mirela Kopjar<sup>1</sup>

<sup>1</sup>Josip Juraj Strossmayer University of Osijek, Faculty of Food Technology, F. Kuhača 18,  
31000 Osijek, Croatia

<sup>2</sup>Department of Food, Bioprocessing and Nutrition Sciences, North Carolina State  
University, Raleigh, NC 27695, USA

Vanillin is a natural product occurring in tropical specie *Vanilla planifolia*. It is used as a flavor enhancer in the food industry, perfumery and pharmaceuticals [1]. It has been previously reported that vanillin is more than a flavoring agent and could serve as a potential antioxidant [2]. Considering the importance of vanillin application in the food area, we applied the encapsulation technique using vibration technology (Encapsulator B-390) to produce alginate and alginate/chitosan hydrogel beads containing vanillin as core material. The aim of the study was to investigate the effect of chitosan addition to wall material on vanillin concentration. Results showed that the addition of chitosan (0.5%, 1%, 2% and 3%) caused a decrease in vanillin concentration determined by the HPLC method compared to a sample containing only alginate as wall material. However, chitosan addition caused an increase in antioxidant activities, which were determined spectrophotometrically since chitosan enhances antioxidant activity. Formulated hydrogel beads are potential delivery systems of vanillin and could be used as an ingredient in functional foods as all components used in their preparation are nutritionally rich and safe for consumption.

**Keywords:** vanillin, alginate, hydrogel, beads, chitosan

[1] K. N. Waliszewski, V. T. Pardio, S. L. Ovando, *Food Chem.* 101 (2006) 1059-1062.

[2] S. S. Kumar, K. I. Priyadarsini, K. B. Sainis, *Redox Report* 7 (2002) 35-40.

### Acknowledgement

This work was supported by the Croatian Science Foundation under project (IP-2019-04-5749) “Design, fabrication and testing of biopolymer gels as delivery systems for bioactive and volatile compounds in innovative functional foods (bioACTIVEgels)”, Young Researchers’s Career Development Project – Training of New Doctoral Students (DOK-2020-01-4205).





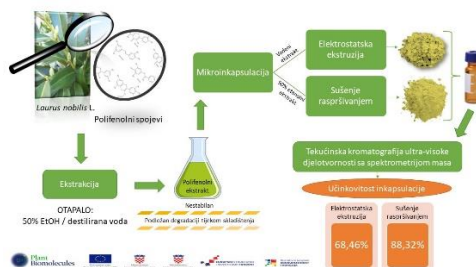
## INKAPSULACIJA POLIFENOLNOG EKSTRAKTA LISTA LOVORA (*Laurus nobilis* L.) PRIMJENOM SUŠENJA RASPRŠIVANJEM I ELEKTROSTATSKE EKSTRUZIJE ENCAPSULATION OF LAUREL (*Laurus nobilis* L.) LEAF POLYPHENOLS BY SPRAY-DRYING AND ELECTROSTATIC EXTRUSION

Erika Dobrosravić, Ivona Elez Garofulić, Zoran Zorić, Marija Kristina Josipović,  
David Kolanović, Verica Dragović-Uzelac

Sveučilište u Zagrebu, Prehrambeno-biotehnoški fakultet, Pierottijeva 6, 10 000 Zagreb, Hrvatska

Lovor (*Laurus nobilis* L.) je zimzeleni mediteranski gm čije se lišće stoljećima koristilo u narodnoj medicini zbog svojih blagotvornih učinaka na zdravlje koji se uvelike mogu pripisati sadržaju polifenola. Budući da su polifenoli nestabilni i skloni gubljenju svojih aktivnih svojstava tijekom skladištenja, od velike je važnosti poboljšati njihovu stabilnost kako bi bili primjenjivi u industriji. To se može postići različitim metodama inkapsulacije među kojima je najčešće korištena metoda sušenja raspršivanjem (SR) u kojoj se tekući ekstrakt s otopljenim nosačem propušta kroz struju vrućeg zraka prilikom čega dolazi do isparavanja otapala te nastaje prah s bioaktivnim molekulama inkapsuliranim u zaštitni omotač nosača. Elektrostatska ekstruzija (EE) je metoda u kojoj se pomoću elektrostatske sile ekstrakt s otopljenim nosačem propušta kroz mlaznicu te u kontaktu sa želirajućom otopinom nastaju uniformne kuglice gela s inkapsuliranim bioaktivnim spojevima. U ovom istraživanju, 50 % etanolni ekstrakt lovorovog lista inkapsuliran je primjenom SR pri prethodno definiranim optimalnim uvjetima (120 °C; mješavina β-ciklodekstrin:maltodekstrin (1:1); omjer uzorak: nosač 1:2), a vodeni ekstrakt je inkapsuliran primjenom EE također pri prethodno definiranim optimalnim uvjetima (1,0 % otopina alginata u ekstraktu; 1,5 % CaCl<sub>2</sub> uz 0,5 % kitozana kao želirajuća otopina). Dobiveni prah je otopljen u 80% metanolu, a gel-kuglice u 5% otopini natrijeva citrata te su zajedno s inicijalnim ekstraktima analizirani primjenom tekućinske kromatografije ultra-visoke djelotvornosti s masenom spektrometrijom (UPLC/MS-MS). Učinkovitost inkapsulacije ukupnih polifenola kod SR iznosila je 88,32 %, a kod EE 68,46 %. Kod SR najuspješnije inkapsulirana skupina bili su flavan-3-oli (95,67 %), a kod EE flavoni (90,82 %). Najslabije inkapsulirana skupina kod SR bile su fenolne kiseline (76,10 %), a kod EE proantocijanidini (6,38 %). Rezultati su pokazali prednost primjene SR nad EE u cilju postizanja veće učinkovitosti inkapsulacije, a još jedna prednost se nalazi u mogućnosti primjene vodenih otopina etanola za ekstrakciju polifenola čime se kombiniraju maksimalna učinkovitost ekstrakcije i inkapsulacije, dok se EE primjenjuje samo na vodenim ekstraktima. Unatoč tome, obje metode pokazale su relativno visoke postotke inkapsulacije te će budući odabir metode ovisiti prije svega o konačnoj namjeni kapsuliranih sustava.

**Ključne riječi:** lovor, polifenoli, inkapsulacija, sušenje raspršivanjem, elektrostatska ekstruzija





**UTJECAJ PROCESNIH PARAMETARA TIJEKOM  
REVERZNE OSMOZE NA ZADRŽAVANJE ORGANSKIH  
KISELINA U KONCENTRATIMA KONVENCIONALNOG I  
EKOLOŠKOG VINA CABERNET SAUVIGNON  
THE INFLUENCE OF PROCESSING PARAMETERS DURING  
REVERSE OSMOSIS ON ORGANIC ACIDS RETENTION IN  
CONVENTIONAL AND ECOLOGICAL CABERNET  
SAUVIGNON WINE CONCENTRATES**

Ivana Ivić<sup>1</sup>, Ivana Buljeta<sup>1</sup>, Mirela Kopjar<sup>1</sup>, Dubravko Pichler<sup>2</sup>,  
Josip Mesić<sup>3</sup>, Anita Pichler<sup>1</sup>

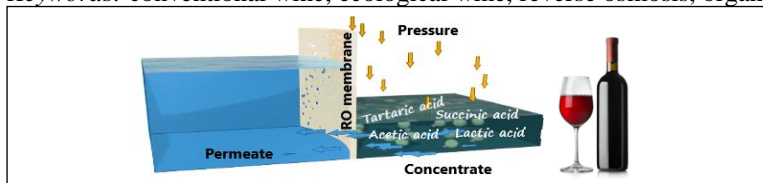
<sup>1</sup> Josip Juraj Strossmayer University of Osijek, Faculty of Food Technology Osijek, Franje  
Kuhača 18, 31000 Osijek, Croatia

<sup>2</sup> Water supply - Osijek, Poljski put 1, 31000 Osijek, Croatia

<sup>3</sup> Polytechnic in Požega, Vukovarska 17, 34000 Požega, Croatia

The organic acid content in red wine is very important due to its impact on wine aroma and it differs between wine varieties. Most common organic acids in red wine are tartaric, acetic, lactic or succinic acid. Their concentrations depend on wine production and storage conditions. Wine production procedures can include membrane filtration of wine, such as reverse osmosis (RO), that is used for wine concentration and chemical composition correction. The aim of this study was to investigate the influence of different pressures (2.5, 3.5, 4.5 and 5.5 MPa) and temperature regimes (with and without cooling) during reverse osmosis process on organic acid content in conventional and ecological Cabernet Sauvignon red wine concentrates. The results showed that initial concentrations of all acids decreased after RO process, but the retention of organic acids was higher if higher pressure and cooling was applied, especially at 5.5 MPa with cooling. However, the pressure of 2.5 MPa with cooling was also favourable for organic acids retention in conventional wine concentrate. Higher retention of tartaric and succinic acid was achieved in ecological wine concentrates, and higher retention of lactic acid was achieved in conventional wine concentrates at same processing parameters. The retention of acetic acid was similar in both wine concentrates, and its initial concentration decreased for more than 50%. The PCA analysis showed visible changes in organic acid profile of both wines, with differences between concentrates obtained at different operating conditions.

**Keywords:** conventional wine, ecological wine, reverse osmosis, organic acid, retention



## **KAZEIN I PROTEINI SIRUTKE KAO NOSAČI FENOLNIH SPOJEVA ARONIJE CASEIN AND WHEY PROTEINS AS CARRIERS OF CHOKEBERRY PHENOLICS**

Indira Kosović<sup>1</sup>, Ivana Buljeta<sup>1</sup>, Josip Šimunović<sup>2</sup>, Anita Pichler<sup>1</sup>,  
Mirela Kopjar<sup>1</sup>

<sup>1</sup>Faculty of Food Technology Osijek, Josip Juraj Strossmayer University of Osijek, Franje  
Kuhača 18, 31 000 Osijek, Croatia

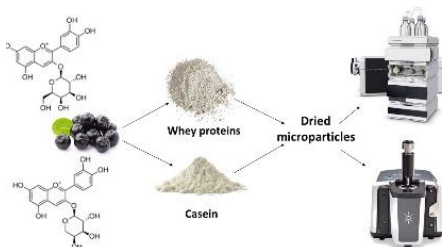
<sup>2</sup>Department of Food, Bioprocessing and Nutrition Sciences, North Carolina State  
University, Raleigh, NC 27 695, USA

Phenolic compounds are one of the most important bioactive food components related to antioxidant, anti-inflammatory and antimicrobial activity. The aim of this study was to investigate the binding of chokeberry phenolics to casein and whey proteins (with and without lecithin). For the purpose of investigation, freeze-dried chokeberry juice/protein microparticles were prepared. Total phenolics and proanthocyanidins as well as antioxidant activity (DPPH, ABTS, FRAP and CUPRAC assay) were determined spectrophotometrically, while contents of individual phenolic components were evaluated by HPLC method. Color parameters were evaluated and IR spectra were recorded. The highest total phenolic and proanthocyanidin contents had a chokeberry juice/whey protein (59.46 mg GAE/g and 54.79 mg PB2/g, respectively) and the lowest had a chokeberry juice/casein (15.65 mg GAE/g and 6.51 mg PB2/g, respectively) microparticles. Results of antioxidant activities followed the same trend as it was obtained for total phenolics. IR spectra confirmed the binding of phenolics on proteins. Results of this research showed that whey proteins higher affinity for chokeberry phenolics than casein and these microparticles can be used in the food industry as bioactive food additives.

*Keywords:* chokeberry juice, casein, whey proteins, phenolics

### **Acknowledgment**

This study was financially supported by the Croatian Science Foundation through grant PZS-2019-02-1595.

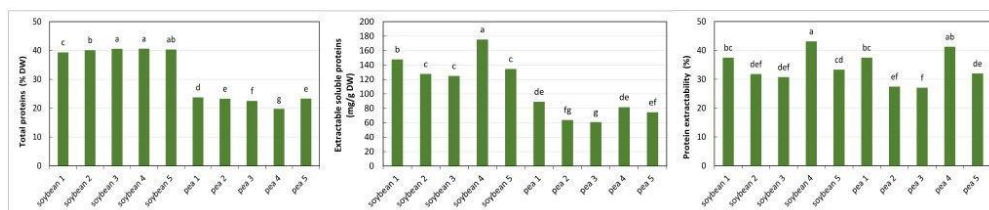


## LEGUMINOZE KAO VAŽAN IZVOR BILJNIH PROTEINA LEGUMES AS IMPORTANT SOURCES OF PLANT PROTEINS

Marija Kovačević Babić, Marijana Tucak, Aleksandra Sudarić,  
Tihomir Čupić, Marija Viljevac Vuletić, Daniela Horvat  
Agricultural Institute Osijek, Južno predgrađe 17, 31000 Osijek, Croatia

Proteins represent one of the most concentrated nutrients in legumes and they can be easily used as components in innovative human foods and therefore, have attracted interest of food industry. Legume proteins extractable in dilute salt solutions belong to the globulin family of seed storage proteins and are called legumins (11S), vicilins (7S) and convicilin (15S). The content of water soluble proteins is a critical factor in food quality and production of isolated soybean proteins. The total grain proteins of soybean and pea varieties were determined on Infratec 1241 Grain Analyzer, while the total soluble proteins were analyzed by the HPLC. Proteins extractability (%) was calculated as a ratio of total soluble proteins and total grain proteins on a dry weight basis (DM). On average, soybean varieties contained 40.22% of total grain proteins compared to 22.46% in peas, while the content of total soluble proteins varied from 124.80 mg/g<sub>DM</sub> to 175.36 mg/g<sub>DM</sub> in soybeans and from 60.84 mg/g<sub>DM</sub> to 89.06 mg/g<sub>DM</sub> in peas. Extractability of soluble proteins varied from 30.74% to 43.16% in soybeans and from 27.05% to 41.26% in peas, which means that the content and extractability of soluble proteins depends on the type and variety of legumes.

**Keywords:** legumes, total grain proteins, water soluble proteins, HPLC



## KONTAMINACIJA HRVATSKIH TRADICIONALNIH MESNIH PROIZVODA OKRATOKSINOM A I PLIJESNIMA PRODUCENTIMA U POVEZNICI SA REGIONALNIM VREMENSKIM UVJETIMA CONTAMINATION OF CROATIAN TRADITIONAL MEAT PRODUCTS WITH OCHRATOXIN A AND IT'S MOULD PRODUCERS IN RELATION TO REGIONAL WEATHER

Tina Lešić<sup>1</sup>, Ana Vulić<sup>1</sup>, Manuela Zadravec<sup>1</sup>, Nada Vahčić<sup>2</sup>, Irena Perković<sup>3</sup>,  
Bojan Šarkanj<sup>4</sup>, Nina Kudumija<sup>1</sup>, Jelka Pleadin<sup>1</sup>

<sup>1</sup>Croatian Veterinary Institute, Savska Cesta 143, 10000 Zagreb

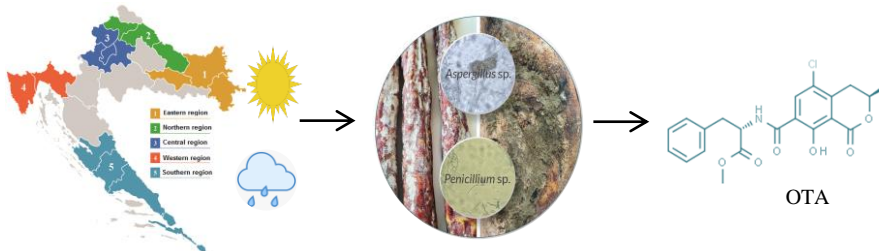
<sup>2</sup>University of Zagreb, Faculty of Food Technology and Biotechnology, Pierottijeva 6,  
10000 Zagreb, Croatia

<sup>3</sup>Croatian Veterinary Institute, Veterinary Institute Vinkovci, Josipa Kozarca 24,  
32100 Vinkovci, Croatia

<sup>4</sup>University North, Department of Food Technology, Žarka Dolinara 1,  
48000 Koprivnica, Croatia

Ochratoxin A (OTA) is the most common mycotoxin contaminant of traditional meat products (TMPs). It can be produced by different *Aspergillus* and *Penicillium* species that overgrow the surface of TMPs during ripening, facilitated by uncontrolled traditional household production and local weather. The aim of this study was to investigate into OTA contamination and its mould producers by virtue of analysing 120 TMP samples produced in 5 Croatian regions (Eastern, Northern, Central, Western, and Southern), and to relate this contamination to regional weather during products' maturation. Mould species were identified by beta-tubulin and calmodulin loci sequencing, while OTA concentrations were determined using LC-MS/MS (liquid chromatography-tandem mass spectrometry). OTA was detected in the concentration range of 0.33-4.81 µg/kg in 7% of the samples. Three potential ochratoxigenic species were isolated: *P. nordicum* (8%), *A. tubingensis* (5%), and *A. welwitschiae* (2%). The samples coming from the Western region had the highest average OTA concentration (1.93±2.04 µg/kg) and yielded the highest number of ochratoxigenic isolates. The average temperature during the products' ripening was 15 °C, i.e., optimal for OTA production, by *P. nordicum* that was predominantly isolated. Unlike other regions with moderate climate, in the Southern region having a hot and dry weather resembling of subtropics, neither OTA nor *P. nordicum* were detected, suggesting that OTA was mainly produced by the *Penicillium* rather than the *Aspergillus* species in the moderate climatic regions.

**Keywords:** mycotoxins, sausages, *Penicillium*, *Aspergillus*, temperature



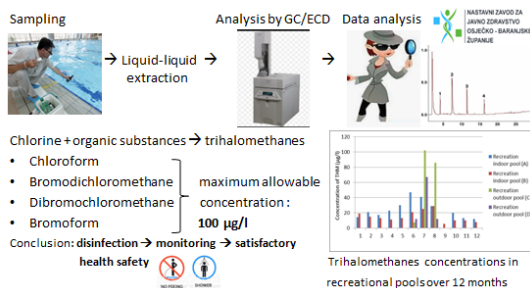
# **PRAĆENJE KONCENTRACIJE TRIHALOMETANA KAO JEDNOG OD INDIKATORA ZDRAVSTVENE ISPRAVNOSTI BAZENSKIH VODA NA PODRUČJU OSJEČKO-BARANJSKE I VUKOVARSKO-SRIJEMSKJE ŽUPANIJE MONITORING OF CONCENTRATION OF TRIHALOMETHANES AS ONE OF THE INDICATORS OF HEALTH SAFETY MANAGEMENT OF POOL WATERS IN THE AREA OF OSIJEK-BARANJA AND VUKOVAR-SRIJEM COUNTY**

Tanja Marković, Hrvoje Babić, Leontina Toth, Danijela Bezik, Snježana Benkotić  
Teaching Institute of Public Health Osijek – Baranja County, Ulica Franje Krežme 1,  
31000 Osijek, Croatia

Considering the use of swimming pools for public purposes (spa, rehabilitation and recreational), it is important to ensure acceptable sanitary-technical and hygienic conditions defined by legislation and thus ensure the continuous health safety of pool water. Disinfection plays an important role in maintaining the quality of pool water. Water disinfection is the process of destroying pathogenic bacteria and reducing the total number of all live bacteria to prevent the transmission of disease through water. The most commonly used disinfectant is chlorine. During the chlorination process, chlorine can react with the organic substances present in the water (sweat, urine, oils) creating a series of by-products known as trihalomethanes. Based on numerous studies of trihalomethanes effect on human health, they are classified as carcinogenic and mutagenic compounds, and their excessive intake can lead to a number of health problems (damage to the liver, kidneys and central nervous system). This study investigates trihalomethane concentrations in pool waters at bathing areas in the area of Osijek-Baranja and Vukovar-Srijem county, in 2020 (182 analyzed samples) and 2021 (233 analyzed samples). Measurements were performed on a gas chromatograph with an electron capture detector (GC-ECD) according to HRN EN ISO 10301. [1] According to the results, we can conclude that the concentration of trihalomethane is in accordance with legislation and, in this sense, health safety was satisfactory.

**Keywords:** pool water, disinfection, chlorine, trihalomethanes

[1] HRN EN ISO 10301 – Water quality – Determination of highly volatile halogenated hydrocarbons – Gas chromatographic methods (ISO 10301:1997; EN ISO 10301:1997)

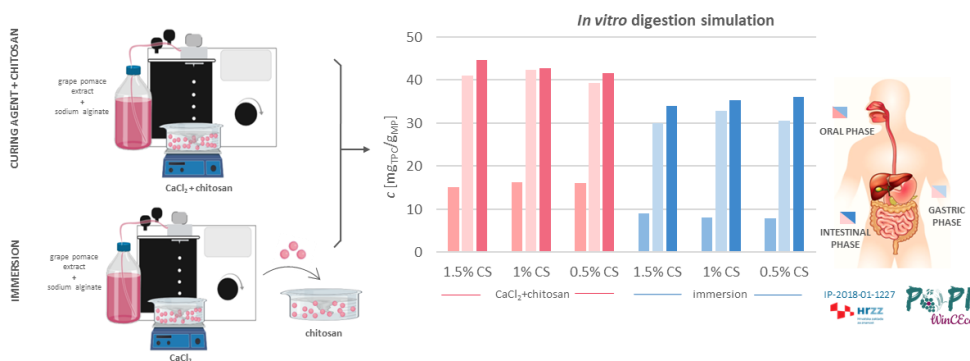


## IN VITRO OTPUŠTANJE FENOLNIH SPOJEVA IZ ALGINAT/KITIZAN MIKROČESTICA IN VITRO RELEASE OF PHENOLIC COMPOUNDS FROM ALGINATE/CHITOSAN MICROPARTICLES

Josipa Martinović, Gabriela Perković, Gordana Šelo, Ana-Marija Klarić,  
Mirela Planinić, Marina Tišma, Ana Bucić-Kojić  
Josip Juraj Strossmayer University of Osijek, Faculty of Food Technology Osijek, Franje  
Kuhača 18, 31000 Osijek, Croatia

In this work, phenol-rich microparticles loaded with grape pomace extract were prepared by the ionic gelation method using sodium alginate (3% w/v) and chitosan (0.5%, 1.0%, or 1.5% w/v) as coatings and 0.25 M CaCl<sub>2</sub> as curing agent. The influence of the two methods of adding chitosan (A - chitosan was mixed with CaCl<sub>2</sub> and B - alginate hydrogels were immersed in chitosan) on the encapsulation efficiency (EE) and *in vitro* release of phenolic compounds (TPC) from alginate/chitosan microparticles was studied. The hydrogels obtained were freeze-dried, and the dried microparticles (MP) were then used to study the release of TPC during simulated enzyme-free digestion *in vitro* in the mouth, stomach, and intestine for 243 min. In the A method, the highest EE (75.81%) was obtained when 1.5% chitosan was used and the lowest when the chitosan concentration was 0.5%. In the B method, the reverse order was observed, with the highest EE (57.52%) obtained with 0.5% chitosan and the lowest with chitosan concentration of 1.5%. The results of simulated digestion showed a faster release of TPC when the microparticles were prepared by adding chitosan to CaCl<sub>2</sub> than when the immersion method was used. In general, the most TPC was released in the gastric phase (92.23 – 99.01% for the A method and 84.85 – 93.17% for the B method), while the cumulative TPC content after 243 min of digestion was in the range of 41.59 – 44.58 mg<sub>TPC</sub>/g<sub>MP</sub> for the A method and 34.08 – 36.03 mg<sub>TPC</sub>/g<sub>MP</sub> for the B method).

**Keywords:** phenolic compounds, ionic gelation, sodium alginate, chitosan, *in vitro* digestion

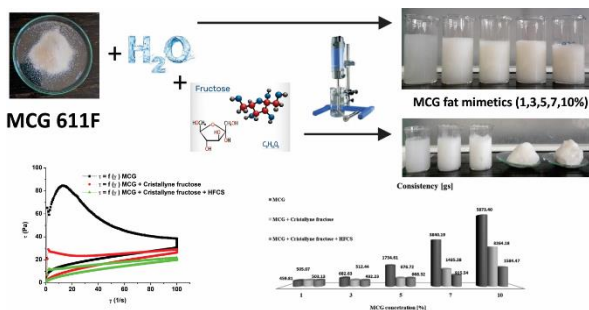


## REOLOŠKE OSOBINE CELULOZNOG ZAMENJIVAČA MASTI PRI DODATKU FRUKTOZNIH ZASLAĐIVAČA RHEOLOGICAL PROPERTIES OF CELLULOSE FAT MIMETIC WITH THE ADITION OF FRUCTOSE SWEETENERS

Ivana Nikolić, Ljubica Dokić, Biljana Pajin, Zita Šereš, Dragana Šoronja–  
Simović, Ivana Lončarević, Nikola Maravić, Jovana Petrović, Jana Zahorec  
Tehnološki fakultet Novi Sad, Univerzitet u Novom Sadu, Bulevar cara Lazara 1,  
21000 Novi Sad, Serbia

The combination of fat mimetics and starch sweeteners is applicable in low-energy and low-fat food products. In this paper, the influence of fructose sweeteners on the rheological and textural characteristics of MCG 611F fat mimetic with different concentrations (1, 3, 5, 7 and 10%) was analyzed. MCG 611F consists of colloidal microcrystalline cellulose (MCC) and sodium carboxymethyl cellulose (NaCMC). The amount of sweetener in the mixture with the fat mimetic was 20%. The effect of pure crystalline fructose and a mixture of crystalline fructose and high fructose corn syrup in a ratio of 1:1 was investigated. With the addition of pure crystalline fructose, values of the rheological parameters: the yield stress,  $\tau_0$ , decreased for 41.35–77.84%, and the thixotropic loop area,  $A_0$ , for 70.39–78.93%. By adding a mixture of sweeteners, this decrease was additionally increased for 10% for both rheological parameters. The presence of sweeteners significantly disturbed the crosslinking of the three-dimensional structure of the MCG gel. At higher gel concentrations of 5, 7 and 10%, the dominance of the elastic modulus  $G'$  was preserved. Accordingly, the texture parameters: consistency, hardness, cohesiveness and viscosity index were reduced. These negative effects of sweeteners on the rheological and textural properties of fat mimetic gels can be avoided by the correct order of addition of raw materials in production and by enabling hydration of the gel before the addition of small molecule components.

**Keywords:** cellulose fat mimetics, fructose sweeteners, rheology, texture



**Acknowledgments:**  
This research was supported by the  
Ministry of Education, Science and  
Technological Development,  
Republic of Serbia;  
Program (451-03-68/2022-  
14/200134).



## UTJECAJ ZAMRZAVANJA I MARINIRANJA NA NUTRITIVNA I MIKROBIOLOŠKA SVOJSTVA ZELENIH ŠPAROGA

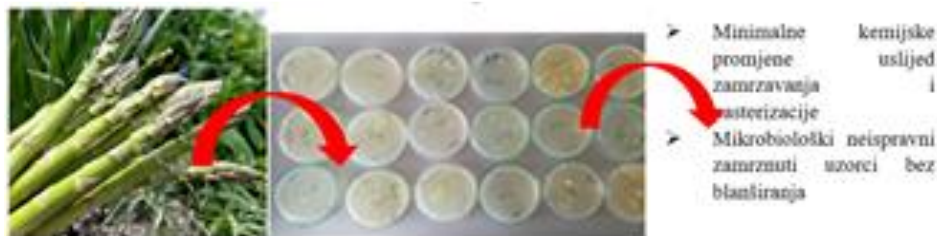
### THE INFLUENCE OF FREEZING AND MARINATING ON THE NUTRITIONAL AND MICROBIOLOGICAL PROPERTIES OF GREEN ASPARAGUS

Valentina Obradović<sup>1</sup>, Ines Krznarić Došen<sup>1</sup>, Irena Perković<sup>2</sup>, Maja Ergović  
Ravančić<sup>1</sup>, Svjetlana Škrabal<sup>1</sup>, Helena Marčetić<sup>1</sup>

<sup>1</sup>Veučilište u Požezi, Vukovarska 17, 34 000 Požega, Hrvatska

<sup>2</sup>Veterinarski zavod Vinkovci, I. i J. Kozarca 24, 32100 Vinkovci, Hrvatska

Zelena šparoga se najčešće prodaje kao svježa uz primjenu konzerviranja hlađenjem. Ipak, relativno kratka sezona berbe, koja tek u trećoj godini uzgoja traje do dva mjeseca, nameće potrebu i za drugim metodama konzerviranja. U ovom radu su zelene šparoge sorte *Asparagus argenteuil* konzervirane pasterizacijom u slano kiselom naljevu (10 uzoraka) i zamrzavanjem (10 uzoraka). Nakon šest mjeseci skladištenja ispitani su slijedeći mikrobiološki parametri: *Enterobacteriaceae*, koagulaza pozitivni stafilokoki/*Staphylococcus aureus*, sulfitoreducirajuće klostridije, *Salmonella*, *Listeria monocytogenes*, aerobne mezofilne bakterije, kvasci i plijesni. Određeni su i slijedeći kemijski parametri: udio vode, masti, ugljikohidrata, bjelančevina, pepela, šećera i soli. Šparoge koje nisu bile blanširane prije zamrzavanja nisu zadovoljile mikrobiološke kriterije za zelenu šparogu, upućujući na nužnost pravilne pripreme prije zamrzavanja, dok su svi pasterizirani uzorci imali zadovoljavajuće mikrobiološke parametre. Oba postupka konzerviranja su uzrokovali minimalne promjene kemijskog sastava u odnosu na svježnu zelenu šparogu, uz nešto manje vrijednosti bjelančevina kod mariniranih šparoga zbog denaturacije uslijed termičke obrade.





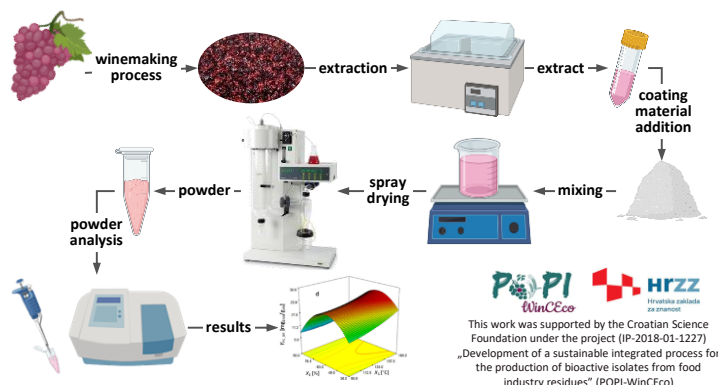
## OPTIMIRANJE PROCESA SUŠENJA RASPRŠIVANJEM EKSTRAKTA TROPA GROŽĐA OPTIMIZATION OF THE SPRAY DRYING PROCESS OF GRAPE POMACE EXTRACT

Gabriela Perković, Mirela Planinić, Josipa Martinović, Gordana Šelo,  
Marina Tišma, Ana Bucić-Kojić

Josip Juraj Strossmayer University of Osijek, Faculty of Food Technology Osijek, Franje  
Kuhača 18, 31000 Osijek, Croatia

Spray drying is one of the most commonly used encapsulation techniques in the food industry. By using coating material, various active ingredients are protected by the encapsulation process. The aim of this study was to find optimal spray drying conditions to achieve maximum encapsulation efficiency and protection of phenolic compounds from liquid grape pomace extract when 1% sodium alginate is used as coating. The liquid extract was prepared under the previously determined optimal conditions for solid-liquid extraction (temperature: 80 °C, time: 120 min, liquid/solid ratio: 40 mL/g, shaking bath: 200 rpm). A Box-Behnken design was used to investigate the influence of drying conditions such as air inlet temperature (160–200 °C), feed flow rate (4–8 mL/min), and volume of added liquid pomace extract (50–150 mL) and their interaction on the phenolic content of the grape pomace powder. The encapsulation efficiency was more than 56% in all experiments performed. Optimal conditions for spray drying were established, such as an air inlet temperature of 180 °C, a feed flow rate of 6 mL/min, and a volume of 150 mL of liquid pomace extract. Under these conditions, the predicted value for the yield of total phenolic compounds was 30.50 mg/g<sub>powder</sub>.

**Keywords:** grape pomace extract, phenolic compounds, response surface methodology, sodium alginate, spray drying



## SENZORNE KARAKTERISTIKE ČAJNOG PECIVA OBOGAĆENOG EKSTRUDIRANIM REZANCIMA ŠEĆERNE REPE

### SENSORY CHARACTERISTICS OF COOKIES ENRICHED WITH EXTRUDED SUGAR BEET PULP

Jovana Petrović<sup>1</sup>, Biljana Pajin<sup>1</sup>, Dragana Šoronja-Simović<sup>1</sup>,

Ivana Lončarević<sup>1</sup>, Antun Jozinović<sup>2</sup>, Dušan Rakić<sup>1</sup>,

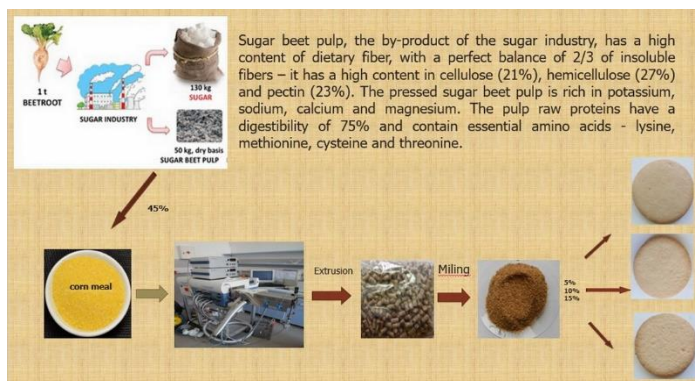
Ivana Nikolić<sup>1</sup>, Zita Šereš<sup>1</sup>, Nikola Maravić<sup>1</sup>

<sup>1</sup>Faculty of Technology, University of Novi Sad, Bul. Cara Lazara 1, 21000 Novi Sad, Serbia

<sup>2</sup>Josip Juraj Strossmayer University of Osijek, Faculty of Food Technology Osijek, Franje Kuhača 18, Osijek, Croatia

Every year, large quantities of sugar beet pulp are produced in Serbia as well as all over the world (about 120 million tones). Beet pulp contains 70-80% of dietary fiber which have a positive effect on human cholesterol. Compared to cereal fibers mainly used in biscuit production, sugar beet fibers have a perfect ratio of 2/3 insoluble fiber, contain no phytic acid and gluten free. In this work, extruded sugar beet pulp (ratio of corn grits:sugar beet pulp in extrudate was 55:45) is used for improving the nutritional quality of cookies which are world –spread consumption, especially among children. Wheat flour in cookies is replaced with extrudates in the amount of 5, 10 and 15%. Cookie samples were evaluated by a panel comprising of 10 trained members, food technologists. The addition of the extrudate led to an increase in the hardness, graininess, poorer appearance of the cookie surface with more pronounced cracks and slight deformation of the shape.

*Keywords:* extruded sugar beet pulp, food waste valorization, cookie quality, sensory analysis



*Acknowledgements:* The research was financed by the Ministry of Education, Science and Technological Development of the Republic of Serbia, Project No. 451-03-68/2022-14/200134.

## **SENZORSKA, FIZIKALNO - KEMIJSKA I MIKROBIOLOŠKA KVALITETA SVJEŽIH SIREVA NA TRŽIŠTU ORGANOLEPTIC, PHYSICAL - CHEMICAL AND MICROBIOLOGICAL QUALITY OF FRESH CHEESE ON THE MARKET**

Svjetlana Škrabal, Maja Ergović Ravančić, Valentina Obradović,  
Helena Marčetić, Tanja Abramović

Veleučilište u Požegi, Vukovarska 17, 34000 Požega, Hrvatska

Svježi sir je visoko vrijedna namirnica. Potrošači u Republici Hrvatskoj ga relativno često konzumiraju u svježem stanju. U ovom radu je analizirano pet uzoraka svježih sireva različitih proizvođača. Uzorci su kupljeni u jednom trgovačkom centru. Cilj istraživanja je bio utvrditi kakvoću svježih sireva na tržištu, te ju usporediti sa zakonskom regulativom. Uzorci sireva su analizirani na kiselost, udio vode, udio masti, senzorska svojstva, *Salmonella spp.*, *Escherichiu coli*, *Staphylococcus aureus*, *Listeriu monocytogenes*, te kvasce i plijesni. Rezultati istraživanja su pokazali da su svi analizirani uzorci sireva bili u skladu s mikrobiološkim kriterijima i zahtjevima za fizikalno – kemijskim parametrima kakvoće. Prilikom senzorskog ocjenjivanja dobili su različite ocjene. Upravo njihova senzorska svojstva biti će presudna pri odabiru pojedinog sira za konzumaciju. S obzirom da su svježi sirevi lakao pokvarljiva namirnica specifičnih senzorskih svojstava, njihova proizvodnja je vrlo zahtjevan tehnološki proces u kom se moraju strogo poštivati pravila dobre proizvođačke i higijenske prakse.

*Ključne riječi:* svježi sir, fizikalno kemijski parametri, mikrobiološka kvaliteta, senzorska svojstva



## UTJECAJ EKSTRAKCIJE POTPOMOŽNE MIKROVALOVIMA NA PRINOS POLIFENOLA IZ KORE RAJČICE

### EFFECT OF MICROWAVE-ASSISTED EXTRACTION ON THE RECOVERY OF POLYPHENOLS FROM TOMATO WASTE

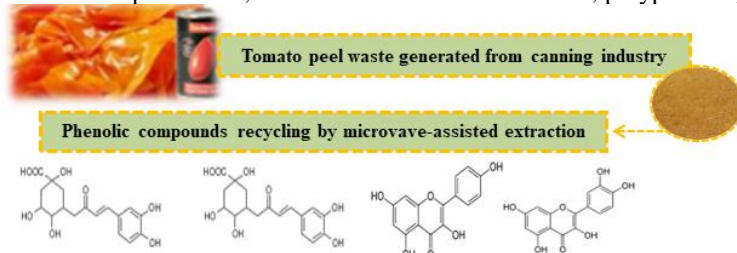
Marina Tranfić Bakić<sup>a</sup>, Sandra Pedisić<sup>b</sup>, Zoran Zorić<sup>b</sup>,  
Verica Dragović-Uzelac<sup>b</sup>, Antonela Ninčević Grassino<sup>b</sup>

<sup>a</sup>Faculty of Chemistry and Technology, University of Split, Ruđera Boškovića 35,  
21000 Split, Croatia

<sup>b</sup>Faculty of Food Technology and Biotechnology, University of Zagreb, Pierottijeva 6,  
10000 Zagreb, Croatia

The edible fruit of the tomato (*Solanum lycopersicum*) is one of the most widely produced and consumed vegetables in the world, either fresh or processed in the form of canned tomatoes, sauce, juice, ketchup, and soup. Industrial processing of tomatoes generates significant amounts of waste, consisting mainly of tomato peels and seeds, but also leaves and stems. The management of by-products from tomato processing is an important problem for tomato processing companies, as these wastes are released into the environment. Normally, some of this waste is reused for animal feed through composting or drying. However, modern environmentally sound technologies offer more efficient strategies for recycling these by-products and reusing them as a sustainable source of various nutrients and highly biologically active compounds such as polyphenols. In this context, the present study describes the application of microwave-assisted extraction (MAE) as an innovative technique for the isolation of polyphenols from tomato peel waste. The effects of solvents, i.e. water and aqueous solution of HCl (1%, v/v), methanol (50 and 70%, v/v), with or without addition of 1% HCl and ethanol (50 and 70% v/v), temperatures (25, 55 and 90 °C) and times (5 and 10 min) were evaluated by HPLC-DAD analyses in terms of phenolic compounds recovery. Of the extraction parameters evaluated, temperatures and solvents have a significant effect on the yield of individual phenolic compounds. Different combinations of these parameters lead to the isolation of different amounts of individual phenolic compounds. Kaemferol-3-O-rutinoside (8.5 to 142.5 mg/kg), *p*-coumaric acid (3 to 111.5 mg/kg), and chlorogenic acid derivative (10.5 to 109 mg/kg) are found in high amounts. On the other hand, the extraction time has no significant ( $p > 0.05$ ) influence on the recovery of phenolic compounds. In conclusion, HPLC-DAD analyses show that polyphenols were isolated in remarkable amounts with minimal time (5 min), using MAE as an innovative and environmentally friendly technique.

**Ključne riječi:** tomato peel waste, microwaves-assisted extraction, polyphenols, HPLC-DAD



## SINTEZA I BIOLOŠKA AKTIVNOST AMIDINO SUPSTITUIRANIH BENZIMIDAZOLA I BENZOTIAZOLA SYNTHESIS AND BIOLOGICAL ACTIVITY OF AMIDINO SUBSTITUTED BENZIMIDAZOLES AND BENZOTHIAZOLES

Anja Beč<sup>1</sup>, Teo Tomić<sup>1</sup>, Livio Racan<sup>2</sup>, Leentje Persoons<sup>3</sup>, Dirk Daelemans<sup>3</sup>,  
Mihailo Banjanac<sup>4</sup>, Vedrana Radovanović<sup>4</sup> and Marijana Hranjec<sup>1</sup>

<sup>1</sup>Faculty of Chemical Engineering and Technology, University of Zagreb, Marulićev trg 19,  
10 000 Zagreb, Croatia

<sup>2</sup>Department of Applied Chemistry, Faculty of Textile Technology, University of Zagreb,  
HR-10000 Zagreb, Croatia

<sup>3</sup>KU Leuven, Department of Microbiology, Immunology and Transplantation, Rega  
Institute, Leuven, Belgium

<sup>4</sup>Pharmacology *in vitro*, Selvita Ltd. Prilaz baruna Filipovića 29, 10000 Zagreb, Croatia

Due to the great biological importance of benzimidazole and benzothiazole derived derivatives, nowadays there is still an increasing interest in medicinal and pharmaceutical chemistry for using this unavoidable structural motifs in the rational design of novel drugs [1]. Suchlike derivatives display a broad spectrum of different biological features such as anticancer, antiviral, antioxidant, antibacterial, antifungal, antihistaminic, anti-inflammatory, *etc* [2]. Amidines are structural parts of numerous biologically active compounds like many important medical and biochemical agents. By introduction of amidino functional groups at the termini of the molecule, the biological activity could be significantly improved because of interaction with an electronegatively charged biological molecule such as DNA [3]. Herein we present the synthesis and biological evaluation of novel amidino substituted benzimidazole and benzothiazole derivatives substituted with 2-hydroxyphenyl ring in the position 2. All compounds were tested for their antiproliferative activity on several human cancer cells as well as for antibacterial activity *in vitro*.

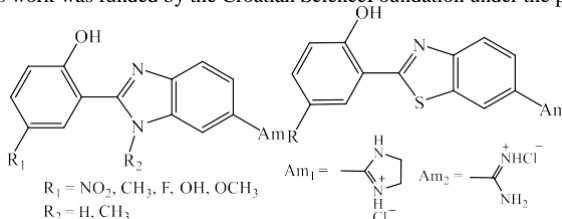
**Keywords:** antiproliferative and antibacterial activity, benzimidazoles, benzothiazoles

[1] S. R. Brishty *et al.*, *Front. Pharmacol.* 12 (2021) 762807.

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**Acknowledgments:** This work was funded by the Croatian Science Foundation under the project IP-2018-01-4379.



## SINTEZA I BIOLOŠKA AKTIVNOST NOVIH AMIDINO-SUPSTITUIRANIH IMIDAZO[4,5-*b*]PIRIDINA SYNTHESIS AND BIOLOGICAL ACTIVITY OF NOVEL AMIDINO-SUBSTITUTED IMIDAZO[4,5-*b*]PYRIDINES

Ida Boček<sup>1</sup>, Leentje Persoons<sup>2</sup>, Dirk Daelemans<sup>2</sup>, Mihailo Banjanac<sup>3</sup>,  
Vedrana Radovanović<sup>3</sup>, Marijeta Kralj<sup>4</sup>, Katarina Zlatić<sup>1</sup>,  
Robert Vianello<sup>5</sup> and Marijana Hranjec<sup>1</sup>

<sup>1</sup>Faculty of Chemical Engineering and Technology, University of Zagreb, 10000 Zagreb, Croatia

<sup>2</sup>Department of Microbiology and Immunology, Rega Institute, Leuven, Belgium;

<sup>3</sup>Pharmacology *in vitro*, Selvita, 10000 Zagreb, Croatia

<sup>4</sup>Laboratory for the Computational Design and Synthesis of Functional Materials, Ruđer Bošković Institute, 10000 Zagreb, Croatia

<sup>5</sup>Division of Molecular Medicine, Institute Ruđer Bošković, 10000 Zagreb, Croatia

Imidazo-pyridines are important scaffold in organic and medicinal chemistry due to their promising biological activity [1]. Some of the derivatives have already found application in medicine, while many others are currently in clinical testing

In this work, we have synthesized novel amidino-substituted derivatives of imidazo[4,5-*b*]pyridine [2]. Main precursors for the synthesis of targeted derivatives were prepared by DMSO-mediated cyclization [3]. Unsubstituted amidines were prepared using lithium hexamethyldisilazane, while other were obtained by Pinner reaction. The structures of newly prepared compounds were confirmed by means of <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy as well as MS spectrometry.

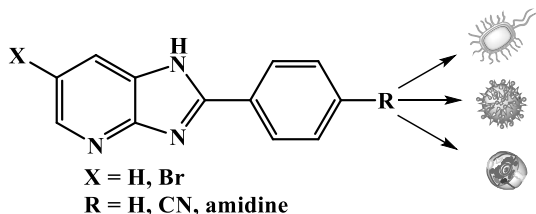
All prepared compounds were evaluated for their antitumor activity *in vitro* on several human cancer cells as well as for their antiviral and antibacterial activity.

**Keywords:** imidazo[4,5-*b*]pyridines, amidines, biological evaluation

[1] B. Lončar, *et al.*, *Eur. J. Med. Chem.* 217 (2021) 113342.

[2] Y. Chai, *et al.*, *J. Org. Chem.* 79 (2014) 852–866.

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**Acknowledgments:** This work was funded by the Croatian Science Foundation under the projects IP-2018-01-4379 and IP-2020-02-8090.

## DEVELOPMENT AND VALIDATION OF A NOVEL CE METHOD FOR SIMULTANEOUS ANALYSIS OF RIBOCICLIB, LETROZOLE AND IBUPROFEN RAZVOJ I VALIDACIJA NOVE CE METODE ZA ISTOVREMENU ANALIZU RIBOCIKLIBA, LETROZOLA I IBUPROFENA

Josipa Božić<sup>1</sup>, Zvonimir Mlinarić<sup>2</sup>, Lu Turković<sup>2</sup>, Biljana Nigović<sup>2</sup>, Miranda Sertić<sup>2</sup>

<sup>1</sup>Faculty of Science, University of Zagreb, Horvatovac 102a, Zagreb, Croatia

<sup>2</sup>Faculty of Pharmacy and Biochemistry, University of Zagreb, Ante Kovačića 1, Zagreb, Croatia

Breast cancer is the most common cancer worldwide while the HR<sup>+</sup>/HER2<sup>-</sup> subtype is the most prevalent [1]. Locally advanced or metastatic HR<sup>+</sup>/HER2<sup>-</sup> breast cancers are treated with the combination of CDK4/6 inhibitors and drugs with anti-estrogen effects. One of the common combinations used in clinical practice is ribociclib with letrozole [2]. Many breast cancer patients suffer from various comorbidities and side effects. Thus, different drug classes are regularly used in clinical practice, painkiller ibuprofen being one of the most common. Because of that, we developed a capillary electrophoresis (CE) method for the simultaneous determination of ribociclib, letrozole, and ibuprofen since drugs metabolized by the same enzymes can have interactions. During method development, different buffer types (borate and phosphate with and without SDS) and additives and surfactants (SBE- $\beta$ -CD and i-PrOH) were tested. Separation was achieved with 75 mM phosphate, 8.5 mM sulfobutylether- $\beta$ -cyclodextrin, and 5% i-PrOH. The optimal conditions were 15 kV, 25 °C and 5 s hydrodynamic injection under 50 mbar. The developed method was validated according to the ICH guidelines and was shown to be linear in the range of 1 to 75  $\mu\text{g mL}^{-1}$  ( $r > 0.9957$ ). Intra-day and inter-day repeatabilities were evaluated for method precision with acceptable RSD values. The robustness of the method was tested by changing applied voltage ( $\pm 0.5$  kV), cyclodextrin concentration ( $\pm 0.5$  mM), and temperature ( $\pm 2$  °C) one variable at a time, and the changes in peak areas and migration times were shown to be in the range of 0.34 to 7.27 %. The validated method is the basis for the further development of an even more sensitive method capable of detecting low plasma concentrations of these drugs using innovative sample preparation techniques and coupling to the mass detector which could then be applied to standard clinical practice.

**Keywords:** breast cancer, capillary electrophoresis, ribociclib, letrozole, ibuprofen

[1] Shah et al., *The Oncologist*. 2020. 25, e900–e908.

[2] Im et al. *New England Journal of Medicine*. 2019. 381(4), 307–316.



This research was funded by Croatian Science Foundation, grant numbers HRZZ-UIP-2019-04-8461 and DOK-2021-02-4595.



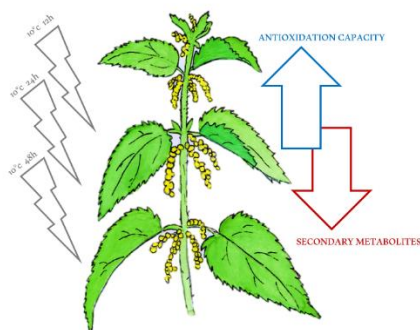
## UTJECAJ NISKE TEMPERATURE NA ANTIOKSIDATIVNU AKTIVNOST KOPRIVE INFLUENCE OF LOW TEMPERATURE ON THE ANTIOXIDANT ACTIVITY OF NETTLE

Sarah Butigan, Selma Mlinarić

Odjel za biologiju, Sveučilište J. J. Strossmayera u Osijeku, Cara Hadrijana 8/A,  
31000 Osijek, Croatia

Nettle (*Urtica dioica* L.) is a traditional medicinal plant in Croatia. It is considered as an important source of natural antioxidants that have a positive effect on the human health by fighting various diseases and slowing down aging. Nettle grows in different habitats and can easily adapt to changes in environmental conditions. However, prolonged exposure to a certain environmental factor, such as low temperature, can negatively affect the growth and development of plants causing increased formation of reactive oxygen species and the occurrence of oxidative stress. In such conditions, plants activate a highly effective antioxidant system. The aim of this research was to determine the influence of low temperature on nettle's antioxidant activity. The nettles were grown under controlled conditions (temperature  $22 \pm 1$  °C, photoperiod 16h/8h, light intensity  $\sim 100 \mu\text{mol m}^{-2}\text{s}^{-1}$ ). When they reached adult stage, they were exposed to low temperature (10 °C) for various time periods: 12h, 24h and 48h. Untreated plants were considered as a control group. In order to describe the antioxidant activity, the iron reduction antioxidant capacity (FRAP), the content of total soluble polyphenols (PHE) and the content of ascorbic acid (AA) were determined. Exposure to low temperature after only 12h led to a decrease in AA compared to the control group, while the content of PHE did not change during exposure to low temperature. On the other hand, only long-term exposure to low temperature (48h) led to an increase in the antioxidant capacity of the nettle plants. The results indicate that prolonged exposure of nettles to low temperatures promotes the activation of the antioxidant system, while even short exposure to these conditions affects the reduction of secondary metabolites.

**Keywords:** *Urtica dioica*, antioxidant activity, oxidative stress





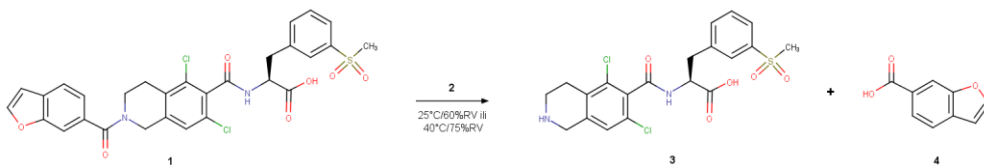
## UTJECAJ VITAMINA E NA STABILNOST OTOPINE LIFITEGRASTA INFLUENCE OF VITAMIN E ON THE STABILITY OF LIFITEGRAST SOLUTION

Karla Dubaić, Ivan Sušanj, Anja Kovač, Nina Popović, Nicole Mesaroš,  
Josipa Šumonja, Sofija Ivković, Maša Safundžić Kučuk, Leo Štefan  
JADRAN GALENSKI LABORATORIJ d.d. Svilno 20, 51000 Rijeka, Hrvatska

Lifitegrast (*S*)-2-[2-(benzofuran-6-karbonil)-5,7-dikloro-1,2,3,4-tetrahidroizokinolin-6-karboksamido]-3-[3-(metilsulfonyl)fenil] propanska kiselina, **1**), djeluje kao LFA-1/ICAM-1 inhibitor, a na tržištu se nalazi kao lijek odobren za liječenje bolesti suhog oka [1]. Tijekom studija stabilnosti u okviru predformulacijskih istraživanja ispitan je utjecaj vitamina E u vodotopljivoj TPGS formi (**2**) na stabilnost **1**. Prototipovi otopine lifitegrasta pripremljeni su bez **2** kao i uz dodatak različitih udjela **2** (0,01 % - 0,5 %) te su izloženi uvjetima 25 °C/60 %RV i 40 °C/75 %RV u periodu od 28 dana. Tijekom studije ispitivani su kritični atributi kvalitete, poput osobina, pH, sadržaja lifitegrasta i njegovih onečišćenja. Dodatno, u cilju praćenja profila razgradnje, razvijene su metode tekućinske kromatografije visoke razlučivosti za određivanje sadržaja lifitegrasta i onečišćenja. Pri ispitanim uvjetima, osobine i pH bili su unutar očekivanih vrijednosti. Uočeno je da porast temperature, kao i koncentracije **2**, utječe na razgradnju **1** pri čemu su utvrđena dva glavna onečišćenja: (*S*)-2-(5,7-dikloro-1,2,3,4-tetrahidroizokinolin-6-karboksamido)-3-[3-(metilsulfonyl)fenil]propanska kiselina (onečišćenje D, **3**) i benzofuran-6-karboksilna kiselina (onečišćenje C, **4**). Rezultati ukazuju da **2** sudjeluje u oksidativnoj hidrolizi **1** pri ispitanim uvjetima.

*Ključne riječi:* stabilnost, vitamin E, lifitegrast, onečišćenja

[1] J. R. Yerrabelly, R. Kommera, V. R. Kasireddy, V. R. Ghojala, H. Yerrabelly, *ChemistrySelect*. 5 (2020) 3355.



## SUPRESIJA RASTA TUMORSKIH STANICA IZLOŽENIH DJELOVANJU NOVIH VANADIJEVIH KOMPLEKSA SUPPRESSION OF TUMOUR CELLS GROWTH EXPOSED TO NOVEL VANADIUM COMPLEXES

Nikolina Filipović<sup>1</sup>, Berislav Marković<sup>1</sup>, Stjepan Šarić<sup>1</sup>,  
Katarina Mišković Špoljarić<sup>2</sup>

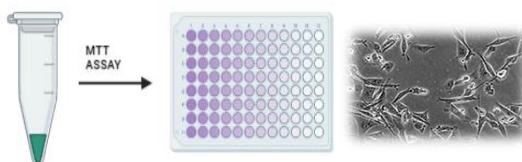
<sup>1</sup>Josip Juraj Strossmayer University of Osijek, Department of Chemistry,  
Ulica cara Hadrijana 8/a, 31000 Osijek, Croatia

<sup>2</sup>Josip Juraj Strossmayer University of Osijek, Faculty of Medicine,  
Josipa Hutlera 4, 31000 Osijek, Croatia

In the last 15 years, significant progress has been accomplished in synthesizing new metal compounds with an emphasis on transition metals [1]. The focus of our research is new complexes of vanadium and their antiproliferative abilities on cancer cell lines. The vanadium complexes were synthesized from V<sub>2</sub>O<sub>5</sub> (V<sub>1</sub> group of compounds) and VOSO<sub>4</sub>·x H<sub>2</sub>O (V<sub>2</sub> group of compounds), and ligands from the hydroxypyronone group: chromone-2-carboxylic acid and cumalic acid. After synthesis, using classical solution chemistry in the stoichiometric ratio (1:1, metal: ligand), the compounds were dissolved in water (10<sup>-3</sup> mol / dm<sup>3</sup>) and subjected to MTT assay (cytotoxicity test). In addition to the complexes, the activity of the ligands was also tested. The assay was performed on 6 cancer cell lines (Caco-2, HT-29, Hep-G2, KATO III, NCI-H 358, MDA-MB 231) and one normal human cell line (MRC-5). The results show that both groups of vanadium compounds demonstrate exceptional cytotoxicity against human cancer cells (MDA-MB 231): the cell survival at the highest concentrations (10<sup>-5</sup> mol/dm<sup>3</sup>) is 29%. The antiproliferative effect was also observed on the following cell lines: KATO III (V<sub>1</sub>: 58.2%, V<sub>2</sub>: 51.3%), Hep-G2 (V<sub>1</sub>: 66.9%, V<sub>2</sub>: 59.4%), NCI-H358 (V<sub>1</sub>: 58.1%, V<sub>2</sub>: 58.4%). The inhibitory effect on the HT-29 and Caco-2 cell lines is less than 25%. Unlike the compounds, the ligands did not show antiproliferative activity on any cell line and the survival was > 95%. Based on such results, it can be concluded that the newly synthesized groups of vanadium complexes have the potential for future researches on antiproliferative activity on various cancer cell lines with an emphasis on breast cancer (MDA-MB 231).

**Keywords:** vanadium complexes, cytotoxicity, hydroxypyronones, MTT assay

[1] S.Kowalski, D.Wyrzykowski, I.Inkielewicz–Stepniak, Molecular and Cellular Mechanisms of Cytotoxic activity of Vanadium compounds against Cancer Cells, *Molecules*, **25**, 2020.



## COVID-19 INFEKCIJA I NEURODEGENERACIJA: POTENCIJALNA VEZA OTKRIVENA RAČUNALNIM SIMULACIJAMA

### COVID-19 INFECTION AND NEURODEGENERATION: A POTENTIAL LINK REVEALED BY COMPUTATIONAL SIMULATIONS

Lucija Hok<sup>a</sup>, Hrvoje Rimac<sup>b</sup>, Janez Mavri<sup>c</sup>, Robert Vianello<sup>a</sup>

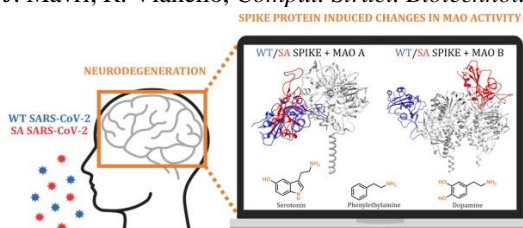
<sup>a</sup>Ruder Bošković Institute, 10000 Zagreb, Croatia

<sup>b</sup>University of Zagreb, Faculty of Pharmacy and Biochemistry, 10000 Zagreb, Croatia

<sup>c</sup>National Institute of Chemistry, 1000 Ljubljana, Slovenia

Although COVID-19 has been primarily associated with pneumonia, recent data show that its causative agent, the SARS-CoV-2 coronavirus, can infect many vital organs beyond the lungs, including the heart, kidneys and the brain. The literature agrees that COVID-19 is likely to have long-term mental health effects on infected individuals, which signifies a need to understand the role of the virus in the pathophysiology of brain disorders that is currently unknown and widely debated. Our docking and molecular dynamics simulations [1] show that the affinity of the spike protein from the wild type (WT) and the South African B.1.351 (SA) variant towards MAO enzymes is comparable to that for its ACE2 receptor. This allows for the WT/SA...MAO complex formation, which changes MAO affinities for their neurotransmitter substrates, thereby impacting their metabolic conversion and misbalancing their levels. Knowing that this fine regulation is strongly linked with the etiology of various brain pathologies, these results are the first to highlight the possibility that the interference with the brain MAO catalytic activity is responsible for the increased neurodegenerative illnesses following a COVID-19 infection, thus placing a neurobiological link between these two conditions in the spotlight. Since the obtained insight suggests that a more contagious SA variant causes even larger disturbances, and with new and more problematic strains likely emerging in the near future, we firmly advise that the presented prospect of the SARS-CoV-2 induced neurological complications should not be ignored, but rather requires further clinical investigations to achieve an early diagnosis and timely therapeutic interventions.

**Keywords:** neurodegeneration, SARS-CoV-2 spike protein, South African B.1.351 variant  
[1] L. Hok, H. Rimac, J. Mavri, R. Vianello, *Comput. Struct. Biotechnol. J.* 20 (2022) 1254.



## BIOMIMETIČKA KROMATOGRAFIJA: UČINKOVIT ALAT ZA PROCJENU BIORASPOLOŽIVOSTI ALOINA I ALOE-EMODINA BIOMIMETIC CHROMATOGRAPHY: EFFECTIVE TOOL FOR BIOAVAILABILITY EVALUATION OF ALOIN AND ALOE-EMODIN

Mario-Livio Jeličić, Jelena Kovačić, Daniela Amidžić Klarić, Ana Mornar  
University of Zagreb Faculty of Pharmacy and Biochemistry, Ante Kovačića 1,  
10000 Zagreb, Croatia

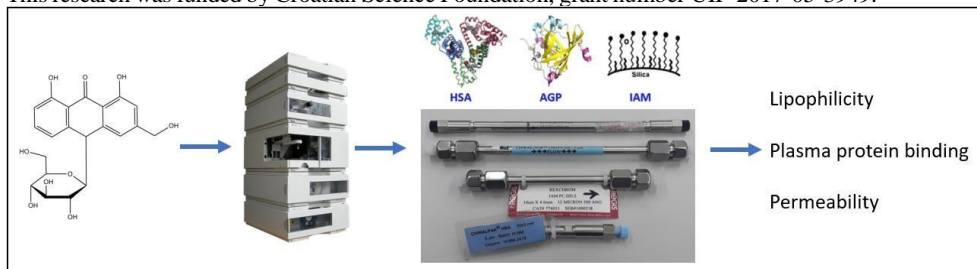
*Aloe vera* (syn.: *Aloe barbadensis* Miller) is the most commercialized Aloe species belonging to the Xanthorrhoeaceae family. Aloin is the major anthraquinone of aloe and characterized as the C-glycoside of aloe-emodin. Due to polyphenolic structure, aloin and aloe-emodin are considered as physiologically active compounds responsible for aloe biological effects such as reduction of inflammation. Despite the frequent use of aloe, limited information is available for their bioavailability which is a very common phenomenon for other phytochemicals as well. A study providing deeper mechanistic insights into the bioavailability of aloin and aloe-emodin is essential to develop better treatment strategies in the future based on botanical products.

Although traditional evaluation of drugs bioavailability and performance in human body require long lasting and expensive clinical studies, a more affordable and faster approach is being developed. Innovative biomimetic chromatographic methods have shown to be good alternative for such studies.

The aim of this work was to evaluate parameters such as hydrophobicity, lipophilicity, and plasma protein binding using chromatographic tools, especially growing population of biomimetic columns mimicking cell membranes, as well as ones containing plasma proteins (human serum albumin (HSA) and alpha-1-acid glycoprotein (AGP)). As expected, aloin as glycoside showed lower hydrophobicity ( $R_{M0}=1.85$ ,  $\log k_0=1.37$ ) compared to aloe-emodin ( $R_{M0}=3.06$ ,  $\log k_0=3.01$ ). On the other hand, aloin showed superior affinity to phospholipids compared to aloe-emodin ( $\Delta \log k_{0 \text{ IAM}}=1.68$ ). Both compounds showed the higher affinity for HSA (62.7% aloin; 97.5% aloe-emodin) than AGP (44.1% aloin; 84.2% aloe-emodin).

**Keywords:** botanicals, inflammatory bowel disease, biomimetic chromatography

This research was funded by Croatian Science Foundation, grant number UIP-2017-05-3949.



# PROCJENA ELEMENATA U TRAGOVIMA I TEŠKIH METALA KAO ONEČIŠĆENJA U DODACIMA PREHRANI KOJI SE KORISTE U LIJEČENJU UPALNIH BOLESTI CRIJEVA

## TRACE AND HEAVY METAL IMPURITY EVALUATION IN DIETARY SUPPLEMENTS USED IN THE TREATMENT OF INFLAMMATORY BOWEL DISEASE

Ilija Klarić<sup>1</sup>, Jelena Kovačić<sup>2</sup>, Mario-Livio Jeličić<sup>2</sup>, Ana Mornar<sup>2</sup>,  
Snježana Zubčić<sup>3</sup>, Daniela Amidžić Klarić<sup>2</sup>

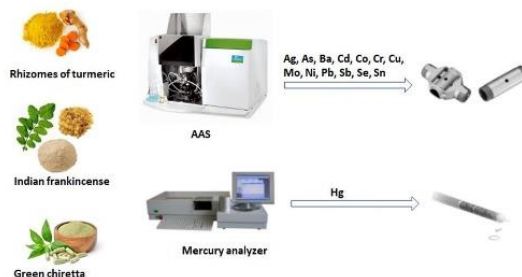
<sup>1</sup>Public Health Brčko DC, R. Dž. Čauševića 1, Brčko DC, B&H

<sup>2</sup>Faculty of Pharmacy and Biochemistry, Ante Kovačića 1, 10000 Zagreb, Croatia

<sup>3</sup>Agency for Medical Products and Medical Devices of Croatia, Ksaverska cesta 4,  
10000 Zagreb, Croatia

Trace and heavy metal impurity in dietary supplements (DS) poses a serious potential risk to health. Furthermore, trace metals play a significant role in reactions that lead to the formation of the active chemical plant constituents and are responsible for their curative and toxic properties. For all mentioned above, this study aimed to evaluate the content of metal impurity in DS containing one or more plant species used to alleviate the symptoms of inflammatory bowel disease (IBD): Indian frankincense, Green chiretta and turmeric. Fifty-four collected samples were in different dosage forms: tablet, hard and soft capsule, tea mixture, bulk and tincture. Total Hg content in the studied samples was analyzed using mercury analyzer, while the contents of Ag, As, Ba, Cd, Co, Cr, Cu, Mo, Ni, Pb, Sb, Se and Sn were analyzed by GF-AAS after microwave digestion. The obtained results of metal impurities were in a wide range. In conclusion, trace and heavy metal impurity in DS used in treating IBD were borderline or higher than the safety level. Notably, Pb and Hg posed the highest risk.

*Keywords:* metal impurity, dietary supplements, inflammatory bowel diseases



This research was funded by Croatian Science Foundation, grant number UIP-2017-05-3949.

## MIKROEKSTRAKCIJA ZAPAKIRANIM SORBENSOM DERIVATA ANDROGRAFOLIDA U LJUDSKOJ PLAZMI MICRO-EXTRACTION BY PACKED SORBENT (MEPS) OF ANDROGRAPHOLIDE'S DERIVATES IN HUMAN PLASMA

Jelena Kovačić, Daniela Amidžić-Klarić, Mario-Livio Jeličić, Ana Mornar  
Faculty of Pharmacy and Biochemistry, University of Zagreb, A. Kovačića 1,  
10000 Zagreb, Croatia

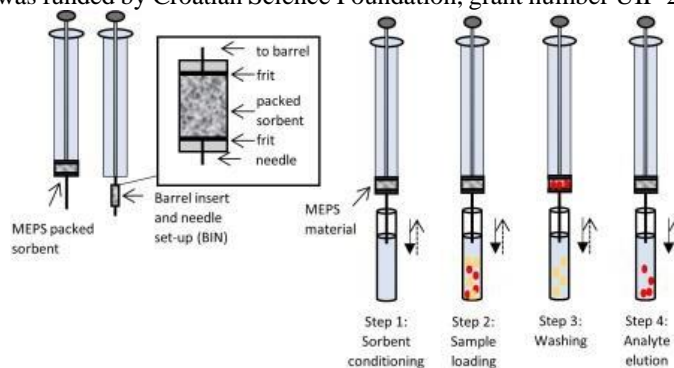
Andrographolides are diterpenoids found in the plant of *Andrographis paniculata* (Burm.f.) Nees (Acanthaceae) and widely used in traditional medicine, exhibiting anti-inflammatory property. In this research, a novel micro-extraction by packed sorbent (MEPS) procedure for sample preparation was examined with the aim of extraction of pharmacological active andrographolide, neoandrographolide and 14-deoxyandrographolide from plasma samples. The analysis of samples was performed using developed and validated high-performance liquid chromatography with diode array detection (HPLC/DAD) method.

The validation results showed acceptable linearity of the method ( $R^2 > 0.99$ ) for all analytes within the calibration range. Acceptable accuracy and precision of the method were indicated by recovery of 91–100% and Relative Standard Deviation (RSD) values below 7.6%. The extraction recovery was found to be between 91.04 and 100.34% with RSD values not higher than 11.5%. The limit of quantification was found to be between 62 and 322 ng/mL while the limit of detection was found between 18 and 97 ng/mL. Short-term (1 - 3 days at room temperature) and long-term stability (3 days at  $-80\text{ }^\circ\text{C}$ ) were also tested and showed no significant difference (RSDs were lower than 14.8%).

The development of this fast and easy MEPS pretreatment procedure granted agreeable validation results and it represents a bioanalytical improvement (cheaper, greener and less time-consuming) over classical solid-phase extraction methods.

**Keyword:** MEPS, human plasma, HPLC

This research was funded by Croatian Science Foundation, grant number UIP-2017-05-3949.



## ENERGETSKI STATUS U STANIČNIM SFERAMA OVISNO O PODRIJEKLU STANICA, VELIČINI I DOSTUPNOSTI NUTRIENTA

### ENERGY STATUS IN CELL SPHERES DEPENDING ON CELL ORIGIN, SIZE AND NUTRIENT AVAILABILITY

Marijana Leventić, Ena Main, Matej Ruška and Ljubica Glavaš-Obrovac  
Faculty of Medicine Osijek, Josip Juraj Strossmayer University of Osijek, J. Huttlera 4,  
31000 Osijek, Croatia

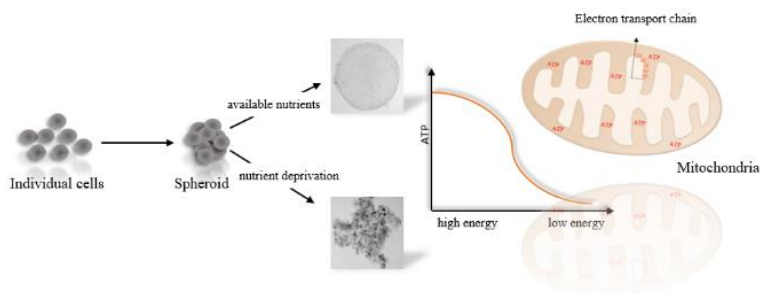
Unique cell properties and cell growth conditions directly influence the energy status of the cell, while the energy status itself directly affects the metabolic activity that supports or suppresses a specific cell function. Information about the metabolic status of the cell spheroids can provide a valuable input for further research of the metabolic activity of tissue-like models.

The goal of our research was to determine how the change in the cell growth conditions affects the changes in the energy status of the cell. The evaluation was focused on the three main parameters, namely the sphere size, the nutrient availability from the growing medium and the cell type used to form the spheres.

Two different cell lines were used to form the spheres: the normal MRC-5 cell line and the glioblastoma D54 cell line. Spheroids were grown under different controlled nutrient availability conditions and different time points in low adherent plates with V-bottom. Cells in the spheres were labelled with TMRE dye for detection of changes in mitochondrial membrane potential. We used the colorimetric ATP assay to determine the levels of ATP in cells lysate, and the colorimetric LDH assay to measure the enzyme activity of the lactate dehydrogenase.

The obtained results indicate that the energy status of the cells in the spheres is in direct correlation with the level of the nutrient source, while the dissociated spheres, changes in mitochondrial potential, ATP levels and enzyme activity indicated a deficit in the energy levels required for the normal cell function.

*Keywords:* energy status, cell spheres, ATP, mitochondrial potential





## ANTIPROLIFERATIVNA I PROTUUPALNA AKTIVNOST PREGNANSKOG STEROIDA IZOLIRANOG IZ KORALJA, *Eunicella cavolini* IZ JADRANSKOG MORA ANTIPROLIFERATIVE AND ANTI-INFLAMMATORY ACTIVITY OF PREGNANE STEROID ISOLATED FROM THE ADRIATIC SEA CORAL, *Eunicella cavolini*

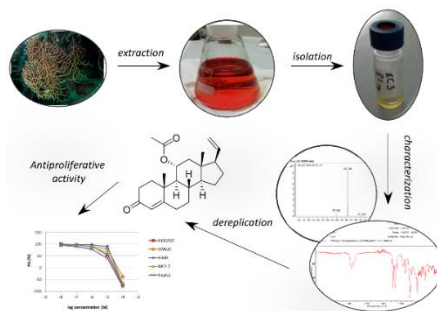
Dario Matulja<sup>1</sup>, Sandra Kraljević Pavelić<sup>2</sup>, Dean Marković<sup>1</sup>  
<sup>1</sup>Department of Biotechnology, University of Rijeka, Radmile Matejčić 2,  
51000 Rijeka, Croatia  
<sup>2</sup>Faculty of Health Studies, University of Rijeka, Viktora Cara Emina 5,  
51000 Rijeka, Croatia

Gorgonian corals of the genus *Eunicella* are well-known sources of structurally diverse secondary metabolites including terpenoids, steroids as well as alkaloids to lower extent. Detailed research studies of those compounds are scarce and they have been examined mostly as anticancer agents on several cell lines since [1]. Therefore, within the Adriatic Sea bioprospecting programme, we have carried out the extraction of the coral, *Eunicella cavolini* (Koch, 1887). Upon dereplication by using spectroscopic data and MarinLit database, we successfully isolated a pregnane steroid and connected it to previously isolated compound [2]. Furthermore, the isolated steroid was screened for antiproliferative activity against four cancer and one non-transformed cell line accompanied with evaluation of anti-inflammatory potential by using assays of albumin denaturation and soybean lipoxygenase inhibitions. The natural compound exhibited non-selective activity against tested cell lines with the highest activity towards hepatocellular carcinoma (HepG2) ( $IC_{50} = 6 \mu\text{M}$ ). Finally, at the concentrations of 309.4 and 118.6  $\mu\text{M}$ , pregnane steroid inhibited 50% of soybean lipoxygenase and albumin denaturation, respectively.

**Keywords:** *Eunicella cavolini*, pregnane steroid, anticancer, anti-inflammatory

[1] D. Matulja *et al.*, *Molecules* 25 (2020) 129

[2] E. Ioannou *et al.*, *Tetrahedron* 64 (2008) 11797-11801





**MEHANOKEMIJSKA SINTEZA I STRUKTURNA  
KARAKTERIZACIJA NOVIH 1,2,3-TRIAZOLNIH  
DERIVATA 2-ARILBENZOTIAZOLA  
MECHANOCHEMICAL SYNTHESIS AND STRUCTURAL  
CHARACTERIZATION OF NOVEL 1,2,3-TRIAZOLYL 2-  
ARYL BENZOTHIAZOLE DERIVATIVES**

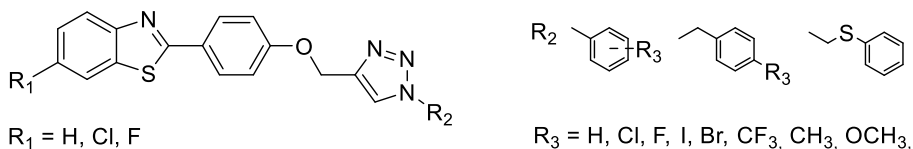
Ivana Sokol, Hanja Mlinar, Kristina Olujić, Tatjana Gazivoda Kraljević  
Department of Organic Chemistry, Faculty of Chemical Engineering and Technology,  
University of Zagreb, Marulićev trg 20, 10000 Zagreb, Croatia

In recent decades, benzofused azoles, which containing heteroatoms form the structures of many biologically active compounds. Benzothiazole is used for various therapeutic applications such as antitumor, antimicrobial, antiviral, anti-inflammatory and other activities.[1] Among the azoles, the 1,2,3-triazoles has a widespread occurrence as pharmacophore or linker in different compounds due their structural features that enable it to mimic different functional groups as a bioisostere. Thus, the 1,2,3-triazole moiety is present in the structure of the antiviral drug Ribavirin, which shows a broad spectrum of activity against several RNA and DNA viruses. Coupling of benzothiazoles to triazole cores can result in enhanced biological activities, as was obtained for 2-mercaptobenzothiazole and 1,2,3-triazole derivative which demonstrated potent selective COX-2 inhibition comparable with the standard drug ibuprofen.[2]

In this work, we present mechanochemical synthesis of target 1,2,3-triazolyl derivatives of 2-aryl benzothiazole. 2-aryl benzothiazoles were prepared by cyclization reaction of 6-substituted 2-amino thiophenole with propargylated benzaldehyde which were then converted by Huisgen 1,3-dipolar cycloaddition using copper(II) acetate as catalyst in ball mill to desired triazolyl 2-arylbenzothiazole derivatives. The structures of all newly prepared benzothiazole derivatives were confirmed by <sup>1</sup>H and <sup>13</sup>C-NMR spectroscopy.

**Keywords:** benzothiazole, 1,2,3-triazole, mechanochemical synthesis

- [1] S.G. Agalave, S.R. Maujan, S. Vandana, Click Chemistry, Asian J. Chem. 6 (2011) 2696  
[2] S. Shafi, M. Mahboob Alam, N. Mulakayala, C. Mulakayala, G. Vanaja, A.M. Kalle, M.S. Alam, Eur. J. Med. Chem. 49 (2012) 324



## GINKO (*Ginkgo biloba* L.) AS A SOURCE OF BIFLAVONOIDS WITH BIOLOGICAL ACTIVITY

Dunja Šamec<sup>1</sup>, Bojan Šarkanj<sup>1</sup>, Erna Karalija<sup>2</sup>

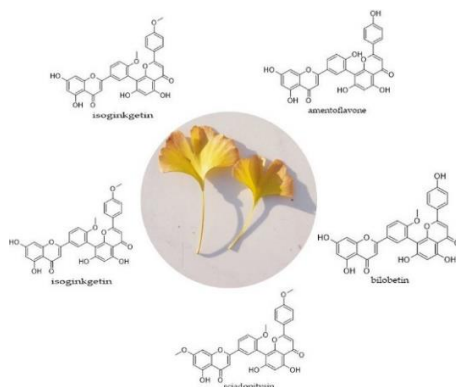
<sup>1</sup>Department of Food Technology, University Center Koprivnica, University North, Trg Dr. Žarka Dolinara 1, 48 000, Koprivnica, Croatia

<sup>2</sup>Department for Biology, Faculty of Science, University of Sarajevo, Zmaja od Bosne 33-35, 71000 Sarajevo, Bosnia and Herzegovina

Flavonoids exist as aglycones, glycosides, or dimeric forms called biflavonoids. Biflavonoids presence is commonly reported in plants used in traditional and modern medicine, indicating their potential health benefits. Biflavonoids are not present in all plant species, but are found only in some species. One of them is ginkgo (*Ginkgo biloba* L.), a well-known medicinal plant used in traditional and Western medicine. Unfortunately, most phytochemical studies published on ginkgo in recent years have neglected biflavonoids as important bioactive components that have come into scientific focus as important health-promoting compounds. So, the aim of this work was to conduct a comprehensive literature review on the presence of biflavonoids in ginkgo and to summarize data on the chemistry, diversity, and biological factors affecting their presence in ginkgo, as well as their bioactive and health-related properties. To date, the presence of 13 biflavonoids in ginkgo has been demonstrated, of which amentoflavone, bilobetin, sciadopitysin, ginkgetin, and isoginkgetin are the most common. Their role in plants remains unknown, but their bioactivity and potential role in treating human health are better understood and are associated with antioxidant, anticancer, antiviral, antibacterial, antifungal, and anti-inflammatory activities, as well as their potential role in treating cardiovascular, metabolic, and neurodegenerative diseases.

**Keywords:** biflavonoids, ginkgo, biological activity

**Funding:** “This work has been supported by Croatian Science Foundation project no. UIP-2019-04-1018.



**ODREĐIVANJE *IN VIVO* GENOTOKSIČNOG UČINKA  
DOBRIČICE (*Glechoma hederacea* L.) I UTJECAJ NA  
HEMATOLOŠKE I BIOKEMIJSKE PARAMETRE  
KRVI ŠTAKORA  
*IN VIVO* GENOTOXICITY OF GROUND IVY (*Glechoma  
hederacea* L.) AND EFFECT ON HEMATOLOGICAL AND  
BIOCHEMICAL BLOOD PARAMETERS OF RAT**

Danijela Šeremet<sup>1</sup>, Ana Mandura Jarić<sup>1</sup>, Vesna Benković<sup>2</sup>, Anica Horvat  
Knežević<sup>2</sup>, Vedran Balta<sup>2</sup>, Sofia Ana Blažević<sup>2</sup>, Ivana Žepić<sup>1</sup>,  
Draženka Komes<sup>1</sup>

<sup>1</sup>Faculty of Food Technology and Biotechnology, University of Zagreb, Pierottijeva ulica 6,  
10000 Zagreb, Croatia

<sup>2</sup>Faculty of Science, University of Zagreb, Rooseveltov trg 6, 10000 Zagreb, Croatia

Ground ivy (*Glechoma hederacea* L.), a member of the *Lamiacea* family, has been used in folk medicine for generations. The aim of the present study was to evaluate *in vivo* genotoxicity of the water extract of ground ivy and to determine whether there was an effect on hematological and biochemical parameters of blood. The experiment involved 12 Sprague Dawley rats, divided into 4 groups – 2 control groups (female and male) and 2 experimental groups (female and male) which were treated *per os* with ground ivy extract at a dose of 200 mg of freeze-dried extract per kg of rat for 14 days. The care and use of the experimental animals were in accordance with Croatian animal welfare laws and guidelines. All animals survived the experiments and their white blood, liver and kidney cells were subjected to alkaline comet assay in which tail length and intensity of DNA were determined. According to the obtained results there were no evidence of genotoxic activity after exposure to the ground ivy extract. The detected hematological and biochemical blood parameters did not indicate any adverse effect of the ground ivy extract.

**Keywords:** ground ivy, genotoxicity, hematological and biochemical blood parameters

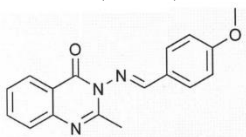


## DERIVATI SCHIFF-OVIH BAZA KAO POTENCIJALNI INHIBITORI ACETILKOLINESTERAZE – *In vitro* STUDIJA SCHIFF BASE DERIVATIVES AS POTENTIAL ACETYLCHOLINESTERASE INHIBITORS- AN *In vitro* STUDY

Domagoj Šubarić<sup>1</sup>, Mario Komar<sup>2</sup>, Maja Karnoš<sup>1</sup>, Drago Bešlo<sup>1</sup>, Vesna Rastija<sup>1</sup>  
<sup>1</sup>Faculty of Agrobiotechnical sciences, J.J. Strossmayer University of, Osijek, Vladimira  
Preloga 1, 31000 Osijek, Croatia

<sup>2</sup>Faculty of Food Technology, J.J. Strossmayer University of, Osijek, Franje Kuhača 18,  
31000 Osijek, Croatia

Schiff base derivatives were synthesized by utilizing the green chemistry methods such as microwave-assisted, ultrasound-assisted and mechanochemical synthesis. [1] Acetylcholinesterase inhibitors are widely recognised as potential drugs for treating symptoms of the Alzheimer's disease. Inhibitory properties of AChE inhibitors have been used for the development of active compounds in plant protection treatments. Twenty-four Schiff base derivatives were tested as potential acetylcholinesterase inhibitors. *In vitro* experiment has been conducted on a 96-well microplate UV-Vis reader by utilizing the modified Ellman's method. [2] Absorbance readings were obtained by measuring at the wavelength of 412 nm. Donepezil was used as a standard acetylcholinesterase inhibitor. The highest percentage of inhibition was obtained with the compound **10** (Fig. 1), 34.58%, while the lowest inhibition percentage was obtained with compound **26** (3.88%).

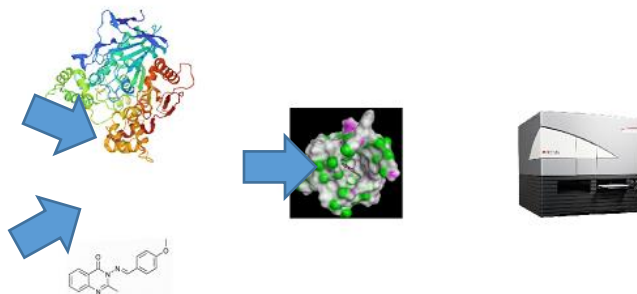


**Figure 1.** Compound 10

**Keywords:** Schiff base, acetylcholinesterase, inhibition

[1] M. Komar, F. Prašnikar, T. Kraljević Gazivoda, K. Aladić, M. Molnar, *Curr. Green Chem.* 8(1) (2021) 62-69.

[2] G.L. Ellman, K.D. Courtney, V. Andres, R.M. Featherstone, *Biochemical Pharmacology*, 7(2) (1961) 88-95.



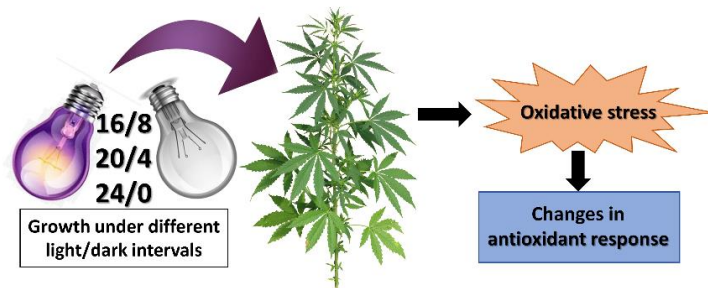
**TRAJANJE SVJETLOSNIH INTERVALA MIJENJA  
ANTIOKSIDACIJSKI ODGOVOR  
INDUSTRIJSKE KONOPLJE  
DURATION OF LIGHT INTERVALS CHANGES  
ANTIOXIDANT RESPONSE OF INDUSTRIAL HEMP**

Antonia Vicić<sup>1</sup>, Selma Mlinarić<sup>2</sup>, Lidija Begović<sup>2</sup>, Martina Šrajer Gajdošik<sup>1</sup>  
<sup>1</sup>Department of Chemistry, J.J. Strossmayer University of Osijek, Ulica cara Hadrijana 8/A,  
31000 Osijek, Croatia

<sup>2</sup>Department of Biology, J.J. Strossmayer University of Osijek, Ulica cara Hadrijana 8/A,  
31000 Osijek, Croatia

Industrial hemp (*Cannabis sativa* L. subsp. *sativa*) is one of the oldest cultivated plants used for many purposes throughout centuries. It has been valued for its nutritional and medicinal properties. Industrial hemp is primary a short-day plant but it can endure great changes in daylight intensity and length which can promote oxidative damage. Therefore, plants must modify their antioxidative responses to combat this stress. In this study, the antioxidative response of two hemp cultivars (USO and Finola) grown under violet light ( $\sim 250 \mu\text{mol m}^{-2} \text{s}^{-1}$ ) and different light/dark intervals (18/6, 20/4 and 24/0) was investigated. To determine antioxidative potential, ferric reducing antioxidant power (FRAP) and scavenging effect on the 1,1-diphenyl-2-picrylhydrazyl free radical (DPPH) assays were employed. The content of total polyphenols was determined spectrophotometrically using Folin-Ciocalteu reagent. Highest FRAP values were observed at 20/4 in both cultivars. DPPH assay showed similar results as FRAP, except that no statistical difference was observed between 16/8 and 20/4 values for the Finola cultivar. The total phenolic content in both cultivars showed the highest values at 20/4 as well, correlating with other two methods and suggesting that phenolic compounds are likely to contribute to radical scavenging activity. All results indicate that 20/4 light interval causes the most stress in plants possibly inducing free radical formation and consequent increase in overall nonenzymatic antioxidant response in order to preserve important bioactive components.

**Keywords:** industrial hemp, antioxidative response, DPPH, FRAP, total phenolic content



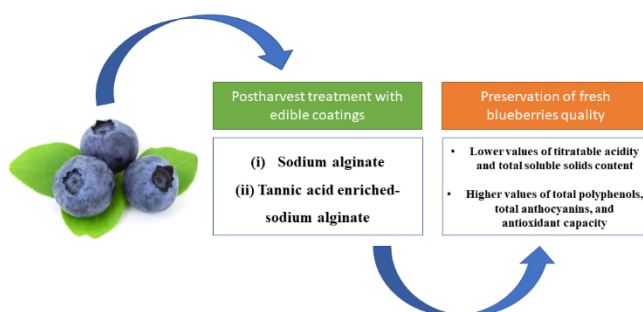
## THE EFFECT OF EDIBLE COATINGS ON THE QUALITY OF FRESH BLUEBERRIES

Slaven Jurić, Ana Jakoplić, Kristina Vlahoviček Kahlina,  
Marija Sigurnjak Bureš, Luna Maslov Bandić

University of Zagreb, Faculty of Agriculture, Department of Chemistry, Svetosimunska 25,  
10 000 Zagreb, Croatia

Blueberries (*Vaccinium corymbosum* L.) are well known for their great taste, high concentration of bioactive compounds, and numerous health benefits they offer to consumers. Fresh blueberries are very sensitive during the postharvest period mainly caused by water loss, mold decomposition, and metabolic changes. Blueberries have a shelf life of 7 to 40 days at 4 °C, depending on characteristics such as fruit cultivar, storage conditions, and maturity harvest technique. Edible coatings are used to extend the shelf life of perishable fruits like blueberries. This research reports use of two types of hydrogel coatings in postharvest treatment of fresh blueberries: (i) sodium alginate (2% (w/v)) (ii) and tannic acid (1% (w/v)) enriched sodium alginate (2% (w/v)). Fruit quality was evaluated for weight loss, titratable acidity, total soluble solids content, total polyphenolic content, total anthocyanin content, and antioxidant capacity. Sodium alginate coated samples showed lower values of total soluble solids content and titratable acidity compared to the control samples while tannic acid-enriched sodium alginate coated samples had significantly higher values of total polyphenols, total anthocyanins, and antioxidant capacity.

**Keywords:** blueberries, edible coatings, sodium alginate, tannic acid, bioactive compounds



## RAČUNALNI PROBIR DERIVATA KINAZOLINONA KAO POTENCIJALNIH ANTIFUNGALNIH TVARI A COMPUTATIONAL SCREENING OF QUINAZOLINONE DERIVATIVES AS POTENTIAL ANTIFUNGAL AGENTS

Maja Karnas<sup>1</sup>, Mario Komar<sup>2</sup>, Dejan Agić<sup>1</sup>, Vesna Rastija<sup>1</sup>,  
Domagoj Šubarić<sup>1</sup>, Maja Molnar<sup>2</sup>

<sup>1</sup>Faculty of Agrobiotechnical Sciences Osijek, Josip Juraj Strossmayer University of Osijek,  
Vladimira Preloga 1, 31000 Osijek, Croatia

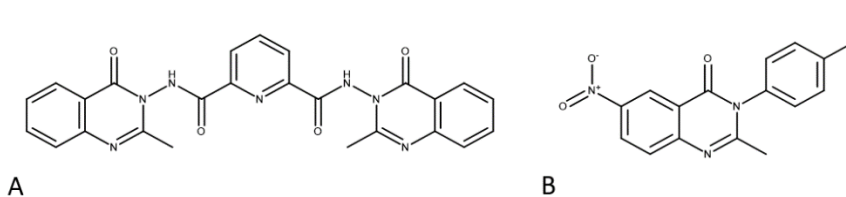
<sup>2</sup>Faculty of Food Technology Osijek, Josip Juraj Strossmayer University of Osijek, Franje  
Kuhača 18, 31000 Osijek, Croatia

Phytopathogenic fungi are one of the leading causes of plant diseases that reduce crop quality and cause huge yield losses. The control of fungal plant diseases is important for reducing or preventing these losses. The excessive use of available fungicides over a long period of time has increased the fungal resistance and become a major ecological issue, giving the incentive to find new antifungal agents. Quinazolinone is a common heterocyclic nitrogen scaffold, widely present in natural products. Its derivatives exert a variety of biological activities, such as antitumor, antiviral, antibacterial and antifungal [1]. The aim of this study was to examine a potential antifungal activity of several structurally different, recently synthesized new quinazolinone derivatives [2] using a computational approach. A molecular docking analysis has been performed on two fungal chitinases, type A (PDB ID: 2XUC) and B (PDB ID: 2IUZ), involved in chitin decomposition, cell wall degradation and remodeling. Molecular docking has shown that all tested compounds bind near the enzyme active sites. The most promising compounds were *N*<sup>2</sup>,*N*<sup>6</sup>-bis(2-methyl-4-oxoquinazolin-3(4*H*)-yl)pyridine-2,6-dicarboxamide for chitinase A, and 3-(4-methoxyphenyl)-2-methyl-6-nitroquinazolin-4(3*H*)-one for chitinase B.

*Keywords:* quinazolinones, molecular docking, chitinase

[1] J.-W. Peng, X.-D. Yin, H. Li, K.-Y. Ma, Z.-J. Zhang, R. Zhou, Y.-L. Wang, G.-F. Hu, Y.-Q. Liu, *J. Agric. Food Chem.* 69 (2021) 16, 4604–4614.

[2] M. Komar, M. Molnar, A. Konjarević, *Croat. Chem. Acta* 92 (2019) 4, 511–517.



## Optimizacija ekstrakcije karotenoida iz kore *Citrus unshiu* korištenjem zelenih otapala Optimization of carotenoid extraction from *Citrus unshiu* peels using green solvents

Luna Maslov Bandić, Kristina Vlahoviček Kahlina,  
Marija Sigurnjak Bureš, Slaven Jurić

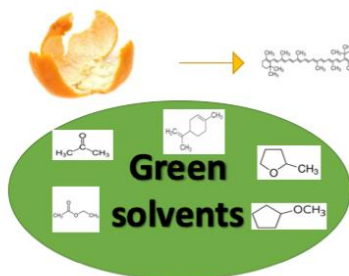
University of Zagreb, Faculty of Agriculture, Department of Chemistry, Svetosimunska 25,  
10 000 Zagreb, Croatia

Sample treatment is one of the most contaminant steps in the analytical process, mainly due to the high consumption of energy and petrol-based organic solvents, which involve a high environmental impact [1]. One of the most promising strategies to reduce the side effects of the analytical methodology consists of the substitution of organic solvents with a greener alternative. Carotenoids belong to a group of organic chemical compounds. They are naturally occurring pigments in citrus peel. Standard extraction methods of carotenoids from citrus peel use *n*-hexane.

Our goal was an optimization of solid-liquid extraction of carotenoids from *Citrus unshiu* peels using green solvents: acetone, ethyl acetate, limonene, 2-methyl tetrahydrofuran, cyclopentyl methyl ether. Response surface methodology (RSM) using the central composite designs (CCD) approach was used. Total carotenoids were determined spectrophotometrically. Optimized conditions of time, temperature, and type of solvent were 65 min, 65 °C with cyclopentyl methyl ether giving carotenoid content of 10.51 mg/L. Compared with the conventional solvent hexane gave an increase of 37.29%. Also, other green solvents gave significantly higher results compared to hexane. Using green solvents to extract carotenoids from mandarin peels could be recommended as an alternative to *n*-hexane.

**Keywords:** green solvents, carotenoids, extraction, citrus peel

[1] S. Armenta, F. Esteve-Turrillas, S. Garrigues, M. de la Guardia, *Green Anal Chem* 1 (2022) 100007.





## EDU-CLIC: EDUKACIJA ZA ODRŽIVO GOSPODARENJE KOMUNALNIM OTPADOM

### EDU-CLIC: EDUCATION FOR SUSTAINABLE MUNICIPAL SOLID WASTE MANAGEMENT

Jurislav Babić<sup>1</sup>, Natalija Velić<sup>1</sup>, Antun Jozinović<sup>1</sup>, Darko Velić<sup>1</sup>, Sandra Budžaki<sup>1</sup>, Mario Panjičko<sup>2</sup>, Goran Vujić<sup>3</sup>, Dušan Milovanović<sup>3</sup>, Milan Mirić<sup>4</sup>

<sup>1</sup>Josip Juraj Strossmayer University of Osijek, Faculty of Food Technology Osijek, Franje Kuhača 18, 31000 Osijek, Croatia

<sup>2</sup>CROTEH Ltd., Centre for the development of Sustainable, 10000 Zagreb, Croatia

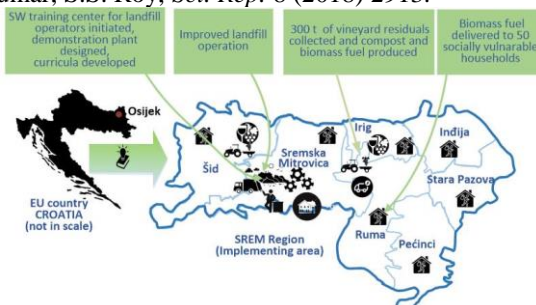
<sup>3</sup>University of Novi Sad, Faculty of Technical Sciences, 21000 Novi Sad, Serbia

<sup>4</sup>Regional development agency Srem, 22400 Ruma, Serbia

The aim of this paper is to demonstrate the importance of education for sustainable municipal solid waste (MSW) management, using the EDU-CLIC project as an example. Landfills are significant contributors to the national carbon footprint worldwide, as they are considered the third largest anthropogenic source of methane emissions [1]. In order to make MSW management more sustainable, environmental education and waste management education are crucial, as they raise public awareness and enable the implementation of efficient and sustainable modern waste management systems, which not only depend on the implementation of appropriate technical and economic strategies, but cannot function without the contribution of people (both qualified professionals and citizens in general). The educational-professional project "EDUcation for CLimate Change mitigation in the municipal solid waste sector" is a part of the European Climate Initiative (EUKI) of the German Federal Ministry for Economic Affairs and Climate Action (BMWK). The project EDU-CLIC aims to create the infrastructure for a training centre for landfill operators and to develop a curriculum to train operators in sustainable MSW management. In addition, the project aims to upgrade an existing landfill in Sremska Mitrovica, Serbia (the country where the project is being implemented), which will serve as both a demonstration centre and a blueprint for future modern MSW centres in the region. Project activities aim to promote the implementation of more sustainable on-site MSW management practises to achieve a long-term goal - reducing greenhouse gas emissions from landfills and thereby mitigating the negative environmental impacts of landfills.

**Keywords:** municipal solid waste management, education, landfill

[1] C.K. Singh, A. Kumar, S.S. Roy, *Sci. Rep.* 8 (2018) 2913.



## ISKORISTIVOST SLAME ZA SEKUNDARNU AMBALAŽU OTISNUTU OFSETNOM I BAKROTISKARSKOM TEHNIKOM TISKA USABILITY OF STRAW FOR SECONDARY PACKAGING PRINTED BY OFFSET AND GRAVURE PRINTING TECHNIQUES

Irena Bates, Ivana Plazonić, Valentina Radić Seleš, Maja Rudolf,  
Katja Petric Maretić

University of Zagreb, Faculty of Graphic Arts, Getaldićeva 2, 10000 Zagreb, Croatia

Packaging is the material with which the product is wrapped or inside which the product is placed. The main function of packaging is to protect the packaged product, identify it and place it on the market, and to ensure the original shape of the packaged goods. The trend today is to reduce the global amount of packaging waste by recycling the same waste or reusing other available waste materials, while maintaining the required quality of the packaging thus produced. Cereal grains which include wheat, rye, barley, oats, rice, corn, millet, sorghum, wheat, spelt and others, are staple foods for human and animal consumption. Each year, large quantities of stalks are left in the fields after harvesting, and after drying in the sun is mostly treated as waste. Given the high availability of cereals worldwide, cereal straw could be more usefully utilized as an alternative source of fiber for secondary packaging. Therefore, the printing paper substrates were formed from the straw pulp of three different cereal species (wheat, barley and triticale) and mixed with recycled wood pulp in a 3:7 ratio. Since offset and gravure printing are used globally to print absorbent packaging, in this study we analyzed the black prints made by these two printing techniques. The usability of the printed papers with straw pulp for secondary packaging was observed based on the penetration of the ink into the printing substrate. It was found that the composition of the paper substrate has no effect on the depth of ink penetration into the printing substrate, so that cereal straw can be used as waste material for the production of secondary packaging. In general, prints with gravure inks have lower ink penetration compared to offset inks.

**Ključne riječi:** gravure printing, offset printing, packaging, ink penetration, straw pulps

**Acknowledgement:** This work has been supported in part by Croatian Science Foundation under the project "Printability, quality and utilization of substrates with non-wood fibers" (UIP-2017-05-2573).



## BIORAZGRADNJA POLI(VINIL-KLORIDA) KVASCEM *Candida parapsilosis*

### BIODEGRADATION OF POLYVINYL CHLORIDE BY YEAST *Candida parapsilosis*

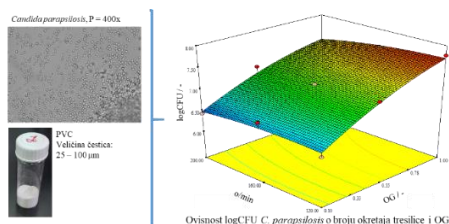
Kristina Bule<sup>1</sup>, Marija Kuštro<sup>1</sup>, Dubravka Tavra<sup>1</sup>, Martina Miloloža<sup>1</sup>,  
Viktorija Prevarić<sup>1</sup>, Matija Cvetnić<sup>1</sup>, Šime Ukić<sup>1</sup>, Tomislav Bolanča<sup>1,2</sup>,  
Marinko Markić<sup>1</sup>, Dajana Kučić Grgić<sup>1</sup>

<sup>1</sup>Sveučilište u Zagrebu, Fakultet kemijskog inženjerstva i tehnologije,  
Marulićev trg 19, 10000 Zagreb, Hrvatska

<sup>2</sup>Sveučilište Sjever, Trg dr. Žarka Dolinara 1, 48000 Koprivnica, Hrvatska

Visoke koncentracije mikroplastike (MP) u okolišu predstavljaju prijetnju čovječanstvu i zato se u posljednje vrijeme intenzivno istražuju moguća rješenja uklanjanja MP-a iz okoliša. Cilj ovoga rada bio je ispitati utjecaj različitih parametara na biorazgradnju MP-a poli(vinil-klorida) (PVC) primjenom kvasca *Candida parapsilosis* uz određivanje optimalnih uvjeta procesa. Ispitan je utjecaj pH-vrijednosti medija (3, 5 i 7), optičke gustoće (OG = 0,1, 0,5 i 1,0) i broj okretaja rotacijske tresilice (120, 160 i 200 o/min). Tijekom 30 dana procesa pratio se ukupan broj živih stanica kvasaca (CFU), koncentracija ukupnog, organskog i anorganskog ugljika u sustavu (TC, TOC i TIC) te se LC/MS analizom pratio sastav vodene faze. Tijekom biorazgradnje PVC-a postoji opasnost od nastanka toksičnih nusprodukata zbog čega se ispitala i toksičnost vodene faze nakon procesa primjenom morske bakterije *Vibrio fischeri*. MP PVC je analiziran prije i nakon procesa biorazgradnje primjenom FTIR-ATR spektroskopije. Dobiveni rezultati obrađeni su u programu *Desing Expert*, OG i broj okretaja rotacijske tresilice pokazali su se kao signifikantni parametri, dok promjena pH-vrijednosti medija nije imala velikog utjecaja na proces. Dobiveni optimalni uvjeti procesa su pH-vrijednost = 4,38, broj okretaja rotacijske tresilice = 120 o/min i OG = 1,0.

**Ključne riječi:** mikroplastika, biorazgradnja, *Candida parapsilosis*, poli(vinil-klorid)



#### ZAHVALA

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## PYROLITIC DEGRADATION OF FILTER CAKE AFTER MEMBRANE FILTRATION OF TEXTILE WASHING EFFLUENT

Mirjana Čurlin<sup>1</sup>, Tanja Pušić<sup>2</sup>, Tea Kaurin<sup>2</sup>, Nino Dimitrov<sup>3</sup>,  
Branka Vojnović<sup>2</sup>, Agata Vinčić<sup>2</sup>

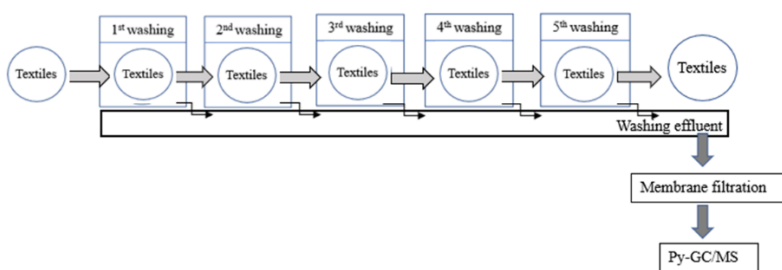
<sup>1</sup>Faculty of Food and Biotechnology, University of Zagreb, Pierottijeva 6, 10000 Zagreb, Croatia

<sup>2</sup>Faculty of Textile Technology, University of Zagreb, Prilaz baruna Filipovića 28 a, 10000 Zagreb, Croatia

<sup>3</sup>Croatian Institute of Public Health, Rockefellerova 7, 10000 Zagreb, Croatia

The mixed cotton/polyester textiles were washed in 5 cycles according to the standard procedure with and without detergent. The wastewater generated during washing was cumulatively collected and solid particles were separated by membrane filtration to identify released particles from the textiles, which represent potential environmental pollution with microplastic particles. By applying the pyrolytic decomposition method with the Py-GC/MS instrument, a qualitative and quantitative analysis of the particles released in the washing process was performed. The results of the analysis indicate the presence of chemical compounds characteristic of the decomposition of polymeric and cellulosic materials. The obtained results are used for the analysis of the estimation of the release of microplastic particles during washing.

*Keywords:* washing process, Cotton/PES textiles, release of particles pyrolytic degradation



**PRIKAZ OCJENE KEMIJSKOG STANJA POVRŠINSKIH  
VODA KOPAČKOG RITA NA TEMELJU ANALIZE  
ODABRANIH TEŠKIH METALA KROZ  
JEDNOGODIŠNJE VREMENSKO RAZDOBLJE  
EVALUATION OF CHEMICAL STATUS OF KOPAČKI RIT  
SURFACE WATER BODIES THROUGH ANALYSIS OF  
SELECTED HEAVY METALS THROUGH ONE-YEAR  
PERIOD**

Ivan Damjanović<sup>1</sup>, Hrvoje Sučić<sup>1</sup>, Danijela Bezik<sup>1</sup>, Mirna Habuda-Stanić<sup>2</sup>,  
Dario Kolarić<sup>1</sup>, Zdenka Šušić<sup>1</sup>, Leontina Toth<sup>1</sup>, Barbara Petrovicky Šveiger<sup>1</sup>,  
Marika Kralj<sup>1</sup>, Ines Ružkan<sup>1</sup>, Mirna Tokić<sup>1</sup>, Mirta Eberhard<sup>1</sup>, Tanja  
Marković<sup>1</sup>, Hrvoje Babić<sup>1</sup>, Nataša Turić<sup>1</sup>, Snježana Benkotić<sup>1</sup>

<sup>1</sup>Teaching Institute of Public Health for the Osijek – Baranja County, Drinska 8, 31000  
Osijek, Croatia

<sup>2</sup>Josip Juraj Strossmayer University of Osijek, Faculty of Food Technology Osijek, F.  
Kuhača 18, 31000 Osijek, Croatia

Wetlands are the most productive ecosystems on Earth. Due to the undergoing wet – dry cycles, they ensure the diversity of ecological conditions in the same habitat and support high biodiversity. The dynamics of the Kopački rit wetland floodplain water regime is a consequence of its geographical location in the area of the Drava – Danube confluence. The chemical status of surface water is based not only on the annual average concentrations (AAC) of the substances, but also on the maximum annual concentration (MAC). Heavy metals are among the most dangerous inorganic pollutants due to biodegradability, bioaccumulation, toxicity at low concentrations and due to incorporation into food chains. Dissolved in water, they are in ionic form and non-biodegradable and tend to accumulate in living things in the process of bioaccumulation. As part of the Naturavita project in the Nature Park Kopački rit, sampling and analysis of mercury, nickel, cadmium, lead and their compounds were carried out at 19 locations through one-year period of 12 field survey cycles. According to the obtained results, at all sampling locations, the measured average (AAC) and maximum annual concentrations (MAC) do not exceed allowable concentration according to Regulation on water quality standard (OG 96/2019). Good chemical status has been achieved at all sampling locations.

*Keywords:* surface waters, Kopački rit Nature Park, wetland ecosystems, heavy metals, bioaccumulation

## SADRŽAJ PM<sub>2.5</sub> U ZRAKU ZAPADNOG DIJELA GRADA ZAGREBA

### PM<sub>2.5</sub> CONTENT IN AIR IN WESTERN PART OF CITY ZAGREB

Valentina Gluščić, Ranka Godec, Gordana Pehnc, Ivan Bešlić  
Institut za medicinska istraživanja i medicinu rada, Ksaverska cesta 2, 10000 Zagreb,  
Hrvatska

Onečišćujuće tvari raspršene u zraku koje se razlikuju po obliku, sastavu i veličini nazivamo lebdeće čestice. Lebdeće čestice su smjese krutih i tekućih tvari koje mogu nastati iz različitih prirodnih (mineralna prašina, morski aerosoli, erupcije vulkana) i antropogenih izvora (emisije stacionarnih i mobilnih izvora, gorenje biomase, poljoprivreda i dr.) ili su nastale fotokemijskim reakcijama iz plinovitih prekursora. Frakcija lebdećih čestica PM<sub>2.5</sub> zbog aerodinamičkog promjera manjeg od 2,5 µm može dublje prodrijeti u organizam čovjeka i potencijalno je opasna za zdravlje ljudi, ali i sav živi svijet.

Sadržaj PM<sub>2.5</sub> čine različite vrste organskih i anorganskih spojeva koji mogu ujedno i biti markeri za određivanje izvora iz kojih su lebdeće čestice nastale. Stoga je, ispitujući sadržaj lebdećih čestica, moguće dobiti odgovor o različitim karakteristikama izvora kao što su: vrsta, intenzitet te vremenska i/ili prostorna raspodjela. Svrha ovog istraživanja bila je ispitati masene koncentracije u vodi topivih aniona (Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, CH<sub>3</sub>COO<sup>-</sup>, HCOO<sup>-</sup>) i kationa (Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>) u PM<sub>2.5</sub> i njihove odnose s ciljem određivanja prisutnih izvora onečišćenja. Uzorci PM<sub>2.5</sub> sakupljeni su u periodu od mjesec dana na mjernoj postaji u zapadnom dijelu grada s jakom gustoćom prometa. Ovo su prva kontinuirana mjerenja masenih koncentracija PM<sub>2.5</sub> i sadržaja anorganskih i organskih aniona i kationa u PM<sub>2.5</sub> frakciji na toj lokaciji. Rezultati upućuju na prisutnost različitih primarnih (mobilni, stacionarni) i sekundarnih izvora. Istraživanja je potrebno nastaviti kako bi se ispitala vremenska razdioba te dobila bolja karakterizacija izvora i njihovih doprinosa ukupnom onečišćenju zraka u zapadnom dijelu grada Zagreba.

*Ključne riječi:* lebdeće čestice, anioni, kationi, urbana mjerna postaja



## RAZINE UGLJIKA U LEBDEĆIM ČESTICAMA PM<sub>2,5</sub> I PM<sub>1</sub> U ZRAKU

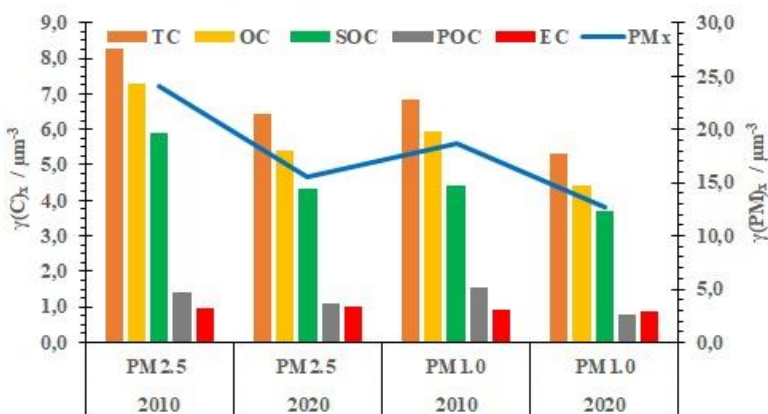
### CARBON LEVELS IN AIRBORNE PM<sub>2.5</sub> AND PM<sub>1</sub> PARTICULATE MATTER

Ranka Godec, Krešimir Šega, Martina Šilović Hujčić, Ivan Bešlić

Institut za medicinska istraživanja i medicinu rada, Ksaverska c. 2, 10000 Zagreb, Hrvatska

Lebdeće čestice su jedno od glavnih onečišćenja zraka, a sadrže velik broj organskih i anorganskih spojeva. Iako organski spojevi čine oko 10 % do 70 % ukupne mase lebdećih čestica u atmosferi, koncentracije, sastav i mehanizmi formiranja organskih čestica nisu potpuno razjašnjeni, a jedan od razloga je i to što se organska tvar sastoji od stotina pojedinačnih spojeva različitih kemijskih i termodinamičkih svojstava. Niti jednom analitičkom tehnikom trenutno nije moguće analizirati cijeli raspon organskih spojeva u česticama. Svrha ovog istraživanja bila je odrediti razine različitih oblika ugljika u respirabilnim lebdećim česticama PM<sub>2,5</sub> i PM<sub>1</sub> (aerodinamičkog promjera manjeg od 2,5 i 1  $\mu\text{m}$ ). 24-satni uzorci sakupljeni su svakodnevno u 2010. i 2020. godini na jednoj urbanoj pozadinskoj lokaciji u Zagrebu te je promatrano jesu li se promijenile razine pojedinih oblika ugljika nakon 10 godina.

*Ključne riječi:* EC, OC, sezonska raspodjela, SOC



## USPOREDBA DENITRIFICIRAJUĆE DEFOSFATACIJE PRI PULSONOM I STUPNJEVITOM DODAVANJU ELEKTRON AKCEPTORA THE COMPARISON OF DENITRIFYING DEPHOSPHATATION AT PULSE AND STEP ADDITION OF ELECTRON ACCEPTOR

Dijana Grgas<sup>1</sup>, Ana Marija Prskalo<sup>1</sup>, Tea Štefanac<sup>1</sup>, Mirna Habuda-Stanić<sup>2</sup>,  
Sanja Radman<sup>3</sup>, Tibela Landeka Dragičević<sup>1</sup>

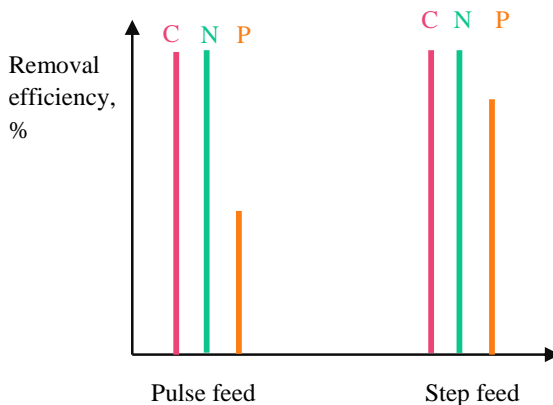
<sup>1</sup>University of Zagreb, Faculty of Food Technology and Biotechnology, Pierotti Str. 6, 10000  
Zagreb, Croatia

<sup>2</sup>J. J. Strossmayer University of Osijek, Faculty of Food Technology Osijek, F. Kuhača 18,  
31000 Osijek, Croatia

<sup>3</sup>University of Split, Faculty of Chemistry and Technology, R. Boškovića 35, 21000 Split,  
Croatia

The experiments of denitrifying dephosphatation with acetate as the carbon source and nitrite as electron acceptor were performed in two identical sequencing batch reactors (SBR). One reactor was fed with 70 mg NO<sub>2</sub>-N/L at once (pulse feed), and the second reactor was fed with 70 mg NO<sub>2</sub>-N/L added in seven steps (step feed), each step of 10 mg NO<sub>2</sub>-N/L. The experiments were performed at COD/N ratio 3 and N/P ratio 4. The results showed that 70 mg NO<sub>2</sub>-N/L added at once inhibited the denitrifying dephosphatation process. Contrary, the addition of 70 mg NO<sub>2</sub>-N/L in seven steps, each of 10 mg NO<sub>2</sub>-N/L, was beneficial for the C, N and P removal.

**Keywords:** denitrifying dephosphatation, electron acceptor, nitrite inhibition





## OBRADA OTPADNE VODE GRADA AEROBNIM GRANULAMA MUNICIPAL WASTEWATER TREATMENT BY AEROBIC GRANULES

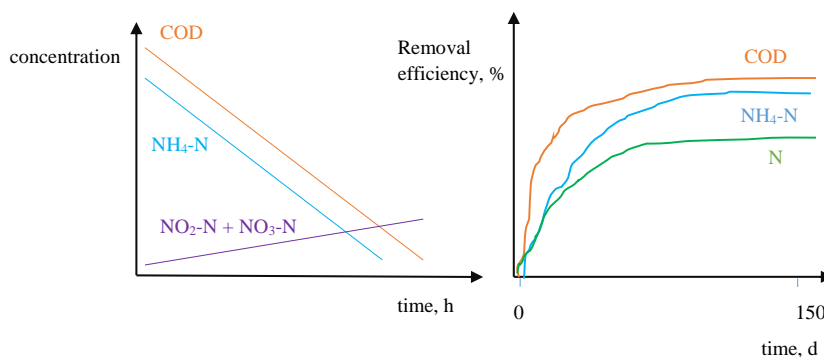
Dijana Grgas<sup>1</sup>, Marija Biškup<sup>1</sup>, Mirjana Galant<sup>2</sup>, Tea Štefanac<sup>1</sup>,  
Tibela Landeka Dragičević<sup>1</sup>

<sup>1</sup>University of Zagreb, Faculty of Food Technology and Biotechnology, Pierotti Str. 6, 10000  
Zagreb, Croatia

<sup>2</sup>Usluga odvodnja d.o.o., Šime Kurelića 22, 52000 Pazin, Croatia

The potential of aerobic granules for the municipal wastewater treatment was investigated. The synthetic wastewater with acetate as the carbon source at the COD/N ratio 4 was used. The experiments were performed at volumetric exchange ratio of 50% with mature granules in the sequencing batch reactor (SBR). The simultaneous nitrification and denitrification (SND) was responsible for nitrogen (N) removal. The granules formation were maintained during the 150 days of experiments. The chemical oxygen demand (COD) and  $\text{NH}_4\text{-N}$  removal was recorded over 90%, however, the COD/N ratio was not enough for the complete denitrification of  $\text{NO}_2\text{-N}$  and  $\text{NO}_3\text{-N}$ .

*Keywords:* aerobic granules, municipal wastewater, low C/N ratio



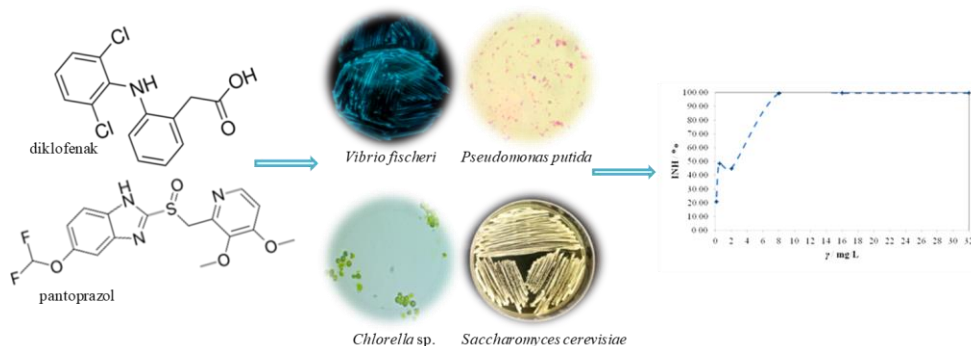
## ISPITIVANJE EKOTOKSIČNOSTI DIKLOFENAKA I PANTOPRAZOLA INVESTIGATION OF ECOTOXICITY OF DICLOFENAC AND PANTOPRAZOLE

Karlo Grgurević, Martina Miloloža, Dajana Kučić Grgić

Fakultet kemijskog inženjerstva i tehnologije Sveučilišta u Zagrebu, Trg Marka Marulića 19,  
10000 Zagreb, Hrvatska

Usljed antropogenog djelovanja, ksenobiotici dopijevaju u okoliš. Ksenobiotici, među koje se ubrajaju farmaceutici, antibiotici, otrovi te pesticidi, su tvari koje su biološki aktivne, a zaostaju u okolišu u visokim koncentracijama s obzirom na njihovu jaku postojanost i bioakumulaciju. Prema tome, potrebno je istraživati njihov utjecaj na organizme u okolišu. U ovome je radu istraživana ekotoksičnost dvaju ksenobiotika, diklofenaka i pantoprazola, na četiri testna organizma: morskoj bakteriji *Vibrio fischeri*, bakteriji *Pseudomonas putida*, mikroalgi roda *Chlorella*, te kvascu *Saccharomyces cerevisiae*. Ispitivan je ekotoksični utjecaj svakog navedenog ksenobiotika, ali i njihove smjese u omjerima 1:1, 2:1 i 1:2. Za navedeno je proveden test ekotoksičnosti s *V. fischeri* tijekom 30 min izloženosti uz praćenje smanjenja bioluminiscencije bakterije. Ukupan broj živih stanica bakterija (CFU) *P. putida* te mikroalgi *Chlorella* sp., pratio se tijekom 3 dana provedbe pokusa u svrhu uočavanja ekotoksičnog utjecaja na rast navedenih mikroorganizama. Tijekom istog vremena izloženosti, provodio se i pokus sa *S. cerevisiae* u kojem se pratio volumen nastalog CO<sub>2</sub>, odnosno volumen istisnute tekućine. Rezultati promjene inhibicije u odnosu na ispitivane koncentracije diklofenaka i pantoprazola su prikazani karakterističnom krivuljom doza-odgovor, a najosjetljiviji testni organizmi pokazali su se *S. cerevisiae* te *V. fischeri*.

**Ključne riječi:** ekotoksičnost, *Vibrio fischeri*, *Pseudomonas putida*, *Chlorella* sp., *Saccharomyces cerevisiae*



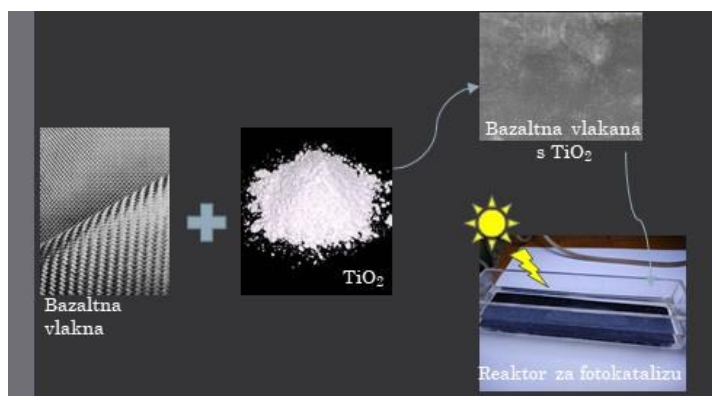
## BAZALTNA VLAKNA KAO NOSIIOC FOTOKATLIZATORA TITAN(IV) OKSIDA BASALT FIBERS AS A CARRIER OF TITANIUM(IV) OXIDE PHOTOCATALYST

Igor Jajčinović, Ivan Brnardić, Lidija Peharec

Metalurški fakultet Sveučilišta u Zagrebu, Aleja narodnih heroja 3, 44000 Sisak, Hrvatska

Razvojem analitičkih metoda dolazi do pronalaska sve većeg broja mikroonečišćujućih tvari kao što su farmaceutici i pesticidi u otpadnim vodama ali i u vodama za piće. Za pročišćavanje voda od mikronečišćujućih tvari u svijetu se koristi aktivni ugljen čija uporaba zahtijeva procese regeneracije radi slabljenja njegovog djelovanja. Posljednjih nekoliko godina intenzivno se radi na pronalaženju novih metoda pročišćavanja vode ali i zraka od ove vrste onečišćenja. Napredne oksidacijske metode pokazuju veliki potencijal za pročišćavanje ove vrste onečišćenja, a pogotovo uporaba titan(IV) oksida.  $\text{TiO}_2$  nije toksičan i lako je dostupan ima i dobra fotokatalitička svojstva što pozitivno utječe na njegov izbor kod pročišćavanja od mikroonečišćujućih tvari. Kako bi se poboljšala fotokatalitička svojstva i povećala učinkovitost,  $\text{TiO}_2$  se može dopirati sa različitim elementima kao što su srebro, dušik i slično. U ovom radu provedena je imobilizacija  $\text{TiO}_2$  na mreže od bazaltnih vlakana različitim metodama kako bi se poboljšala fotokatalitička aktivnost  $\text{TiO}_2$ . Bazaltna vlakna koriste se kao nosači fotokatalizatora radi lakšeg uklanjanja fotokatalizatora iz pročišćene vode ali i za poboljšanje fotokatalitičke aktivnosti.

*Ključne riječi:* fotokataliza,  $\text{TiO}_2$ , bazaltna vlakna



## AUTOMATSKO BROJANJE BAKTERIJSKIH KOLONIJA AUTOMATED COUNTING OF BACTERIAL COLONIES

Karlo Josić<sup>1</sup>, Martina Miloloža<sup>2</sup>, Dajana Kučić Grgić<sup>2</sup>

<sup>1</sup>Visoko učilište Algebra, Gradišćanska 24, 10000 Zagreb, Hrvatska

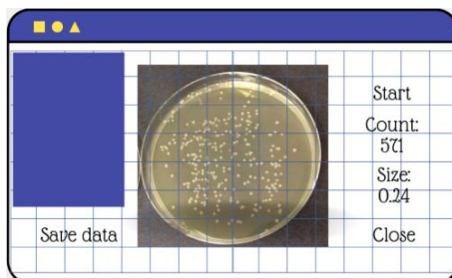
<sup>2</sup>Fakultet kemijskog inženjerstva i tehnologije Sveučilišta u Zagrebu, Trg Marka Marulića  
19, 10000 Zagreb, Hrvatska

Mikrobiološka istraživanja podrazumijevaju uzgoj mikroorganizama na hranjivoj podlozi u Petrijevim zdjelicama uz primjenu i u poljoprivredne, prehrambene te medicinske svrhe [1]. Izrasle kolonije se prebrojavaju u svrhu određivanja ukupnog broja živih stanica bakterija (*Colony Forming Units*, CFU). Određivanje CFU može biti dugotrajan postupak, pogotovo u slučaju gustog uzorka, prilikom kojeg se može lako pogriješiti. U svrhu ubrzavanja provedbe ove analize te značajne uštede vremena mikrobiolozima, postojeća se pokušava unaprijediti uz računalnu tehnologiju. U ovome radu dati će se pregled postojećih rješenja. Prvi uređaj koji se koristio za automatsko brojanje kolonija korišten je 1957. godine [1]. Slika Petrijeve zdjelice se skenirala na CRT zaslonu pomoću fotomultiplikatora, a obrada digitalizirane slike se vršila pomoću računala. Stoga, glavni dijelovi automatskog brojača su kamera i računalo s odgovarajućim softverom za obradu slike. Novija inačica koja je ispitivana čini *Sony cyber shot* kamera uz Biowizard softver za analizu slike [1]. U usporedbi s ručnim brojanjem kolonija i drugim komercijalnim softverima, dobiveni su bolji rezultati o parametrima kolonija uz kraće vrijeme analize primjenom Biowizard-a. Nekoliko automatiziranih sustava za brojanje kolonija je komercijalno dostupno (poput ProtoCOL, Whitley aCOLyte, AID BacSpot), ali nemaju široku upotrebu zbog njihove visoke cijene [2]. Stoga je potrebno usmjeriti daljnja istraživanja u razvoj i povećanje preciznosti automatiziranog sustava uz dostupnost za laboratorijske upotrebe.

*Ključne riječi:* mikrobiologija, CFU, automatsko brojanje kolonija, programiranje, softveri

[1] S. Raju, A. H.G., A. V. Krishnan, D. Naryanan, V. Gangadhran, S. C. Paul, *J. Multi. Dent. Res.* 5 (2019) 17-19.

[2] S. D. Brugger, C. Baumberger, M. Jost, W. Jenni, U. Brugger, K. Mühlemann, *PlosOne.* 7 (2012) e33695.



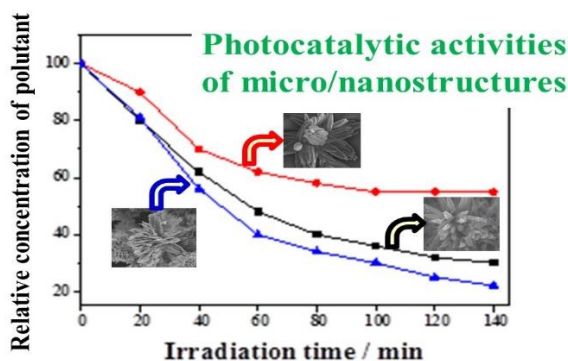
## MIKRO/NANOSTRUKTURE ZA FOTOKATALITIČKO PROČIŠĆAVANJE VODE MICRO/NANOSTRUCTURES FOR PHOTOCATALYTIC WATER TREATMENT

Magdy Lučić Lavčević, Luka Gujinović

Faculty of Chemistry and Technology, University of Split, Ruđera Boškovića 35,  
21000 Split, Croatia

In recent years, many researchers have focused on developing simple methods for a large-scale synthesis of nanoscale materials with full control of morphology, because size, shape, crystal structure and porosity are crucial factors in determining their chemical, optical, and electrical properties. Among nanoscale materials, hierarchical metal oxides are particularly important, owing to their advantages such as high surface area and multiscale porosity, which enhance their photocatalytic and antimicrobial activity. Zinc oxide is well known as a material that forms various hierarchical morphologies at the micro- and nanoscale, which act as excellent photocatalysts in the case of ultraviolet irradiation. However, some morphologies can also provide zinc oxide catalysts that are functional in the sunlight. Photocatalytic degradation of an organic dye, as a model pollutant, was studied in sunlight, in aqueous solutions with hierarchical porous micro/nanostructures of zinc oxide in the form of flowers. Flowers have been successfully obtained by three different methods: introducing an organic surfactant during a solution phase route, introducing microalgal surfactant in a green synthesis route and using a template-based synthesis. Morphology of these complex structures was characterized by scanning electron microscopy, X-ray diffraction and scattering analysis. Their morphological characteristics were compared and correlated to their photocatalytic activities.

*Keywords:* nanostructures, ZnO, photocatalyst



## RASPOZNAVANJE KARBONATNIH ČESTICA U VODI DISTINGUISHING CARBONATE PARTICLES IN WATER

Aleksandar Maksimović, Vlasta Mohaček Grošev  
Institut Ruđer Bošković, Bijenička c. 54, 10000 Zagreb, Hrvatska

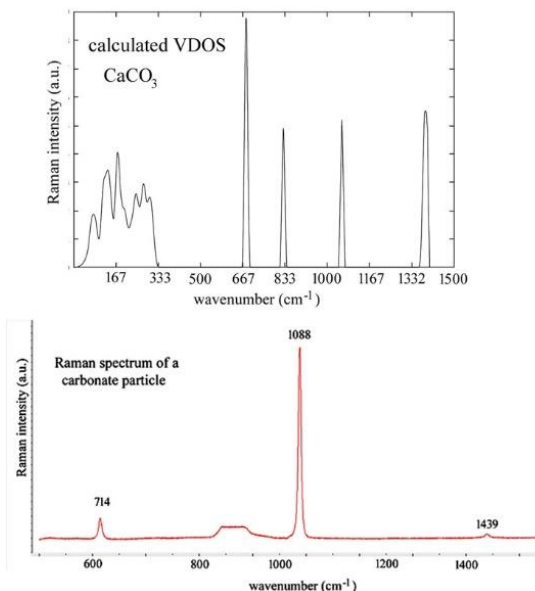
U sklopu analize filtrata vode koja se provodi u sklopu projekta JamINNO+ [1] koristeći metodu Ramanove spektroskopije, pokazalo se da je mnoštvo čestica karbonatnog porijekla [2]. Analizirajući vibracije kristalnih sistema  $XCO_3$  ( $X=Ca, Mg, Zn$ ) programom YPHON [3], dobivene su vibracije nešto nižih valnih brojeva od opaženih (vidi sliku). Totalno simetrična vibracija  $CO_3^{2-}$  iona pojavljuje se na najnižim valnim brojevima u kalcitu  $CaCO_3$ , na najvišim u  $MgCO_3$ , dok je za  $ZnCO_3$  između oba spomenuta. Najveći broj čestica u vodi je kalcitnog sastava.

*Ključne riječi:* kalcit, vibracijska gustoća stanja (eng. VDOS) Raman, mikroplastika

[1] „Razvoj funkcionalnog pića u održivoj ambalaži JamINNO+“, projekt iz poziva Ministarstva gospodarstva i održivog razvoja broj KK.01.2.1.02

[2] N. V. Kalinin, A. V. Saleev, I. Benzen, *Computer Optics* 42 (2018) 263.

[3] Y. Wang, L.-Q. Chen, Z.-K. Liu, *Comp. Phys. Comm.* 185 (2014) 2950.



**FOLIJARNA APLIKACIJA KAOLINA SMANJUJE  
 OKSIDACIJSKI STRES, POBOLJŠAVA FOTOSINTETSKU  
 UČINKOVITOST I SADRŽAJ KLOROFILA U LISTOVIMA  
 KRUŠKE TIJEKOM LJETNOG STRESA  
 FOLIAR APPLICATION OF KAOLIN CLAY REDUCES  
 OXIDATIVE STRESS, IMPROVE PHOTOSYNTHETIC  
 EFFICIENCY AND CHLOROPHYLL CONTENT IN THE  
 LEAVES OF PEER TREES DURING SUMMER STRESS**

Ines Mihaljević, Marija Viljevac Vuletić, Dominik Vuković, Vesna Tomaš  
 Agricultural institute Osijek, Južno predgrađe 17, 31000 Osijek, Croatia

Kaolin is natural clay, and its spray application creates a thin protective layer on the plant surface. It protects plants from adverse abiotic stresses, which improves their yield and quality. In this experiment, a kaolin particle film application was tested on pear leaves during summer conditions, with the aim of evaluate the benefits of kaolin under stressful conditions (high temperature and excessive irradiation). The investigation was carried out in experimental orchard of Agricultural institute Osijek, Croatia. Two pear cultivars were included in experiment: Abate Fetel and Conferance. We analysed and compared photosynthetic efficiency, chlorophyll and carotenoid contents, MDA, H<sub>2</sub>O<sub>2</sub>, phenols and enzymatic antioxidative activity between kaolin sprayed and water sprayed (control) plants under field conditions during warm day. The obtained results indicate that kaolin clay application could improve the leaf physiology, chlorophyll content, and photosynthetic efficiency of pear trees subjected to heat and excessive light. Kaolin reduced oxidative stress, alleviated membrane damage and regulated the activities of antioxidant enzymes. Therefore, kaolin application in pear trees has shown potential as a summer stress prevention strategy. This study provides insights into the physiological adaptation of pear trees to high temperature and excessive light after kaolin applications, which may be also useful in production of other fruit trees affected by climate changes.

*Keywords:* kaolin clay, pear, oxidative stress, photosynthesis

Abate fetel	PI <sub>total</sub>	Chl <i>a + b</i>	Car	MDA	H <sub>2</sub> O <sub>2</sub>	PPO	GPOD	Phenols
<b>Control</b>	3.21	1.28	0.21	18.66	17.86	9.47	0.95	42.66
<b>Kaolin</b>	4.99	1.45	0.23	16.72	14.65	6.16	0.45	44.23
	*	*	ns	*	*	*	*	ns

Conferance	PI <sub>total</sub>	Chl <i>a + b</i>	Car	MDA	H <sub>2</sub> O <sub>2</sub>	PPO	GPOD	Phenols
<b>Control</b>	3.42	1.37	0.22	19.44	17.80	12.47	1.09	52.10
<b>Kaolin</b>	6.07	1.65	0.25	17.98	16.63	8.56	1.20	45.37
	*	*	*	*	ns	*	ns	*

\*PI<sub>total</sub>-photosynthetic efficiency; Chl *a+b*-total chlorophyll content; Car-carotenoid content; MDA- malondialdehyde content; H<sub>2</sub>O<sub>2</sub>-hydrogen peroxide; PPO- polyphenol oxidase activity; GPOD- guaiacol peroxidase activity; Phenols- total phenols content

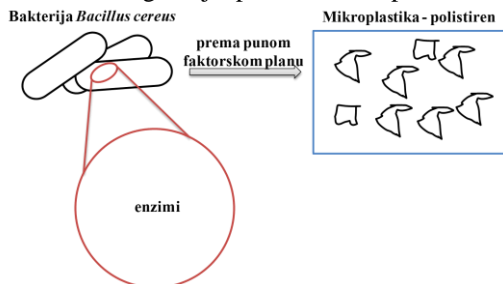
**ODREĐIVANJE OPTIMALNIH UVJETA  
BIORAZGRADNJE MIKROPLASTIKE PRIMJENOM  
BAKTERIJE *Bacillus cereus*  
DETERMINATION OF OPTIMAL CONDITIONS FOR  
MICROPLASTICS BIODEGRADATION BY BACTERIUM  
*Bacillus cereus***

Martina Miloloža, Kristina Bule, Viktorija Prevarić, Matija Cvetnić,  
Marinko Markić, Tomislav Bolanča, Vesna Očelić Bulatović,  
Šime Ukić, Dajana Kučić Grgić

<sup>1</sup>Fakultet kemijskog inženjerstva i tehnologije Sveučilišta u Zagrebu,  
Trg Marka Marulića 19, 10 000 Zagreb, Hrvatska

Od 1970. godine pozornost znanstvenika usmjerena je na onečišćenje okoliša mikroplastikom. Mikroplastikom se definiraju čestice veličine manje od 5 mm. Pronađene su u svim sastavnicama okoliša, oceanima, morima, rijekama, jezerima, sedimentu te tlu, ali i čak u hrani. Zaostajanjem u okolišu i bioakumulacijom čestica mikroplastike u vodenim organizmima predstavlja ekološki rizik. S obzirom na navedeno potrebno je istraživati postupke uklanjanja mikroplastike iz okoliša. Perspektivan postupak je bioremedijacija onečišćenoga okoliša primjenom bakterija. U ovome su radu određivani optimalni uvjeti biorazgradnje polistirena primjenom bakterije *Bacillus cereus*. Pokus se proveo prema punom faktorskom planu (eng. *Full Factorial design*) uz ispitivanje 3 čimbenika (veličina čestica mikroplastike, koncentracija mikroplastike i broj okretaja rotacijske tresilice) na 3 razine (najniža, srednja i najviša vrijednost). Tijekom 30 dana provođenja pokusa pratio se ukupni broj živih stanica bakterije (CFU), koncentracije ukupnog, organskog i anorganskog ugljika te su se čestice mikroplastike analizirale FTIR spektroskopijom. CFU se mijenjao tijekom provedbe pokusa, odnosno uočene su eksponencijalna i stacionarna faza rasta bakterije. Koncentracija organskog i anorganskog ugljika mijenjala se po istom trendu kao i CFU. Prema rezultatima FTIR spektroskopije, potvrđeno je narušavanje strukture čestica polistirena. Provedeno istraživanje ukazuje da ispitivana bakterijska kultura ima sposobnost biorazgradnje čestica mikroplastika.

**Ključne riječi:** mikroplastika, biorazgradnja, puni faktorski plan, *Bacillus cereus*





## AQUATIC TOXICITY OF MICROPLASTICS AND MICROCRYSTALLINE CELLULOSE USED AS ABRASIVES IN COSMETICS

Martina Miloloža<sup>1</sup>, Ula Rozman<sup>2</sup>, Dajana Kučić Grgić<sup>1</sup>, Gabriela Kalčikova<sup>2</sup>

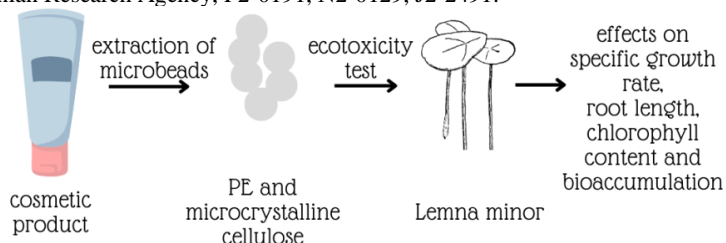
<sup>1</sup>University of Zagreb, Faculty of Chemical Engineering and Technology,  
Trg Marka Marulića 19, 10 000 Zagreb, Croatia

<sup>2</sup>University of Ljubljana, Faculty of Chemistry and Chemical Engineering, Večna pot 113,  
1000 Ljubljana, Slovenia

Pollution by microplastics, i.e. particles smaller than 1 mm, is an environmental problem because these particles are detected in all environmental components. One of the sources of microplastics are cosmetic products where microplastics, called microbeads, are used as abrasives. In latest years, the use of microplastics in cosmetics have been limited and these abrasive materials have been replaced by various materials e.g. by microcrystalline cellulose and other materials that have not been yet tested for possible adverse effects. In this context, the ecotoxicity of polyethylene microplastics and microcrystalline cellulose particles extracted from a cosmetic product was tested by using duckweed *Lemna minor* growth inhibition test. The experiment was performed in 100 mL beakers containing 50 mL Steinberg medium, *Lemna minor* and polyethylene microplastics or microcrystalline celluloses particles (100 mg/L). The experiment was performed in a climate chamber at  $24 \pm 2$  °C and high humidity (> 70%) with a photoperiod of 16/8 h (light/dark) during an exposure time of 7 days. The effects of both particles on specific growth rate, root length and chlorophyll content were monitored. The bioaccumulation of particles on *Lemna minor* biomass was also investigated. Results showed no significant effects of both particles on specific growth rate and chlorophyll contents, but microcrystalline cellulose particles affected the root length of *Lemna minor* and accumulated on plant biomass in higher quantity in comparison to polyethylene microplastics.

**Keywords:** microplastics, microbeads, polyethylene, microcrystalline cellulose particles, ecotoxicity, *Lemna minor*

**Acknowledgments:** This work was financed by the Croatian Science Foundation through project entitled Advanced Water Treatment Technologies for Microplastics Removal (AdWaTMiR) (IP-2019-04-9661) and the Slovenian Research Agency, P2-0191, N2-0129, J2-2491.



## INFLUENCE OF WHEAT PULP IN PRINTING SUBSTRATE ON THE CHEMICAL STABILITY OF GRAVURE PRINTS UTJECAJ PŠENIČNE PULPE U TISKARSKOJ PODLOZI NA KEMIJSKU STABILNOST BAKROTISKARSKIH OTISAKA

Ivana Plazonić, Valentina Radić Seleš, Maja Rudolf,  
Katja Petric Maretić, Irena Bates

University of Zagreb, Faculty of Graphic Arts, Getaldićeva 2, 10000 Zagreb, Croatia

Today, the global emphasis is on the importance and necessity of recycling all types of waste. In the paper industry, waste paper has been a very important raw material for decades resulting in recycled cellulose fibres. As cellulose fibres become shorter with each recycling cycle, it is necessary to add virgin fibres to the paper pulp to achieve the required quality and stability of the formed paper. Enriching the pulp of recycled fibres with alternative non-wood fibres could be one of the environmentally friendly approaches to paper production. Wheat straw, as a by-product of globally available field crop, has imposed itself as a logical choice of alternative raw material. From the pulp of recycled fibres and from pulp admixture of 70% of recycled fibres and 30% of wheat fibres, laboratory papers were formed and served as the printing substrates for this study. The possibility of using such papers as printing substrates was assessed based on the chemical stability of the prints produced by the gravure printing technique with two types of inks (conventional and UV). Namely, gravure is the most common technique in printing packaging and the chemical stability of prints is one of the very important requirements in packaging printing.

*Keywords:* chemical stability, gravure prints, printing substrate, wheat pulp

**Acknowledgment:** This work has been supported in part by Croatian Science Foundation under the project „Printability, quality and utilization of substrates with non-wood fibres“ (UIP-2017-05-2573)



## OPTIMAL REMOVAL OF TOLPERISONE FROM WATERS BY PHOTOCATALYSIS, NANOTECHNOLOGY AND CHEMOMETRICS

Predrag Putnik<sup>1</sup>, Szabolcs Bognár<sup>2</sup>, Ivana Maksimović<sup>3</sup>, Branko Velebit<sup>4</sup>,  
Marina Putnik-Delić<sup>3</sup>, Daniela Šojić Merkulov<sup>2</sup>

<sup>1</sup>University North, Department of Food Technology, Trg dr. Žarka Dolinara 1, 48000 Koprivnica, Croatia

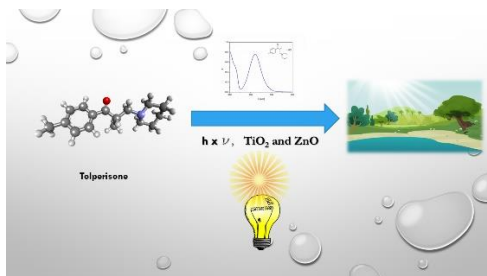
<sup>2</sup>University of Novi Sad, Faculty of Sciences, Department of Chemistry, Biochemistry and Environmental Protection, Trg Dositeja Obradovića 3, 21000 Novi Sad, Serbia

<sup>3</sup>University of Novi Sad, Faculty of Agriculture, Trg Dositeja Obradovića 8, 21000 Novi Sad, Serbia

<sup>4</sup>Institute of Meat Hygiene and Technology, Kaćanskog 13, 11040 Belgrade, Serbia

Environmental pollution with various pharmaceuticals is becoming serious global issue. When various chemicals are released into environmental waters above capacity for their removal they disturb the ecosystems of flora and fauna in both, water and (indirectly) in terrestrial ecosystems. For instance, pharmaceutical compounds as tolperisone (TLP) are toxic for waters, especially for plants and should be removed from environment. One promising option for water purification is heterogenous photocatalytic degradation with different photocatalysts. Consequently, this research employed the photodegradation of the TLP with two photocatalysts, TiO<sub>2</sub> and ZnO under simulated solar and UV irradiation. Evaluated parameters included optimal catalyst loading, length of irradiation, type of light, and degradation of TLP was monitored by the UFLC-DAD and LC-ESI-MS. Environmental toxicity of TLP in plants was examined with wheat evaluating germination, biomass production and photosynthetic pigments of the plant. Chemometric analysis was used to evaluate experimental relations in results. Data showed that the best removal of TLP was with TiO<sub>2</sub>, at optimal catalyst loading of 1.0 mg/cm<sup>3</sup> after 60.83 min of irradiation under UV light. Moreover, it was detected that germination, biomass production, and chlorophyll b (Chl b) were not related with percentage of TLP after irradiation. Whereas, chlorophyll a (Chl a) ( $r=-0.61$ ,  $p\leq 0.05$ ), Chl a+b ( $r=-0.56$ ,  $p\leq 0.05$ ), and carotenoid (car) ( $r=-0.57$ ,  $p\leq 0.05$ ) were strongly inversely (negatively) correlated with TLP concentration, while Chl a+b/car ( $r=0.36$ ,  $p\leq 0.05$ ) was moderately (positively) related.

**Keywords:** Photosynthetic pigments; Toxicity mechanism; Wheat biomass germination; Tolperisone; TiO<sub>2</sub>/ZnO

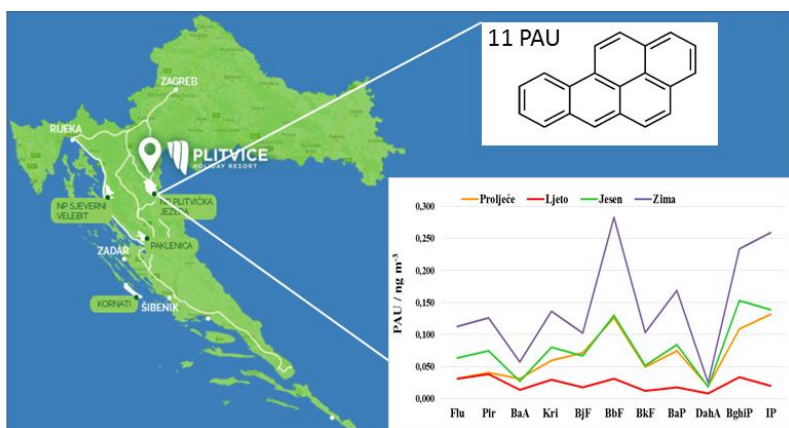


## POLICIKLIČKI AROMATSKI UGLJIKOVODICI U ZRAKU NACIONALNOG PARKA PLITVIČKA JEZERA POLYCYCLIC AROMATIC HYDROCARBONS IN THE AIR AT THE PLITVICE NATIONAL PARK

Zdravka Sever Štrukil, Ivana Jakovljević, Gordana Pehnc, Ivan Bešlić  
Institut za medicinska istraživanja i medicinu rada, Ksaverska cesta 2, 10000 Zagreb,  
Hrvatska

Policiklički aromatski ugljikovodici (PAU) su vrlo rasprostranjeni u okolišu, a mogu nastati prirodnim putem ili antropogenim utjecajem. Emisija PAU iz prirodnih izvora znatno je niža od one koju uzrokuje ljudska djelatnost, pri čemu koncentracija PAU ovisi o načinu proizvodnje energije, gustoći prometa, industrijskoj emisiji, grijanju u kućanstvima i dr. Na pozadinskoj mjernoj postaji udaljenoj nekoliko kilometara od izravnog utjecaja lokalnih izvora onečišćenja unutar najstarijeg nacionalnog parka u Hrvatskoj, NP Plitvička jezera provedeno je uzorkovanje PM<sub>10</sub> frakcije lebdećih čestica sakupljanjem 24-satnih uzoraka neprekidno tijekom 30 dana u svakom godišnjem dobu u 2021. godini. Koncentracije 11 mjerenih PAU (fluoranten (Flu), piren (Pir), benzo(a)antracen (BaA), krizen (Kri), benzo(j)fluoranten (BjF), benzo(b)fluoranten (BbF), benzo(k)fluoranten (BkF), benzo(a)piren (BaP), dibenzo(a,h)antracen (DahA), benzo(ghi)perilen (BghiP) i indeno(1,2,3-cd)piren (IP)) određene su kromatografijom visoke djelotvornosti (HPLC) s fluorescentnim detektorom. Masene koncentracije PAU bile su niske za sve mjerene PAU i kretale su se u rasponu 0,008 ng m<sup>-3</sup> za DahA do 0,283 ng m<sup>-3</sup> za BbF, te pokazuju sezonsku ovisnost s koncentracijama tri do dvanaest puta višim u zimi nego ljeti.

*Ključne riječi:* PM<sub>10</sub> frakcija, HPLC, sezonske varijacije



## Praćenje i suzbijanje *Halyomorpha halys* u nasadu kruške u istočnoj Slavoniji

### Monitoring and control of *Halyomorpha halys* in a pear orchard in Eastern Slavonia

Vesna Tomaš<sup>1</sup>, Ines Mihaljević<sup>1</sup>, Dominik Vuković<sup>1</sup>,  
Marija Viljevac Vuletić<sup>1</sup>, Željko Budinščak<sup>2</sup>

<sup>1</sup>Agricultural institute Osijek, Južno predgrađe 17, 31000 Osijek, Hrvatska

<sup>2</sup>Hrvatska agencija za poljoprivredu i hranu, Centar za zaštitu bilja, Gorice 68b, 10000 Zagreb, Hrvatska

*Halyomorpha halys* je invazivna, polifagna vrsta stjenice, porijeklom iz istočne Azije. U Hrvatskoj je prvi puta otkrivena 2017. godine u Rijeci, Primorsko-goranska županija. U posljednje dvije godine bilježimo njezino pojavljivanje u sve većem broju kao i sve učestalije štete na plodovima kruške. Pokus je postavljen na pokusnom nasadu kruške Poljoprivrednog instituta Osijek, Odjela za voćarstvo. Cilj ovog istraživanja je bio utvrditi učinkovitost četiri tretmana (T1- acetamid+ polimeri (0,05 % + 0,15 %); T2- spiroetramat + polimeri (0,15 % + 0,15 %); T3-deltametrin + polimeri (0,05 % + 0,15 %); T4-tretman s vodom, kontrolni tretman) u suzbijanju razvojnog stadija ličinki (L1-L5) i imaga po principu metode “privuci i ubij”. U pokusni nasad je postavljen feromon za praćenje štetnika. Oko feromona obilježena su pokusna stabla (tri stabla po tretmanu u dva ponavljanja, reda). Ispod pokusnih stabala postavljena je bijela agrotekstilna podloga za lakše praćenje uginule populacije štetnika nakon tretmana u vremenskim intervalima od 5, 24 i 48 sati. Najbolji rezultat pokazao je tretman 1 u odnosu na ostale tretmane u istraživanju u sva tri praćenja.

*Ključne riječi:* *Halyomorpha halys*, invazivna vrsta, kruška, suzbijanje, praćenje

TRETMAN	LIČINKE (L1-L5)	IMAGO
1	35.11 a	0,88 a
2	9.83 b	0,05 b
3	5.55 b	0,05 b
4	0.00 b	0,00 b

## FILTRATION OF COKING WASTEWATER THROUGH GRANULAR ACTIVATED CARBON FILTER SEEDED WITH BIOMASS

Ana Tutić<sup>1</sup>, Viktorija Prevarić<sup>2</sup>, Martina Miloloža<sup>2</sup>, Šime Ukić<sup>2</sup>,  
Dajana Kučić Grgić<sup>2</sup>, Marinko Markić<sup>2</sup>, Laszlo Sipos<sup>2</sup>

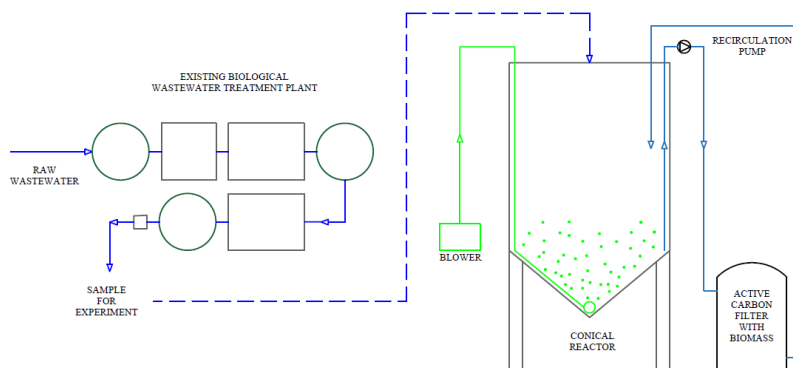
<sup>1</sup>BP group d.o.o., Glavna 2, 31309 Kneževi Vinogradi, Croatia

<sup>2</sup>University of Zagreb, Faculty of Chemical Engineering and Technology,  
Marulićev trg 20, 10000 Zagreb, Croatia

Granular activated carbon (GAC) was used as a support for biomass growth in biological filtration process treating coking wastewater with the aim of reducing ammonia concentration. Advantages of such media are high specific surface area, porous microstructure and low production cost [1]. Wastewater after treatment in a two-stage biological plant, using activated sludge technology is subjected to biological filtration. The wastewater enters a conical reactor, volume 15 L, which is aerated via a perforated tube and a blower, from where it is recirculated to the activated carbon column seeded with activated sludge from municipal wastewater treatment plant. Kinetic experiments were performed for 24 hours and samples were collected through that period. Ammonia concentration was reduced from 56.39 mg/L and 66.31 mg/L to 14.62 mg/L and 19.95 mg/L, respectively.

**Keywords:** coking wastewater, filtration, GAC, biology

[1] Z. Wenjie, W. Huaqin, D.R. Joseph, J. Yue, *Global NEST J.* 17 (2015) No 3.



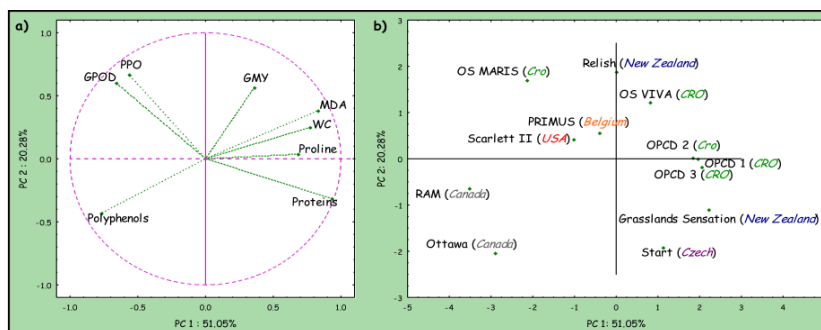
**Figure 1.** Treatment of cooking wastewater

## UTJECAJ TOPLINSKOG VALA NA FIZIOLOŠKI STATUS I PRINOS ZELENE MASE CRVENE DJETELINE HEAT WAVE IMPACT ON PHYSIOLOGICAL STATUS AND GREEN MASS YIELD OF RED CLOVER

Marija Viljevac Vuletić, Daniela Horvat, Marija Kovačević Babić,  
Tihomir Čupić, Marijana Tucak  
Agricultural Institute Osijek, Južno predgrađe 17, 31 000 Osijek, Croatia

Heat wave, as a result of climate change, is an increasingly common phenomenon in eastern Croatia. During the early summer of 2021, eastern Slavonia experienced a severe heat wave with maximal daily temperature peak at 38.9 °C. Here, we report impact of heatwave on plant antioxidative status after unfavorable conditions and consequently on green mass yield (GMY) of 12 red clover cultivars or breeding populations of different origin and therefore, different tolerance to heat. Canadian cultivars Ottawa and RAM converged with the lowest water content (WC) and the highest polyphenols which indicates that polyphenols played a leading role in the stress response of those cultivars. Heat wave response of cultivar OS MARIS was arranged by activation of enzymes guaiacol peroxidase (GPOD) and polyphenol oxidase (PPO). Heat wave activated both enzymatic and non-enzymatic response mechanisms and ultimately influenced GMY. Principal component analysis (PCA) grouped Croatian cultivar OS VIVA and OPCDs in the same quadrant with GMY indicating that heat the least influenced GMY in those cultivars and therefore sort out them as potential source of tolerance to stressful conditions.

**Keywords:** antioxidative status, climate change, heat stress tolerance



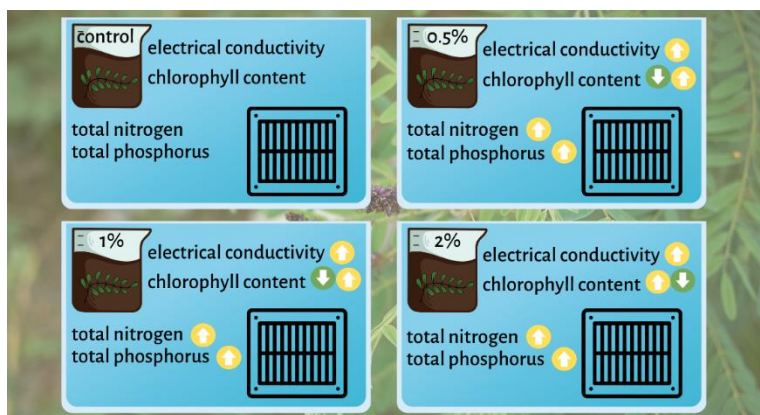


## FITOTOKSIČNI UTJECAJ ČIVITNJAČE (*AMORPHA FRUTICOSA* L.) NA RAZVOJ OBRAŠTAJA PHYTOTOXIC EFFECT OF INDIGOSBUSH (*AMORPHA FRUTICOSA* L.) ON PERIPHYTON DEVELOPMENT

Tanja Žuna Pfeiffer, Dubravka Špoljarić Maronić, Filip Stević, Mario Šimić,  
Nikolina Bek, Matej Šag, Ljiljana Krstin  
Department of Biology, Josip Juraj Strossmayer University of Osijek,  
Ulica cara Hadrijana 8/A, 31000 Osijek, Croatia

Indigobush (*Amorpha fruticosa* L.) is a deciduous shrub which extensively occupies forest edges, riversides, roadsides and many other habitat types. Allelochemicals in leaves of this invasive plant have strong phytotoxic effects and inhibit seed germination and seedling growth. In natural environments, during the decomposition of its dead mass (e.g. leaves), allelochemicals could be released into the aquatic systems. The aim of this study was to investigate the influence of the indigobush aqueous extracts (0.05, 1 and 2 %) on physical and chemical parameters as well as on periphyton development in the experimental aquatic systems. All concentrations of leaf extract caused changes in the aquatic environments - electrical conductivity, total nitrogen and total phosphorus content has a higher value compared to the control. This offered favourable conditions for periphyton development. On the last sampling day periphyton biomass in all treatments was higher than in the control. Chlorophyll content varied during the study indicating changes in the periphytic algal assemblages. The results suggest that the rapid invasion of indigobush along the riversides may affect aquatic environments and their biotic communities.

**Keywords:** experimental aquatic system, aqueous extracts, invasive plant, algae





## ISPITIVANJE KVALITETE SREDSTVA ZA SMANJENJE EMISIJE DUŠIČNIH OKSIDA DIZELSKIH VOZILA QUALITY TESTING OF THE DIESEL EXHAUST FLUID FOR REDUCING NITROGEN OXIDE EMISSION

INA D&R Central Testing Laboratory Staff

INA- Oil & Gas company, Refinery & Marketing- Development BU,  
 R&D Central Testing Laboratory, Lovinčičeva 4,10 000, Zagreb, Croatia

INA R&D Central testing laboratory is equipped with state of modern analytical instruments and our analytical services are backed by qualified and experienced staff members. It requires important for developing new products and quality control of motor fuel oils at all levels of the chain: from production to logistics and end usage. Road transport remains the main source of toxic NO<sub>x</sub> (nitrogen oxide) emissions because new European standards require a further reduction in hazardous air pollutants and emissions for diesel vehicles: passenger vehicles, trucks, construction, agricultural equipment and rail and marine engines. In 2022 the new regulation is an integral part of the EU's Green Deal, Sustainable and Smart Mobility Strategy and Zero Pollution Action Plan. The diesel exhaust fluid, AdBlue is an inexpensive and efficient option for lowering NO<sub>x</sub> emissions. The solution is added to a separate storage tank in diesel-powered vehicles equipped with a selective catalytic reduction (SCR) technology system. This system aims to significantly reduce emissions of nitrogen oxide (NO<sub>x</sub>) which are harmful to the environment and thus meet the stringent emission limits set by European standards (Euro 6) - which are standard for the control of toxic air emissions. This paper describes the results of a full range of prompt quality testing and analysis services of the diesel exhaust fluid (DEF), conforming to international test specifications ISO 22241 standards [1], [2], [3]. The introduction of some new test standard methods will certainly affect the further improvement of the quality of processes and services for external and internal customers and the efficiency of the business performance in our laboratory. This will allow for increased competitiveness and better market positioning which will ultimately affect the profitability of the entire company.

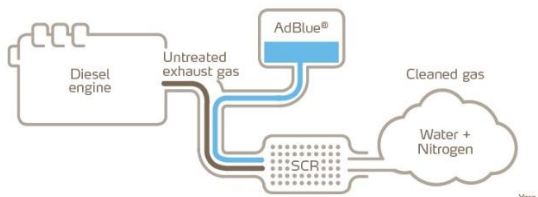
**Keywords:** diesel motor fuels, diesel exhaust fluid, control of toxic air emissions

[1] ISO 22241-1, Diesel engines -NO<sub>x</sub> reduction agent AUS 32 — Part 1: Quality requirements

[2] ISO 22241-2, Diesel engines — NO<sub>x</sub> reduction agent AUS 32 — Part 2: Test methods

[3] ISO 22241-2, Diesel engines — NO<sub>x</sub> reduction agent AUS 32 — Part 3: Handling, transportation and storage

Pollutant	Emission limits for diesel vehicles	
	Euro 5	Euro 6
HC+ NO <sub>x</sub> / gkm <sup>-1</sup>	0,23	0,17
NO <sub>x</sub> / gkm <sup>-1</sup>	0,18	0,08



**8. Susret mladih kemičara/  
*8<sup>th</sup> Meeting of Young Chemists***

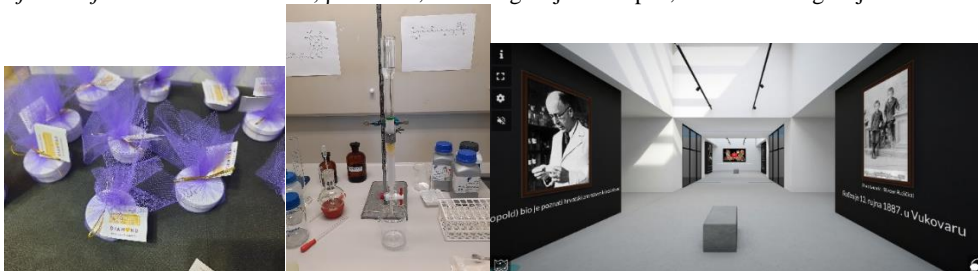
**LAVOSLAV RUŽIČKA - OSAM POČASNIH DOKTORATA ZA 8.  
SUSRET MLADIH KEMIČARA  
LAVOSLAV RUŽIČKA - EIGHT HONORARY DOCTORATES FOR  
THE 8th MEETING OF YOUNG CHEMISTS**

**Erika Mičić, Matej Maljak, Marko Šeper, Leonarda Puđa, Kiara Lemac, Anja Vinković, Marta Atanasovski, Antonija Milić, Nataša Vinković**

Gimnazija Vukovar, Šamac 2, 32000 Vukovar, Hrvatska

Očuvanje kulturne baštine i identiteta zadaća je svih nas kako bismo ostavili u nasljeđe budućim generacijama. Vođeni tom idejom inspiraciju smo pronašli u znanstvenom radu našeg sugrađanina, nobelovca Lavoslava Ružičke. Iz njegovog širokog opusa i djelovanja odabrali smo segment koji smo prilagodili vremenu u kojem živimo te ga predstavili kroz eksperimentalni rad, aktivno učenje i različite digitalne alate. Kako je Lavoslav Ružička proučavao terpene i terpenoide te za proučavanje terpena dobio Nobelovu nagradu, odlučili smo krenuti njegovim stopama. Odlučili smo proučavati terpenoide, izolirati terpenoid  $\beta$ -karoten iz špinata primjenom TLC kromatografije i kromatografije na stupcu te izolirani  $\beta$ -karoten koristiti u kremama koje proizvode naši gimnazijalci zajedno s mentoricom prof. Antonijom Milić. Uz eksperimentalni dio izolacije pigmenta koristili smo različite digitalne alate kako bismo na suvremen način prikazali naše rezultate, ali i lik i djelo našeg nobelovca. Cilj rada nam je prikazati život Lavoslava Ružičke kroz digitalni alat Art Gallery, njegov znanstveni put kroz digitalni alate Genially i Trip line u suradnji s prof. Natašom Vinković. Izolirati i kemijski dokazati terpenoid  $\beta$ -karoten iz smrznutog špinata te upotrijebiti  $\beta$ -karoten u proizvodnji krema s obzirom da  $\beta$ -karoten štiti kožu od štetnih vanjskih utjecaja, a sluznici osigurava prijeko potrebnu vlažnost pretvorbom u vitamin A. Odabrali smo kromatografiju na stupcu jer se kolonska kromatografija najčešće koristi za separaciju uzorka kako bi se izdvojila željena komponenta iz smjese, a TLC kromatografiju kako bismo izdvojili komponentu iz smjese na temelju njihovog različitog polariteta. Svaki korak istraživanja prikazali smo interaktivnim digitalnim plakatom koji ćemo predstaviti. Ovim smo radom uspjeli prezentirati zakonitosti i spoznaje na suvremen način prilagođen svim izazovima suvremene civilizacije. Budući da je Lavoslav Ružička laureat osam počasnih doktorata, a rad prezentiramo na 8. Susretu mladih kemičara, mislimo da smo indikativnim naslovom rada uspjeli zainteresirati znanstvenu javnost.

*Ključne riječi:* Lavoslav Ružička,  $\beta$ -karoten, kromatografija na stupcu, TLC kromatografija



## ODREĐIVANJE KOFEINA U ČAJU DETERMINATION OF CAFFEINE IN TEA

Centner Ena, Matuš Vladimira, Radić Maja

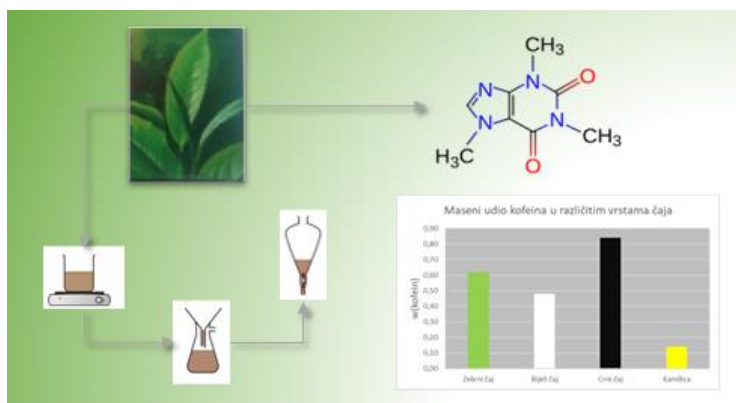
Tehnička škola Nikole Tesle Vukovar, Blage Zadre 4, 32010 Vukovar, Hrvatska

Alkaloidi su prirodni organski spojevi jakog djelovanja: već u malim količinama djeluju na središnji živčani sustav čovjeka i životinja. Poznato je više od 5000 vrsta alkaloida u preko 4000 vrsta biljaka, a najpoznatiji su morfin, kodein i heroin iz opijuma, nikotin iz lista duhana, kofein iz kave i listova čaja, strihnin iz sjemenki strihnosa, kokain iz lista koke, kinin iz kore kininovca i atropin iz velebilja. U biljkama su obično prisutni u obliku soli, rijetko u obliku slobodnih baza, a u biljci je obično jedan glavni alkaloid i više sporednih.

U ovom radu određen je maseni udio kofeina u različitim uzorcima čaja: zeleni čaj, bijeli čaj, crni čaj i kamilica, a od metoda korištene su ekstrakcija i filtracija.

Kofein je prirodni alkaloid ksantina, a spada u skupinu purinskih alkaloida. Svi purinski alkaloidi imaju nadražujući učinak na živčani sustav i srce, imaju djelovanje diuretika i protuotrova za različite vrste toksičnih tvari. Čisti kofein je bijeli kristalni prah u obliku dugih iglica bez mirisa i gorkog okusa. Djeluje kao stimulans, odnosno privremeno odgađa umor i pospanost, ali slično kao i alkohol uzrokuje dehidraciju organizma te treba biti oprezan prilikom konzumiranja prehrambenih proizvoda koji sadrže kofein.

*Gljučne riječi:* alkaloid, kofein, ekstrakcija



## KEMIJA FOTOGRAFSKOG PROCESA I FIZIKA SVJETLOSTI CHEMISTRY BEHIND THE PHOTOGRAPHIC PROCESS AND THE PHYSICS OF LIGHT

Karolina Dvojković<sup>1</sup>, Ana Kujundžić<sup>1</sup>, Marinela Ižaković Ivić<sup>2</sup>,  
Ivan Matijanić<sup>2</sup>,

<sup>1</sup>Gimnazija Vukovar, Šamac 2, 32000 Vukovar, Hrvatska

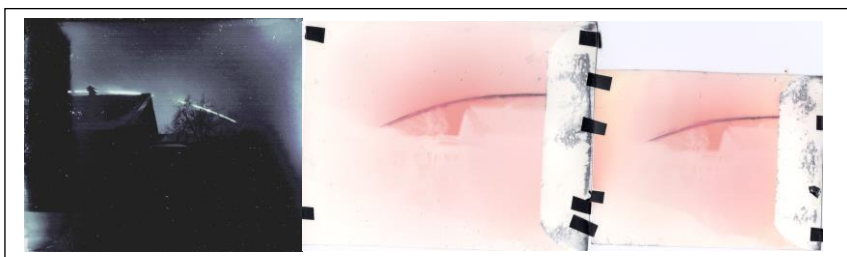
<sup>2</sup>Srednja škola Valpovo, Dr. Franje Tuđmana 2, 31550 Valpovo, Hrvatska

Riječ fotografija potječe od grčkih riječi *phos* (svjetlo) i *graphis* (crtanje). Stoga, fotografija se može definirati kao tehnika digitalnog ili kemijskog zapisivanja prizora na materijalu koji je osjetljiv na svjetlost. Primjena fotografije je široka, od dokumentarne svrhe, pa sve do umjetnosti i stvaralaštva. Fotografija je imala iznimnu važnost za Lavoslava Ružičku. Volio je ljepotu i sklad, a kako je zavolio vrtlarstvo, imao je i svoj vrt gdje je stvarao prava remek-djela. Najviše je volio ruže i alpske biljke. Zbog toga je svoje radove ovjekovječio fotoaparatom. Fotografija kao proces snimanja točnog odraza svjetla izvrsna je podloga za proučavanje kemijskih procesa. Različiti izvori svjetla i različite fotografske tehnike omogućuju učeniku ne samo razumijevanje kemijskih i fizičkih reakcija i procesa nego i ekskluzivan umjetnički izričaj. Sraz klasičnih i digitalnih fotografskih postupaka nudi bezbrojne praktične, kreativne, zabavne mogućnosti za istraživanje.

*Ključne riječi:* kemija, fizika, svjetlost, fotografski procesi, fotografija

[1] L. F. A. Mason, *Photographic Processing Chemistry*, The Focal Press, London, 1975.

[2] V. Henč-Bartolić, P. Kulišić, *Valovi i optika*, Školska knjiga, Zagreb, 1991.



## ISPITIVANJE KAKVOĆE RUČNO RAĐENOG PRIRODNOG SAPUNA TESTING THE QUALITY OF HANDMADE NATURAL SOAP

Nika Đuzel, Josipa Jurčević, Antea Kukulj, Kristina Trogrlić, Slavica Jukić  
Katolički školski centar "Don Bosco", Opća gimnazija, S. Radića b.b., 72230 Žepče, BiH

Razvitkom svijesti o štetnosti sintetičkih tvari u sredstvima za higijenu na zdravlje i okoliš, sve je veća potražnja za prirodnim sapunima. Cilj ovog rada bio je istražiti sapun pripremljen saponifikacijom maslinova, palmina, kokosova i ricinusova ulja s natrijevom lužinom. Sapun je dobiven postupkom na hladno. Obojen je prirodnim bojama, a mirisna komponenta je eterično ulje lavande. Kakvoća ovog sapuna utvrđena je kemijskom analizom i istraživanjem mišljenja korisnika ovog proizvoda. Kemijskom analizom određeni su sadržaji ukupnih alkalija, ukupnih masnih kiselina, pH vrijednost i kritična micelarna koncentracija te su uspoređeni s vrijednostima komercijalnog toaletnog sapuna. Dobiveni rezultati ukazuju na određene prednosti prirodnih sapuna.

*Ključne riječi:* prirodni sapun, saponifikacija, analiza



## UTJECAJ INHIBITORA NA AKTIVNOST SALIVARNE AMILAZE INFLUENCE OF INHIBITORS ON SALIVARY AMILASE ACTIVITY

Helena Floreani<sup>1</sup>, Teuta Muharemi<sup>1</sup>, Lucija Hunjadi<sup>1</sup>, Ivor Janković<sup>1</sup>,  
Silvija Krnić<sup>1</sup>, Nikolina Filipović<sup>2</sup>

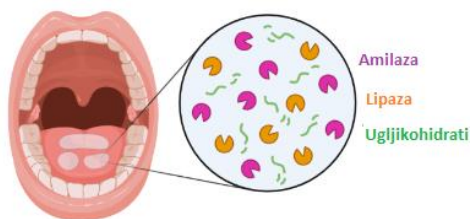
<sup>1</sup>III. gimnazija Osijek, Ul. Kamila Firingera 14, 31000 Osijek, Hrvatska

<sup>2</sup>Sveučilište J. J. Strossmayera u Osijeku, Odjel za kemiju, Ul. Cara Hadrijana 8/a,  
31000 Osijek, Hrvatska

Cilj ovog učeničkog istraživačkog rada je poticanje znatiželje za otkrivanjem svijeta oko sebe te osposobljavanje za samostalne aktivnosti učenja i istraživanja. Tijekom izrade ovog istraživanja, učenici su primijenili usvojena znanja naučena u predmetu Kemija, a koja se tiču građe enzima, povezanosti građe sa svojstvima enzima kao i načinima njihove denaturacije. Učenici su se upoznali sa  $\alpha$ -amilazom (salivarna amilaza) kao najvažnijim probavnim enzimom sline koji započinje razgradnju ugljikohidrata u usnoj šupljini i želudcu. Provedeni su pokusi prilikom kojih su ispitani čimbenici poput promjene pH i temperature te njihov utjecaj na aktivnost amilaze iz sline. Rezultati su dokazali da enzimi imaju optimalnu temperaturu i pH koji im omogućavaju normalno funkcioniranje te da će ih uvjeti drugačiji od optimalnih u potpunosti inaktivirati. Svrha je kroz jednostavan pokus povezati postojeća znanja iz područja kemije i biologije. Dobivene rezultate učenici su analizirali te prikazali i predstavili kao rezultate istraživanja drugim učenicima. Učenici su na konkretnom primjeru upoznali znanstvenu metodologiju i organizaciju istraživanja te svladali pojedine tehnike i metode istraživanja. Ovaj rad primjer je dobre prakse kako učenici uče postavljati istraživačka pitanja, predviđati ili postavljati hipoteze, samostalno opažati, razvrstavati, uspoređivati, statistički obrađivati i vrednovati podatke te zaključivati. U ovom istraživačkom radu sudjelovalo je 4 učenika različite dobne starosti. Svaki je učenik imao svoj zadatak za dodatno istraživanje koje su tada zajedno objedinili u cjelovit rad i izložili ostalim učenicima u svojim razredima.

*Ključne riječi:* izolacija DNA iz biljnog materijala, integracija biologije i kemije

[1] Odluka o donošenju kurikuluma za nastavni predmet Kemije za osnovne škole i gimnazije u Republici Hrvatskoj - [https://narodne-novine.nn.hr/clanci/sluzbeni/2019\\_01\\_10\\_208.html](https://narodne-novine.nn.hr/clanci/sluzbeni/2019_01_10_208.html)



**ANTIOKSIDACIJSKI KAPACITET POVRĆA  
UZGOJENOG U ŠKOLSKOM VRTU  
KŠC „DON BOSCO“ ŽEPČE  
ANTIOXIDATIVE CAPACITY OF VEGETABLE GROWN  
IN THE KŠC „DON BOSCO“ ŽEPČE**

Magdalena Jurić, Sandra Maglica, Renata Šimić, Maja Spajić  
Katolički školski centar „Don Bosco“ Tehničko-obrtnička škola Žepče, Stjepana Radića b.b.,  
72230 Žepče, BiH

Lisnato povrće je važan dio prehrane zbog visoke nutritivne i niske energetske vrijednosti. Uz bogat sadržaj vitamina lisnato povrće pokazuje visok antioksidativni učinak.

Cilj ovog rada bio je odrediti sadržaj biološki aktivnih spojeva u blitvi i špinatu uzgojenim na ekološki način u školskom vrtu KŠC „Don Bosco“ Žepče. Ispitivan je sadržaj ukupnih fenola i antioksidacijska aktivnost u svježim uzorcima i uzorcima konzervirani smrzavanjem u razdoblju od mjesec dana. U radu je korištena UZV ekstrakcija biološki aktivnih komponenti. Udio ukupnih fenola određen je spektrofotometrijskom Folin-Ciocalteu metodom, a antioksidacijska aktivnost ispitana je različitim metodama, ovisno o mehanizmu djelovanja: DPPH metoda (2,2-difenil-pikrilhidrazil) i ABTS metoda (2,2-azinobis(3-etilbenzotiazilin-6-sulfonat)). Dobiveni rezultati se nedvojbeno razlikuju, no svi ispitivani uzorci pokazuju izrazito dobar antioksidacijski potencijal i udio ukupnih fenola.

*Ključne riječi:* špinat, blitva, Folin-Ciocalteu, ABTS, DPPH



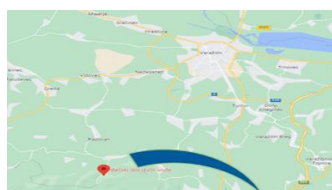
## PRAĆENJE KVALITETE VODE PRIRODNOG IZVORA BELSKI DOL MONITORING THE WATER QUALITY OF NATURAL SOURCE BELSKI DOL

Petra Novak Mlinarić, Tamara Tkalec-Car

Graditeljska prirodoslovna i rudarska škola, Hallerova aleja 3, 42000 Varaždin, Hrvatska

U današnje vrijeme sve je veći interes i potreba za kvalitetnom vodom, no istovremeno zbog sve intenzivnijeg industrijskog i poljoprivrednog razvoja te utjecaja urbanih sredina na okoliš, degradacija kvalitetne podzemne vode gotovo je neizbježna. Nažalost izuzetak nisu ni podzemne vode Varaždinske županije čiju posebnu vrijednost čine mnogobrojni prirodni izvori vode. Iz tog razloga zaštita podzemnih voda trebala bi biti jedan od glavnih preduvjeta za daljnji razvoj regije i poboljšanje kvalitete života. Maleno mjesto Bela u Varaždinskoj županiji ima svoj vlastiti vodovod izgrađen 60- tih godina prošlog stoljeća, a voda kojom se opskrbljuje dolazi iz prirodnog izvora Belski dol. Mještani imaju svoju vlastitu vodovodnu mrežu koja se nalazi ispod županijskog vodovodnog sustava. Cilj ovog rada je praćenje kvalitete izvorske vode Belski dol tijekom godine dana te utvrđivanje onečišćenja, ako postoji i u kojem obujmu. Provedena su istraživanja pH, mutnoće, električne provodnosti, koncentracije nitrata i klorida. Uočeno je da tijekom godine voda ima ujednačenu vrijednost pH i električne provodnosti dok je udio nitrata nešto veći tijekom pojačane poljoprivredne aktivnosti, a koncentracija klorida je povećana u zimskom periodu kada se sole okolne ceste. Svi parametri tijekom čitave godine su na donjim granicama prema Pravilniku o zdravstvenoj ispravnosti vode za piće što nam govori da je voda iz izvora Belski dol izvrsne kvalitete.

*Glavne riječi:* prirodni izvor vode, pitka voda, nitrati, kloridi



Datum uzorkovanja	pH	Vodljivost µS/cm	Mutnoća	Nitrati mg/l	Kloridi mg/l
16.01.2021.	7,51	449	0,00	3,55	7,09
05.02.2021.	7,72	457	0,00	3,65	7,25
04.03.2021.	7,35	450	0,00	3,68	8,05
02.04.2021.	7,52	457	0,02	3,91	4,26
07.05.2021.	7,34	456	0,46	3,98	4,07
04.06.2021.	7,27	458	0,67	3,97	3,85
08.07.2021.	7,34	458	1,82	4,00	4,72
13.08.2021.	7,47	452	0,75	3,69	4,83
09.09.2021.	7,60	459	0,67	3,82	4,80
15.10.2021.	7,37	461	0,48	3,66	4,66
12.11.2021.	7,73	459	0,00	3,60	5,23



## JEDNOSTAVNIM PUTEM DO SLOŽENIH MOLEKULA THE EASY WAY TO COMPLEX MOLECULES

Maja Skrenković<sup>1</sup>, Anja Kovač<sup>1</sup>, Dominik Vučković<sup>1</sup>, Adrian Čukić<sup>1</sup>,  
Kristina Kristek<sup>1</sup>, Nikolina Filipović<sup>2</sup>

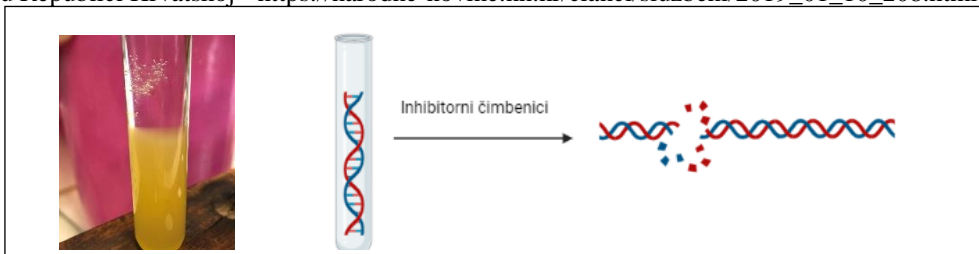
<sup>1</sup>III. gimnazija Osijek, Ul. Kamila Firingera 14, 31000, Osijek, Hrvatska

<sup>2</sup>Sveučilište J. J. Strossmayera u Osijeku, Odjel za kemiju, Ul. Cara Hadrijana 8/a,  
31000 Osijek, Hrvatska

Kemija je jedna od temeljnih prirodoslovnih znanosti koja proučava sastav, građu, svojstva i pretvorbe tvari. Učenje i poučavanje predmeta Kemija temelji se na stjecanju znanja i vještina složenim kognitivnim procesima percepcije (opažanja), znanstvene komunikacije (prikazivanje opaženoga i rasprava) te rasuđivanja (analiza rasprave, vrednovanje i donošenja zaključaka). Kemijski pokus obuhvaća sve navedene kognitivne procese, stoga je kao dio iskustvenoga učenja temeljna nastavna aktivnost.[1] Uvažavajući temelje koje nam nalaže kurikulum osmislili smo rad u kojem su učenici imali priliku primjeniti usvojena znanja na primjeru izolacije DNA molekule voća. Kemijske veze, molekulska međudjelovanja, polarnost, prostorni oblik molekula, topljivost i proces otapanja, metode razdvajanja sastojaka iz smjese, fizikalne i kemijske promjene, kiselost i lužnatost tvari, sve su to pojmovi i sadržaji koje su učenici naučili u predmetu Kemija, a sada su korišteni u svrhu razumjevanja građe ove važne molekule i time stavljeni u kontekst i konkretno primjenjeni. Provedena je izolacija DNA iz kivija i banane te je dobivena puno veća količina DNA molekula iz kivija. Izolirane DNA molekule izložene su inhibitornim čimbenicima poput visoke temperature, kiselina, lužina i soli teških metala. Analizirani su rezultati nakon čega su učenici dobili zadatak prikazati i predstaviti rezultate istraživanja drugim učenicima. U istraživanju je sudjelovalo 4 učenika i svaki je učenik imao svoju temu i zadatak za dodatno istraživanje koje su tada zajedno objedinili u cjelovit rad i izložili ostalim učenicima u svojim razredima. Svrha ovog rada je predstaviti primjer dobre prakse kako iskoristiti i povezati postojeća znanja iz područja kemije i biologije kroz jednostavan pokus izolacije DNA na način da je ona vidljiva golim okom, a potom ju analizirati kako bismo razumjeli njenu građu i važnost kao molekule koja nosi sve informacije potrebne za normalno funkcioniranje jednog organizma.

*Ključne riječi:* izolacija DNA iz biljnog materijala, integracija biologije i kemije

[1] Odluka o donošenju kurikuluma za nastavni predmet Kemije za osnovne škole i gimnazije u Republici Hrvatskoj - [https://narodne-novine.nn.hr/clanci/sluzbeni/2019\\_01\\_10\\_208.html](https://narodne-novine.nn.hr/clanci/sluzbeni/2019_01_10_208.html)



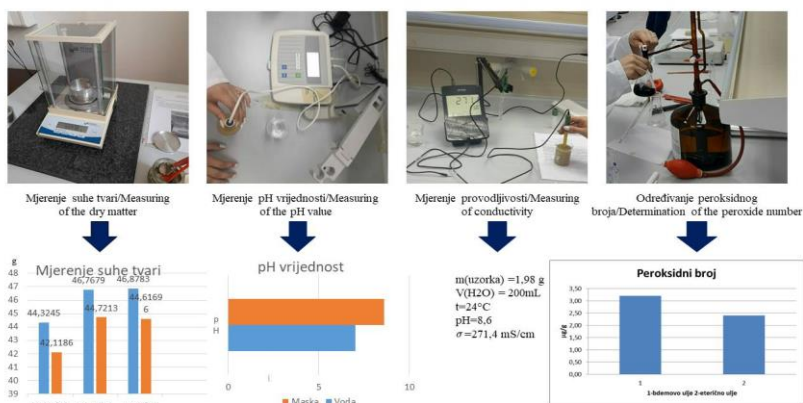
## ISPITIVANJE FIZIKALNO-KEMIJSKIH PARAMETARA MASKE ZA LICE OD ZELENE GLINE TESTING OF PHYSICO-CHEMICAL PARAMETERS OF GREEN CLAY FACE MASK

Vanja Perković, Ana Penava, Marko Tomas

Katolički školski centar „Don Bosco“, Opća gimnazija, Stjepana Radića b.b., 72230 Žepče,  
Bosna i Hercegovina

Cilj rada bio je dobiti proizvod koji ne sadrži štetne kemikalije, a daje blistavost, djeluje hidratacijski, te smiruje crvenilo i upalne procese kože lica. Maska za lice pripremljena za ovu analizu sadrži ventiliranu zelenu glinu i prirodne sastojke poput hidrolata lavande, ulja badema i eteričnog ulja čajevca. Zelena glina sadrži prirodne i netretirane nutrijente koji djeluju remineralizirajuće i detoksirajuće te podižu imunitet organizma. Mješanjem lavande i čajevca dobiva se proizvod dobrog antibakterijskog i protuupalnog djelovanja. Kvaliteta ispitivane maske utvrđena je ispitivanjem fizikalno-kemijskih parametara; pH-vrijednost, mjerenje vodljivosti, analiza teksture, određivanje peroksidnog broja po Wheeleru, određivanje vlažnosti standardnom metodom (ISO 665;1991), te recenzijom koju su dali učenici naše škole.

*Ključne riječi:* maska za lice, zelena glina, peroksidni broj po Wheeleru



## ENERGETSKI NAPITCI ENERGY DRINKS

Nikolina Velikić, Željana Milić, Đurđevka Pecikozić  
Tehnička škola Nikole Tesle, Blage Zadre 4, 32000 Vukovar, Hrvatska

Energetski napitci su bezalkoholni napitci koji povećavaju mentalne i kognitivne sposobnosti, Glavni potrošači ove vrste napitaka su adolescenti, mladi i sportaši, odnosno osobe koje zbog ubrzanog načina života žele na brz i jednostavan način održati ili povratiti energiju.

Većina osoba koje konzumiraju energetske napitke nisu upoznate s njihovim sastavom niti s posljedicama prekomjernog konzumiranja. Energetski napitci sadrže sastojke koji u ljudskom organizmu potiču razbuđivanje i brzu proizvodnju energije, a jedan od sastojaka je kofein.

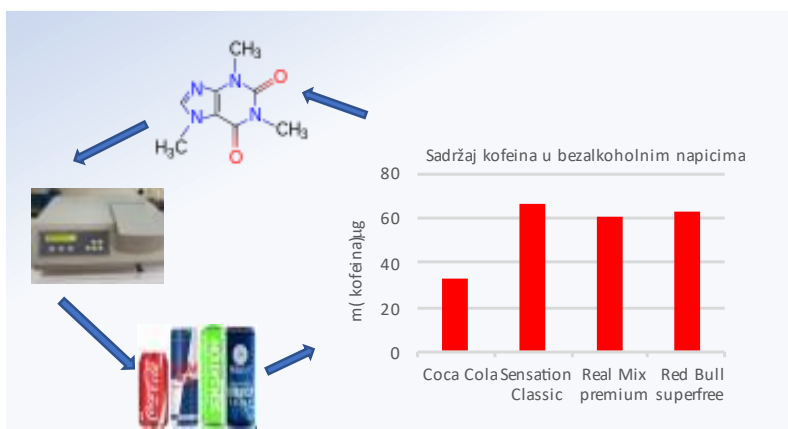
U ovom radu određen je sadržaj kofeina u četiri bezalkoholna napitka koja mladi najčešće konzumiraju Coca Cola, Sensation Classic energy drink, Real Mix premium energy drink, Red Bull sugar free.

Za određivanje sadržaja kofeina korištena je spektrofotometrijska metoda. Analizirani su isti alikvoti Coca Cole i energetskih napitaka i utvrđeno je da u Coca Coli ima dvostruko manje kofeina nego u energetskim napitcima.

Nekoliko studija pokazuje da je „sigurna“ količina kofeina za većinu odraslih, zdravih osoba oko 400 mg dnevno.

Kofein izaziva ovisnost i dehidrira organizam, dehidracija može biti ozbiljna, čak i smrtonosna.

*Ključne riječi:* energetski napitci, spektrofotometrija, kofein, ovisnost



## UTJECAJ RAZLIČITIH TEMPERATURA ČUVANJA NA SVOJSTVA PIVA KONTAMINIRANOG S *LACTOBACILLUS BREVIS* INFLUENCE OF DIFFERENT STORAGE TEMPERATURES ON THE PROPERTIES OF BEER CONTAMINATED WITH *LACTOBACILLUS BREVIS*

Antonio Mamić<sup>1</sup>, Kale Marković<sup>1</sup>, Dorotea Štefanac<sup>1</sup>, Nika Vitas<sup>1</sup>,  
Jasminka Žiža<sup>1</sup>, Ivana Ćosić<sup>2</sup>, Bojan Matijević<sup>2</sup>

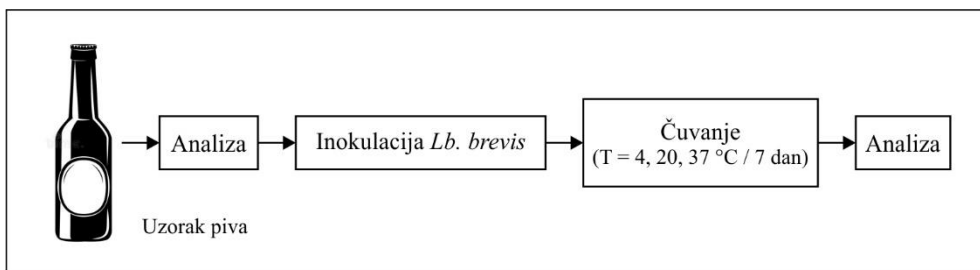
<sup>1</sup>Gimnazija Karlovac, Rakovac 4, 47000 Karlovac, Hrvatska

<sup>2</sup>Veleučilište u Karlovcu, Trg J.J. Strossmayera 9, 47000 Karlovac, Hrvatska

Pojava nepoželjnih mikroorganizama (kontaminanta) može uzrokovati promjenu senzorskih svojstava (okusa, mirisa i izgleda) piva i činiti ga neupotrebljivim za piće [1]. Posebnu pažnja treba posvetiti mikrobiološkoj kontroli piva, pravovremenom otkrivanju izvora i vrste kontaminacije. *Lactobacillus brevis* je gram – pozitivna bakterija koja se koristi u industriji za proizvodnju fermentirane hrane. Međutim, ovu bakteriju se povezuje i sa kvarenjem hrane i pića, posebice piva [1]. Cilj rada je istražiti intenzitet promjena svojstava piva kontaminiranog sa *Lb. brevis* i čuvanog pri različitim temperaturama. Uzorci piva kontaminirani su sa *Lb. brevis* i čuvani pri različitim temperaturama, T = 4, 20 i 37 °C, kroz 7 dana. U pivu prije i nakon čuvanja praćena su sljedeća svojstva: pH – vrijednost, ekstrakt u osnovnoj sladovini, udio alkohola, gorčina, polifenoli, boja i bistroća. Također, određen je i ukupan broj *stanica Lb. brevis*.

**Ključne riječi:** čuvanje, kontaminacija, *Lactobacillus brevis*, pivo, svojstva

[1] Feyereisen, M., Mahony, J., Lugli, G.A., Ventura, M., Horst, N., Franz, C.M.A.P., Noben, J., O’Sullivan, T., van Sinderen, D., Isolation and Characterization of *Lactobacillus brevis*, *Viruses* 11 (2019), 1 – 16.



## BUNARI OSJEČKO-BARANJSKE ŽUPANIJE WELLS IN OSIJEK-BARANJA COUNTY

Igor Prašnikar<sup>1</sup>, Tatjana Varga<sup>2</sup>,

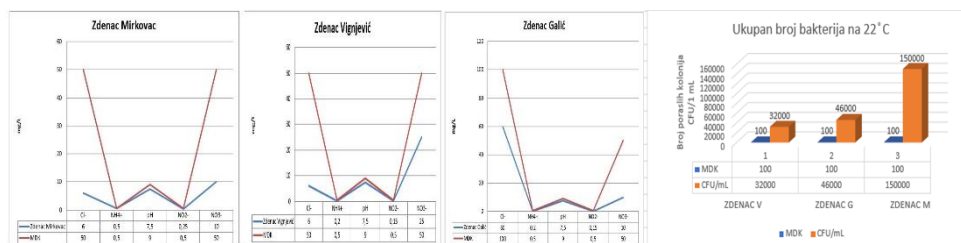
Nina Radaković<sup>3</sup>, Lara Vrajić<sup>4</sup>, Maja Vranić<sup>5</sup>

Tehnička škola i prirodoslovna gimnazija Ruđera Boškovića, Vukovarska cesta 209,  
31000 Osijek, Hrvatska

Cilj je ovog rada je prikazati kemijsku i mikrobiološku (bakterije i gljivice) kvalitetu vode iz bunara na području Donjeg Grada u Osijeku, Nemetina i Mirkovca, čime bi se dobilo i uvid stanje podzemnih voda koje navodnjavaju istraživane bunare. Za provedbu istraživanja odabrane su brze metode rada. Kemijska analiza vode, kvantitativno određivanje  $\text{Cl}^-$ ,  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  i  $\text{NO}_2^-$  iona, te određivanje pH vode provedeno je pomoću Merckovog terenskog laboratorija. Mikrobiološka analiza provedena je pomoću fleksibilnih nosača s hranjivim podlogama za ukupan rast bakterija s jedne strane i sa selektivnim podlogama s druge strane nosača: ljubičasto-crveni žučni glukozni agar za bakterija iz por. *Enterobacteriaceae*, ljubičasto-crveni žučni laktozni agar za koliformne bakterije, te Rose Bengal agar za plijesni i kvasce. Inkubacija uzoraka vode na hranjivim podlogama za opći rast bakterija provedena je na 22 °C tijekom dva dana, prije brojanja jedinica za formiranje kolonija (CFU).

Dobiveni rezultati ukazuju na povećan ukupan broj bakterija, broj bakterija fekalnog onečišćenja i plijesni u odnosu na službeno preporučene/dopuštene vrijednosti, stoga ispitivana bunarska voda nije pogodna za piće. Kemijskom analizom vode dobiveni su zadovoljavajući rezultati, te je ispitivana bunarska voda kemijski prihvatljiva za piće.

**Ključne riječi:** bunari, voda, kemijska analiza, mikrobiološka analiza, rezultati



**Sponzorska predavanja/*Sponsors lectures***

## PROIZVODNJA NATRIJEVOG HIPOKLORITA NA MJESTU POTROŠNJE, DEZINFEKCIJSKA SREDSTVA NA BAZI NATRIJEVOG HIPOKLORITA/AKTIVNOG KLORA PRODUCTION OF SODIUM HYPOCHLORITE *IN SITU*, SODIUM HYPOCHLORITE/ACTIVE CHLORINE BASED DISINFECTANTS

Miloš Tomišić

Sigma d.o.o., Ivana Milutinovića 77, 25220 Crvenka, Srbija  
office@hlorogen.com

HLOOROGEN je postrojenje za elektrolitičku proizvodnju klora u obliku otopine natrijevog hipoklorita (NaOCl) na mjestu njegove potrošnje (*in situ*), i to na potpuno siguran način.

Sustav je dizajniran tako da omogući potpuno sigurno kloriranje vode, jer se tijekom rada ne stvara plinoviti klor. Proizvodnja otopine natrijevog hipoklorita je jednostavna, jer zahtijeva samo sol, omekšanu vodu i struju, pa su operativni troškovi višestruko niži u usporedbi s korištenjem plinskog klora ili komercijalnog natrijevog hipoklorita. Sustav je automatiziran, zahtijeva minimalno održavanje i jednostavan je za korištenje. Dezinfekcija natrijevim hipokloritom na licu mjesta optimalno je i rašireno rješenje na velikim sustavima kao zamjena za plinoviti klor. Vijek trajanja sustava je 25 godina.

Dezinfekcijska sredstva na bazi natrijevog hipoklorita/aktivnog klora učinkovita su u borbi protiv bakterija, gljivica i virusa. Europska agencija za kemikalije odobrila je uporabu biocidnih proizvoda čija je aktivna tvar aktivni klor u sledećim vrstama proizvoda: Biocidni proizvodi za osobnu higijenu ljudi; Dezinfekcijska sredstva i algacidi koji nisu namijenjeni za izravnu upotrebu na ljudima ili životinjama; Biocidni proizvodi u veterinarskoj higijeni; Dezinfekcijska sredstva na području hrane i hrane za životinje; Dezinfekcijska sredstva za pitku vodu. Učinkovitost, sastav i sigurnost dezinfekcijskih sredstava Aqualor H je dokazana u vodećim domaćim i europskim laboratorijama.

*Ključne riječi:* natrij hipoklorit/aktivni klor, elektroliza, dezinfekcija, pitka voda





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