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24th and 25th
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XIV Meeting of Young Chemical Engineers

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BOOK OF ABSTRACTS

Knjiga sažetaka

Zagreb, Croatia, 24th and 25th February 2022


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HRVATSKO DRUŠTVO KEMIJSKIH INŽENJERA I TEHNOLOGA

SVEUČILIŠTE U ZAGREBU
FAKULTET KEMIJSKOG INŽENJERSTVA I TEHNOLOGIJE

XIV. SUSRET MLADIH KEMIJSKIH INŽENJERA

KNJIGA SAŽETAKA

XIV MEETING OF YOUNG CHEMICAL ENGINEERS

BOOK OF ABSTRACTS

Zagreb, 24. i 25. veljače 2022.

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UVODNIK

Susret mladih kemijskih inženjera (SMLKI) je dugogodišnji projekt djelatnika Fakulteta kemijskog inženjerstva i tehnologije koji tradicionalno promiču kemijsko-inženjersku disciplinu i ističu važnost kontinuiranog razvoja kemijskog inženjerstva i kemije u Republici Hrvatskoj. Susret se tradicionalno održava svake dvije godine od 1996. u organizaciji Hrvatskog društva kemijskih inženjera i tehnologa i Fakulteta kemijskog inženjerstva i tehnologije Sveučilišta u Zagrebu, a ove godine po prvi puta postaje međunarodni skup. XIV. susret mladih kemijskih inženjera održava se 24. i 25. veljače 2022. godine na Fakultetu kemijskog inženjerstva i tehnologije u Zagrebu.

Ovaj znanstveno-stručni skup okuplja mlade znanstvenike koji će kroz sedam sekcija razmijeniti svoja iskustva i znanja stečena radom u industriji, na sveučilištima, institutima i drugim ustanovama te prezentirati rezultate svojih istraživanja u području kemijskog inženjerstva i kemije. Cilj susreta je afirmirati mlade stručnjake i struku predstavljanjem rezultata postignutih tijekom studija, izrade završnih, diplomskih i znanstveno-stručnih radova. Mladi znanstvenici razmijenit će nova dostignuća u području kemijskog inženjerstva i kemije, novim tehnikama i tehnologijama. Susret nastoji skrenuti pozornost na nužnost interdisciplinarnosti istraživanja, razvoja i provedbe proizvodnih procesa te ponuditi mogućnost otvorenog dijaloga između akademije i privrede.

Na ovogodišnji Susret prijavilo se 264 sudionika sa 193 rada. Tijekom dva radna dana održat će se 2 plenarna, 6 pozvanih, 23 sekcijska predavanja uz 162 posterska priopćenja i 6 izlaganja sponzora. Ove godine nagrađuju se najbolja posterska priopćenja i najbolje izlaganje u kategoriji sekcijskih predavanja, a cjeloviti radovi sa Susreta objavit će se u posebnom izdanju časopisa Kemija u industriji. Radovi će prije objavljivanja proći standardni postupak recenzije. Rok za slanje radova je 8. svibnja 2022.

Hvala svima koji su doprinijeli organizaciji XIV. susreta mladih kemijskih inženjera. Svim sudionicima želim uspješan rad i ugodno druženje!

Predsjednik Znanstveno-organizacijskog odbora
Izv. prof. dr. sc. Krunoslav Žižek

FOREWORD

The Meeting of Young Chemical Engineers (SMLKI) is a long-standing project of employees of the Faculty of Chemical Engineering and Technology, who traditionally promote the discipline of chemical engineering and demonstrate the importance for its continuous development in the Republic of Croatia. Organized by the Croatian Society of Chemical Engineers and the Faculty of Chemical Engineering and Technology, the Meeting has traditionally been held biennially since 1996 and this year, for the first time, it will be an international meeting. XIV Meeting of Young Chemical Engineers is held on February 24-25, 2022 at the Faculty of Chemical Engineering and Technology in Zagreb.

This scientific and professional meeting will gather young scientists who will share their experience and knowledge from industry, universities, research institutes and other institutions in its seven sections and present their research results in the field of chemical engineering and chemistry. The aim of the Meeting is to strengthen the young experts and our profession by presenting the results of their bachelor's and master's theses obtained during their studies. In addition, young scientists will share their valuable experiences and achievements in the field of chemical engineering and chemistry using new techniques and technologies. The Meeting seeks to focus on the essence of interdisciplinary research, development and enforcement of production processes and provide an opportunity for open dialog between science and industry.

This year's Meeting will gather 264 participants with 193 presentations. Two working days will feature 2 plenary lectures, 6 invited lectures, 23 section lectures with 162 poster presentations and 6 sponsor presentations. This year, prizes will be awarded for best poster presentations and the best oral presentation, while full papers from the Meeting will be considered for publication in the special issue of the journal Chemistry in Industry. Prior to publication, papers will undergo a standard peer review process. The deadline for submission of full manuscripts is May 8, 2022.

Many thanks to all who contributed to the organization of the XIV Meeting of Young Chemical Engineers. I wish all participants a successful and enjoyable conference!

Chair of the Scientific and Organizing Committee
Assoc. Prof. Krunoslav Žižek

SADRŽAJ
CONTENTS

PLENARNA PREDAVANJA / *PLENARY LECTURES*

POZVANA PREDAVANJA / *INVITED LECTURES*

USMENA IZLAGANJA / *ORAL PRESENTATIONS*

POSTERSKA IZLAGANJA / *POSTER PRESENTATIONS*

PLENARNA PREDAVANJA
PLENARY LECTURES

4^TH INDUSTRIAL REVOLUTION DRIVEN BY DIGITALIZATION AND DIGITAL TWIN

Steffen Wagner

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We are witnessing the entry of humanity into the fourth industrial revolution, which is gaining a momentum. We are still at the very beginning, but changes and spheres in which great changes will take place are already in sight. Unlike the first three, the fourth industrial revolution is experienced by humanity consciously, and on top of that, it is actively and consciously designed. Siemens, as one of the leading, globally present technical and technological institutions, is actively contributing to changes in ecosystems with its visions and solutions. AI, Optogenetics, Batteries, CO_2 reduction, Cloud/Edge computing, Autonomous systems, Data collection and data analytics… are only a few aspects of driving activities in different industries.

Example: Owner operators in the process industry are usually collecting, and own a huge amount of production data. However, this data needs to be turned into value by providing actionable insights on the status of operations and equipment of a specific production site. The combination of different data sources – like engineering and/or process measured data etc. - in real time, and an instant interpretation of the process context, will significantly increase transparency, the quality of decision making and thereby operational efficiency. Based on “as-is” data, rather than just “as-built” data, direct value can be generated through applications in the field of asset management, predictive analytics and artificial intelligence. Transparent processes are enabling the right decisions for planning, optimizing and continuously improving industrial plant operations. In addition, insights from this data can also be used to enable new business models for the owner operator as well as its suppliers.

Digital twin is an unavoidable aspect of the digital transformation of our ecosystem.

PROXIDRUGS: NEW THERAPEUTIC OPTIONS FOR NUMEROUS DISEASES

Ivan Đikić

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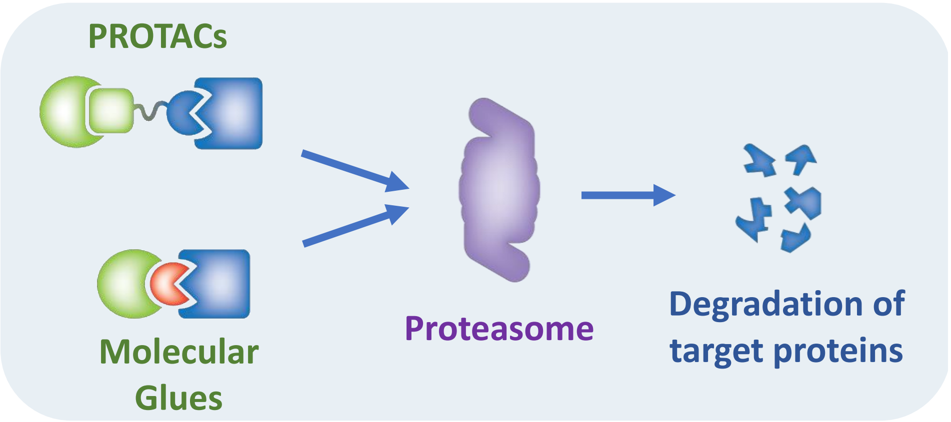
The new class of proximity-inducing drugs allows for the degradation of disease-relevant target structures (proteins, nucleic acids, organelles) thus opening up new therapeutic options in numerous diseases. The respective drugs usually are small, bifunctional molecules which direct target structures straight towards the cellular waste system. Whilst 80% of proteins are still deemed to be undruggable, a large proportion of these is thought to be targetable by the new strategy. Together with academic and industrial partners, Goethe University Frankfurt has established the BMBF-funded Cluster4Future PROXIDRUGS. Key piece of the Cluster is a technology platform for drug discovery and preclinical development. The Cluster aims at systematically improving the new class of proximity-inducing drugs and establishing a toolbox that can quickly adapted to different target structures and disease settings. The Cluster comprises ten different research projects focusing on cutting-edge challenges, such as the development of novel degradation strategies, the solubility enhancement of target proteins, the validation of molecular degraders in neuronal models, the creation of proximity-based agents against bacterial and viral pathogens, of novel E3 ligands and structured linkers and the development of versatile assays, screening and molecular profiling platforms for the identification and characterization of molecular degraders; and targeted trapping of drugs in cells or cell compartments. The research projects are accompanied by an integrative roof project testing and implementing efficient innovation and data processing structures. The Cluster will especially benefit from the knowhow of all partners and from the facilities and available screening libraries at the newly established *Frankfurt Center for Innovation and Technologies* and at the Fraunhofer ITMP.

PROXIDRUGS



Targeted degradation as new mode of action for drugs

POZVANA PREDAVANJA
INVITED LECTURES

PLASMA TECHNOLOGY: AN INNOVATIVE TOOL TO ENGINEER CHEMICAL REACTIONS

Stephanie Ognier, Mengxue Zhang, Michaël Tatoulian

IRCP-UMR8247, Equipe 2PM, Chimie ParisTech-PSL, IPGG, Paris, France
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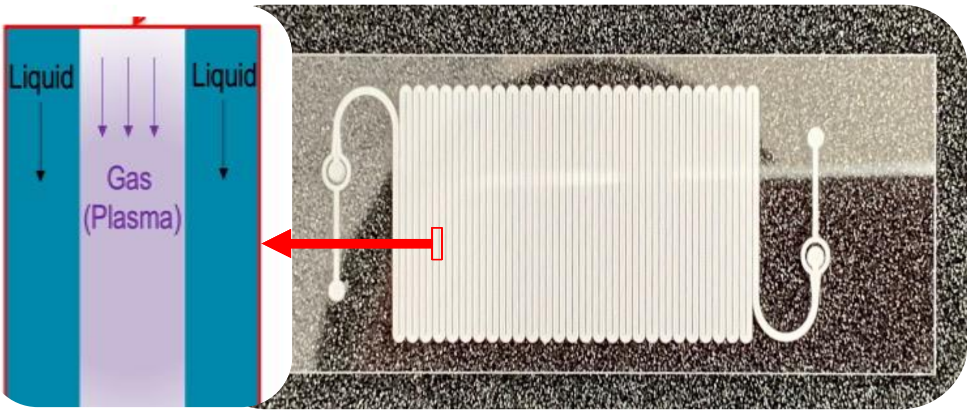
Plasma is a powerful technology for the generation of reactive species without any catalyst. It is currently used for the modification of materials in several areas of industry but underused in the field of small molecules due to the lack of accessible plasma reactor in liquid phase. The "Plasma, Processes, Microsystems" team (2PM), headed by Prof. M. Tatoulian, has developed therefore since 2013 gas-liquid two-phase flows micro-structured reactors coupled to plasma devices able to generate in a controlled way gaseous reactive radical species in close contact to a flowing liquid phase.
Preliminary results demonstrated the proof of concept with various types of cyclohexane and benzene functionalizations using different gases (O_2, H_2, NH_3, CO). Since then, this unique association of plasma and microfluidics is studied to explore new functionalization reactions, such as acylation or methylation, starting from various types of substrates. The presentation aims to show that plasma technology could open the way to the development of new synthetic routes, by functionalizing organic molecules in a simple and effective way in metal-free conditions (no catalyst) at ambient temperature and pressure.



Glass microreactor and a zoom on a microfluidic channel

PROBLEM SOLVING IN THE PHARMACEUTICAL INDUSTRY, 3 CASE STUDIES

Jerome Le Cunff

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Being an engineer in the pharmaceutical industry especially in research and manufacturing requires a wide range of knowledge and skills. Encountering a problem does not offer any guarantee that a solution can be found, and when a solution does exist other constrains such as resource availability, feasibility and timelines add another layer of complexity. The task of the engineer is to come up with the best available solution in the given situation and to be able to help reach a decision that would bring the most benefits to the project or the manufacturing process. In this lecture 3 of such problems will be presented in the analytical development, formulation development and in the manufacturing science and technology. The first case study is the sodium interference from in-use samples on ion chromatography for the analysis of a pharmaceutical finished product stability. Since the in-use solution contained 0.9% NaCl the signal from the sodium ion would mask all other peaks in the chromatogram. The second case study, dealing with manufacturing process development is the problem of rehumidification of the finished product at the end of the lyophilization process. The product required to contain a narrow range of water content to form a stable monohydrate form. The third case study is from the manufacturing process itself, dealing with the problem of predicting stability of products that are manufactured on a new line. Predicting the stability of product requires relatively complex mathematical model that also fit with the actual chemical processes and using generic equation to try and fit the data was not applicable. These three case studies will help illustrate the approach to problem solving and the solutions that where all implemented in our company.

APPLICATIONS OF VIBRATIONAL SPECTROSCOPY IN MICROBIAL BIOTECHNOLOGY

Volha Shapaval, Achim Kohler, Valeria Tafintseva, Simona Dzurendova, Dana Byrtusova, Johanna Karin Hillevi Blomqvist, Anne Marie Langseter, Gergely Kosa, Kristin Forfang, Boris Zimmermann

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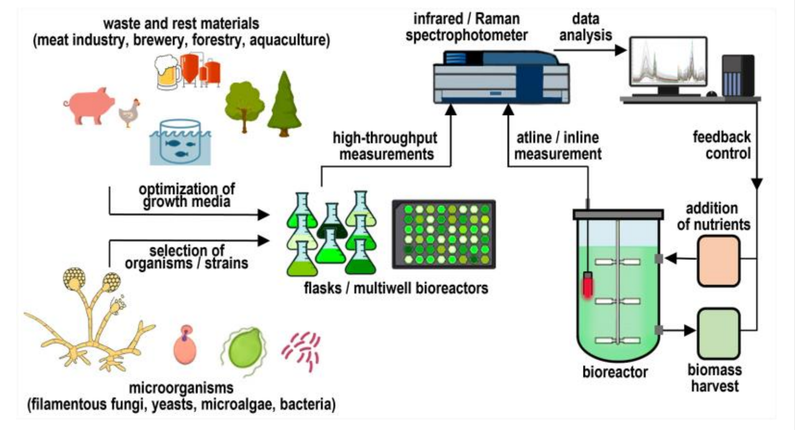
Microorganisms, such as microalgae, yeasts, filamentous fungi and bacteria, are powerful cell factories for substance synthesis. Since they can produce various metabolites, including structural and enzymatic proteins, lipids, carbohydrates, biopolymers, pigments, alcohols, and antibiotics, they have found use in the fields of industrial, pharmaceutical and agro-environmental biotechnology. Microbial biotechnology based on fermentation processes is expanding in the fields of food, feed, energy, chemical and material bio-based industries to drive the green transition to a circular and sustainable economy. Bioprocess development requires technologies for process monitoring and high throughput screening, and in this respect vibrational (infrared and Raman) spectroscopy techniques have seen rapid advance and application in the recent years. Infrared and Raman spectroscopies are considered as fast, inexpensive, and highly sensitive methods for analysis of biological samples, and thus have emerged as the dominant biospectroscopy techniques. Both techniques are excellent for obtaining comprehensive and detailed information in biotechnology since they can simultaneously measure broad chemical profiles of the chemical constituents present in the bioprocess via detection of numerous functional groups. Since infrared and Raman spectra are unique and characteristic, they are often referred to as spectral "fingerprints" of biosamples. The spectra can be used for identification, classification and chemical characterization, as well as in regression-based analyses for tracking biochemical changes between samples or over time. This rich spectroscopic data is usually interpreted by using chemometrics, classical machine learning, and deep learning data analyses methods. Various measurement modes allow microscopy imaging of microorganisms at nanometer and micrometer scale, high throughput measurements of hundreds of samples, and online time-dependent measurements with fibre-optic systems. Here, spectroscopy-based research conducted by the Biospectroscopy and Data Modeling Group at the Norwegian University of Life Sciences will be presented. The group has extensive collaboration with the Norwegian food, feed and biotechnology industry in valorisation of waste and rest materials, such as animal slaughter sideproducts from meat industry, rest biomass from brewery, woody lignocellulose sideproducts from forestry, and sludge from aquaculture industry. These waste and rest materials can be utilised and converted by microorganisms into food, feed, nutraceuticals, biofuels, and biopolymers.



ENGINEERING, ECONOMICS OR MANAGEMENT? WHAT IS THE MOST IMPORTANT AND YOUR CHOICE?

Jakov Mihaljević

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It could be said that engineering is a profession that combines knowledge from technical, mathematical and natural sciences acquired through learning, experience and practice and is applied to economic development. As a company, INA provides engineers with the opportunity for personal development through various business positions where the importance of applying economic principles in the analysis of engineering decisions can be seen. Engineers are reaching solutions for various unfavourable situations, and in order to achieve this, it is often necessary to direct a group of people towards achieving the goal in the most efficient and cost-effective way. The question is, is today's engineer tomorrow's manager?

NANOPARTICLE-BASED CONDUCTIVE INKS FOR INKJET PRINTING OF PLANAR ELECTRODES

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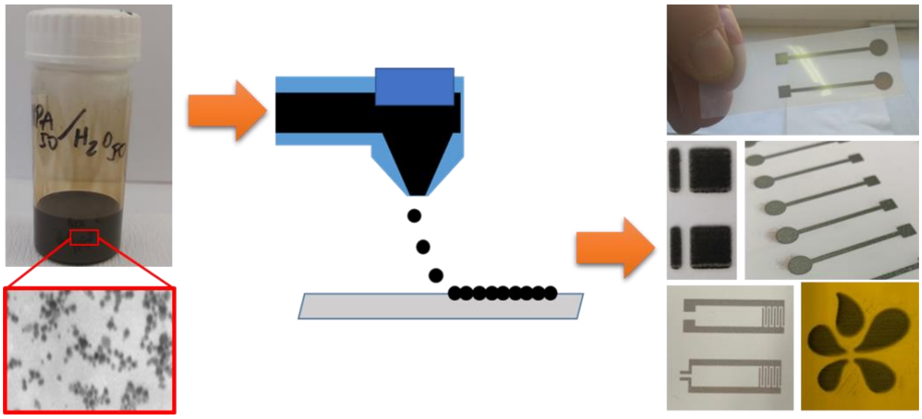
Miniaturized planar electrodes are needed to enable emerging sensor applications, such as wearable (bio)chemical sensing. While there are different ways of fabricating such electrodes, inkjet printing of conductive features presents a greener, scalable, and cost-effective fabrication technology. A key challenge in the process of printing electrodes is the formulation of a conductive ink with suitable properties. Metal and carbon nanoparticles are the most common conductive materials used for this purpose. However, the selected particles should be small enough to pass through the printer nozzle and remain stable in the formulated suspension without aggregating. For effective inkjet printing, the fluid dynamic parameters (viscosity, density and surface tension) of the ink must be optimized. Wetting of the substrate and adhesion must also be considered. Finally, post-processing of the printed electrodes is needed to remove stabilizers and additives, thereby improving the electrical conductivity. While thermal processing is the gold standard, high temperatures may limit the choice of substrate and alternative processing technologies are sought.

In this presentation, development of planar electrodes via inkjet printing will be illustrated using two examples: a conductive ink based on silver nanoparticles and a conductive ink based on graphene nanosheets. The entire process will be explained: from nanoparticle synthesis and stabilization, ink formulation and optimization, to inkjet printing on plastic sheets. Finally, the potential of flash lamp annealing for post-processing of the electrodes will be reviewed.

The Croatian Science Foundation funded this research, grant UIP-2020-02-9139.



UTJECAJ DJELOVANJA ULTRAZVUKA U ŠARŽNOM KRISTALIZATORU NA KINETIKU NUKLEACIJE I RASTA KRISTALA

INFLUENCE OF ULTRASOUND IRRADIATION IN BATCH CRYSTALLIZER ON NUCLEATION AND CRYSTAL GROWTH KINETICS

Marija Ćosić

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Iako je kristalizacija jedna od najstarijih jediničnih operacija, pronalaženje procesnih uvjeta kojima bi se dobili kristali željenih karakteristika i danas predstavlja veliki izazov. Karakteristike kristaličnog produkta određene su kinetikom dvaju osnovnih koraka kristalizacije, a to su nukleacija i rast kristala. U posljednje vrijeme velika je pažnja usmjerena na utjecaj ultrazvučnog djelovanja na kinetiku navedenih procesa. Naime, djelovanjem ultrazvuka unutar matične otopine dolazi do pojave ultrazvučne kavitacije. Ova pojava može ubrzati nukleaciju, povećati brzinu prijenosa tvari pri rastu kristala, s obzirom na to da smanjuje debljinu difuzijskog sloja na granici faza kristal/matična otopina, ali isto tako djelovati i na samu površinu kristala. U ovom predavanju dat će se uvid u recentna istraživanja utjecaja ultrazvuka na kinetiku nukleacije i rasta kristala boraksa tijekom kristalizacije u šaržnom kristalizatoru sa i bez mehaničkog miješanja. Primjena ultrazvuka i povećanje njegove amplitude i pulsa značajno utječe na širinu metastabilne zone te promjenu koncentracije matične otopine tijekom perioda rasta kristala u odnosu na sustave bez ultrazvuka. Međutim, unatoč izraženom utjecaju na parametre kristalizacije ultrazvuk nije u mogućnosti suspendirati nastale kristale i tako osigurati osnovni zahtjev za njihov neometani rast u suspenziji. Kako odabrati uvjete miješanja za provedbu sonokristalizacije? Kako izgledaju raspodjele veličina rastućih kristala tijekom različitih uvjeta sonokristalizacije? Kako se mijenja konačna veličina i oblik dobivenih kristala s promjenom parametara ultrazvuka te koliko se snage privede sustavu tijekom sonokristalizacije sa i bez miješanja? Odgovore na navedena, ali i druga pitanja o sonokristalizaciji će se dati tijekom predavanja.

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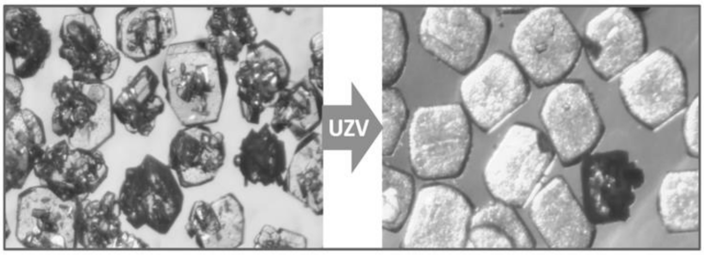

USMENA IZLAGANJA
ORAL PRESENTATIONS

INFLUENCE OF STATIC MIXER GEOMETRY ON BIODIESEL SYNTHESIS

Ivan Karlo Cingesar, Domagoj Vrsaljko

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Biodiesel is considered a promising fuel alternative to fossil fuels [1]. Vegetable oils, along with animal fats and wastes, are considered the best feedstocks for biodiesel production. Vegetable oils are converted into biodiesel by transesterification with methanol [2]. The current trend in biodiesel production is towards millifluidic and microfluidic devices, which are often custom-built reactionware. The reactionware is often produced using additive manufacturing, which means that laboratory devices are produced that are specifically tailored to the desired reaction.

In this work, the Computational Fluid Dynamics (CFD) program was used to simulate fluid flow in a microreactor modeled using CAD (computer-aided design) software. CFD predicted how the fluid would behave and provided initial results. After the initial CFD simulations, biodiesel production was conducted in the laboratory. Two types of microreactors were 3D-printed, a tubular microreactor and a "vortex" microreactor. In both reactors, the reaction was carried out four times with four different residence times: 1, 2, 4 and 8 minutes. The obtained mixture of products and unconverted reagents was separated using a centrifuge. The biodiesel was then characterized by gas chromatography (GC) and Fourier transform infrared spectroscopy (FTIR) with ATR crystal. The dead volumes predicted by the software CFD in the modeled "vortex" microreactor were confirmed by experiments. The conversion in the tubular microreactor is higher due to the dead volume in the "vortex" microreactor.

This work has been supported by European Regional Development Fund under the project: OS-Mi (KK.01.1.1.04.0006) and by Croatian Science Foundation under the project DOK-2020-01-8955.

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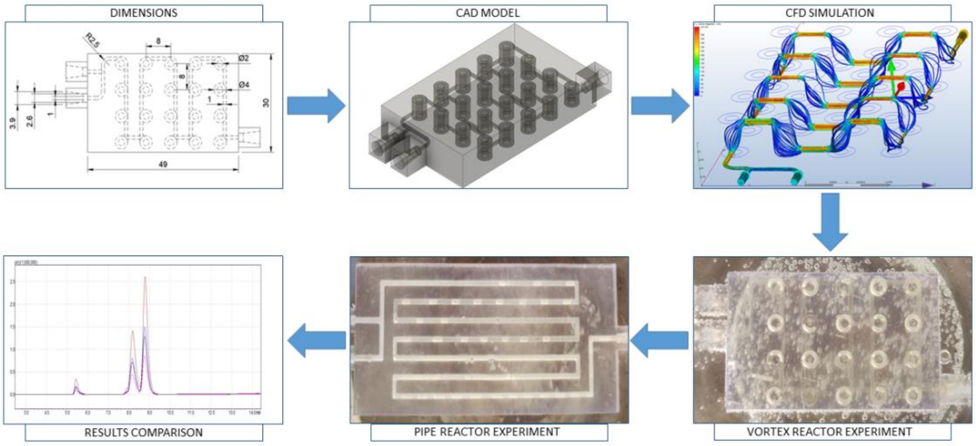

FLEKSIBILNI KRISTALI KADMIJEVIH(II) HALOGENIDA S DIKLORPIRIDINSKIM LIGANDIMA

FLEXIBLE CRYSTALS OF CADMIUM(II) HALOGENIDES WITH DICHLOROPYRIDINE LIGANDS

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Kristali – tvari uređene strukture koja osigurava kontroliran i efikasan prijenos energije, iako su do sada intenzivno istraživani, često su zanemarivani kod dizajna novih, pametnih uređaja zbog svoje krtosti i lomljivosti. Nedavno otkriće molekulskih kristala prilagodljivih na vanjski mehanički podražaj rezultiralo je značajnim pomakom prema razmatranju kristalnih materijala kao potencijalnih kandidata za primjenu u naprednim tehnologijama. No, unatoč iznimnom interesu znanstvene zajednice za ovo novoopisano svojstvo kristalne tvari, čemu svjedoči streloviti porast broja literaturnih navoda koji opisuju fleksibilne organske, ali i metalo-organske molekulske kristale, još uvijek nije jasno koji su strukturni čimbenici odgovorni za opremanje molekulskih kristala adaptivnim svojstvima [1].
Kristalni 1D koordinacijski polimeri kadmija(II) pokazali su se izvrsnim kandidatima za sustavno proučavanje mehaničke fleksibilnosti [2-4]. Nedavnim istraživanjima uočeno je da serije kristala 1D kadmijevih(II) polimera s 3-halogenpiridinskim te halogenpirazinskim ligandima pokazuju širok raspon mehaničkih odziva različitih stupnjeva i vrsta (od plastične do elastične savitljivosti) [2-4]. Kako bi se dodatno istražio utjecaj strukturnih parametara na savitljivost, u ovom radu proučavani su kristali koji u svojoj strukturi sadrže 3,5-diklorpiridinski ligand. Opaženi visoki stupnjevi elastičnog odziva su kvantificirani, te korelirani s jakošću i usmjerenošću međumolekulskih interakcija.

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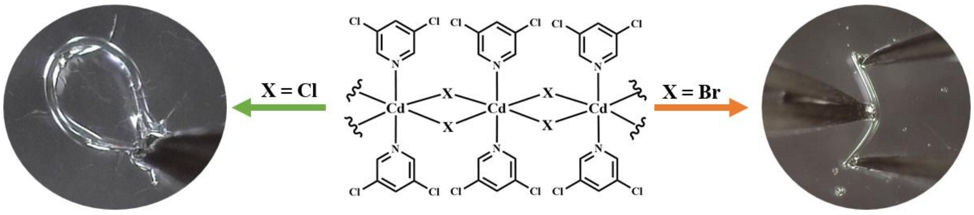

THE INFLUENCE OF THE ALCOHOL BUTANOL STRUCTURAL BRANCHING AND THE FEEDSTOCK TYPE ON THE SYNTHESIS AND APPLICATION PROPERTIES OF FATTY ACID (ISO)BUTYL ESTERS

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Biodiesel, as a renewable fuel, is interesting to researchers due to its advantages over mineral diesel, e.g. lower toxicity, higher lubricity, lower sulfur content or biodegradability. In this research, different biodiesels were synthesized using sunflower oil, rapeseed oil, coconut oil, animal fat or waste cooking oil as a triglyceride sources and butanol or isobutanol, as an alcohol. Butanol can be obtained via fermentation processes [1], therefore contributing to the sustainability of biodiesel production, whereas the presence of structural branching can influence final application fuel properties, i.e. low-temperature properties [2]. Potassium hydroxide was used to catalyze transesterification reactions. After nuclear magnetic resonance analysis of each synthesized biodiesel, reaction conversions were calculated and compared. When butanol was used, the highest conversion of 99.99 % was achieved in majority of reaction systems, at upper limit parameter values. However, the presence of structural branching changes interactions between reactants, resulting in the conversion above 96 % only in the specific cases, e.g. isobutanol/rapeseed oil system with the molar reactant ratio of 12:1. Furthermore, to investigate the influence of structural differences in fatty acid and alcohol moieties on biodiesel application properties, biodiesels obtained from sunflower oil were purified and their density, viscosity, cold filter plugging point and lubricity was analyzed according to standardized tests.

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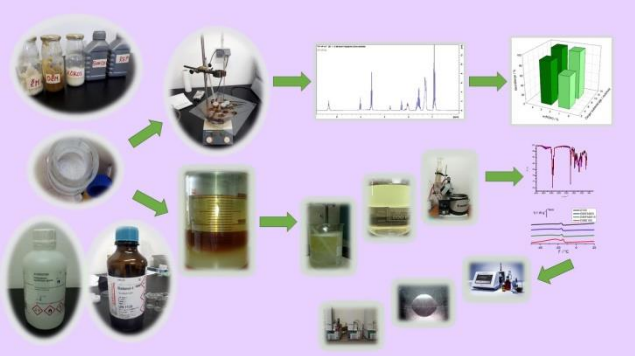

Figure 1. The path of the synthesis, purification and analysis of biodiesel

COMPUTATIONAL STUDY OF NEURODEGENERATION RELATED TO COVID-19 INFECTION

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Although COVID-19 has been primarily associated with pneumonia, recent data show that the SARS-CoV-2 virus can infect other vital organs, such as heart, kidneys and 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 [1]. Our docking and molecular dynamics simulations [2] show that affinities of spike proteins from the wild type (WT) and South African (SA) variant for MAO enzymes are comparable to those for their ACE2 receptors. This allows for the spike·MAO complex formation, which changes MAO affinities for its neurotransmitters, thus eventually impacting rates of their metabolic conversions and misbalancing their levels. Knowing this fine regulation is strongly linked with the etiology of various neurodegenerative disorders, these results highlight the possibility that the interference with the brain MAO activity is responsible for the increased neurodegeneration following the COVID-19 infection. Since the obtained insight suggests a more contagious SA variant would produce even larger disturbances, and with new and more problematic strains likely emerging in the near future, we firmly advise that the demonstrated prospect for the SARS-CoV-2 induced neurological complications should not be ignored, rather requires further clinical investigation in order to achieve early diagnosis and timely treatment.

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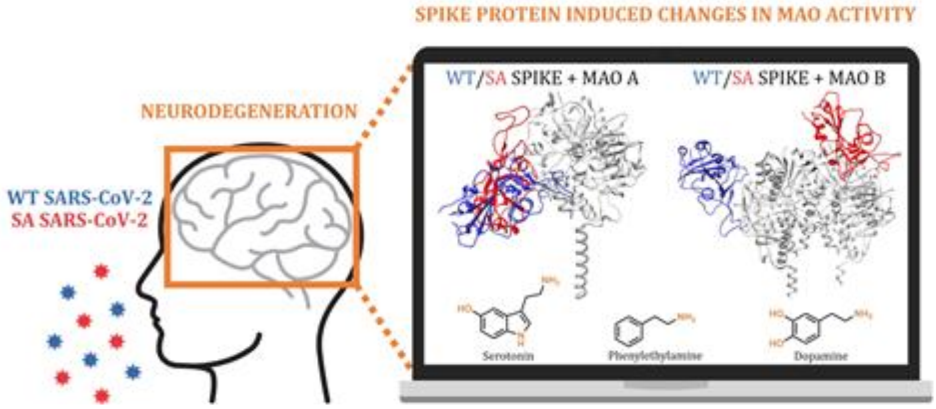

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UTJECAJ $[Ni(NCS)_2(L)_4]$ (L = py, 4-mepy, 3,5-lut) KOMPLEKSA NA SINTEZU SILIKALITA-1

EFFECT OF $[Ni(NCS)_2(L)_4]$ (L = py, 4-mepy, 3,5-lut) COMPLEXES ON THE SYNTHESIS OF SILICALITE-1

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Silikalit-1 (SIL-1) je zeolit strukturnog tipa MFI čije su karakteristike i sinteza već dobro poznate [1], a u istraživanjima se koristi za proučavanje kristalnog rasta [2]. Kao i njegov poznatiji alumosilikatni analog ZSM-5, ima široku industrijsku primjenu kao katalizotor i adsorbens [3]. SIL-1 sve se češće koristi u dizajnu tankih filmova i membrana, a uobičajena sinteza SIL-1 uključuje geliranje silicijevog dioksida (SiO_2) u smjesi vode, amonijevog fluorida (NH_4F) koji služi kao mineralizator i tetrapropilamonijevog bromida (TPABr) koji ima ulogu usmjerivača strukture. Uobičajeni omjeri reaktanata su: 1 SiO_2 : 0.08 (TPA)Br : 0.04 NH_4F : 20 H_2O. U literaturi [1] je također spomenuto kako dodatak mineralizatora (NH_4F) skraćuje vrijeme reakcije i povećava veličinu kristalita produkta.

Kako bi se ispitao utjecaj sterički zahtjevnih metalnih kompleksa na sintezu i kristalizaciju SIL-1 korišteni su niklovi(II) kompleksi tipa: $[Ni(NCS)_2(L)_4]$ (L = piridin; py, 4-metilpridin; 4-mepy, 3,5-lutidin; 3,5-lut). Reakcije su provedene s TPABr i bez usmjerivača strukture u cilju izučavanja kompleksa kao potencijalnih usmjerivača strukture za sintezu zeolita. Tijekom sinteze u trajanju od 21 dana reakcijske su smjese uzorkovane svakih 24 sata te su produkti analizirani IR spektroskopijom, difrakcijom rentgenskog zračenja na praškastom uzorku (PXRD) i optičkom mikroskopijom. Zaključeno je kako niklovi kompleksi navedenog tipa imaju značajan utjecaj na sintezu SIL-1 u vidu brzine reakcije, dobivenog produkta, morfologije kristala i kristalnih intermedijera.

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SYNTHESIS AND CHARACTERIZATION OF MULTILAYER NANOCAPSULES MADE OF WEAK POLYELECTROLYTES

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Polyelectrolytes are macromolecules (e.g. polymers) with dissociating functional groups which can carry positive or negative charge in solution. By alternating adsorption of positively and negatively charged polyelectrolytes on a substrate surface, thin films called polyelectrolyte multilayers are formed. In the case of adsorption on colloidal particles followed by the dissolution of the template, it is possible to prepare hollow polyelectrolyte capsules of colloidal dimensions. Due to a large number of available polymeric compounds and easily tunable multilayer properties, these systems find their application in various fields such as biomedicine and catalysis. In this study, hollow nanocapsules made of weak polyelectrolytes, poly(allylamine) (PAH) and poly(acrylic acid) (PAA) were successfully designed, synthesized and characterized. The formation of the polyelectrolyte multilayer on fully biocompatible hydroxyapatite (HA) nanoparticles was monitored by measuring the electrophoretic mobility of particles. After the optimization of the substrate decomposition conditions, hollow polyelectrolyte capsules were prepared by dissolution of the template in the presence of HCl. Further characterization was performed using infrared spectroscopy, energy dispersion X-ray analysis, dynamic light scattering, scanning electron microscopy and atomic force microscopy. With these methods, the chemical composition, structure, size and morphology of obtained nanocapsules were determined. It was found that the capsules are of a rather narrow size distribution ranging from 100 to 250 nm with a flexible capsule wall being only a few tens of nanometers thick. Moreover, the dispersions of capsules were stable for at least 40 days. This extreme stability of nanocapsules could be attributed to their small dimensions, low mass and high surface charge.

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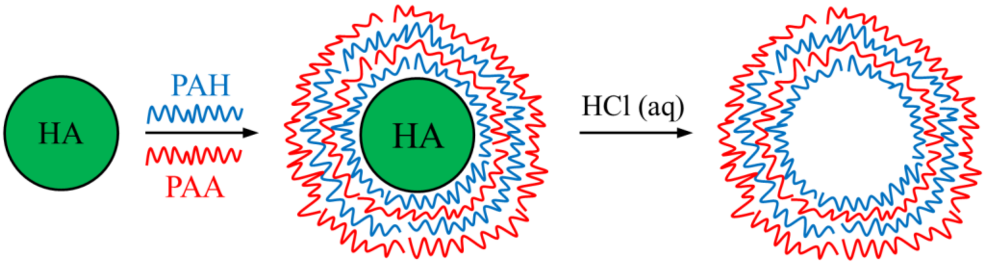

LASER ABLATION INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY (LA-ICP-MS)

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Laser ablation (LA) as a solid sampling technique for inductively coupled plasma-mass spectrometry (LA-ICP-MS) provides major, minor and trace elements information with wide element coverage, low limits of detection and wide dynamic range with minimal sample preparation. Further advantages include its suitability for microanalysis, depth profiling and two- or three- dimensional elemental mapping or imaging [1]. The method LA-ICP-MS is applicable to variety of sample types including geological, environmental, biological and forensic samples. Samples with different physical properties can be ablated: solid or liquid (e.g. blood samples), powdered or crystalline, conductive or non-conductive, opaque or transparent. In geosciences, LA-ICP-MS has been employed in trace element mapping of various rock, mineral and ore samples. The technique has also been applied in trace metal mapping of elemental and nanoparticle uptake in animal and plant tissue. Imaging of certain elements in paleontological samples by LA-ICP-MS has been performed in order to study migratory and dietary changes in modern and fossil organisms [2]. However, complex methodology and a lack of available calibration and referent standards render the method rather limited for routine analytical purposes.

The aim of our study was to present application of LA-ICP-MS in the quantification of selected elements in different matrices. The selection of samples was focused on the materials, which were of the most similar matrix as referent glass material NIST, SRM 612. For this reason, geological sample of quartz and iron nanoparticles embedded in silica pellets were chosen. The results demonstrated the ability of method to determine up to ten elements on semi-quantitative level. By comparison to referent material the interference effects were found negligible.

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RAZVOJ *INKJET* TISKANE ČVRSTOFAZNE Ag/AgCl REFERENTNE ELEKTRODE

THE DEVELOPMENT OF AN INKJET PRINTED SOLID STATE Ag/AgCl REFERENCE ELECTRODE

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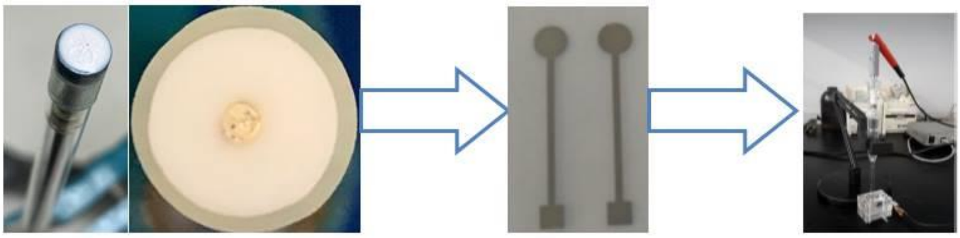
Razvoj čvrtofaznih referentnih elektroda stabilnog potencijala nužan je za integraciju u minijaturizirane potenciometrijske senzorske sustave. Ovdje su predstavljeni prvi koraci u razvoju čvrstofaznih plošnih Ag/AgCl tiskanih referentnih elektroda. Ispitane su dvije izvedbe čvrstofaznih elektroda: 1. štapićasta Ag-elektroda je kemijski klorirana primjenom željezova(III) klorida te površinski oslojena referentnom membranom na bazi poli(vinil butirala) (PVB); 2. formulirana je referentna Ag/AgCl pasta primjenom inovativne tehnike fotoredukcije intenzivnom pulsirajućom svjetlošću (IPL) i nanesena na štapićastu elektrodu od staklastog ugljika. Optimirani su uvjeti kemijskog kloriranja i fotoredukcije te potreban volumen PVB-membrane i referentne paste. Ispitan je odziv elektroda u vodenim otopinama KCl različitih koncentracija; u oba slučaja ostvaren je prihvatljiv naponski odziv. Nadalje je ispitan odziv u otopinama različitih soli, uključujući $NaNO_3$, NaCl te $CaCl_2$; ispitan je utjecaj pH na elektrodni odziv te je izvršena usporedna karakterizacija komercijalne ionsko-selektivne elektrode uz pripravljene čvrstofazne referentne elektrode te konvencionalnu Ag/AgCl elektrodu s unutarnjim elektrolitom. Konačno, izvršen je transfer optimiranih referentnih membrana na inkjet otisnutu srebrnu elektrodu u svrhu demonstracije plošne referentne elektrode.

Ovaj rad financirala je Hrvatska zaklada za znanost projektom UIP-2020-02-9139.



EFFECT OF DIFFERENT MORPHOLOGY OF LEAD DIOXIDE IN COMPOSITE WITH GRAPHITIC CARBON NITRIDE FOR ELECTROCHEMICAL DEGRADATION OF FLUORESCENT TAG DYES

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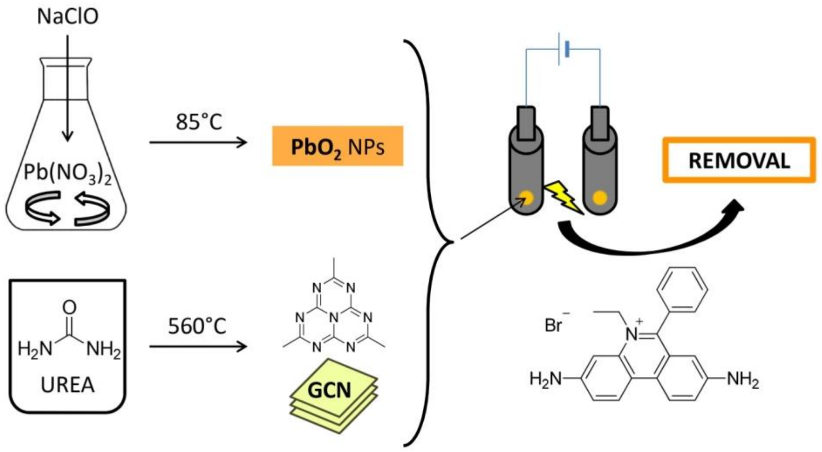
Dyes such as fluorescein, eosins, and ethidium bromide are widely used in medicine and molecular biology. Electrochemical advanced oxidative processes could be utilized to remove these compounds from aqueous waste in a simple and environmentally compatible way. Graphitic carbon nitride (GCN) has shown excellent electrocatalytical properties. Lead dioxide is one of the most effective materials used in electrocatalysis.

A new composite material was prepared from graphitic carbon nitride and lead oxides. Lead dioxides were prepared using different growth-directing compounds by a solvothermal synthesis. GCN was prepared from urea. Finally, PbO_2/GCN composite was prepared. The electrocatalytic properties of the materials and composite are closely related to their structure. Modified carbon electrodes were prepared by coating the surface of graphite rods with PbO_2, GCN, and the PbO_2/GCN composite. Electrochemical properties of these electrodes were examined using cyclic voltammetry and EIS. Morphological characterization was done by XRD, SEM, Z seizer, BET analysis and FTIR. The best electrode material was used for the degradation experiments. A method for degrading ethidium bromide as a model is being developed, optimizing the experimental parameters (electrolyte concentration, pH, current density).



KEMIJSKO INŽENJERSTVO, KAUZALNOST I UMJETNA INTELIGENCIJA

CHEMICAL ENGINEERING, CAUSALITY AND ARTIFICIAL INTELLIGENCE

Želimir Kurtanjek

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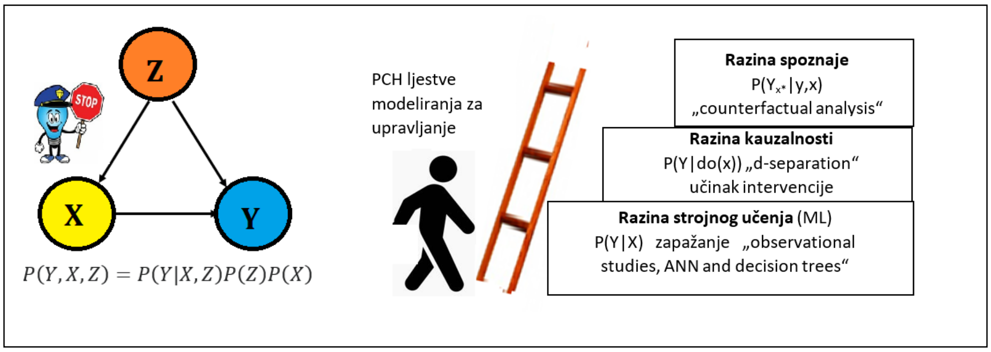
Razvoj umjetne inteligencije (UI) je osnova revolucije i promjene paradigme u znanosti, tehnologijama i životu ljudi u 21. stoljeću. U radu su ističe bitan utjecaj UI u području kemijskog inženjerstva. Sadašnji početni razvoj UI usmjeren je na razvoj sustava s adaptivnom programiranom robotikom, umjetni vid, i analizu velikih podataka. Bitni korak prema umjetnoj općoj inteligencije (UOI) je prijenos sposobnosti zaključivanja s čovjeka na stroj. U radu su dane osnove metodologije razvoja inteligentnih računalnih modela u kemijskom inženjerstvu primjenom Bayesovih mreža kojima se omogućuje kauzalno zaključivanje i stjecanje novih (kontrakauzalnih) spoznaja. Opisani su primjeri modela dirigirane evolucije enzima za proizvodnju biogoriva iz celulozne sirovine, predikcije 3D strukture proteina na osnovu primarne sekvencije aminokiselina, i algoritma procjene kauzalnih učinaka poslovnih odluka. Prikazani su rezultati vlastitog istraživanja strukturnog kauzalnog modela (SCM) evaluacije učinka produkata razgradnje lignoceluloznih supstrata na aktivnost LPMO (lytic-polysaccharide monooxygenase) enzima. SCM model zasniva se na primjeni molekularnih deskriptora supstrata i regularizaciji LASSO (least absolute shrinkage and selection operator) i strojnim učenjem RF (random forest) algoritma. Rezultati pokazuju značajnu prednost SCM modela u odnosu na regresijski OSL (ordinary least squares) model. Točnost SCM modela procijenjena je simuliranim slučajnim uzorkovanjem (bootstrap) i pokazuje za red veličine manju pogrešku u odnosu na klasični OSL model. Također je dan prikaz računalne osnove (software) u otvorenoj računalnoj platformi Github.



RAZVOJ AMINONAFTALENSKIH FOTOUKLONJIVIH ZAŠTITNIH SKUPINA

DEVELOPMENT OF AMINONAPHTHALENE PHOTOREMOVABLE PROTECTING GROUPS

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Zaštitne skupine u višestupnjevitoj organskoj kemiji zauzimaju veliku ulogu. Fotouklonjive zaštitne skupine (fotokavezi) uklanjaju se fotokemijskom reakcijom, što omogućuje selektivnost jer se pobuđuje samo kromofor od interesa, bez utjecaja na druge skupine. S obzirom da za odvijanje tih reakcija nisu potrebni reagensi niti katalizatori, fotokavezi se sve više primjenjuju u biologiji i medicini [1].

Među najpoznatijim fotokavezima ističu se derivati *ortho*-nitrobenzilnog alkohola, koji apsorbiraju svjetlost u vidljivom području, što im je omogućilo široku primjenu. Međutim, radi nekoliko nedostataka javila se potreba za daljnjim razvojem fotokaveza [2]. Kao potencijalni fotokavezi za karboksilne kiseline i alkohole proučavani su i *ortho*-, *meta*- i *para*-supstituirani hidroksimetilanilini [3]. Iako su se pokazali kao dobri fotokavezi, njihov nedostatak je što apsorbiraju zračenje valnih duljina kraćih od 300 nm, te je potrebno pripraviti nove derivate koji će apsorbirati fotone valne duljine slične vidljivoj svjetlosti (eng. *near visible light*).

Shodno tome, sintetiziran je niz novih aminonaftalenskih derivata kao potencijalnih fotokaveza pri čemu je detaljno ispitana njihova fotokemijska reaktivnost, koja se znatno mijenja ovisno o položaju supstituenata na naftalenskoj jezgri. Njihova potencijalna primjenjivost demonstrirana je zaštitom biološki važnih molekula te lijekova, poput ibuprofena, ketoprofena, aminokiseline fenilalanina, neurotransmitera GABA i glukoze.

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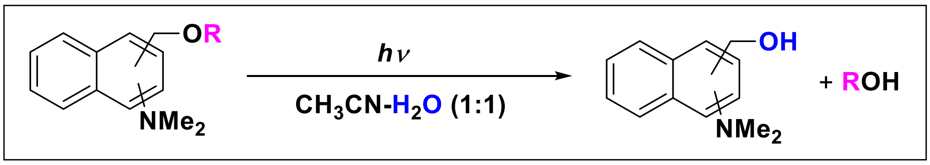

SYNTHESIS OF BIMETALLIC–CHITOSAN COMPLEXES AS ANTIBACTERIAL MATERIALS

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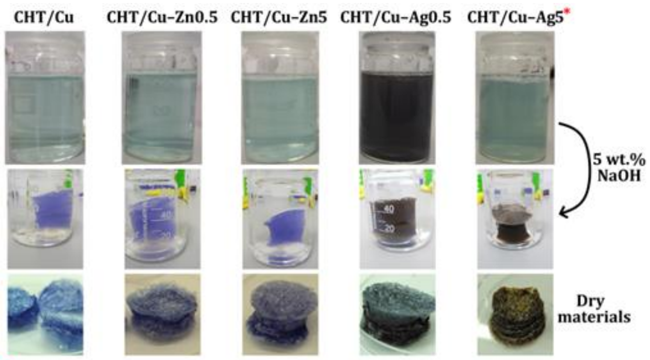
Chitosan-based hydrogels have found many applications in biomedicine due to their biocompatibility, biodegradability and bioactivity. Chitosan (CHT) is a non–toxic, polycationic biopolymer with antibacterial properties which can be improved through complexation with transition metals such as copper, zinc and silver. Cu^{2+}, Zn^{2+} and Ag^{+} ions are used in biomedicine due to beneficial properties in the repair and regeneration of different tissues. Furthermore, the addition of these metal ions into CHT matrix enhances antibacterial properties against Gram-positive and Gram-negative bacteria. The strong affinity of these ions towards $–NH_2$ and –OH groups of chitosan is responsible for the complexation process that can be used to prepare stable hydrogels with defined structure and improved antibacterial properties. To date, there is no study conducted on the synthesis of chitosan-based materials through simultaneous complexation with two metal ions. Therefore, the aim of this work was to investigate the structural properties and stability of chitosan-based hydrogels when two different metal ions are added into CHT solution.

In this work, the complex solutions (CHT/Cu, CHT/Cu–M0.5 and CHT/Cu–M5) were *in situ* prepared by mixing the appropriate volume of 1.2 wt.% CHT solution (medium molecular weight, degree of deacetylation = 85 %) and solutions of metal ions according to their volume ratio: $V_{\mathrm{CHT}}/(V_{\mathrm{Cu2+}}+V_{\mathrm{M}})=7.33$, where M is the solution of Zn^{2+} or Ag^{+} ions with two different concentrations. The molar ratio of amino groups and Zn^{2+} or Ag^{+} ions was adjusted to $n(–NH_2):n(M)=1:0.009$ and 1:0.09. In the case of Cu^{2+} ions, ratio was constant in all complexes with value of $n(–NH_2):n(Cu^{2+}) = 1:0.09$. Due to poor solubility of Ag acetate, CHT/Cu–Ag5 complex solution was prepared with minor changes. The prepared solutions of complexes were neutralized with 5 wt.% NaOH solution during 24 h and obtained hydrogels were extensively washed with distilled water until pH neutral. The prepared hydrogels were then frozen and lyophilized to obtain dry materials which were characterized by ATR-FTIR spectroscopy and their morphology was investigated by SEM.

The preliminary results show the stable and porous microstructure of all prepared hydrogels. The addition of a second metal ion increases stability of hydrogels, in comparison with CHT/Cu hydrogels. Furthermore, shifts in absorption bands in FTIR spectra of all samples indicate successful complexation of CHT with metal ions. The results imply strong interactions of metal ions with $–NH_2$ and –OH groups of chitosan and that complexation process can be used as a potential method for obtaining stable bimetallic–chitosan hydrogels as antibacterial materials.



*Due to poor solubility of Ag acetate, CHT/Cu–Ag5 complex solution was prepared with minor changes.

ELECTRICAL AND STRUCTURAL PROPERTIES OF Na_2O-V_2O_5-P_2O_5-Nb_2O_5 GLASSES

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With the growing interest in the development of solid-state batteries, the study of the electrical properties of alkali phosphate-based glasses has attracted considerable attention due to their great potential for application as electrolytes and/or electrode materials. In particular, research has focused on the improvement of ionic conductivity in these glasses, which is achieved by introducing a second glass-former that causes non-linear variation of ionic conductivity, a phenomenon known as *mixed glass former effect* (MGFE). The MGFE has been thoroughly studied in glasses with conventional glass-formers (B_2O_3, SiO_2, P_2O_5, GeO_2), yet there are scarce reports regarding the glass systems where a conventional glass-former is substituted by the conditional one, such as V_2O_5 and Nb_2O_5 [1,2].

In this work, glasses of the quaternary system $35Na_2O–10V_2O_5–(55 – x)P_2O_5–xNb_2O_5$, with x in mol%, were prepared and investigated in order to verify the MGFE in the presence of two conditional glass formers, Nb_2O_5 and V_2O_5. The latter is added due to its stabilizing effect on the glass structure, as it is involved in the glass network formation and its fraction is kept constant. The glasses are synthesized by the melt-quenching method and the parameters of synthesis are optimized to obtain the desired products whose amorphous character is confirmed by PXRD. The glass transition temperatures are determined by DTA, while their (micro)structural properties are evaluated by SEM-EDS analysis and infrared spectroscopy. The electrical properties of prepared glasses are studied by impedance spectroscopy (IS) in a wide frequency (0.01 Hz – 1 MHz) and temperature (-90 °C – 240 °C) range. The correlation between the structural changes occurring upon glass-formers exchange, and certain physico-chemical properties of these glasses is discussed in detail.

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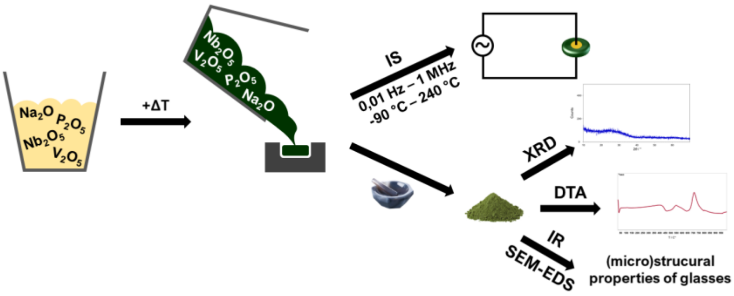

Figure 1. A schematic representation of the study of $35Na_2O–10V_2O_5–(55 – x)P_2O_5–xNb_2O_5$ glasses

PREPARATION OF NEW FUNCTIONAL FILAMENTS – PET-G/TiO_2 AND PET-G/TiO_2/CNT COMPOSITES

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The aim of this work was to produce a new functional filament using glycol-modified polyethylene terephthalate (PET-G) as a polymer matrix with the addition of titanium dioxide (TiO_2) and carbon nanotube (CNT) fillers. The composite filament produced is used to manufacture static mixers on the 3D-printer using additive manufacturing technology – fused filament fabrication (FFF).

The addition of the fillers modifies the physico-chemical properties of the polymer and gives the polymer photocatalytic properties. TiO_2 as a photocatalyst can decompose organic matter under the influence of ultraviolet (UV) light source, such as sunlight for example. CNT is added to the composite to enhance the photocatalytic effect of the TiO_2. The addition of the fillers also changes the mechanical properties of the composite compared to PET-G itself.

The fillers were added to the polymer matrix in several different ratios. The mechanical properties of the prepared composites were determined. Eight static mixers were successfully manufactured, seven from composite filaments with different filler ratios and one from pure PET-G filament. The manufactured static mixers (Fig. 1.) will later be used to decompose organic pollution in water in the presence of sunlight.

This work has been supported by European Regional Development Fund under the project: OS-Mi (KK.01.1.1.04.0006) and by Croatian Science Foundation under the projects DOK-2020-01-8955 and DOK-2021-02-5999.

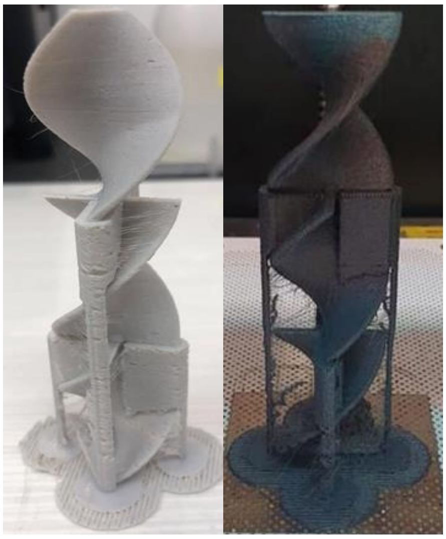

Figure 1. 3D-printed static mixers from different filler ratio composites

EPR UVID U MAGNETSKA SVOJSTVA DVOMETALNIH BAKAR/CINK MOF-74 MATERIJALA

EPR INSIGHT INTO MAGNETIC PROPERTIES OF BIMETALLIC COPPER/ZINC MOF-74 MATERIALS

Valentina Martinez[1], Senada Muratović[1], Bahar Karadeniz[1], Yulia Krupskaya[2], Vladislav Kataev[2], Dijana Žilić[1], Krunoslav Užarević[1]

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Metal-organske mreže (MOF-ovi) su kristalni, porozni materijali u kojima su metalni centri premošćujućim organskim ligandima povezani u ponavljajuće koordinacijske jedinice. MOF-74 je dobro istražena metal-organska mreža karakteristične saćaste strukture, koja joj pruža raznolika svojstva. Razvijene su brojne strategije za pripremu i modifikaciju dvometalnih MOF-ova kako bi se istražio doprinos sinergističkog efekta dvaju metala na svojstva ovih materijala [1]. Pritom se za mehanokemijsku sintezu pokazalo da osigurava dobru kontrolu nad stehiometrijskim omjerom dvaju metala u MM'-MOF-74 [2].

Naš cilj je bio proučiti kakav utjecaj izbor prekursora odnosno sintetskog pristupa ima na raspodjelu bakra i cinka u mreži, preciznije, da li je ona ravnomjerna ili postoje domene pojedinih metala. U tu svrhu mehanokemijski su pripravljeni bimetalni bakar/cink MOF-74 materijali. Iako nisu uočene strukturne razlike između sintetiziranih materijala, spektroskopija elektronske paramagnetske rezonancije (EPR) otkriva da im raspodjela metala u mreži nije jednaka. Ovo je dodatno pojašnjeno uz *in situ* praćenje reakcija difrakcijom sinkrotronskog rentgenskog zračenja na polikristalnom uzorku, kojim su uočeni različiti mehanizmi sklapanja mreže.

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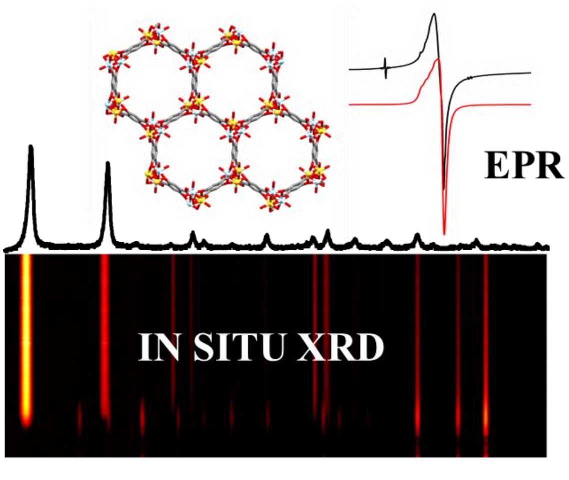

BIORAZGRADNJA MIKROPLASTIKE POLISTIRENA PRIMJENOM BAKTERIJSKIH KULTURA

BIODEGRADATION OF MICROPLASTICS POLYSTYRENE USING BACTERIAL CULTURE

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Posljedica nezaustavljivog rasta proizvodnje plastike i neadekvatnog odlaganja plastičnog otpada postaje globalni izazov. Velike su količine plastike u okolišu pod direktnim utjecajem biotičkih i abiotičkih faktora uslijed kojih dolazi do usitnjavanja čestica i nastajanja sitnih čestica plastike, odnosno mikroplastike (MP). Uslijed akumulacije MP-a, čestica manjih od 5 mm, predstavljaju sve veće globalno onečišćenje, a zbog njenih malih dimenzija teško ju je analizirati i ukloniti iz okoliša. Biološka razgradivost polimera ovisi o fizikalnim i kemijskim svojstvima polimera, abiotičkim svojstvima, ali i o svojstvima samih mikroorganizama. U ovom radu ispitivana je biorazgradnja čestica polistirena (PS) primjenom bakterije *Bacillus cereus*. PS se široko koristi zbog svojih dobrih mehaničkih svojstava, relativno niske cijene te stabilnosti. Cilj ovoga istraživanja bio je ispitati optimalne uvjete za proces biorazgradnje MP-a primjenom navedene bakterijske kulture. Dizajn eksperimenta se provodio prema Full Factorial dizajnu (FF) prema kombinaciji za tri ispitivana čimbenika – veličina MP-a, koncentracija MP-a, i broj okretaja rotacijske tresilice – na tri razine (minimalna, srednja i maksimalna vrijednost). Tijekom 30 dana provedbe pokusa biorazgradnje, praćena je promjena optičke gustoće (OG) te ukupni broj izraslih kolonija bakterija (CFU). U vodenoj fazi određivane su vrijednosti ukupnog (TC), organskog (TOC) i anorganskog (IC) ugljika te koncentracije aniona i kationa. LC/MS analizom identificirani su otpušteni aditivi s čestica MP-a te razgradni produkti potencijalno nastali prilikom biorazgradnje MP-a. Strukturne promjene PS-a određene su FTIR-ATR spektroskopijom. Rezultati pokusa ukazuju da je bolji rast bakterije *Bacillus cereus* uočen pri koncentraciji PS-a od 500 mg/L te brzini okretaja od 150 o/min. S obzirom na navedeno, ispitivana bakterijska kultura ima sposobnost biorazgradnje mikroplastike.

Ovo istraživanje financira Hrvatska zaklada za znanost: Projekt IP-04-2019-9661 (AdWaTMiR); Primjena naprednih tehnologija obrade voda za uklanjanje mikroplastike.

UTJECAJ MOLIBDENOVOG(VI) OKSIDA NA STRUKTURU I POLARONSKU PROVODNOST VANADATNO-FOSFATNIH STAKALA

INFLUENCE OF MOLYBDENUM(VI) OXIDE ON THE STRUCTURE AND POLARONIC CONDUCTIVITY OF VANADIUM PHOSPHATE GLASSES

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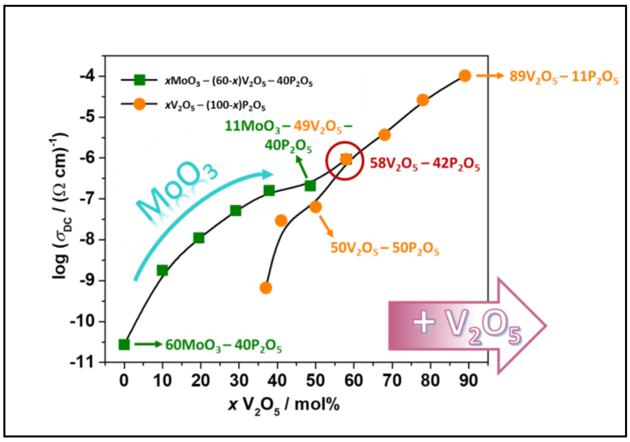
Oksidna stakla koja sadrže okside prijelaznih metala (TMO) kao što su V_2O_5, MoO_3, WO_3 i Fe_2O_3 od velikog su znanstvenog interesa zbog svoje potencijalne primjene u fotonici, kao elementi elektroničkih sklopova, senzori plina, itd. Električna vodljivost u ovim staklima posljedica je skokova malih polarona između iona prijelaznih metala u različitim oksidacijskim stanjima te ovisi o količini oksida prijelaznog metala, udjelu iona prijelaznog metala u različitim oksidacijskim stanjima te njihovoj međusobnoj udaljenosti. Među raznim prijelaznim metalnim oksidima koji se mogu ugraditi u oksidna stakla, vanadijev (V) oksid je posebno atraktivan jer sudjeluje u formiranju strukturne mreže stakla i stoga se može dodavati u velikim količinama. Također, zanimljivo je istražiti kako dodatak drugog TMO-a utječe na polaronsku vodljivost u ovim staklima zbog mogućeg prijenosa elektrona preko različitih TM iona, kao i modifikacije strukturne mreže koja može, ali i ne mora, pogodovati transportu polarona. U ovom istraživanju, serija binarnih $xV_2O_5–(100–x)P_2O_5$ stakala sa širokim rasponom sastava od $x = 41$ do $x = 89$ mol% i ternarnih $(60–x)MoO_3–xV_2O_5–40P_2O_5$ stakala s $x = 0$-49 mol%, pripremljene su metodom naglog hlađenja taline. Struktura i električna svojstva dobivenih uzoraka stakala ispitana su Ramanovom i impedancijskom spektroskopijom. Udio V^{4+} iona, V^{4+}/V_{tot} (binarni sustav), te zbroj iona V^{4+} i Mo^{5+}, $(V^{4+}+Mo^{5+})/(V+Mo)_{tot}$ (ternarni sustav) određeni su iz temperaturne ovisnosti magnetizacije mjerene SQUID magnetometrom. DC vodljivost stakala u binarnom sustavu raste gotovo linearno s povećanjem V_2O_5 dostižući najveću vodljivost od $1{,}03\times10^{-4}$ $(\Omega\ cm)^{-1}$ pri 30 °C za staklo s 89 mol% V_2O_5. Također, povećanje udjela V_2O_5 uz istovremeno smanjenje udjela MoO_3 u ternarnoj seriji stakala uzrokuje snažno povećanje vodljivosti do 40 mol% V_2O_5 nakon čega slijedi blagi porast za veći sadržaj V_2O_5. Usporedba stakla iz binarne i ternarne serije s približno istom količinom V_2O_5 pokazala je nešto veće vrijednosti vodljivosti za stakla s MoO_3 što ukazuje na mali, ali evidentan pozitivan utjecaj molibdena na električna svojstva najvjerojatnije putem strukturnih modifikacija fosfatne mreže koje ubrzavaju polaronski transport između vanadijevih iona.



POVEĆANJE IONSKE VODLJIVOSTI NATRIJEVOG FOSFATNOG STAKLA DODATKOM WO_3 I MoO_3

ENHANCEMENT OF IONIC CONDUCTIVITY IN SODIUM PHOPSHATE GLASSES BY ADDITION OF WO_3 AND MoO_3

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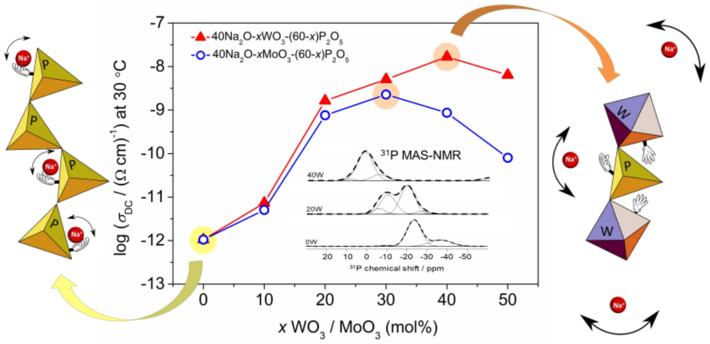
Fosfatna stakla koja sadrže alkalijske i prijelazne metalne okside intenzivno se istražuju posljednjih godina zbog jednostavne i ekonomične priprave te dobrih fizikalno-kemijskih svojstava. Ovi su materijali posebice interesantni za primjenu kao čvrsti elektroliti zbog mogućnosti dodatka relativno velike količine alkalijskih oksida (≤50 mol%). Ipak, dosadašnja su istraživanja pokazala da je ionska vodljivost niska i pri visokim koncentracijama ovih iona zbog njihove slabe pokretljivosti. U ovom smo istraživanju pokazali kako se pokretljivost alkalijskih iona u ovim materijalima može znatno povećati dodatkom WO_3 i MoO_3. Istraživanje je provedeno na dvije serije stakala pripravljene naglim hlađenjem taline: $40Na_2O–xMoO_3–(60-x)P_2O_5$ i $40Na_2O–xWO_3–(60-x)P_2O_5$; x = 0-50 mol%. Metodom impedancijske spektroskopije (IS) određena su električna svojstva stakala te se pokazalo kako ionska provodnost raste preko četiri reda veličine s dodatkom WO_3, te oko tri reda veličine u slučaju MoO_3 (Slika 1). Osim toga, dobivena je i maksimalna vrijednost provodnosti pri 30 mol% MoO_3 i 40 mol% WO_3. Kako bi se dobio uvid u strukturne promjene nastale dodatkom navedenih oksida korištena je ^{31}P MAS-NMR spektroskopija. Rezultati su pokazali kako ugradnja volframovih i molibdenovih poliedara u fosfatnu mrežu odnosno nastanak P-O-W/Mo veza prati isti trend ovisnosti o sastavu stakla kao i ionska provodnost. Navedeno upućuje da nastajanje miješanih volframovih/molibdenovih-fosfatnih jedinica ubrzava transport Na^+ iona te značajno poboljšava ionsku vodljivost ovih materijala.



Slika 1. Povećanje ionske vodljivosti natrijevog fosfatnog stakla dodatkom WO_3 i MoO_3.

IMPROVEMENT OF GRANULOMETRIC PROPERTIES OF CRYSTALS BY CONSTANT SUPERSATURATION FEEDBACK CONTROL

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The aim of this work was to investigate different control policies of the batch cooling crystallizer on the granulometric properties of obtained crystals. The study was conducted by computer simulation using population balance modeling in Simulink [1]. The Population balance was solved using the conservation element/solution element (CESE) method and consequently the dynamic evolution of crystal size distribution was obtained. The system under study consisted of 1 L batch crystallizer with water as solvent and potassium nitrate as solute. The cooling system was not modeled because of the slow nature of the crystallization process and almost instant reaction of thermostat in real life application. The crystallizer was cooled from 32 °C to 20 °C with the starting concentration being saturation concentration at 32 °C. The crystallizer was seeded with 2 g of KNO_3 and crystal size distribution of seeds was taken to be normal with mean 200 μm and standard deviation of 50 μm. Two temperature control policies were investigated, namely open loop linear cooling and closed loop (feedback) constant supersaturation control. For open loop linear cooling, different cooling rates were investigated and for the case of closed loop control, different supersaturations were investigated. The linear control policy had shorter operating time, but gave a significantly bigger ratio of nucleated crystals in the final product. Increasing the cooling rate resulted in a higher ratio of nucleated crystals which is considered to be a negative effect. On the other hand, constant supersaturation control had longer operating time, but resulted in a smaller ratio of nucleated crystals in the product. In conclusion, constant supersaturation feedback control is preferred because of improved granulometric properties of the product in comparison with linear open loop cooling policy.

This research is funded by European Structural and Investment Funds, grant number KK.01.1.1.07.0017 (CrystAPC – Crystallization Advanced Process Control).

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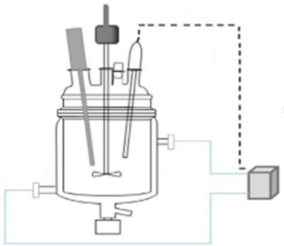
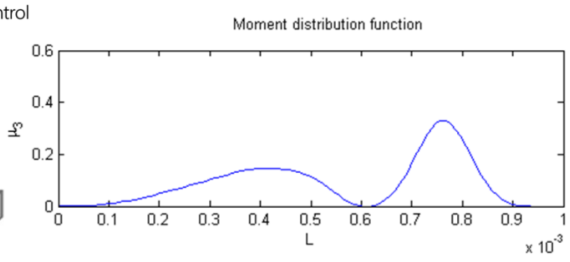
CrystAPC
crystallization advanced process control





KOORDINACIJSKE PUZZLE S KOMPLEKSNIM SPOJEVIMA MOLIBDENA SA SCHIFFOVIMA BAZAMA

COORDINATION PUZZLES WITH MOLYBDENUM SCHIFF BASE COMPLEXES

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The coordination chemistry of molybdenum has been growing rapidly due to the rich biochemical and catalytical properties of the obtained complexes [1,2]. Molybdenum Schiff's base complexes are of particular interest because MoO_2L type of complexes possess open coordination site that can be utilized for substrate binding properties [3]. Furthermore, hydrazone ligands are the most important pharmacophoric cores of several anti-inflammatory, antinociceptive, and antiplatelet drugs [4]. In light of the mentioned, two ligands obtained from nitrobenzaldehyde were prepared and coordinated to the MoO_2^{2+} core. If the reactions were performed in alcohols, mononuclear complexes, $[MoO_2(L^{1\ \mathrm{or}\ 2})(D)]$, D=donor molecule, were obateined. When acetonitrile was used as the solvent, the polynuclear $[MoO_2(L^1)]_n$ or mononuclear complex $[MoO_2(L^2)(H_2O)]$ was obtained. All the complexes were analysed and identified by IR-ATR, TG analysis, while molecular and crystal structure was determined by X-Ray diffraction. It has been noticed that grinding of $[MoO_2(L^2)(D)]$ alters the crystal structure and obtained compounds correspond to $[MoO_2(L^2)]_n$. After exposure to alcohol vapors, the starting compounds $[MoO_2(L^2)(D)]$ were obtained. Further research perspective is to test the obtained complexes as the catalysts in the oxidation reactions following the principles of green chemistry.

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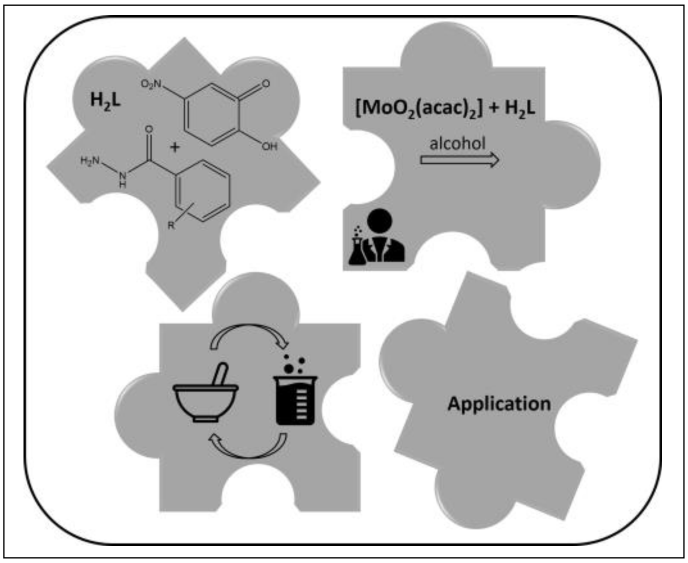

CHARACTERISATION OF CALCIUM ALUMINATE CEMENT HYDRATION

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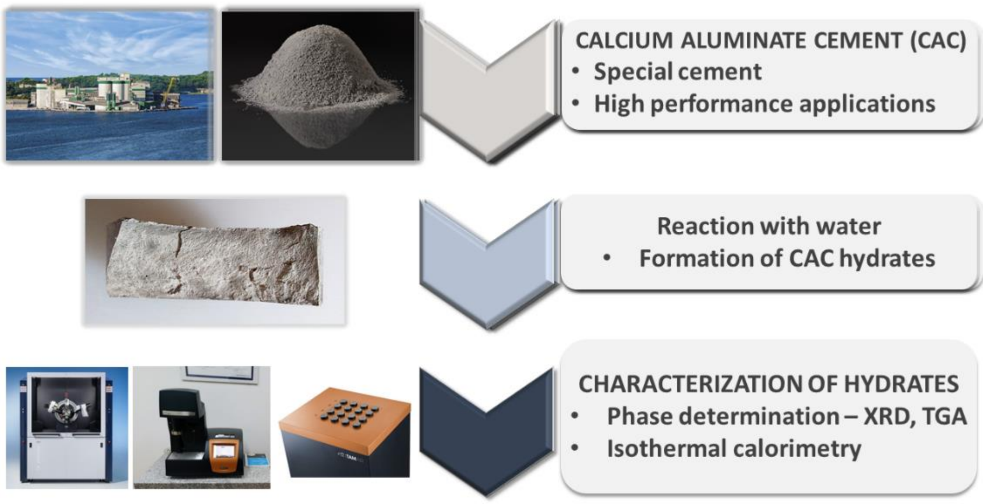
After water, cement is the second most widely used substance in the world and the largest manufactured product by mass. Calcium aluminate cement (CAC) is a special cement used for high-performance applications (resistance to chemical attack, high early strength, refractory use, abrasion resistance, and/or use at low ambient temperatures). Monocalcium aluminate, CA, the main constituent of CAC, reacts with water to form a series of calcium aluminate hydrates. Therefore, the main objective of the present paper is to determine the occurring hydrated phases of CAC paste. Moreover, complementary analytical methods such as X-ray diffraction analysis, thermogravimetric analysis and isothermal calorimetry will be presented to characterise hydration of CAC.



MACHINE-LEARNING IN CHEMISTRY

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Machine learning (ML) approaches are widely used to analyse and model various types of problems, including those related to chemistry. The basic premise is to have a large enough and reliable dataset that is used for training and testing a predictive model. In the presentation, process of selecting ML method (like Random Forest or Graph Neural Network) and building of predictive models will be demonstrated in the field of design of novel chemicals with biological activities, such as drugs and agrochemicals.

The authors are thankful to the European Union (European Regional Development Fund - the Competitiveness and Cohesion Operational Program), for funding this study through the project Bioprospecting of the Adriatic Sea (KK.01.1.1.01.0002), granted to The Centre of Excellence for Marine Bioprospecting—BioProCro.

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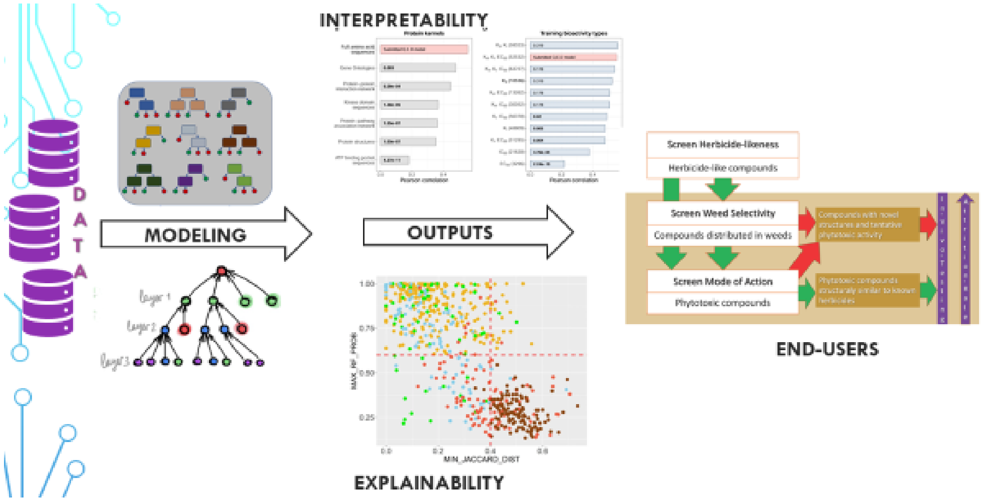

CHARACTERIZATION OF HISTORICAL MORTARS AND IDENTIFICATION OF THEIR PREPARATION TECHNOLOGY: ROMAN MILITARY CAMP VIMINACIUM

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Recent technological developments in the field of material science and applied chemistry have led to the fact that technological research is an inevitable procedure and first step in the diagnosis of historical buildings state. This research required a multidisciplinary approach and brought very valuable scientific knowledge and data for conservation practice [1,2]. The aim of our research paper was detailed characterization of historical mortars from the Roman period: Roman military camp Viminacium [3]. In situ and laboratory examination of the sampled materials included: visual observations, stereo-optical and digital microscopy, spectrophotometry and colorimetry, mineralogical and petrological analyses, physical-mechanical tests, thermal characterization, mechanical and chemical separation of aggregates and binders, and characterization of samples, binders and aggregates. These examinations of historical mortar samples gave information about mortars composition, their technology of preparation, as well as information about their degradation. Data obtained through mortar analyses. Moreover, the obtained results contribute to the knowledge base about Roman mortars on the Danube Limes in Serbia. Furthermore, gained results were taken as the starting point in designing compatible restoration mortar.

The authors are grateful for the support of the Science Fund of the Republic of Serbia, through the Program for Excellent Projects of Young Researchers - PROMIS, Grant Agreement #6067004, Project acronym MoDeCo2000.

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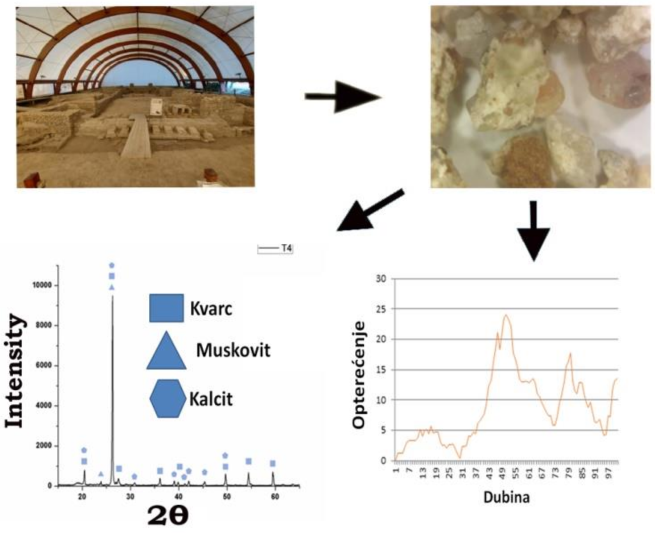

POSTERSKA IZLAGANJA
POSTER PRESENTATIONS

Analiza sinteza i vođenje procesa
Process analysis, synthesis and design

AN IMPROVED SPECTROPHOTOMETRIC METHOD FOR THE DETERMINATION OF PEROXIDE VALUE IN FATS FOR CHOCOLATE PRODUCTION

Veronika Barišić, Ivana Flanjak, Antun Jozinović, Jurislav Babić, Drago Šubarić, Đurđica Ačkar

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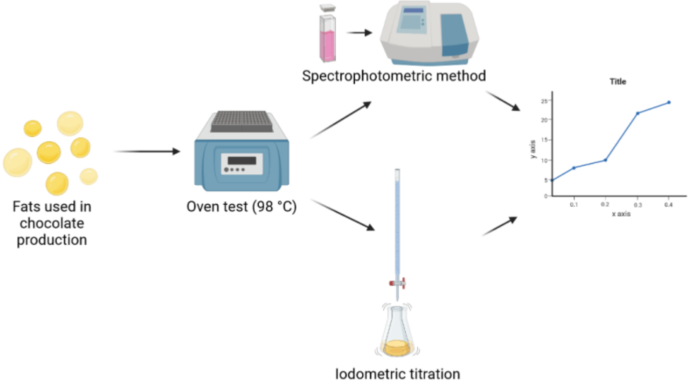
Chocolates are confectionery products with contents of fat, predominantly cocoa butter. Along with cocoa butter, different cocoa butter equivalents can be used. During storage, oxidation of fats may occur and influence shelf-life of chocolate. Usually, iodometric titration is used for the determination of peroxide value. However, the spectrophotometric method, based on the ability of peroxides to oxidize ferrous ions to ferric ions, uses fewer chemicals and is faster compared to the titration method. The aim of this research was to evaluate if the spectrophotometric method can be used in routine analysis of peroxide value. Five types of fats used in chocolate production were examined: four different samples of cocoa butter and blend of vegetable fats. To determine the span of peroxide value, and to accelerate the increase of the peroxide value of fats, samples were kept in a ventilator oven at 98 °C until limit of spectrophotometric method was reached (conditions based on the Oven test). Before the experiment, the spectrophotometric method was validated and limits of detection and quantification were determined. For all analysed fats, samples were taken in regular intervals of storage and peroxide value was determined both spectrophotometrically and by titration. Results showed limits and advantages of the spectrophotometric method for peroxide value determination compared to iodometric titration. Results showed that spectrophotometric method can be used for determination of peroxide value of fats for chocolate production. Also, the resistance of non-deodorized cocoa butter to peroxide formation was recorded.



INFLUENCE OF DISACCHARIDES ON COMPLEX FORMATION OF β-CYCLODEXTRIN WITH CATECHIN

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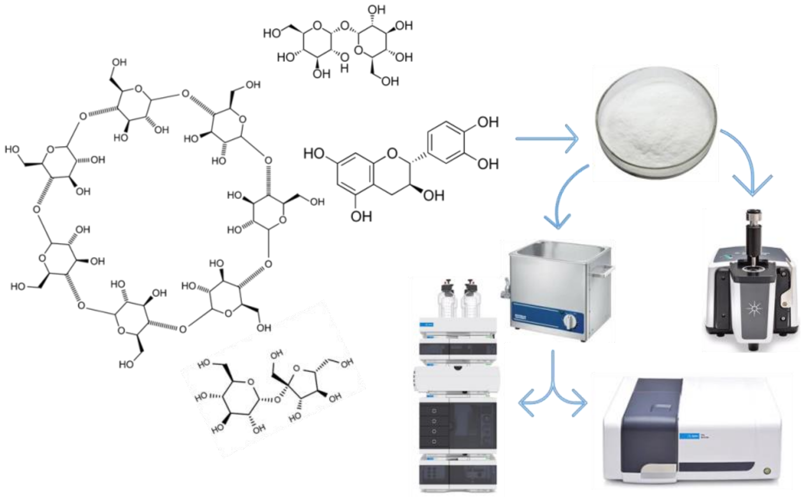
Catechin is a naturally occurring polyphenol that belongs to a group of flavonoids. Considering catechin's positive antimicrobial, antiallergic, anti-inflammatory and anticancer effects, it's a compound with potential applications in foods and drugs. Its shortcomings, such as light and oxygen sensitivity, sparingly water solubility and astringency, could be overcome by encapsulation. In the present study, inclusion complex of catechin with β-cyclodextrin using co-precipitation method, followed by freeze-drying, was prepared and analyzed. Influence of disaccharides (trehalose and sucrose) addition on catechin encapsulation was also investigated. Catechin concentrations were determined by HPLC analysis, and the antioxidant activity of the samples was assessed. Additionally, FTIR analysis was performed to confirm encapsulation. The results showed that catechin concentrations in samples ranged from 3.12 mg/g to 3.35 mg/g and that the addition of disaccharides negatively affected catechin encapsulation. Antioxidant activity had the same trend and increased with higher catechin concentrations in samples. By observing IR spectrum, it was noticed that some bands at β-cyclodextrin were shifted when catechin was present, which could be related to formation of intra-molecular hydrogen bonds. These results contribute to better insight into catechin behavior in food systems where disaccharides are usually present. Also, catechin/β-cyclodextrin inclusion complex could find its application in food products as an ingredient for antioxidants enrichment.



COMPARISON OF LINEAR CALIBRATION MODELS FOR PREDICTING GLYCINE CONCENTRATION

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Accurate measurement of solution concentration is of great importance for crystallization processes since supersaturation is prerequisite for nucleation and crystal growth. The development of process analytical technologies (PAT) enables the continuous measurements of process parameters for the production of high-quality drug products. The current solute concentration among with solubility curve provides information on supersaturation in the solution and thus allows implementation of feedback supersaturation control (SSC). The most commonly used method for in-situ concentration measurements is using ATR-FTIR spectroscopy. The IR absorbance of the dissolved compound is dependent on its concentration in the solution, as well as the temperature of the solvent. Therefore, a calibration is necessary to convert absorbance data into solution concentration [1]. In this work, ATR-FTIR spectra with the corresponding temperature of solutions with different concentrations are used to build two different calibration models: partial least squares regression (PLSR) and principal component regression (PCR) to monitor the concentration of glycine solution in real-time. Cross-validation was used to choose the right number of components to avoid overfitting the model. After visualizing ATR-FTIR spectra, the characteristic absorption bands were marked in the region between 1200 and 1800 cm^{-1}. The original dataset (W) and the subdivided dataset (C) were preprocessed using several different mathematical treatments (scaling, normalization, standardization and Savitzky-Golay smoothing) and used to build calibration models. Results show that, PLSR has better predictive performance in comparison to PCR with the same number of components used.

This research is funded by European Structural and Investment Funds, grant number KK.01.1.1.07.0017 (CrystAPC – Crystallization Advanced Process Control).

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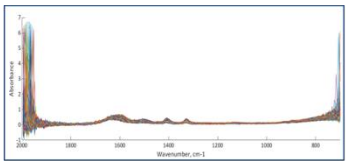

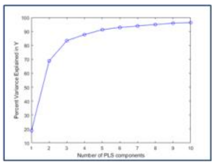

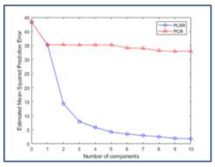

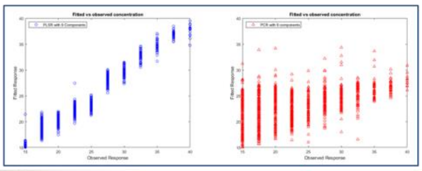

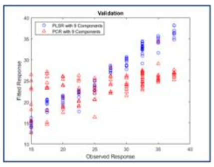

Europska unija
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REPUBLIKA HRVATSKA
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EUROPSKI STRUKTURNI I INVESTICIJSKI FONDOVI
Operativni program KONKURENTNOST I KOHEZIJA
CrystAPC
crystallization advanced process control

TRADITIONAL APPLE CULTIVARS POLYPHENOLIC PROFILE ANALYSIS AND THEIR RESISTANCE TO INFECTION BY *PENICILLIUM EXPANSUM*

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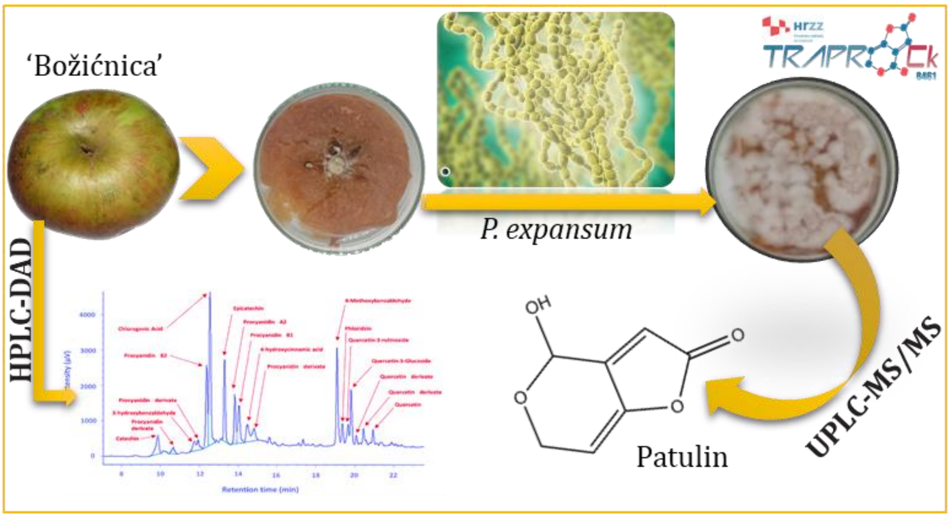
Traditional apple cultivars contain a higher amount of polyphenolic compounds which are the bearers of apple resistance to plant diseases. Some of the biological activities of polyphenols are antimutagenic, antiphlogistic, antioxidant activity and antifungal activity. Due to that, it seems like traditional apple cultivars possess great potential for apple fruit resistance on *Penicillium expansum* infection. It is confirmed that traditional apple varieties contain higher levels of polyphenols like flavanols, phenolic acids, procyanidins, dihydrochalcones and flavan-3-ols. Seven traditional apple cultivars (´Paradija´, ´Srčika´, ´Mašanka´, ´Kanada´, ´Božičnica´, ´Ivandija´ and ´Šampanjka´) from Croatia were analysed by high- performance liquid chromatography with diode-array detectors for the content of polyphenolic compounds. The resistance of traditional apple cultivars to infection by *P. expansum* (CBS 325.48) was performed mycelia grown on potato dextrose agar at 29 °C; inoculated 1 cm thick apple slices were incubated at 29 °C until the *P. expansum* colony reaches the diameter of 9 cm. Patulin content was determined by UPLC-MS/MS method.
Results showed that 17 phenolic compounds were detected in traditional apple cultivars. The highest amount of catechin (114.89 ± 2.6 µg/mL), epicatechin (229.81 ± 5.97 µg/mL), chlorogenic acid (3028.78 ± 34.17 µg/mL) and quercetin (18.92 ± 2.38 µg/mL) had ˙Božićnica˙. The highest content of phloridzin (117.75 ± 2.06 µg/mL), phloretin (48.23 ± 0.77 µg/mL), quercetin-3-rutinoside (41.65 ± 0.93 µg/mL) and procyanidin B2 (250.12 ± 2.93 µg/mL) had ˙Srčika˙. Moreover, the highest content of 4-hydrixycinnamic acid (54.59 ± 1.36 µg/mL) and 2-6-dimethoxybenzoic acid (352.8 ± 25.55 µg/mL) had ˙Kanada˙ and the highest content of procyanidin A2 (55.11 ± 1.75 µg/mL) and procyanidin B1 (39.52 ± 1.14 µg/mL) had ˙Paradija˙. However, patulin wasn´t detected in any up mentioned apple cultivars.

Here presented data are part of the project "The possibility of exploiting traditional apple cultivars for the production of apples and apple juice with the reduced patulin content" supported by Croatian Science Foundation (UIP-2020-02-8461).



DETERMINATION OF CANNABINOIDS IN *CANNABIS SATIVA* EXTRACTS OBTAINED BY CONVENTIONAL AND DEEP EUTECTIC SOLVENTS

Martina Jakovljević Kovač, Mario Komar, Melita Lončarić, Stela Jokić, Maja Molnar

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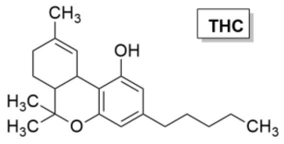
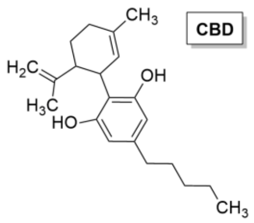
Currently, there is a growing market demand for products derived from industrial hemp for food, recreational and medical use. This plant is widely known to be the major source of cannabinoids, including cannabidiol (CBD), cannabidiolic acid (CBDA), tetrahydrocannabinol (THC), cannabichromene (CBC), cannabigerol (CBG), and cannabinol (CBN). Cannabinoids are very significant group with strong remedial potential against inflammation, depression, nausea and epilepsy. On the other hand, THC is mostly responsible for psychotropic activities, so it is a controlled substance. Given that, cannabinoids are carriers of biological activity of industrial hemp, which is increasingly used in various forms (food, cosmetics or tinctures), it is important not just to develop a fast and reliable method of quantification of cannabinoids in hemp samples but to find the most suitable solvent and extraction conditions.

The aim of this paper was to select the most suitable solvent and conditions among conventional (aqueous ethanol solutions (30-70% (*v*/*v*)), ethanol, methanol, acetonitrile) and hydrophobic deep eutectic solvents (hDESs), as well as the development of HPLC method for the detection of cannabinoids in prepared extracts.

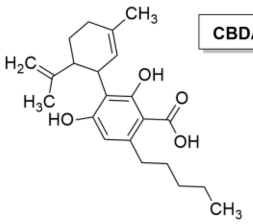
Depending on the conditions used and the solvent, different cannabinoids were extracted. The solvents show different ability to extract cannabinoids, so the conclusion about a universal solvent for all cannabinoids cannot be made. However, in terms of CBD, as the best known cannabinoid and its precursor, CBDA, the most suitable solvent is ethanol when extracted at 70 °C for 30 min. On the other hand, the most suitable hDES is a menthol:acetic acid (1: 1) for 60 min at 70 °C. Using ethanol as solvent 7.57 ug/mg of plant CBD and 100.25 ug/mg of plant CBDA was extracted, while by using menthol: acetic acid (1:1) 10.0 ug/mg of plant CBD and 128.67 ug/mg of plant CBDA was extracted proving that hDES can be a good substitute in the extraction of bioactive components from industrial hemp.



THC



CBD



CBDA

RENDGENSKA STRUKTURNA ANALIZA U RAZREDU−INTEGRIRANO POUČAVANJE

X–RAY STRUCTURAL ANALYSIS IN THE CLASSROOM–INTEGRATED TEACHING

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Korištenje novih tehnologija može znatno doprinijeti osuvremenjavanju metoda i sadržaja poučavanja kemije kroz integrirani pristup temeljnim prirodoznanstvenim pojmovima. Rendgenska difrakcija praha temeljna je analitička tehnika koja se koristi u mnogim laboratorijima, a u očekivanim učeničkim predznanjima i kurikulumskim ciljevima srednjoškolske kemije i fizike nalaze se svi potrebni pojmovi dostatni za upoznavanje ove metode.

U našem radu predložen je izbor sadržaja i nastavnih aktivnosti primjerenih učenicima četvrtog razreda gimnazije, kroz integrirano poučavanje u 90-minutnom nastavnom satu kroz studiju slučaja. Cilj rada je potaknuti nastavnike u istraživanju novih metoda i postupaka pri usvajanju sadržaja vezanih uz građu kristalnih tvari rabeći rendgensku strukturnu analizu. Predloženi didaktički materijali pogodni su za nastavni scenarij kada se rabe ustupljeni ili dostupni podatci difrakcijskih pokusa u okviru redovne nastave. Tijekom provedbe učenik upoznaje, istražuje i rabi dostupne otvorene baze kristalografskih podataka i pripadne COD ID (*Crystallography Open Database Identity Document*)[1], CIF datoteku (*Crystallographic Information File*), program *Mercury* [2] koji omogućuje kvalitativnu analizu difraktograma praha nepoznatog uzorka i vizualizaciju struktura molekula uzorka, a pruža i razne druge mogućnosti (poput istraživanja duljine veza između atoma, slaganje atoma/iona/molekula u jediničnoj ćeliji, analizu međumolekulskih interakcija, itd.). Tijekom ovakve nastavne učenici povezuju i produbljuju postojeća znanja iz *kemije, fizike* i *računalstva* i spoznaju svrhu 'učenja' često apstraktnih temeljnih pojmova.

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STUDIJA SLUČAJA

potrebno odrediti identitet nepoznatih praškastih uzoraka ⇨

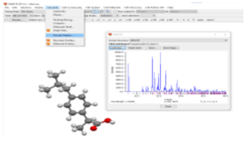
snimanje rendgenograma praha promatra se očitanjem QR koda ⇨

uz svaki uzorak učenik dobiva COD ID; na raspolaganju su i neoznačeni difraktogrami analiziranih prahova ⇨

Crystallography Open Database

COD ID; CIF;

Mercury - izračun difraktograma praha



usporedba s eksperimentalnim podatcima

identifikacija uzorka

APPLICATION OF INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY (ICP-MS) IN ANALYSIS OF SORPTION OF SELECTED LANTHANIDES ON IRON NANOPARTICLES

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Rare Earth Elements (REEs) are widely used in chemical engineering, nuclear industry, metallurgy, electronics and computer technology because of their unique properties. It is of great importance to fulfil ever-increasing demands for recycling those elements from REEs containing products as well as wastewater [1].

Among a number of available methods, adsorption of metal cations from water solutions has gained wide attention because of its simplicity, high efficiency and low cost. Zero-valent iron nanoparticles (nZVI) demonstrate unique sorption and magnetic properties, which are of great advantage in terms of magnetic separation and re-use without loss of efficiency [2]. Iron nanoparticles are often surface modified by use of coating reagents.

In this work, dipicolinic acid (pyridine-2,6-dicarboxylic acid, PDCA) was used for the surface modification [3]. In order to confirm the efficiency of functionalization, nZVIs were characterized with Fourier transform infrared spectroscopy (FTIR). Modification success was confirmed through assignation of vibration bands that correspond to PDCA bonding onto nanoparticles. Size of prepared nanoparticles was estimated by use of atomic force microscopy (AFM).

Sorption of selected REEs and actinides from aqueous solutions (Y, La, Ce, Sm, Eu, Gd, Dy, Er, Th, U) on neutral and functionalized nZVI was analysed by inductively coupled plasma-mass spectrometry (ICP-MS). Unique performance capability of this method allow the sensitive determination of ions in the heavy masses range, even in the cases when elemental isotopic composition is extremely complex. Measured results confirmed the different capacity for metal ion sorption in the nZVI and functionalized PDCA-nZVI mediums.

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PRAĆENJE NASTAJANJA NASLAGA POMOĆU MODELA NEURONSKIH MREŽA S PROCIJENJENIM NEMJERENIM PROCESNIM VARIJABLAMA U IZMJENJIVAČIMA TOPLINE ZA PREDGRIJAVANJE SIROVE NAFTE

FOULING DEPOSTION MONITORING USING NEURAL NETWORK MODELS WITH ESTIMATED UNMEASURED PROCESS VARIABLES IN CRUDE OIL PRE-HEAT HEAT EXCHANGERS

Nikola Rimac, Željka Ujević Andrijić

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Zbog nastajanja naslaga u izmjenjivačima topline dolazi do smanjenja efikasnosti rada izmjenjivača te povećanja troškova održavanja, kao i posljedično veće potrošnje energenata te povećane emisije CO_2. Gotovo polovica ukupnih operacijskih troškova rafinerije odlazi na gubitke uslijed nastanka naslaga u sekciji izmjenjivača topline za predgrijavanje sirove nafte prije atmosferske destilacije [1]. Mehanizam nastajanja naslaga zbog svoje kompleksnosti nije lako opisati. Praćenjem nastajanja naslaga mogu se predvidjeti potencijalni kvarovi izmjenjivača topline te omogućiti planirano čišćenje u svrhu smanjenja potrošnje energenata. Na osnovi dostupnih mjerenja procesnih varijabli te fizikalno-kemijskih svojstava ulaznih sirovih nafti mogu se razviti napredni identifikacijski modeli poput modela neuronskih mreža [2]. U ovom radu razvijeni su modeli neuronskih mreža za čiji je razvoj potrebno imati kontinuirano prikupljane podatke s mjernih instrumenata. Prikazan je način identifikacije nastanka naslaga, odnosno *fouling* faktora modelom neuronskih mreža u setu izmjenjivača topline u sekciji predgrijavanja sirove nafte čije su nemjerene varijable (temperature na ulazima tople struje) procijenjene na osnovi poznatih okolnih varijabli prema jednadžbama dizajna izmjenjivača topline i fizikalno-kemijskim karakteristikama sirove nafte. Rezultat ovog postupka daje informaciju o brzini i tendenciji nastanka naslaga u izmjenjivačima topline koja može poslužiti kao dostatna informacija za planiranje budućih čišćenja time umanjujući rizik od nenadanih troškova održavanja i povećanja potrošnje energenata.

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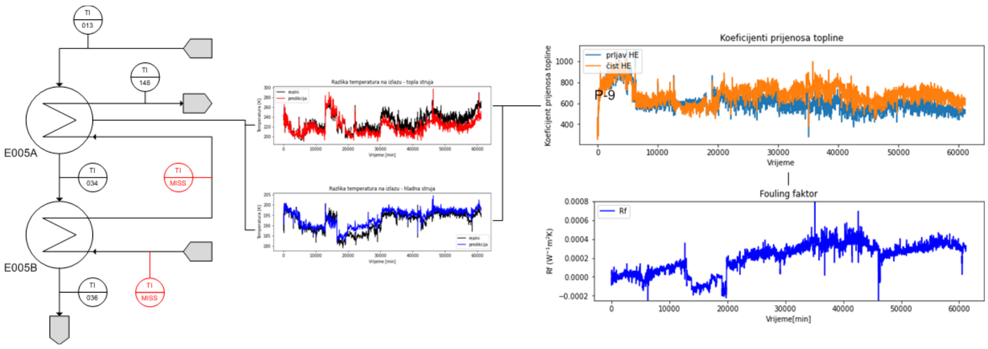

Biokemijsko inženjerstvo
Biochemical engineering

EVALUACIJA NITRILAZA KAO BIOKATALIZATORA ZA SINTEZU (*R*)-4-KLORO-3-HIDROKSIBUTANSKE KISELINE

EVALUATION OF NITRILASES AS BIOCATALYSTS FOR THE SYNTHESIS OF (*R*)-4-CHLORO-3-HYDROXYBUTYRIC ACID

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Enzimi nitrilaze, bez stvaranja slobodnih amidnih međuprodukata, kataliziraju reakcije hidrolize nitrila u karboksilne kiseline i amonijak [1]. Stoga se nitrilaza može koristiti kao biokatalizator u reakcijama pretvorbe (*R*)-4-kloro-3-hidroksibutironitrila (KHB) u (*R*)-4-kloro-3-hidroksibutansku kiselinu, pri čemu dolazi do spontane ciklizacije produkta u (*R*)-3-hidroksi-γ-butirolakton (HBL) (slika 1).

HBL je koristan kiralni građevni blok s primjenom u sintezi različitih polimera, otapala i farmaceutika. Postoje brojni kemijski putevi sinteze HBL-a, no većina ima nedostatke poput skupih ili opasnih reaktanata, intenzivnih procesnih uvjeta, te niskih iskorištenja i selektivnosti, što uzrokuje poskupljenje procesa izdvajanja produkta. Nasuprot tome, enzimski katalizirani procesi koriste blage reakcijske uvjete, postižu visoku selektivnost te mogu pružiti ekonomski isplativ postupak sinteze ove vrijedne kemikalije [2,3].

U ovom radu provedena je evaluacija 24 nitrilaze. Tijekom ispitivanja korišteni su isti početni uvjeti, koncentracija supstrata (KHB) i masena koncentracija nitrilaza, dok se reakcija pratila 6 sati. Enzim s najvećim iskorištenjem na produktu izabran je za sljedeći korak, kinetičko istraživanje. Određeni su kinetički parametri nitrilazom katalizirane sinteze (*R*)-4-kloro-3-hidroksibutanske kiseline iz (*R*)-4-kloro-3-hidroksibutironitrila.

Ovaj rad financira se projektom CATPHARMA (KK.01.1.1.04.0013).

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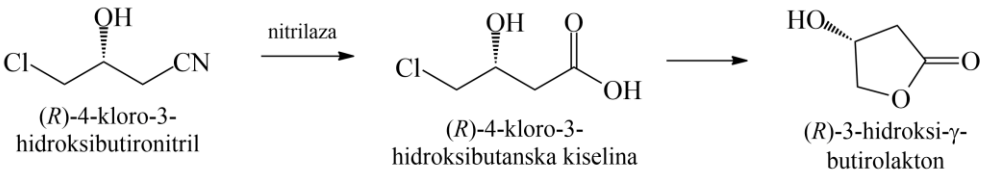

Slika 1. Reakcijska shema konverzije (*R*)-4-kloro-3-hidroksibutironitrila u (*R*)-4-kloro-3-hidroksibutansku kiselinu te spontana ciklizacija u (*R*)-3-hidroksi-γ-butirolakton

RATIONAL DESIGN OF DEEP EUTECTIC SOLVENTS FOR LIPASE CATALYZED KINETIC RESOLUTION (*R*,*S*)-1-PHENYLETHANOL

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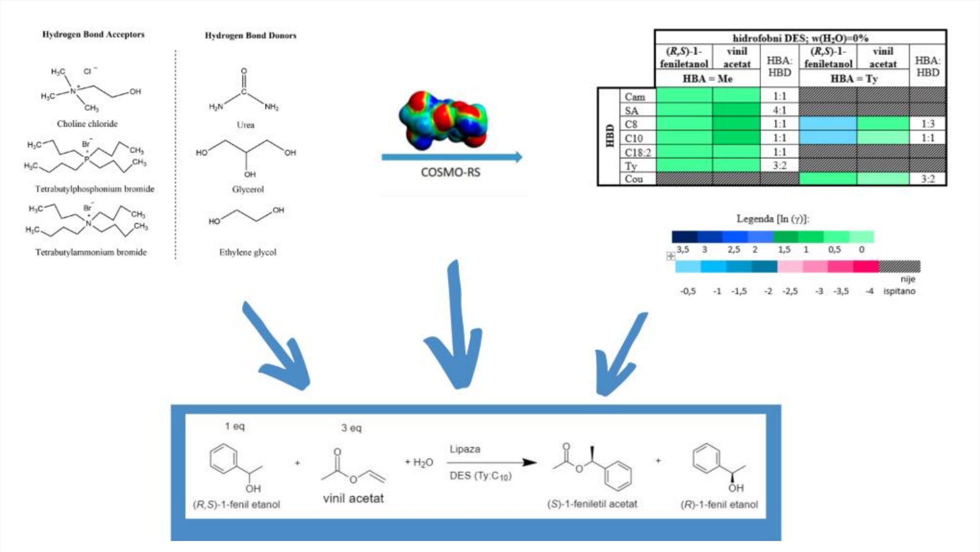
Deep eutectic solvents (DESs), as a green alternative to organic solvents from non-renewable sources, show their potential for future industrial applications and the potential of green chemistry as such through research and implementation in enzyme-catalyzed reactions. In this paper, eutectic solvents were investigated for kinetic resolution using the software program COSMO based on the evaluation of the solubility of the substrates vinyl acetate and (*R*,*S*)-1-phenylethanol. Kinetic resolution was carried out in selected eutectic solvents and the success of the reaction was monitored in the hydrophobic deep eutectic solvent (Ty:C_{10}) and compared to both hydrophilic deep eutectic solvent (ChClU10%) and the organic solvent ethyl acetate (classically used). Conversion and enantiomeric excess values were used to evaluate the success of the reaction. Thymol:decanoic acid (Ty:C_{10}) proved to be the best solvent among the tested solvents for carrying out the esterification reaction of (*R*,*S*)-1-phenylethanol with the highest conversion rate of 53.04%. The enantiomeric excess is satisfactory and is more than 97% for all three solvents used. Moreover, the enantiomeric excess (ee) is highest for our most successful solvent Ty:C_{10} and its value is 98.80%.

Results were obtained during research under the Croatian Science Foundation project (No. 7712) “Rational design of natural deep eutectic solvents for the preparation and formulation of chiral drugs”.



	hidrofobni DES; w(H_2O)=0%					
	(*R*,*S*)-1-feniletanol	vinil acetat	HBA:HBD	(*R*,*S*)-1-feniletanol	vinil acetat	HBA:HBD
HBD	**HBA = Me**			**HBA = Ty**		
Cam	🟩	🟩	1:1	▨	▨	▨
SA	🟩	🟩	4:1	▨	▨	▨
C8	🟩	🟩	1:1	🟦	🟩	1:3
C10	🟩	🟩	1:1	🟦	🟩	1:1
C18:2	🟩	🟩	1:1	▨	▨	▨
Ty	🟩	🟩	3:2	▨	▨	▨
Cou	▨	▨	▨	🟩	🟩	3:2

NUTRITIONAL SYSTEM BIOLOGY: ADVANTAGES, APPLICATIONS AND FUTURE PERSPECTIVE

Dora Givošev, Ivona Buljan, Josipa Jurčić, Martina Kosić, Franka Maretić, Antonija Matos, Sara Nadoveza, Anđela Sinković, Maja Benković, Tamara Jurina, Davor Valinger, Jasenka Gajdoš Kljusurić, Ana Jurinjak Tušek

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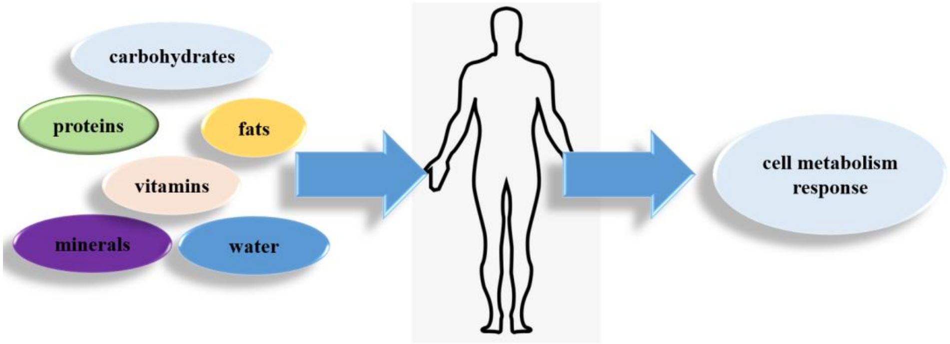
To better understand biological systems and changes that occur in them, scientists have developed a more holistic approach – systems biology. Systems biology combines several "-omics" disciplines: genomics, transcriptomics, proteomics, and metabolomics in order to obtain a large amount of data. This approach was soon recognized as a useful tool for nutritional research because it provides the opportunity to understand how different physiological systems interact with each other and with specific nutrients under different conditions. It can also be used to analyse and predict changes that take place in a cell over time, for example in the aging process and in the development of disease.
The advantages of using systems biology in nutrition research are numerous. Rather than focusing on an isolated nutrient and its metabolic pathway, it allows analysis of changes in that pathway, taking into account various conditions in the system, such as concentrations of other nutrients and enzymes. Physiological systems dynamically adapt to these changes to maintain homeostasis. One of the most important aspects of nutrition is its connection and correlation with health and disease. Systems biology can help in understanding how each nutrient affects health, but also how an individual's health status affects nutrient utilization and metabolism.
In this paper, an overview of the basics of systems biology in nutrition will be presented, with a focus on the benefits of this approach and the future perspective of this field.



KINETIČKA KARAKTERIZACIJA IMOBILIZIRANE ALDOLAZE

KINETICAL CHARACTERIZATION OF IMMOBILIZED ALDOLASE

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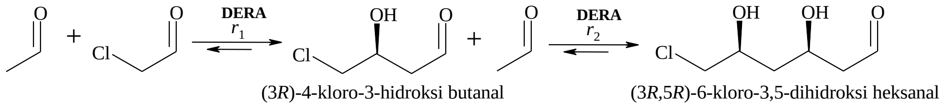
Prekursor bočnog lanca statina koji je jedan od najtraženijih farmaceutika se sintetizira korištenjem kemijskih i biokatalitičkih metoda. Aldolna adicija acetaldehida i kloroacetaldehida katalizirana enzimom deoksiriboza-fosfat aldolazom (DERA) (slika 1) je metoda čija je prednost proizvodnja enantiomerno čistog produkta, ali veliki nedostatak je deaktivacija enzima DERA u prisutnosti aldehida. Imobilizacija enzima na čvrsti nosioc je jedan od načina za povećanje stabilnosti enzima. Modeliranje kinetike reakcije, te uspostavljanje matematičkog modela procesa omogućuje razvoj i intenzifikaciju enzimski katalizirane reakcije.
U ovom radu, enzim DERA je imobiliziran na magnetske nanočestice kovalentnim vezanjem. Za funkcionalizaciju nosioca korišten je 3-aminopropiltrietoksilan (APTES), a za aktivaciju benzokinon. Kinetička karakterizacija DERA-e je provedena u prvom i drugom stupnju reakcije. U oba slučaja kinetika je opisana dvosupstratnom Michaelis-Menteničinom jednadžbom. Ispitana je i deaktivacija enzima u prisutnosti različitih koncentracija acetaldehida i kloroacetaldehida.



Slika 1. Reakcije aldolne adicije acetaldehida i kloroacetaldehida katalizirana enzimom DERA.

PREPARATION OF DEFATTED WHEAT FLOUR

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The purpose of this study was to prepare a defatted white wheat flour. Fats in flour are an important ingredient of wheat flour, which affects its structural and mechanical properties and the texture of baked products [1]. Nowadays, a healthy diet plays a significant role in the choice of food products. Certainly, customers are becoming careful and paying more attention to food quality. The idea of creating low-calorie, high-nutrient products is very favorable. This problem can be solved by developing innovative technology and using non-traditional methods to reduce the weight fraction of fat and thus increase the nutritional value and extend the shelf life of white wheat flour. For this purpose, supercritical fluid technology was used to perform experiments on white wheat flour. The CO_2 used in this technique was in its supercritical state, which was achieved when the processing temperature and pressure conditions were above the critical point [2]. The flour was exposed to $SCCO_2$ conditions at 300 bar for 24 h and 35 °C. It was found that $SCCO_2$ successfully extracted fats from white wheat flour, which was confirmed by the extraction of residual fat from $SCCO_2$-treated white wheat flour. For comparison, extraction of fat by the Soxhlet method with petroleum ether was also performed on untreated white wheat flour, where it was found that the fat content in $SCCO_2$-treated white wheat flour was lower by 20%.

On the other hand, the chemical composition and physical state of fats are significant in developing the necessary structure of dough and baked goods. Therefore, the rheological and baking tests were performed to confirm the suitability of $SCCO_2$-treated wheat flour for baking products.

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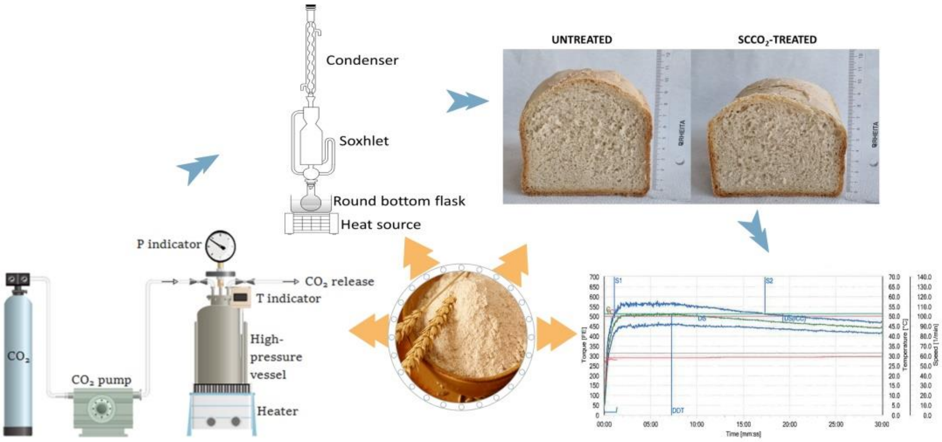

BIOKEMIJSKA OSNOVA ODABRANIH SLUČAJEVA IZ TV SERIJE “UVOD U ANATOMIJU”

BIOCHEMICAL BASIS OF SELECTED CASES FROM THE TV SHOW „GREY'S ANATOMY“

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Popularna serija *Uvod u anatomiju (Grey's Anatomy)* prikazuje se na malim ekranima već dva desetljeća. Slučajevi koji su u seriji često su inspirirani stvarnim slučajevima, a ponajviše se baziraju na kirurškim zahvatima. No, tijekom 18 sezona serije pojavili su se i slučajevi koji u svojoj pozadini imaju različite biokemijske osnove koje utječu na toksičnost i farmakološku aktivnost lijeka. Inspiracija za ove slučajeve pronađena je u biomedicinskim časopisima u kojima su opisani odgovarajući slučajevi iz prakse. U ovom radu dajemo pregled tih slučajeva i njihovu biokemijsku pozadinu. U prvom slučaju prisutni simptomi posljedica su neurotoksičnosti kobalta koja proizlazi iz njegovog utjecaja na hemostazu složenih biokemijskih reakcija (Fentonova reakcija, peroksidacija lipida i aktivacija proteaza i fosfolipaze A2 što vodi do oštećenja mijelinske ovojnice neurona). Stvaranja neurotoksina u drugom slučaju posljedica je interakcije biljnog lijeka i kemoterapeutskog sredstva, a u pozadini ima metabolizam/biotransformaciju dimetilsulfoksida. Obrađen je i slučaj pacijentice koja se probudila iz anestezije jer je brzi metabolizator korištenog anestetika. Kod brzih metabolizatora biotransformacija anestetika je ubrzana pa se pri normalnim dozama gubi farmakološki učinak. U posljednjem slučaju opisana je promijenjena boje mokraće kao rezultat hidroksilacije i glukuronidacije lijeka amitriptilina. Televizijske serije kao što je *Uvod u anatomiju* populariziraju znanost i mogu izazvati interes za studiranje u područjima biomedicine i biotehničkih znanosti.

SAHARIFIKACIJA LIGNOCELULOZNE BIOMASE ENZIMSKIM KOKTELOM IZ *T. LANUGINOSUS*

SACCHARIFICATION OF LIGNOCELLULOSIC BIOMASS BY ENZYME COCKTAIL FROM *T. LANUGINOSUS*

Marko Kolarić, Davor Mamuzić, Darijo Šibalić, Marina Tišma

Sveučilište Josipa Jurja Strossmayera u Osijeku, Prehrambeno-tehnološki fakultet Osijek,
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Thermomyces lanuginosus je termofilna gljiva koja tijekom uzgoja na lignoceluloznim supstratima proizvodi hidrolitičke enzime koji kataliziraju razgradnju hemiceluloze do jednostavnih šećera [1]. U ovom radu istraživana je mogućnost proizvodnje šećernog hidrolizata iz lignocelulozne sirovine primjenom nepročišćenog koktela enzima iz *T. lanuginosus*. U prvom dijelu istraživanja proveden je uzgoj *T. lanuginosus* na pljevici ječma na način da je 30 g supstrata (w_{H2O} = 70 %) inokulirano s 5 micelijskih diskova kulture (*Ø* = 1 cm) te inkubirano pri 45 °C. Tijekom 9 dana fermentacije, svaka 24 sata uzorci su ekstrahirani u citratnom puferu (pH = 6; 0,1 M) u svrhu proizvodnje enzimskog koktela koji sadrži enzime ksilanazu i *β*-glukozidazu. Maksimalne aktivnosti enzima ksilazana (3642 U $\mathrm{cm^{-3}}$, 30120 U $\mathrm{g_{st}^{-1}}$) i *β*-glukozidaza (4,5 U $\mathrm{cm^{-3}}$, 37 U $\mathrm{g_{st}^{-1}}$) izmjerene su nakon osmog dana fermentacije. Proizvedeni koktel enzima korišten je u sljedećim eksperimentima. U drugom dijelu istraživanja proveden je šaržni eksperiment saharifikacije pljevice ječma s nepročišćenim enzimskim koktelom u trajanju od 18 sati (45 °C, 350 rpm). Nakon saharifikacije DNS metodom su izmjerene koncentracije reducirajućih šećera u hidrolizatu (189 mg $\mathrm{g_{st}^{-1}}$). S obzirom da je nakon enzimske hidrolize došlo do povećanja koncentracije reducirajućih šećera za 13,5 puta, ova istraživanja biti će temelj daljnjeg razvoja ekološki i ekonomski održivog procesa proizvodnje bioetanola iz lignoceluloznih sirovina.

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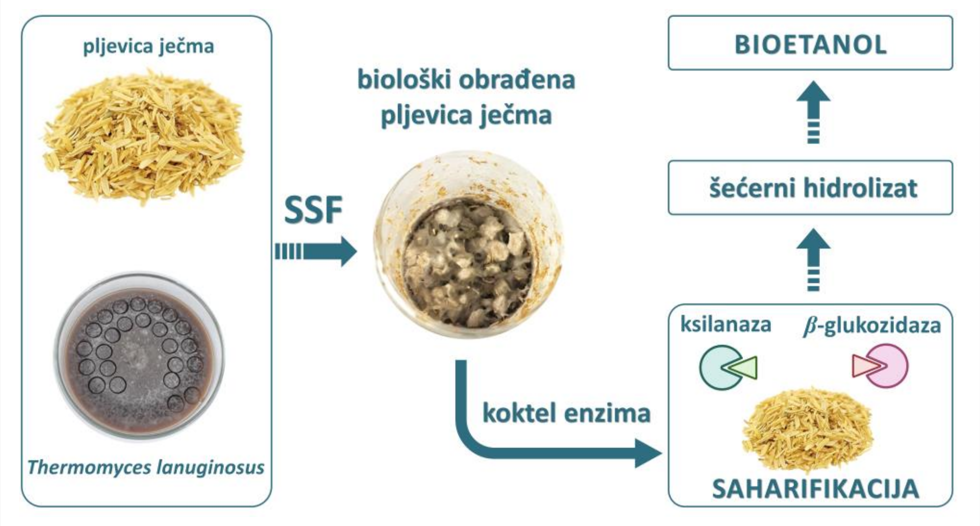

AMERICAN BLUEBERRIES (*VACCINIUM CORYMBOSUM* L.) AS A SOURCE OF BIOACTIVE SUBSTANCES

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American blueberries (*Vaccinium corymbosum* L.) are considered to be a rich source of various important bioactive substances that have numerous positive effects on human health, such as vitamins and different phenolic compounds, including flavonoids and anthocyanidins. Among others, they show good antioxidant, anti-inflammatory, anticancer, and antiproliferative properties [1,2].

Our study determined the activities of six selected enzymes and the concentration of total proteins by the Bradford method in juice and extracts obtained from pomace of American blueberries. Fresh and dehydrated blueberry juices were used for analyses, as well as ethanol extracts from fresh and dehydrated pomace, which were dried in a fruit dryer. Ethanol extracts were obtained by the Soxhlet extraction method. The activities of peroxidase, protease, laccase, α-amylase, glucoamylase, and transglutaminase were determined by specific enzymatic assays.

With this study, we confirmed the presence of all analysed enzymes in all four samples from blueberries. The highest enzyme activity in the tested samples was shown by the enzymes glucoamylase and cellulase, with enzyme activity above 2 U/mL. According to the results obtained, blueberries are an excellent natural source of bioactive substances, including proteins and enzymes, and thus have a great potential for use in various industries such as pharmaceuticals, medicine, food, and cosmetics.

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EXOTIC FRUIT PEELS AS A SOURCE OF BIOACTIVE AND HIGH VALUE-ADDED COMPOUNDS

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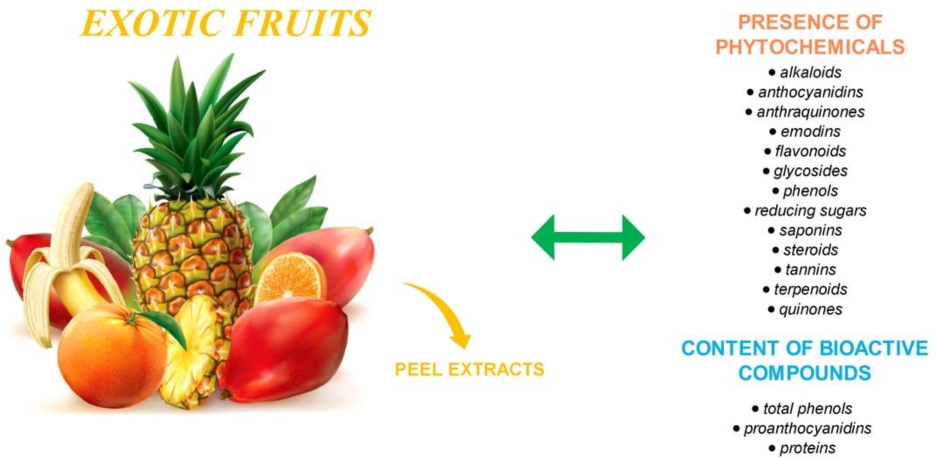
Most of herbal medicines are obtained from leaves, stems, flowers, and fruits and may be in some cases great alternative to drugs. Fruit peels, seeds, kernels, and pits are discarded in most cases, but various studies carried out on fruit wastes revealed the presence of different bioactive constituents, which can be a source of high value-added compounds for various applications. Therefore, the aim of our work was to investigate different fruit wastes (peels) of exotic fruits (banana, orange, pineapple, pomegranate, avocado, and mango) for the possible use of these biowaste as a source of bioactive and high value-added compounds.

Samples of exotic fruit peels were prepared from dried peels and by homogenization in water as a solvent. Initially, qualitative analysis of the presence of various phytochemicals (alkaloids, phenols, anthraquinones, terpenoids, tannins, reducing sugars, flavonoids, anthocyanidins, emodins, saponins, quinones, steroids, glycosides) was performed, and the contents of reducing sugars, proanthocyanidins, total phenols and proteins in the obtained homogenates were additionally quantified by spectrophotometric methods.

The study showed that homogenates of exotic fruit peels are full of various phytochemicals. Pomegranate peels homogenate contained the highest content of reducing sugars, avocado peels homogenate the highest content of proanthocyanidins, and mango peels homogenate the highest content of total phenols and proteins.

Based on obtained results, natural homogenates of fruit wastes may be used to obtain various bioactive components with added value. Therefore, homogenates of exotic fruit peels, which are otherwise hugely discarded in fruit processing, could be used for inclusion in various materials for applications in food (e.g., food packaging), pharmaceutical (e.g., ointments, patches), and cosmetic (e.g., creams, gels, lotions) industries.



LOVE OR COMPULSION RELATIONSHIP BETWEEN MYELIN BASIC PROTEIN AND PHOSPHATIDYLCHOLINE LIPIDS

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Myelin is a multilayer membrane tightly wrapped around the axon of neurons, allowing efficient transmission of neural impulses. Slight changes in distributions of lipids in myelin membranes affect their adhesive properties, as well as their bonding with myelin basic protein MBP, one of the most important myelin-associated proteins. With its high content of positively charged residues, unstructured MBP binds to the anionic lipids of the cytoplasmic leaflets, which causes balance changes between charged lipids and alternations in the lateral organization of the model myelin bilayers [1]. All these changes appear in neurodegenerative diseases such as multiple sclerosis (MS) and encephalomyelitis (EAE) [2]. It is not yet known what role MBP confinement plays in the efficiency of its adsorption to lipid bilayer made from zwitterionic lipid 1,2-dipalmitoyl-sn-glycero-3-phosphocholine (DPPC), which constitutes about 40% of myelin lipids [3]. Using the several types of calorimetric and spectroscopic techniques, such as FT-IR and CD spectroscopy, UV-Vis spectrometry, ITC and DSC calorimetry our goal is to unravel the impact of MBP on phase transition temperatures (T_p, T_m) of DPPC multilamellar and unilamellar liposomes and their structural arrangements [4]. All experimental results are supported with computational study.

We thank Croatian Science Foundation for the financial support within the project „Model of demyelination on a molecular scale at physiological and pathological conditions“ (HrZZ UIP-2020-02-7669).

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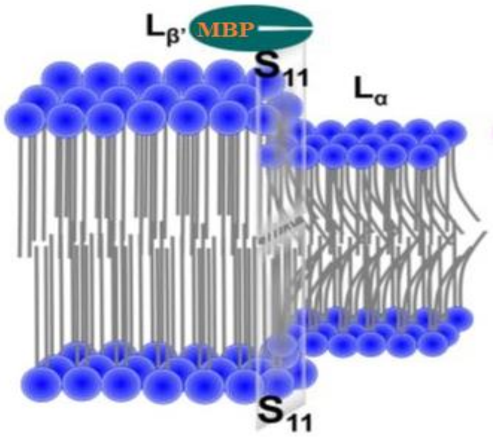

Figure 1. Possible position of MBP protein on DPPC unilamellar liposomes between gel ($L_{\beta'}$) and fluid (L_{α}) phase.

IMOBILIZACIJA HALOGENHIDRIN-DEHALOGENAZE METODOM KAPSULIRANJA U METALO-ORGANSKE MREŽE

IMMOBILIZATION OF HALOHYDRIN DEHALOGENASE VIA ENCAPSULATION IN METAL-ORGANIC FRAMEWORKS

Nevena Milčić[1], Petra Marin[2], Mirela Kovačević[1], Magdalena Kolić[1], Krešimir Kos[1], Martina Sudar[1], Katja Vasić[3], Gordana Hojnik Podrepšek[3], Mateja Primožič[3], Maja Leitgeb[3], Maja Majerić Elenkov[2], Zvjezdana Findrik Blažević[1]

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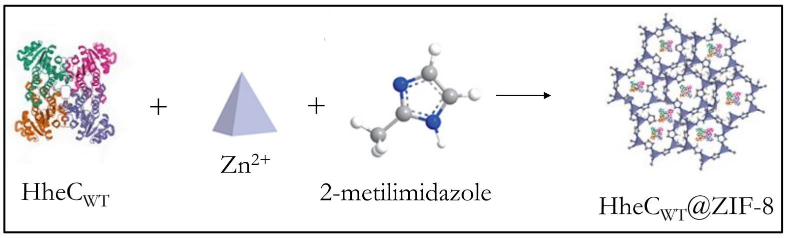
Halogenhidrin-dehalogenaza tipa C (HheC iz *Agrobacterium radiobacter*) zauzima važno mjesto u industrijskoj biokatalizi zahvaljujući visokoj enantioselektivnosti i mogućnosti sinteze raznovrsnih β-supstituiranih alkohola i epoksida [1]. Zbog hidrolitičke nestabilnosti i ograničene topljivosti supstrata epoksida, HheC-katalizirane reakcije mogu se provoditi u alternativnim medijima poput organskih otapala. Pritom otapala mogu imati štetan utjecaj na strukturna i katalitička svojstva enzima. Stoga se operacijska stabilnost enzima može povećati metodama imobilizacije poput kapsuliranja u metalo-organske mreže (engl. *metal-organic frameworks* – MOFs). MOF su porozni materijali visokog stupnja kristaliničnosti koji mogu zaštititi enzim od nepovoljnih reakcijskih uvjeta. Zeolitne imidazolne mreže (ZIF) moguće je sintetizirati pri biokompatibnilim uvjetima gdje enzim služi kao nukleus kristalizacije [2]. U ovom radu ispitana je mogućnost sinteze HheC@ZIF-8 s ciljem povećanja stabilnosti prilikom biokatalize u organskom mediju.

Ovaj rad izrađen je u okviru projekta „Enzimska sinteza fluoriranih kiralnih građevnih blokova“ EnzyFluor (IP-2018-01-4493) financiranog sredstvima Hrvatske zaklade za znanost te hrvatsko-slovenskog bilateralnog projekta „Stabilizacija halogenhidrin-dehalogenaza radi upotrebe u nekovencionalnim medijima“.

[1] Z. Findrik Blažević et al., Adv. Synth. Catal. 363(2) (2021) 388-410.
[2] W. Liang et al., Chem. Rev. 121 (2021) 1077−1129.



BIORAZGRADNJA KSENOBIOTIKA POMOĆU OKOLIŠNIH MIKROORGANIZAMA

BIODEGRADATION OF XENOBIOTICS BY ENVIRONMENTAL MICROORGANISMS

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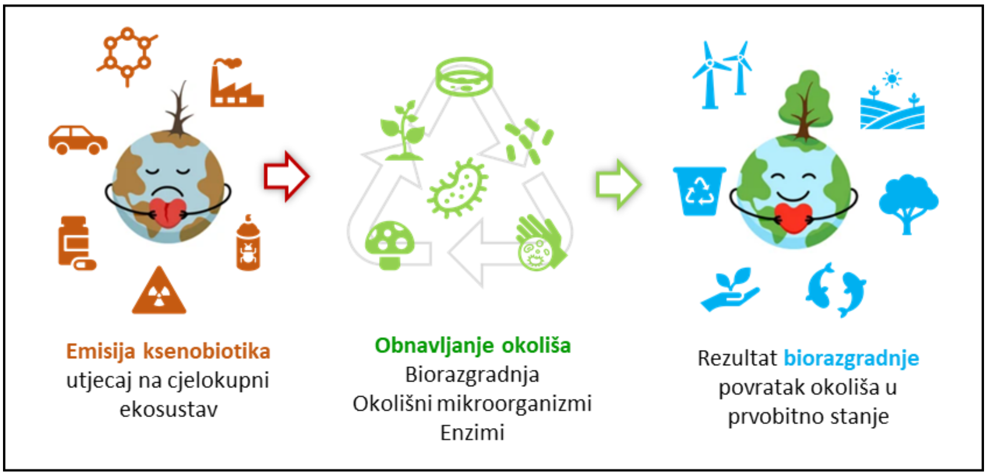
Posljednjih nekoliko desetljeća, kao posljedica ubrzane industrijalizacije, modernizacije i porasta broja svjetskog stanovništva, dolazi do povećane emisije ksenobiotika u sve sastavnice okoliša. Onečišćenje okoliša uzrokovano ksenobioticima stvara poremećaje u ekosustavima. Mikrobne zajednice imaju značajnu ulogu u funkcioniranju ekosustava i sposobne su razgraditi širok raspon spojeva. Ksenobiotici u okolišu su otporni na razgradnju, a glavni razlog je taj što ih prirodno prisutni mikroorganizmi ne mogu prepoznati i stoga ne ulaze u uobičajene metaboličke putove. Zbog velikog metaboličkog potencijala, mikroorganizmi se mogu prilagoditi novim supstratima, pri čemu proizvode enzime odgovorne za razgradnju što može biti učinkovito sredstvo za detoksikaciju okoliša. U ovom radu prikazat će se odabrane specifične mikrobiološke kulture za biorazgradnju ksenobiotika baziranu na metaboličkom potencijalu i svojstvima koja omogućuju stanici funkcionalnu aktivnost i otpornost prema uvjetima u onečišćenom okolišu kako bi se doprinijelo većoj učinkovitosti procesa.



TRANSFORMACIJA HERBICIDA U OKOLIŠU POMOĆU AUTOHTONIH MIKROORGANIZAMA

TRANSFORMATION OF HERBICIDES IN ENVIRONMENT WITH INDIGENOUS MICROORGANISMS

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Marija Vuković Domanovac

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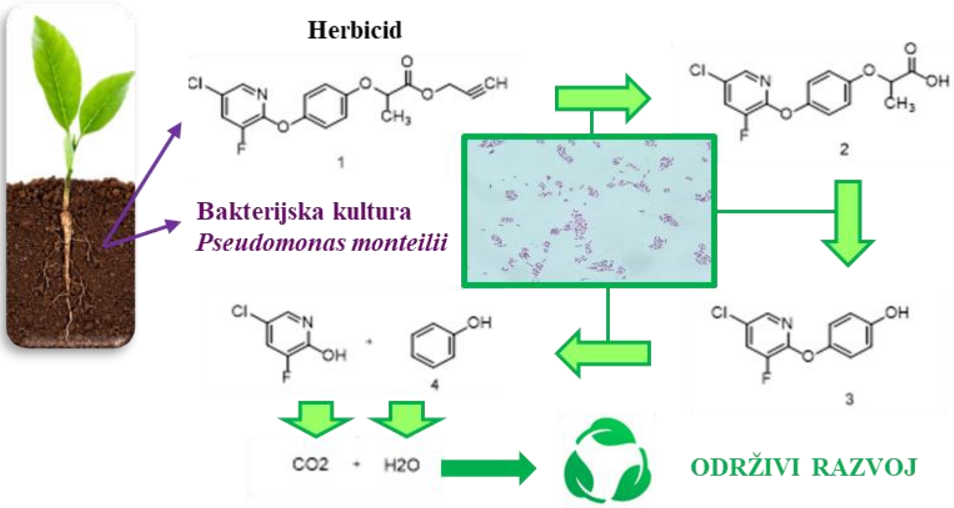
Prekomjerna upotreba herbicida tijekom proteklog stoljeća dovela je do njihovog širenja i akumulacije u različitim okolišnim aspektima, uključujući sastavnice okoliša, kao što su tlo, voda, zrak te žive organizme. Toksičan učinak, koji se povezuje s djelovanjem ovakvih široko rasprostranjenih organskih kemikalija, može ostaviti različite posljedice na zdravlje živih organizama uključujući i čovjeka. U ovom radu iz tla onečišćenog herbicidom pendimetalinom izolirane su bakterijske vrste koje pripadaju rodovima *Bacillus* i *Pseudomonas*. Nadalje je s izoliranim bakterijskim kulturama istraživan put i mehanizam biorazgradnje pendimetalina te je provedena spektroskopska karakterizacija herbicida uz prikaz puteva biorazgradnje. Procjena bioloških aktivnosti početnih herbicidnih spojeva te njihovih konačnih produkata provedena je pomoću softvera PASS. Rezultati procjene biološke aktivnosti ukazuju na smanjenje toksičnih učinaka krajnjih produkata biorazgradnje u odnosu na početne herbicidne spojeve. Na temelju navedenog, potvrđen je potencijal autohtonih mikroorganizama u biorazgradnji herbicida i njihova uloga u postizanju održivosti okoliša.



NOVI MIKROBNI IZVORI KOJI SE MOGU KORISTITI U BIOREMEDIJACIJI

NOVEL MICROBIAL SOURCES FOR USE IN BIOREMEDIATION

Lea Raos, Karla Radak, Marija Vuković Domanovac

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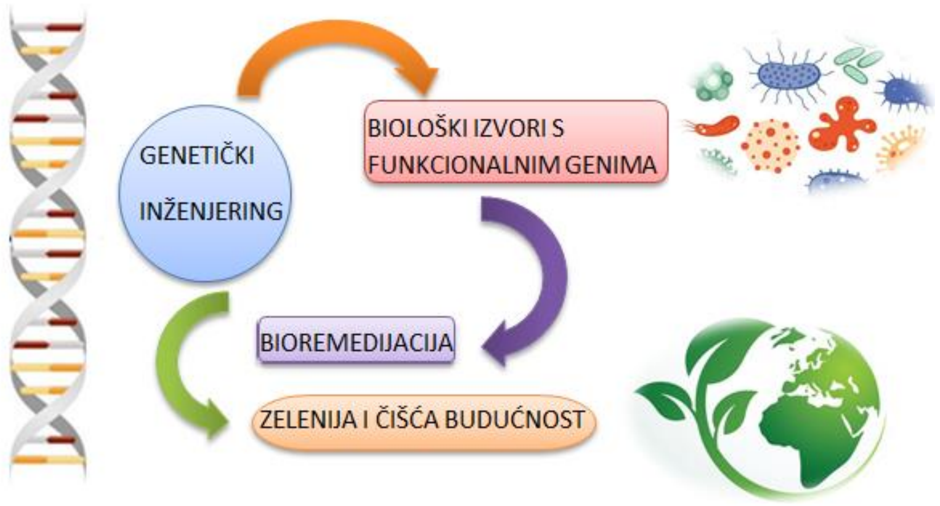
Danas, u 21. stoljeću, s velikom stopom rasta ljudske populacije, svijet se suočava s onečišćenjem prirodnih resursa. Sukladno tome, vrijeme je za iskorištavanje okolišno prihvatljivih postupaka za vraćanje okoliša u prvobitno stanje. U potrazi za mikrobnim izvorima koji imaju sposobnost uklanjanja određene onečišćujuće tvari istražuju se njima već onečišćena područja. Bioremedijacija je istraživački intenzivna tehnologija koja zahtijeva razumijevanje mikrobnih procesa te se za potencijalnu primjenu razvijaju inovativni mikroorganizmi. U ovom radu prikazat će se dostupni i noviji mikrobni izvori dobiveni primjenom genetičkog inženjerstva koji se mogu spojiti s tehnikama bioremedijacije za uspješnu primjenu kako bi se krenulo prema zelenijoj i čišćoj budućnosti.



BIOLOŠKA OBRADA PIVSKOG TROPA S *TRAMETES VERSICOLOR* U SVRHU PROIZVODNJE HIDROLITIČKIH ENZIMA

BIOLOGICAL TREATMENT OF BREWER'S SPENT GRAIN BY *TRAMETES VERSICOLOR* FOR THE PRODUCTION OF HYDROLYTIC ENZYMES

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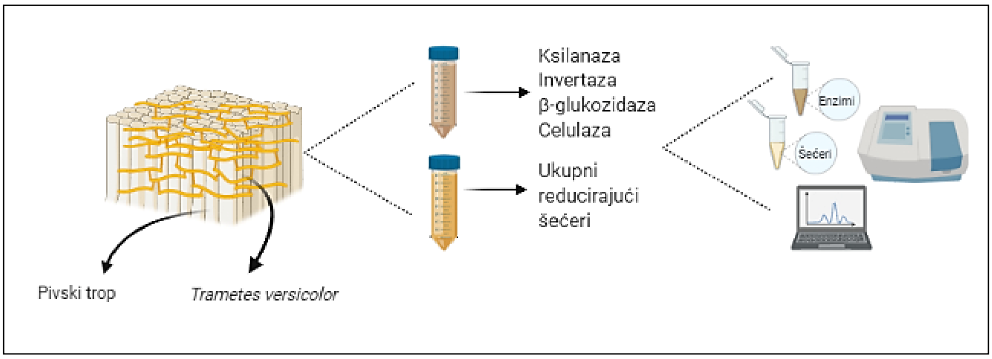
Pivski trop je jedan od glavnih nusproizvoda pivarske industrije. Najčešće se upotrebljava kao stočna hrana, a u posljednje vrijeme zauzima značajno mjesto u znanstvenim istraživanjima u svrhu primjene u proizvodnji visokovrijednih produkata i biogoriva.
U ovome radu istražena je mogućnost proizvodnje hidrolitičkih enzima (ksilanaze, invertaze, celulaze i β-glukozidaze) i reducirajućih šećera, tijekom 15 dana uzgoja *Trametes versicolor* na pivskom tropu. Dokazano je da je *Trametes versicolor* dobar proizvođač ksilanaze i invertaze, pri čemu su maksimalne volumne aktivnosti enzima postignute nakon 15. dana: *V.A.* (ksilanaza) = 511,19 U/cm^3 i *V.A.* (invertaza) = 186,25 U/cm^3. Maksimalna volumna aktivnost β-glukozidaze postignuta je nakon 12. dana (*V.A.* = 4,34 U/ cm^3), a celulaze nakon 10. dana (*V.A.* = 0,074 U/ cm^3).
Početna koncentracija ukupnih reducirajućih šećera u vodenom ekstraktu neobrađenog pivskog tropa iznosila je 2,72 mg$_{\text{glukoze}}$/g$_{\text{s.t.}}$, a nakon biološke obrade zbog aktivnosti hidrolitičkih enzima, došlo je do povećanja koncentracije ukupnih reducirajućih šećera na 19,56 mg$_{\text{glukoze}}$/g$_{\text{s.t.}}$.



GLUTARALDEHYDE ACTIVATION ON SODIUM ALGINATE BEADS FOR LACCASE IMMOBILIZATION

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In terms of modern green chemistry, eco-friendly and simple approaches, using enzymes for various industries are encouraged. Entrapment of enzyme within a polymer matrix, such as alginate (Alg), is the simplest immobilization method, where solution of sodium Alg is added dropwise to a $CaCl_2$ solution. When calcium ions permeate through alginate beads, more gelation happens, which increases the beads' hardness. Properties, such as size of beads, enzyme leakage degree, its stability and porosity are optimized through Alg and Ca concentrations, as well as contact time in $CaCl_2$ solution and the use of cross-linking agents. Alg beads were prepared by adding Alg solution to $CaCl_2$, where they were stored to achieve a certain degree of hardness. Obtained Alg beads were collected and further activated with cross-linking agent glutaraldehyde (GA). The optimization of GA concentration and activation time was carried out at room T under orbital stirring. Enzyme immobilization with GA activated Alg beads was performed to optimize the time of immobilization. Enzyme efficiency was determined using Bradford method, while residual activity of laccase was determined spectrophotometrically. After optimization of process parameters in immobilization protocol, the highest residual activity and immobilization efficiency were achieved, resulting in 88% and 97%, respectively. Results suggest GA activation on Alg beads increases laccase activity, which shows that the proposed simple immobilization approach has potential in various applications, such as wastewater treatment or others [1-3].

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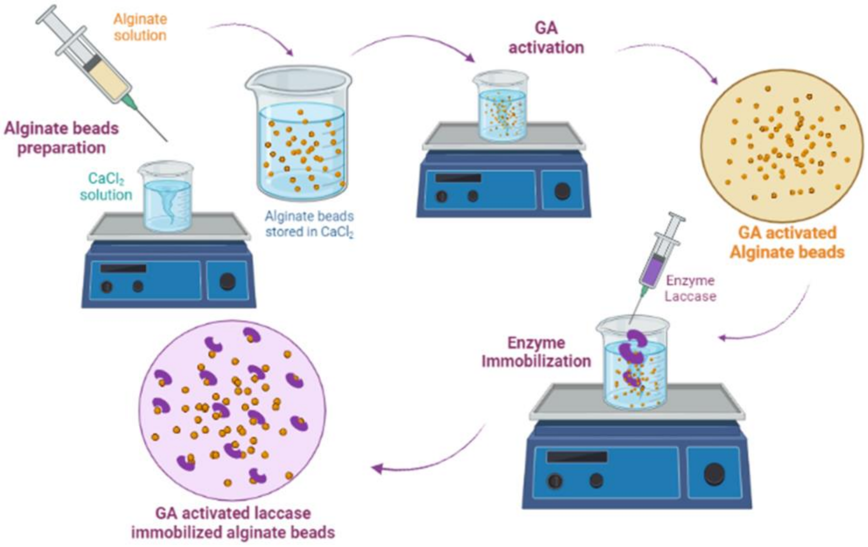
[3] D. A. Morales Urrea, A. V. Fernandez Gimenez, Y. E. Rodriguez, E. M. Contreras, Process Saf. Environ. Prot. 156 (2021) 134-143.



Ekoinženjerstvo
Environmental engineering

ECOTOXICITY DETERMINATION OF XENOBIOTICS BY CRUSTACEAN *Daphnia magna* AND BACTERIA *Vibrio fischeri*

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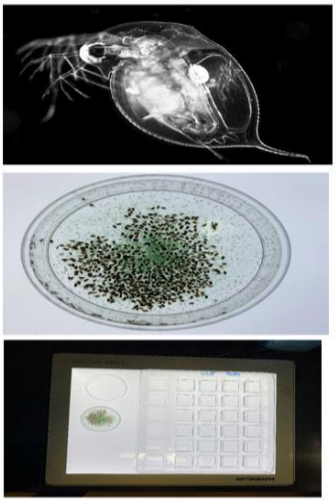
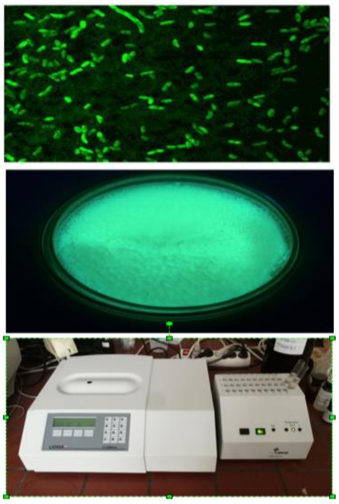
The risk assessment of the impact of xenobiotics on the environment is mainly focused on the analysis of the effect of pure substances, and less on their mixtures, although mixtures are most often present in the environment. In this paper, the ecotoxicity of standard solutions of the xenobiotics acetamiprid, clothianidin, thiacloprid and microplastics (shredded plastic bottles (PET) and bottle cap (PP)) and their binary and ternary mixtures was tested. Ecotoxicity was tested according to the standard method ISO 6341:2012 using crustacean *Daphnia magna* and the standard method ISO 11348-3:2007 using the luminescent bacterium *Vibrio fischeri*. Chromatographic HPLC-DAD analysis of samples was also performed. The same growth trend of the toxicity curve was observed in all tested xenobiotics. The inhibition of the tested organisms increases with increasing concentration of solutions. In the experiment with *Daphnia magna*, clothianidin (I = 90%) proved to be the most toxic, followed by acetamiprid and thiacloprid (I = 85%) and microplastics (I = 10%). The mixture of microplastics and thiacloprid showed a synergistic effect between the components. In the experiment with *Vibrio fischeri*, acetamiprid (I = 88.28%) proved to be the most toxic, followed by thiacloprid (I = 51.22%) and microplastics (I = 0.5%). Clothianidin did not cause bacterial culture inhibition. All binary mixtures of pesticides and microplastics and binary mixture of pesticides showed a synergistic effect between the components. Only a mixture of acetamiprid and thiacloprid and a ternary mixture of pesticides showed an antagonistic effect among the components. Chromatographic HPLC-DAD analysis revealed the release of the new microplastic compound into the aqueous medium.

This paper was prepared as part of the project Advanced Water Treatment Technologies for Microplastics Removal (IP-2019-04-9661, AdWaTMiR).





COPPER ION REMOVAL FROM CONTAMINATED WATER USING BENTONITE

Mediha Biberović[1], Ajla Mandalović[2], Amra Odobašić[3], Melisa Ahmetović[4]

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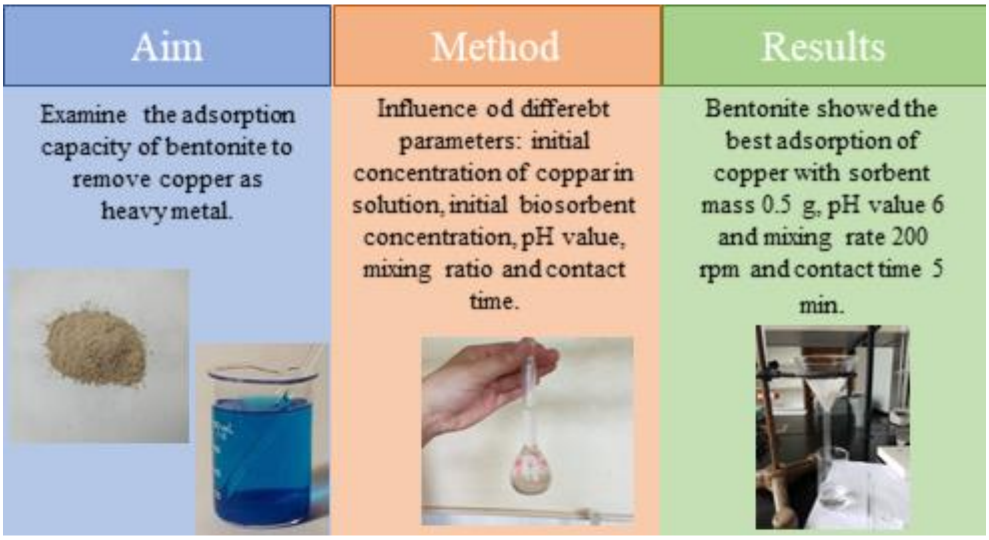
A major environmental problem worldwide is pollution of watercourses with heavy metals as a result of rapid population growth, industrialization and economic development. Given this, the aim of study was to examine the possibility of using bentonite from the Šipovo site (Bosnia and Hercegovina) for the removal of copper ions (Cu^{2+}) and to determine its adsorption capacity. Bentonite is a type of highly plastic clay that has the ability to expand and turn into a gel when in humid conditions. It is formed by the deposition of volcanic ash in humid conditions. It consists mainly of montmorillonite which is mineral found in clay.

In this paper, the adsorption capacity of bentonite for removal of copper as a heavy metal from contaminated water was examined, depending on various parameters such as initial concentration of copper in solution, initial sorbent concentration, pH value (pH = 2 and pH = 6), mixing rate (200 rpm and 250 rpm) and contact time (5 min and 15 min). The results showed that the adsorption capacity of bentonite decreases with increasing concentration of copper ions. The best results were obtained at bentonite concentration $5.5 \cdot 10^{-5}$ mol/50 ml and pH value 6, at 200 rpm and contact time of 5 min. Bentonite can be used as an effective sorption agent to remove copper ions, and as a material derived from nature, it is easily available and economically viable.



Aim

Examine the adsorption capacity of bentonite to remove copper as heavy metal.

Method

Influence od differebt parameters: initial concentration of coppar in solution, initial biosorbent concentration, pH value, mixing ratio and contact time.

Results

Bentonite showed the best adsorption of copper with sorbent mass 0.5 g, pH value 6 and mixing rate 200 rpm and contact time 5 min.

PROCJENA ČISTOĆE I KVALITETE DALMATINSKOG I KONTINENTALNOG MACERATA SMILJA

PURITY AND QUALITY ASSESSMENT OF DALMATIAN AND CONTINENTAL IMMORTELLE MACERATE

Barbara Bilandžija[1], Lucija Bilandžija[1], Lea Pollak[2], Suzana Inić[1]

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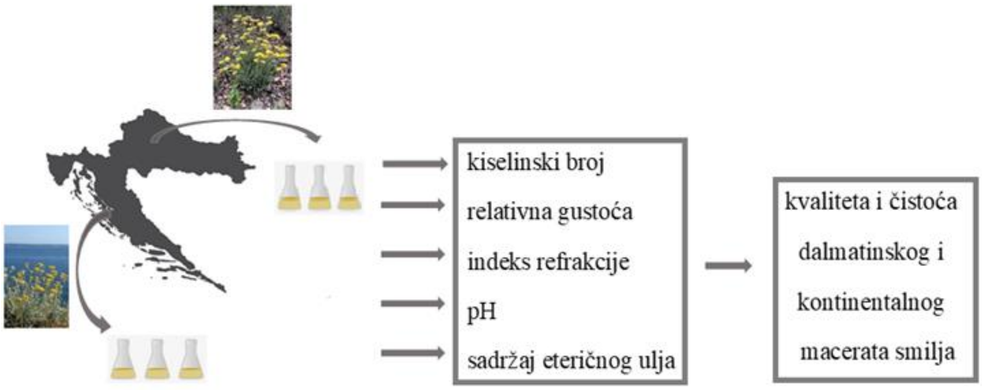
Smilje (*Helichrysum italicum* (Roth) G. Don) je mediteranska biljka koja zbog brojnih ljekovitih svojstava ima dugogodišnju primjenu u tradicionalnoj medicini. Budući da danas sve više raste interes farmaceutske i kozmetičke industrije za različitim pripravcima smilja, javlja se potreba za uvođenjem referentnih vrijednosti fizikalnih i kemijskih parametara koji bi se koristili u procjeni čistoće i kvalitete tih pripravaka. Cilj ovoga rada je procijeniti i usporediti čistoću i kvalitetu uzoraka macerata dalmatinskog i kontinentalnog smilja u maslinovom ulju (n=6) mjerenjem kemijskih parametara (kiselinski broj), fizikalnih parametara (relativna gustoća, indeks refrakcije), pH vrijednosti i sadržaja eteričnog ulja. Izmjerena vrijednost kiselinskog broja uzoraka ispitivanih macerata iznosila je između 1,71 i 2,88 mg KOH/g, relativna gustoća bila je između 0,905 i 0,988, a indeks refrakcije iznosio je između 1,4691 i 1,4743. Izmjerena pH vrijednost bila je u rasponu između 4,40 i 5,25, a sadržaj eteričnog ulja je bio od <0,08 do 0,51 %. Budući da nema referentnih vrijednosti ovih parametara za macerat smilja, izmjerene vrijednosti uspoređene su s referentnim vrijednostima za eterično ulje smilja i maslinovo ulje koje su dostupne u literaturi. Provedena ispitivanja su pokazala da nema značajnih razlika u izmjerenim parametrima između uzoraka macerata dalmatinskog i kontinentalnog smilja pa se može zaključiti da nema razlika u njihovoj čistoći i kvaliteti.



FIZIKALNO-KEMIJSKA I MIKROBIOLOŠKA KARAKTERIZACIJA RAZLIČITIH VRSTA TLA NA PODRUČJU BOSNE I HERCEGOVINE

PHSYSICO-CHEMICAL AND MICROBIOLOGICAL CHARACTERIZATION OF DIFFERENT SOIL TYPES IN BOSNIA AND HERZEGOVINA

Ivana Bošnjak, Martina Miloloža, Dajana Kučić Grgić

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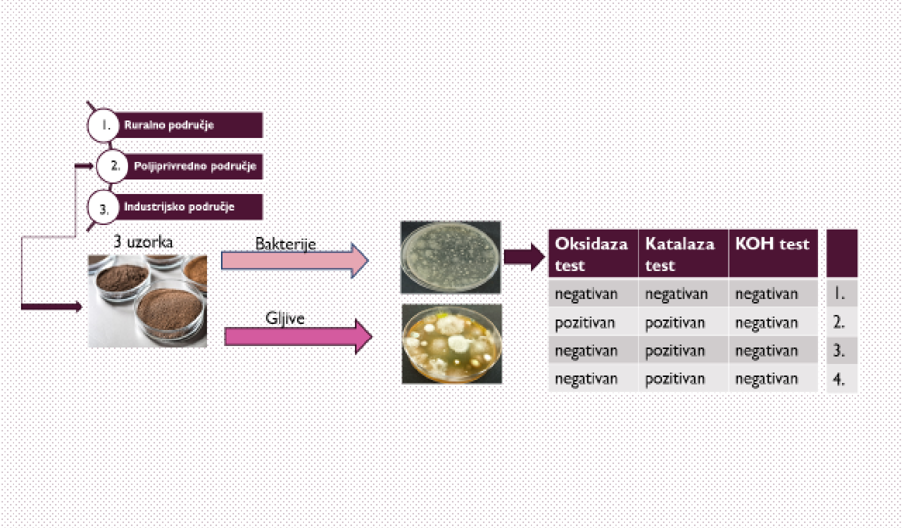
Tlo je rastresiti površinski sloj Zemljine kore. Sastoji se od mineralnih tvari, vode,zraka, gline i nužno sadrži biološku, organsku komponentu. Tlo je četverofazni (čvrsta faza + otopina + zrak + živi organizmi) strukturirani sustav. U čvrstoj fazi ističu se čestice pijeska, sitnoga pijeska, praha, gline i koloidne čestice. Tekuća faza tla sastoji se uglavnom od vode u kojoj su koloidno dispergirane različite anorganske i organske tvari. Organizme tla čine mnogobrojne i raznolike vrste, činitelji tvorbe tla: virusi, bakterije, gljive, alge, više biljke (podzemni korijen), kišne gliste i kukci. U ovom radu prikupljena su tri uzorka tla sa različitih lokacija. Prvi uzorak prikupljen je u ruralnom planinskom području, drugi je dio poljoprivrednog područja (polje pšenice), a treći uzorak je prikupljen uz industrijsko postrojenje za proizvodnju željeza. Odrađena je fizikalno-kemijska i mikrobiološka analiza za sva tri uzorka. Fizikalno-kemijska analiza obuhvaćala je određivanje udjela vlage svakog pojedinog tla, vodljivosti, koncentracije otopljenoga kisika te pH-vrijednosti. Za pobližu identifikaciju bakterija, provedeni su biokemijski testovi (katalaza i oksidaza test) te KOH test uz bojanje po Gramu i Schaffer-Fultonu. Završni korak identifikacije bakterija obuhvaćao je provedbu API stripa. Plijesni su se identificirale uz pomoć Bergenyevog priručnika te mikroskopskom analizom.



Oksidaza test	Katalaza test	KOH test	
negativan	negativan	negativan	1.
pozitivan	pozitivan	negativan	2.
negativan	pozitivan	negativan	3.
negativan	pozitivan	negativan	4.

BIORAZGRADNJA MIKROPLASTIKE PVC-A PRIMJENOM KVASACA *Trichosporon* sp. I *Rhodotorula glutinis* IZOLIRANIH IZ OKOLIŠA

BIODEGRADATION OF PVC MICROPLASTIC USING YEAST *Trichosporon* sp. AND *Rhodotorula glutinis* ISOLATED FROM THE ENVIRONMENT

Kristina Bule[1], Marija Kuštro, Dubravka Tavra, Martina Miloloža, Viktorija Prevarić, Matija Cvetnić[1], Šime Ukić[1], Tomislav Bolanča[1,2], Marinko Markić[1], Dajana Kučić Grgić[1]

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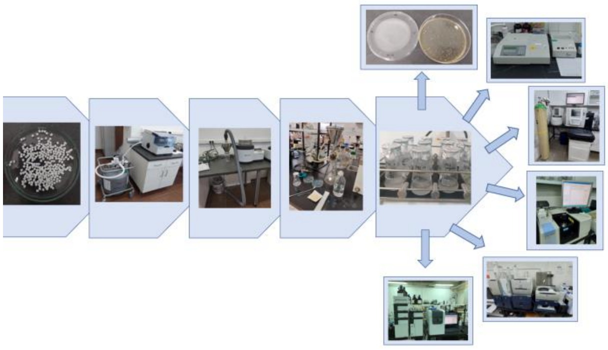
Onečišćenje vodnog okoliša mikroplastikom (MP) sve više zabrinjava znanstvenu zajednicu. Sve veće količine akumuliranog plastičnog otpada zahtijevaju nove metode i tehnologije uklanjanja MP-a koje će zadovoljiti tehnološke, ekonomske, ali i ekološke zahtjeve, stoga se okreće biološkom uklanjanju. Kvasci su gotovo neistraženi mikroorganizmi u ovom području i zato je u ovom istraživanju ispitana biorazgradnja mikroplastičnih čestica poli(vinil-klorid)-a, PVC, tijekom 30 dana primjenom kvasaca *Trichosporon* sp. i *Rhodotorula glutinis* izoliranih iz okoliša. Tijekom procesa pratila se optička gustoća (OG), broj živih stanica kvasaca (CFU), morfološke promjene, koncentracija ukupnog, organskog i anorganskog ugljika, koncentracija aniona i kationa te se primjenom LC-MS-a pratio mogući nastanak novih produkata poput oligomera i dimera. Čestice PVC-a analizirane su prije i nakon procesa biorazgradnje primjenom ATR-FTIR spektroskopije. Ispitan je i utjecaj glukoze na proces biorazgradnje. Prema rezultatima, oba kvasca pokazuju učinkovitiju biorazgradnju MP-a uz dodatak glukoze. S obzirom na intenzivniji porast CFU-a kod *R. glutinis* možemo zaključiti da se *R. glutinis* bolje prilagodila navedenim uvjetima od *Trichosporona* sp., što ujedno ukazuje i na bolju biorazgradnju PVC-a. Ovo otvara mogućnost za daljnja ispitivanja u svrhu bolje biorazgradnje i predlaže se ispitivanje optimalnih uvjeta samoga procesa.

Ovaj rad izrađen je u sklopu projekta Primjena naprednih tehnologija obrade voda za uklanjanje mikroplastike (AdWaTMiR) (IP-2019-04-9661) financiranog od Hrvatske zaklade za znanost.



RAČUNALNO PREDVIĐANJE p*K*a VRIJEDNOSTI MORINA

COMPUTATIONAL PREDICTION OF p*K*a VALUES OF MORIN

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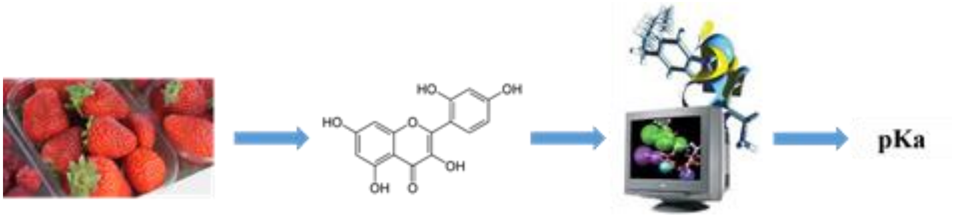
Favonoid morin, nazvan prema biljnoj porodici *Moraceae* (dudovke), predmet je brojnih znanstvenih istraživanja. Ovaj prehrambeni bioflavonoid pokazuje niz različitih bioaktivnosti, kao što su antioksidacijska, protuupalna, neuroprotektivna, kardio-protektivna, antidijabetička i antimikrobna aktivnost. U ovom je radu određena p*K*a vrijednost morina primjenom programa ACD/p*K*a. ACD/p*K*a je računalni program za precizan izračun konstanti kiselo-bazne ionizacije, odnosno za izračun p*K*a. Za neke prirodne spojeve, osobito polifenole, eksperimentalne vrijednosti p*K*a nisu dostupne, dok se u literaturi mogu naći izračunate vrijednosti dobivene primjenom raznih programa. Ove vrijednosti mogu imati veliki značaj u rasvjetljivanju mehanizma na kojima se temelje neke od bioaktivnosti, primjerice antioksidacijska aktivnost. Predviđanje p*K*a vrijednosti omogućuje i predviđanje redoslijeda deprotonacije hidroksilnih skupina morina, što također pomaže u utvrđivanju mehanizama na kojima se temelji pojedina bioaktivnost.



ODREĐIVANJE EKOTOKSIČNOSTI KSENOBIOTIKA PRISUTNIH U OKOLIŠU

DETERMINATION OF ECOTOXICITY OF XENOBIOTICS PRESENT IN THE ENVIRONMENT

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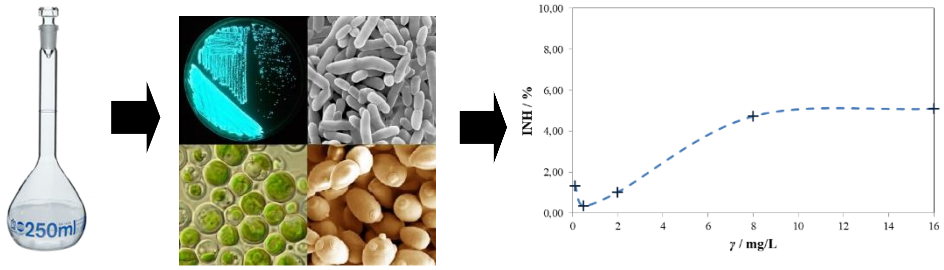
Neprestanim antropogenim djelovanjem povećava se emisija ksenobiotika u okolišu. Ksenobiotici se definiraju kao sintetske tvari koje su strane određenom ekološkom sustavu, a imaju određenu biološku aktivnost. U njih ubrajamo farmaceutike, antibiotike, otrove, pesticide i slično. Zabrinjavajuće svojstvo ksenobiotika njihovo je nakupljanje u visokim koncentracijama u organizmima i okolišu, što je uzrokovano njihovom jakom postojanošću i bioakumulacijom. Iz tog razloga imaju iznimno štetan utjecaj na ljudsko zdravlje i okoliš. U ovom radu ispitana je ekotoksičnost dvaju ksenobiotika: diklofenaka i pantoprazola te njihovih smjesa u različitim omjerima; 1:1, 2:1 i 1:2. Ekotoksičnost ksenobiotika na mikroorganizmima zasniva se na inhibiciji različitih bioloških svojstava koja su karakteristična za ispitivane mikroorganizme. Ispitivanja su se provodila na mikroorganizmima: *Vibrio fischeri*, *Pseudomonas putida*, *Chlorella* sp. te *Saccharomyces cerevisiae*. Za ispitivanje ekotoksičnosti primjenom morske bakterije *Vibrio fischeri* proučavala se inhibicija bioluminiscencije u prisutnosti ksenobiotika, nakon 30 minuta. Primjenom bakterije *Pseudomonas putida* i zelenih mikroalgi *Chlorella* sp., određivana je *CFU* (eng. *Colony Forming Units*) vrijednost u svrhu izračuna inhibicije rasta spomenutih mikroorganizama pri različitim ispitivanim koncentracijama ksenobiotika. Prilikom provedbe testa toksičnosti primjenom kvasca *Saccharomyces cerevisiae*, pratio se volumen ugljikovog dioksida, CO_2, čije je nastajanje inhibirano pri različitim koncentracijama ksenobiotika s obzirom na inhibiciju procesa fermentacije. Mjerenja su se provodila svakih 24 sata u razdoblju od 72 sata. Konačni rezultati ispitivanja ekološkog rizika prikazani su krivuljom doza-odgovor, a prikazivale su promjene mjerenih svojstava u vremenu ili promjene inhibicije u ovisnosti o koncentraciji ksenobiotika. Također, ekološki rizik iskazan je i EC_{20} te EC_{50} vrijednostima (eng. *effective concentration*), prema kojima se klasificira toksičnost ispitivane tvari.



SORPTION OF THREE ORGANIC MICROPOLLUTANTS BY POWDERED ACTIVATED CARBON: KINETICS, ISOTHERMS AND EFFECT OF HUMIC ACIDS

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Organic micropollutants (OMPs) present in wastewater have brough into focus these last years. Despite their low concentrations in wastewater effluents (ng/L - µg/L), they entail potential risks for human health and environment due to their occurrence and persistence [1]. Among the innovative treatment technologies used, adsorption onto powdered activated carbon (PAC) seems a promising option for the removal of OMPs. However, previous studies have found that the dissolved organic matter (DOM) present in the wastewater is main factor limiting the adsorption of OMPs onto activated carbon [2,3]. Yet it is not clear what effects DOM constituents have on OMPs adsorption. In this study, adsorption batch tests were performed in ultra-pure water and humic acid solution for the removal of diclofenac, sulfamethoxazole and trimethoprim by testing two different PAC concentrations (0.1g/L and 1g/L). Kinetic experimental data obtained were fitted to Lagergren's pseudo first order, pseudo-second order and intraparticle diffusion model. In order to describe the mechanism of adsorption, the data obtained were fitted to linear (Kd), Freundlich and Langmuir isotherms. Matrix effect caused by the presence of humic acids is expected to decrease the adsorption of OMPs according to the DOM present in the solutions.

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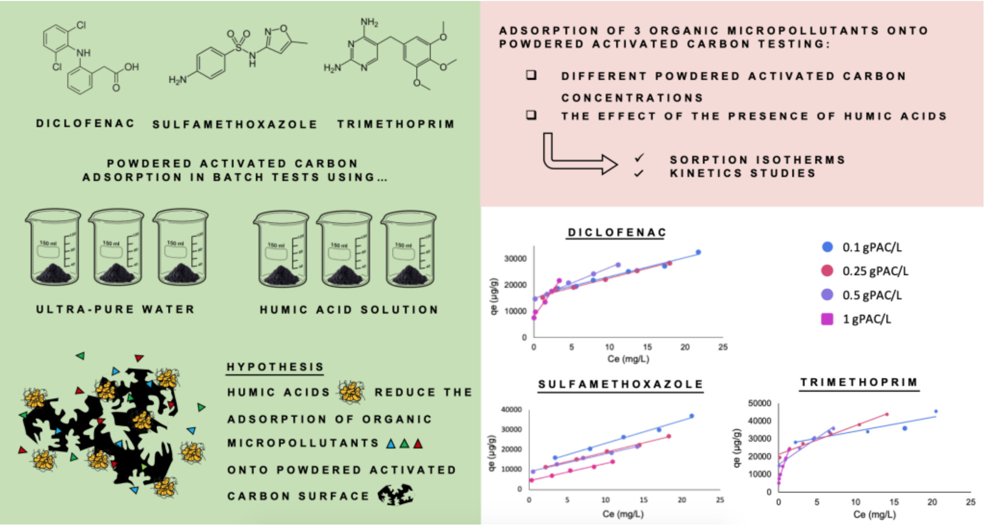

UDIO PAU U PRAŠINI IZ UNUTARNJEG PROSTORA AUTOMOBILA

CONTENT OF PAHs IN DUST COLLECTED INSIDE THE CARS

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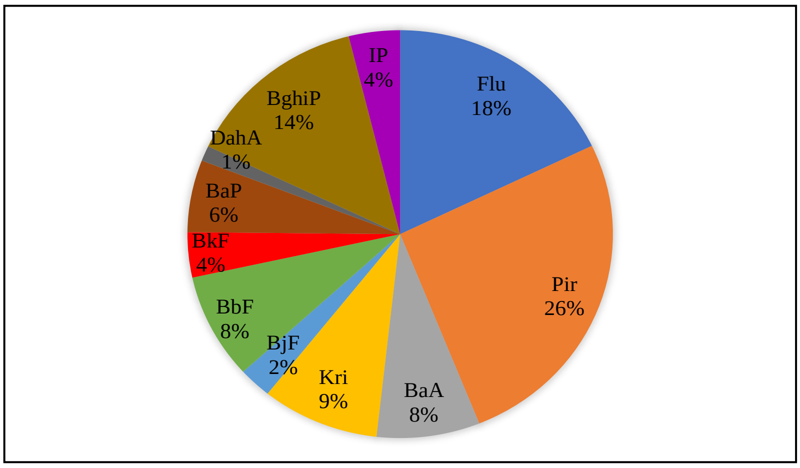
Policiklički aromatski ugljikovodici (PAU) su organski spojevi koju imaju veliku sposobnost bioakumulacije te kancerogeno i mutageno djelovanje na zdravlje ljudi. PAU-i su prisutni kako u vanjskom tako i u unutarnjem zraku. U unutarnjim prostorima osim u zraku mogu biti vezani na čestice prašine te se unos kod ljudi odvija ne samo inhalacijom nego i ingestijom te dermalnom apsorpcijom. Zbog toga prašina može biti dobar pokazatelj izloženosti ljudi karcinogenim onečišćenjima prisutnim u zatvorenim prostorima. Cilj ovog istraživanja je odrediti ukupnu koncentraciju mjerenih PAU te udio pojedinog PAU-a u sumi PAU (ΣPAU) u prašini sakupljenoj unutar automobila.

U ovom istraživanju sakupljena je prašina unutarnjeg prostora 22 automobila s motorom na dizelsko ili benzin gorivo. Ekstrakcija PAU iz uzoraka prašine provodila se ubrzanom ekstrakcijom s otapalom pri temperaturi od 125 °C i tlaku 1500 psi (~103 bara). Ekstrakti uzoraka upareni su do suhog na uparivaču te su zatim otopljeni u acetonitrilu. Tekućinskom kromatografijom visoke djelotvornosti određivano je 11 PAU: floranten (Flu), piren (Pir), benzo(a)antracen (BaA), krizen (Kri), benzo(b)fluoranen (BbF), benzo(j)fluoranten (BjF), benzo(k)fluoranten (BkF), benzo(a)piren (BaP), dibenzo(ah)antracen (DahA), benzo(ghi)perilen (BghiP) i indeno(1,2,3,-cd)piren (IP). Ukupna koncentracija za sve PAU-e (ΣPAU) kretala se od 0,39 µg g^{-1} do 12,1 µg g^{-1}. Najveću zastupljenost u ΣPAU imali su Pir (26%), Flu (18%) i BghiP (14%), dok je zastupljenost Kri bila 9%, a BaA i BbF 8%. Udio BaP iznosio je 6%, dok su ostali PAU-i bili ispod 5%. Ovo istraživanje pokazuje da putnici u automobilima mogu biti izloženi povišenim razinama PAU-a, ali je udio toksičnih PAU-a (BaP i DahA) u prašini iz automobila u manjoj mjeri zastupljen od ostalih manje opasnih PAU-a.

Istraživanje je dijelom financirano sredstvima projekta Hrvatske zaklade za znanost (UIP-2017-05-6713)



EVALUATION OF WATER MATRIX EFFECT ON DEGRADATION OF PHARMACEUTICALS

Ana Krpina[1], Amin Samzadeh[1], Matija Cvetnić[1], Lidija Furač[1], Viktorija Prevarić[1], Šime Ukić[1], Tomislav Bolanča[1,2]

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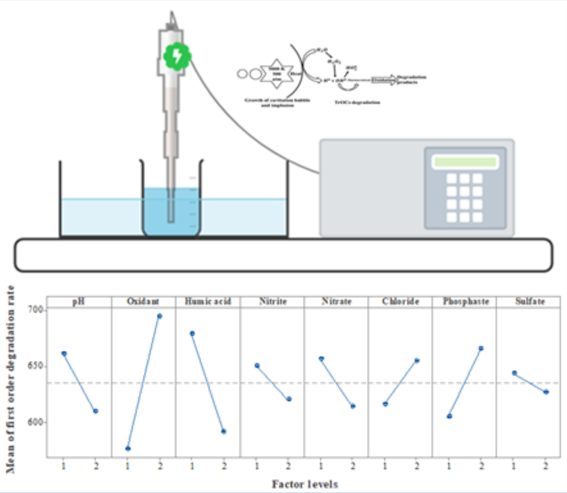
In this study one widely used recalcitrant pharmaceutical that has potential to be on the watch list was chosen for its degradation study. There was an evaluatation of the influence of several water matrix factors on pharmaceutical degradation with advanced oxidation processes (AOPs). To the best of our knowledge so far, there has been no research comparing UV-C, ultrasound (US) and microwave (MW) based processes under different operational parameters (oxidant dosage, pH, humic acid, nitrite ion, nitrate ion, chloride ion, phosphate ion and sulfate ion). Each of these factors depending on the degradation process, had synergistic or inhibitory effect on degradation rate of studied pharmaceutical. Design of the experiment that was used was Taguchi method. It shows significant results and indicates the effect of studied factors on degradation processes that, in most cases, were in agreement with previous literature findings, also it reduces the number of required experiments, time, and costs. Water matrix constituents had a significant impact on the degradation efficiency.



INFLUENCE OF HYDROGEN PEROXIDE ON THE DEGRADATION OF ANTHELMINTICS IN WASTEWATER

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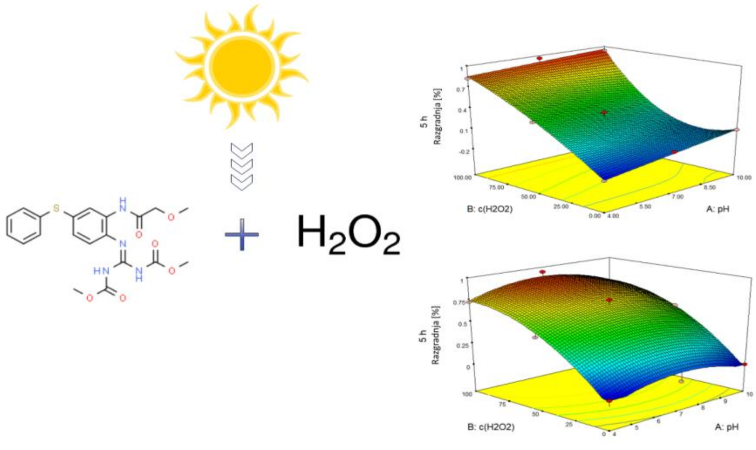
Antiparasitics are among the new water pollutants, given that their potential negative impact on the environment has recently been highlighted. By secretions of animals and humans, they can easily reach the soil and water where they have negative impact on other organisms. Also, the presence of microplastics in water is a growing problem with confirmed negative effect on human and animal health. Microplastics are smaller than 5 nm in size and have an extremely heterogeneous composition, which makes its effective elimination from water a great challenge and frequent subject of research. In this research, using HPLC equipment, the composition of degradation products according to the similarities of the absorption spectrum was analysed for the antiparasitic febantel. Degradation of antiparasitic was attempted by mechanical mixing in the presence of hydrogen peroxide. Solar radiation was also simulated in order to research the possibility of antiparasitics degradation by the action of photons. These simulated conditions were also examined in the presence of microplastics to monitor its possible impact on degradation. The results showed different percentage degradation. The amount of degradation products varies depending on the pH value and concentration of hydrogen peroxide.

This paper was prepared as part of the project Advanced Water Treatment Technologies for Microplastics Removal (IP-2019-04-9661, AdWaTMiR).



ENHANCEMENT OF SOLAR DRIVEN DEGRADATION OF CIPROFLOXACIN BY PHOTODEPOSITED AG AND FE ONTO ISO-TYPE HOMOJUNCTION BIVO$_4$ SURFACE

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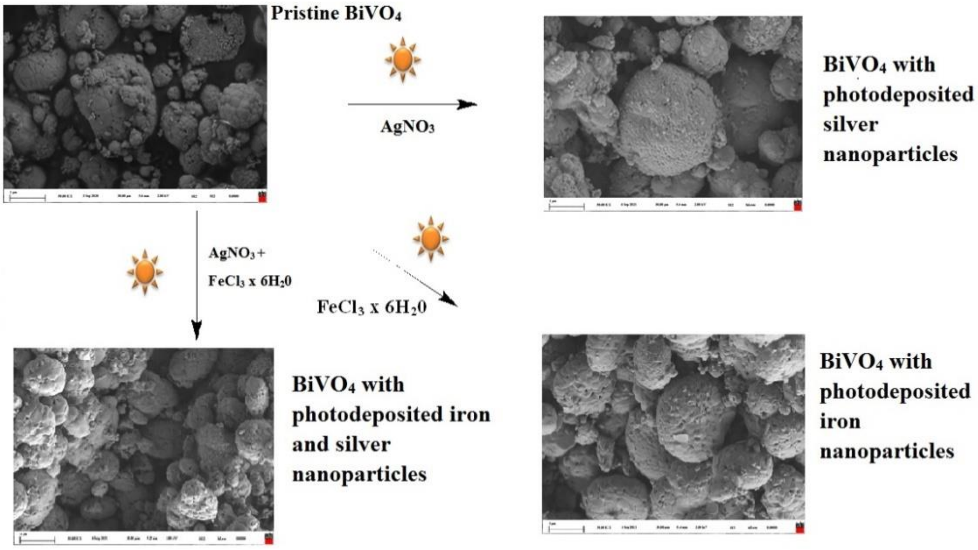
After synthesis of iso-type homojunction (monoclinic-tetragonal) $BiVO_4$ material, this material was enhanced by photodeposition of silver and iron separately. The newly synthesized materials shown to enhance photocatalytic degradation of ciprofloxacin (CIP), antibiotic from the European commission's Watch list. These enhancements happened due to different effects. Photodepsotion of silver enhanced the degradation of CIP, due to the effects of silver lowering the recombination in the material. Iron compound served as a photo-Fenton reagent which activated the production of hydroxyl radicals from hydrogen peroxide in photocatalytic reaction with H_2O_2.

The goal of this study was to get both enhancements (recombination decrease and photo-Fenton activation of H_2O_2) in one material for an increase in CIP degradation. For that purpose, we combined the synthesis methods for the best photocatalyst from our previous research to see whether we will get the above mentioned combination of effects. The new materials were categorized by XRD, DRS, and SEM. All the new materials showed better solar light photocatalytic performance in CIP degradation then pristine $BiVO_4$.



MODELING OF THE INTERACTIONS OF ORGANIC POLLUTANTS AND MICROPLASTICS IN THE WATER

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Ana-Marija Pitner[1], Matej Viljevac[1], Marin Kovačić[1], Bruno Grassl[2],
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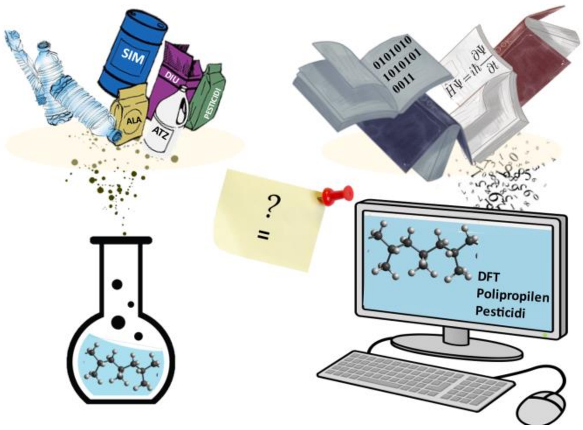
The presence of contaminants of emerging concern (CECs) in aquatic environment represents the risk due to potential adverse effects on both human health and the environment. The term CECs does not only apply to chemical contaminants but to the microplastics (MPs) as well. As MPs may interact with the co-pollutants present in water through sorption, they may serve as vectors for adsorbed chemicals, altering their environmental behavior and overall toxicity. Aging due to common atmospheric stressors such as ultraviolet radiation, temperature, humidity and oxygen leads to micro- as well as macro-scale degradation of MP which may have significant influence on interactions MP/co-pollutants. Since photo-degradation is one of the dominant processes, the intention of this work was to determine change in bulk and surface PP properties caused by UV-aging. We investigated adsorption behavior of pesticides on pristine and aged MPs,-aiming to establish correlation between structural characteristics of MPs and adsorption capacity at varied conditions. For that purpose, polypropylene (PP) MPs were used as the most abundant type in aquatic environment and atrazine and alachlor as the representatives of widely used pesticides. The adsorption experiments were performed according to statistical experimental design, whereas the particle size and the level of MPs aging, as well as pH and temperature were used as influential factors. The results were modelled using the principles of response surface methodology and the corresponding adsorption isotherms were established. The nature of the adsorption, bonding types and the adsorption energies were further studied by density functional theory (DFT).

This study has been fully supported by the Croatian Science Foundation under the project Microplastics in water; fate and behavior and removal ReMiCRO (IP-2020-02-6033).



KARAKTERIZACIJA KOMINE GROŽĐA I PRAĆENJE NJEZINE PROMJENE TIJEKOM POSTUPKA SILAŽE

CHARACTERIZATION OF GRAPE POMACE AND MONITORING OF ITS CHANGES DURING THE SILAGE

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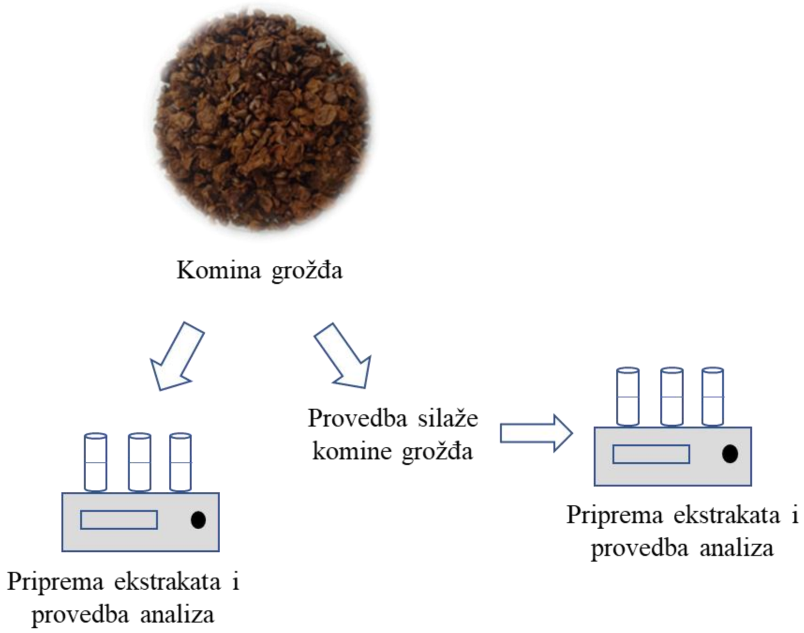
Komina grožđa je glavni nusproizvod proizvodnje vina. Ukoliko se komina grožđa odlaže na odlagališta može imati nepovoljne posljedice na okoliš te se stoga u posljednjih nekoliko godina istražuju načini iskorištavanja komine grožđa. S obzirom da se komina proizvodi jednom godišnje (u vrijeme berbe), potrebno je osigurati adekvatne načine skladištenja komine prilikom čega je važno očuvanje njezinih karakteristika. Osim sušenja, kao alternativna metoda provodi se siliranje što podrazumijeva konzerviranje vlažnih usjeva koji se dalje koriste kao krmiva. Tijekom siliranja odvija se fermentacija u anaerobnim uvjetima gdje bakterije mliječne kiseline prevode vodotopljive ugljikohidrate u mliječnu kiselinu što se očituje smanjenjem pH vrijednosti. U ovom radu provedena je silaža komine grožđa u 4 odvojena eksperimenta: komine kao kontrole, komine uz dodatak inokuluma bakterija mliječne kiseline, komine uz dodatak zeolita te komine uz dodatak inokuluma i zeolita. Uzorci su pohranjeni na temperaturu od 18-20 ºC te su periodički uzimani. Analizirani su parametri poput udjela suhe tvari, pH vrijednosti, sadržaja polifenola i tanina i drugi s ciljem praćenja uspješnosti procesa silaže.



MODELIRANJE PROCESA SUŠENJA KOMINE GROŽĐA

MODELLING OF DRYING PROCESS OF GRAPE POMACE

Tea Sokač, Veronika Gunjević Anita Pušek, Ana Jurinjak Tušek, Filip Dujmić, Mladen Brnčić, Ivana Radojčić Redovniković

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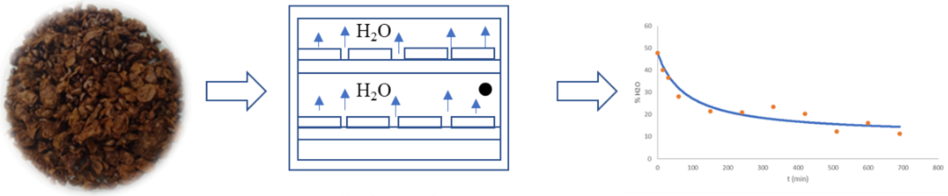
Tijekom proizvodnje vina, 20-25 % od ukupne korištene mase grožđa završi kao otpad. Nepropisno odlaganje ovog otpada predstavlja rizik za okoliš, a kao moguće rješenje ovog problema može biti iskorištavanje komine grožđa kao sirovine za nove proizvode. S obzirom da komina grožđa nije dostupna tijekom cijele godine, važno je pronaći prihvatljiv način procesa sušenja s ciljem očuvanja početnih karakteristika komine. U ovom istraživanju provedeno je sušenje komine grožđa u vakuum sušari pri različitim temperaturama (35, 50 i 70 °C). Procesi sušenja su opisani matematičkim modelima u svrhu odabira onog koji najbolje opisuje sušenje. Dobiveni rezultati pokazali su da je sušenje u vakuum sušari na 70 °C najpovoljnija metoda uzevši u obzir vrijeme sušenja i utrošak energije.



Komina grožđa

Sušenje u vakuum sušari pri različitim temperaturama

Opisivanje kinetike sušenja matematičkim modelima

DOPRINOS GORENJA BIOMASE ONEČIŠĆENJU ZRAKA U GRADU ZAGREBU

BIOMASS BURNING CONTRIBUTION TO AIR POLLUTION IN ZAGREB CITY

Suzana Sopčić, Gordana Pehnec, Ivan Bešlić

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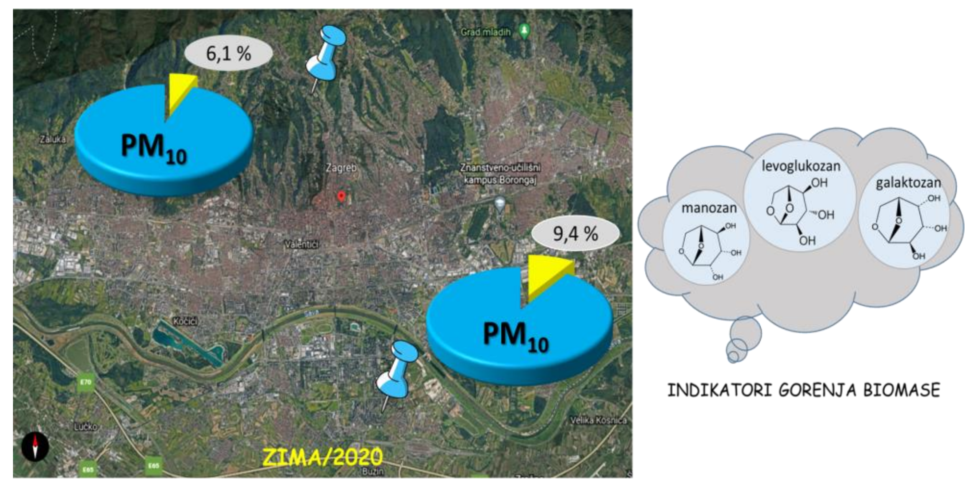
Posljednjih godina sve se više promiče korištenje biomase kao alternativnog izvora energije s ciljem smanjenja široke upotrebe fosilnih goriva. Uz prednosti poput dostupnosti, cijene te kružnog ciklusa ugljikovog dioksida, gorenje biomase manje je povoljno iz aspekta oslobođenih lebdećih čestica. Kako bi se pratio doprinos gorenja biomase ukupnoj koncentraciji oslobođenih lebdećih čestica najčešće su ispitivani kalijevi ioni te policiklički aromatski ugljikovodici. S obzirom da oni ne spadaju u grupu jedinstvenih markera, u posljednjih nekoliko godina se za indikaciju onečišćenja gorenjem biomase koriste celulozno specifični derivati monosaharida poznatiji kao anhidrošećeri. Anhidrošećeri nastaju isključivo pirolizom celuloze i hemiceluloze što ih čini preciznijim i specifičnim indikatorima za onečišćenje zraka gorenjem biomase. Glavni predstavnik anhidrošećera je levoglukozan, čije su koncentracije najveće, no formiraju se i njegovi izomeri manozan i galaktozan, ali u nešto nižim koncentracijama. Cilj ovog rada bio je istražiti doprinos gorenja biomase onečišćenju zraka u gradu Zagrebu praćenjem koncentracija levoglukozana, manozana i galaktozana u lebdećim česticama. Za tu svrhu paralelno su sakupljane lebdeće čestice aerodimaničkog promjera < 10 μm (PM$_{10}$) na mjernim postajama u sjevernom i južnom dijelu grada Zagreba. Period sakupljanja bio je 30 dana u svakoj sezoni 2020. godine. Masene koncentracije lebdećih čestica određene su gravimetrijskom metodom, dok su masene koncentracije anhidrošećera određene analitičkom metodom anionske izmjenjivačke kromatografije visoke djelotvornosti s pulsnom amperometrijskom detekcijom. Rezultati su pokazali značajnu sezonsku razliku i koncentracija lebdećih čestica i koncentracija anhidošećera na obje mjerne postaje. Na mjernoj postaji u južnom dijelu grada koncentracije anhidrošećera bile su veće u odnosu na sjevernu mjernu postaju, te su pratile sezonski trend: zima, jesen, proljeće, ljeto,što je u skladu sa sezonom grijanja u kućanstvima. Udio anhidrošećera u lebdećim česticama u zimskoj sezoni kada je njihova koncentracija najveća iznosio je 9,4 % na južnoj mjernoj postaji, dok je na sjevernoj mjernoj postaji taj udio iznosio 6,1 %.



RAZGRADNJA MIKROPLASTIKE PRIMJENOM UV-C/H_2O_2 PROCESA

MICROPLASTIC DEGRADATION BY UV-C/H_2O_2 PROCESS

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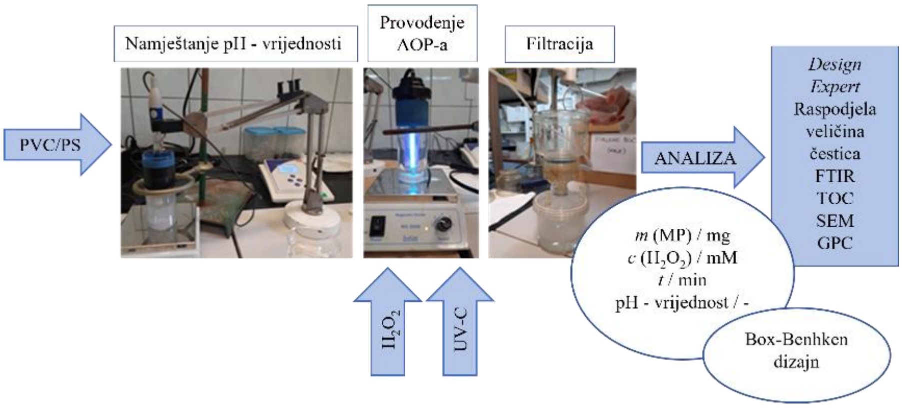
Mikroplastikom (MP) se smatraju sve plastične čestice manje od 5 mm koje zbog svojih svojstava mogu štetno utjecati na živi svijet. Konvencionalne metode za obradu voda nisu dovoljno učinkovite za uklanjanje MP-a te se u tu svrhu razmatra primjena naprednih oksidacijskih procesa (eng. *Advanced Oxidation Process*, AOP). AOP procesi temelje se na nastanku reaktivnih radikala koji mogu razgraditi organske onečišćujuće tvari. Provedeno je ispitivanje razgradnje MP-a polistirena (PS) i poli(vinil-klorida) (PVC), primjenom UV-C/H_2O_2 procesa. Eksperimenti su provedeni prema Box-Behnken dizajnu pri čemu se ispitao utjecaj mase MP-a, koncentracija oksidacijskog sredstva, pH – vrijednost i vrijeme izlaganja UV-C zračenju, na razgradnju MP-a. Čestice MP-a, prije i nakon razgradnje, okarakterizirane su FTIR spektroskopijom, SEM i GPC analizom, a vodena faza TOC analizom. Određena je i raspodjela veličina čestica prije i nakon razgradnje. U računalnom programu *Design Expert* 7.1.5. određeni su optimalni uvjeti UV-C/H_2O_2 procesa za razgradnju obje vrste MP-a. Na temelju dobivenih rezultata utvrđeno je kako je primjenom UV-C/H_2O_2 procesa nastupila djelomična fragmentacija čestica i njihova površinska razgradnja. Učinkovitija razgradnja uočena je za PVC. Optimalni uvjeti za razgradnju PS-a su vrijeme trajanja procesa 82,62 min, koncentracija H_2O_2 19,54 mM uz masu PS-a 30,42 mg i pH – vrijednost medija 6,25. Optimalni uvjeti za razgradnju PVC-a su vrijeme trajanja procesa 89,84 min pri 9,72 mM koncentraciji H_2O_2 uz masu PVC-a od 34,26 mg i pH – vrijednost medija 7,03. Koncentracija oksidansa i vrijeme izlaganja UV-C zračenju pokazali su se značajnim parametrima.

Autori se zahvaljuju financijskoj podršci Hrvatske zaklade za znanost za projekt pod nazivom Primjena naprednih tehnologija obrade voda za uklanjanje mikroplastike (AdWaTMiR) (IP-2019-04-9661).



KINETIKA BIOREMEDIJACIJE OTPADNE VODE POMOĆU MIKROORGANIZAMA

KINETICS OF BIOREMEDIATION OF WASTEWATER BY MICROORGANISMS

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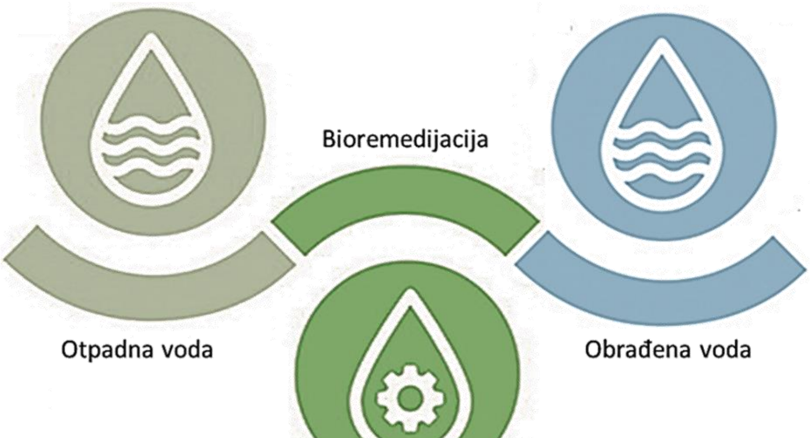
Sve veća zabrinutost zbog degradacije okoliša, onečišćenja vodnog tijela i nedostatka čiste vode, zaokupila je interes istraživača za postizanje ciljeva održivog razvoja. Primjena bioloških procesa za obradu otpadnih voda se kategorizira kao čista tehnologija zbog iskorištavanja potencijala prirodno prisutnih mikrobioloških konzorcija. Bioremedijacija je skup bioloških postupaka za uklanjanje onečišćujućih tvari u okolišu u kontroliranim uvjetima. Istraživanja su pokazala da se izravnom inokulacijom mikroorganizama može poboljšati sposobnost razgradnje organskih onečišćujućih tvari, a može biti i jedini način da se osigura zatvoren ciklus uz nultu emisiju otpadnih voda. Matematički modeli i kinetički parametri važni su za predviđanje učinkovitosti biološke obrade otpadne vode. U ovom radu je istražena bioremedijacija organskih tvari u procjednoj vodi dobivenoj iz biootpada. Pokusi su provedeni u šaržnom reaktoru pri okolišnoj temperaturi uz biostimulaciju autohtonih i bioaugmentaciju ezogenih mikrobnih kultura izoliranih iz herbicidom onečišćenog tla. Dobivena vrijednost biorazgradljivosti supstrata iznosi > 0,50 što ukazuje na odabir biološke obrade. Kako bi se dobio uvid u tijek uklanjanja organskih onečišćujućih tvari, provedena je kinetička analiza istraživanog procesa pomoću matematičkih modela.



KINETIKA RAZGRADNJE PANTOPRAZOLA U VODI

PANTOPRAZOLE DEGRADATION KINETICS IN WATER

Vjeran Sunko[1], Viktorija Prevarić[1], Matija Cvetnić[1], Lidija Furač[1], Šime Ukić[1], Kristina Bule[1], Martina Miloloža[1], Dajana Kučić Grgić[1], Marinko Markić[1], Bruna Babić[1], Danijela Ašperger[1], Tomislav Bolanča[1,2]

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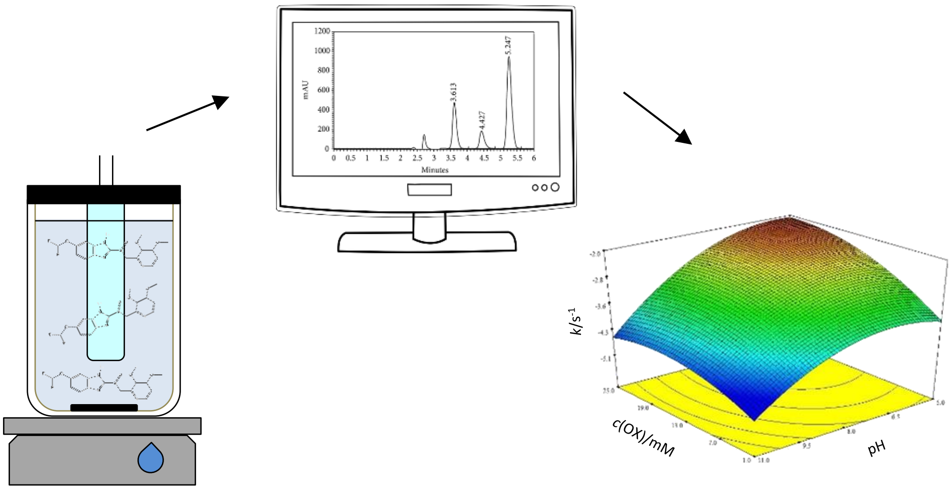
Pantoprazol je jedan od često upotrebljavanih farmaceutika, a koristi se za liječenje bolesti probavnog sustava. Tragovi pantoprazola i njegovih metabolita pronađeni su u uzorcima vode. Zbog toksičnih učinaka potrebno je ispitati mehanizme njegove razgradnje s ciljem pronalaska adekvatnog načina njegovog uklanjanja vodenog okoliša.

U ovom je radu određena toksičnost otopine pantoprazola na bioluminiscentnim bakterijama *Vibrio Fischeri*, mjerenjem inhibicije nakon kontaktnog vremena od 30 minuta. Toksičnost je iskazana kao EC_{50} vrijednost te iznosi 0,04 mM. Nakon toga praćena je kinetika razgradnje pantoprazola u vodi pod utjecajem UV-C/H_2O_2 i UV-C/$Na_2S_2O_8$ naprednih oksidacijskih procesa. Također je ispitan i utjecaj UV-C zračenja samostalno bez dodatka oksidansa. Kod izvođenja pokusa razgradnje primijenjen je potpuni faktorski dizajn eksperimenta gdje je promatran utjecaj koncentracije dodanog oksidansa i pH-vrijednosti otopine, a optimalni uvjeti određeni su metodom odzivne površine. Uzorci su analizirani na HPLC uređaju s UV detektorom. U oba procesa određena je kinetika razgradnje pseudo-prvog reda. Iako je već i primjena samog UV-C zračenja u određenoj mjeri pokazala razgradnju pantoprazola, dodatak oksidansa u oba slučaja pokazuje značajno bolju razgradnju.



BIORAZGRADLJIVOST ORGANSKE FRAKCIJE IZ MIJEŠANOG KOMUNALNOG OTPADA

BIODEGRADABILITY OF ORGANIC FRACTION FROM MIXED MUNICIPAL SOLID WASTE

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Potrošačke navike modernog društva dovode do rasta ukupnih količina otpada što je jedan od najznačajnijih ekoloških problema današnjice. Cjeloviti sustav gospodarenja otpadom daje nam jasne naputke i mjere u svrhu rješavanja ovog problema. Unatoč sve većem odvojenom sakupljanju otpada, miješani komunalni otpad je još uvijek dominantan tok otpada. Procjena biorazgradljivosti biorazgradljive organske frakcije miješanog komunalnog otpada omogućuje uvid u početne uvjete procesa te kvalitetan odabir biološke obrade kao okolišno prihvatljivog rješenja. U ovom radu za procjenu biorazgradljivosti korišteni su realni uzorci biorazgradljive organske frakcije iz miješanog komunalnog otpada. Rezultati pokazuju da je udio biorazgradljive frakcije u miješanom komunalnom otpadu u prosjeku visok i iznosi 73,62±1,50 %. Visoka prosječna vrijednost omjera BPK_5/KPK od 0,78±0,04 ukazuje na mogućnost biološke obrade.

POBOLJŠANJE BIOREMEDIJACIJSKOG POTENCIJALA MIKROORGANIZAMA KOJI RAZGRAĐUJU KSENOBIOTIKE

ENHANCING BIOREMEDIATION POTENTIAL OF XENOBIOTIC-DEGRADING MICROORGANISMS

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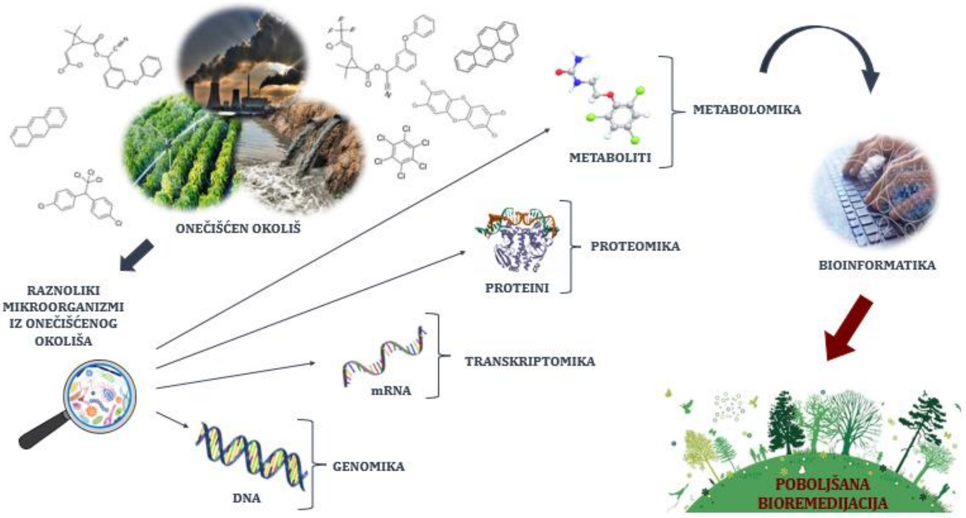
Globalno onečišćenje ksenobioticima predstavlja stalnu antropogenu prijetnju i izaziva ozbiljnu zabrinutost za okoliš. Mnogi ksenobiotski spojevi smanjuju kakvoću okoliša zbog svoje toksičnosti, postojanosti i ograničene biorazgradljivosti što uključuje i visok potencijalni rizik za ljude i životinje. Metabolizam mikroba smatra se najvažnijim mehanizmom razgradnje takvih spojeva te čini osnovu za strategiju bioremedijacije. Tehnike bioremedijacije imaju za cilj ubrzati prirodni proces razgradnje optimiranjem uvjeta u kojima se on događa. U ovom radu, prikazat će se napredne tehnologije koje se koriste za karakterizaciju složenih mikrobnih zajednica. Razumijevanjem njihovih strukturnih i funkcionalnih aspekata može se doprinijeti u poboljšanju bioremedijacijskog potencijala u uklanjanju ksenobiotika.



APPLICATION OF FERRATE FOR REMOVAL OF MICROPLASTICS IN WATER

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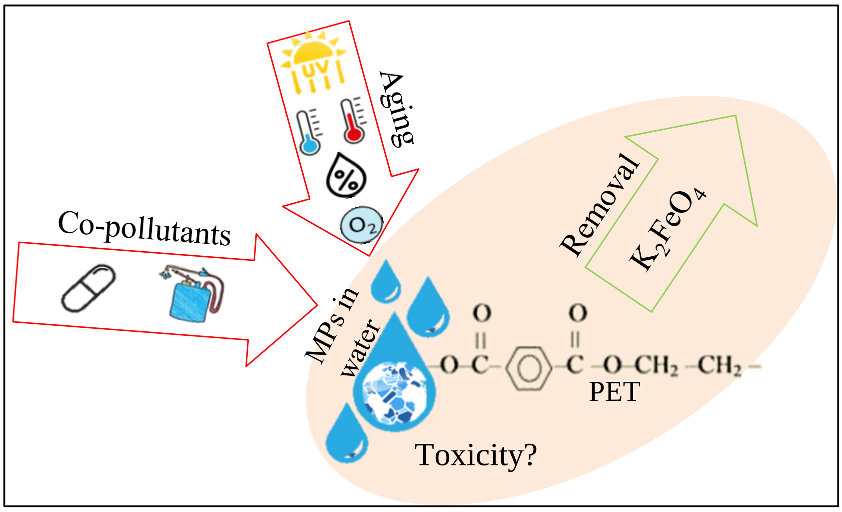
Contaminants of emerging concern (CECs), including microplastics (MPs), in aquatic systems are recognized as potentially harmful to human health and the environment. Atmospheric conditions cause aging of MPs, resulting in surface and structural changes in material. Pristine MPs in water pose a certain risk on their own, but even worse MPs show the ability to interact with co-pollutants in water, behaving as vectors for other pollutants. Both aging of MPs and sorption of co-pollutants on MPs can completely alter MPs environmental behavior and toxicity. Potassium ferrate, K_2FeO_4, a strong oxidant and coagulant stands out as a potentially great candidate for removal of MPs from water. The main drawback is a narrow interval of pH values where the spontaneous K_2FeO_4 reduction is the lowest and oxidation activity towards MPs highest. The aim of this work was to investigate optimal pH conditions K_2FeO_4 towards MP removal and correlate these conditions with toxicity to the freshwater planktonic crustacean *Daphnia magna* and the green algae *Selenastrum capricornutum (Pseudokirchneriella subcapitata)*. For that purpose, a Britton-Robinson buffer was prepared and the stability and activity of K_2FeO_4 were examined by UV-visible spectroscopy, at different pH values: 4, 7, and 10. Poly(ethylene terephthalate) (PET) in the form of shredded bottles and commercial foils were aged under ultraviolet radiation were used as representative sample of MPs. Oxidative effect experiments of K_2FeO_4 on UV-aged PET films were carried out during 180 min, by stepwise addition of K_2FeO_4, followed by quantification of K_2FeO_4 removal by coagulation and toxicity experiments. Acute toxicity bioassays were performed according to the standard procedures using *Daphnia magna*, (ISO 6341:2012) and *Selenastrum capricornutum (Pseudokirchneriella subcapitata)*, (ISO 8692:2012).

This study has been fully supported by the Croatian Science Foundation under the project Microplastics in water; fate and behavior and removal ReMiCRO (IP-2020-02-6033).



ISOLATION AND IDENTIFICATION OF MICROORGANISMS FROM THE REAL COKING WASTEWATER

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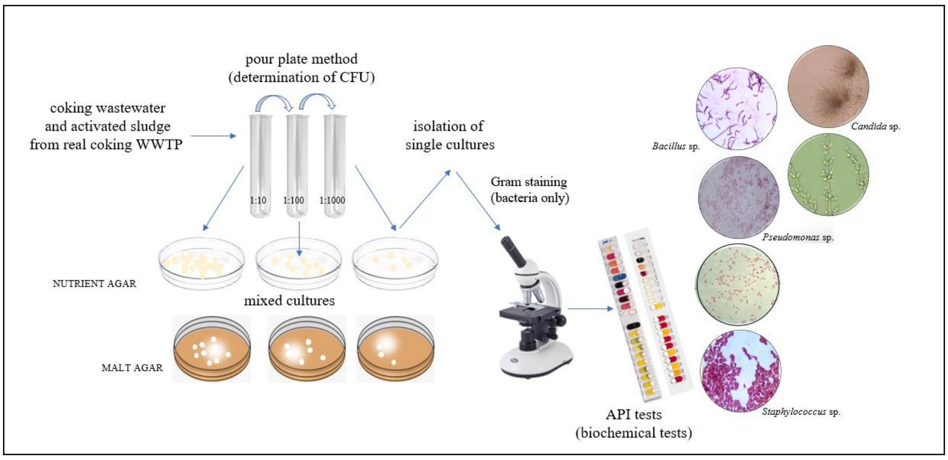
Coke industries around the world produce large amounts of distinctly toxic wastewater of complex composition, known as coking wastewater. Coking wastewater represents a significant environmental issue in terms of both, quantity and quality. It consists of number of toxic compounds, such as phenolic compounds, cyanides and thiocyanates, among many others. In addition to toxicity, these compounds are characterized by carcinogenicity, mutagenicity and teratogenicity. If coking wastewater of such composition is not adequately treated, it poses a potential hazard to both, people and nature. This study involves isolation and identification of microorganisms naturally present in real coking wastewater treatment plant. Three different bacteria strains (two Gram positive, (*Bacillus* sp. and *Staphylococcus* sp.) and one Gram negative (*Pseudomonas* sp.)), as well as one yeast (*Candida* sp.) were isolated and identified from mixture of coking wastewater and activated sludge. Since there is a general need to optimize biological treatment of coking wastewater to achieve environmentally friendly, cost-effective and efficient technology, detailed study and understanding of biological processes is crucial, therefore the isolation and identification of microbial species is the first step in this great challenge.

This research was supported by project „Optimization of existing biological wastewater treatment plant of coke industry“. Special thanks to all associates, including Faculty of Chemical Engineering and Technology and company Bor-plastika d.o.o.



KEMIJSKI ADITIVI PRISUTNI U PLASTICI

CHEMICAL ADDITIVES PRESENT IN PLASTICS

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Čestice nezbrinute plastike koje nekontrolirano završavaju u okolišu zajedno s kemijskim aditivima, čiji dodatak među ostalim služi poboljšanju svojstava, ozbiljno prijete okolišu i organizmima. Određene kemikalije u prošlosti korištene kao aditivi danas su kvalificirane kao tvari posebno zabrinjavajućih svojstava (*eng. substances of very high concern*, SVHC), čiji je popis predložila i Europska agencija za kemikalije, ili kao postojane organske onečišćujuće tvari (*eng. Persistent Organic Pollutants*, POPs) [1]. Porastom svjesnosti o njihovim negativnim utjecajima, sve više se provode ekotoksikološka ispitivanja na različitim organizmima. U ovom radu dan je pregled najčešće korištenih aditiva te rezultati provedenih ekotoksikoloških ispitivanja na polibromiranim difenil eterima i teškim metalima. U jednom od ispitivanja, praćen je utjecaj PBDE-47, PBDE-99 i PBDE-209 na embrije zebrica te je otkriveno da je došlo do subletalnih promjena uključujući kašnjenje u razvoju, zastoj krvi, smanjenog broja otkucaja srca, deformacije repa i glave, te zakrivljenost kralježnice [2]. Iako aditivi na bazi metala, koji se najviše koriste kao stabilizatori, inertna punila i pigmenti [3], imaju važne uloge, prevelike količine teških metala mogu izazvati autoimune i neurološke bolesti, kardiovaskularne bolesti, hipertenziju, neplodnost, oštećenje jetre i bubrega, deformacije kostiju, hiperglikemiju, dijabetes, te mnoge druge negativne učinke [4,5].

Ovo istraživanje financira Hrvatska zaklada za znanost: Projekt IP-04-2019-9661 (AdWaTMiR); Primjena naprednih tehnologija obrade voda za uklanjanje mikroplastike.

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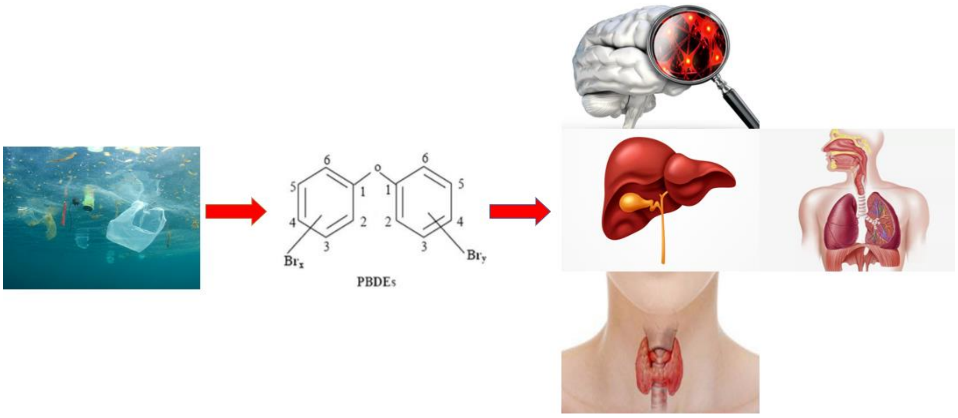

Mehanički, toplinski i separacijski procesi

Mechanical, thermal and separation processes

PREDVIĐANJE TOPLJIVOSTI RIVAROKSABANA U ORGANSKIM OTAPALIMA PRIMJENOM WILSONOVA MODELA TE MODELA, NRTL, UNIQUAC I COSMO-RS

PREDICTION OF SOLUBILITY OF RIVAROXABAN IN ORGANIC SOLVENTS BY THE WILSON, NRTL, UNIQUAC AND COSMO-RS MODELS

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Rivaroksaban je lijek za liječenje i prevenciju nastajanja krvnih ugrušaka u žilama iz reda novih oralnih antikoagulansa (NOAK). Budući da NOAK ne ulaze u interakciju s drugim lijekovima niti zahtijevaju rutinsko praćenje, pogodna su alternativa dosadašnjim antagonistima vitamina K. U ovom radu prikazana je procjena topljivosti dvaju kristalnih oblika rivaroksabana u sedam organskih otapala: acetonitrilu, metil-acetatu, 1,4-dioksanu, acetonu, 2-butanonu, 3-pentanonu i 2-heksanonu, primjenom Wilsonova modela te modela NRTL, UNIQUAC i COSMO-RS. Od prva tri modela, jedino Wilsonov korektno opisuje topljivost u cijelome području sastava. Model COSMO-RS predviđa najbolju topljivost rivaroksabana u acetonitrilu i acetonu, iako je eksperimentom utvrđeno da se rivaroksaban najbolje otapa u 1,4-dioksanu [1]. Međutim, predviđa najmanju topljivost rivaroksabana u 2-heksanonu, što je u skladu s eksperimentalnim podacima [1].

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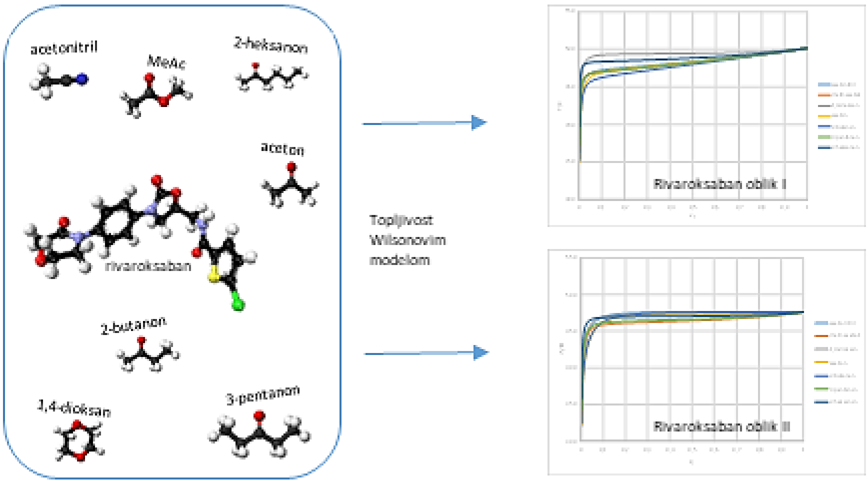

OPTIMIZATION OF HIGH VOLTAGE ELECTRIC DISCHARGE EKSTRACTION OF PHENOLICS FROM MANDARIN PEEL

Marija Banožić, Silvija Šafranko, Dora Bogadi, Stela Jokić

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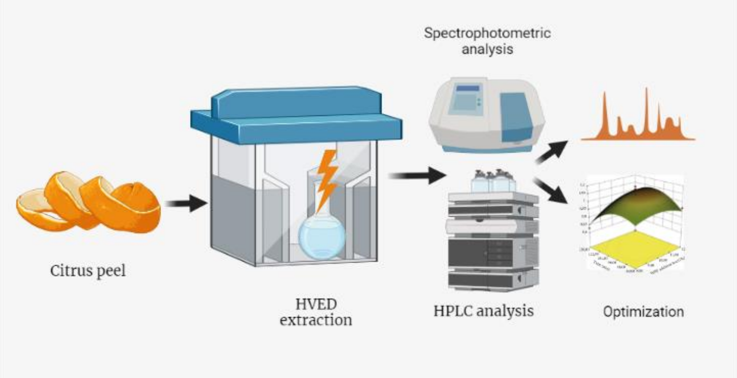
This study aimed to investigate the possibility of applying an high voltage electric discharge (HVED) extraction for the separation of phenolic compounds from the citrus peel (Mandarin, Okitsu variety). Mandarin peel represent citrus by-product generated during the growth and fresh fruit processing. In this study, the influence of three process parameters: time (5-15 min), frequency (40-100 Hz) and solvent/solid ratio (200-400 mL/g) on the extraction yield and bioactive compounds content in obtained extracts were investigated. The antiradical activity and the total phenolic content of the extracts were determined using spectrophotometric assays. The identification and quantification of individual phenolics were performed using high performance liquid chromatography with a diode array detector (HPLC-DAD). Based on the obtained experimental data, the extraction process was optimized using the Design Expert® software. Optimal parameters are defined as follows, for maximum extraction yield: solvent/solid ratio 285.93 mL/g, frequency 73.38 Hz and time of 14.84 min, for maximum hesperidin concentration: solvent/solid ratio 366.19 mL/g, frequency of 97.56 Hz and time of 5.10 min and for maximum narirutin concentration solvent/solid ratio 200 mL/g, frequency of 70 Hz and time of 15 min. The predicted data were experimentally confirmed with an error range of ± 10%. This study clarified that citrus by-products are valuable raw materials rich in phenoliccompounds. Also, using an innovative non-thermal extraction method with green solvent (water) it is possible to obtain satisfying content of bioactive compounds in citrus peel extracts.

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).



PREDVIĐANJE RAVNOTEŽE PARA-KAPLJEVINA U TROKOMPONENTNOME SUSTAVU NA OSNOVI PARAMETARA MODELA KOEFICIJENTA AKTIVNOSTI IZ DVOKOMPONENTNIH SUSTAVA

PREDICTING VAPOR-LIQUID EQUILIBRIUM IN THE THREE-COMPONENT SYSTEM USING PARAMETERS OF ACTIVITY COEFFICENT MODELS OBTAINED FROM TWO-COMPONENT SYSTEMS

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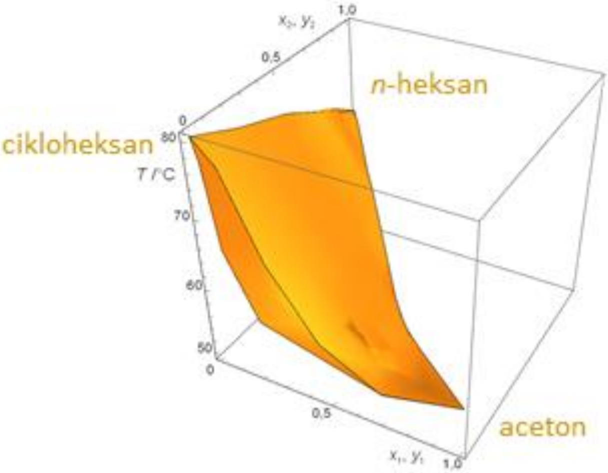
Ideja o primjeni parametara modela izračunatih iz dvokomponentnih sustava za predviđanje svojstava srodnih trokomponentnih sustava važna je radi brzih termodinamičkih proračuna jer se može izostaviti mukotrpan i dugotrajan eksperimentalni postupak u trokomponentnim sustavima. U ovom je istraživanju eksperimentalno određena ravnoteža para-kapljevina u trokomponentnome sustavu aceton(1) – *n*-heksan(2) – cikloheksan(3) pri atmosferskome tlaku te prikazan postupak modeliranja primjenom parametara modela iz dvokomponentnih sustava. Iz literaturnih podataka o odgovarajućim dvokomponentnim sustavima aceton(1) – *n*-heksan(2), aceton(1) – cikloheksan(3) te *n*-heksan(2) – cikloheksan(3), izračunati su parametri koeficijenata aktivnosti modela Wilson, NRTL i UNIQUAC. Iz parametara modela određenih u dvokomponentnim sustavima izračunati su ravnotežni tlakovi i ekscesne Gibbsove energije u trokomponentnom sustavu. Najbolje slaganje eksperimenta i modela dobiveno je kod modela UNIQUAC.



MODELIRANJE FAZNE RAVNOTEŽE PARA-KAPLJEVINA U DVOKOMPONENTNOME SUSTAVU ACETON – CIKLOHEKSAN

MODELING OF VAPOR-LIQUID PHASE EQUILIBRIUM IN THE TWO-COMPONENT SYSTEM ACETONE – CYCLOHEXANE

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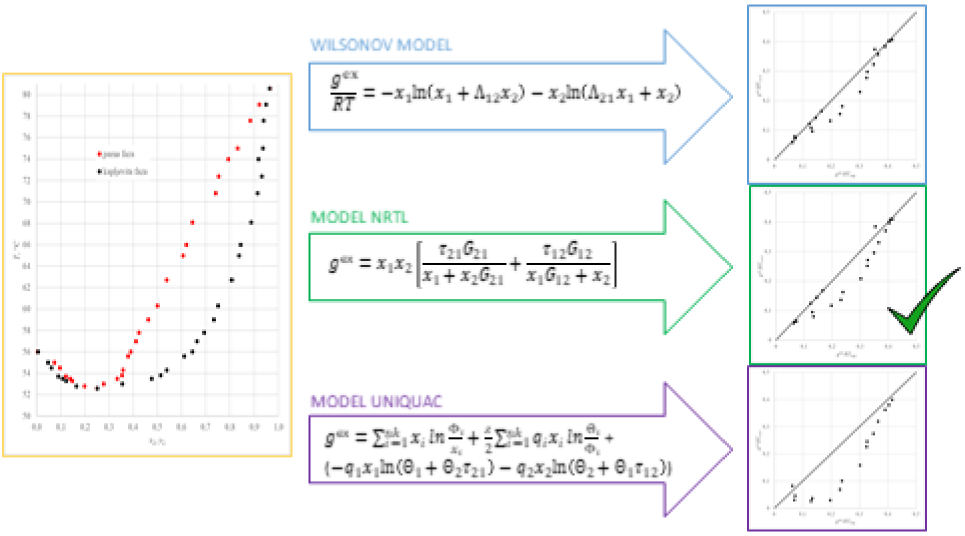
Razmatranje termodinamičkih osnova fazne ravnoteže para-kapljevina s kemijsko-inženjerskog pogleda služi opisu ponašanja brojnih tehnika u industriji koje uključuje prisutnost spomenutih faza. S tim je ciljem u ovome radu Hunsmannovom aparaturom eksperimentalno određena ravnoteža para-kapljevina u uvjetima stalnoga atmosferskog tlaka. Iz tako dobivenih ravnotežnih sastava faza i ravnotežne temperature, termodinamičkim proračunima izračunati su parametri modela koeficijenata aktivnosti, i to Wilsonova, NRTL-a i UNIQUAC-a. Iz dobivenih parametara izračunati su dijagrami vrenja i ekscesne Gibbsove energije te su uspoređeni s eksperimentalnim podatcima. Na osnovi usporedbe može se zaključiti kako se istraživani dvokomponentni sustav najbolje može opisati modelom koeficijenta aktivnosti NRTL. Eksperimentalni podatci ukazuju na azeotropno ponašanje sustava aceton(1) – cikloheksan(2) s minumumom vrelišta koji se postiže pri 52,6 °C.



KARAKTERIZACIJA UF/NF/RO MEMBRANA KORIŠTENIH U SVRHU OBRADE TEKSTILNE OTPADNE VODE

CHARACTERIZATION OF UF/NF/RO MEMBRANES USED FOR TEXTILE WASTEWATER TREATMENT

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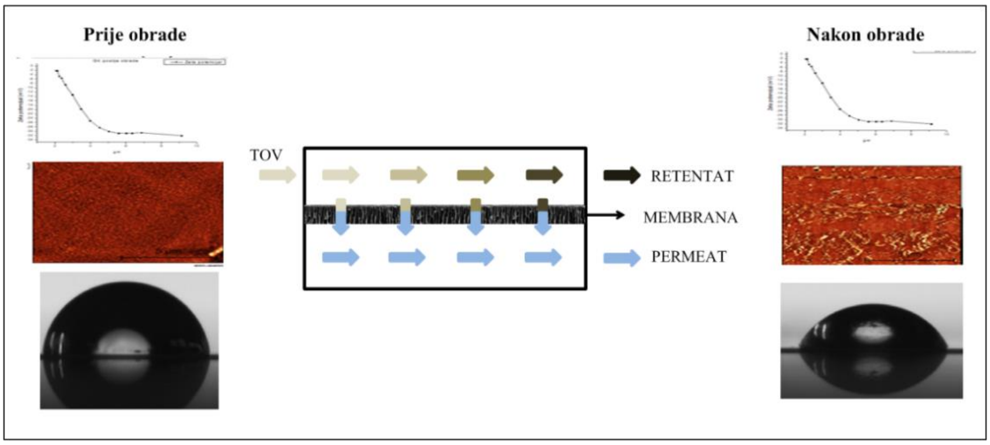
U ovome radu napravljena je karakterizacija četiri ultrafiltracijske membrane (GH, GK, PT i PU) granične molekulske mase 2, 3, 5 i 10 kDa, dviju nanofiltracijskih membrana (NF90 i NF) 100 - 200 i 150 - 300 Da te jedne reverzno osmotske membrane (XLE) 100 Da prije i nakon obrade tekstilnom otpadnom vodom (TOV). Određeni su zeta potencijali, hidrofobnost/hidrofilnost, hrapavost površine, spektri valnih duljina infracrvenim spektrofotometrom s Fourierovom transformacijom (FTIR) i površinski morfološki prikazi pomoću mikroskopije atomskim sila (AFM). Dobivenim mjerenjima utvrđene su promjene na membranama nakon obrade TOV-e. Nakon obrade TOV-e kod UF membrana, posebice GK i PT, došlo je do smanjenja zeta potencijala zbog pojačanih elektrostatskih interakcija dok je kod GH membrane uočeno povećanje zeta potencijala. Također je pokazano AFM-om da su sve ispitivane membrane homogene. Na membranama GH, GK i PT nakon obrade TOV-e pokazuje se povećanje hrapavosti površine. FTIR spektrima utvrdilo se stvaranje novih pikova na svim membranama što potvrđuje adsorpciju otopljenih tvari na površini membrana. Kontaktni kutovi novih nekorištenih membrana pokazali su hidrofilnost površine (kontaktni kutovi 50,67° - 61,04°). Nakon obrade TOV-e, GH, GK i PT membrane pokazuju povećanje kontaktnog kuta, a samim time i blago povećanu hidrofobnost površina.



STABILNOST EMULZIJA I INVERZIJA FAZA U SUSTAVIMA ULJE – VODA

WATER-OIL SYSTEMS: STABILITY OF EMULSIONS AND PHASE INVERSION

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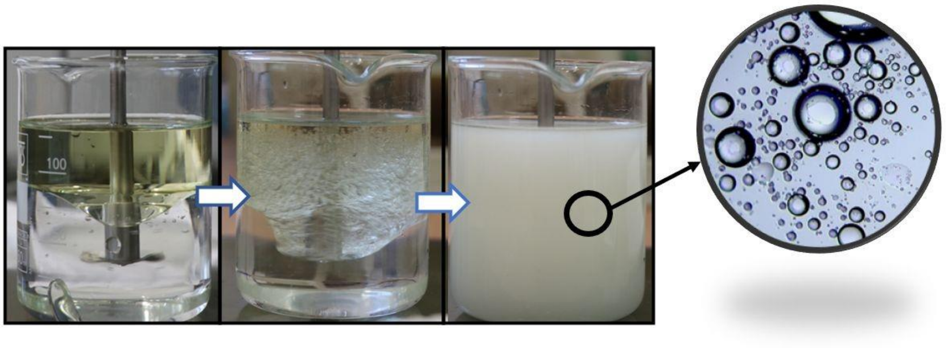
Istražen je utjecaj svojstava ulja i volumnog udjela vode na stabilnost emulzija i inverziju faza. Odabrano je šest jestivih ulja koja se razlikuju po kemijskom sastavu (suncokretovo, biljno, bučino, kukuruzno, kikiriki i maslinovo). Istražen je utjecaj temperature na gustoću, viskoznost i površinsku napetost ulja a navedene su ovisnosti prikazane odgovarajućim korelacijskim jednadžbama. Gustoća i površinska napetost ulja opadaju linearno s porastom temperature dok je utjecaj temperature na viskoznost opisana jednadžbom Arrheniusovog tipa. Ovisnost površinske napetosti o viskoznosti ulja opisana je Pelofskyjevom empirijskom jednadžbom. Viskoznost i gustoća emulzija procijenjene su na temelju podataka o pojedinačnim fazama. Miješanje dviju nemješljivih kapljevina provedeno je u posudi Rushtonovih dimenzija opremljenoj turbinskim miješalom s četiri lopatice nagnute pod kutem od 45°. Volumni udio vode mijenjan je u intervalu od 10 do 90 % a maksimalna brzina vrtnje miješala odgovarala je brzini potrebnoj da se osigura stanje potpune disperzije. Definirana su područja u kojem je ulje, odnosno voda kontinuirana faza. Na temelju ovisnosti snage potrebne za miješanje i pripadajući režim strujanja razvijena je korelacijska jednadžba koja omogućava procjenu značajke snage uz poznatu viskoznost emulzije. Raspodjela masnih kiselina u uljima te udio slobodnih masnih kiselina i ostalih površinski aktivnih tvari utječu na međupovršinsku napetost a time i sklonost sustava koalescenciji te stabilnost emulzija.

Ovaj rad izrađen je unutar projekta Razvoj sustava za ispitivanje višefaznih strujanja i izgaranja s ciljem povećanja istraživačkih aktivnosti znanstvenog i poslovnog sektora, KK.01.1.1.04.0070., sufinanciranog od strane Europske unije, sredstvima Europskog fonda za regionalni razvoj, Operativni program Konkurentnost i kohezija 2014.-2020.



EKSTRAKCIJA KOFEINA IZ ČAJA EKOLOŠKI PRIHVATLJIVIM OTAPALIMA

EXTRACTION OF CAFFEINE FROM TEA WITH ECO-FRIENDLY SOLVENTS

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U ovom je radu istražena mogućnost primjene niskotemperaturnih eutektičkih otapala (*deep eutectic solvent, DES*) za ekstrakciju kofeina iz tri vrste čaja (crni, zeleni i yerba mate) koji sadrže različit početni udio kofeina. Pripravljena su četiri otapala s različitim udjelom vode: kolin klorid : limunska kiselina, 2:1 s 30 % vode (DES1); jabučna kiselina:glukoza:glicerol, 1:1:1 s 30 % vode (DES2); mliječna kiselina:glicerol, 2:1 s 10 % vode (DES3) i kolin klorid:jabučna kiselina, 1:1 s 30 % vode (DES4). Šaržna je ekstrakcija provedena pri sobnoj temperaturi uz stalan maseni omjer listića čaja i otapala. Koncentracija kofeina određena je primjenom UV/Vis spektroskopije. Modelom COSMO RS procijenjena je topljivost kofeina u pripravljenim otapalima. Prema modelu topljivost kofeina raste u sljedećem smjeru: DES2 > DES 3 > DES 4 > DES1. Učinkovitost ekstrakcije kofeina iz čaja yerba mate mijenja se u smjeru procijenjenom modelom COSMO RS. Za ekstrakciju kofeina iz crnog i zelenog čaja najučinkovitije je otapalo DES1 dok se najmanje učinkovitim pokazalo otapalo DES2. Razlika vjerojatno potječe od ekstrakcije i drugih spojeva osim kofeina iz crnog i zelenog čaja. Crni i zeleni čaj potječu od iste biljke (*Camellia sinensis*) dok se čaj yerba mate dobiva iz lišća istoimene južnoameričke biljke (*Ilex paraguariensis*).
Eksperimentalno je određena toksičnost otapala (bakterijom *V. fischeri*) i antimikrobna aktivnost (testom osjetljivosti) ekstrakata.

KONTINUIRANA EKSTRAKCIJSKA DEACIDIFIKACIJA SIROVINE ZA SINTEZU BIODIZELA

CONTINUOUS EXTRACTIVE DEACIDIFICATION OF FEEDSTOCK FOR BIODIESEL SYNTHESIS

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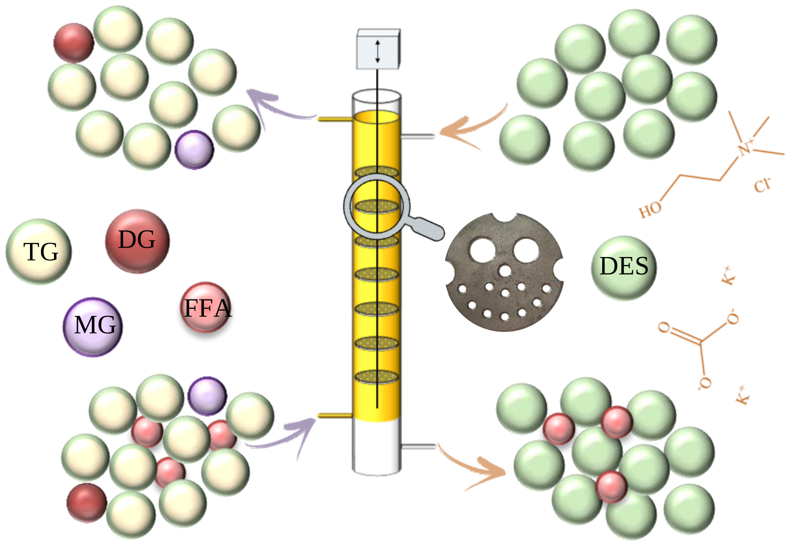
Istraživanja pokazuju da će do 2030. svjetska potreba za energijom narasti za 50 %, zbog čega se, kao zamjena za fosilna goriva, sve više koriste alternativni izvori energije (obnovljivi izvori i biogoriva). Biodizel je održiv, obnovljiv, netoksičan i čist izvor energije, koji se proizvodi reakcijom transesterifikacije životinjskih masti, biljnih ulja ili otpadnog jestivog ulja. Visoki sadržaj slobodnih masnih kiselina (engl. *free fatty acids*, *FFA*) i vlage u otpadnom ulju može dovesti do saponifikacije, zbog čega se ulje u predobradi pročišćava. Suvišak *FFA* može se uspješno ukloniti ekstrakcijskom deacidifikacijom uz upotrebu ekološki prihvatljivih niskotemperaturnih eutektičkih otapala. U ovom je radu istražen utjecaj frekvencije pulzacija plitica i masenog omjera otapala i ulja na djelotvornost kontinuirane ekstrakcijske deacidifikacije otpadnog jestivog ulja s 1,71 % *FFA* pomoću niskotemperaturnog eutektičkog otapala kalijev karbonat-etilen-glikol (1:10). Eksperimenti su provedeni tijekom 20, 25 i 30 minuta. Istražen je utjecaj frekvencija pulzacije plitica (10, 15 i 20 min^{-1}) i masenog omjera otapala i ulja (0,26:1, 0,35:1 i 0,46:1) na djelotvornost kontinuirane ekstrakcijske deacidifikacije. Stacionarno stanje je u svim eksperimentima postignuto nakon 20 minuta. Na djelotvornost procesa utječu kvaliteta sirovine, maseni omjer otapala i ulja te hidrodinamički uvjeti. Najveća djelotvornost (> 96 %) postignuta je pri frekvenciji pulzacija plitica 15 min^{-1} i masenom omjeru 0,35:1. Volumni koeficijent prijenosa tvari veći je na strani kontinuirane faze (ulja), što znači da se glavni otpor prijenosu tvari nalazi na strani disperzne faze (otapala). Kontinuirana ekstrakcijska deacidifikacija daje zadovoljavajuće rezultate s visokom djelotvornošću, no za industrijsku će primjenu biti potrebno dodatno istraživanje i optimizacija uvjeta provedbe procesa.

Ovaj rad izrađen je unutar projekta Razvoj sustava za ispitivanje višefaznih strujanja i izgaranja s ciljem povećanja istraživačkih aktivnosti znanstvenog i poslovnog sektora, KK.01.1.1.04.0070., sufinanciranog od strane Europske unije, sredstvima Europskog fonda za regionalni razvoj, Operativni program Konkurentnost i kohezija 2014.-2020.



Reakcijsko inženjerstvo
Reaction engineering

PREPARATION AND CHARACTERISATION OF TIO_2/ZIF-8 HYBRID PHOTOCATALYST FOR PHOTODEGRADATION OF NEONICOTIONIDE INSECTICIDES

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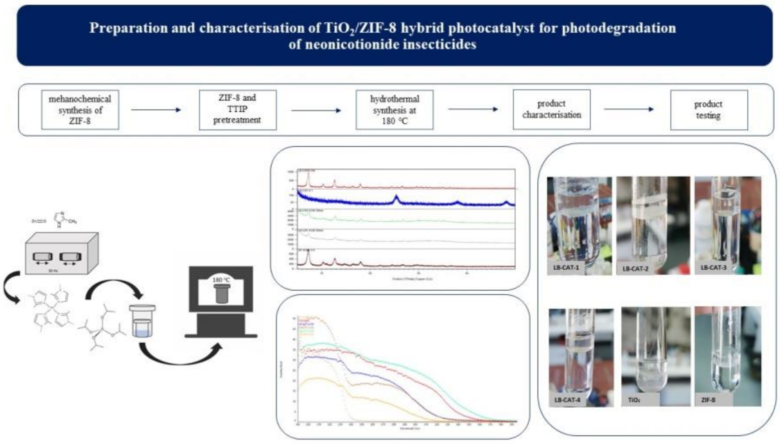
The aim of this study was to prepare and characterize a visible light responsive hybrid TiO_2/ZIF-8 photocatalyst with potential application for the photodegradation of neonicotinoid insecticides [1]. For this purpose, a hydrothermal synthesis of a hybrid TiO_2/ZIF-8 composite catalyst was carried out using mechanochemically synthesized ZIF-8 and titanium tetraisopropoxide as titanium precursor [2]. Characterization of the prepared hybrid materials was carried out by various techniques, such as powder X-ray diffraction (XRD), and UV-Vis diffuse reflectance spectroscopy (UV-Vis/DRS). To determine the polarity of the products and reactants, a simple test was performed in a solution of hexane and water.

The prepared ZIF-8/TiO_2 composites showed increased absorption of visible radiation between 400 and 800 nm.

[1] L. Rui, L. Wei, J. Chun, H. Qinyu, W. Yinzhen, 825 (2020) 154008
[2] P.J. Beldon, L. Fabian, R.S. Stein, A. Thirumurugan, A.K. Cheetham, T. Friščić, Angew. Chem. Int. 49 (2010) 9640–9643.



REAKTIVNI KISIKOVI RADIKALI U FOTOKATALITIČKOJ RAZGRADNJI NEONIKOTINOIDA

REACTIVE OXYGEN RADICALS IN PHOTOCATALYTIC DECOMPOSITION OF NEONICOTINOIDS

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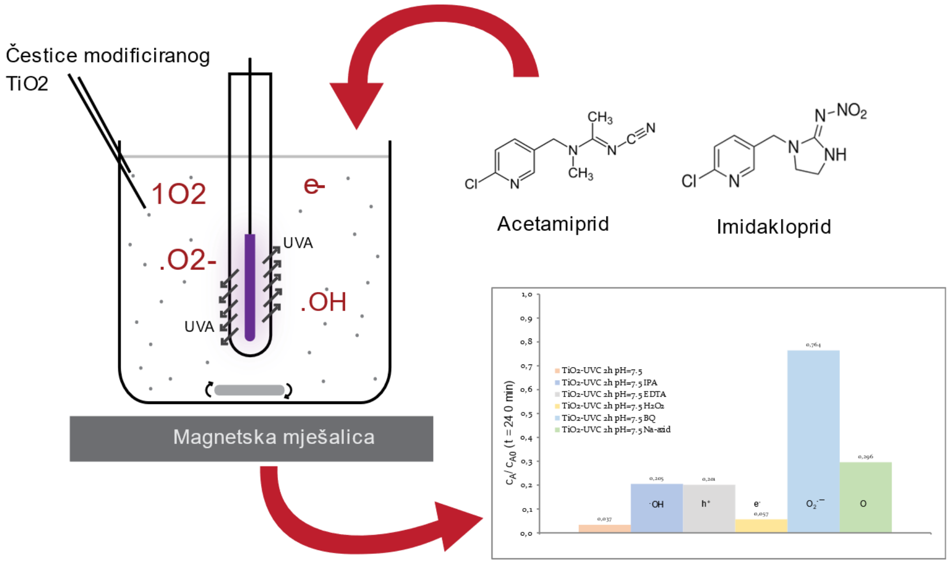
Neonikotonoidni insekticidi (ili neonikotinoidi) su 2018. godine uvršteni na proširenu tzv. "watch" listu Europske komisije unutar Okvirne direktive o vodama zbog potvrđenog rizika i opasnosti za vodni okoliš. Njihovo uklanjanje jedan je od izazova kojim se bave mnoga istraživanja. Cilj ovog istraživanja je odrediti reaktivne kisikove radikale ključne za uspješno provođenje fotokatalitičke razgradnje modelnih komponenti neonikotinoida (imidakloprida i acetamiprida) primjenom modificiranih TiO_2 fotokatalizatora. Istraživanja su provedena u kotlastom fotoreaktoru, a kao izvor zračenja korištena je UVP Pen Ray lampa (UVA, λ=365 nm). Ispitan je utjecaj pH otopine na fotokatalitičku razgradnju te je uspoređena fotolitička i fotokatalitička razgradnja pri optimalnoj pH vrijednosti. Za određivanje reaktivnih kisikovih radikala koristili su se tzv. hvatači i to izopropanol, natrijev azid i p-benzokinon za određivanje $OH^{\bullet}$, $^1O_2$ i $O_2^{-\bullet}$ radikala te H_2O_2 za e^-. Mogućnost razgradnje izravnom oksidacijom adsorbiranog organskog zagađivala sa šupljinama valentnog pojasa (h^+) provjerila se dodatnim ispitivanjem uz primjenu EDTA-Na_2. Zaključci o utjecaju reaktivnih kisikovih radikala na učinkovitosti fotokatalitičke razgradnje donijeti su temelju određivanja promjene koncentracije modelne komponente kao funkcije vremena ozračivanja u prisutnosti prethodno spomenutih spojeva.

Ovaj je rad financirala Hrvatska zaklada za znanost projektom Intenzifikacija fotokatalitičkih i katalitičkih procesa za obradu otpadnih voda i otpadnih plinova, IN-PhotoCat (IP-2018-01-8669).



EKSTRAKCIJA ENZIMA *ENDO*-1,4-KSILANAZA VODENIM DVOFAZNIM SUSTAVIMA

EXTRACTION OF THE ENZYME *ENDO*-1,4,-XYLANASE IN AQUEOUS TWO-PHASE SYSTEMS

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Anita Šalić

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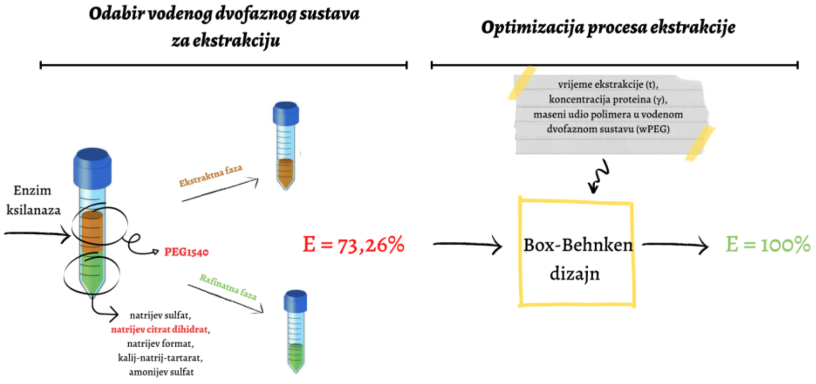
Enzim *endo*-1,4-ksilanaza, ili skraćeno ksilanaza, je hidrolitički enzim koji nasumično cijepa *β*-1,4 vezu polisaharida ksilana u ksilozu. Enzim ksilanaza drugi je najkorišteniji industrijski enzim, odmah nakon enzima lipaza. Koristi se u različitim industrijskim granama, a najviše u industrije celuloze i papira gdje se koristi kao sredstvo za izbjeljivanje te u prehrambenoj industriji gdje se upotrebljava u svrhu poboljšanja kvalitete tijesta, pri ekstrakciji kave te u proizvodnji piva i sokova. Zbog sve veće potrebe za enzimom ksilanaza, posljednjih se nekoliko desetljeća neprestano traga za novim izvorima ovog enzima. Enzim ksilanaza je ekstracelularni enzim, a proizvode ga mikroorganizmi kao što su gljive, bakterije i kvasci. Tijekom svoga rasta mikroorganizmi, osim ksilanaze, proizvode i druge ekstracelularne enzime te sekundarne metabolite. Kako bi dobili enzim ksilanaza pogodan za industrijsku upotrebu, enzim je u pravilu potrebno pročistiti. Kao jedna od učinkovitih i jeftinih metoda pročišćavanja enzima ksilanaza koristi se i ekstrakcija vodenim dvofaznim sustavima. Prednosti ove metode prema drugim metodama pročišćavanja enzima su: kratko vrijeme trajanja procesa, niska cijena ekstrakcijskog sredstva, mala potrošnja energije, velika iskorištenja, veliki kapacitet ekstrakcijskog procesa te relativno jednostavno uvećanje procesa.

U ovom radu provedena ekstrakcija enzima ksilanaza porijeklom iz *Trametes versicolor* vodenim dvofaznima sustavima na bazi polietilenglikola (PEG1540) i različitih soli (natrijev sulfat, natrijev citrat dihidrat, natrijev format, kalij-natrij-tartarat i amonijev sulfat). Preliminarna istraživanja pokazala su kako se najveća učinkovitost ekstrakcije od 73,26 % postiže upotrebom vodenog dvofaznog sustava natrijev citrat dihidrat-voda-PEG1540. Kako bi se postigla veća učinkovitost ekstrakcije, provedena je optimizacija procesa korištenjem eksperimentalnog Box-Behnken dizajna na tri razine s tri faktora pri čemu je analiziran utjecaj vremena ekstrakcije (t), koncentracije proteina (γ) i masenog udjela polimera u vodenom dvofaznom sustavu (w_{PEG}) na učinkovitost ekstrakcije enzima ksilanza. Pri optimalnim procesnim uvjetima (γ = 0,3 mg/mL, w_{PEG} = 0,21 i t = 15 min) postignuta je maksimalna učinkovitost ekstrakcije enzima ksilanaza od 100 %.



INVESTIGATION OF THE POTENTIAL OF STEREOLITHOGRAPHY AS A POSSIBLE METHOD FOR THE PRODUCTION OF CERAMIC MONOLITHIC CATALYSTS

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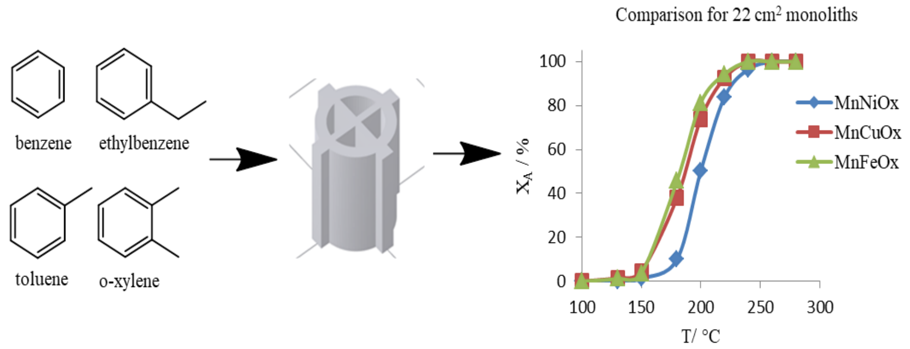
In chemical engineering, the term monolith refers to structures with clearly defined and invariable geometry. They are usually produced by extrusion (ceramic monoliths, usually made of synthetic cordierite) or by coiling and grooving (metal monoliths, usually made of stainless steel). In recent years, the possibility of 3D printing, i.e. additive manufacturing (AM), has been explored for various applications in the field of biotechnology and chemical sciences, but also in the field of catalytic reaction engineering as an advanced method to fabricate complex monolithic catalysts/reactors from different materials.

In this work, stereolithography (SLA) was used to fabricate ceramic monolithic catalyst carriers for the preparation of potential monolithic catalysts for the catalytic oxidation of a benzene/toluene/ethylbenzene/o-xylene (BTEX) gaseous mixture. This approach involves the preparation of inert catalyst carriers, on the surface of which the catalytically active components are subsequently deposited using the impregnation technique. The prepared monolithic catalysts differed in the characteristic geometry of the channels, resulting in different geometric surface areas (11 cm^2, 15 cm^2, 20 cm^2, and 22 cm^2) of the monolithic catalysts. As catalyst precursors, 1 M aqueous solutions of manganese(II) nitrate tetrahydrate, copper(II) nitrate trihydrate, iron(III) nitrate nonahydrate, and nickel(II) nitrate hexahydrate were used. Two-component mixed oxides of manganese and transition metals (Fe, Cu and Ni) were used as catalytically active components.

As expected, the conversion of the BTEX components increased with increasing temperature, and characteristic S-shaped curves (i.e., self-ignition curves) were obtained. The carrier with a geometric surface area of 22 cm^2 proved to be the best, as expected, while in terms of the chemical composition of the catalyst, the best results were obtained with MnFeOx, followed by MnCuOx with very similar conversion values, and MnNiOx, which proved to be less catalytically active under the tested operating conditions.

Croatian Science Foundation has supported this work under the project IN-PhotoCat (IP-2018-01-8669).



CHARACTERIZATION OF pH SENSOR FILMS PREPARED BY THE SOL-GEL METHOD

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The aim of this work is to determine the working range of the pH indicator after immobilization, to characterize the functional groups using Fourier-transform infrared spectroscopy (FTIR), and to determine whether the hydrophilicity of the surface changes when the coating is applied. In addition, the effect of post-curing and swelling of polyacrylate test plates in various solvents on coating adhesion was investigated. The degree of cure (DOC) of the plates was determined using DSC method.

The test plates were manufactured using stereolithography (SLA) 3D-printing technology (Clear material) and sol-gel method was used to prepare the pH sensor films. The mixture for sensor film coating was prepared using silane precursors tetraethoxysilane (TEOS) and phenyltrimethoxysilane (FTMS), ethanol/water as solvent and hydrochloric acid (HCl) as catalyst for the sol-gel process with the addition of pH indicators. The indicators used in this work were methyl red and litmus.

The functionality of the sensor film was investigated by placing the test plates covered with pH sensor films in ten solutions with different pH values. After the test, it can be seen that the pH sensor films change color depending on the pH of the solution (Fig. 1).

This work has been supported by European Regional Development Fund under the project: OS-Mi (KK.01.1.1.04.0006) and by Croatian Science Foundation under the project DOK-2021-02-5999.

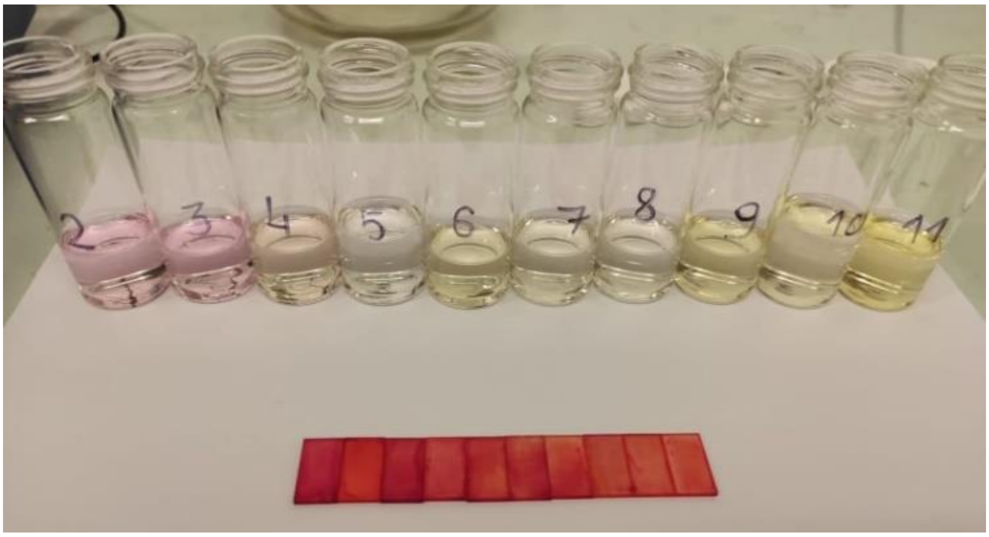

Figure 1. Test plates coated with sensor films after 3 days in solutions with pH values 2-11

EKSTRAKCIJA LAKAZE VODENIM DVOFAZNIM SUSTAVIMA: OPTIMIZACIJA I INTENZIFIKACIJA PROCESA

LACCASE EXTRACTION BY AQUEOUS TWO-PHASE SYSTEMS: PROCESS OPTIMIZATION AND INTENSIFICATION

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Enzim lakaza pripada skupini polifenol oksidaza. S obzirom da može katalizirati reakcije velikog broja supstrata, primjenjuje se u brojnim biotransformacijama kao što su oksidacije organskih i anorganskih supstrata, ksenobiotika, pesticida itd. Izvor enzima lakaza su najčešće različite biljke i gljive. Kako bi korištenje enzima u industriji bilo ekonomski opravdano, potrebno je proizvesti enzim visoke čistoće i aktivnosti te prihvatljive cijene. Enzim lakaza industrijski se u pravilu proizvodi submerznom fermentacijom, ali se sve češće koristi i proizvodnja na čvrstim nosačima jer se u ovom procesu kao supstrat može koristiti otpad iz različitih industrija. Prilikom rasta gljiva na kompleksnim podlogama kakve su čvrsti nosači dolazi do proizvodnje različitih enzima te je stoga na ovaj način proizveden enzim lakazu potrebno odvojiti različitim tehnikama pročišćavanja od drugih enzima i ostalih komponenata fermentacijske podloge. Pročišćavanje enzima, pa tako i pročišćavanje enzima lakaza je skup proces te se stoga sve više radi na razvoju održivih, jeftinih, “zelenih” i učinkovitih metoda pročišćavanja enzima. Jedna od takvih metoda je i ekstrakcija pomoću vodenih dvofaznih sustava primjena kojih se pokazala učinkovitom pri pročišćavanju osjetljivih biomolekula kao što su enzimi.

U ovom radu provedeno je pročišćavanje enzima lakaza porijeklom iz *Trametes versicolor* proizvedenog fermentacijom na čvrstim nosačima ekstrakcijom pomoću vodenog dvofaznog sustava PEG1500-H_2O-$(NH_4)_2SO_4$. Optimizacija procesa ekstrakcije provedena je korištenjem Box-Behnken dizajna na tri razine s tri faktora prilikom koje je analiziran utjecaj vremena ekstrakcije (t), koncentracije proteina (γ) i masnog udjela polimera u vodenom dvofaznom sustavu (w_{PEG}) na faktor pročišćavanja (*FP*) enzima lakaza. Dobiveni rezultati pokazali su da se najveći faktor pročišćavanja enzima lakaza, $FP = 2{,}5$ postiže pri $t = 15$ min, $\gamma = 1{,}6$ mg/mL i $w_{PEG} = 0{,}179$. Kako bi se proces dodatno intenzivirao, ekstrakcija enzima lakaza provedena je i u mikroekstraktoru pri optimalnim uvjetima.

REGIOSELECTIVE OXOFUNCTIONALIZATION OF STEROIDS IN DEEP EUTECTIC SOLVENTS

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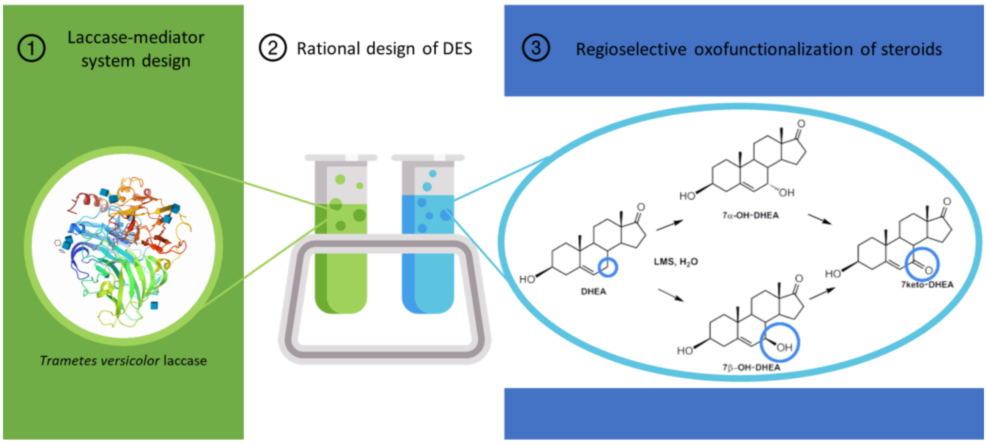
Steroid production occupies a prominent place in the pharmaceutical industry, where steroids, after antibiotics, represent the second most important group of pharmaceutics. One of the major transformations in their synthesis path is oxofunctionalization, a regioselective introduction of oxygen into the gonane nucleus that can be catalysed by laccases. With the help of mediator systems, these enzymes can catalyse a wide range of organic substrates. Since most steroid compounds are not water-soluble, the use of deep eutectic solvents (DES) can overcome the disadvantages of common organic solvents. The aim of this research is to investigate the possible use of DES for *Trametes versicolor* laccase-mediated regioselective oxofunctionalization of 3*β*-hydroxyandrost-5-en-17-one to 3*β*-hydroxyandrost-5-en-7,17-dione, an important compound in medicine and pharmaceutics. The Conductor-like Screening Model for Real Solvents (COSMO-RS) was used to predict substrate solubility and to design a two-phase reaction system compatible with all reaction constituents. Three reaction parameters (substrate, mediator and enzyme concentration) were optimised by response surface methodology to obtain high product yield. This research applies both empirical methods and mathematical models to find one solvent with optimal characteristics for this specific requirement.



PRIMJENA PROTOČNIH MILI- I MIKROREAKTORA U SINTEZI HETEROCIKLIČKIH ANALOGA REZVERATROLA

APPLICATION OF FLOW MILI- AND MICROREACTORS IN THE SYNTHESIS OF HETEROCYCLIC RESVERATROL ANALOGUES

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In organic chemistry, more and more attention is paid to synthesis in milli- and micro-flow systems (flow chemistry). This approach has numerous advantages over batch synthesis such as higher efficiency, environmental friendliness and safety and the advantage that all toxic and corrosive reagents are handeled in a closed system [1]. In this work, a series of reactions will be carried out for the synthesis of new heterocyclic resveratrol analogues by batch synthesis, and in milli- and micro-reactors in which the reaction conditions will be optimized to increase efficiency and safety and enhance the process. A selective and convenient way to form a carbon-carbon double bond is through the Wittig reaction and its modifications. This reaction is one of the most important and versatile reactions in organic chemistry for the synthesis of alkenes with unambiguous positioning of the double bond [2, 3]. An aldehyde and a Wittig salt are introduced into the reactor where they react by treatment with aqueous sodium hydroxide to form the corresponding unsaturated Wittig product. The results obtained by batch synthesis and flow synthesis were compared and presented in this work.

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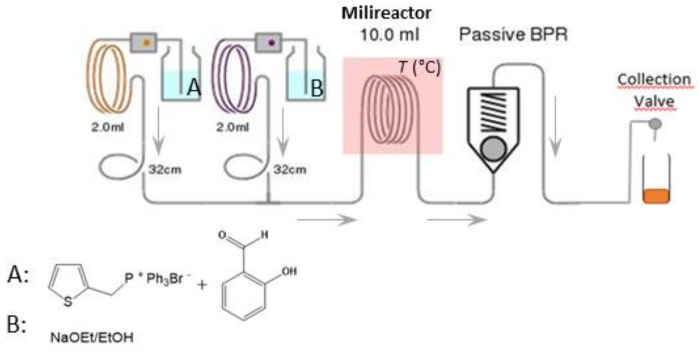

PHOTOCATALYTIC DEGRADATION OF IMIDACLOPRID UNDER NATURAL SUNLIGHT

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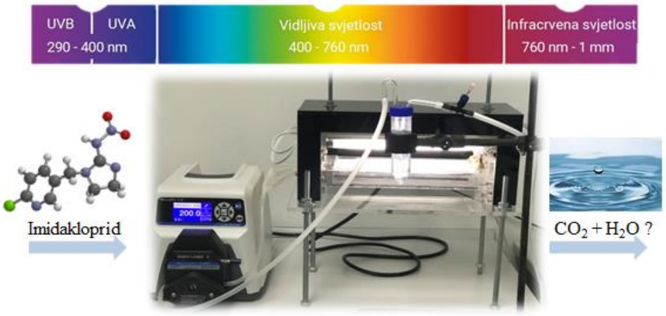
Pollution of the environment, especially of the aquatic ecosystem, is one of the most serious problems today. Due to their high toxicity, strong bioaccumulation in the environment and high persistence, a relatively new group of insecticides - neonicotinoids - pose a serious threat to the ecosystem and the health of living organisms. Since conventional water treatment methods do not allow the complete removal of pesticides from polluted waters, a large amount of scientific research today is focused on the development of environmentally friendly and energy-efficient treatment methods. Heterogeneous photocatalysis is carried out in the presence of a solid semiconductor material and under the influence of sunlight as a radiation source. Due to its properties such as high photochemical stability, oxidative efficiency, availability and non-toxicity, the most commonly used photocatalyst is titanium dioxide (TiO_2). Despite its many advantages, the high energy of the bandgap, i.e., the need for UV radiation for excitation, is a factor limiting the use of TiO_2 in solar systems. In this work, photolytic and photocatalytic degradation of the neonicotinoid insecticide imidacloprid was investigated with Sun as a radiation source. Investigations were carried out in a plate photoreactor under recirculating reaction conditions with an immobilized photocatalyst (TiO_2). To reduce the bandgap, TiO_2 was modified by prior irradiation with UVC radiation. The experiments were performed at a constant initial reactant concentration (10 ppm) and at a constant pH of the reaction solution (pH = 6.5). The influence of the recirculation flow (50 - 300 $cm^3\ min^{-1}$) and the surface area of the photocatalyst exposed to radiation on the rate of degradation of the model component was studied. The course of imidacloprid degradation was followed by high performance liquid chromatography (HPLC), while the degradation intermediates were identified by QT of analysis. The test results indicated the possibility of photocatalytic degradation of imidacloprid using Sun, a clean and alternative energy source, as a radiation source. In the presence of the prepared photocatalyst, the reaction rate is significantly increased. Higher conversions of imidacloprid were achieved at higher recirculation flows and larger surface area of the photocatalyst exposed to radiation.

This work has been supported by Croatian Science Foundation under the project IN-PhotoCat (IP-2018-01-8669).



Primijenjena kemija
Applied chemistry

WHEN HYDROPHOBIC CAVITIES MEET BENZENE DERIVATIVES

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Macrocyclic receptors such as cucurbit [7]uril (CB7) and β-cyclodextrin (β-CD) have found their use in various scientific fields and branches of industry as suitable receptors and solubilizers for hydrophobic compounds in aqueous solutions. This is attributed to favorable desolvation of the guest and the host cavity as well as their spatial compatibility [1]. Benzene derivatives containing functionalities with different electron-donor properties were chosen as guests for investigation of substituent impact on the hydrophobically driven hosting. Their complexation with CB7 and β-CD in water (Figure 1) was explored by means of isothermal titration microcalorimetry and NMR spectroscopy. The complexes with guests functionalized with electron-donor groups were more stable as a result of a more favorable reaction enthalpy. Most of the examined host-guest systems showed distinct temperature dependence of $\Delta_r H°$ and $\Delta_r S°$, resulting in an almost complete temperature independence of reaction Gibbs energy. The complexation thermodynamics was in agreement with the classical interpretation of the hydrophobic effect at lower temperatures and the non-classical explanation at higher ones [1,2].

This research was fully supported by the Croatian Science Foundation (project MacroSol, IP-2019-04-9560) and European Regional Development Fund (project CIuK, KK.01.1.1.02.0016).

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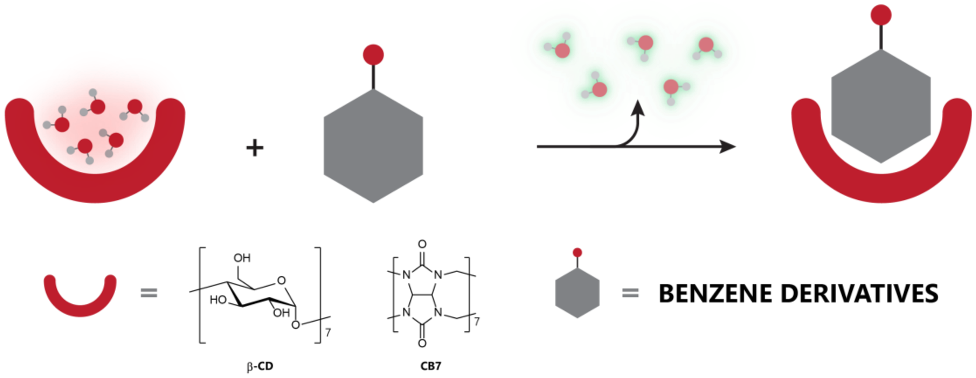

Figure 1. Schematic representation of the complexation process.

TRIAZOLYLCOUMARIN-DERIVED PSEUDOPEPTIDES: SYNTHESIS AND FLUORESCENCE PROPERTIES

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Supramolecular gels based on low-weight molecules have attracted considerable research interest due to their potential applications in fields such as molecular electronics, light-energy conversion, catalysis, cosmetics and drug delivery systems [1]. Coumarins are a very large class of compounds containing the unique 2H-chromen-2-one motif. Coumarin derivatives are widely found in nature, especially in plants and are components of several essential oils. The coumarin compounds are increasingly used in the design of small-molecule fluorescent chemosensors because of its excellent biocompatibility, strong and stable fluorescence emission, and good structural flexibility [2]. In aim of design of fluorescent pseudopeptides, novel products containing coumarin chromophore linked via a triazole ring to an amino acid derivatives were synthesised using Cu-catalized “click” reaction. Their photophysical properties were fully investigated by UV-vis and fluorescence spectreoscopy. In all tested derivatives, excitation at 323 nm shows a wide band with a maximum of fluorescence at 389 nm. In addition to good fluorescent properties, synthesized triazolylcoumarin derivatives also show gelator properties, especially in the DMSO/H_2O system, where fluorescent gels were obtained.

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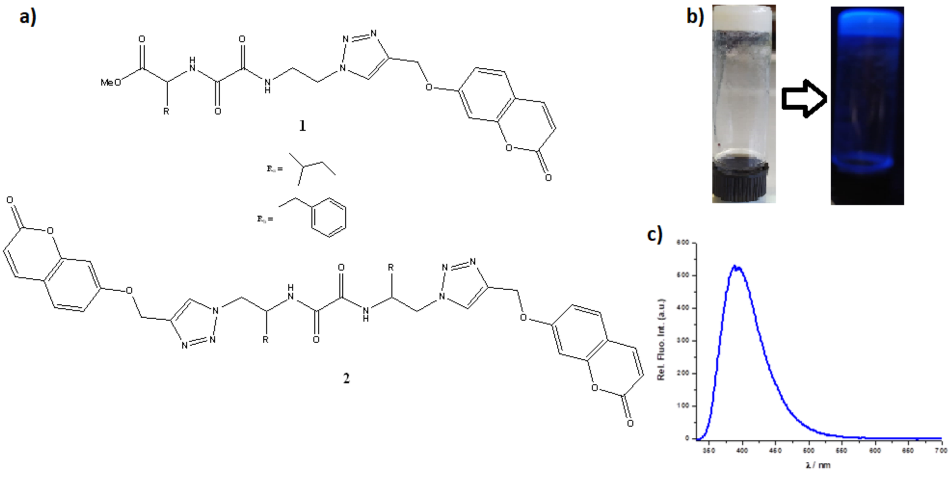

Figure 1. a) general structure of novel bis(triazolylcoumarin)-derived pseudopeptides, b) coumarine gel in DMSO/H_2O, c) fluorescence spectra of triazolylcoumarin

RAZVOJ IONSKO SELEKTIVNIH ELEKTRODA BEZ UNUTARNJEG ELEKTROLITA NA BAZI UGLJIKOVIH NANOCJEVČICA

DEVELOPMENT OF SOLID CONTACT ION-SELECTIVE ELECTRODES BASED ON CARBON NANOTUBES

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Razvoj čvrstih kontakata za ion-selektivne elektrode bez unutarnjeg elektrolita bitan je za razvoj modernih potenciometrijskih senzora sa značajnim poboljšanjem u ponovljivosti i stabilnosti odziva [1]. Radi svojih odličnih svojstava električne vodljivosti, kemijske stabilnosti i mehaničke otpornosti, ugljikovi nanomaterijali pokazali su se prikladni za izradu čvrstih kontakata, a prevladavanje problema njihova dispergiranja ključno je za različite metode depozicije i jednostavnu izradu minijaturiziranih ion-selektivnih elektroda bez unutarnjeg elektrolita. Disperzije višestjenih ugljikovih nanocjevčica (MWCNT) pripremljene su u apsolutnom etanolu uz dodatak polivinil-butirala (PVB) u različitim omjerima ultrazvučnim miješanjem. Stabilnost disperzija karakterizirana je UV-Vis spektroskopijom. Vodljivost tankih filmova pripremljenih rotacijskim oblaganjem izmjerena je metodom mjerenja otpora u četiri točke. Na temelju dobivenih rezultata odabrana je najprikladnija disperzija za izradu ion-selektivnih elektroda za detekciju amonijevih iona (NH_4^+) bez unutarnjeg elektrolita. Ion-selektivne elektrode pripremljene su nakapavanjem različitih volumena odabrane disperzije i otopljene ion-selektivne membrane s nonaktinom kao ionoforom na grafitnu disk elektrodu. Provedenim potenciometrijskim mjerenjima elektrodama su određeni osjetljivost, linearnost i ponovljivost te je utvrđen omjer čvrstog kontakta i ion-selektivne membrane za izradu elektrode koja daje optimalne rezultate.

Ovaj rad financirala je Hrvatska zaklada za znanost projektom UIP-2020-02-9139.

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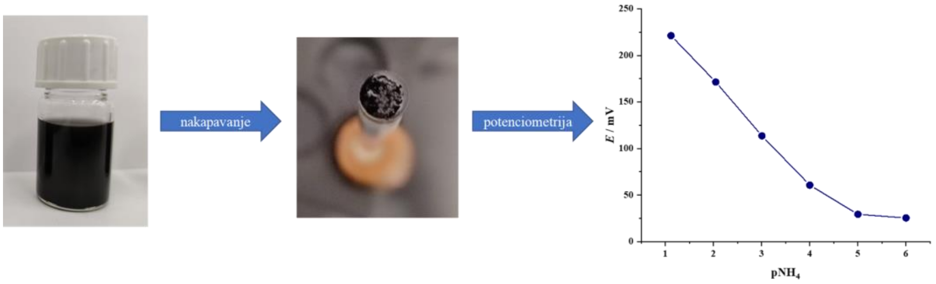

SINTEZA NOVIH 2,6-DISUPSTITUIRANIH IMIDAZO[4,5-*b*]PIRIDINA SUZUKIJEVOM REAKCIJOM

SYNTHESIS OF NOVEL 2,6-DISUBSTITUTED IMIDAZO[4,5-*b*]PYRIDINES BY SUZUKI COUPLING

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Moderna medicinska kemija zahtijeva sintezu velikog broja spojeva koji sadrže farmakoforne heterocikličke strukturne jedinice koje su uklopljene u različite molekulske strukture. Među istaknutim dušikovim heterociklima, veliki značaj imaju derivati imidazo[4,5-*b*]piridina zbog širokog spektra biološke aktivnosti i farmakoloških svojstava [1]. U odnosu na slične analoge, slabo su istraženi zbog niskih iskorištenja reakcija, velikog broja sintetskih koraka, otežane izolacije produkata te brojnih nusprodukata. Iz navedenih razloga znanstvenici su usmjereni na direktnu funkcionalizaciju imidazo[4,5-*b*]piridinske jezgre reakcijama kataliziranim prijelaznim metalima. Upotreba različitih prijelaznih metala u organometalnoj kemiji rezultirala je uspješnom sintezom brojnih arilnih, oligomernih i polimernih aromatskih i heterocikličkih spojeva.

Novi derivati imidazo[4,5-*b*]piridina sintetizirani su Suzuki-Miyaura križnim povezivanjem [2]. Reakcije su optimirane u sustavu otapala s različitim bazama i katalizatorima, a istraživan je i utjecaj elektrofilnog i nukleofilnog supstituenta na bornim kiselinama. U danim reakcijskim uvjetima nije bilo potrebno korištenje zaštitne skupine.

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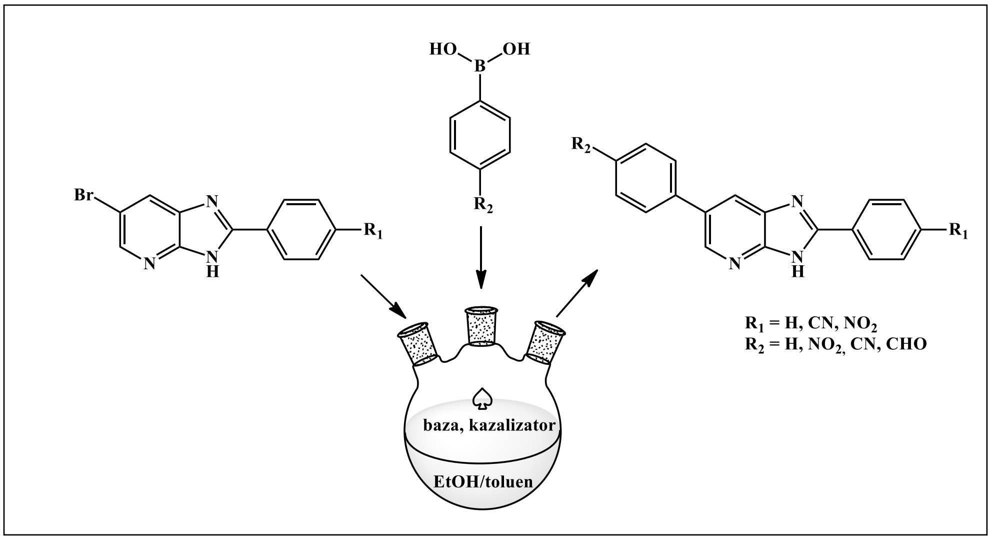

SINTEZA FOTOKEMIJSKI REAKTIVNIH ETINILFENOLNIH BODIPY SPOJEVA S POTENCIJALNOM PRIMJENOM ZA LIJEČENJE KARCINOMA

SYNTHESIS OF PHOTOCHEMICALLY REACTIVE ETHYNYLPHENOL BODIPY COMPOUNDS WITH POTENTIAL APPLICATION FOR CANCER TREATMENT

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Fotodinamička terapija često je korištena metoda za liječenje karcinoma temeljena na uporabi fotosenzibilizatora koji apsorbiraju svjetlo i prenose apsorbiranu energiju na kisik kako bi nastao singletni kisik i druge reaktivne vrste koje su odgovorne za citotoksične učinke [1]. Međutim, stanice karcinoma često su hipoksične, čineći ovaj pristup neučinkovitim. Kao rješenje problema dizajnirali smo niz molekula koje nisu toksične, ali nakon izlaganja svjetlu u fotokemijskoj reakciji stvaraju citotoksične vrste, kinon-metide (QM). QM su važni intermedijeri u kemiji fenola, poznati po svojoj biološkoj aktivnosti zbog reaktivnosti s biološki važnim molekulama kao što su DNK i proteini [2]. Ovaj rad opisuje derivatizaciju fluorescentne BODIPY boje u prekursor QM sa značajno pomaknutom apsorpcijom prema crvenom dijelu elektromagnetskog spektra kao posljedicom produljene konjugacije kromofora s etinilfenolnom skupinom. BODIPY spojevi naročito su zanimljivi zbog njihovih izvanrednih fotofizičkih svojstava koja se lako mogu mijenjati sintetskim modifikacijama [3]. Fotofizička svojstva sintetiziranih spojeva ispitana su UV-Vis te stacionarnom i vremenski razlučenom fluorescencijskom spektroskopijom. Fotokemijska reaktivnost ispitana je osvjetljavanjem u metanolu, dok su HPLC analizom detektirani adukti metanola, potvrđujući očekivane QM kao intermedijare u reakcijama [4]. Dobiveni rezultati posebno su zanimljivi zato jer ispitivani spojevi pokazuje neuobičajenu anti-Kasha fotokemijsku reaktivnost. Posljedično, novosintetizirane molekule imaju potencijal za razvoj fotoaktivirajućih fluorescentnih markera za različite biološki važne molekule kao što su proteini i DNK.

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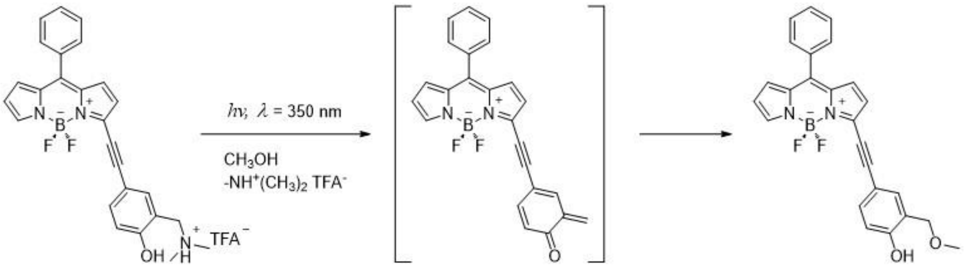

1b

2b

3b

BODIPY QM

Slika 1. Fotometanoliza etinilfenolnog BODIPY spoja preko reaktivnog QM.

APPLICATION OF BIVO₄ FOR THE PHOTOELECTROCATALYTIC DEGRADATION OF AROMATIC COMPOUNDS

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Aromatic organic components in wastewater widely come from a variety of industries such as medicine, paper, food preservatives and antiseptics, and etc. Some of them like Phenol are extremely hazardous and their disposal in the environment may have catastrophic impact on human health. Thus, there is great interest in the kinetics study of aromatic organic components degradation in order to develop new techniques to effectively treat these pollutants for wastewater purification. Recently, the combination of Photocatalysis (PC) and electrochemical oxidation (EC), referred to as photoelectrochemical (PEC) technology, has attracted increasing interest since it resolves the inherent challenges of both PC and EC processes as low efficiency and energy consuming, respectively.
In this work, PEC degradation of three different organic pollutants (Phenol (Ph), Salicylic acid (SA), and 5-Aminosalicylic acid(5-ASA)) was investigated using $BiVO_4$ as a solar light activated material. Moreover, the effect of reduced graphene oxide (rGO) in PEC degradation was studied. $BiVO_4$ showed different efficiency for removal of different organic pollutants (5-ASA>SA>Ph) and the presented layer of rGO incredibly improved the $BiVO_4$ efficiency for all studied organic pollutants degradation. The influence of initial concentration, pH, and applied voltages on PEC degradation was studied.

This work has been fully supported by Croatian Science Foundation under the project IP-2018-01-1982 and European Structural and Investment Funds, Water Purification and Energy Conversion using Novel Composite Materials and Solar Irradiation, KK.01.1.1.04.0001.

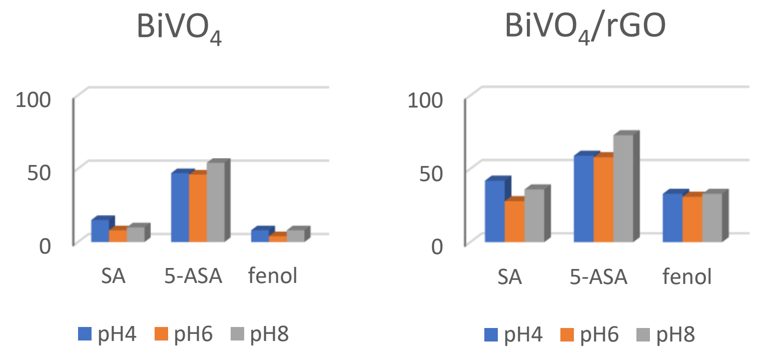

Figure 1. Degradation efficiency of different aromatic compaunds at $BiVO_4$ and $BiVO_4$/rGO electrodes at different pH values and voltage of 1.3 V

SYNTHESIS OF NOVEL ISOXAZOLE OR OXIME TETHERED URACIL–PYRIDINE HYBRIDS

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Since the discovery of platinum coordination compound cisplatin, the spotlights are directed to rational design of metal compounds that showed various biological activity such anticancer, antimicrobial, antiviral and antidiabetic [1]. Pyridine itself is a monodentate ligand having capability to bind metal producing the range of pyridine coordinated complexes of transition metals [2]. Uracil nucleosides with various functional groups at the C-5 position have been investigated for their anticancer activity [3]. Novel C-5 substituted uracil derivatives bearing isoxazole moiety were synthesized by 1,3-dipolar cycloaddition of *N*-1 propargylated uracil derivatives and pyridine-2-aldoxime. On the other hand, oxime linker was introduced by alkylation reaction of C-5 substituted uracil derivatives with corresponding alkylating agent in the presence of base. Linear, aromatic, and cyclopropyl alkynyl moieties were introduced at C-5 position of uracil using a palladium catalyzed crosscoupling Sonogashira reaction. Synthesized pyridine based uracil ligands will be used for the preparation of metal complexes with the aim to evalute their antiproliferative activity.

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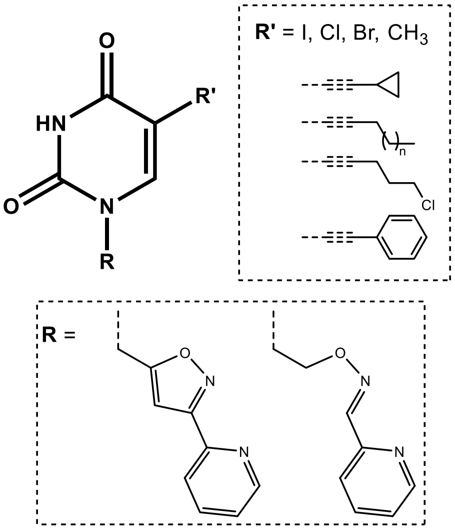

ODREĐIVANJE SORPCIJSKOG AFINITETA KRIZOTINIBA PREMA TiO_2 IMOBILIZIRANIM FOTOKATALIZATORIMA

DETERMINATION OF SORPTION AFFINITY OF CRIZOTINIB FOR TiO_2 IMMOBILIZED PHOTOCATALYSTS

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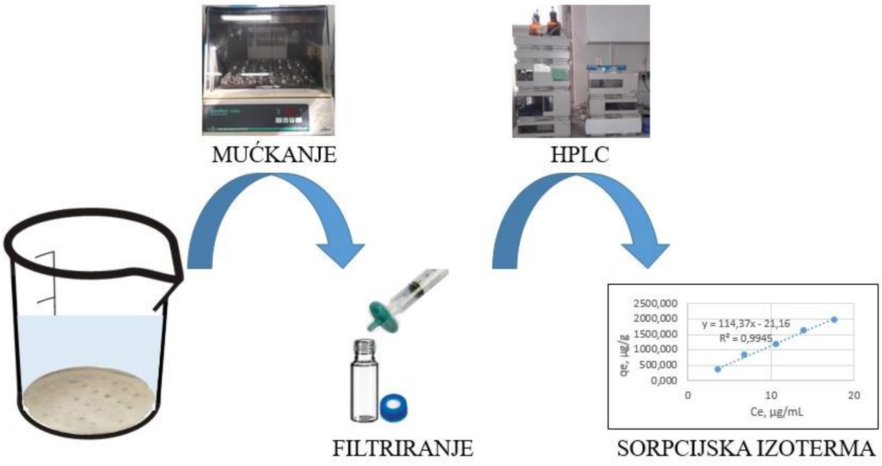
Farmaceutici su biološki aktivne tvari čija je okolišna koncentracija u posljednje vrijeme u porastu zbog neadekvatnog zbrinjavanja i konvencionalnih metoda obrade vode koje ne pokazuju zadovoljavajuću učinkovitost uklanjanja istih. U okolišu se nalaze u vrlo niskim koncentracijama (reda veličine nekoliko ng/L do nekoliko µg/L) zbog čega se ubrajaju u skupinu „novih zagađivala“ za koja ne postoji zakonska regulativa o ispuštanju u okoliš. Činjenica da u ekosustavu nisu prisutni u enormnim količinama poput nekih drugih zagađivala nije zanemariva upravo zato što su takve supstance djelotvorne pri vrlo malim koncentracijama.

Usporedbom niza metoda utvrđeno je da fotokatalitička razgradnja ima najveću učinkovitost uklanjanja farmaceutika iz vodenog okoliša. Budući da je glavni preduvjet za provedbu tog procesa sorpcija farmaceutika, proveden je eksperiment u kojemu se ispitivala sorpcija krizotiniba na mrežice s imobiliziranim TiO_2 te mrežice s imobiliziranim TiO_2 i ugljikovim nanocjevčicama. Pritom se pratio utjecaj kinetike sorpcije, pH vrijednosti, temperature, ionske jakosti i mase imobiliziranog fotokatalizatora TiO_2. Ispitivani parametri opisivali su se linearnom sorpcijskom izotermom, čije vrijednosti regresijskog koeficijenta (R^2) i koeficijenta raspodjele (K_d) ukazuju kako porastom vrijednosti navedenih parametara raste i sorpcija ispitivanog farmaceutika, osim u slučaju utjecaja ionske jakosti gdje se sorpcija smanjuje porastom iste. Promatrajući sorpciju na dvjema različitim mrežicama utvrđen je veći sorpcijski afinitet krizotiniba prema mrežicama s imobiliziranim TiO_2 i ugljikovim nanocjevčicama što je posljedica njihove veće specifične površine, tj. broja aktivnih mjesta na koje se farmaceutik može vezati.



SINTEZA I SPEKTROSKOPSKA KARAKTERIZACIJA *N*-SUPSTITUIRANIH BENZIMIDAZOLA KAO POTENCIJALNIH SENZORA ZA pH U VODENIM OTOPINAMA

SYNTHESIS AND SPECTROSCOPIC CHARACTERIZATION OF *N*-SUBSTITUTED BENZIMIDAZOLES AS POTENTIAL pH SENSORS IN AQUEOUS SOLUTIONS

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Benzimidazolna strukturna jedinica, osim za sintezu heterocikličkih spojeva u organskoj i medicinskoj kemiji, svoju primjenu pronalazi u razvoju optoelektroničkih uređaja i optičkih kemosenzora [1]. Molekularni sustavi temeljeni na benzimidazolima daju pH inducirani spektralni odziv u vidljivom području UV spektra s velikim vrijednostima molarnih apsorpcijskih koeficijenata [2]. Kondenzacijom 2-amino-5cijano-*N*-fenilbenzimidazola s 4-*N*,*N*-dietilamino-2-hidroksibenzaldehidom pripređena je ciljana Schiffova baza, dok su akrilonitrilni derivati benzimidazola pripređeni reakcijom aldolne kondenzacije iz *N*-supstituiranih 2-cijanometilbenzimidazola i 4-*N*,*N*-dietilaminobenzaldehida. Strukture pripređenih spojeva su potvrđene ^{1}H i ^{13}C NMR spektroskopijom. U šest otapala različitih polarnosti provedena je i njihova spektroskopska karakterizacija UV/Vid i fluorimetrijskom spektroskopijom kao i spektroskopske titracije s puferima različitih pH vrijednosti.

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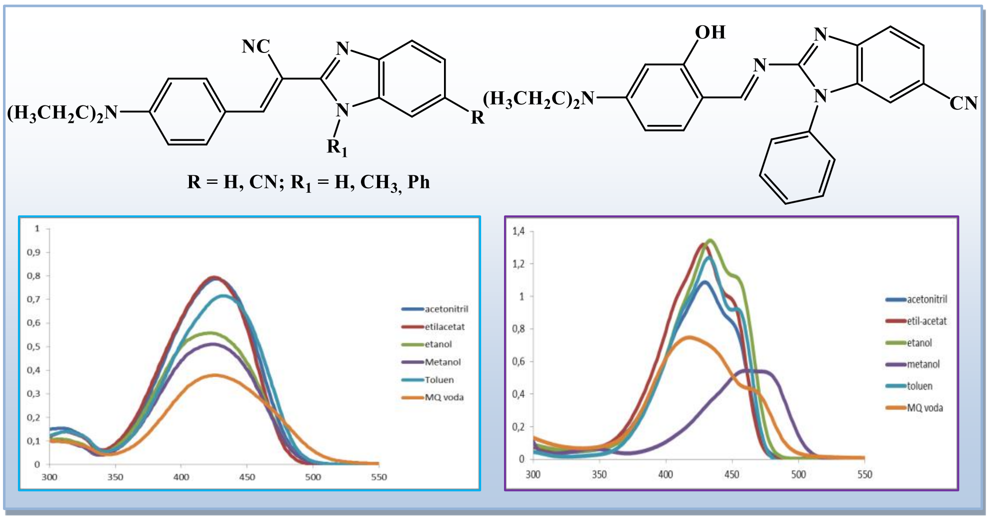

TOTAL PHENOLIC AND FLAVONOID CONTENT OF METHANOLIC EXTRACTS FROM *CORNUS MAS* L. AND *CORNUS OFFICINALIS* SIEBOLD & ZUCC. LEAVES AND FRUITS

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In this study, total phenolic and flavonoid content of methanolic extracts of leaves and fruits from six samples of *Cornus mas* L. and one sample of *Cornus officinalis* Siebold & Zucc., Cornaceae, have been investigated. Samples were air-dried, milled and extracted with methanol in an ultrasonic bath. After filtration, organic solvent was removed using a rotary evaporator and the remaining samples were suspended in distilled water, frozen and afterward subjected to lyophilization. Total phenolic content and flavonoid content were evaluated spectrophotometrically in aqueous solutions of obtained lyophilizates using the Folin-Ciocalteu method [1] and the $AlCl_3$ method [2], respectively. Pearson's correlation coefficient (r) was used to establish the relationship between leaf and fruit total phenolic and flavonoid content ($\alpha = 0.05$). Data analysis was performed in Microsoft Excel (2013).
Total phenolic content of *C. mas* leaf and fruit extracts ranged from 195.32 ± 1.59 to 311.21 ± 1.22 mg gallic acid equivalent (GAE)/g dry extract (DE) and from 9.69 ± 0.58 to 16.63 ± 0.26 mg GAE/g DE, respectively. Total phenolic contents of *C. officinalis* leaf and fruit extracts were 286.70 ± 1.90 mg GAE/g DE and 13.56 ± 0.15 mg GAE/g DE, respectively. Flavonoid content in leaf extracts of *C. mas* ranged from 1.20 ± 0.06 to 4.51 ± 0.22 mg quercetin equivalent (QE)/g DE, while flavonoid content in fruit extracts ranged from 0.18 ± 0.04 to 1.07 ± 0.02 mg QE/ g DE. Flavonoid contents of *C. officinalis* leaf and fruit extracts were 3.66 ± 0.03 and 0.42 ± 0.03 mg QE/g DE, respectively. Very strong negative correlation was observed between total phenolic contents in leaves and fruits of *C. mas* (r = -0.94, P = 0.005), while between leaf and fruit flavonoid contents of *C. mas* very strong positive correlation was observed (r = 0.90, P = 0.016).

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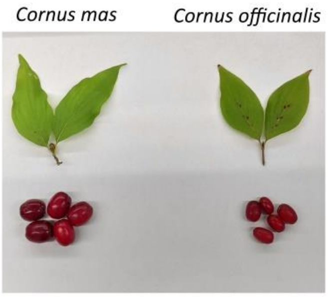

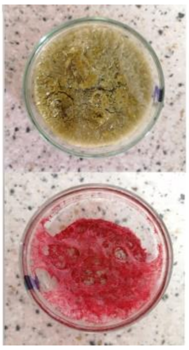

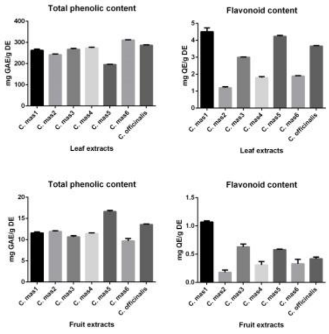

ANALYSIS OF ANTIOXIDANT ACTIVITY AND CONTENT OF POLYPHENOLS AND FLAVONOIDS IN AQUEOUS, ETANOLIC AND HYDROETHANOL EXTRACTS OF HIBISCUS

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Hibiscus is a widely used plant, which has been proven to have numerous positive effects on human health, such as lowering blood pressure, maintaining optimal blood cholesterol levels, liver protection, prevention of oxidative stress, etc. In this study, the content of polyphenols, flavonoids and antioxidant capacity of aqueous, ethanolic and hydroethanolic (50/50 *v*/*v*) hibiscus extracts, prepared by maceration and ultrasonic extraction, was analysed. Analysis of antioxidant activity was performed *in vitro*, using FRAP and DPPH methods. The results showed that the mixture of water and ethanol had a significantly higher effect of extraction of bioactive components from hibiscus than the remaining two solvents. The lowest content of polyphenols and flavonoids, and thus the weakest antioxidant activity was recorded in extracts prepared in absolute ethanol. By comparing the efficiency of the techniques used, maceration proved to be slightly more efficient in the case of aqueous and hydroethanol extracts, while higher polyphenol content and higher antioxidant activity were observed in ethanolic extracts prepared by ultrasonic extraction.

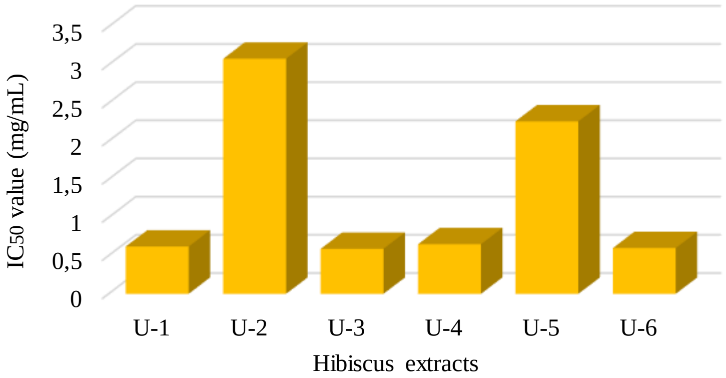

Figure 1. Efficacy of extracts in inhibition of DPPH radicals

SYNTHESIS, CHARACTERIZATION, ANTIOXIDANT AND ANTIMICROBIAL ACTIVITY OF SILVER(I) COMPLEXES WITH SCHIFF BASES DERIVED FROM NINHYDRIN AND SELECTED NON-POLAR AMINO ACIDS

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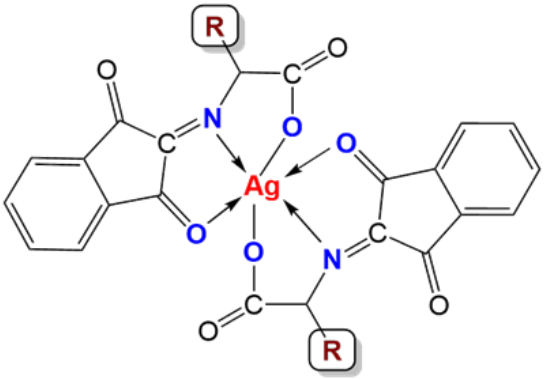
The chemistry of imines and its complexes is an important area of research due to the wide application of these components in various industries. A large number of these complexes have shown significant antimicrobial, antitumor and antioxidant activity *in vitro* and *in vivo*. In this research, two silver(I) complexes with imine derived from ninhydrin and selected hydrophobic amino acids (alanine and valine) were synthesized and characterized. Structural characterization was performed using spectroscopic methods. *In vitro* antioxidant activity was tested using FRAP and DPPH methods, while antibacterial activity was tested by diffusion technique on reference bacterial strains. Based on spectral data, it is assumed that the ligand coordinates the metal ion as a tridentate ONO donor ligand, with the coordination of the oxygen atom of the carbonyl group of ninhydrin, the nitrogen atom of the newly formed imine group and the oxygen atom of the carboxylic group of the amino acid. The metal complex containing the amino acid valine showed significant antioxidant activity under *in vitro* conditions, in contrast to the complex with alanine, which showed significantly poorer efficacy in inhibiting free radicals. The antibacterial activity of the synthesized complexes is extremely weak, with slightly better inhibition of gram-positive compared to gram-negative bacteria.



QSAR ANALYSIS OF QUINAZOLINONE SCHIFF BASES' ANTIFUNGAL ACTIVITY

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Plant diseases and pests are responsible for many losses in agricultural production worldwide, proving that their control is crucial for crop farming today. The use of plant protection products has effectively limited these losses. However, some of the active ingredients of these products are toxic for humans and fauna or cause groundwater and soil pollution. Therefore, there is an urgent need to find new, environmentally and toxicologically acceptable active ingredients for plant protection [1]. In this study, we have tested the antifungal activity of 19 quinazolinone based Schiff bases [2] against *Sclerotinia sclerotiorum* (Lib.) de Bary, a necrotrophic fungal pathogen causing disease in a variety of plants. Most of the tested compounds showed very good fungal growth inhibition at 0.8 μmol/mL, with 8 compounds inhibiting mycelial growth by more than 80 %.

QSAR techniques provide an insight into the relationship between structure and biological activity of compounds, presenting an alternative path for the design and development of new active ingredients for plant protection. To elucidate important structural and physicochemical characteristics of tested quinazolinone Schiff bases related to their increased antifungal activity, a QSAR analysis was performed.

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ODREĐIVANJE I USPOREDBA KONCENTRACIJE VITAMINA C U ODABRANOM VOĆU I VOĆNIM PRERAĐEVINAMA

DETERMINATION AND COMPARISON OF VITAMIN C CONCENTRATION IN SELECTED FRUIT AND FRUIT PRODUCTS

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Vitamin C je vrlo snažan antioksidans prisutan u voću i povrću. U ovom radu, jodometrijska titracija je upotrijebljena za ispitivanje efekta skladištenja i vrste obrade na koncentraciju askorbinske kiseline u voću i voćnim prerađevinama. Metoda je jednostavna i praktična za brzo određivanje vitamina C. Dobivene vrijednosti uspoređene su s USDA bazom podataka. Korišten je svježi, smrznuti i obrađeni voćni materijal. Između ostalog, od voća je ispitana aronija, brusnica, borovnica, drenjina, goji, razne sorte jabuke, mango, tayberry i crna višnja. Suhi biljni materijal ispitan je u dva oblika, kao suhi materijal i u obliku čajne infuzije. Uspoređivanjem eksperimentalnih vrijednosti s vrijednostima USDA baze podataka uočene su velike razlike u sadržaju vitamina C u voću i voćnim prerađevinama. U odnosu na voćne prerađevine, svježe voće sadrži najveću koncentraciju vitamina C te njegovom preradbom dolazi do gubitka samog vitamina zbog njegovih kemijskih svojstava. Suhi biljni materijal je najsiromašniji vitaminom C, dok se dobar udio vitamina nalazi u svježem i smrznutom voću.

MEHANOKEMIJSKA SINTEZA NOVIH DERIVATA BENZOTIAZOLA S POTENCIJALNIM ANTITUMORSKIM DJELOVANJEM

MECHANOCHEMICAL SYNTHESIS OF NOVEL BENZOTHIAZOLE DERIVATIVES WITH ANTITUMORAL POTENTIAL

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Nedostatci postojeće antitumorske terapije doveli su do razvoja novih kemoterapeutika u čemu je prepoznata važnost benzotiazola. Derivati benzotiazola pokazuju značajno antitumorsko, antimikrobno i antioksidativno djelovanje [1]. Uz benzotiazol, značajnu ulogu u medicinskoj kemiji imaju i 1,2,3-triazoli, bioizosteri amida koji zbog rigidne strukture i stabilnosti u različitim fiziološkim uvjetima, predstavljaju idealne poveznice u sintezi biološki aktivnih spojeva. Uz to, moguće ih je lako pripraviti klik reakcijom-Huisgenovom 1,3-dipolarnom cikloadicijom [2]. Mehanokemija se danas smatra izvrsnom metodom zelene kemije, kojom se uvelike smanjuje ili čak potpuno izbjegava upotreba otapala i omogućuje neke sinteze koje je nemoguće provesti u otopini [3]. U ovom radu opisana je sinteza novih 1,2,3-triazolnih derivata benzotiazola. Mikrovalovima potpomognutom reakcijom 2-hidroksibenzaldehida i propargil-bromida uz K_2CO_3 kao bazu, pripravljen je 2-propargilbenzaldehid koji je ciklizacijom s *ortho*-aminotiofenolom uz $Na_2S_2O_5$ preveden u propargilirani derivat benzotiazola koji je potom mehanokemijskim klik reakcijama s odgovarajućim aromatskim azidima i uz $Cu(OAc)_2$ kao katalizator preveden u ciljane 1,2,3-triazolne derivate benzotiazola. Strukture svih novopripravljenih spojeva potvrđene su ^{1}H- i ^{13}C-NMR spektroskopijom, a moguće biološke mete i farmakološko djelovanje sintetiziranih spojeva predviđeni su *in silico* analizom (PASS).

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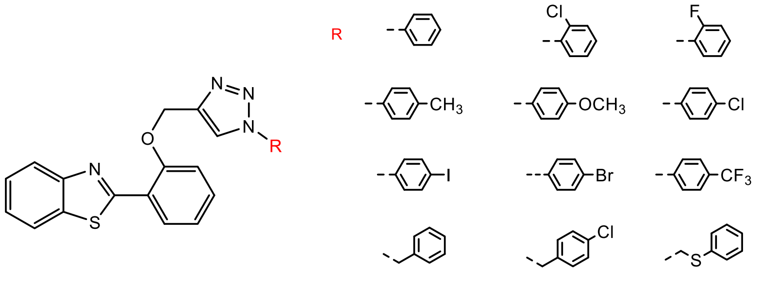

HYDROPHOBIC CAVITIES AND DIAMANTANES

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Diamantane derivatives are excellent guests for cucurbit[7]uril (CB7), forming complexes with stability constants reaching above petamolar values in water [1]. However, their inclusion within hydrophobic cavities was rarely explored in non-aqueous solutions. We have therefore studied the solvent (water, formamide, ethylene glycol) and temperature effects on the complexation of diamantane alcohols (Figure 1) with CB7 and β- and γ-cyclodextrin by means of isothermal microcalorimetry and NMR spectroscopy. Complex stability constants were much higher in water due to less unfavorable $\Delta_r S°$. The reactions involving apical alcohols were the most exergonic. A significant temperature dependence of $\Delta_r H°$ and $\Delta_r S°$ resulted in an almost perfect enthalpy-entropy compensation for most of the studied host-guest systems. The thermodynamic complexation parameters were in agreement with the classical rationale of the hydrophobic effect at lower temperatures and non-classical explanation at higher ones [2,3]. The results of ^{1}H NMR titrations were in accord with the thermodynamic studies and have revealed an interesting difference in complex formation kinetics between cucurbit[7]uril and β-cyclodextrin hosts.

This research was fully supported by the Croatian Science Foundation (projects MacroSol, IP-2019-04-9560 and DiamMat, UIP-2017-05-9653) and European Regional Development Fund (project CIuK, KK.01.1.1.02.0016).

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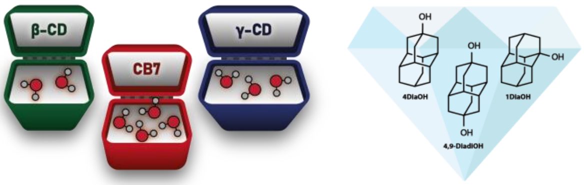

Figure 1. Schematic representation of the investigated hosts and guests

HPLC METODA ZA ISPITIVANJE KINETIKE ENZIMSKE METILACIJE 6-MERKAPTOPURINA

HPLC METHOD FOR 6-MERCAPTOPURINE ENZYMATIC METHYLATION KINETICS ASSESSMENT

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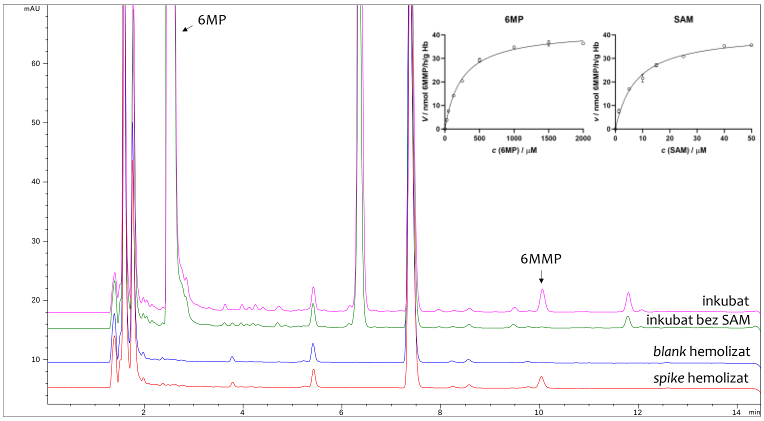
Tiopurin S-metiltransferaza (TPMT, E.C. 2.1.1.67) citosolni je enzim koji metilira sulfhidrilne skupine kako aromatskih, tako i heterocikličkih spojeva. Primjeri lijekova koje TPMT inaktivira su azatioprin, 6-merkaptopurin (6MP) i 6-tiogvanin koji se koriste kao imunosupresivi za liječenje leukemija, ali i upalnih bolesti crijeva. Cilj ovog istraživanja bio je razviti HPLC metodu za određivanje 6-metilmerkaptopurina (6MMP) kao metabolita 6-merkaptopurina u biološkom uzorku hemolizata kako bi se odredila enzimska kinetika, ali i postavili temelji za ispitivanje eventualnih interakcija biljnih dodataka prehrani sa lijekovima koji se metaboliziraju preko TPMT, a koje bi mogle dovesti do promjena u njihovim terapijskim koncentracijama. Krv korištena za istraživanje izvađena je zdravom dobrovoljcu na antikoagulant EDTA, eritrociti su odvojeni od krvne plazme, lizirani sa suviškom hladne ultračiste vode te skladišteni na -20 °C. Razvijena je HPLC metoda u trajanju od 22 min. Kao nepokretna faza korištena je Cortecs Phenyl kolona (150 × 4,6 mm, veličina čestica 2,7 um). Provedena je gradijentna eluacija s dvije sastavnice mobilne faze (0,1 % mravlje kiseline u vodi, odnosno metanolu). Reakcijske otopine sadržavale su hemolizat, 6MP, S-adenozilmetionin (SAM, kofaktor u reakcijama metilacije), ditiotreitol i $HClO_4$ pomoću koje je reakcija zaustavljana nakon inkubacije. Uzorci su inkubirani 90 minuta na 37 °C. Nakon utvrđivanja selektivnosti kao ključnog validacijskog parametra, ispitani su linearnost (r = 0,9994), točnost (analitički prinosi između 97,07 % i 98,69 %) te preciznost (RSD = 0,81 %, n = 6; analiza varijance pokazala je statistički neznačajnu razliku prinosa za α = 0,05 kroz tri dana). Nadalje, ispitana je kinetika metilacije 6MP putem TPMT pri čemu kao produkt nastaje 6MMP. V_{max} za 6MP iznosio je 41,94 nmol 6MMP/h/g Hb, a K_m 239,5 µM. V_{max} za SAM bio je 40,93 nmol 6MMP/h/g Hb, a K_m 7,6 µM. Dobiveni rezultati poslužit će daljnjem ispitivanju mogućnosti interakcija biljnih dodataka prehrani i terapije azatioprinom ili 6MP.

Ovaj rad je sufinancirala Hrvatska zaklada za znanost projektom [UIP-2017-05-3949].



ADSORPTION STUDY OF POLYPHENOLS FROM APPLES AND *β*-GLUCAN FROM BARLEY

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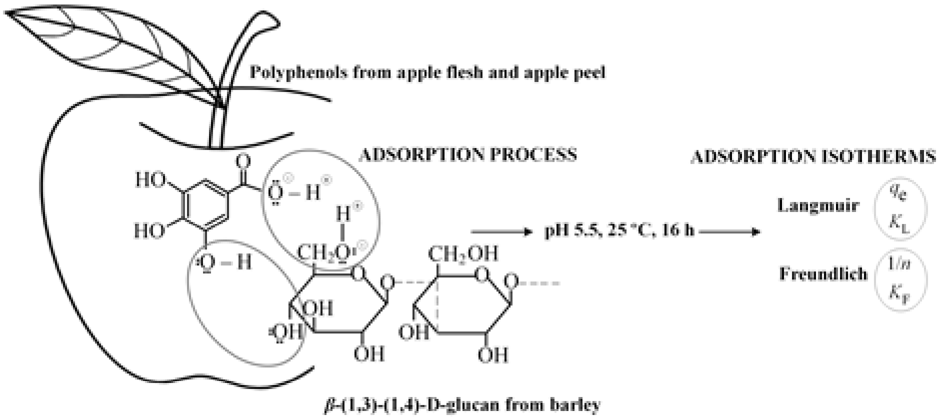
Polyphenols are secondary plant metabolites that can be found in different sources like apples. Since apples are available around whole year, they are a good source of polyphenols in the human diet. Polyphenols showed numerous bioactivities. They can interact with other food constituents like dietary fiber. One of the dietary fiber which can be found in different cerals is *β*-glucan. It was shown that *β*-glucan can interact with polyphenols and these interaction can influence the potentially beneficial bioactivities of polyphenols. Polyphenols and *β*-glucan interactions can be studyed through the adsorption process, where polyphenol is an adsorbate and *β*-glucan is an adsorbent. In equilibrium, different adsorption models like Freundlich and Langmuir can be applied in order to obtain the parameters of these models. The aim of these work was to study the adsorption between polyphenols from apple peel and flesh and *β*-glucan from barley. Polyphenols were extracted by ultrasound assisted extraction from apple peel and flesh with 80 % methanol. The adsorption was conducted between polyphenols from apple peel and flesh at 25 °C and pH 5.5. During the adsorption, polyphenols adsorbed onto *β*-glucan. The un-adsorbed polyphenols were determined by reversed-phase high performance liquid chromatography (RP-HPLC). After the adsorption process, adsorption models like Freundlich and Langmuir were applied. The results showed that polyphenols from apple peel showed slighty higher adsorption capacity then polyphenols from apple flesh. Also, adsorption proces between polyphenols and *β*-glucan were favoured.



SYNTHESIS AND BIOLOGICAL ACTIVITY OF NOVEL QUINOLINE AND COUMARIN HYBRIDS BRIDGED BY 1,2,3-TRIAZOLE RING

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The field of drug discovery is constantly advancing in its quest to find new biologically active compounds. Recently, an emerging trend in medical chemistry is molecular hybridization, which is often used as a key strategy in drug design [1]. It includes combining known biologically active moieties as scaffolds to build a new molecule that could retain properties, or potentially have new activity. Coumarin and quinoline are widely used in pharmaceuticals, as well as in new molecular hybrids. Triazole ring are also important linkage, building block and pharmachophore in molecular hybrids with quinolines and coumarins [2,3].

In this work, we present synthesis of novel hybrids of quinoline and coumarin bridged with 1,2,3-triazole ring. The methylazido coumarins were prepared by cyclization of corresponding phenols and ethyl 4-chloroacetoacetate, followed by azidation. The hybrids bridged with 1,2,3-triazole (1-35) were prepared using Cu-catalyzed Huisgen-1,3-dipolar cycloaddition reaction. Antitumor activity of novel molecular hybrids was examined against human tumor cell lines: glioblastoma, pancreatic adenocarcinoma, colorectal carcinoma, lung carcinoma, acute lymphoblastic leukemia, acute myeloid leukemia, chronic myeloid leukemia and non-Hodgkin lymphoma.

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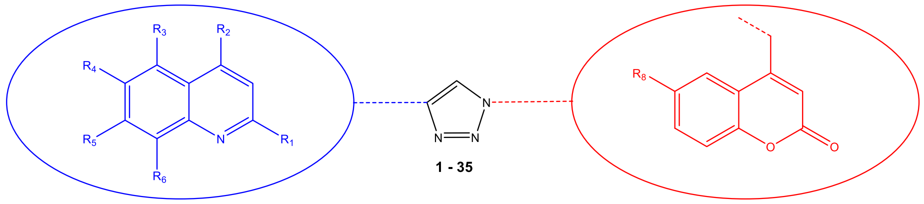

1 - 35

R_1 = CF_3
R_2 = OH_2C ---
R_3 = Cl
R_4 = OCH_3
R_5 = OCH_3
R_6 = CF_3, OH_2C ---

R_7 = OH, OCH_3, F, OCH_2CH_3, $C(CH_3)_3$, Cl, Br

DEVELOPMENT AND USAGE SMART PLANT EXTRACT BASED GELS IN pH MEASUREMENT

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In chemical analysis, most of the chemicals used can be replaced by the less harmful chemicals or natural reagents obtained from the extract of some plants. Natural reagents isolated from plants are just as good as synthetic ones, but also environmentally friendly. The aim of this study was to determine the possibility of using turmeric and red cabbage extract in the preparation and application of "green" gels in controlling the pH of different samples, with special emphasis on fresh food. Gels with plant extracts have been successfully used to determine the pH value and to assess the quality and freshness of short shelf life foods. Such gels can also be used as environmentally friendly "smart" packaging, especially those products that are sensitive to oxidation or whose change freshness is accompanied by a change in pH.

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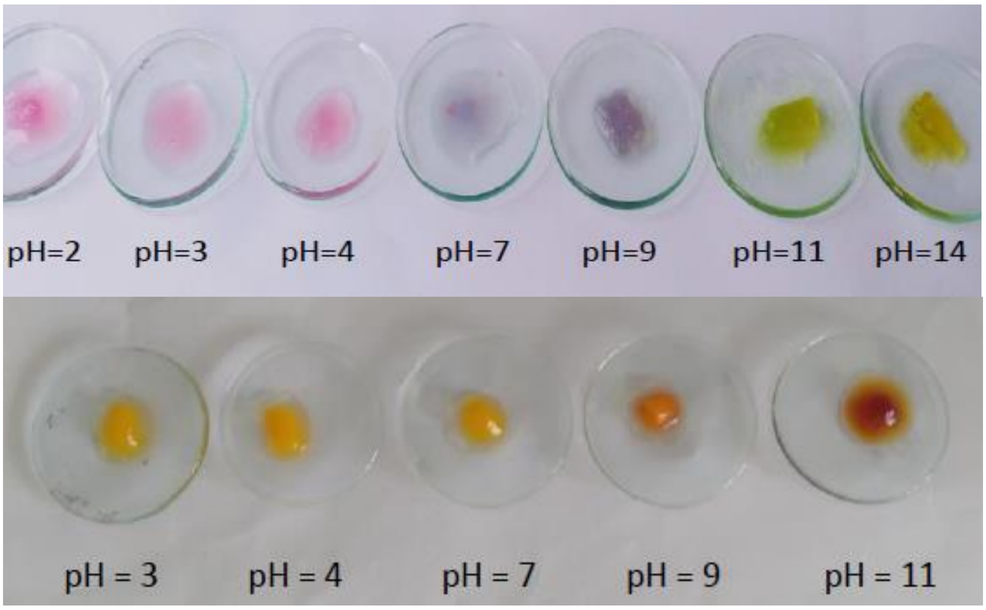

NEW UNCHARGED 2-THIENOSTILBENES OXIMES AS REACTIVATORS OF CHOLINESTERASES

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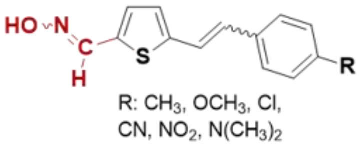
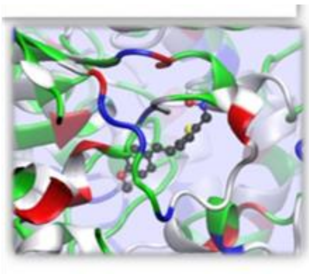
Oximes, the symptomatic drugs currently were used as inhibitors of acetylcholinesterase (AChE) and butyrylcholinesterase (BuChE) in the treatment of neurological disorders such as Alzheimer's and Parkinson's disease. The inhibition of acetylcholinesterase (AChE) and butyrylcholinesterase (BChE) by organophosphates (OPs) as nerve agents and pesticides compromises normal cholinergic nerve signal transduction in the peripheral and central nervous systems (CNS) leading to cholinergic crisis. The treatment comprises an antimuscarinic drug and an oxime reactivator of the inhibited enzyme. Oximes in use have quaternary nitrogens, and therefore poorly cross the brain–blood barrier. In this work, we synthesized novel uncharged thienostilbene oximes by sequence of three reactions in very high yields. Eight *trans*,*anti*- and *trans*,*syn*-isomers of oximes were tested as reactivators of nerve-agent-inhibited AChE and BChE. Four derivatives reactivated cyclosarin-inhibited BChE up to 70% in two hours of reactivation, and docking studies confirmed their productive interactions with the active site of cyclosarin-inhibited BChE.

Based on the moderate binding affinity of both AChE and BChE for all selected oximes, these compounds present a new class of oximes with the potential for further development of CNS-active therapeutics in OP poisoning.

This research was partially funded by the Croatian Science Foundation (project IP-2018-01-7683).





KALIJ SMANJUJE CITOTOKSIČNOST TALIJA
POTASSIUM PREVENTS THALLIUM CYTOTOXICITY

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Talij je jedan od najtoksičnijih kemijskih elemenata [1]. Ion talija (Tl^+) ima atomski radijus približno jednak radijusu iona kalija (K^+) te se pretpostavlja da talij ulazi u stanicu pomoću Na^+/K^+ ATP-aze [2]. U ovom je istraživanju ispitan protektivni učinak kalija na toksičnost talija tako što je pet staničnih linija (HepG2, HaCaT, pk15, SH-SY5Y i V79) tretirano s talijevim (I) acetatom (koncentracijski raspon: 15,6 do 125 µg/ml, 24 h) ili s talijevim (I) acetatom (koncentracijski raspon: 15,6 do 125 µg/ml, 24 h) zajedno s kalijevim (I) acetatatom (500 µg/ml, 24 h) te je praćena vijabilnost stanica MTT testom. Dobiveni rezultati citotoksičnosti statistički su uspoređeni višestrukim *t*-testovima (korekcija po Benjamini-Hochbergu) te modelom mješovitih efekata analize varijance (ANOVA). Talij je bio citotoksičan za sve stanične linije, a njegova citotoksičnost bila je ovisna o koncentraciji. U odnosu na tretman s talijem i kalijem zajedno, tretman samo s talijem bio je toksičniji za sve stanične linije. Nakon zajedničkog tretmana s talijem i kalijem zabilježena je statistički značajno niža citotoksičnost u odnosu na tretman samo s talijem kod svih staničnih linija osim kod V79 stanične linije. Rezultati istraživanja upućuju da kalij može spriječiti citotoksični učinak talija, što potvrđuje pretpostavku da Tl^+ koristi membranske proteine K^+ za ulazak u stanicu.

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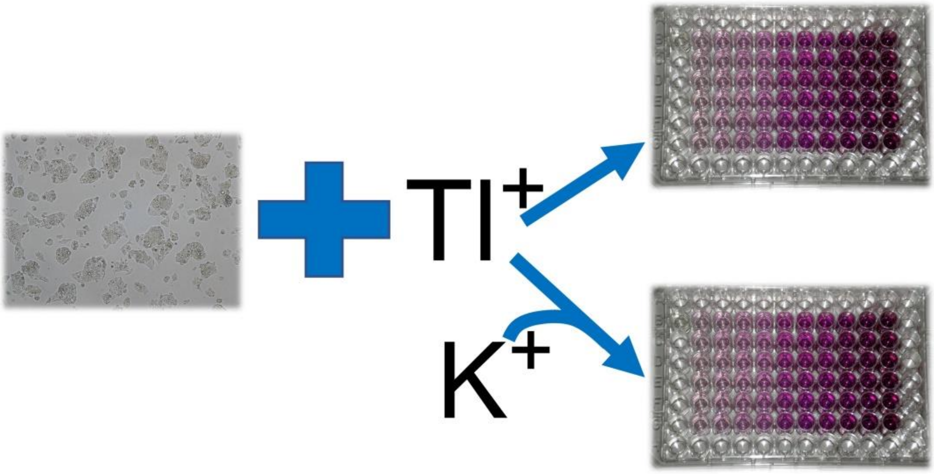

HSS-GC-FID ANALYSIS OF RESIDUAL SOLVENTS IN FOOD SUPPLEMENTS USED IN THE TREATMENT OF INFLAMMATORY BOWEL DISEASE

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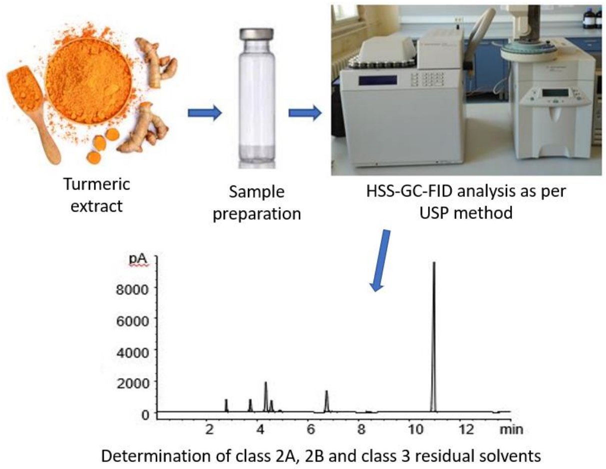
There is an ever-increasing number of food supplements on the global market - products containing concentrated sources of nutrients intended for supplementing the intake of those nutrients from a normal diet. However, due to loose legal regulations in many countries, these products do not undergo the same quality control other medicinal products do. Some of these food supplements may pose public health risks due to the presence of residual solvents in them not being properly reported. Residual solvents are volatile organic chemical substances that may have been used or produced in the preparation of a medicinal product. According to the Globally Harmonized System (GHS) Hazard Classification they are classified from Class 1 to Class 3 based on their potential dangers for human health.

In order to determine the presence of residual solvents in food supplements used for the treatment of inflammatory bowel disease method <467> defined by the United States Pharmacopeia was used. Multiple samples from the Croatian market were prepared and analysed using headspace gas chromatography/flame ionization detection (HS-GC-FID) and then compared with chromatograms of analysed standards containing Class 2A, Class 2B, and Class 3 residual solvents, as defined by the GHS Classification.

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



NOVEL 1,2,3- TRIAZOLE DERIVATIVES OF BENZOKSAZOLE: SYNTHESIS, STRUCTURAL CHARACTERIZATION AND BIOLOGICAL ACTIVITY

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Cancer is one of the main causes of death worldwide along with cardiovascular diseases. Due to its high mortality rate and frequency, medicinal chemists are rapidly developing new, potent antitumor agents. Benzoxazoles are structural isosters of natural nucleotides and represent an important class of heterocyclic compounds exhibiting exceptional pharmacological activities such as anticancer, anti-inflammatory and antiviral. In addition, some of them have found application as fluorescent whitening agents and functional materials [1-2].

Utilizing conventional and green synthetic methods, novel derivatives of benzoxazole containing 1,2,3-triazole ring as a linker were prepared. Propargylated 2-aminobenzoxazole and 2-thiobenzoxazole were prepared in a two-step reaction including cyclization reaction of 2-aminophenol using di(imidazole-1-yl)methanimine or carbon disulfide, and subsequent N-alkylation reaction with propargyl bromide as an alkylating reagent. 2-amino- and 2-thiobenzoxazole derivatives with 1,2,3-triazole moiety were synthesized by Cu(I) catalyzed click reaction of 2-propargylated benzoxazole derivatives with corresponding azides. The most potent activity against acute lymphoblastic leukemia (DND-41, IC_{50}= 1 μM) showed benzoxazole derivative consisting of coumarin ring linked *via* 1,2,3-triazole.

This work was founded by Pliva Hrvatska d.o.o. and Croatian Science Foundation (HRZZ-IP-2018-01-4682).

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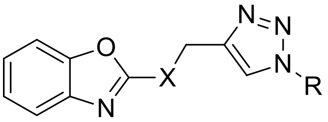

R: alkyl, aryl, coumarin
X: NH, S

SYNTHESIS OF NOVEL NITRO AND CYANO SUBSTITUTED BENZOTHIAZOLES USING GREEN CHEMISTRY METHODS

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The development of efficient and environmentally friendly chemical processes for the synthesis of biologically active molecules constitutes a major challenge for chemists in organic synthesis [1]. Benzofused heteroaromatic compounds, in particular benzothiazoles, are common structural scaffold of biologically active compounds and natural products [2-4]. Herein, we have synthesized novel 6-substituted 2-arylbenzothiazole derivatives with varied aromatic and aliphatic unit at phenyl ring. Key benzothiazole intermediates were obtained by condensation of bis(2-amino-5-nitrophenyl) disulphide or bis(2-amino-5-cyanophenyl) disulphide with corresponding benzaldehydes using environmentally friendly solvent glycerol. Finally, targeted 2,6-disubstituted benzothiazoles were synthesized by *O*-alkylation using green synthetic methods, such as ultrasound assisted synthesis and mechanochemical synthesis. The ultrasound assisted method was more effective in terms of reducing the reaction time and enhancing the product yield compared to that of the classical solution-based and mechanochemical synthesis.

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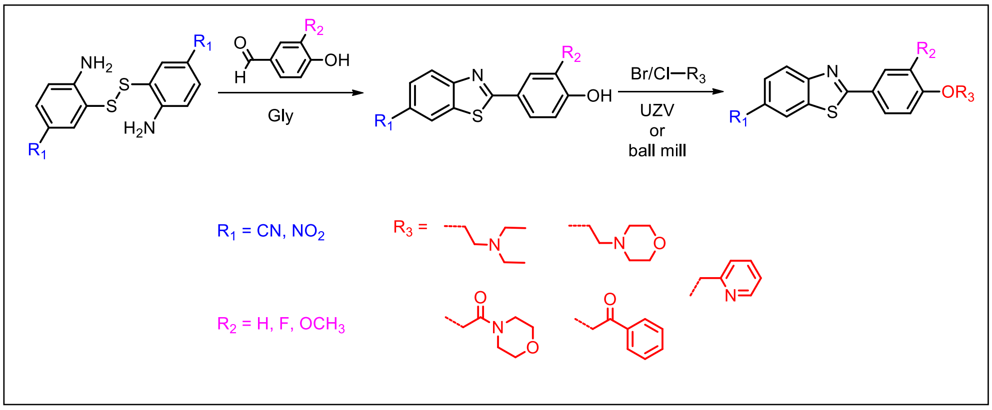

FOTOELEKTROKEMIJSKO DOBIVANJE VODIKA POTPOMOGNUTO ASKORBINSKOM KISELINOM

PHOTOELECTROCATALYTIC HYDROGEN PRODUCTION SUPPORTED BY ASCORBIC ACID

Gabrijela Radić, Dajana Balaić, Gabriela Antonije Oreški, Hrvoje Kušić, Marijana Kraljić Roković

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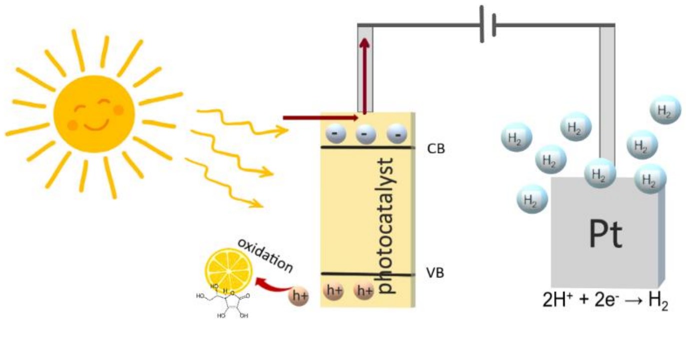
U posljednje vrijeme raste interes za istraživanjem i korištenjem fotoelektrokemijskih procesa, spoja elektrokemijske oksidacije i fotokatalitičkih procesa. Kombinacijom napona i svjetlosne pobude elektroni s fotoanode vanjskim strujnim krugom putuju do katode gdje se odvijaju reakcije redukcije. Fotoanodni materijali su poluvodiči kod kojih svjetlosnom pobudom dolazi do stvaranja brzo rekombinirajućih parova elektron-šupljina. Kako bi se spriječila rekombinacija koriste se različiti *hvatači šupljina* poput metanola ili askorbinske kiseline. TiO_2 je već vrlo dobro istražen fotokatalitički materijal, popularan zbog kemijske stabilnosti, niske cijene i netoksičnosti, ali energetski procijep od 3,2 eV dopušta apsorpciju svjetlosti samo iz ultraljubičastog (UV) dijela spektra. Kako bi se prevladao taj nedostatak istražuju se i drugi fotokatalitički materijali poput SnS_2, čiji energetski procijep od oko 2,2 eV omogućuje apsorpciju fotona iz vidljivog dijela spektra. Cilj ovog rada bila je usporedba elektrokemijskih odziva ispitivanih fotokatalitičkih materijala pri različitim koncentracijama askorbinske kiseline i odabir najpogodnijih uvjeta za proizvodnju vodika. Reakcija redukcije vodika odvijala se na platinskoj katodi u troelektrodnom sustavu uz TiO_2 i SnS_2 kao fotoanode. Elektrokemijska karakterizacija fotokatalitičkih materijala provedena je metodama linearne polarizacije (LSV), elektrokemijske impedancijske spektroskopije (EIS), kronoamperometrije (CA) i mjerenjem potencijala otvorenog kruga (OCP). Količina dobivenog vodika praćena je tijekom 2h a najistaknutiji rezultati dobiveni su korištenjem 10 mM otopine askorbinske kiseline.

Rad je u potpunosti financirala Hrvatska zaklada za znanost u okviru znanstvenog istraživačkog projekta IP-2018-01-1982 voditelja Hrvoja Kušića.



SYNTHESIS, STRUCTURAL CHARACTERIZATION AND ANTIBACTERIAL EVALUATIONS OF NOVEL 1,2,3-TRIAZOLE DERIVATIVES OF BENZOXAZOLES

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In the field of drug discovery and development, biologically important heterocycles, such us benzoxazole, known as „privileged structures“ play an important role as promising future drug candidates beacuse of their versatile binding properties for different biotargets [1]. Benzoxazole derivatives have shown a wide range of biological activities such as antimicrobial, antiviral, anticancer and antioxidant. The benzoxazole core is part of several drugs such as flunoxaprofen, benoxaprofen, tafaimids, caboxamycinare. 1,2,3-triazole is a well-known scaffold that has a widespread occurrence in different compounds due their structural features that enable it to mimic different functional groups as a bioisostere [2,3]. Deep eutectic solvents (DES) represents a novel class of green solvents in organic chemistry with high application in many areas. Thus, in this work novel benzoxazole derivatives bearing 1,2,3-triazole as a linker were synthesized by Cu(I) catalyzed click reaction of *O*-propargylated benzoxazoles with corresponding azides in DESs (ChCl/glycerol; L-carnitine/urea; D-sorbitol/urea/NH_4Cl), Structures of novel compounds were confirmed by ^{1}H- and ^{13}C-NMR spectroscopy. Antibacterial evaluations of novel benzoxazole derivatives were performed on bacterial strains: *Escherichia coli, Enterococcus Faecalis, Klebsiella Pneumonia, Pseudomonas aeruginosa* and *Staphylococcus aureus*.

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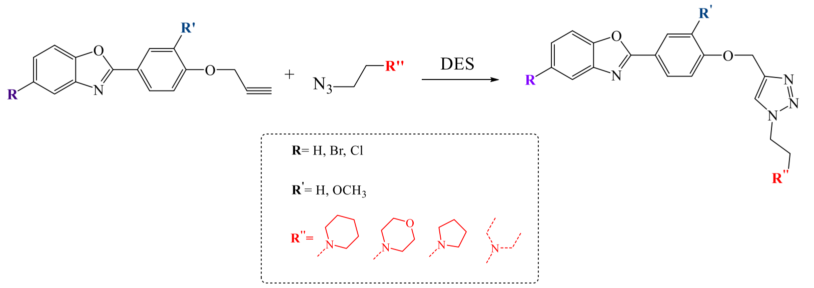

MOSS AND LICHEN AS BIOINDICATORS OF AIR POLLUTION WITH Cd, Cr, Cu AND Pb IN URBAN AREA OF SARAJEVO

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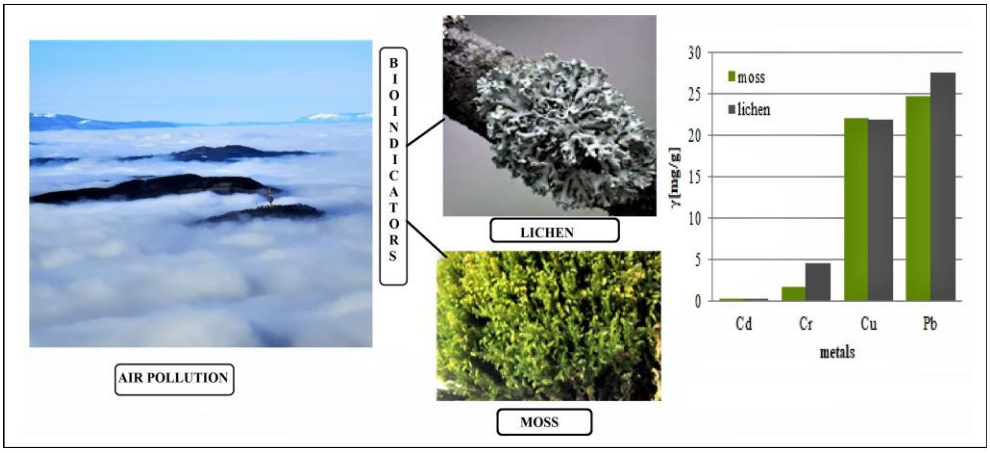
Sarajevo, Bosnia and Herzegovina, is one of the world's cities which has problems with air pollution especially in winter periods. In this study heavy metals (Cd, Cr, Cu, and Pb) in lichen (*Hypogymnia physodes*) and moss (*Hypnum cupressiforme*) were used for the monitoring of air pollution in urban area of Sarajevo. The metal analysis was performed by flame atomic absorption spectrometry (FAAS). The content of determined metals in moss was: Cd (0,12 mg/g), Cr (1,75 mg/g), Cu (22,13 mg/g) and Pb (24,68 mg/g) and in lichen Cd (0,17 mg/g), Cr (4,51 mg/g), Cu (21,87 mg/g) and Pb (27,68).

The content of all analyzed heavy metals, except Cu, was higher in lichens. The concentration of Cu and Pb in moss, and the concentration of Cr in lichens, indicate higher air pollution and the concentration of Cu, Pb indicate medium air pollution compared to other European cities. In general, the higer content of metals in lichens and mosses is due to the high level of particles rich in heavy metals in the air.



DFT I FT-IR STUDIJA GEOPOLIMERNE STRUKTURE

DFT AND FT-IR STUDY OF GEOPOLYMER STRUCTURE

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U tumačenju spektrometrijskih analiza uvelike mogu pomoći i kvantnokemijski izračuni područja očekivanih različitih vibracijskih modova za pojedini sustav. Za tu svrhu primijenjena je teorija funkcionala gustoće (engl. *Density Functional Theory*, *DFT*) s funkcionalom B3LYP i skupom baznih funkcija 6-311++G(d,p) unutar programskog paketa *Gaussian 09*. Proračun IR spektra proveden je nakon optimizacije modela fragmenata geopolimerne strukture, u vodenom mediju, koja se prema Davidovitsu naziva poli(sialat-disilokso) [1]. Spomenuta struktura je amorfna struktura aluminosilikata. Dobiveni rezultati pokazuju podudarnost izračunatog IR spektra s eksperimentalno dobivenim podacima sintetiziranog poli(sialat-disilokso) iz metakaolina pomoću natrijevog silikata. Parametri sinteze postavljeni su na molarni omjer 1 Na_2O : 1 Al_2O_3 : 4 SiO_2.

Financijska sredstva za izradu rada osigurana su u okviru projekta “Alternativna veziva za beton (ABC): Razumijevanje mikrostrukture za predviđanje trajnosti“, oznaka projekta: UIP-05-2017-4767, koji je financiran od strane Hrvatske zaklade za znanost.

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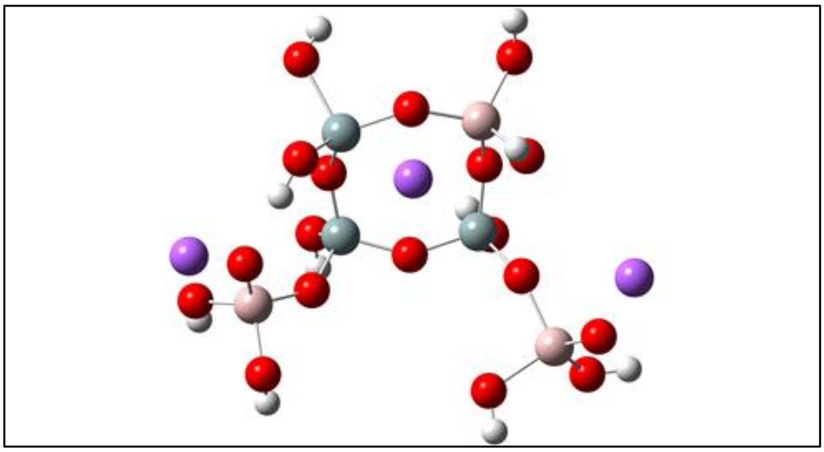

ISTRAŽIVANJE UPOTREBE ODABRANIH OTAPALA U PRIPREMI KISELO-BAZNIH INDIKATORA OD ODABRANOG JAGODIČASTOG VOĆA

STUDY OF THE APPLICATION OF SELECTED SOLVENTS IN THE PREPARATION OF ALTERNATIVE ACID-BASE INDICATORS FROM SELECTED FRESH SOFT FRUIT

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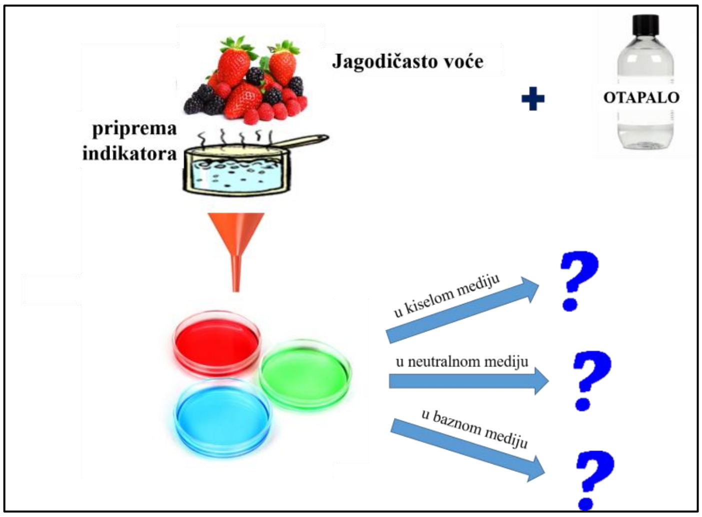
Kiselo-bazni indikatori dio su nastave kemije koji se lako može popratiti samostalnim praktičnim radom učenika primjenom zanimljivih pokusa. Ukoliko su pokusi povezani sa svakodnevnim životom, istraživanja su pokazala da se gradivo lakše uči i duže pamti. Naša prethodna ispitivanja su pokazala kako se biljni materijal može uspješno koristiti u nastavi kemije. U ovom radu su prethodna istraživanja proširena te uključuju primjenu odabranih otapala u pripremi kiselo-baznih indikatora na bazi jagodičastog voća. U tu je svrhu od otapala korištena voda, aceton, etanol i metanol, a od voća su ispitani svježi i suhi plodovi jagode, šumske jagode, kupine, maline, crne maline te crnog, crvenog i bijelog duda. Provedeno je preliminarno ispitivanje sa svakim otapalom, kako bi od odabranih otapala odabrali najbolja dva. Nakon toga, ispitana je uspješnost primjene odabranih razrjeđenja otapala s vodom, pa su tako ispitana 25, 50 i 75 %-tno razrjeđenje kako bi se utvrdilo optimalno. Iako su sva ispitana otapala pokazala potencijal primjene u pripremi alternativnih indikatora, etanol i metanol u 50 % i 75 %-tnom razrjeđenju su se pokazala vizualno najboljima. Od ispitanog voća, najboljim su se pokazali indikatori pripremljeni od kupina i crnih malina. Međutim, primjenom odabranih otapala može se brzo i jeftino pripremiti kiselo-bazni indikator sa svim ispitanim voćem, koji ima mogućnost primjene u modernoj učionici kemije.



SINTEZA, ANTIBAKTERIJSKA I ANTITUMORSKA ISPITIVANJA NOVIH 2-ARIL SUPSTITUIRANIH DERIVATA BENZIMIDAZOLA

SYNTHESIS ANTIBACTERIAL AND ANTITUMOR EVALUATIONS OF NOVEL 2-ARYL SUBSTITUTED BENZIMIDAZOLE DERIVATIVES

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Benzimidazol je važan farmakofor i smatra se povlaštenom strukturom u medicinskoj kemiji [1]. Derivati benzimidazola pokazuju brojne farmakološke aktivnosti poput antituberkulostatske, antimalarijske, antimikrobne, antivirusne, antitumorske i protuupalne [2]. 1,2,3-triazolni prsten kao dušikov heterociklički gradivni blok ima značajnu ulogu u dizajnu i sintezi lijekova budući da ne predstavlja samo pasivnu poveznicu. nego je i farmakofor jer se lako povezuje s biološkim metama putem vodikovih veza i dipolnih interakcija [3]. U ovom radu je prikazana sinteza i biološka ispitivanja novih derivata 2-arilbenzimidazola premoštenih 1,2,3-triazolnim prstenom. Ultrazvukom potpomognutom reakcijom ciklizacije O-alkiliranih benzaldehida s različito supstituiranim 1,2-diaminobenzenom sintetizirani su 2-arilbenzimidazoli. 1,2,3-triazolni derivati benzimidazola pripravljeni su Huisgenovom 1,3-dipolarnom cikloadicijom s odgovarajućim azidima. Antitumorska ispitivanja derivata benzimidazola su pokazala da derivat 2-arilbenzimidazola s N,N-dietilnim supstituentom ima najizraženiju antitumorsku aktivnost protiv tumorskih staničnih linija porijeklom iz čovjeka: adenokarcinom gušterače (Capan-1, IC_{50} = 2,2 μM), karcinom pluća (NCI-H46, IC_{50} = 2,2 μM), akutna limfoblastična leukemija (DND-41, IC_{50} = 2,6 μM), kronična mijeloična leukemija (K-562, IC_{50} = 2,0 μM) i non-Hodgkinov limfom (Z-138, IC_{50} = 2,0 μM). Ispitano je i antibakterijsko djelovanje novopripravljenih spojeva na bakterijskim stanicama Escherichia coli, Enterococcus Faecalis, Klebsiella Pneumonia, Pseudomonas aeruginosa, Staphylococcus aureus. Najizraženiju inhibiciju (MIC> 88-98 %) je pokazao 6-klor-benzimidazolni derivat s morfolinskim supstituentom na bakteriju Enterococcus Faecalis pri svim ispitanim koncentracijama (256-0,25 mg/L).

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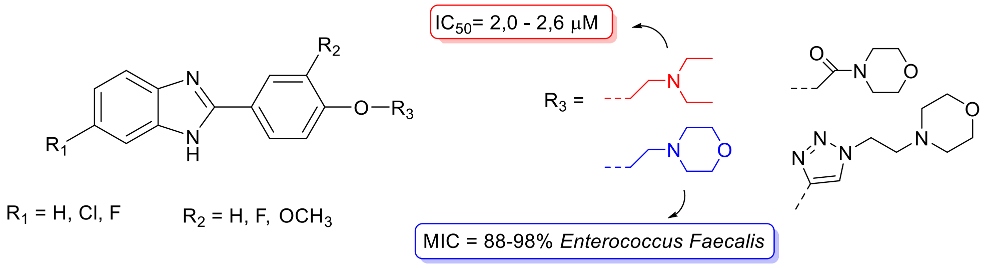

AMINE AND ETHER BIS-1,2,3-TRIAZOLE LIGANDS AND THEIR TRANSITION METAL COMPLEXES

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The stereochemistry of flexible tridentate ligands influences many important properties like stability and reactivity in a chemical or biological environment [1,2]. Metal coordination with bis-1,2,3-triazole ligands is an unexplored area of research in comparison to the structurally related dipicolylamine derivatives [3]. In this work, bis-1,2,3-triazole derivatives with unsubstituted *N*- and *O*-central donor atoms were prepared using *click* chemistry by the reaction of aromatic azides with dipropargylamine and dipropargyl ether, respectively. Coordination of transition metals was studied in solution by NMR and UV-Vis spectrometry, along with characterisation in solid-state by single-crystal X-ray crystallography. Our research has shown that these types of ligands prefer formation of ML_2 metal complexes. Study of the stereochemical preferences is currently underway as these ligands are able to form *cis*-, *trans-fac* or *mer*-isomers.

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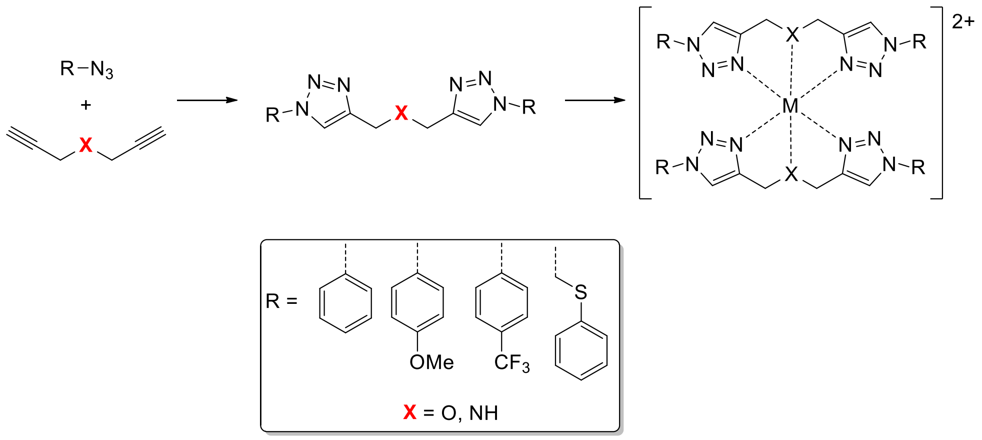

THE CONTENT OF HEAVY METALS IN DIFFERENT SPICES AND HERBS PURCHASED FROM LOCAL MARKET OF SARAJEVO

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The intake of heavy metals for the consumption of edible herbs can have long-term consequences for human health. That was the reason for setting the limits for heavy metals from foodstuffs and medicinal products by health authorities (WHO/US EPA). Heavy metal monitoring in food, like spices and herbs provides basic information on safety aspects in regulatory processes as well as nutritional values. This study aimed to measurements of the concentration of common heavy metals like cadmium, lead, copper, iron and zinc, in selected spices and herbs (*Matricaria chamomilla*, *Mentha piperita*, *Rosa canina*, *Salvia officinalis*, *Thymus vulgaris*, *Origanum vulgare*, *Petroselinum crispum*, *Salvia rosmarinus* and *Ocimum basilicum*) often consumed in the Bosnia and Herzegovina. Microwave-assisted digestion was applied for the dissolution of the samples and heavy metals concentration was determined using AAS. All element concentrations were measured on a dry weight basis. The daily intake for investigated spices and herbs was calculated too. The results for the determination of heavy metals showed varied concentrations in the spices and herb samples. The concentration (mg kg^{-1}) ranges were measured as follows: 0.11-0.12 for Cd, 0.34-7.10 for Pb, 3.49-11.97 for Cu, 665.70-220.80 for Fe and 15.42-55.23 for Zn. In conclusion, metal exposure through consumption of spices and investigated herbs does not seem to be of health concern to the adult population of Sarajevo.

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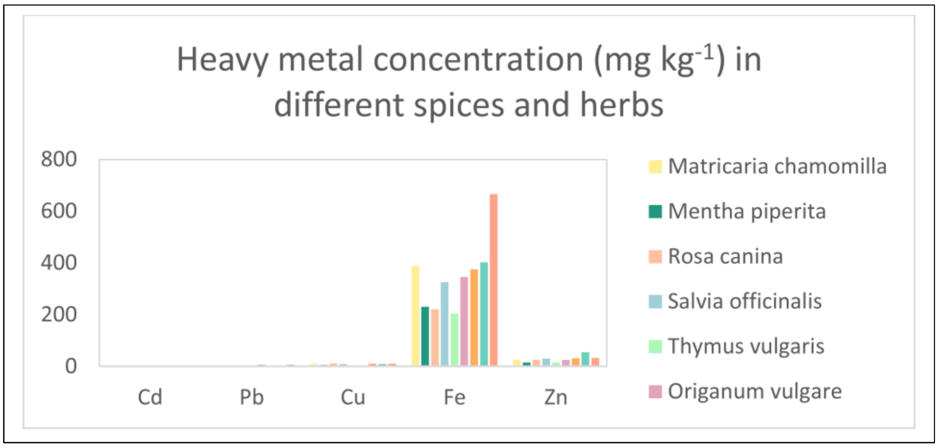

PRIPRAVA I KARAKTERIZACIJA POLIMERNOG SPOJA CINKOVOG BROMIDA S 1-METILIMIDAZOLOM

PREPARATION AND CHARACTERIZATION OF A POLYMERIC COMPOUND OF ZINC BROMIDE WITH 1-METHYLIMIDAZOLE

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Koordinacijski spojevi imidazola i njegovih derivata s ionima cinka imaju važnu ulogu u medicinskoj kemiji jer pokazuju značajnu biološku aktivnost kao antibakterijska, analgetička, antikancerogena i terapeutska sredstva. Kao bočni ogranak aminokiseline histidin, imidazol koordinira metalne ione mnogih metaloenzima. Biološka uloga kompleksa koji sadrže imidazolni prsten može se povezati s dva atoma dušika koji imaju različita svojstva: deprotonirani atom dušika može koordinirati atom prijelaznog metala, dok protonirani atom dušika sudjeluje u vodikovoj vezi [1-3]. U sklopu našeg proučavanja koordinacijskih spojeva cinka s derivatima imidazola sintetiziran je refluksom u metanolu polimerni koordinacijski spoj cinkovog bromida s 1-metilimidazolom (1-Meimi), $[ZnBr_2(1\text{-Meimi})]_n$ (**1**). Kristalna struktura je određena rendgenskom difrakcijom na jediničnom kristalu. Atom cinka koordiniran je s tri atoma broma i jednim atomom dušika iz 1-metilimidazola. Jedan bromov atom je premošćujući te nastaje 1D polimer. Rentgenskom strukturnom analizom na polikristalnom uzorku nađeno je da nakon otapanja u etanolu kristalizira monomer spoja u kojem je cink koordiniran s dva atoma broma i dva atoma dušika iz 1-metilimidazola, $[ZnBr_2(1\text{-Meimi})_2]$ (**2**), već poznate structure [4]. Oba spoja kristaliziraju u monoklinskom sustavu, **1** u prostornoj grupi *Cc* a **2** u $P2_1/n$.

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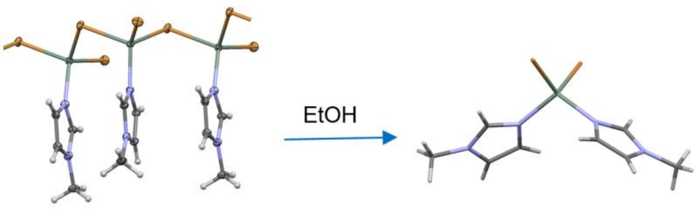

$[ZnBr_2(1\text{-Meimi})]_n$

$[ZnBr_2(1\text{-Meimi})_2]$

CHARACTERIZATION OF ROMAN MORTARS FROM TWO ARCHEOLOGICAL SITES: TRAJAN'S BRIDGE AND ROMAN CASTRUM DIANA, KARATAS

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Historical mortars are composite materials made of binders and aggregates that were used in the construction of water tanks, Roman baths, mosaics, aqueducts, frescoes, etc. Due to the specific composition, Roman mortars are characterized by excellent strength and durability, as evidenced by numerous Roman buildings that have been preserved to this day. During the restoration and conservation of cultural heritage buildings, it is necessary to use compatible materials with appropriate physical, chemical, mechanical and aesthetic properties, which could be used for conservation of the original historical materials without compromising the durability and specificity of the analyzed building [1-3]. The aim of our work was the examination of the composition, properties, and production technology of Roman mortars from two archeological sites in Serbia (Trajan's Bridge and Karatas, Diana). Trajan's Bridge was constructed between 103 and 105 AD by the order of Roman emperor Trajan. Diana was an auxiliary fort located near Danube cataracts 8 km upstream from present-day Kladovo [4,5]. The used methods were: optical microscopy, drilling resistance measurements, XRD, TG, TG-MS, water absorption, mercury porosimetry, SEM-EDS, chemical separation of binders and aggregates, and FTIR analysis. The gained results revealed interesting facts about how advanced the Romans were in the production technology of mortars, which has been stable from the 2nd century until now.

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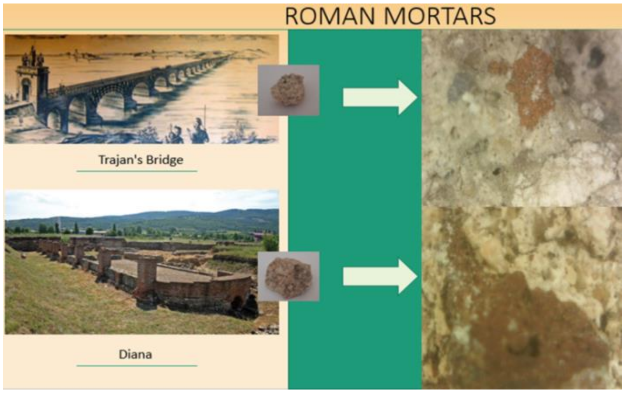

SINTEZA I ANTIOKSIDATIVNA AKTIVNOST DERIVATA BENZIMIDAZOLA I IMIDAZO[4,5-*b*]PIRIDINA

SYNTHESIS AND ANTIOXIDATIVE ACTIVITY OF BENZIMIDAZOLE AND IMIDAZO[4,5-*b*]PYRIDINES

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Spojevi koji u svojoj strukturi sadrže jezgru imidazo[4,5-*b*]piridina i benzimidazola smatraju se strukturnim analozima purina, te su predmet velikog interesa u istraživanju organskih i medicinskih kemičara zbog širokog spektra različitih bioloških aktivnosti i pozitivnih farmakoloških svojstava koje pokazuju. Sastavni su dio strukture brojnih lijekova poput antihelmintika, antivirotika, antiparazitika, antimikotika, analgetika i antitumorskih lijekova. Aktivnost ovih spojeva značajno ovisi o funkcionalnim skupinama i supstituentima koji su vezani na heterocikličkoj jezgri. Sinteza hidroksi supstituiranih amida *N*-benzimidazola i iminokumarinskih derivata imidazo[4,5-*b*]piridina provedena je klasičnim reakcijama organske sinteze i sintezom potpomognutom mikrovalovima. Ciljani derivati benzimidazola sintetizirani su uklanjanjem zaštitnih metoksi skupina spojeva u reakciji s BBr_3 pri niskoj temperaturi uz uspješno uklanjanje samo jedne zaštitne skupine.

Iminokumarinski derivati imidazo[4,5-*b*]piridina sintetizirani su reakcijom kondenzacije 5-supstituiranih salicilbenzaldehida s 2-cijanometilimidazo[4,5-*b*]piridinima.[2] Strukture novosintetiziranih spojeva potvrđene su ^{1}H, ^{13}C i 2D NMR spektroskopijom. Antioksidativna aktivnost sintetiziranih spojeva ispitana je metodama DPPH i FRAP.

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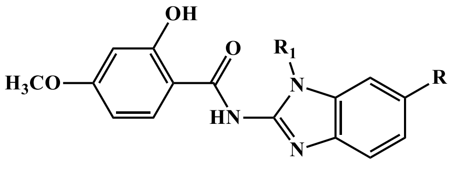
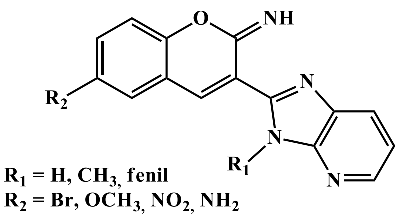


R = H, CN, R_1 = H, CH_3,$CH_2CH(CH_3)_2$



R_1 = H, CH_3, fenil
R_2 = Br, OCH_3, NO_2, NH_2

ANTIFUNGAL AND INHIBITORY ACTIVITY OF SCHIFF BASES – AN *IN SILICO* STUDY

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In silico methods are used for a rational approach in screening, optimization, and the design of newly synthesized compounds as potential agents in plant protection. The tested compounds are quinazolinone-based Schiff bases synthesized by the means of the green chemistry procedures, such as microwave-assisted, ultrasound-assisted, and mechano-chemical synthesis [1]. The aim of the study is to evaluate the inhibitory activity of mentioned compounds on enzymes that have a crucial role in the growth and spreading of plant pathogenic fungi, such as *Macrophomina phaseolina*, *Sclerotinia sclerotiorum*, *Fusarium oxysporum* f. sp. *Lycopersici* and *F. culmorum* [2]. *In silico* study was performed by the use of molecular docking on enzymes responsible for the fungal growth: demethylase ((CYP51), pdb ID: 5eah), chitinase (pdb ID: 4txe), transferase (N-myristoyltransferase, pdb ID: 2p6g), as well as enzymes responsible for the degradation of the plant cell-wall: endoglucanase I (pdb ID: 4ovw), proteinase K (pdb ID: 2pwb), pectinase (endopolygalacturonase, pdb ID: 1czf). The binding affinity and interactions with the active sites of enzymes was determined the mode of action of the most active compounds against fungi.

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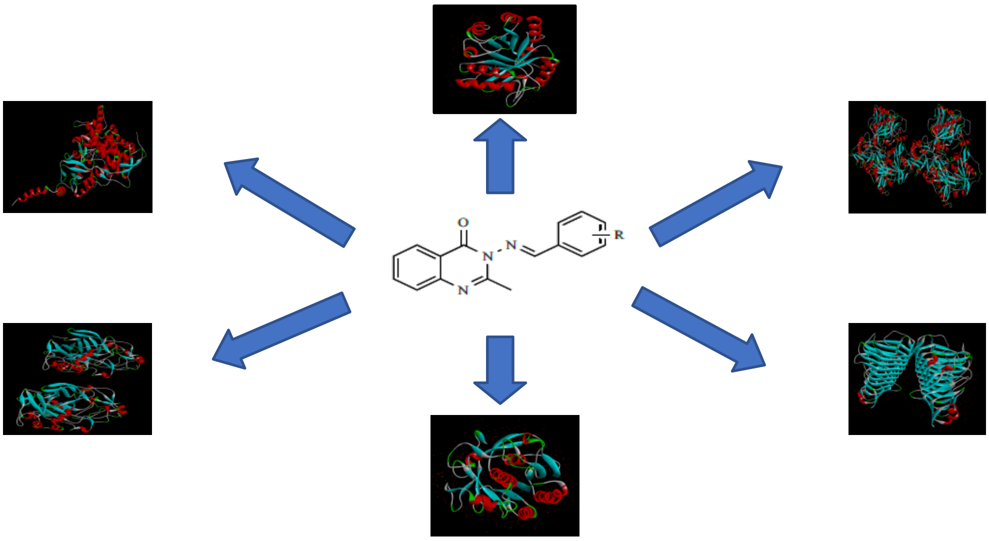

INFLUENCE OF LEUCINE CHIRALITY ON CONFORMATIONAL PREFERENCES AND BILOGIOCAL ACTIVITY OF FERROCENE DIPEPTIDE DERIVED FROM FERROCENE-1,1'-DIAMINE AND LEUCINE

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Ferrocene peptides are often used as peptidomimetics because it is known that the conjugation of ferrocene core (Fcd, Fca, Fcda) and different amino acids leads to the formation of intramolecular hydrogen bonds that induce the formation of several elements of secondary structure [1,2]. Addition of L- or D-leucine to antimicrobial peptide brevinin-1OS can affect improvement of antibacterial and anticancer activity to be ten times stronger than parent peptide [3].

To examine the influence of ferrocene synthone itself, the chirality of leucine (D- / L-) and the influence of protecting groups on the chiral arrangement and biological activity of prepared peptides, we decided to prepare homochiral and heterochiral ferrocene dipeptides Ac-L(D)-Leu-NH-Fn-NH-L(D)-Leu-Boc (1-4).

The prepared dipeptides were examined by spectroscopic analysis (IR, NMR, and CD spectroscopy), followed by biological evaluation which included determination of antimicrobial activity (disk-diffusion method and nutrient broth dilution method with determination of MIC values) and determination of antioxidant activity (DPPH and FRAP methods).

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

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Figure 1. Ferrocene dipeptide **I**

CAFFEINE – ELECTROCHEMICAL BEHAVIOUR ON THE SURFACE OF SWNT ELECTRODE

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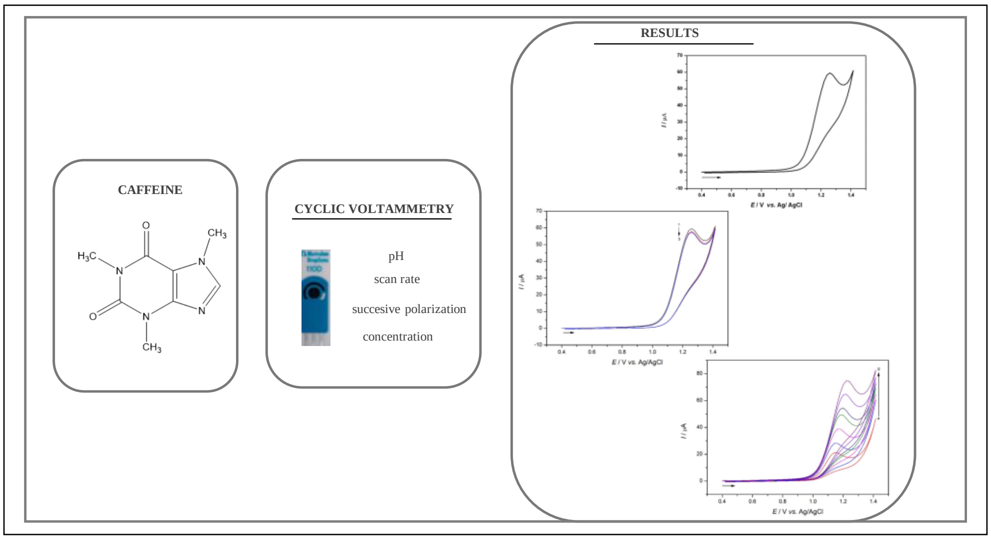
Caffeine is a white crystalline powder, bitter in taste and odourless. It is an alkaloid from the xanthine group. The main sources of caffeine are coffee, energy drinks, dietary supplements. Caffeine is electroactive species and therefore, the aim of this work was to investigate the electrochemical behaviour of caffeine on the surface of single-walled carbon nanotubes (SWCNT) electrode as a working electrode. The investigated cyclic voltammetry conditions were as follow the effect of pH values of inert buffer, the concentration of caffeine, polarization rate, and multiple consecutive polarization. The electrochemical behaviour of caffeine on the surface of the SWCNT electrode had shown irreversible electrode reaction and diffusion-controlled process. The effect of concentration had shown linear increase in anode current response with increasing analyte concentration (R^2 = 0.9999; *LOD* = 4.4 mg L^{-1}; *LOQ* = 14.8 mg L^{-1}). The cyclic voltammetry had shown as an applicable method to the characterization of caffeine.



HYDROPHOBIC EFFECT – COMPARISON OF AROMATIC AND ALIPHATIC ALCOHOLS

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Derivatives of adamantane and similar rigid aliphatic structures are known as suitable guests for cyclodextrins and cucurbit[7]uril in water [1,2]. While hosting of aliphatic compounds was frequently explored, the inclusion of aromatic functionalities within cyclodextrins and cucurbiturils is far less investigated. Furthermore, the binding thermodynamics of aromatic and structurally similar aliphatic guests was never systematically compared. Therefore, the complexation of 2-naphthol and its hydrogenated analogues (Figure 1) with cucurbit[7]uril and cyclodextrins in water was explored by means of isothermal titration microcalorimetry, fluorimetry, spectrophotometry, and NMR spectroscopy. Significant influence of guest aromaticity on complexation thermodynamics was observed – the reactions involving aliphatic guest were remarkably more entropically favourable, leading to higher complex stability constants compared to the ones with aromatic analogues. Reaction enthalpy and entropy of the majority of examined systems varied substantially with temperature, resulting in nearly complete enthalpy-entropy compensation (weak temperature dependence of $\Delta_r G°$). The complexation thermodynamics at lower temperatures was in agreement with the classical interpretation of the hydrophobic effect, while the binding at higher temperatures could be rationalized by the non-classical rationale [1,2].

This research was fully supported by the Croatian Science Foundation (project MacroSol, IP-2019-04-9560) and European Regional Development Fund (project CIuK, KK.01.1.1.02.0016).

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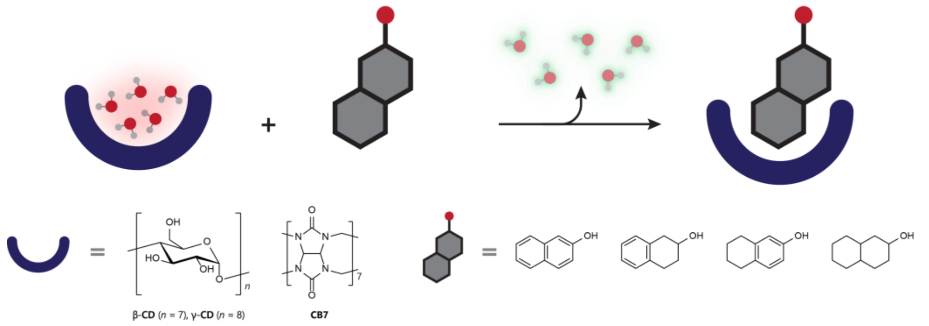

Figure 1. Schematic representation of the complexation

RAČUNALNA STUDIJA MEHANIZMOM TEMELJENIH IREVERZIBILNIH INHIBITORA ENZIMA MONOAMIN-OKSIDAZE B

COMPUTATIONAL STUDY OF THE MONOAMINE OXIDASE B MECHANISM-BASED IRREVERSIBLE INHIBITORS

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Monoamin-oksidaza B (MAO B) flavoenzim je odgovoran za metabolizam endogenih i egzogenih amina, uključujući monoaminske neutransmitere čija je narušena homeostaza implicirana kod razvitka mnogih neurodgenerativnih oboljenja. MAO B predstavlja osnovnu farmakološku metu za liječenje Alzheimerove i Parkinsonove bolesti. Komercijalni lijekovi, selegilin i razagilin, administriraju se uz dijetalne restrikcije te, u većim dozama, gube selektivnost što rezultira učestalijim nuspojavama većeg intenziteta [1]. Stoga, postoji pritisak tržišta za razvitkom novih, mehanizmom temeljenih inhibitora MAO B enzima. Za dizajn novih inhibitora razvijen je inovativni pristup koji uključuje spajanje temeljnih aromatskih struktura [2] s propagilaminskom jezgrom koja je prisutna kod komercijalno dostupnih lijekova koji ciljaju MAO enzime [3]. Metodom molekulskog pristajanja i potom simulacijama molekulske dinamike, dobiveni su povoljniji termodinamički profili vezanja novodizajniranih liganada u aktivno mjesto MAO B enzima, te će se kinetički profili inhibitorne aktivnosti okarakterizirati pristupom kvantno-mehaničkog klastera.

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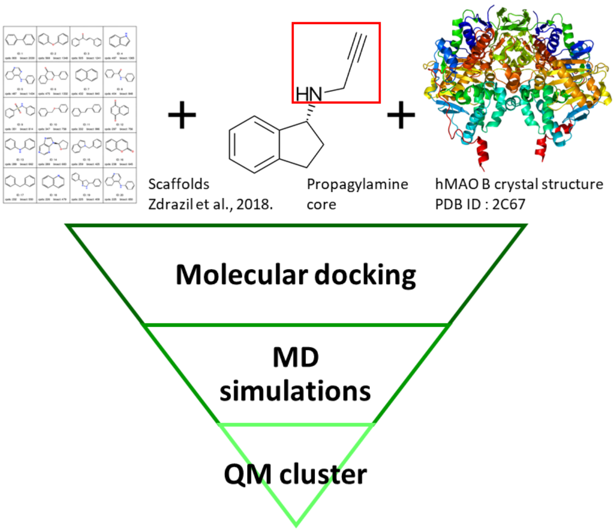

ISPITIVANJE KINETIKE MEHANIČKI AKTIVIRANE OLIGOMERIZACIJE NIKLOVOG(II) DIBENZOILMETANATA RAMANOVOM SPEKTROSKOPIJOM *IN SITU*

INVESTIGATION OF KINETICS OF MECHANICALLY ACTIVATED OLIGOMERIZATION OF NICKEL(II) DIBENZOYLMETHANATE BY *IN SITU* RAMAN SPECTROSCOPY

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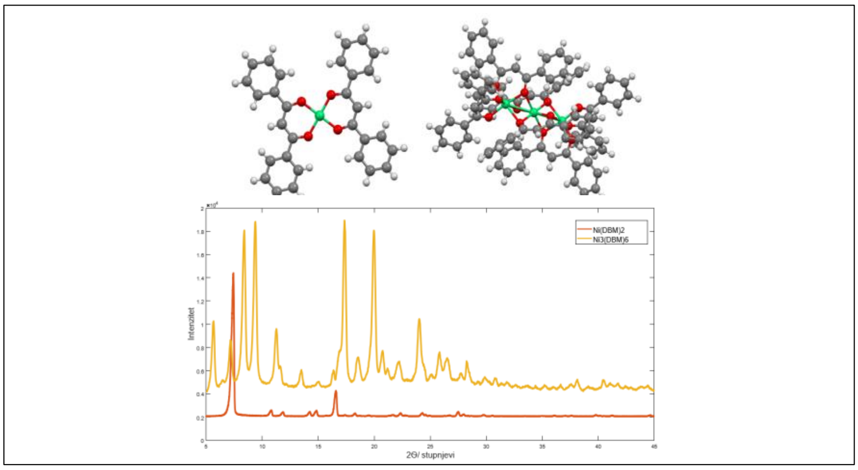
Primjena mehanokemijskih postupaka na industrijskoj skali ograničena je radi nepotpunog razumijevanja mehanizama mehanokemijskih reakcija. U ovom radu istraživan je utjecaj frekvencije mljevenja, materijala i mase kuglica na mehanokemijsku oligomerizaciju niklovog(II) dibenzoilmetanata primjenom Ramanove spektroskopije *in situ*. Pripravljeni spojevi karakterizirani su rendgenskom difrakcijom, XRD, i termogravimetrijskom analizom. Izabrani modelni sustav jednostupanjska je reakcija trimerizacije čija se brzina povećava porastom frekvencije mljevenja, korištenjem većeg promjera kuglica za mljevenje kao i materijala veće gustoće (ahat < cirkonijev dioksid < nehrđajući čelik < volframov karbid). Praćeni parametri bitno utječu na prijenos energije te reaktivnost sustava što je i potvrđeno kinetičkim reakcijskim profilima i numeričkim simulacijama. Dobiveni rezultati od velike su važnosti za optimizaciju mehanokemijskih procesa kao i njihovo dublje razumijevanje.



NOVI UVID U REGIOSELEKTIVNOST HOFMANN-LÖFFLER-FREYTAGOVE REAKCIJE

NEW INSIGHT INTO REGIOSELECTIVITY OF HOFMANN-LÖFFLER-FREYTAG REACTIONS

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Moderne inačice Hoffmann-Löffler-Freytag (HLF) reakcije proučavaju se na velikom broju sustava kako bi se funkcionalizirali udaljeni nefunkcionalizirani (alkanski) ugljici [1]. Naročitu primjenu pronalaze u farmaceutskoj industriji prilikom funkcionalizacije u kasnoj fazi (late-stage functionalization) nefunkcionaliziranih alkilnih lanaca u spojevima uzora pri čemu nastaju mnogi novi kandidati za lijekove [2]. Jedan od češće korištenih protokola uključuje induciranu pregradnju sulfonamida s jodom uz ko-oksidans. U toj reakciji nastaje jodosulfonamid kao međuprodukt koji uslijed fotokemijske aktivacije homolitčkim cijepanjem N-I veze stvara *N*-radikal. Uz pomoć reakcija prijenosa atoma vodika (HAT-reakcija) pregrađuje se u termodinamički stabilniju strukturu *C*-radikala. Nastali C-radikal može reagirati s atomom joda pri čemu nastaje aktivirani udaljeni C-atom. Daljnjom se obradom takav spoj ciklizira. Uočena je regioselektivnost HLF reakcije; produkti 1,5-HAT reakcije češće nastaju od produkata 1,6-HAT reakcije, unatoč termodinamičkim pretpostavkama o stabilnosti C5 i C6 radikala. Cilj rada je odrediti kinetičke i termodinamičke parametre koji diktiraju regioselektivnost reakcije. Korištene su kvantno-kemijske metode koje su validirane tijekom termodinamičkog proučavanja tipičnog sustava [3]. Sustavnim ispitivanjem reakcija koje se pregrađuju putem 1,4-, 1,5-, 1,6-HAT i stvaraju sekundarne *C*-radikale uočena je nepovoljna barijera strukturnog peteročlanog prstena u prijelaznom stanju, dok približno jednaku barijeru imaju strukture prijelaznih stanja koje sadrže šesteročlane i sedmeročlane prstene. Navedenim istraživanjem rasvijetlit će se uvjeti koji su potrebni za upravljanje regioselektivnošću HFL reakcija na sulfonamidima.

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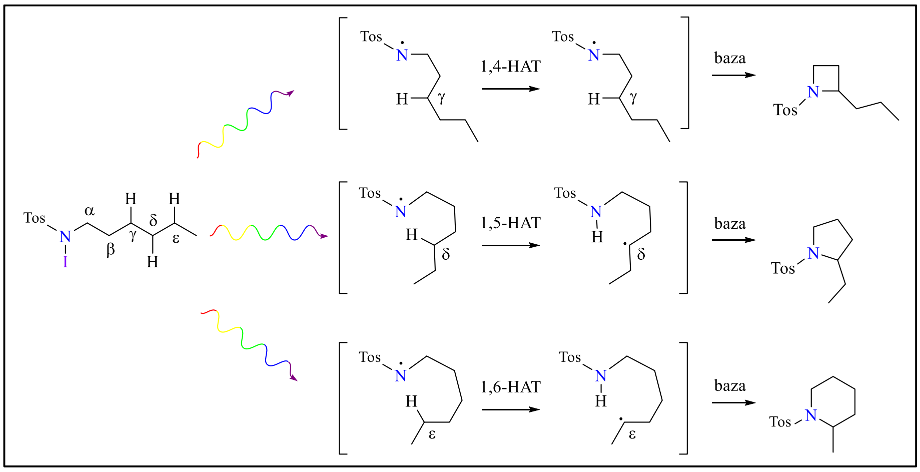

Razvoj materijala i proizvoda
Materials and products development

PREVENTION OF MICROBIAL DETERIORATION OF ADDITIVIZED WASTE EMULSION

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Preservatives are natural or synthetic substances added to products in order to inhibit or retard spoilage (development of microorganisms). Their application can improve not only product’s shelf life by preventing microbial deterioration, but also its initial properties and appearance. Preservatives are especially important in the preservation of water-based products with biodegradable constituents [1].

Waste emulsion for road construction was homogenized and enhanced by additives. Emulsion properties such as its appearance, odour and physical changes were observed in order to determine its stability. It was found that an additivized emulsion was susceptible to microbial deterioration only 7 days after its preparation.

In this research, application of four different preservatives (sodium acetate, sodium benzoate, potassium metabisulfite and Preventol® B2) was investigated in order to prolong shelf life of an enhanced waste emulsion. Emulsions with various concentrations of preservatives were prepared and monitored daily during eight weeks for changes in appearance and odour caused by microbial deterioration.

It was found that the addition of sodium benzoate and potassium metabisulfite in lowest tested concentrations (0.25 g preservative per 100 g non-additivized emulsion) was successful in preventing microbial deterioration since no changes in odour or appearance have occurred throughout eight weeks. However, detailed microbiological investigation should be obtained in order to confirm these findings.

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DETERMINATION OF ADHESIVITY OF TWO WASTE EMULSIONS BY WATER IMMERSION TEST

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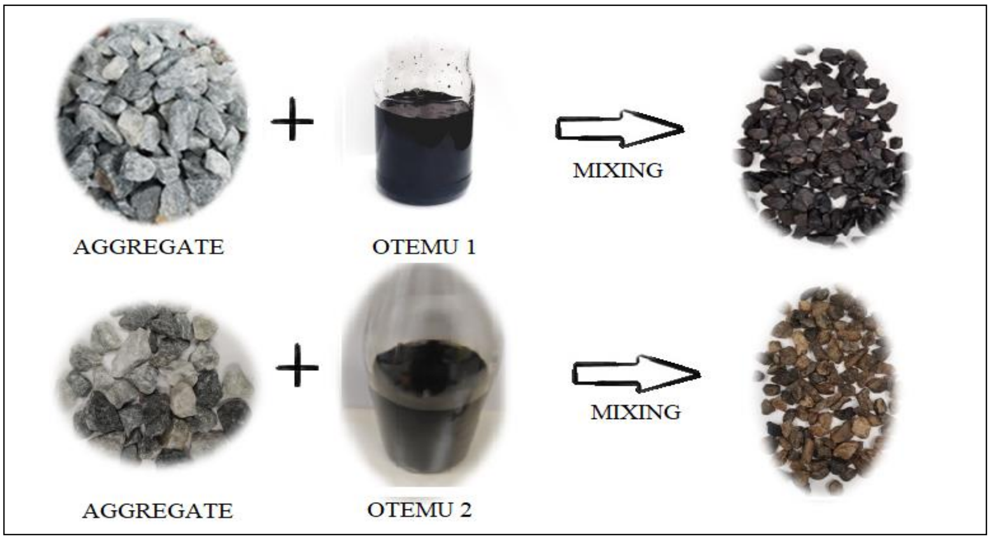
The water immersion test provides a qualitative assessment of binding ability of a bituminous emulsion. After the aggregate (stone) has been coated by emulsion and cured for a period of time the emulsion coating should display stability in water. The wholeness of aggregate coverage (given in percentage) by binder is an important parameter in road construction and is a basic test of the effectiveness of the waste emulsion in further use.

In this study, two waste emulsions (OTEMU 1 and OTEMU 2) with different properties were analyzed. The first step was the mechanical mixing of the aggregate and the waste emulsions (binder) with the help of a spoon. When testing the influence of water on binder adhesion, the mixture of waste emulsion binder and aggregate is first allowed to cure and then immersed in water under certain conditions. The percentage of aggregate surface covered with binder is visually assessed. The percentage of coverage of aggregates with OTEMU 1 was 90%, while the percentage of coverage of aggregates with OTEMU 2 was less than 50%.



VIŠEKOMPONENTNA MEHANOKEMIJSKA SINTEZA KOKRISTALA SOLI BAKRA(II) S PERHALOGENIRANIM DONORIMA HALOGENSKE VEZE

MULTICOMPONENT MECHANOCHEMICAL SYNTHESIS OF COCRYSTALS OF COPPER(II) SALTS WITH PERHALOGENATED HALOGEN BOND DONORS

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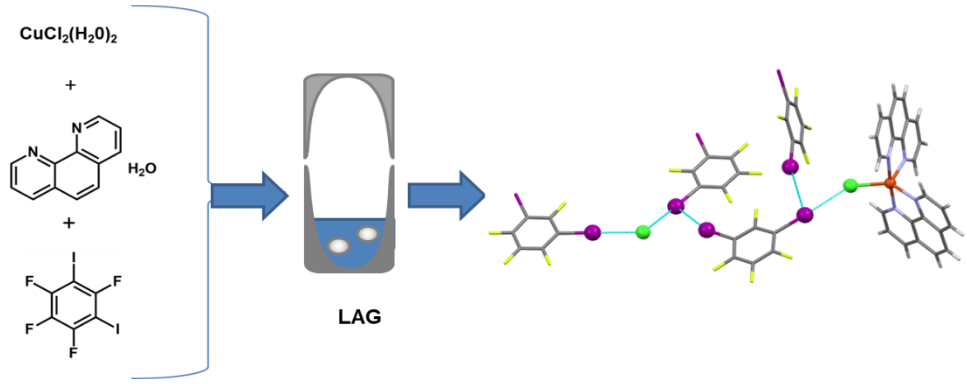
Jedan od smjerova istraživanja višekomponentnih metalo-organskih krutina je dizajn i sinteza kokristala soli [1]. Ranija istraživanja pokazala su kako je višekomponentna mehanokemijska sinteza u jednom koraku praktična metoda za pripravu metalo-organskih kokristala [2]. Na temelju toga u ovom radu izučavana je mogućnost kokristalizacije soli bis(1,10-fenantrolin)kloridobakrova(II) klorida s perhalogeniranim donorima halogenske veze: 1,2-dijodtetrafluorbenzenom (**12tfib**), 1,3-dijodtetrafluorbenzenom (**13tfib**), 1,4-dijodtetrafluorbenzenom (**14tfib**) i 1,3,5-trijod-2,4,6-trifluorbenzenom (**135tfib**). Pokusi kokristalizacije mehanokemijskom sintezom napravljeni su na dva načina. Prvi pristup uključivao je mljevenje kompleksne soli bakra(II) s donorima u različitim stehiometrijskim omjerima, dok je drugi pristup uključivao mljevenje bakrova(II) klorida dihidrata, 1,10-fenantrolina monohidrata (**phen**) i donora u različitim stehiometrijskim omjerima. Rezultati mehanokemijske sinteze praćeni su difrakcijom rentgenskih zraka na praškastom uzorku. U oba pristupa s **12tfib** i **135tfib** dobiveni su kokristali stehiometrije 1:2 (Cu(II) sol : donor). U sintezi s **13tfib** pripravljen je kokristal stehiometrije 1:4, a s **14tfib** i sa soli kompleksa bakra(II) dobiveni su kokristali stehiometrije 1:2 i 1:3. Nadalje, sintezom iz otopine pripravljeno je svih pet kokristala soli, a dobiveni produkti istovjetni su produktima pripravljenim mljevenjem. Rendgenskom strukturnom analizom utvrđeno je da se halogenska veza I···Cl ostvaruje između atoma joda donora halogenske veze i koordiniranog te nekoordiniranog kloridnog atoma. Od pet kokristala u njih četiri molekule su halogenskim vezama povezane u lance, dok u jednom tvore diskretni kompleks.

[1] V. Nemec, K. Lisac, N. Bedeković, L. Fotović, V. Stilinović, D. Cinčić, Cryst Eng Comm 23 (2021) 3063-3083.
[2] K. Lisac, S. Cepić, M. Herak i D. Cinčić, Chem methods (2021)



PROPERTIES OF HYDROPHOBIC DEEP EUTECTIC SOLVENTS IMPORTANT FOR THEIR PHARMACEUTICAL APPLICATION

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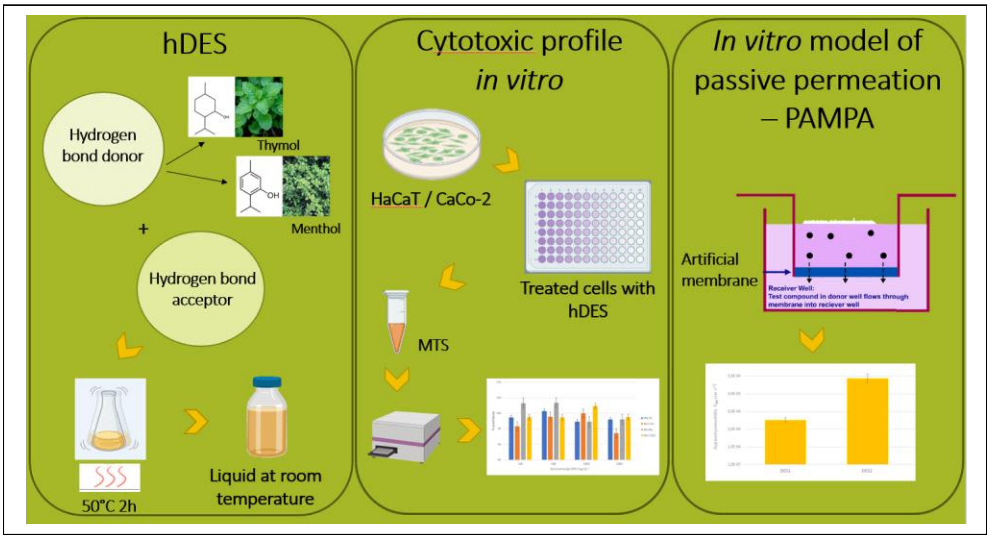
Deep Eutectic Solvents (DESs) are in the focus of fundamental, but also applicative researches in the field of Green Chemistry. Their green character arises from the fact that DESs are non-toxic and non-flammable, as well as easily synthetized from cheap and renewable compounds. Recently, a new window is opened with subclass of DESs, hydrophobic DESs (hDESs), which could be of great value for the pharmaceutical and cosmetic industry. hDESs can overpass the problems that occur with the compounds poorly soluble in water by increasing their solubility, permeability and bioavailability. In order to safely use it in aforementioned industries it is of great importance to test their cytotoxicity and their own permeability potential. Therefore, in the presented work we have synthetized eight hydrophobic DESs and evaluated their cytotoxic profile *in vitro* on two human cell lines CaCo-2 and HaCaT. The Parallel Artificial Membrane Permeability Assay (PAMPA) was applied as an *in vitro* model of passive permeation to determine potential of hDESs to be used as a solvent or a carrier for different compounds of interest.



MODIFICATION OF BRONZE FOR IMPROVING CORROSION PROTECION OF ACRYLIC RESIN

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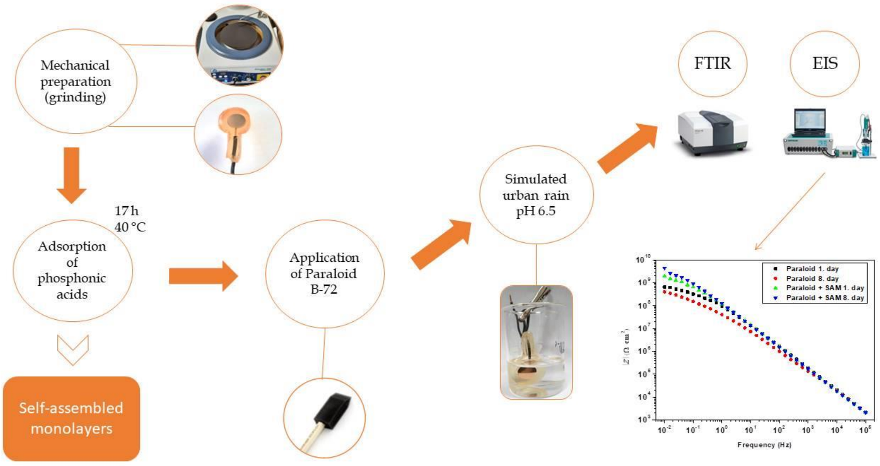
Bronze works of art and cultural heritage are exposed to pollution in open or closed atmospheres. They are susceptible to corrosion processes that lead to changes in their appearance and stability. To reduce the deterioration of cultural heritage, corrosion protection is used, which must meet the requirements of conservation ethics. Today, the most commonly used protective coating is acrylic resin, Paraloid B-72, whose drawback is the short-term protection.

In this work the combination of self-assembled monolayers of selected phosphonic acids with Paraloid B-72 is examined, which improves corrosion protection due to better adhesion between the coating and the metal surface. The protective coating is applied with a brush on metal substrates. Further, the properties of untreated and treated surfaces are compared.

The protective effect of the obtained coating systems are studied by electrochemical impedance spectroscopy (EIS) in a simulated urban rain solution at pH 6.5. The structure of the self-assembled monolayers and the acrylic coating are determined by Fourier transform infrared spectroscopy (FTIR).

This work has been fully supported by Croatian Science Foundation under the project IP-2019-04-5030.



KOKRISTALI S BAKROVIM(II) KOMPLEKSIMA KAO DONORIMA HALOGENSKE VEZE

COCRYSTALS WITH COPPER(II) COMPLEXES AS HALOGEN BOND DONORS

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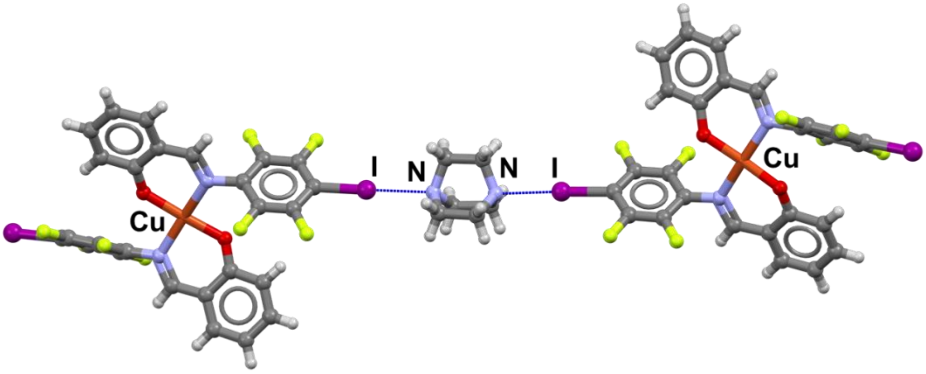
U dizajnu metaloorganskih višekomponentnih kristala temeljenih na halogenskoj vezi [1], metaloorganski kompleksi mogu se koristiti kao akceptori ili donori halogenske veze što ovisi o funkcionalizaciji periferije organskog liganda. Odabranom funkcionalizacijom liganda omogućuje se nastanak specifičnih interakcija između kompleksa i okruženja u kojem se on nalazi. U dosadašnjim istraživanjima, metaloorganski kompleksi daleko su češće izučavani kao akceptori halogenske veze [2].

U ovom istraživanju po prvi put pripravljeni su kokristali u kojima je donor halogenske veze iminski bakrov(II) kompleks. Imin koji je korišten kao ligand pripravljen je kondenzacijom 2,3,5,6-tetrafluor-4-jodanilina i salicilaldehida (itfasal). Nadalje, pripravljeni su bakrovi(II) kompleksi Cu(itfasal)$_2$ i Cu(piridin)(itfasal)$_2$ koji su kokristalizirani s akceptorom halogenske veze 1,4-diazabiciklo[2.2.2]oktanom (dabco) u stehiometrijskom omjeru 1:1. Pripravljeni spojevi okarakterizirani su metodama difrakcije rentgenskog zračenja na jediničnom kristalu i praškastom uzorku te su im određena termička svojstva. Strukturna analiza pokazala je da je u oba pripravljena kokristala ostvarena ciljana halogenska veza I···N između atoma joda perhalogenirane periferije metaloorganskih jedinica i dušikovih atoma molekule dabco. Također, u oba kokristala molekule se povezuju halogenskim vezama u lance koji se nadalje povezuju u tri dimenzije kontaktima C–H···C i C–H···F.

[1] G. Cavallo, P. Metrangolo, R. Milani, T. Pilati, A. Priimagi, G. Resnati, G. Terraneo, Chem. Rev. 116 (2016) 2478.
[2] V. Nemec, K. Lisac, N. Bedeković, L. Fotović, V. Stilinović, D. Cinčić, CrystEngComm 23 (2021) 3063.



SINTEZA I PROČIŠĆAVANJE BIOADITIVA ZA DIZELSKO GORIVO NA OSNOVI LEVULINSKE KISELINE

SYNTHESIS AND PURIFICATION OF DIESEL FUEL BIOADDITIVES BASED ON LEVULINIC ACID

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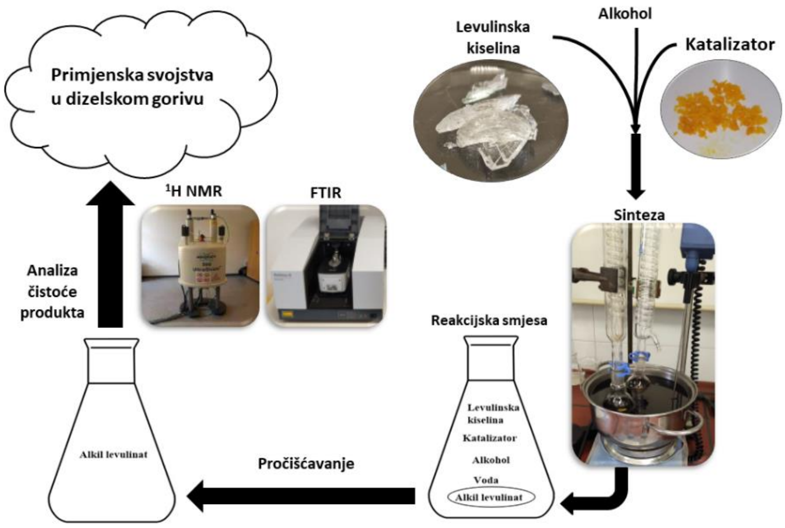
Motorna goriva neizostavni su proizvodi naftne industrije koji se najviše koriste u automobilskoj industriji i općenito u prijevozu. Važno je da goriva zadovoljavaju zahtjeve kvalitete regulirane normama. Dodatak aditiva ponekad je neizostavan dio kako bi se ti zahtjevi zadovoljili, a u novijem razdoblju istraživanja su sve više usmjerena na sintezu aditiva iz obnovljivih sirovina. Levulinska kiselina pokazuje izniman potencijal kao sirovina za sintezu bioaditiva jer se može jednostavno sintetizirati iz celuloze dobivene iz biootpada. U ovome radu sintetizirani su alkil levulinati procesom esterifikacije, reakcijom levulinske kiseline i raznih alkohola uz kiseli katalizator $FeCl_3$. Kako bi se istražilo na koji način utječe duljina alkilnog lanca na primjenska svojstva sintetiziranih alkil levulinata u sintezama su korišteni alkoholi različitih duljina lanaca - metanol, pentanol i oktanol. Pročišćavanje produkta sinteze izvodilo se ekstrakcijom i uparavanjem u rotacionom uparivaču. Uspješnost pročišćavanja potvrdila se infracrvenom spektroskopijom s Fourierovom transformacijom (FTIR) te ^{1}H nuklearnom magnetskom rezonancijom. Nakon uspješnog pročišćavanja ispitana su fizikalna svojstva aditiva te njihov utjecaj na poboljšanje mazivosti i niskotemperaturnih svojstva dizelskog goriva.



TETRAEDARSKI KOMPLEKSI CoX_2L (X = Cl, Br i I) KAO AKCEPTORI HALOGENSKE VEZE U METALOORGANSKIM KOKRISTALIMA

TETRAHEDRAL COMPLEXES CoX_2L (X = Cl, Br and I) AS HALOGEN BOND ACCEPTORS IN METAL−ORGANIC COCRYSTALS

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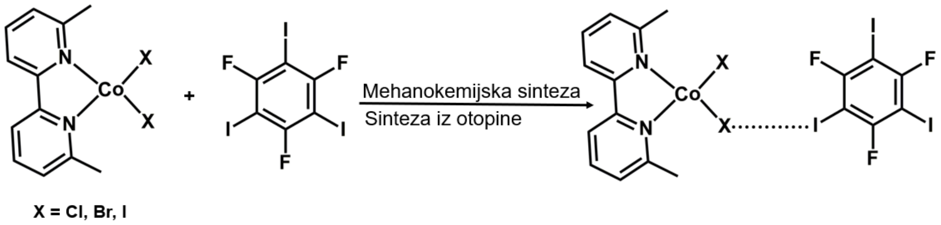
Posljednjih dvadesetak godina brojna istraživanja usmjerena su na izučavanje halogenskih veza u kristalnom inženjerstvu metaloorganskih krutina [1]. Neutralni metaloorganski spojevi koji sadrže halogenido ligande kao akceptore halogenske veze pokazali su se kao pouzdani građevni blokovi u dizajnu i sintezi metaloorganskih kokristala [2]. Pretraživanjem literature ustanovljeno je da je značajan broj istraživanja usmjeren na višekomponentne metaloorganske materijale s perhalogeniranim aromatima kao donorima halogenske veze.

S ciljem izučavanja novih metaloorganskih kokristala u kojem su molekule povezane halogenskim vezama, u ovom radu odabrani su i pripravljeni tetraedarski **CoX_2L** kompleksi (X= Cl, Br, I ; L= 6,6'-dimetil-2,2'-bipiridin (**6-bpy**)) te je ispitan njihov potencijal u ulozi akceptora halogenske veze. Kao donori halogenske veze korišteni su 1,3-dijodtetrafluorbenzen (**13tfib**), 1,4-dijodtetrafluorbenzen (**14tfib**) te 1,3,5-trijod-2,4,6-trifluorbenzen (**135tfib**). Mehanokemijskom sintezom i sintezom iz otopine uspješno je pripravljeno pet novih kokristala koji sadrže **13tfib** ili **135tfib** kao donore halogenske veze. Mehanokemijski pokusi s donorom **14tfib** pokazali su da dolazi do kokristalizacije samo s kompleksom **CoI_2(6-bpy)**, dok sinteza iz otopine nije bila uspješna s niti jednim kompleksom. Kokristali dobiveni iz otopine analizirani su difrakcijom rendgenskog zračenja na jediničnom kristalu. Rendgenska strukturna analiza kokristala pokazala je da su metaloorganske građevne jedinice u kristalu povezane halogenskim vezama Co-X···I s molekulama donora halogenske veze pri čemu tvore diskretne supramolekulske komplekse. Nadalje, u strukturama koje sadrže **135tfib** diskretni supramolekulski kompleksi povezani su halogenskim vezama I···I između susjednih molekula **135tfib**.

[1] G. Cavallo, P. Metrangolo, R. Milani, T. Pilati, A. Priimägi, G. Resnati, G. Terraneo, The Halogen Bond. Chem. Rev., 116 (2016) 2478–2601.

[2] V. Nemec, K Lisac, N. Bedeković, L. Fotović, V. Stilinović, D. Cinčić, CrystEngComm 23 (2021) 3063.



ALGINATE HYDROGEL BEADS AS CARRIERS OF WINE POLYPHENOLS

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The development of more nutritious, safe to eat and functional foods is one of the main challenges that the food industry is currently facing. Microencapsulation technology uses polyphenols and other bioactives that benefit human health and utilizes them to form gel systems as alginate hydrogel beads. In this study, Cabernet Sauvignon red wine concentrates were subjected to the process of microencapsulation. To perform the microencapsulation process, the B-390 BUCHI encapsulator was used under fixed conditions (1000 µm nozzle, 200 mbar, 200 Hz, 1000 V). By dropping mixtures of wine concentrate and alginate (3% A), alginate/xanthan (3% A, 0.1% X) or alginate/carboxymethylcellulose (3% A, 0.1% C) in the calcium chloride solution (5%), hydrogel beads were obtained and the influence of the wall material composition on the polyphenols' encapsulation was investigated. Individual polyphenols in the hydrogel beads were evaluated using HPLC analysis and the results showed that malvidin-3-glucoside, gallic acid, catechin and rutin were predominant components. The antioxidant activity of hydrogel beads was determined spectrophotometrically. The most effective formulation was alginate alone. Formulated alginate hydrogel beads as carriers of red wine polyphenols could be further used to enhance the nutritional value of foods and beverages into which they are added.

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' Career Development Project – Training of New Doctoral Students (DOK-2020-01-4205).

OSVJEŽI SVOJE ROKOVE - UZ DOBRO PIVO LAKŠE PAMTIM ŠTIVO

REFRESH YOUR FINALS - A GOOD BEER WHILE YOU STUDY MAKES THE MIND LESS CLOUDY

Franka Delonga, Natalija Bulaš, Lucija Divić, Martina Kukoleča, Nina Lucić, Karmen Periša, Anita Pitarević, Danica Sinovčić, Marina Velić

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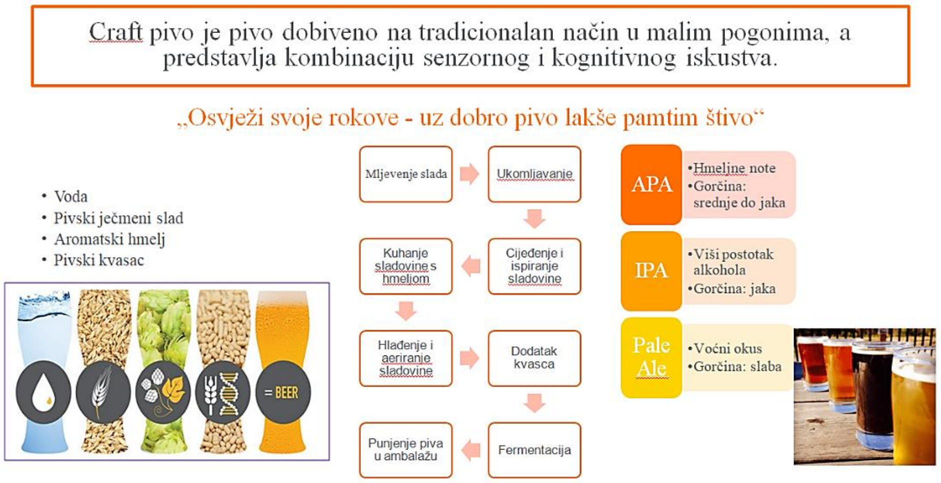
U sklopu studentskog projekta „Osvježi svoje rokove - uz dobro pivo lakše pamtim štivo“, kojeg financira Studentski zbor Sveučilišta u Splitu i Kemijsko-tehnološki fakultet u Splitu, devet studentica diplomskog studija Prehrambene tehnologije odlučilo se na proizvodnju craft piva. Tijekom projekta razvila se suradnja s craft pivovarama iz Splita, Zadra i Dubrovnika koje su pomagale u razvijanju recepture i korištenju potrebne aparature. Također, prilikom nabave određenih sirovina za proizvodnju, tvrtke, OPG-ovi, kao i profesori s fakulteta, pružili su potporu projektu što je uvelike olakšalo početak i provedbu samog projekta.

Cilj projekta bio je osmišljavanje optimalne recepture i manipulacija s parametrima proizvodnje kako bi se proizvelo craft pivo inovativnih i specifičnih organoleptičkih karakteristika. Eksperimentalno nemjerljivi ciljevi projekta su uspješan timski rad, upoznavanje s tehnološkim procesom proizvodnje craft piva, organizacija, planiranje i samostalna realizacija projekta, donošenje zaključaka, prezentacija rezultata široj publici te u konačnici usvajanje znanja.

Projekt se sastojao od nabave sirovina i proizvodnje različitih vrsta piva na craft uređaju Grainfather, zatim su piva s najboljim organoleptičkim svojstvima išla na analizu aroma na GCMS uređaj i analizu fizikalnih svojstava. Eksperimentiranjem s okusima ustanovljeno je koje sirovine daju najbolje arome pivu, dok pojedine sirovine sadrže biološki aktivne spojeve koje, osim senzorike, povećavaju i zdravstvenu vrijednost piva te ga potencijalno svrstavaju u kategoriju funkcionalne hrane.

Za sudjelovanje na XIV. susretu mladih kemijskih inženjera odabrana je šarža piva s najboljim svojstvima koju će studentice predstaviti.



Craft pivo je pivo dobiveno na tradicionalan način u malim pogonima, a predstavlja kombinaciju senzornog i kognitivnog iskustva.

„Osvježi svoje rokove - uz dobro pivo lakše pamtim štivo“

- Voda
- Pivski ječmeni slad
- Aromatski hmelj
- Pivski kvasac

APA
- Hmeljne note
- Gorčina: srednje do jaka

IPA
- Viši postotak alkohola
- Gorčina: jaka

Pale Ale
- Voćni okus
- Gorčina: slaba

BORON MODIFIED CHITOSAN SCAFFOLDS CHEMICALLY CROSSLINKED BY GENIPIN

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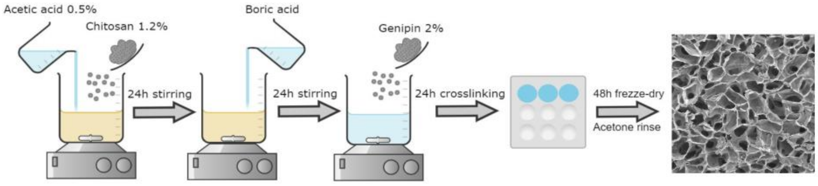
Chitosan scaffolds are an effective biologically active material with versatile application in chemistry and medicine. Chitosan has a polycation nature allowing complex formation with metal ions and many biomolecules such as DNA, proteins and lipids while it's specific structure and functional groups are responsible for antibacterial, hemostatic and analgesic properties. To improve angiogenic and antimicrobial potential chitosan can be modified by boron (borate ions). The aim of this work was to prepare boron modified chitosan scaffolds, using boric acid as a boron precursor, as potential bioactive scaffolds for tissue regeneration. Borate ions tend to form complexes with hydroxyl groups, however, such physical interactions between boron and chitosan functional groups result in poor encapsulation efficiency. To ensure higher boron incorporation, chitosan scaffolds were crosslinked by genipin, a crosslinker with lower cytotoxicity in contrast to glutaraldehyde commonly used to prepare stable chitosan-based materials. The degree of deacetylation (*DD*) and concentration of chitosan solution as well as the concentration of a solvent are important parameters that affect the crosslinking process. Moreover, the addition of boric acid could interfere with the crosslinking process by occupying chitosan functional groups. Here, chitosan scaffolds were modified by different concentrations of boric acid, while the concentration of chitosan solution (1.2 w/v), the concentration of genipin (2% w/w) and the concentration of acetic acid (0.5% v/v) were kept constant. Obtained scaffolds were characterized by scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), differential scanning calorimetry (DSC), Fourier transformation infrared spectroscopy (FTIR), while cytotoxicity was evaluated as a function of materials concentration and exposure time. The results indicated successful incorporation of boron into crosslinked chitosan scaffolds with highly porous structure and low cytotoxicity.



KOMPLEKSNI SPOJEVI KOBALTA(II) S HALOGENIDO LIGANDIMA KAO AKCEPTORIMA HALOGENSKE VEZE

COBALT(II) COMPLEX COMPOUNDS WITH HALIDE LIGANDS AS HALOGEN BOND ACCEPTORS

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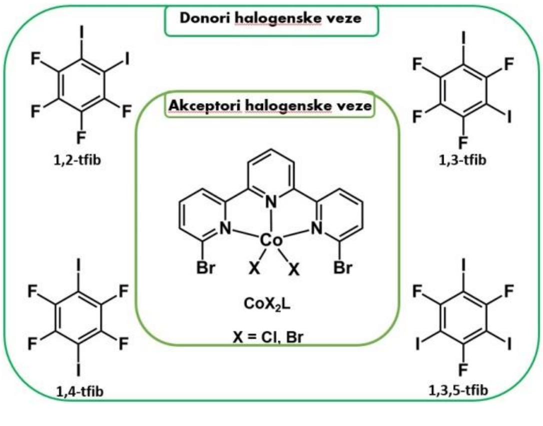
Istraživanje neutralnih metaloorganskih kokristala u kojima su molekule povezane halogenskom vezom danas je vrlo popularna tema u kristalnom inženjerstvu, a u literaturi nalazimo nekoliko strategija dizajna. Najčešće se kao donori halogenske veze koriste perfluorirani jodbenzenski spojevi, a akceptori halogenske veze mogu biti halogenido ili okso ligandi u kompleksnom spoju, atomi vezani na periferiji liganda, zatim atomi liganda koji sudjeluju u koordinaciji s metalnim ionom ili pak sam metalni ion [1].

U svrhu proučavanja halogenida koordiniranih na metalni centar, ali i onih vezanih na periferiji liganda, kao akceptora halogenske veze pripravljeni su kompleksni spojevi **CoCl$_2$L** te **CoBr$_2$L** (L = 6,6´´-dibrom-2,2´:6´,2´´-terpiridin), te su kokristalizirani s odabranim donorima halogenske veze: 1,2-dijodtetrafluorbenzenom (**1,2-tfib**), 1,3-dijodtetraflourbenzenom (**1,3-tfib**), 1,4-dijodtetrafluorbenzenom (**1,4-tfib**) i 1,3,5-trijodtrifluorbenzenom (**1,3,5-tfib**). Kokristalizacija je provedena metodom mljevenja uz prisutnost male količine kapljevine i kristalizacijom iz otopine. Rezultati mehanokemijske sinteze praćeni su difrakcijom rentgenskih zraka na praškastom uzorku, dok su za oba kompleksna spoja i četiri kokristala, (**CoCl$_2$L**(**1,4-tfib**)$_2$, **CoCl$_2$L**(**1,3-tfib**)$_2$, **CoCl$_2$L**(**1,3,5-tfib**)$_2$ i **CoBr$_2$L(1,3-tfib)$_2$**), određene molekulska i kristalna struktura difrakcijom rendgenskih zraka na jediničnim kristalima dobivenim kristalizacijom iz otopine. Strukturna analiza kompleksnih spojeva pokazala je da su molekule povezane halogenskim vezama Br···X−Co (X=Br, Cl) između bromovog atoma na periferiji liganda i klorido odnosno bromido liganda vezanog na kobalt. U strukturama kokristala uočene su halogenske veze između atoma joda donora halogenske veze te halogenida vezanog na metalni centar. Nadalje, bromov atom na periferiji liganda sudjeluje samo u kontaktima Br···H−C, osim u strukturi **CoCl$_2$L**(**1,3,5-tfib**)$_2$ gdje se dvije susjedne molekule kompleksa povezuju halogenskom vezom Br···Cl−Co.

[1] V. Nemec, K. Lisac, N. Bedeković, L. Fotović, V. Stilinović, D. Cinčić, CrystEngComm 23 (2021) 3063-3083.



INFLUENCE OF THE SOURCE OF FEEDSTOCK AND THE REACTION PARAMETERS ON THE SYNTHESIS OF FATTY ACID ISOBUTYL ESTERS

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In the recent decades, the investigation of the alternatives to mineral fuels has sparked the attention of scientists. The research and development of renewable energy includes the synthesis of biofuels, such as biodiesel, due to their sustainability and nontoxicity. The end fuel properties depend on the type of feedstock and alcohol used for its synthesis. Here, fatty acid isobutyl esters were obtained via transesterification reaction between an alcohol isobutanol and different sources of triglycerides, specifically sunflower oil, rapeseed oil, coconut oil, waste cooking oil or animal fat, alongside a catalyst, potassium hydroxide. Reaction time, molar ratio of the reactants and mass fraction of the catalyst were the reaction parameters that were variable during the course of the reaction at the constant temperature of 60 °C. Results show that the conversion above 96% can be achieved at the temperature of 60 °C, after 30 minutes, when the molar ratio of isobutanol to rapeseed oil is 12:1 and the mass fraction of the catalyst is 1 or 3%. The most significant reaction parameters are molar ratio of the reactants and the mass fraction of the catalyst, which increase, generally, leads to the increase in the reaction conversion.

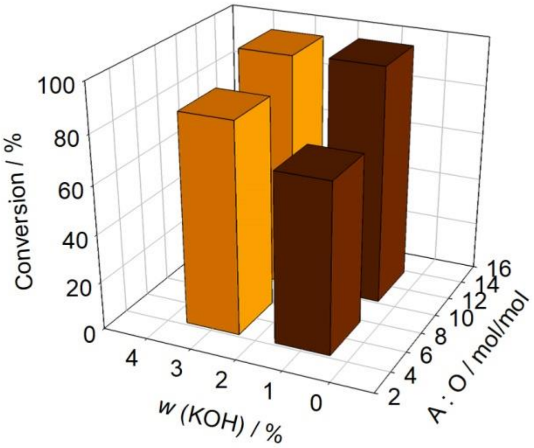

Figure 1. The influence of isobutanol to rapeseed oil molar ratio and mass fraction of KOH on the transesterification reaction conversion

KOMPOZITNI MATERIJALI NA BAZI CEMENTA UZ DODATAK OVČJE VUNE, DRVETA (PAULOWNIA) I STAKLA

COMPOSITE MATERIALS BASED ON CEMENT WITH ADDITION OF SHEEP WOOL, WOOD (PAULOWNIA) AND GLASS

Edina Ibrić, Ajla Mandalović, Mediha Biberović, Elma Zehić, Haris Glušac, Belmin Poljić, Amina Ahmić, Zehrudin Osmanović.

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Pri izradi projekta potrebno je bilo napraviti cementne pločice koje su se koristile kao referentni uzorci, a sastojale su se od cementa, pijeska i vode točno određene gramaže. Cement i pijesak su stavljeni u posudu i dobro izmješani te je postepeno dodavana voda uz konstantno miješanje. Nakon sjedinjavanja komponenti, dobivena masa je dodana u kalupe koji su se nalazili na potresnoj ploči. Nakon toga, kalupi s mortom su ostavljeni na sušenje 24 h nakon čega su vađeni i dobivene pločice odnosno uzorci morta potapani su u vodu, u kojoj su ostali 7 odnosno 28 dana nakon čega su ispitani na čvrstoću i savijanje. Ipitivanje uzoraka je provedeno u laboratoriju u Fabrici cementa u Lukavcu.

Za pripremanje uzoraka sa dodacima drveta - Paulovnije, vune i stakla, princip rada je isti kao i kod pripreme uzoraka morta.

Zaključak prve faze projekta je da je opravdano koristiti navedene materijale u betonskim konstrukcijama, te ako se ostvare dobra izolacijska svojstva, to bi moglo mnogo značiti za razvoj kompozitnih materijala na bazi cementa.

Cilj ovog projekta je bio ispitati utjecaj dodavanja kompozitnih materijala, u ploče na bazi cementa i pijeska, na čvrstoću, toplinsku vodljivost, zvučnu vodljivost te gorivost.

ODREĐIVANJE NESTEHIOMETRIJE KISIKA U PEROVSKITIMA PERMANGANATNOM TITRACIJOM

DETERMINATION OF OXYGEN NONSTOICHIOMETRY IN PEROVSKITES BY PERMANGANATE TITRATION

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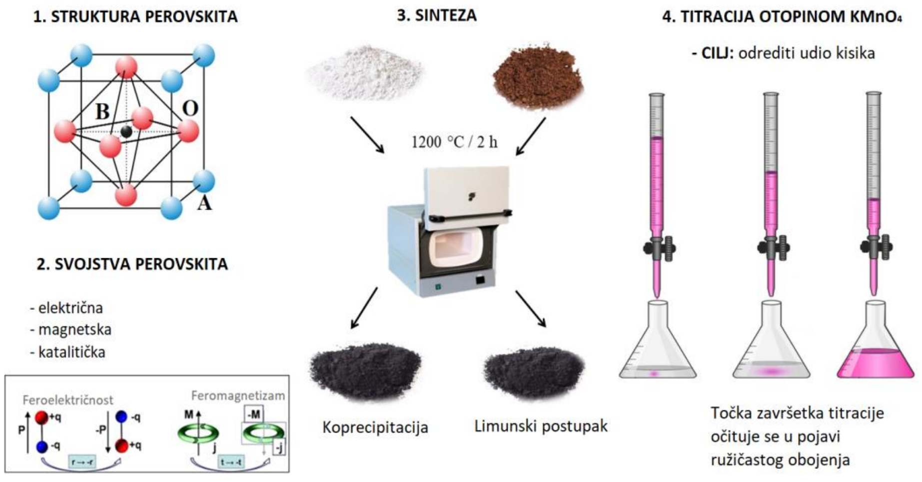
Za potpunu karakterizaciju manganovih perovskita, manganita, vrlo je važan parametar nestehiometrija kisika. Nestehiometrija kisika direktno je povezana s omjerom Mn^{3+}/Mn^{4+} koji utječe na svojstva manganita. Perovskiti bogati kisikom imaju izraženija magnetska svojstva pri sobnoj temperaturi, dok kod onih s deficitom kisika prevladavaju električna svojstva. Postoji nekoliko metoda kojima je moguće odrediti nestehiometriju kisika u perovskitima, kao što su termogravimetrijska analiza (TGA) i volumetrijske metode (titracije).

Cilj ovog rada bio je ispitati primjenjivost metode permanganatne titracije uz Mohrovu sol na određivanje nestehiometrije kisika u manganitima. Postupkom titracije određen je sadržaj kisika u uzorcima $La_{1-x}Sr_xMnO_3$ pripremljenima limunskim (x = 0, 0,1, 0,2 i 0,3) i koprecipitacijskim (x = 0, 0,1, 0,2, 0,3 i 0,5) postupkom sinteze. Utvrđeno je da je metoda permanganatne titracije primjenjiva na određivanje nestehiometrije kisika u manganitima te da ju je moguće jednostavno, brzo i ponovljivo primjenjivati. Osim toga, rezultati su pokazali da je koprecipitacijskim postupkom sinteze moguće proizvesti uzorke s izraženijom nestehiometrijom kisika za primjene u kojima je potrebna velika električna provodnost materijala.



STRUKTURNA ANALIZA *N*-ALKILGLICINA I NJIHOVIH NITRATNIH SOLI

STRUCTURAL ANALYSIS OF *N*-ALKYLGLYCINES AND THEIR NITRATE SALTS

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N-alkylated-amino acids are widely investigated due to their occurrence in bacteria, plant and animal organisms, and humans, as well as their biological functions in metabolic pathways. For instance, *N*-methylglycine is used as a dietary supplement and is investigated as a potential therapeutical agent for treatment of schizophrenia and depression [1]. *N*-ethylglycine is a promising agent for chronic pain treatment [2].

As part of our ongoing investigation of amino acids and their derivatives [3,4], we report synthesis, thermal and crystal structure analysis of four new compounds: *N*-ethylglycine-nitrate (**$H_2EtGlyNO_3$**), *N*-isopropylglycine-nitrate (**$H_2(\textit{i}\text{-PrGly})NO_3$**), *N*-(*n*-propyl)glycine-nitrate (**$H_2(\textit{n}\text{-PrGly})NO_3$**), and *N*-(*n*-propyl)glycine hydrate (**$H(\textit{n}\text{-PrGly})\cdot 1/3H_2O$**). Three *N*-alkylglycine compounds were crystallized as nitrate salts, while *N*-propylglycine was crystallized as a hydrate of a zwitterionic compound. All nitrate salts form 2D layers by hydrogen bonds (Figure 1), with layers connected through weak dispersion interactions of the hydrophobic chains. In **$H(\textit{n}\text{-PrGly})\cdot 1/3H_2O$** a 3D hydrogen-bonded framework is formed.

[1] J. F. Hyslop, S. L. Lovelock, A. J. B. Watson, P. W. Sutton and G.-D. Roiban, J. Biotechnol. 293 (2019) 56-65.

[2] R. Werdehausen, S. Mittnacht, L. A. Bee, M. S. Minett, A. Armbruster, I. Bauer, J. N. Wood, H. Hermanns and V. Eulenburg, Pain 156 (2015) 1647-1659.

[3] D. Vušak, N. Smrečki, S. Muratović, D. Žilić, B. Prugovečki, and D. Matković-Čalogović, RSC Adv. 11 (2021) 23779-23790.

[4] D. Vušak, N. Smrečki, B. Prugovečki, I. Đilović, I. Kirasić, D. Žilić, S. Muratović, and D. Matković-Čalogović, RSC Adv. 9 (2019) 21637-21645.

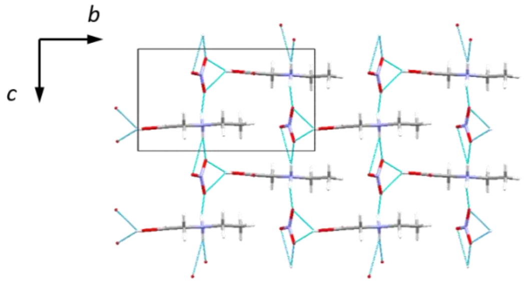

Figure 1. 2D hydrogen-bonded framework in **$H_2EtGlyNO_3$**

UTJECAJ REAKTANATA NA PRIPREMU MANGANITA REAKCIJOM U ČVRSTOM STANJU

INFLUENCE OF THE REACTANTS ON SOLID-STATE REACTION PREPARATION OF MANGANITES

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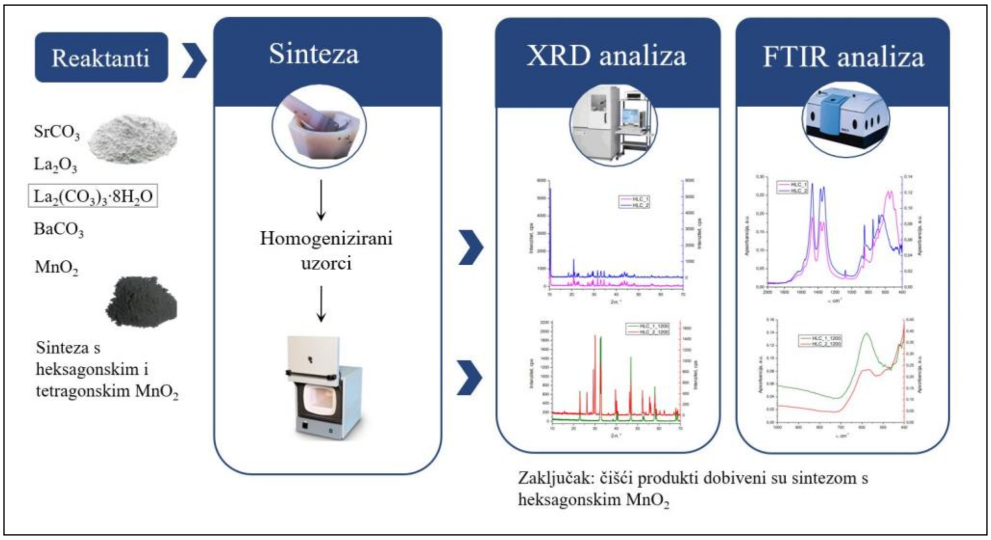
Cilj ovog rada bio je reakcijom u čvrstom stanju sintetizirati stroncijev manganit ($SrMnO_3$), lanatanov manganit ($LaMnO_3$) i barijev manganit ($BaMnO_3$) pomoću dva strukturno različita manganova(IV) oksida (MnO_2) te tako ispitati utjecaj reaktanata na sintezu. Uzorci dobiveni ručnom homogenizacijom žareni su na temperaturama od 1000 °C i 1200 °C.

Za određivanje sastava i strukture sintetiziranih spojeva korištene su rendgenska difrakcijska analiza (XRD) i infracrvena spektroskopija s Fourierovim transformacijama (FTIR). Iste tehnike analize primijenjene su i na dva različita MnO_2 čime je utvrđeno da jedan kristalizira u heksagonskom, a drugi u tetragonskom kristalnom sustavu.

Dobiveni rezultati pokazuju da su sintezom navedenih spojeva iz heksagonskog MnO_2 dobivene čišće manganitne faze.



Zaključak: čišći produkti dobiveni su sintezom s heksagonskim MnO_2

BIORAZGRADNJA AMBALAŽNOG MATERIJALA NA BAZI TERMOPLASTIČNOG ŠKROBA

BIODEGRADATION OF PACKAGING MATERIAL BASED ON THERMOPLASTIC STARCH

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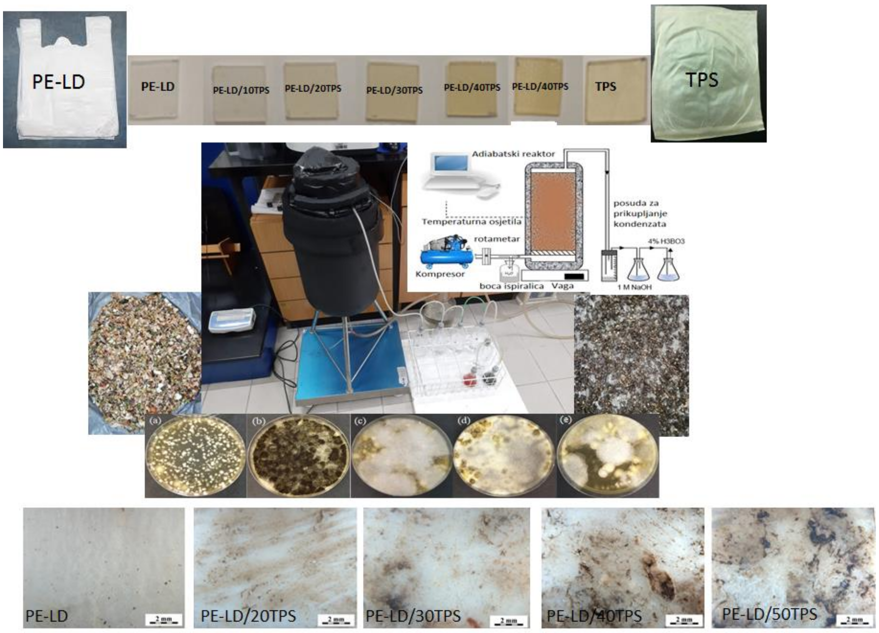
„Stvorili smo ju. Ovisimo o njoj. Utapamo se u njoj.“, slogan je koji jasno opisuje situacija u kojoj se čovječanstvo danas zateklo zbog nastanka velikih količina plastičnog otpada [1]. Stoga je na znanosti da iznađe način kako ekološki zbrinuti plastični otpad, te pronaći materijal koji svim svojim svojstvima konkurira plastičnim sintetskim materijalima, ali nosi i ono najbitnije svojstvo; biorazgradivi materijal.

Povedeni tom idejom, u ovom radu ispitana je biorazgradnja pripremljenih polimernih mješavina polietilena niske gustoće (PE-LD) i termoplastičnog škroba (TPS) procesom kompostiranja u laboratorijskom mjerilu. Tijekom procesa kompostiranja praćene su sve karakteristične procesne veličine važne za provedbu procesa. Postavljen je i matematički model procesa važan za dizajniranje i rad postrojenja za kompostiranje. Biorazgradnja polimernih PE-LD/TPS mješavina pratila se gubitkom mase prije i nakon procesa kompostiranja, kao i promatranjem promjena površine mješavina svjetlosnim (LM) i elektronskim pretražnim mikroskopom (SEM). Veći sadržaj TPS-a u polimernoj PE-LD/TPS mješavini pokazuje značajniju promjenu mase nakon procesa kompostiranja, ubrzava kinetiku razgradnje, te dolazi do izraženije biorazgradnje polimernih mješavina. TPS zbog hidrofilnog karaktera upija i zadržava vlagu iz kompostne mase što pridonosi rastu mikroorganizama, a time i bržoj razgradnji polimernih mješavina. LM i SEM mikroskopijom potvrđena je brža i prodornija biorazgradnja polimernih PE-LD/TPS mješavina.

[1] L. Parker, N. Daly, National Geographic, Washington DC, 2018, 40-91.



UČINAK KRATKOTRAJNOG KONTAKTA S ALKOHOLIMA NA PERFORMANSE KOMERCIJALNIH RO MEMBRANA

EFFECT OF SHORT-TERM CONTACT WITH ALCOHOLS ON THE PERFORMANCES OF COMMERCIAL RO MEMBRANES

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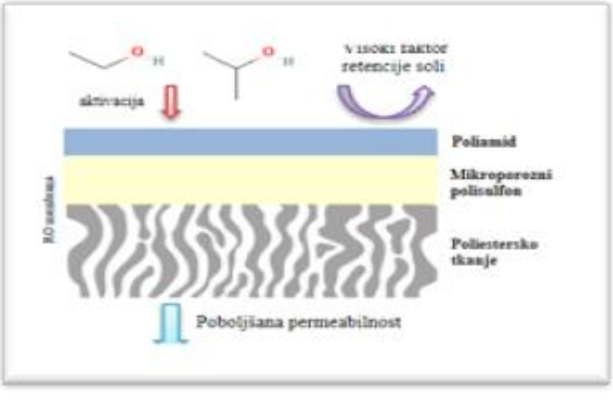
Poliamidne tankoslojne kompozitne membrane (PA – TFC) već se desetljećima primjenjuju za potrebe desalinacije morske i bočate vode te u postupcima obrade pitkih i otpadnih voda. Zbog visoke umreženosti poliamidne strukture koja predstavlja površinski aktivnu i selektivnu barijeru reverzno osmotske (RO) membrane, postiže se visoki stupanj zadržavanja kako anorganskih soli tako i organskih molekula prirodnog i antropogenog porijekla. S druge strane, gusta aktivna površina pruža znatan otpor prijenosu tvari što smanjuje permeabilnost membrane i ima za posljedicu relativno nizak protok. Kako bi se pomirila svojstva između selektivnosti i permeabilnosti RO membrana te postigao kompromis, u novije se vrijeme provode istraživanja utjecaja različitih organskih otapala, poput alkohola, za aktivaciju poliamidnog selektivnog sloja uz marginalno deformiranje polisulfonske potpore. Aktivacijom selektivnog sloja moguće je povećati permeabilnost vode kroz membranu uz zadržavanje visokog koeficijenta retencije soli.
U ovom radu komercijalne RO membrane (BW30LE, ACM5, ACM1, UTC-73AC, XLE) izložene su etilnom, *n*-propilnom te izopropilnom alkoholu u različitim vremenskim intervalima (5 i 60 min). Prije i nakon kratkotrajnog izlaganja alkoholima, ispitivanim membrana su određene performanse, permeabilnost tj. protok čiste vode te faktor zadržavanja jednovalentne (NaCl) i dvovalentne ($CaCl_2$) soli. U istraživanju je je pokazano da se permeabilnost membrana (protok čiste vode) kod aktiviranih membrana povećala (5 – 80 %) u odnosu na permeabilnost tvorničkih membrana, uz neznatan utjecaj na faktor zadržavanja (0,01 – 5 %).



KARAKTERIZACIJA HIDROGELOVA NA OSNOVI CELULOZE I *N*-VINIL-2-PIROLIDONA

CHARACTERIZATION OF HYDROGELS FROM CELLULOSE AND *N*-VINYL-2-PYRROLIDONE

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Celuloza je najrasprostranjeniji biopolimer. Sastavljena je od linearnih lanaca glukoze koji mogu imati od nekoliko stotina do nekoliko tisuća monomernih jedinica povezanih *ß*-(1→4) glikozidnom vezom, a svaka molekula celuloze ima 3 hidroksilne skupine koje joj omogućuju razne modifikacije te umrežavanje lanaca i pripravu hidrogelova. Celuloza je vrlo teško topljiva u vodi i drugim otapalima zbog jakih inter- i intramolekularnih vodikovih veza između pojedinačnih lanaca kao i zbog visokog stupnja kristalnosti (40-60 %) [1].

N-vinil-pirolidon je funkcionalni monomer koji se sastoji od peteročlanog laktama povezanog vinilinom skupinom, te njegovi polimeri imaju važne primjene kao što su filmovi za potencijalnu primjenu u proizvodnji kozmetike, tiskarskih boja, deterdženata, boja, ljepila, plastike, lijekova i farmaceutskih proizvoda [2].

Cilj ovog rada bio je karakterizirati hidrogelove priređene iz celuloze graftirane s *N*-vinil-2-pirolidonom i umrežene s *N*,*N*-metilen-*bis*-amidom (MBA) na dva načina; izravnom sintezom i zračenjem te usporediti njihova svojstva. Omjeri celuloze i *N*-vinil-2-pirolidona u reakcijskoj smjesi bili su 1:1, 1:3 te 1:5 mol/mol, dok je reakcijska smjesa naknadno podvrgavana zračenju od 10, 30 ili 100 kGy. Nakon sinteze hidrogelovi su oblikovani u sfere. Karakterizacija hidrogelova provedena je FTIR spektroskopijom i pretražnom elektronskom mikroskopijom. Temeljem omjera intenziteta karakterističnih vrpci pri 1645-1660 cm^{-1} i 897 cm^{-1} utvrđeno je značajno povećanje nakon zračenja s 10 kGy naspram hidrogela priređenog kemijskom sintezom. Pretražnom elektronskom mikroskopijom utvrđeno je da ozračivanje značajno doprinosi povećanju poroznosti pripravljenog hidrogela kao i da nakon osmotjednog bubrenja sfere pokazuju značajnu deformaciju oblika.

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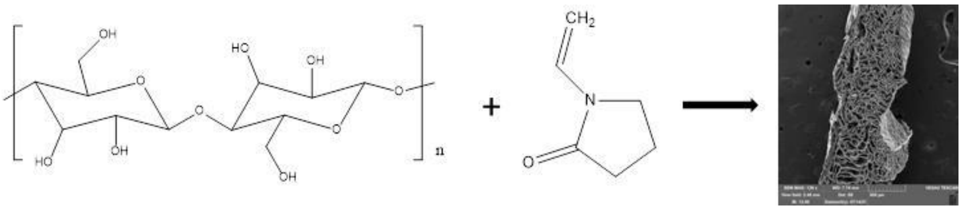
[2] E. Vidović, Polimerni biomaterijali, Predavanje 2, Fakultet kemijskog inženjerstva i tehnologije, Sveučilište u Zagrebu (2021)



PRIPRAVA I KARAKTERIZACIJA KOORDINACIJSKIH SPOJEVA NIKLA(II) S IMIDAZOLOM I ODABRANIM ORGANSKIM KISELINAMA

SYNTHESIS AND CHARACTERIZATION OF NICKEL(II) COORDINATION COMPOUNDS WITH IMIDAZOLE AND SELECTED ORGANIC ACIDS

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Dubravka Matković-Čalogović

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Koordinacijski spojevi imidazola s ionima esencijalnih metala od značaja su između ostalog zbog povezanosti s biološkim sustavima koji sadrže histidinski ostatak u svojoj građi. Priređen je i istražen niz metalnih kompleksa s imidazolom i njegovim derivatima kao modelnih sustava za metaloproteine, a mnogima je dokazano antibakterijsko i antitumorsko djelovanje. Strukturna karakterizacija koordinacijskih spojeva iona esencijalnih metala s navedenim ligandima te miješanih kompleksa derivata imidazola (*N*-donori) i odabranih organskih kiselina (*O*-donori) predstavlja još slabo istraženo područje. Koordinacijski spojevi iona biogenih metala s imidazolom i odabranim organskim kiselinama istražuju se i kao potencijalno funkcionalni porozni materijali [1-4].

U sklopu našeg proučavanja miješanih kompleksa nikla istražena je mogućnost povoljnih uvjeta nastajanja koordinacijskih spojeva nikla(II) s imidazolom i odabranim GRAS (engl. *Generally Recognized As Safe*) organskim kiselinama (pimelinska i sukcinska). U tu svrhu proveden je niz otopinskih i mehanokemijskih sintetskih reakcija. Dobiveni produkti analizirani su difrakcijom rendgenskog zračenja na polikristalnom uzorku. Produktu za kojeg su dobiveni pogodni monokristali, određena je kristalna i molekulska struktura metodom difrakcije rendgenskog zračenja. Dobiveni kompleksni spoj $[\mathrm{Ni}(\mathrm{C_3H_4N_2})_2(\mathrm{C_7H_{11}O_4})_2]$ kristalizira u monoklinskom sustavu, prostornoj grupi *C*2/*c*. Niklov kation je u nepravilnom oktaedarskom okruženju koordiniran s dva dušikova atoma iz imidazolnih prstena te s četiri kisikova atoma dviju karboksilatnih skupina pimelinskih kiselina. Molekule pimelinske kiseline kao didentatni ligand ostvaruju *O*,*O*'-kelatnu koordinaciju metalnog kationa preko jedne karboksilatne skupine. Molekule produkta međusobno se povezuju jakim vodikovim vezama tipa N–H···O i O–H···O.

[1] Y-J. Mu J-X. Xie, Y-G. Ran, B. Han, G-F. Qin, Polyhedron 89 (2015) 20-28.
[2] S. Rojas, T. Devic, P. Horcajada, J. Mater. Chem. B 5 (2017) 2560-2573.
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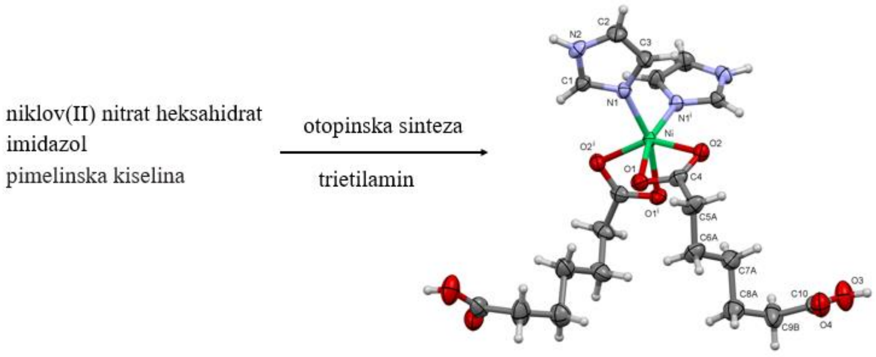

2,2'-BIPIRIDINSKI DERIVATI KAO AKCEPTORI HALOGENSKE VEZE U BINARNIM KRISTALIMA

2,2'-BIPYRIDINE DERIVATIVES AS HALOGEN BOND ACCEPTORS IN MULTICOMPONENT CRYSTALS

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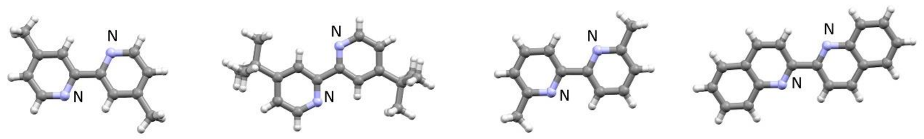
Molekula 2,2'-bipiridina opsežno je proučavana u kemiji koordinacijskih spojeva kao kelatirajući ligand zbog svojih svojstava poput stabilnosti i lakoće funkcionalizacije [1]. Također, 2,2'-bipiridin, kao i iz njega izvedeni derivati, pokazali su se kao zanimljive građevne jedinice u kristalnom inženjerstvu zbog svoje fleksibilnosti i sposobnosti stvaranja različitih supramolekulskih struktura. Upotrebljivost derivata 2,2'-bipiridina kao akceptora halogenske veze slabo je istražena. Akceptorska svojstva istražena su samo kod ariliranih 2,2'-bipiridina gdje je kao donor halogenske veze korišten 1,4-dijodotetrafluorbenzen [2]. U ovom radu istražen je utjecaj različitih alkilnih i arilnih supstituenata na 2,2'-bipiridinu, poglavito u položajima 4 i 6, na mogućnost kokristalizacije s različitim donorima halogenske veze kao što su perfluorirani halobenzeni i *N*-haloimidi. U tu svrhu korištena su četiri derivata 2,2'-bipiridina: 4,4'-dimetil-2,2'-bipiridin (**1**), 4,4'-di-tert-butil-2,2'-bipiridin (**2**), 6,6'-dimetil-2,2'-bipiridin (**3**) i 2,2'-bikinolin (**4**) koji su kokristalizirani sa sedam odabranih donora halogenske veze. Pretraživanje mogućnosti kokristalizacije provedeno je mehanokemijskom sintezom i kristalizacijom iz otopine. Nastali produkti okarakterizirani su difrakcijom rentgenskog zračenja na polikristalnom uzorku. Dobiveno je 14 kokristala od kojih je 10 strukturno okarakterizirano difrakcijom rentgenskog zračenja na jediničnom kristalu. Na temelju dobivenih strukturnih podataka uočeno je da promjenom donora halogenske veze dolazi do promjene konformacije 2,2'-bipiridina, odnosno da dolazi do promjene geometrije iz planarne u neplanarnu, što je posljedica pakiranja molekula u kristalu. Kao dominantna interakcija u gotovo svim kokristalima opažena je halogenska veza I···N.

[1] C. Kaes, A. Katz, M. W. Hosseini, Chem. Rev. 2000, 100, 3553–3590.

[2] R. Ramakrishnan, A. R. Mallia, M. A. Niyas, R. Sethy, M. Hariharan, Cryst. Growth Des. 2016, 16, 6327–6336.



(1) **(2)** **(3)** **(4)**

Slika 1. Korišteni derivati 2,2’-bipiridina

TERNARY COORDINATION COMPOUND OF COPPER(II), 1,10-PHENANTHROLINE AND L-THREONINE: INTERPLAY OF COORDINATION AND PROTONATION

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Ternary coordination compounds of copper(II), amino acids and heterocyclic bases are widely investigated due to their pronounced antiproliferative activity [1,2]. Such compounds are also interesting for investigation in crystal engineering since they are able to form predictive supramolecular synthons, such as π-stacked heterocyclic bases, or $N–H\cdots O_{anion}$ hydrogen bonds. They also form porous architectures making them good candidates for potential application in solvent or gas sorption [1].

In this work, we report synthesis and crystal structure of a novel ternary coordination compound of copper(II), 1,10-phenanthroline (phen) and L-threonine (HThr). In the asymmetric unit of crystal structure, three different coordination species are present: two cations of a type $[Cu(Thr)L(phen)]^+$ ($L = H_2O$ or CH_3OH) and an anion $[Cu(Thr)(SO_4)(phen)]^-$. Besides coordinated water and methanol molecules, crystallization water and methanol molecules are interconnected through hydrogen bonds forming discrete pockets (13% of the unit cell volume). Crystal structure also contains hydrogensulfate ions which form hydrogen bonds with coordinated sulfate ions (Figure 1).

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[2] L. Ruiz-Azuara, M. E. Bravo-Gómez, Curr. Med. Chem. 17 (2010) 3606-3615.

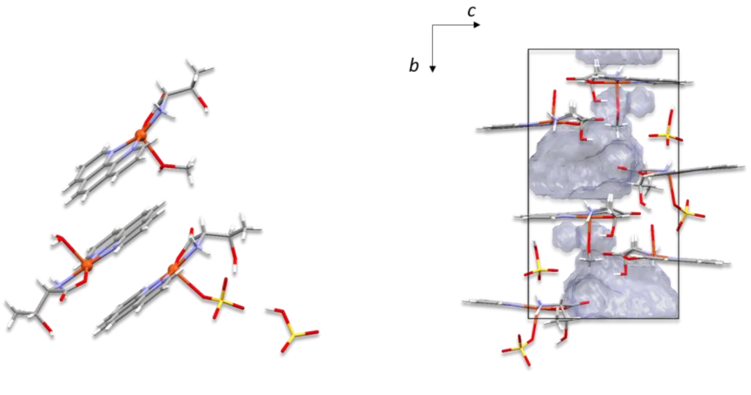

Figure 1. Asymmetric unit of the title compound (left) and pockets of crystallization water and methanol molecules (right). Water and methanol molecules of crystallization are omitted due to clarity.

KOKRISTALIZACIJA PIPERINA S PERFLUORIRANIM DONORIMA HALOGENSKE VEZE

COCRYSTALLIZATION OF PIPERINE AND PERFLUORINATED HALOGEN BOND DONORS

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Halogenska veza, privlačna je interakcija između elektrofilne regije koja sadrži atom halogena X i nukleofila B te tvori supramolekulsku interakciju X···B [1]. Kao takva, halogenska je veza predmet istraživanja supramolekulske kemije i kristalnog inženjerstva zadnjih nekoliko desetljeća. S obzirom na to da su atomi dušika i kisika dobri akceptori halogenske veze [2] moguće je pretpostaviti da će i brojne prirodne organske molekule biti prihvatljivi sučinitelji u tvorbi kokristala povezanih halogenskim vezama.

U ovom radu je metodom kontinuirane ekstrakcije kruto-tekuće iz mljevenog crnog papra izoliran piperin, (**pip**) te su istraživana svojstva piperinskih fukcijskih skupina kao akceptora halogenske veze, kisikovih atoma eterske i karbonilne skupine te piperidinskog dušikovog atoma. Sintezom iz otopine te tekućinom potpomognutom mehanokemijskom sintezom priređena su dva nova kokristala piperina s ditopičnim donorima halogenske veze: 1,4-dijodtetrafluorbenzenom, (**1,4tfib**) i 1,2-dijodtetrafluorbenzenom, (**1,2tfib**). Kristalizacijom iz otopine dobiveni su jedinični kristali kokristala (**pip**)(**1,4tfib**) i (**pip**)$_2$(**1,2tfib**) kojima je molekulska i kristalna struktura određena metodom difrakcije rendgenskog zračenja na jediničnom kristalu. U oba kokristala prisutne su halogenske veze I···O, u kokristalu (**pip**)(**1,4tfib**) one se ostvaruju između dvije neekvivalentne molekule **14tfib** s karbonilnim (d(I1···O1) = 2,796 Å, ∠ (C–I1···O1) = 173,2°) i eterskim kisikovim atomom (d(I2···O2) = 3,190 Å, ∠ (C–I2···O2) = 174,7°), dok se u (**pip**)$_2$(**1,2tfib**) one ostvaruju između molekule **12tfib** i karbonilnih kisikovih atoma dvije neekvivalentne molekule **pip** (d(I1···O1) = 2,990 Å, ∠ (C–I1···O1) = 170,3° ; d(I2···O2) = 2,854 Å, ∠ (C–I2···O2) = 172,13°). Vidljivo je da su u oba slučaja ostvarene halogenske veze linearne i kratke, s parametrima relativnog skraćenja od 8,8 % za eterski i 14–20 % za karbonilni kisikov atom, iz čega je moguće pretpostaviti da je karbonilni kisikov atom piperina dobar akceptor halogenske veze.

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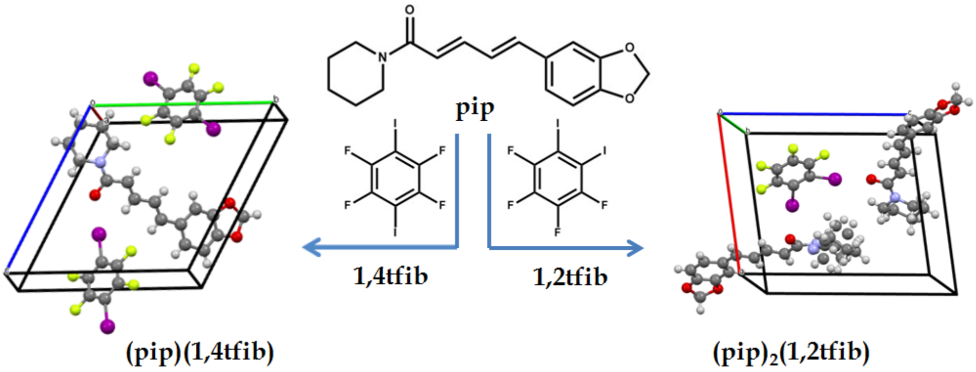

MIKROKAPSULE S I BEZ HITOZANA KAO ANTIMIKROBNA ZAŠTITA NA TEKSTILU

MICROCAPSULES WITH AND WITHOUT CHITOSAN AS AN ANTIMICROBIAL PROTECTIVE COATING ON TEXTILE

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Marko Vinceković[2], Slaven Jurić[2]

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Aktivna sredstva poput nanočestica srebra i srebrov ion poznati su po svojim antimikrobnim svojstvima. Različiti proizvodi koji sadrže navedena sredstva koriste se dugi niz godina u liječenju tegoba kao što su kronične rane. S ciljem izrade medicinskog proizvoda, upotrebom sol-gel postupka su na površinu tekstilnog supstrata nanesene i vezane mikrokapsule koje su u jezgri sadržavale srebrov nitrat, ili nanočestice srebra vezane natrijevim alginatom, plašt sačinjen od cinkovog sulfata, koji je u nekim uzorcima sadržavao i hitozan. Upotrebom ove recepture mikrokapsula omogućeno je kontrolirano otpuštanje antimikrobnog srebra. U ovome radu predstavljeni su rezultati otpuštanja Ag^+ iona u vodenom mediju dobiveni metodom UV/VIS spektrometrije. Zahvaljujući svojoj strukturi, tj. kemijskom sastavu, mikrokapsule su postigle kontrolirano otpuštanje, pri čemu su mikrokapsule koje su sadržavale hitozan otpuštale manje koncentracije Ag^+ iona u odnosu na mikrokapsule bez hitozana.

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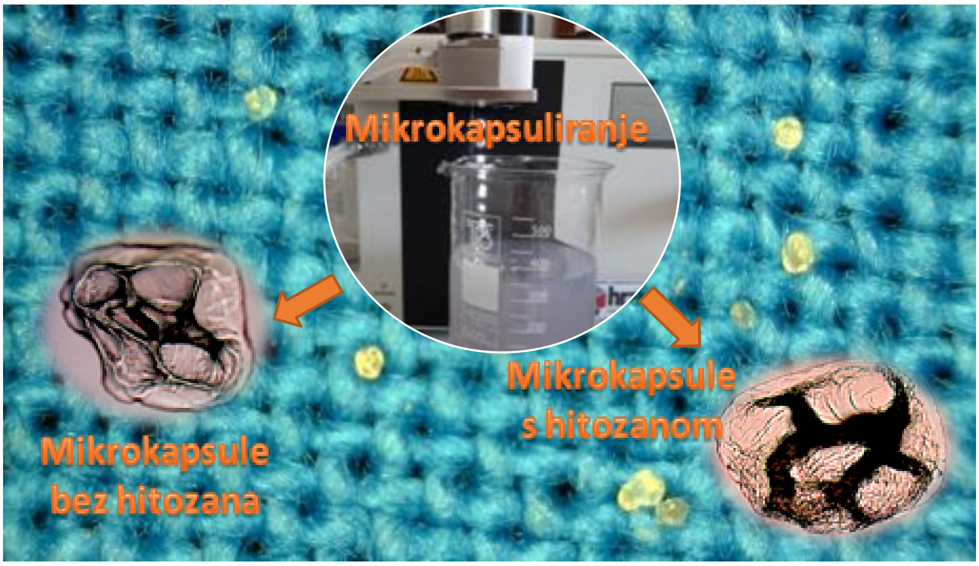

RAZVOJ SINTEZE AMINOSKVARAINA KAO FUNKCIONALNIH MATERIJALA U HIBRIDNIM FOTONAPONSKIM UREĐAJIMA

DEVELOPMENT OF AMINOSQUARINE SYNTHESIS AS FUNCTIONAL MATERIALS IN HYBRID PHOTOVOLTAIC DEVICES

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Solarne ćelije predstavljaju jedan od načina obnovljivog iskorištenja energije uz ekološku svjesnost. Prethodna istraživanja pokazala su da izvrsna svojstva i veliki potencijal za daljnji razvoj imaju ćelije izrađene od malih organskih molekula među kojima se posebno ističu aminoskvaraini [1]. Spojevi s visokim molarnim apsorpcijskim koeficijentom, izraženim i stabilnim optičkim svojstvima, te jednostavnom pripremom, skvaraini su sjajni kandidati za pripremu u organskim fotonaponskim ćelijama [2].

U ovom radu prikazani su rezultati razvoja novih simetričnih i asimetričnih aminoskvaraina, koji bi mogli predstavljati odgovor na zahtjeve za unaprjeđenje učinkovitosti i stabilnosti u području fotonaponskih uređaja. U svrhu optimiranja kemijske i mikrostrukturne kompatibilnosti sintetiziranih spojeva s drugim absorberima u fotonaponskom uređaju, priređena je i u potpunosti okarakterizirana serija različito supstituiranih skvaraina, te je ispitana primjenjivost istih u fotonaponskim sustavima.

[1] J. He, J. Jo, X. Sun, W. Qiao, J. Ok, T. Kim, Z. Li, Adv. Func. Mater. 31 (2020) 2008201
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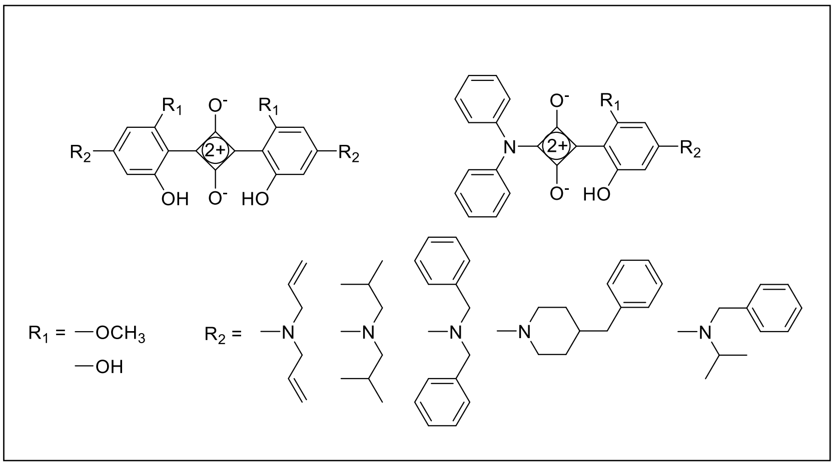

MEĐUMOLEKULSKE INTERAKCIJE OTOPINE POLIALKILMETAKRILATA U MAZIVOM ULJU PAO 4

INTERMOLECULAR INTERACTIONS OF POLYALKYLMETHACRYLATE SOLUTION IN LUBRICANT OIL PAO 4

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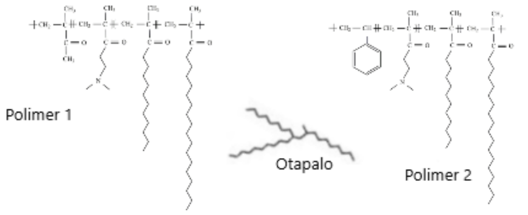
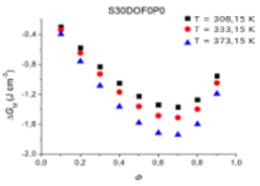
Alkil metakrilatni polimerni aditivi (PAMA) poznati su kao poboljšavala svojstava mazivih ulja poput reoloških svojstava, viskoznosti, indeksa viskoznosti i točke tečenja motornih i transmisijskih ulja. Široku primjenu ovih polimernih aditiva jednakog osnovnog lanca omogućavaju dobro definirana struktura i sastav, a ono iz čega proizlaze različita svojstva metakrilatnih polimera jesu bočni lanci različite duljine i strukture. Također, inkorporacijom stirena u lanac (PSAMA), dobivaju se polimeri poboljšane toplinske stabilnosti. Toplinsko-oksidacijskom razgradnjom mazivog ulja mogu nastati polarni produkti koji se talože i stvaraju mulj na vitalnim dijelovima motora. Uvođenjem funkcionalnog komonomera koji sadrži polarni kisikov ili dušikov atom u bočnom lancu postižu se disperzantna svojstva čime se smanjuje potrošnja goriva i poboljšava mazivost.
Aditivi su u ovom istraživanju sintetizirani radikalskom kopolimerizacijom stirena ili metil metakrilata s dodecil metakrilatom, oktadecil metakrilatom u molarnim udjelima od 30 do 35 % dok je funkcionalni dimetilaminoetil metakrilat dodavan u manjem udjelu od 0 do 10 mol.%. Kako bi se dobio uvid u interakcije PAMA i PSAMA aditiva izračunati su parametri međudjelovanja (Λ_{12}) i Gibbsove energije miješanja (ΔG^{M}), korištenjem Coleman, Graf i Painter metodologije. Rezultati ukazuju da povećanjem udjela DMAEMA dolazi do povećanja parametra međudjelovanja što ukazuje na smanjenje interakcija između kopolimera i mazivog ulja. Također, ΔG^{M} vrijednosti su negativne, što ukazuje na mješljivost u sustavu.





EFFECT OF METAL SUBSTRATE ON PROPERTIES OF POLY(ALLYLAMINE HYDROCHLORIDE) / POLY(ACRYLIC ACID) MULTILAYER

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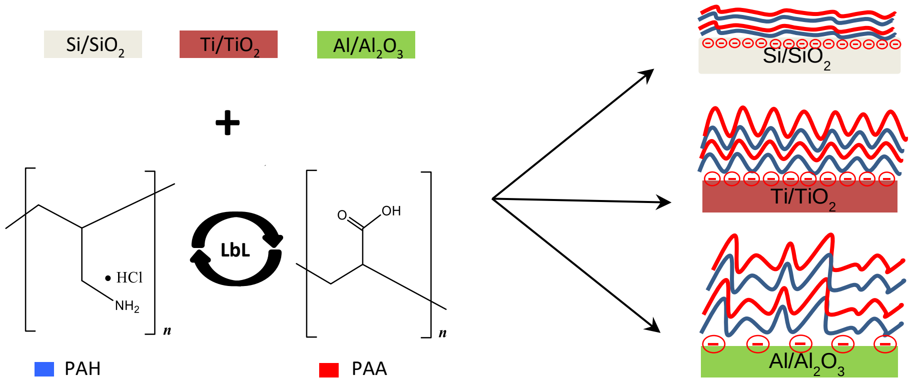
Polyelectrolytes are macromolecules that consist of a repeating sequence of subunits which can be charged in the solution. Positively charged polyelectrolytes are called polycations, while negatively charged are called polyanions. Polyelectrolyte multilayers are films which are formed by alternating adsorption of polycations and polyanions on a surface, most often with layer-by-layer (LbL) method. The properties of a film depend on the polyelectrolyte type, as well as on experimental conditions such as pH, ionic strength, type of the background salt and used substrates. Polyelectrolyte multilayers are also particularly interesting due to their wide application in medicine and biotechnology, especially as antibacterial protection. The aim of presented study was to show how the type of metal substrate affects the properties of multilayer prepared from poly(allylamine hydrochloride), PAH, and poly(acrylic acid), PAA. Commercially available silicon, titanium and aluminum plates were used as metal substrates. The metal substrates were characterized by ellipsometry, atomic force microscopy and contact angle measurements. Afterwards, ten-layer films were prepared on the mentioned substrates and the growth (thickness) of multilayers was monitored by ellipsometry. The morphology and surface roughness of the prepared multilayers was determined by atomic force microscopy. It was observed that the thickness and surface roughness of films increase depending on the used substrate in the order: silicon, titanium and aluminum. These differences could primarily be explained by isoelectric points of used substrates which follow the same trend.

This research was supported by the Croatian Science Foundation under the bilateral Slovenian-Croatian APPLPEMS project (IPS-2020-01-6126).



MECHANICALLY INDUCED FLEXIBILITY OF COPPER(II) COORDINATION POLYMERS CRYSTALS

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It has been noted that inducing mechanical force on crystals could result in distinctive responses: brittle crystals will crack during the application of mechanical force while flexible crystals will bend plastically or elastically in response to mechanical stress [1]. Prompted by recently reported bendability of crystalline coordination compounds [2, 3] we decided to investigate analogous metal-organic systems of copper(II) equipped with pyridine derivatives as ligands, namely $[CuCl_2(4\text{-methylpyridine})_2]_n$ (**1**) and $[CuBr_2(4\text{-methylpyridine})_2]_n$ (**2**). Layering technique was employed for synthesis and crystallization, and it was observed that ethanol and isopropanol produce single crystals of the required quality for further examination. The resulting compounds were characterized by powder X-ray diffraction (PXRD) and molecular and crystal structures were determined using single-crystal X-ray diffraction (SCXRD). Needle-like crystals were isolated and subjected to bending experiments in order to study their mechanical properties. The type of mechanical response was examined using the modified three-point bending method and it was determined that compound **2** showed plastic behavior, unlike compound **1** for which elastic responsiveness was observed, hence the degree of elasticity was calculated.

This research was supported by the Croatian Science Foundation under the project IP-2019-04-1242.

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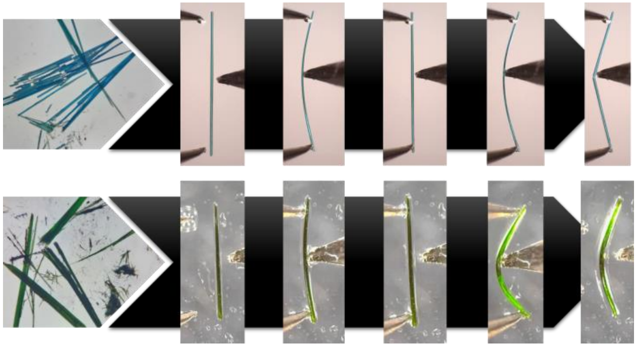

PRIPRAVA MEZOPOROZNE SILIKE

SYNTHESIS OF MESOPOROUS SILICA

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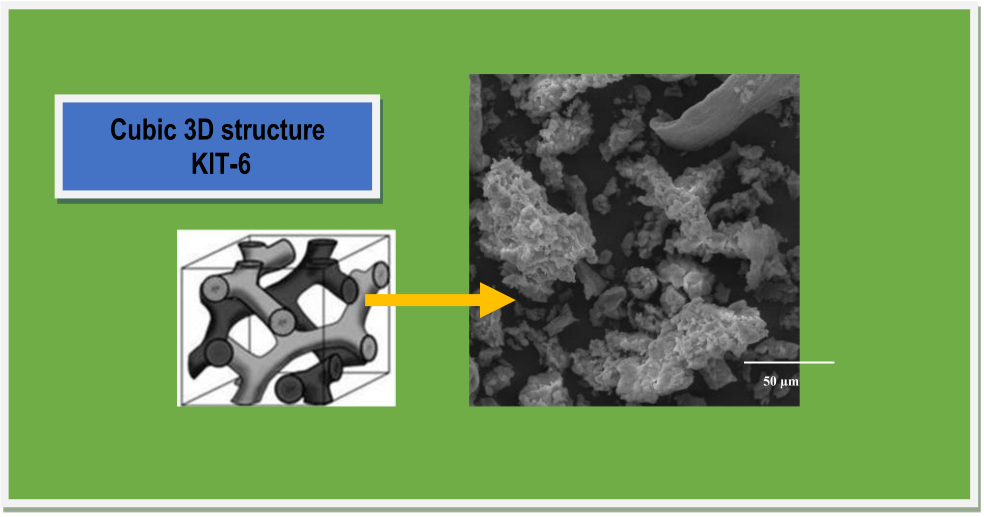
Mesoporous materials are materials that have pore diameter values between 2 and 50 nm according to the IUPAC nomenclature. Due to their unique properties, they have gained a considerable amount of attention within the fields of catalysis, adsorption and ion exchange. Thanks to great specific surface area (SSA) of mesoporous materials, they also play an important role in the synthesis of numerous ceramic materials via the nanocasting technique. Two main structures of mesoporous silica are usually being considered in scientific investigations, and those are the hexagonal SBA-15 (sometimes also known as pseudo-1D structure), and the cubic KIT-6 (3D structure). The goal of this work is to prepare KIT-6 mesoporous silica which will serve as a nanocasting template. The characterization of the material is done using several different characterization techniques, such as FTIR, XRD, N_2 adsorption-desorption isotherms, DTA-TGA, SEM and EDX. Silica was prepared using various aging temperatures (60, 100, 140 °C) which affect the pore sizes and distribution, directly influencing the SSA. In theory, the higher is the aging temperature, the larger are the pores. Different samples were characterized and it has been found that highly pure silica was obtained. Also, it has been proven that the increase of the aging temperature results in the increase of pore size values and SSA (up to 900 m^2 g^{-1}). The relatively easy control of the pore size and distribution, as well as quick and safe template removal make silica-based mesoporous materials very suitable nanocasting agents and open up an opportunity for further development.



UTJECAJ TEMPERATURE NA DJELOTVORNOST INHIBITORA KOROZIJE

INFLUENCE OF TEMPERATURE ON THE EFFECTIVENESS OF CORROSION INHIBITORS

Antonio Pelesk, Helena Otmačić Ćurković

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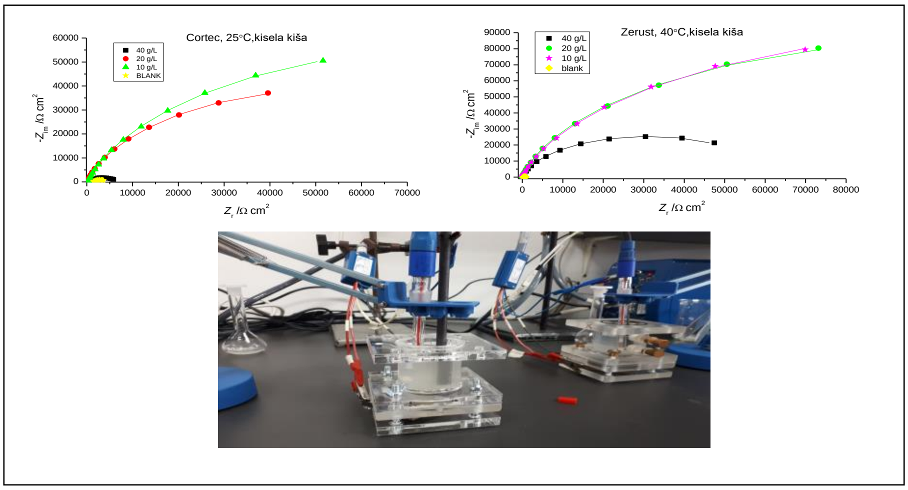
U industriji korozijska zaštita čeličnih konstrukcija je oduvijek bila izazov. Kako bi se postigla zaštita, sve češće su prisutni hlapljivi inhibitori korozije (engl. *Volatile Corrosion Inhibitors*, *VCI*). Ovo istraživanje ima za cilj poboljšati razumijevanje utjecaja temeperature i sastava okoliša na djelotvornost hlapivih inhibitora. U istraživanju će se ispitati djelovanje dvaju komercijalnih praškastih inhibitora korozije na koroziju ugljičnog čelika u otopinama koje simuliraju uvjete u morskom i onečišćenom urbanom okolišu. Ispitivanja su provedena elektrokemijskim metodama - elektrokemijskom impedancijskom spektroskopijom (EIS) i Tafelovom polarizacijom u dva korozijska medija (kisela kiša pH = 6,5; vodena otopina 1 % NaCl) pri 25 i 40 °C. Ispitivanje je rađeno s dva hlapiva inhibitora pri različitim koncentracijama u korozivnom okruženju kako bi se proučila njihova inhibicijska učinkovitost. Na temelju dobivenih rezultata zaključeno je da oba inhibitora smanjuju brzinu korozija čelika pri obje ispitivane temperature, ali da je njihova djelotvornost manja u mediju koji sadrži kloride.



NANOŠENJE ELAIDINSKE KISELINE NA POVRŠINU BAKRA ZA PRIPREMU POLIMERNIH NANOPREVLAKA UMREŽENIH PRIMJENOM γ-ZRAČENJA

APPLICATION OF ELAIDIC ACID ON THE SURFACE OF COPPER FOR PREPARATION OF POLYMER NANOCOATINGS CROSSLINKED USING γ - IRRADIATION

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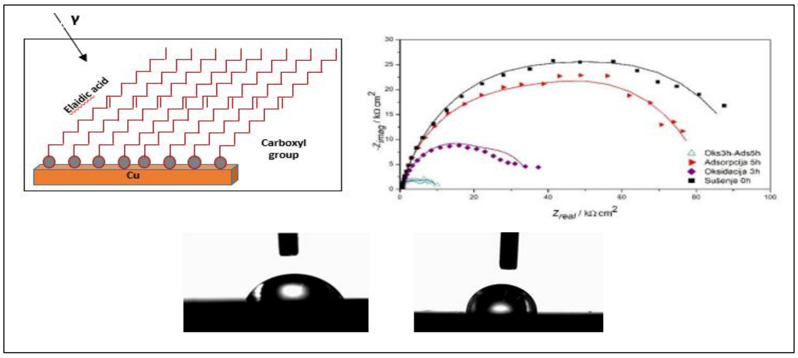
Metali se sve više koriste u svim područjima našeg života. Kako bi spriječili njihovu degradaciju i ostale neželjene posljedice prouzročene djelovanjem korozije, istražuju se nove metode zaštite koje bi trebale biti jednostavnije, jeftinije te bez negativnog utjecaja na okoliš. Jedna od takvih metoda je formiranje samoorganizirajućih molekularnih slojeva (SAM) na površini metala. SAM-ovi su kemisorbirani slojevi molekula koji se iznimno lako nanose, ali isto tako u agresivnim sredinama ih je relativno lako ukloniti sa površine. Umrežavanjem SAM-ova nastaje polimerna prevlaka nano debljine koja u usporedbi sa SAM-om ima veću čvrstoću, dugotrajnost zaštite, otpornija je na prodiranje molekula iz okoliša i dr. Radijacijsko umrežavanje je postupak u kojem se ionizirajuće zračenje koristi za poticanje brzih kemijskih reakcija između monomera i/ili polimera koji se odvijaju uz pomoć slobodnih radikala. Umrežavanje uzrokovano zračenjem je homogeno, brzo i provodi se bez upotrebe često toksičnih otapala ili inicijatora.

U ovom radu ispitivan je utjecaj postupka nanošenja SAM-ova elaidinske kiseline (EA) na površinu bakra, na zaštitna svojstva polimernih nano-prevlaka umreženih γ-zračenjem. Ispitan je utjecaj različitih koncentracija EA i vremena uranjanja bakra u otopinu. Optimalni postupak je uspoređen sa metodom nanošenja EA prskanjem i kistom. Ispitivanja zaštitnih svojstava dobivenih prevlaka su provedena pomoću elektrokemijskih metoda (metoda Tafelove ekstrapolacije i elektrokemijska impedancijska spektroskopija te metoda linearne polarizacije). Goniometrija se koristila za određivanje hidrofobnosti dobivenih polimernih nano-prevlaka. Rezultati su pokazali da je optimalno vrijeme uranjanja (adsorpcija) od 24 h uz oksidaciju od 24 h i bez sušenja. Pri istim uvjetima su uspoređivane metode nanošenja EA na površinu bakra. Sve tri metode nanošenja EA ukazuju na bolja zaštitna svojstva u odnosu na čisti bakar, s opadajućim redoslijedom zaštite: metoda uranjanja, nanošenje kistom te prskanje.

We thank the Croatian Science Foundation (HRZZ IP-2020-02-4344) for supporting the research.



KOOPERATIVNOST HALOGENSKE I PNIKOGENSKE VEZE U KOKRISTALIMA IMINA IZVEDENIH IZ 2-NITROBENZALDEHIDA

COOPERATIVITY OF HALOGEN AND PNICOGEN BONDS IN COCRYSTALS OF 2-NITROBENZALDEHYDE DERIVED IMINES

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Proučavanje halogenskih veza i ostalih interakcija σ-šupljine u višekomponentnim sustavima jedno je od najbrže rastućih područja kristalnog inženjerstva i supramolekulske kemije [1,2]. U kristalnim strukturama različite interakcije σ-šupljine mogu se ostvariti istovremeno, a u tim slučajevima postoji međusobni utjecaj na njihove geometrije, jakost i usmjerenost [3]. Jedna od funkcijskih skupina koja može potencijalno stvarati i halogenske i pnikogenske veze je nitro skupina [4,5].

Kako bi istražili međusobni odnos tih dviju interakcija, u našem istraživanju kristalizacijom iz otopine i tekućinski potpomognutim mljevenjem sintetizirani su imini izvedeni iz 2-nitrobenzaldehida (**nba**) i 4-halogenanilina (**Xan**, X = Cl, Br, I) te njihovi kokristali s 1,3-dijodtetrafluorbenzenom (**13tfib**) i 1,3,5-trijodtrifluorbenzenom (**135tfib**) kao donorima halogenske veze. Rentgenska strukturna analiza potvrdila je uspješnu sintezu šest kokristala stehiometrije 1:1. U svim kokristalima ostvarene su halogenske veze $N_{imin}\cdots I$ između imina i donora halogenske veze, dok su u pet kokristala dodatno ostvarene pnikogenske veze $N_{nitro} \cdots O_{nitro}$ i π-nitro interakcije.

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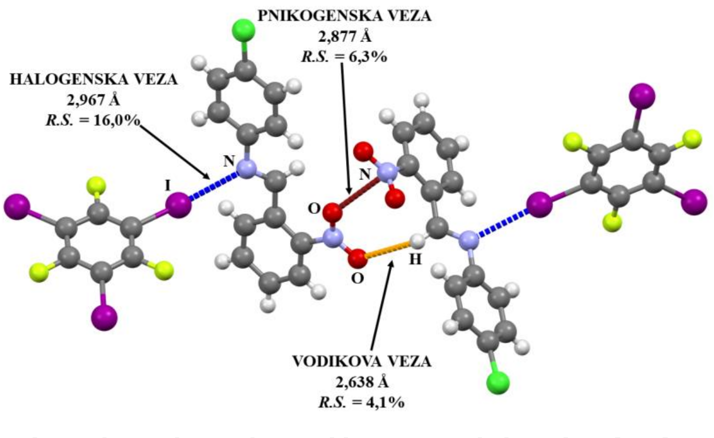

Slika 1. Halogenska, pnikogenska i vodikova veza u kokristalu (**nbaClan**)(**135tfib**)

IZOTIOCIJANTNI SUMPOR KAO AKCEPTOR HALOGENSKE VEZE U KOKRISTALIMA S WERNEROVIM KOORDINACIJSKIM SPOJEVIMA

ISOTHIOCYANATE SULPHUR AS A HALOGEN BOND ACCEPTOR IN COCRYSTALS CONTAINING WERNER COORDINATION COMPOUNDS

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Najviše istraživanja halogenske veze u vidu neutralih akceptora napravljeno je u kokristalima koji sadrže atome dušika i kisika različite funcionalnosti. Sustavi koji sadrže sumpor u ulozi akceptora halogenske veze značajno su manje istraženi. Pretraživanjem baze CSD za izotiocianatni sumpor koordiniran na metal kao akceptor halogenske veze pronađeno je samo četiri slučaja takve interakcije [1]. Riječ je o kokristalima koji sadržavaju komplekse $Co(C_5H_5N)_4(NCS)_2$ ili $Ni(C_7H_7N)_4(NCS)_2$, a koji se svrstavaju u Wernerove koordinacijske spojeve [2]. Wernerovi koordinacijski spojevi su skupina spojeva opće formule MX_2L_2, gdje je M= Ni(II), Co(II), Fe(II), Cu(II), Mn(II), dok je L supstituirani piridin ili α-arilalkilamin [3]. Kako ne postoji sistematično istraživanje halogenske veze s takvim građevnim blokovima, napravljeno je istraživanje na dva Wernerova koordinacijska spoja, koji sadrže isti metalni centar, a razlikuju se samo po metilnoj skupini na ligandu: $Ni(C_5H_5N)_4(NCS)_2$ (**1**) i $Ni(CH_3C_5H_5N)_4(NCS)_2$ (**2**). Navedni kompleksi kokristalizirani su s perhalogeniranim donorima halogenske veze kako bi se izučio akceptorski potencijal izotiocijanatnog sumpora te proučio utjecaj liganda na nastanak supramolekuskih arhitektura. Kao koformeri odabarane su molekule različitih geometrijskih svojstava: 1,2-dijodtetrafluorbenzen (**12tfib**), 1,3-dijodtetrafluorbenzen (**13tfib**), 1,4-dijodtetrafluorbenzen (**14tfib**) i trifluor-1,3,5-trijodbenzen (**135tfib**). Pretraživanje mogućnosti kokristalizacije provedeno je mehanokemijskom sintezom i kristalizacijom iz otopine, uz karakterizaciju nastalih produkata difrakcijom rentgenskog zračenja na polikristalnom uzorku. Dobiveno je osam kokristala, od kojih je šest okarakterizirano difrakcijom rentgenskog zračenja na jediničnom kristalu. Utvrđeno je da je u sintetiziranim kokristalima dominantna interakcija I···S halogenska veza, dok metilna skupina na ligandu utječe značajno na ostvarivanje supramolekulskih arhitektura.

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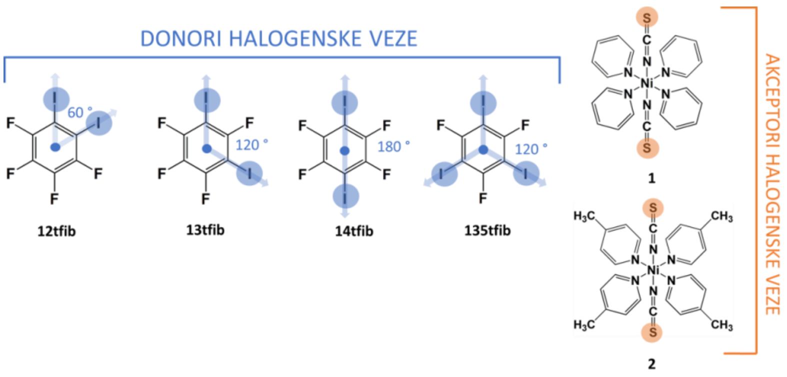

NISKOTEMPERATURNO PONAŠANJE MJEŠAVINA DIZELSKOG GORIVA I ADITIVA NA BAZI 2-(TERT-BUTILAMINO) ETIL METAKRILATA

LOW-TEMPERATURE BEHAVIOR OF DIESEL FORMULATIONS WITH 2-(TERT-BUTYLAMINO)ETHYL METHACRYLATE BASED ADDITIVES

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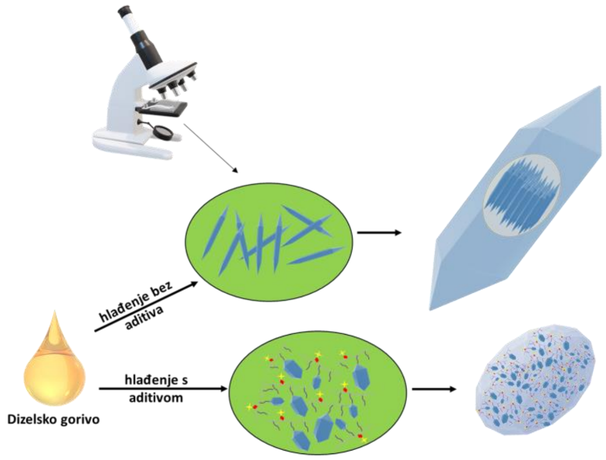
Niske temperature dovode do poteškoća u primjeni dizelskog goriva najčešće povezanih s kristalizacijom parafinskih komponenata dizela. Pri nižim temperaturama parafini kristaliziraju pretežito u kristale igličastog oblika koji se izdvajaju iz dizela i poprečno povezuju tvoreći 3D mrežu. Kao posljedica tog povezivanja dolazi do začepljenja pora filtera goriva u vozilima. Kako bi se navedeno spriječilo, dodaju se aditivi koji poboljšavaju niskotemperaturna svojstva dizela. Njihovim dodatkom moguće je promijeniti veličinu i oblik parafinskih kristala te njihov mehanizam nastanka. Aditivi za poboljšanje niskotemperaturnih svojstava uglavnom su polimeri. Njihova struktura obično se sastoji od nepolarnog alkilnog dijela, tj. bočnog lanca, i polarnog dijela, tj. polarnih skupina. Kada je bočni alkilni lanac slične duljine kao parafini u dizelu, dolazi do kristalizacije i tvori se novi centar nukleacije dok polarni dio utječe na parafinske kristale ograničavajući njihovu veličinu i mijenjajući njihov oblik. U ovome radu istraživan je učinak niza polimernih aditiva na osnovi metakrilata na niskotemperaturno ponašanje neaditiviranog dizela. Serija sintetiziranih aditiva uključivala je kopolimere s različitim molarnim sadržajem dugolančanih i kratkolančanih metakrilata te konstantnim molarnim sadržajem 2-(tert-butilamino) etil metakrilata (TBAEMA). Niskotemperaturno ponašanje promatrano je uz pomoć optičkog mikroskopa s polarizacijom te uz pomoć diferencijalne pretražne kalorimetrije (DSC). Rezultati mikroskopije pokazali su promjenu oblika kristala iz igličastog u sferični uslijed čega je došlo i do sniženja temperature kristalizacije u odnosu na neaditivirani dizel prilikom DSC analize.



ANALIZA POLIALKILMETAKRILATNIH ADITIVA U MAZIVOM ULJU DIFERENCIJALNOM PRETRAŽNOM KALORIMETRIJOM

ANALYSIS OF POLYALKYLMETHACRYLATE ADDITIVES IN LUBRICATION OIL WITH DIFFERENTIAL SCANNING CALORIMETRY

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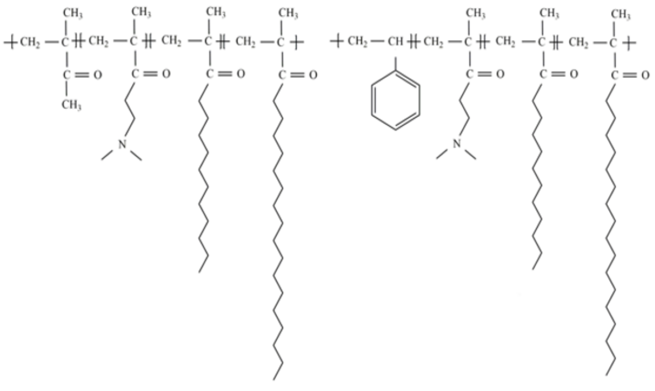
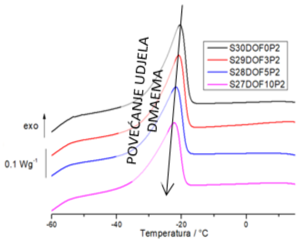
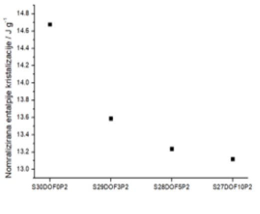
Polialkilmetakrilatni aditivi (PAMA) već se široko primjenjuju u mazivim uljima zahvaljujući tome što ih se vrlo jednostavno može kemijski izmijeniti dodatkom različitih metakrilatnih komonomera zbog slične kopolimerizacijske aktivnosti. Koriste se u cilju poboljšanja reoloških svojstava, indeksa viskoznosti te kao snižavala točke tečenja. Ukupni sastav kopolimera potrebno je poboljšati kako bi se, osim već navedenih, mogli ispuniti zahtjevi za oksidacijskom, toplinskom i smičnom stabilnosti kao i dobrom topljivosti u mazivom ulju. Ono što definira svojstva metakrilatnih aditiva su bočni lanci različite strukture. Kokristalizacijom s parafinima iz ulja snižavala tecišta sprječavaju stvaranje gela i taloženje kristala pomoću dugačkih nepolarnih bočnih lanaca koji formiraju strukturu sličnu češlju. Također, moguće je postići i disperzantna svojstva aditiva inkorporacijom polarnog heteroatoma u bočni lanac, poput dušika ili kisika.

Za ispitivane PAMA i PSAMA aditive koji sadrže funkcionalni dimetilaminoetil metakrilat (DMAEMA) u mazivom PAO 4 ulju diferencijalnom pretražnom kalorimetrijom utvrđeno je da s povećanjem udjela DMAEMA (0 – 10 mol. %) dolazi do sniženja temperature (za do 4 °C) i entalpije kristalizacije (za do 30 %) te udjela kristalne faze kopolimera (za do 25 %). Također, utvrđeno je da povećanjem molekulske mase polimera dolazi do smanjenja temperature kristalizacije ulja.







LA-ICP-MS KARAKTERIZACIJA ANTIMIKROBNIH POLIMERA

LA-ICP-MS CHARACTERIZATION OF ANTIMICROBIAL POLYMERS

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Nanočestice metala i metalnih iona vrlo se često koriste kao učinkovita antimikrobna sredstva na raznim polimerima. Primjena im je raširena u mnogobrojnim suvremenim materijalima: medicinskim materijalima, sportskoj i vojnoj opremi te u predmetima za posebnu namjenu. Problem karakterizacije takvih sofisticiranih materijala predstavljaju koraci uzimanja i pripreme uzorka kojima se ponekad narušavaju osnovna svojstva analita. U ovom će radu stoga biti predstavljena LA-ICP-MS metoda kojom je moguće dobiti točne i pouzdane rezultate kvalitativne i kvantitativne analize više elemenata u tragovima, čak i bez pripreme uzoraka. LA-ICP-MS sustavi visoke razlučivosti obuhvaćaju radno koncentracijsko područje od pg/L do mg/L i posebno su pogodni za istraživanje i karakterizaciju materijala. U svrhu validacije metode mjerenja će biti provedena na certificiranim referentnim materijalima nanočestica metala srebra, definiranih svojstava (koncentracije, veličine, morfologije). Validirana će metoda biti primijenjena na realnim uzorcima antimikrobnih medicinskih materijala s mikrokapsulama ispunjenim srebrovim nanočesticama.

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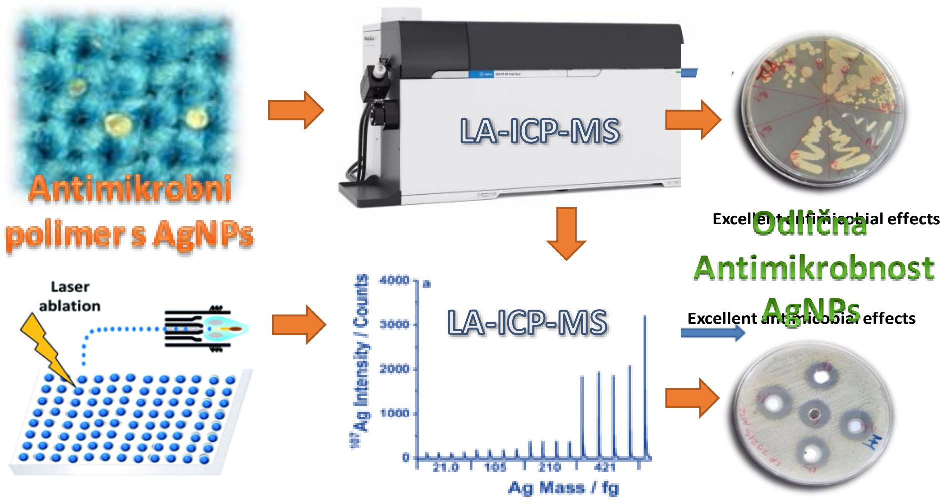

OVERVIEW OF ELECTROACTIVE AND CONDUCTIVE POLYMERS AND THEIR USE IN BIOMEDICINE AS ELECTROSPUN BIOSCAFFOLDS FOR TISSUE AND NERVE REPAIR

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Electroactive/conductive polymers (EAP/ECP) are showing good results as medical textiles for tissue and neural engineering. Applying curent through electroactive textile cells show promising results, where electric stimuly helps faster and better growth of cells on textile scaffolds. Because of their electrical conductivity textiles made of electroactive polymers are great for mimicking real body enviroment where cells are electricly stimulated for growth. Electrical signals are produced and sensed by all cells, not just nerves and muscles; in vivo, these activities build bioelectric circuits that direct individual cell behaviors toward specific anatomical goals. Electrospinning is the best candidate for producing novel electroactive textile meshes that mimic extracelullar matrix. New fields of research is needed on electrospun electroactive polymers, biodegredable and nondegredable textiles. There is a demand for this kind of materials to help diseeses like motor neuron disease, Alzheimer's disease, neurological scoliosis, spinal muscular atrophy (SMA), injured/cut spinal cords. Polymers like polypyrrole (PPy), polyaniline (PANI), polythiophene (PT), polyvinylidene fluoride (PVDF), poly(vinylidene fluoride–trifluoroethylene) (P(VDF–TrFE)) and polyurethane display good electrocunductive properties which can be used in further exploring the electrospun electroactive/conductive textiles fields of study [1,2]. Incorporation of EAP-s with cells brings us closer to achivieng the goal of developing textile composites of organic and non-organic materials that are interweaved and functional together.

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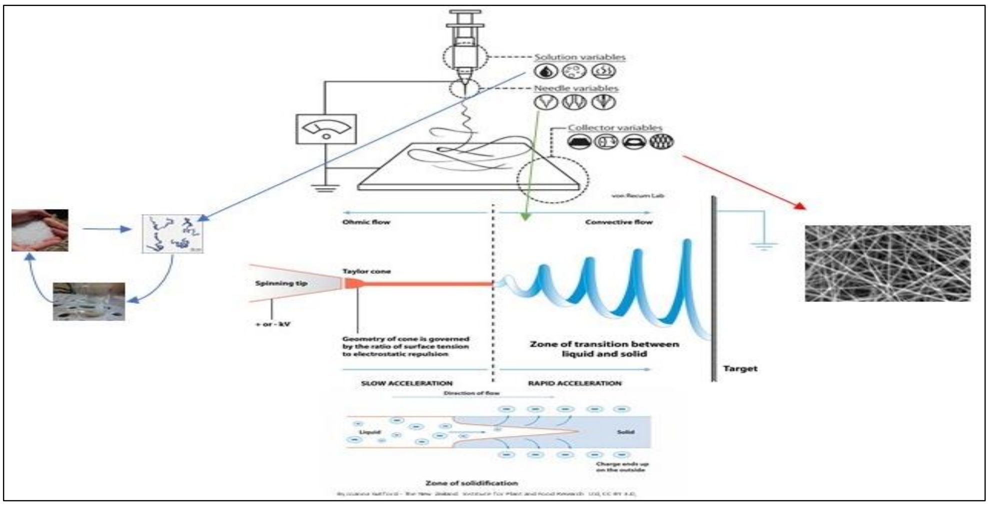

DESIGN OF POROUS CERAMIC BLOCKS BASED ON CLAY MATERIAL AND DIFFERENT PORE FORMING AGENTS

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Porous ceramic blocks are a type of ceramic products that are widely used in private and commercial construction. They are obtained by shaping, drying, and thermal treatment of a plastic mixture of clay material, by adding easily combustible materials. The porous ceramic blocks are one of the most widespread clay products together with bricks. Their porous structure and low heat conductivity are effective tools for improving indoor comfort and for reducing energy consumption. Moreover, binder consumption during masonry and plastering is significantly lower due to the smaller number of joints on the same wall surface and greater precision in the formation of flat walls. Additionally, the advantages of using porous ceramic blocks are fire protection as well as resistance to deformation [1-2].
In this paper, three systems of raw material composites were prepared and tested: composite 1 (low grade clay 100 wt.%), composite 2 (low grade clay 95 wt.% and PEG 2000 5 wt.%), composite 3 (low grade clay 99 wt.% and sawdust 1 wt.%). The raw material components are weighed, manually homogenized, and shaped by pressing into the molds. The samples were allowed to dry for 24 hours under atmospheric conditions, then the drying process was continued in an oven at 105 °C for a period of 1 h. All three systems were treated with the same thermal treatment (maximal temperature 980 °C). The valorization of the raw material composites, as well as of the final products, included the chain of activities, from thermal and chemical-mineralogical characterization, morphological characteristics, particle size distribution, to the textural and mechanical characterization and microstructure by the electron microscopy. The gained results verify the suitability of the used porous ceramic blocks production technology. Produced ceramic blocks are materials with high porosity and adequate mechanical properties, and they could be classified as an effective tool for improvement of the indoor comfort.

The authors would like to acknowledge the support from Ministry of Education, Science and Technological Development (Serbia), project No.: 451-03-9/2022-14/200134.

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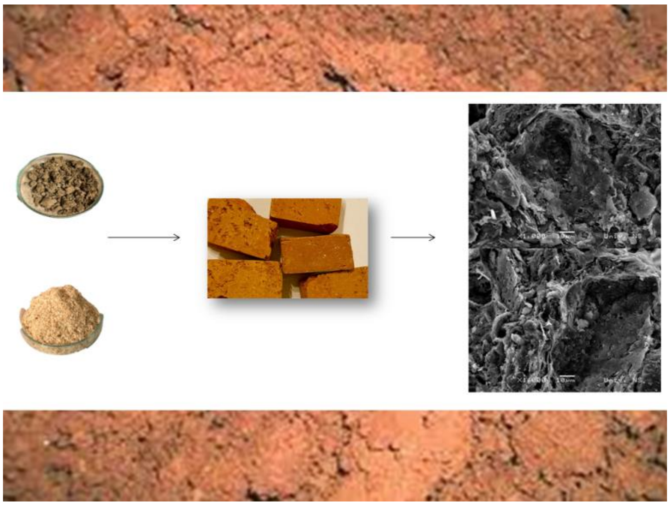

DETERMINATION OF THE OPTIMAL FORMULATION AND COATING PARAMETERS OF BEE PRODUCT ON TEXTILE SUPSTRATE

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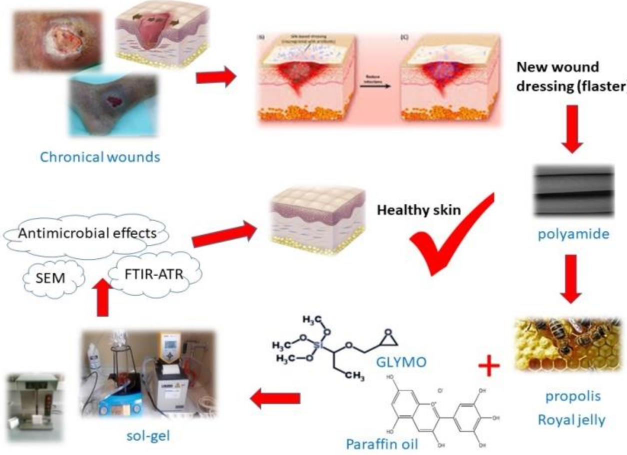
According to the World Health Organization, it is common knowledge that bacterial resistance to antibiotics is one of the major threats to global health. Infections caused by resistant bacteria affect the entire health system where infection with a resistant strain can happen to anyone. Things get more difficult if the wounds heal slowly and require specific medical care. Medical dressings are used to treat such wounds, where the textile plays an important role as a carrier of drugs. The emphasis is on finding new ways of treatment, the application of drugs to textiles, where nature is an inexhaustible source of ideas, especially bee products. Royal jelly and propolis are one of the bee products that have many medicinal properties. Propolis consists of resin, wax and essential oils, vitamins and minerals, but the emphasis is on flavonoids. Flavonoids are found in plant resin and become pharmacologically active by the enzymatic modification that bees make when making propolis. They, in combination with other components of propolis, carry most of the positive effects that propolis has. Propolis has the properties of antibiotics, anaesthetics, antioxidants and antiseptics, so it works great against most viruses, but also fungi and parasites. This paper was focused on the research of the possibilities provided by the application of inorganic-organic substances with royal jelly and propolis, but also the application of natural substances themselves for the modification of polyamide nonwoven textiles. The basic construction characteristics of polyamide nonwoven textiles have been determined. 3-glycidyloxypropyltrimethoxysilane (GLYMO) as the precursor and paraffin for the second treatment were selected. Propolis and royal jelly in stoichiometric proportions to each of the treatments were added. The morphological characteristics of the samples were determined by scanning electron microscope (SEM) and the analysis of samples in the infrared region was performed with the addition for surface analysis (FTIR-ATR). For modified samples by sol-gel process or with the use of only natural means, it is assuming that they could find application in the field of medical textiles (compresses, bandages, plasters, etc.). Given this purpose, the aim of this paper was to find a formulation with as much natural composition as possible, due to ecological requirements, but also the previously mentioned high resistance of bacteria.



RESEARCH AND DEVELOPMENT OF WOUND DRESSINGS WITH BIODEGRADABLE TEXTILE CARRIER

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Skin is a great barrier protecting human body which possesses excellent regenerative properties. Today there is almost no person who has not had a mechanical injury of the skin or mucosa during his life. Sometimes wounds do not heal in a timely fashion, and they require a special approach to healing. Such wounds are called chronic wounds and are treated with systemic and local treatment procedures. There is a large number of products on the market that are combined in treatment, which is expected given the different metabolism of patients (Actisorb Silver 220, Arglaes etc.). In some patients, biofilm is forming; this process takes place very quickly, within a day or two and intensifies inflammation, inhibiting extracellular matrix deposition and tissue repair [1]. This condition places the patients in significant danger and recurrent surgical procedures (wound debridement or even tissue amputation). Existing wound care products have significantly improved the patient care but cannot address the multifactorial nature of impaired wound healing. The ideal wound dressings are supposed to cover the wound, preserve the body water content, be oxygen permeable to allow oxygen access to growing tissue, and prevent the growth of environmental pathogens without interfering with the wound healing [2].
By making dressings for chronic wounds in several layers with the newer methods of textile technology (3D fabrics, fabrics/knits/nonwoven of electrospun fibers) from biodegradable polymers (PGA, PLA, PDS) with active substances, it is possible to contribute to more successful healing of chronic wounds. Active substances (Ag^+, metal/metal oxide nanoparticles, propolis, etc.) are released by different mechanisms of action (pH, chemical bonds, temperature) certainly contribute to the process of local treatment of chronic wounds. The utilized materials are biodegradable and immunocompatible, and do not support cell ingrowth and cellular adhesion so to avoid complications if removal is necessary.

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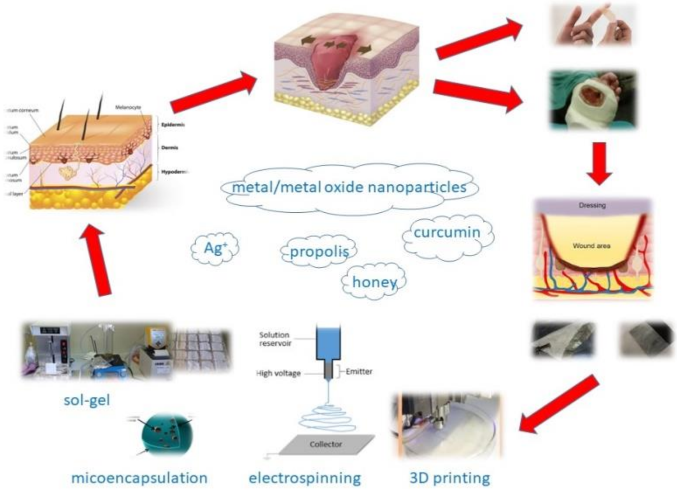

MOLECULAR INTERACTIONS AND THE MISCIBILITY OF POLY(ALKYL METHACRYLATES) BLENDS FROM SOLUTION WITH CELLULOSE NANOCRYSTALS

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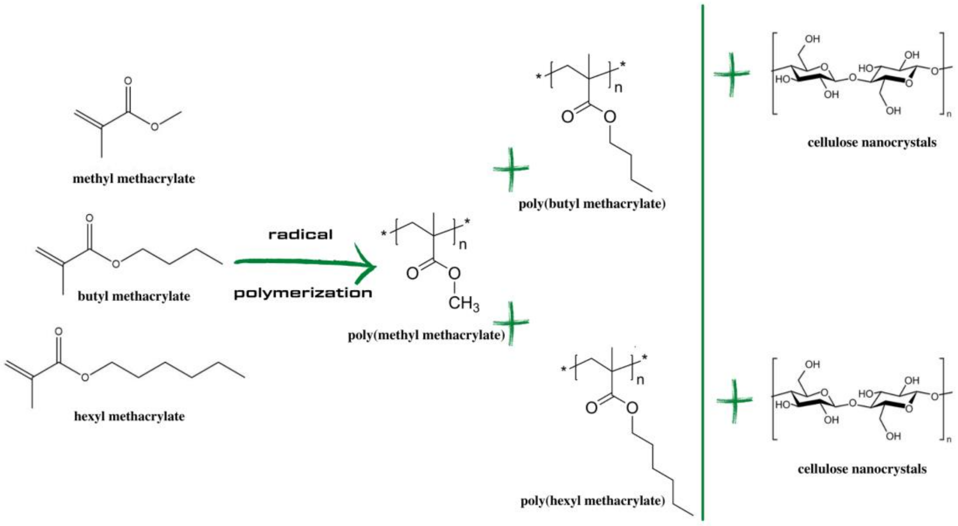
Polymer macromolecules in polymer blends interact by forming strong intermolecular bonds or inter-segment forces usually via hydrogen bonds or between strong dipoles. Polymer blends, whether prepared from polymer melt or solution, are mostly immiscible at the molecular level due to their large molecular mass. The preparation of polymer blends lead to the formation of physical interactions between macromolecules. Such interactions are often localized in a specific area of the polymer macromolecule depending on the present functional groups. The phase behavior in polymer blends, which can be binary, ternary or more, can be modeled using the Flory-Huggins thermodynamic approach. Since we know that the mixture enthalpy is caused by the interactions between the different segments, the polymer-polymer interactions can be predicted by calculating the Gibbs free energy of mixing (ΔG_m).

Poly(methyl methacrylate) (PMMA), poly(butyl methacrylate) (PBMA), poly(hexyl methacrylate) (PHMA) were synthesized by free-radical solution polymerization. Gel permeation chromatography (GPC) was used to determine the relative molecular weight of the synthesized polymers which was used to calculate the Gibbs free energy of mixing. The obtained polymers were dissolved in a common solvent to form a polymer blend. Cellulose nanocrystals were then added to the prepared polymer blends to observe whether cellulose had any effect on the interactions and on the thermal properties, which were monitored by differential scanning calorimetry (DSC). The results showed that the addition of PBMA or PHMA to the PMMA with cellulose nanocrystals changed the interactions of the polymer blends.



HALOGENSKA VEZA U KOKRISTALIMA IMINSKIH DERIVATA MORFOLINA I PIPERAZINA S PERFLUORIRANIM JODBENZENIMA

HALOGEN BONDING IN COCRYSTALS OF MORPHOLINE AND PIPERAZINE CONTAINING IMINE DERIVATES WITH PERFLUORINATED IODOBENZENS

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Halogenska je veza privlačna nekovalentna interakcija između elektrofilnog dijela halogenog atoma (σ-šupljine) i nukleofila [1]. Tijekom posljednjih tridesetak godina ta je interakcija dobila važnu ulogu u kristalnom inženjerstvu, a popis istraživanih donora i akceptora halogenske veze u kontinuiranom je porastu [2].

U ovom radu istraživan je potencijal morfolinske i piperazinske funkcijske skupine kao akceptora halogenske veze, koje su periferno smještene na većim molekulama. U tu svrhu su kondenzacijskom reakcijom *N*-(2-aminoetil)morfolina ili 1-(2-aminoetil)piperazina te acetilacetona ili benzoilacetona pripremljena četiri imina. Dobiveni imini kokristalizirani su s dva perfluorirana donora halogenske veze, 1,4-dijodtetrafluorbenzenom i 1,3,5-trijod-2,4,6-trifluorbenzenom. Metodom isparavanja otapala pripravljeno je osam novih kokristala koji su okarakterizirani metodom difrakcije rentgenskog zračenja na jediničnom kristalu, termogravimetrijskom analizom i razlikovno-pretražnom kalorimetrijom. Strukturna analiza potvrdila je akceptorski potencijal morfolinskog kisika i terminalnog piperazinskog dušika s obzirom da u svim kokristalima sudjeluju u ostvarivanju halogenske veze N/O···I. Analiza relativnih skraćenja i ostalih geometrijskih parametara ostvarenih supramolekulskih interakcija pokazala je da terminalni piperazinski dušikov atom sudjeluje u kraćim i linearnijim halogenskim vezama u odnosu na halogenske veze morfolinskog kisikovog atoma.

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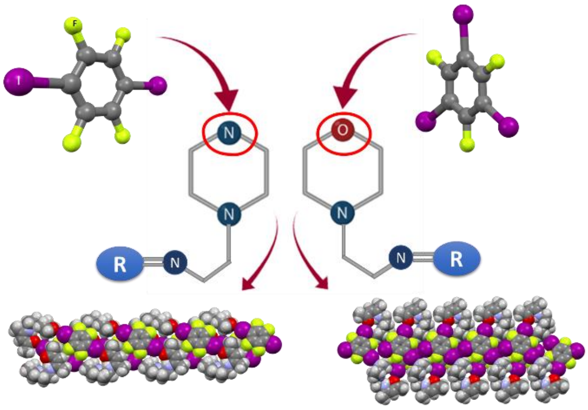

PREPARATION OF GEOPOLYMER BIOCOMPOSITES

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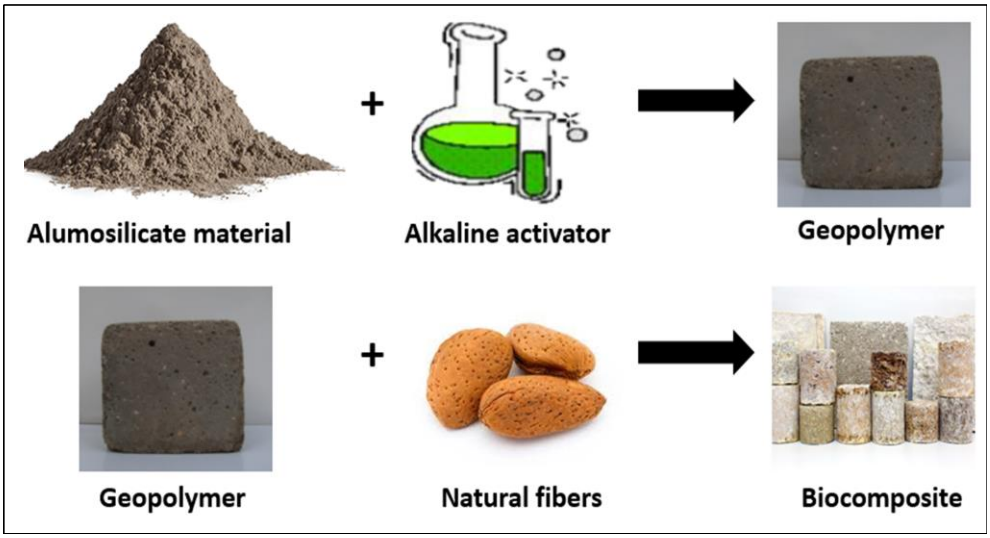
Geopolymers are novel materials made up of aluminosilicate precursors mixed with alkali activation solutions. Common solid precursors are class F fly ash, metakaolin and blast furnace slags, with the main requirement of calcium content not exceeding 10 %. Fly ash and blast furnace slags are waste materials which get reused in these kinds of materials, while metakaolin is kaolin dehydroxylated at temperatures ranging between 500 and 800 °C. Biocomposites are composite materials which utilize natural materials (fibres or particles) as one or more of its components. In this work the preparation of biocomposite based on geopolymer as binder/matrix and almond and hazelnut shell as particle filler was conducted. The influence of NaOH solution pretreatment of nutshell was determined by Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). Thermal properties of prepared composites and its components were analyzed by simultaneous differential thermal and thermogravimetric analysis (DTA/TGA). Optimal solid precursor and activation solution mass ratio was determined as 1.2, and binder and nutshell mass ratio as 1. FTIR and SEM analyses show changes in the pretreated nutshell composition and morphology. The thermal analysis of composites and its components shows typical results for such materials. Further research of different pretreatments, curing conditions and composite components is required for obtaining a proper and applicable material.



SINTEZA HIBRIDNIH PUNILA
HYBRID FILLER SYNTHESIS

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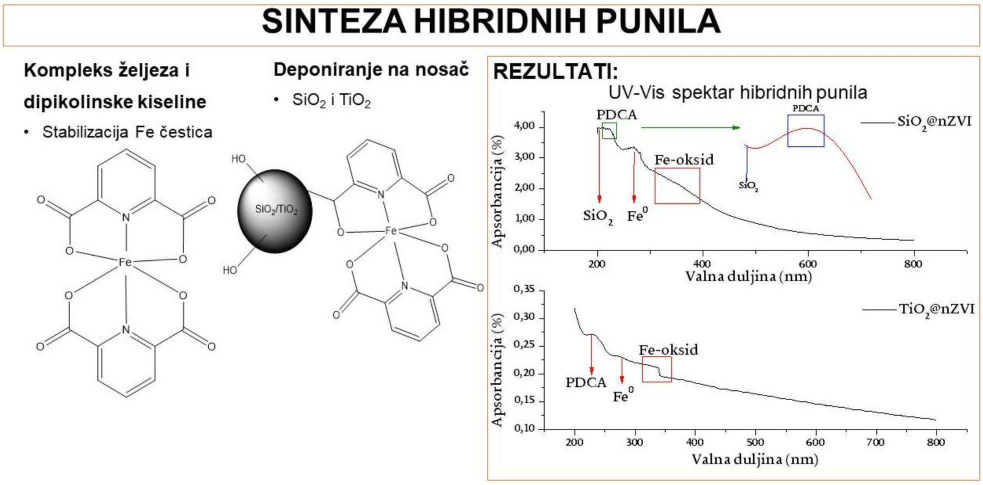
Hibridni materijali, još se nazivaju i hibridnim kompozitima, su novi materijali koji, ukoliko se postignu određene interakcije između konstituenata, pokazuju dobra svojstva oba materijala. Međutim, za to je potrebno ostvariti zadovoljavajuće interakcije, bilo kemijske, molekulske ili strukturne, između konstituenata nanometarskih dimenzija. Prilikom sinteze hibridnog punila u ovom radu korištena su dva komercijalna nanopunila, *n*SiO_2 i *n*TiO_2, koja su služila kao nosači za sintetizirane željezove nanočestice bez naboja (*nano zerovalent iron*, *n*ZVI). Za usporedbu, na isti način, kemijskom sintezom sintetizirane i čestice nZVI. U oba slučaja *n*ZVI stabilizirane su dipikolinskom kiselinom (PDCA). Sintetizirana hibridna punila karakterizirana su različitim tehnikama. Veličina čestica mjerena je DLS metodom na ZetaSizeru. Spektroskopijom u ultraljubičastom i vidljivom području (UV-VIS) potvrđena je prisutnost konstituenata u hibridnom punilu putem apsorbancije UV zračenja. Kemijske interakcije između konstituenata punila analizirane su korištenjem infracrvene spektroskopije s Fourierovim transformacijama (FTIR analizom). Zaključno, provedena je rendgenska difrakcijska analiza (XRD) kako bi se utvrdio mineralni sastav hibridnih punila.



SINTEZA HIBRIDNIH PUNILA

Kompleks željeza i dipikolinske kiseline

- Stabilizacija Fe čestica

Deponiranje na nosač

- SiO_2 i TiO_2

REZULTATI:

UV-Vis spektar hibridnih punila

PRIPREMA I KARAKTERIZACIJA KOMPOZITA POLIETILEN NISKE GUSTOĆE/HEMATIT

PREPARATION AND CHARACTERIZATION OF LOW DENSITY POLYETHYLENE/HEMATITE COMPOSITES

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Emi Govorčin Bajsić[1], Marija Vuković Domanovac[1],
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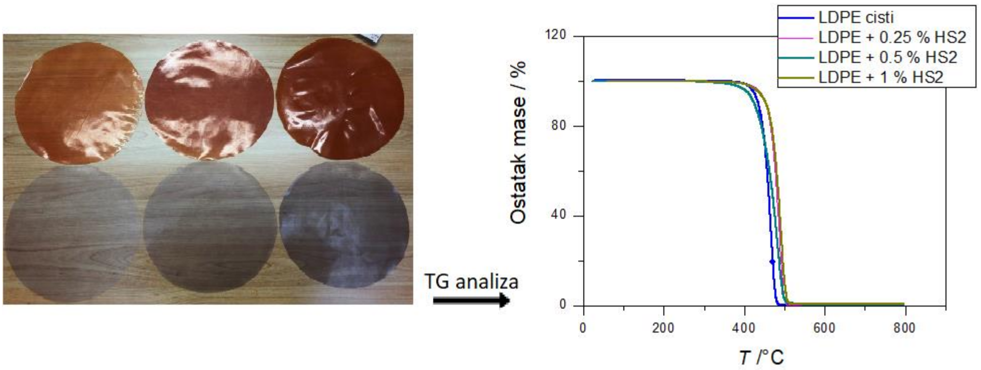
Kompoziti polietilena i željezovih oksida slabije su istraživani u odnosu na druge kompozite polietilena, ali njihovom kombinacijom mogu se dobiti aktivni kompoziti sa širokim područjem primjene. Takvi materijali sadrže aktivne tvari koja imaju različita funkcijska svojstva s ciljem poboljšanja određenih svojstava polimera, a time i produljivanja njegovog životnog vijeka. U tu svrhu najčešće se koriste anorganska punila, među kojima su i željezovi oksidi, koja mogu imati velik utjecaj na mehanička, toplinska, barijerna i ostala svojstva polietilenskih kompozita.

U ovom radu pripremljeni su kompoziti polietilena niske gustoće (LDPE) s česticama hematita (α-Fe_2O_3) različitih veličina, oblika i masenog udjela. Hematit većih dimenzija (oko 100 nm) označen je kao HC1, a onaj manjih dimenzija (oko 2 µm) kao HS2. Udio punila hematita u uzorcima kompozita bio je 0,25, 0,5 i 1 %. Kompoziti LDPE/hematit pripremljeni su u Brabender gnjetilici nakon čega su na hidrauličkoj preši isprešani u folije i pločice. Pripremljenim uzorcima kompozita ispitana su toplinska svojstva metodama termogravimetrijske analize i diferencijalne pretražne kalorimetrije. Odabranim uzorcima polimernih kompozita ispitano je i antimikrobno djelovanje. Rezultati su pokazali da se toplinska stabilnost LDPE-a povećala dodatkom hematita te se iz toga može zaključiti da su navedeni kompoziti toplinski stabilniji. Toplinska stabilnost materijala iznimno se povećala dodatkom čestica hematita manjih dimenzija, HS2, posebice dodatkom najmanjeg udjela hematita od 0,25 % te se navedeni kompozit može smatrati toplinski najstabilnijim uzorkom.



UTJECAJ DODATKA V_2O_5 NA STRUKTURU I PROVODNOST Li_2O-Fe_2O_3-P_2O_5 STAKALA

INFLUENCE OF V_2O_5 ADDITION ON THE STRUCTURE AND CONDUCTIVITY OF Li_2O-Fe_2O_3-P_2O_5 GLASSES

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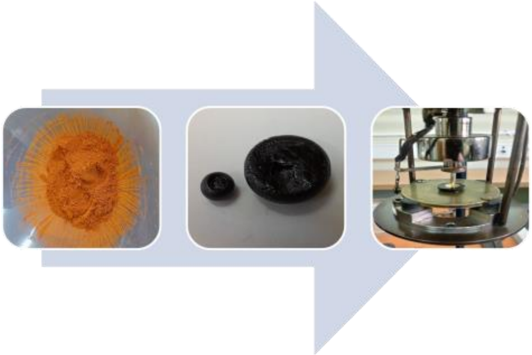
Široka uporaba prenosivih električnih uređaja kao i elektrifikacija transportnog sektora zahtijevaju razvoj naprednih baterija velike gustoće energije. Ipak, današnje litij-ionske baterije ne postižu dovoljno visoke gustoće energije te imaju razmjerno kratak radni vijek. Također, zbog uporabe tekućih elektrolita opasnost od zapaljenja baterije zbog oštećenja je na neprihvatljivoj razini. Jedan od pristupa nadilaženju nedostatcima modernih ionskih baterija općenito je usmjeren ka istraživanju i razvoju novih staklenih i keramičkih materijala pogodnih za čvrste elektrolite i elektrodni materijal. Navedeni materijali pokazuju čitav niz prednosti u odnosu na standardno korištene, kao što su široko područje sastava, izotropna vodljivost, široko temperaturno područje djelovanja, itd. U ovom istraživanju, serija stakla iz sustava Li_2O-Fe_2O_3-V_2O_5-P_2O_5 u kojem se Fe_2O_3 postepeno zamjenjuje s V_2O_5 u širokom rasponu, pripravljena je metodom naglog hlađenja taline. Omjeri pojedinih oksida su održavani tako da odgovaraju $LiFePO_4$ sustavu te su uvjeti priprave istraženi u svrhu dobivanja optimiranih uzoraka s određenim ciljanim karakteristikama. Električni transport u staklima koja sadrže alkalijske i prijelazne metalne okside (TMO) je ionsko-polaronski. Naime, ovisno o količini i mobilnosti Li^+ iona pokazuju ionsku vodljivost, dok polaronska vodljivost ovisi o koncentraciji *malog polarona* odnosno udjelu iona TM u nižim oksidacijskim stanjima. Termička i strukturna svojstva dobivenih uzoraka ispitana su pomoću DTA analize te koristeći PXRD i FTIR metode, dok je uvid u električne karakteristike dobiven metodom impedancijske spektroskopije (IS). Ovo istraživanje ima za cilj pokazati kako dodatak drugog TMOa (V_2O_5) rezultira strukturnim promjenama u dominantnoj amorfnoj matrici što posljedično utječe na električni transport, a sve u svrhu optimiranja i maksimiziranja vodljivosti radi potencijalne primjene u čvrstim ionskim baterijama, što će biti detaljno raspravljeno.



INKJET ISPIS VODLJIVE TINTE NA BAZI POLIMERA POLI(3,4-ETILENDIOKSITIOFENA)

INKJET PRINTING OF CONDUCTING INKS BASED ON POLY(3,4-ETHYLENEDIOXYTHIOPHENE) POLYMER

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Savitljiva tiskana elektronika predstavlja novu generaciju elektroničkih uređaja gdje se koristi poznata metoda *inkjet* (tintnog) ispisa u kombinaciji s novim materijalima kao metoda za tiskanje električnih i optičkih uređaja, posebice onih koji uključuju organske komponente. Tiskana elektronika podrazumijeva ispis vodljivih tinti na različite podloge kako bi se dobila željena električna, mehanička i optička svojstva uređaja, pri čemu se za dobivanje savitljive elektronike koriste polimerne podloge. Tinte za ispis trebaju imati dobru adheziju na podlogu, visoku rezoluciju, minimalnu potrebu za održavanjem pisača i dugi rok trajanja. Najvažnija svojstva tinte koja se trebaju optimirati kako bi se osigurao kvalitetan ispis su viskoznost, površinska napetost, vlaženje i adhezija na podlogu. Uobičajeno se kao materijal za pripremu vodljivih tinti koriste metalne nanočestice poput srebra, zlata, bakra ili aluminija, ali nedostatak takvih tinti je da nemaju svojstvo istezljivosti pa nakon mehaničkih naprezanja može doći do njihovog odvajanje od savitljive podloge. Kao alternativa se sve više istražuju tinte bazirane na vodljivim polimerima kod kojih je uz modifikaciju moguće postići intrinzičku istezljivost uz istovremeno zadržavanje vodljivosti. U radu je sintetiziran graft kopolimer pri čemu je glavni lanac vodljivi poli(3,4-etilendioksitiofen) (PEDOT), a bočni lanci su od poli(akrilat-uretana) (PAU) koji nije vodljiv, ali omogućuje nekovalentno umrežavanje vodikovim vezama čime se postiže istezljivost materijala. Sintetizirani polimer pripremljen je u obliku vodljive tinte, te se *inkjet* ispisao na savitljivu podlogu od poliuretana. Adhezija tiskanog sloja karakterizirana je uranjanjem u vodu i ultrazvučnim testom nakon čega se mikroskopom pratila delaminacija tiskanog polimernog sloja. Također je ispitana i električna provodnost tiskanog sloja kao i njegova istezljivost.

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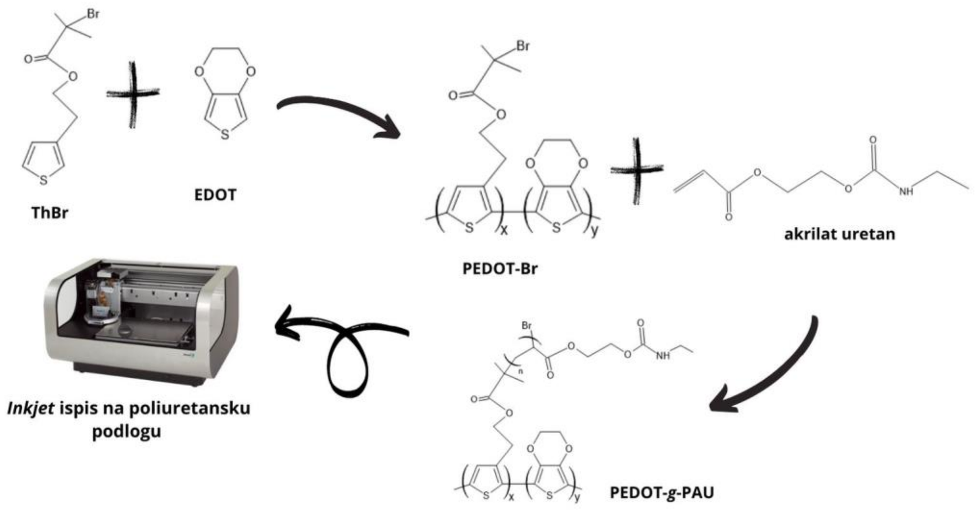

SINTEZA I KARAKTERIZACIJA Ag/SiO$_2$ NANOKOMPOZITA

SYNTHESIS AND CHARACTERISATION OF Ag/SiO$_2$ NANOCOMPOSITES

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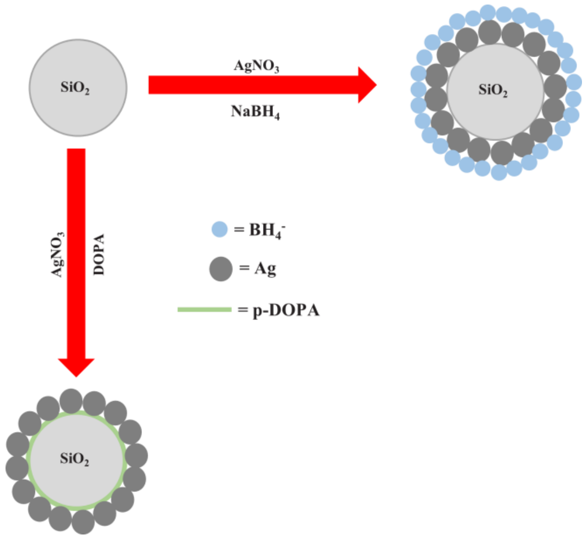
Nanotehnologija je znanstvena disciplina koja se bavi stvarima i pojavama na nanorazini. Nanostrukture predstavljaju veliki izazov zbog njihovih specifičnih svojstava, i fenomenologije koja se zbiva na nanorazini, kao što su problemi velike specifične površine i pojava kvantnih efekata. Posljedično, zadnjih godina značajno se potiču istraživanja u području nanotehnologije, od sinteze različitih nanostrukutra, do njihove primjene u svakodnevnom životu. Cilj ovog rada bio je sintetizirati Ag/SiO$_2$ nanokompozit i okarakterizirati ga. Ag/SiO$_2$ nanokompozit sintetiziran je na dva načina, primjenom dva različita reducensa: natrijev borhidrid (NaBH$_4$) [1] i dopamin hidroklorid (DOPA) [2]. Postupci sinteze djelomično su slični te su izvođeni u podjednakim uvjetima. Pripremljeni nanokompoziti karakterizirani su s tri instrumentalne metode analize: dinamičkim raspršenjem svjetlosti (DLS), UV/VIS spektrofotometrijom i FTIR spektroskopijom. DLS analizom ispitivana je volumna raspodjela veličina čestica gdje je uočena podjednaka raspodjela veličina čestica u oba postupka sinteze. Dok nakon centrifugiranja i ispiranja s dva različita otapala, voda i etanol, dolazi do aglomeracije nanokompozitnih čestica. Stvaranje najvećih aglomerata, s obzirom na otapalo, uočeno je kod uzoraka ispiranih etanolom, dok je korištenjem DOPA-e kao reducirajućeg agensa zabilježena izraženija aglomeracija u priređenom nanokompozitu. Aglomerirane čestice prelaze veličinu od 100 nm, te se one više ne mogu nazvati nanočesticama. FTIR spektroskopijom i UV/VIS spektrofotometrijom dokazana je prisutnost Ag i SiO$_2$ nanočestica u obliku Ag/SiO$_2$ u uzorcima sintetiziranim na oba načina sinteze.

[1] T.T. Le, T.V. Nguyen, T.A. Nguyen, T.T.H. Nguyen, H. Thai, D.L. Tran, D.A. Dinh, T.M. Nguyen, L.T. Lu, Mater. Chem. Phys. 232 (2019) 362-366.
[2] A.W. Jatoi, I.S. Kim, Q.Q. Ni, Carbohydr. Polym. 207 (2019) 640-649.



DINAMIČKO RASPRŠENJE SVIJETLOSTI: RASPODJELA VELIČINE I ZETA POTENCIJAL NANOČESTICA TiO_2 U RAZLIČITIM MATRICAMA

DYNAMIC LIGHT SCATTERING: SIZE DISTRIBUTION AND ZETA POTENTIAL OF TiO_2 NANOPARTICLES IN DIFFERENT MATRICES

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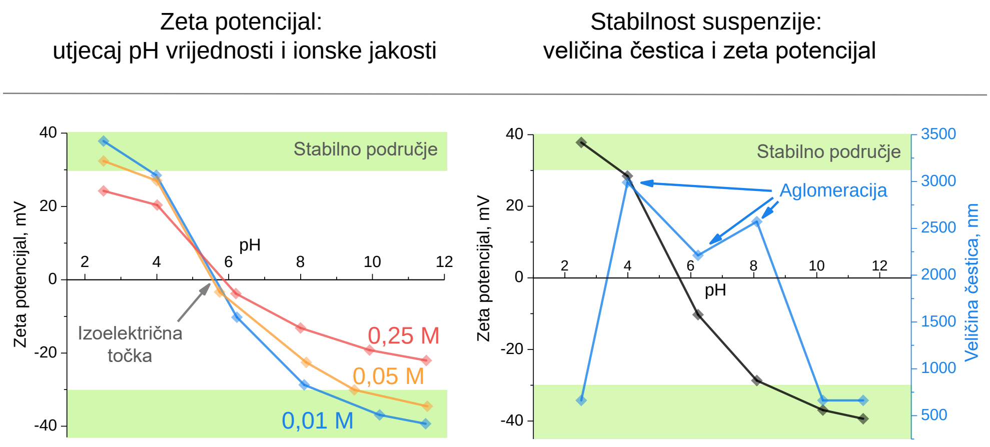
Tehnikom dinamičkog raspršenja svjetlosti (engl. dynamic light scattering, DLS) može se odrediti raspodjela veličina čestica koje podliježu Brownovom gibanju te zeta potencijal čestica prilikom elektroforetskog gibanja u električnom polju. U ovom radu istražen je utjecaj matrice u kojoj su disprgirane nanočestice TiO_2 na raspodjelu veličine i zeta potencijal čestica. Raspodjela veličine i zeta potencijal čestica važni su parametri u određivanju stabilnosti suspenzija. Zeta potencijal ukazuje na stabilnost suspenzije tj. stupanj odbijanja između čestica istovrsnog naboja u suspenziji. Suspenzija je stabilnija što je veća apsolutna vrijednost zeta potencijala. TiO_2 nanočestice dispergirane su u poli-alfa-olefinskom ulju (PAO 6), deioniziranoj vodi te vodenim otopinama različite ionske jakosti i pH vrijednosti. Pomoću DLS metode utvrđeno je da raspodjela veličina čestica izmjerena u deioniziranoj vodi ima 24 puta veću, a u PAO 6 ulju 11 puta veću vrijednost od nominalne (13 nm) što upućuje na aglomeraciju čestica. Izmjeren je i zeta potencijala TiO_2 čestica u vodenoj matrici u širokom rasponu pH vrijednosti i ionske jakosti. Suspenzija se pokazala najstabilnijom pri najmanjoj ionskoj jakosti vodene matrice (0,01 M otopina NaCl) te pri ekstremnim pH vrijednostima ispitanog područja gdje je zeta potencijal imao najveće apsolutne vrijednosti: +37,84 mV pri pH 2,52 i -39,33 mV pri pH 11,48. Smanjena tendencija aglomeraciji vidljiva je iz pomaka raspodijele veličine čestica prema manjim vrijednostima kod pH vrijednosti gdje je izmjerena veća apsolutna vrijednost zeta potencijala od granične vrijednosti za stabilnu suspenziju (>30 mV).


Zeta potencijal:
utjecaj pH vrijednosti i ionske jakosti

Stabilnost suspenzije:
veličina čestica i zeta potencijal

POROUS TERNARY COORDINATION COPMOUNDS OF ZINC, L-SERINE AND 1,10-PHENANTHROLINE

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Zinc is an essential metal and part of over 300 metalloenzymes [1]. Zinc coordination compounds involving amino acids are investigated due to pronounced antitumor, antibacterial and antifungal activities [1,2]. However, crystallographic investigation of ternary coordination compounds involving zinc, amino acids and heterocyclic bases (2,2'-bipyridine and its derivatives) is quite scarce. Only three crystal structures of such ternary coordination compounds were published [3].

As part of our ongoing investigation of ternary coordination compounds of essential metals, amino acids and heterocyclic bases [4], we report synthesis and crystal structure analysis of two novel ternary coordination compounds of zinc, L-serine (HSer) and 1,10-phenanthroline (phen): $[Zn(H_2O)_2(phen)_2][ZnCl(Ser)(phen)]Cl_2\cdot 3H_2O$ (**$1\cdot 3H_2O$**) and $[Zn(H_2O)_2(phen)_2][ZnCl(Ser)(phen)]_2Cl_2\cdot 7.5H_2O$ (**$2\cdot 7.5H_2O$**). Two types of complex entity are present in both coordination compounds, but in different stoichiometric ratios: cationic octahedral $[Zn(H_2O)_2(phen)_2]^{2+}$ and neutral square-pyramidal [ZnCl(Ser)(phen)] species. Both **$1\cdot 3H_2O$** and **$2\cdot 7.5H_2O$** contain infinite 1D channels of crystallization water molecules, occupying 10% and 17% of the unit cell volume, respectively (Figure 1).

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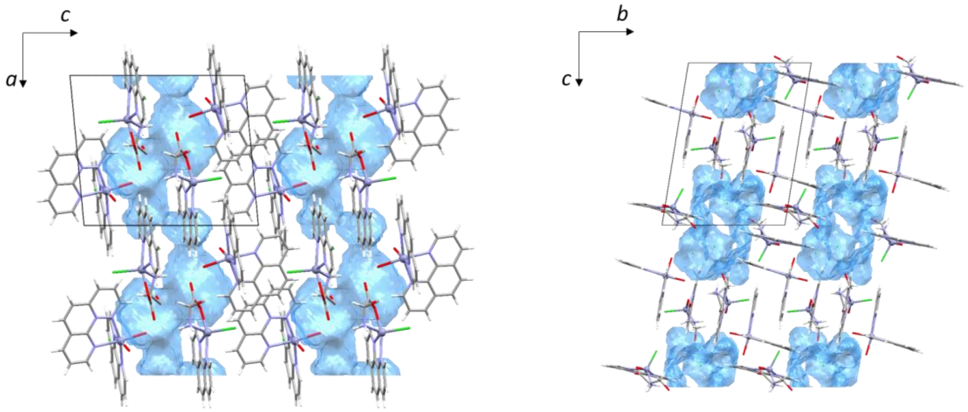
[3] C. R. Groom, I. J. Bruno, M. P. Lightfoot, S. C. Ward, *Acta Cryst.*, 2016, *B72*, 171.

[4] D. Vušak, B. Prugovečki, D. Milić, M. Marković, I. Petković, M. Kralj, D. Matković-Čalogović, Cryst. Growth Des. **17** (2017) 6049.



$1\cdot 3H_2O$ **$2\cdot 7.5H_2O$**

Figure 1. 1D channels of crystallization water molecules in **$1\cdot 3H_2O$** and **$2\cdot 7.5H_2O$**.

SINTEZA I KARAKTERIZACIJA NEUTRALNIH ŽELJEZOVIH NANOČESTICA

SYNTHESIS AND CHARACTERISATION OF NANO ZERO VALENT IRON PARTICLES

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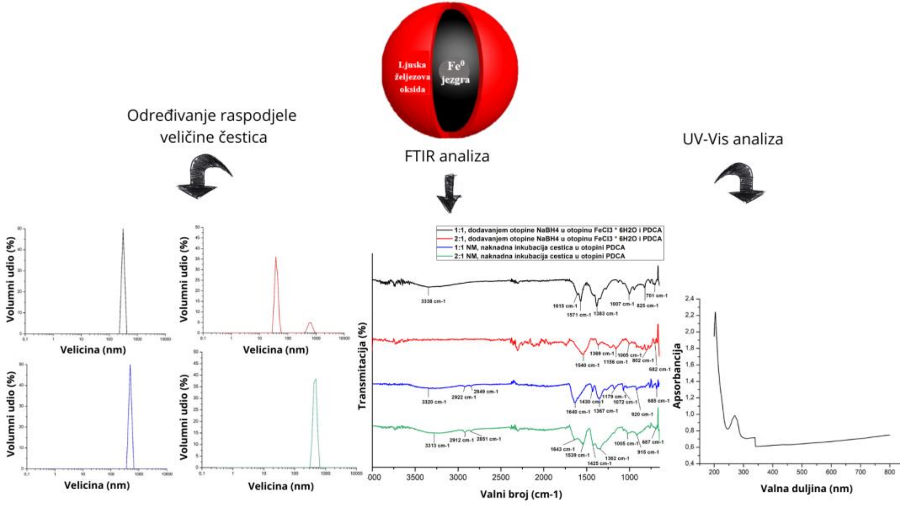
Budući da posjeduju jedinstvena fizikalna i kemijska svojstva, nanočestice su pronašle široku primjenu u industriji. Neutralne nanočestice željeza zbog svoje male veličine, velike specifične površine, magnetskih svojstava i velike redukcijske sposobnosti često se koriste za pročišćavanje onečišćenih voda. Najveći problem ove metode predstavlja nestabilnost i aglomeracija sintetiziranih nanočestica. Iz tog razloga se razvijaju postupci sinteze u svrhu poboljšanja efikasnosti primjene ovih čestica. Cilj rada bila je sinteza neutralnih nanočestica željeza na kemijski način, redukcijom željezove soli, željezova (III) klorida heksahidrata ($FeCl_3 \times 6H_2O$), sa odgovarajućim reducensom, natrijevim borhidridom ($NaBH_4$). Željezove čestice funkcionalizirane su dipikolinskom kiselinom (PDCA) na dva načina: jednokratnim dodavanjem PDCA u otopinu $FeCl_3 \times 6H_2O$ prije redukcije sa $NaBH_4$, a u drugom postupku i naknadnom inkubacijom sintetiziranih nanočestica u PDCA. Pripremljeni su množinski omjeri $FeCl_3 \times 6H_2O$ i PDCA 1:1 i 2:1, kako bi se ispitao utjecaj stabilizatora na veličinu čestica. Sintetizirane željezove nanočestice karakterizirane su infracrvenom spektroskopijom s Fourierovom transformacijom (FTIR), ultraljubičastom - vidljivom spektroskopijom (UV–Vis) te metodom dinamičkog raspršenja svjetlosti (DLS). Analizom raspodjele veličine čestica utvrđena je nanometarska dimenzija sintetiziranih čestica. Naknadno je potvrđeno kako korištenje množinskog omjera $FeCl_3 \times 6H_2O$ i PDCA 2:1 (38 nm) daje manje čestice nego kod omjera 1:1 (veće od 100 nm). FTIR analiza pokazala je da korištenje različitih omjera i različiti načini funkcionalizacije utječu na promjenu strukture ovih nanočestica. Snimljeni spektri pokazuju vrpce koje, prema literaturnim podacima, odgovaraju vibraciji aromatske C-C veze, asimetričnom i simetričnom istezanju karboksilne skupine, vibraciji hidroksilne skupine i istezanju veze između željeza i kisika. Na temelju ovih spektara može se zaključiti o uspješnoj provedbi sinteza nanočestica željeza i njihovoj stabilizaciji sa PDCA. Izuzetak je spektar uzorka dobivenog dodavanjem otopine $NaBH_4$ u otopinu $FeCl_3 \times 6H_2O$ i PDCA korištenjem omjera 2:1 koji se dosta razlikuje od spektara drugih uzoraka, kao i od literaturnih. Premda se u tom spektru pojavljuju neke karakteristične vrpce (primjerice za vezu νFe-O) istovremeno izostaju neke karakteristične vrpce, što ukazuje na to da se PDCA nije vezala na ove nanočestice željeza.



INFLUENCE OF RELATIVE HUMIDITY ON THE SWELLING OF CHITOSAN/POLY(ACRYLIC ACID) NANOFILMS

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Polyelectrolytes are macromolecules in which a significant proportion of functional groups are ionic or easily ionizing. Given the charge of polyelectrolytes in solution, they are divided into polycations and polyanions, and given the degree of ionization in a solution, they are classified as weak and strong polyelectrolytes. By alternating adsorption of positively and negatively charged polyelectrolytes on a solid surface, polyelectrolyte multilayers are formed. This procedure is called layer-by-layer (LbL) method which allows the precise design of nanofilms with desired properties. The main reason that multilayers have been increasingly researched in recent years is their application, for example, in fruit protection, drug delivery, membrane technology, etc. One of the interesting properties of polyelectrolyte coatings is self-healing. For example, a multilayer of chitosan (CS) and poly(acrylic acid) (PAA), was recently prepared and after treatment in an aqueous medium, it healed inflicted mechanical damage. A key factor in this effect is the swelling of the film which is strongly influenced by multilayer interactions. In order to investigate the swelling of CS/PAA thin films, a chamber for controlling the relative humidity of the atmosphere was designed, constructed, and tested using saturated salt solutions which control the relative humidity inside the chamber. In the next step, the LbL method was used to prepare films with different numbers of layers on silica substrate from CS and PAA solutions. The formation and thickness of the LbL film after each adsorbed layer was monitored by ellipsometry. By measuring the thickness of the prepared film during its swelling and drying, the reversibility of these processes, *i.e.* swelling hysteresis, was examined. After that, the thickness of the prepared samples at different humidities was determined. It was found that the thickness of the multilayers increased with increasing humidity and that the swelling of the nanofilms is more pronounced for the films with a higher number of layers.

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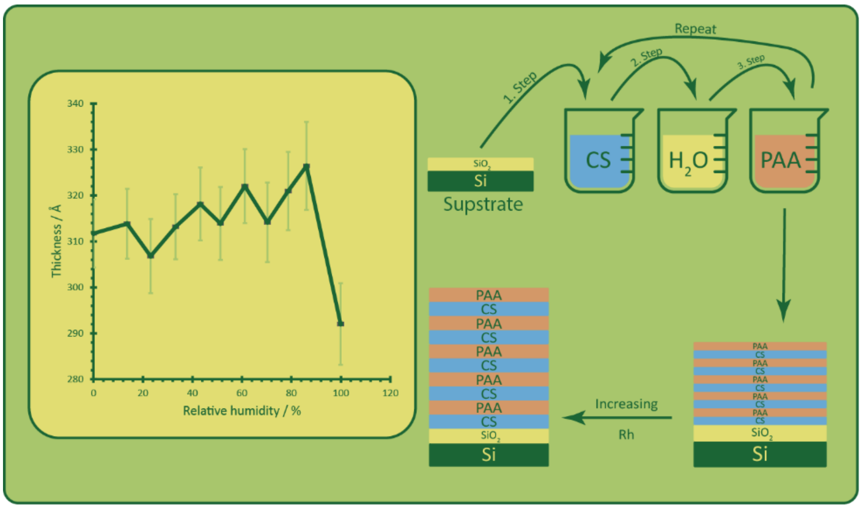

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