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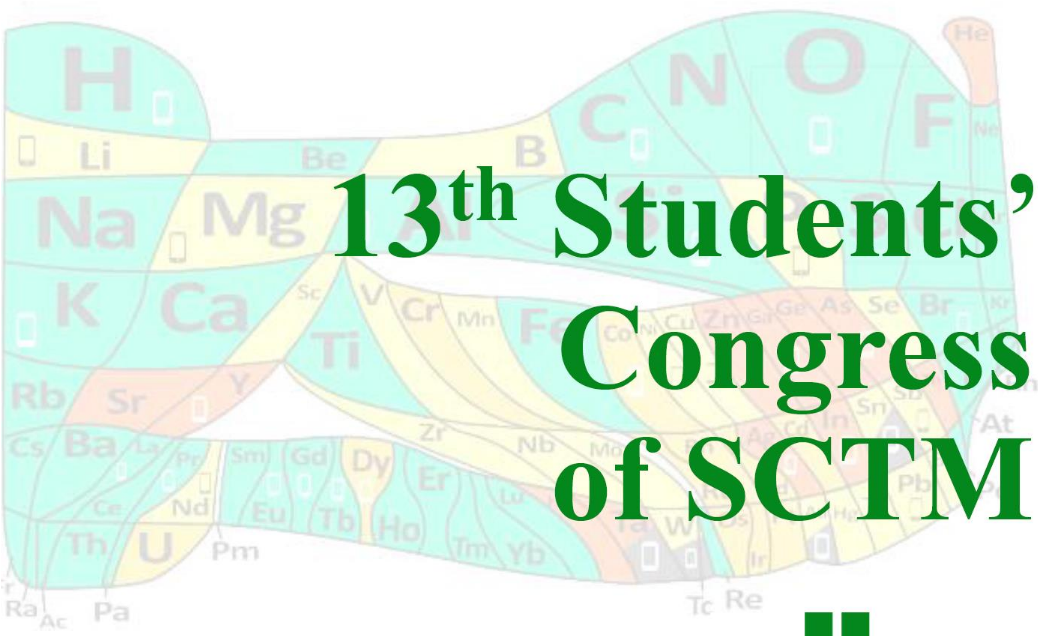

13th Students' Congress of SCTM

CXTM

19–21 September, 2019 |
Institute of Chemistry

Skopje,
Republic of N. Macedonia

Сојуз на хемичарите и технолозите на Македонија

Society of Chemists and Technologists of Macedonia

13th Students' Congress of SCTM

BOOK OF ABSTRACTS

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Сојуз на хемичарите и технолозите на Македонија
Society of Chemists and Technologists of Macedonia
19-21 September 2019, Institute of Chemistry, Skopje

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Plenary Lectures

PL-1

Recent model development for the investigation of drug-delivery systems as well as solid-state electrodes in electrocatalysis or batteries

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This plenary lecture will provide an overview of my recent research activities in the fields of electrocatalysis, battery science and drug-delivery system.

Renewable energy needs to be stored to match demand. The obvious choice is electrochemical water splitting to produce the energy vector H_2, where the sluggish oxygen evolution reaction (OER) at the anode limits the efficiency of this process. Due to its high stability and reasonable activity in the OER, IrO_2-based anodes are considered as a benchmark in acidic water electrolysis. However, even for single-crystalline $IrO_2(110)$ anode the kinetic bottleneck has not been resolved, thereby hampering a rational search for alternative materials. The widely accepted reaction mechanism for the OER in acidic media consists of four proton-coupled electron transfers, in which the OH, O and OOH adsorbate need to be stabilized on the electrocatalyst's surface [1]. By applying the free energy diagram approach [2], asintroduced by Over and Exner, the reaction mechanism and rate-determining reaction step (rds) for the OER over $IrO_2(110)$ is resolved: quite in contrast to common perception, it turns out that not the formation of the OOH adsorbate, but rather the decomposition of the OOH adsorbate under the formation of O_2 is identified as rds at high overpotentials (ηOER > 0.40 V) [3]. This finding is in contrast to the OER over $RuO_2(110)$, where the formation of the OOH adsorbate is kinetically limiting [4]. The different OER kinetics of $IrO_2(110)$ and $RuO_2(110)$ are explained by the introduction of kinetic scaling relations [2,5], which extend the framework of linear scaling relationships by including the applied overpotential and kinetics into the underlying material-screening approach. In this context, an advanced thermodynamic activity descriptor, $|\Delta G(\eta)|$ [6], was recently introduced, which enables to construct overpotential- dependent Volcano curves: in contrast to conventional Volcano plots, this advanced concept accounts for the applied overpotential and also partly for the kinetics [7]. While the combination of kinetic scaling relations and overpotential-dependent Volcano plots is suggested as an improved tool to identify and develop advanced electrode materials within a sustainable hydrogen economy based on water splitting [8], activity-stability Volcano plots have been developed to improve auspicious electrode materials for the application in practice [9]; this framework was originally introduced for the investigation of lithium intercalation in batteries [10] and re-transferred to the field of electrocatalysis.

In the second part of my lecture, an intimate exchange of concepts and ideas between the communities of electrocatalysis and battery science is presented and discussed [11], in that the computational hydrogen electrode approach and Volcano plots from the field of electrocatalysis were translated to a computational lithium electrode [12,13] and activity-stability Volcano curves [10]. In contrast to common approaches in the literature, these advanced methodologies account for the applied electrode potential in the underlying theoretical framework when evaluating the stability and activity of potential battery materials by thermodynamic considerations.

The last part of my lecture addresses a drug-delivery systems (DDS) at the example of the cytostatic doxorubicin (DOX), for which a three-component DDS has been modeled under imitated conditions of the human body: interestingly, the obtained adsorption states of DOX can be described by a Volcano- shaped curve, which provides further evidence for research activities in the field of electrocatalysis how to overcome the Volcano limit and, hence, to enhance turnover [14].

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PL-2

Advanced microscopy techniques in material investigation

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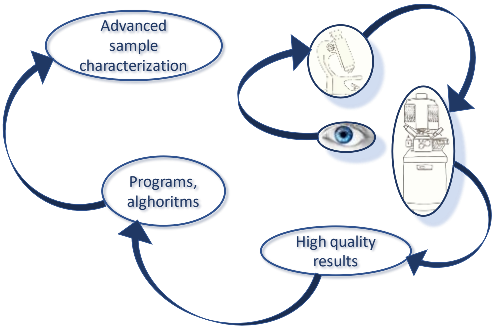
The science of microscopy is a living science that is developing very intensively. The field is very broad and extensive, encompassing many microscopic techniques (light microscopy, confocal microscopy, electron/ion scanning microscopy, X-ray microscopy, ...). Microscopy is increasingly used in various industries (chemical, automobile, glass, ceramic, cement, battery, energy, medicine, environment, food, metal, ...), in diagnostics, treating, researching micro and nano structures, assuring industrial quality excellence, developing and in educational purposes. Depending on the type of sample and the information we want to obtain through microscopy, we choose the appropriate technique. In general, through microscopy, we can directly and indirectly obtain a great deal of information about the sample. For example, microscopy (any kind) can be used for imaging, for deducing microstructural or morphological properties (including tomography), when coupled with spectroscopy it can be used for chemical composition determination or it can be used for direct determination of many physical properties of the sample (mechanical, electrical,…). Additionally, with some post-signal processing using special programs or developed algorithms microscopy gives us many almost unlimited possibilities for advanced sample characterization. Advanced microscopy requires skilful microscopist. During every new microscopy session, obtaining some high quality results seems to be rather time consuming due to adjusting optimal measuring parameters. Nevertheless, investing some time in these initial activities during microscopy is always worthy, since following activities are then much faster and results better. The real time-consuming part comes with post-signal processing and fulfilling the requests of hard pleasing customers.



The lecture will focus on four microscopic techniques (light microscopy, FE-SEM with EDS analysis, correlative microscopy and FIB/SEM microscopy) and their practical applications in material science.

Keywords: microscopic techniques, sample characterization, microstructure.

Acknowledgements: This work was supported by the Ministry of Higher Education, Science and Technology of the Republic of Slovenia through grants P1–0175.

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PL-3

Computational Organic Chemistry. From molecules to nanomaterials

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Nowadays, chemical research is not only focused on the search for new substances or useful materials, but also on the understanding, design and control of their properties. Computational Chemistry[1-3] is in the background of this new trend in chemical research as it provides the appropriate tools for the atomic and molecular description of chemical structures and reactivity, even directing new experimental directions, acting in a predictive way.

In the materials world, graphene was first isolated in 2004, and it sparked a great scientific interest thanks to its peculiar mechanical and electronic properties, which promise to upgrade many technologies, from microelectronics to biosensing and nanomedicine. One way to produce graphene has seen the chemical exfoliation through the interaction with molecules with supramolecular capabilities. Among the many molecules that have been proposed as exfoliating agents of graphite, only a few ones successfully exfoliate and stabilize graphene in aqueous media. Here I will review the development of some environmentally friendly, cheap and simple approach for the synthesis of aqueous soluble few-layer graphene, useful for biological purposes. From theoretical insight, state-of-the-art density functional theory (DFT) calculations within a super-cell slab periodic approach, and comparison with experimental result, we propose that different carbohydrates behave as melamine in a micro-solvation model where the interplay between non-covalent interactions, provides the necessary thermodynamic driving force to stabilize the graphene-water dispersions.

The prepared graphene has been characterized by TEM, X-ray diffraction, TGA, Raman spectroscopy. This study aims to use carbohydrates as exfoliating agents and open up new possibilities for preparing graphene materials, in large-scale, for biological applications.

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PL-4

Biomimetic modelling of metalloenzyme active sites by means of supramolecular bioinorganic edifices

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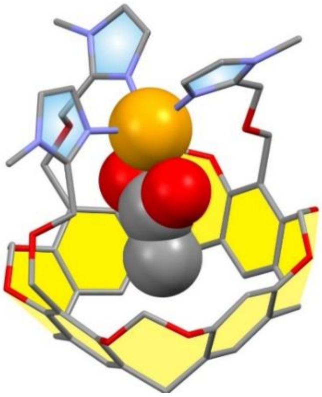
Biomimetic chemistry aims to create novel chemical species inspired by the natural systems such as metalloenzymes. This translates to the catalysts design, but en-route, very often secrets of the mechanisms used by the natural systems are discovered.[1] As an example of the supramolecular approach in biomimetic modelling,[2] the syntheses, structural characterizations, and chemical activity studies of "bowl complexes", based on the resorcin[4]arene scaffold with three or four imidazole-containing coordinating arms grafted at the large rim, will be discussed. These complexes are biomimetic models of a ubiquitous mononuclear active site where three (or four) amino-acid residues hold the metal ion, leaving its one or two coordination sites available for the reversible guest (substrate) binding. The trisimidazole ligand RIm3, as well as the novel, tetraimidazole water soluble ligand WRIm4 were prepared, [3] as well as their complexes with Zn(II), Cu(I) [4] and Cu(II). In the case of the RIm3, spectroscopic studies and X-ray single crystal analysis revealed a 5-coordinate environment for the Zn(II) and Cu(II) centres provided by three imidazole arms, and two extra donors, one embedded inside the resorcinarene cavity, the other in exo position. These two labile sites are occupied by solvent molecules or residual water, and are readily displaced by carboxylate donors, the position of which (endo or exo) is under tight control of the bowl-cavity. The reaction of RIm3 ligand with Zn(II) or Cu(II) acetates led to the formation of the complexes with the acetate anion irreversibly embedded inside the cavity. Cu(II) acetate complex was characterized by the X-ray single crystal analysis, [5] The water soluble WRIm4 ligand is particularly resistant to crystallize. The novel approach to prepare suitable single crystal of its complexes/adducts, including the in-situ host-guest adduct formation and concomitant crystallization of its complexes, by the use of the macromolecular crystallization techniques will be presented.



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Invited Lecture

IL-1

Replication of synthetic information molecules

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Significant progress has been made in the Hunter group towards the development of oligomeric systems equipped with a sequence of phenol and benzoic acid recognition units able to form covalent base pairs. We refer to these systems as information molecules as they encode information in the sequence of the bases. The oligomers can be replicated successfully using covalent templating, however there are partial and scrambled sequences besides the desired product (**Figure 1**) [1].

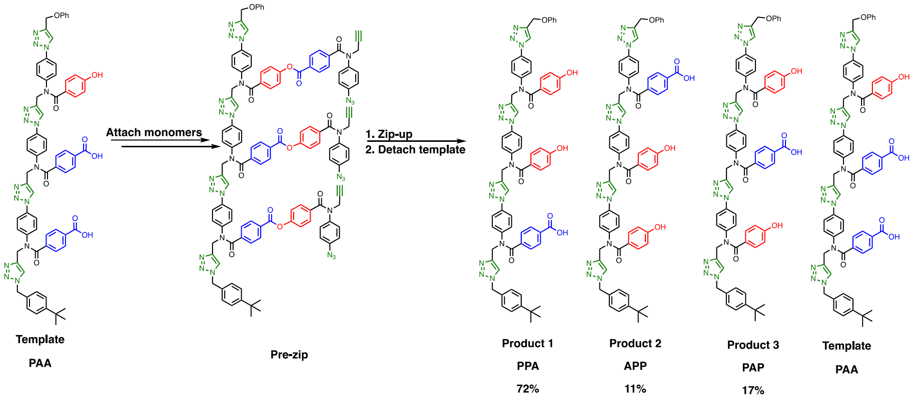

Figure 1: Covalent template directed synthesis on a heterotrimer template.

Here we describe covalent template directed synthesis using porphyrin coordination complexes as the template for oligomer synthesis (**Figure 2**). Selective synthesis of a discreet porphyrin dimer is the subject of my talk.

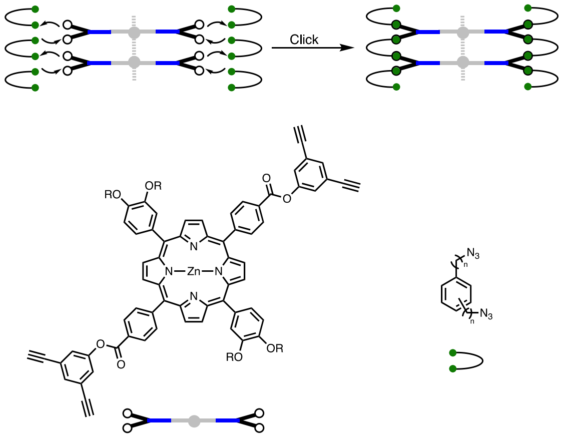

Figure 2: Covalent template directed synthesis on a porphyrin coordination complex template.

Keywords: Information molecules, covalent templating, replication.

Reference:

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Oral Presentations

Analytical and Environmental Chemistry (AEC)

AEC 1

The effect of solvent polarity on the mineral composition of wheatgrass (*Triticum aestivum L.*)

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The aim of this paper was to investigate the content of macroelements, microelements, and toxic metals in the extract of wheatgrass (*Triticum aestivum L.*) determined using inductively coupled plasma optical emission spectrometry. The extracts were prepared with different polarity of methanol or ethanol for 30 min at 60 °C and the liquid-to-solid ratio of 10 cm^3 g^{-1} using ultrasound-assisted extraction technique. Potassium was a dominant macroelement in the wheatgrass extract. The lowest content of potassium (1265.1 mg 100 g^{-1} dry plant material) was noticed in the ethanolic extract, while the highest content of potassium (4706.9 mg 100 g^{-1} dry plant material) was determined in the extract obtained using 50 % (*V*/*V*) ethanol. The presence of microelements, aluminium and boron, in the alcoholic extracts was confirmed, while their content in the aqueous extracts was below the limit of detection. In the ethanolic extract, the high content of aluminium (1798.9 mg 100 g^{-1} dry plant material) and be highoron (145.4 mg 100 g^{-1} dry plant material) were noticed. The extracts with thus mineral composition are considered useful and safe for human health.

AEC 2

Phenolic compounds of *Aronia melanocarpa* from Macedonia: LC/DAD/ESI/MS^n profile and content

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The Aronia genus includes two species: *Aronia melanocarpa* [Michx.] Eliot (black chokeberry) and *Aronia arbutifolia* [L.] Eliot (red chokeberry). Aronia (*Aronia melanocarpa*) berries are a rich source of phenolic compounds, which reveal potential health benefits. Namely, the polyphenols contained in aronia fruits have beneficial physiological effects, as: antioxidant, antimutagenic, anti-inflammatory, anti-cancer and antidiabetic effects.

The focus of this study was oriented towards polyphenol composition and antioxidant activity of samples of Aronia melanocarpa cultivated in Berovo, Macedonia, that were explore using high-performance liquid chromatography (HPLC) coupled to UV diode-array detector (UV-DAD) and electrospray ionization mass spectrometer (ESI-MS) in positive and negative ionization mode, as well as Folin-Ciocalteu, pH-differential and DPPH method. Extracts were prepeared using water:citric acid (98:2 %, *V*/*V*) as a solvent mixture.

Identification of the polyphenols contained in aronia samples is performed by comparing UV and mass spectra with those of appropriate standard substances, but also with previously published results. Three groups of polyphenols were revealed: hydorxycinnamic acids, flavonols (quercetin derivatives) and anthocyanins (cyanidin derivatives).

HPLC/DAD method was used for quantification of the phenolic compounds and the obtained results refer to high content of hydroxylcinnamic acids, which is in the range of 265.9 mg/100 g to 759.3 mg/100 g, followed by anthocyanins in the range of 49.9 mg/100 g to 433.0 mg/100 g, and flavonols 50.3 mg/100g to 112.4 mg/100 g.

Spectrophotometric measurments of total polyphenols, monomeric anthocyanins and radical scavenging activity has been employed as a more practical approach for fast quantification of these compouns. Total polyphenols determined by Folin-Ciocalteu was between 329.6 mg/100 g and 852.6 mg/100 g, expressed as gallic acid equivalents. The content of total monomeric anthocyanins, obtained with pH-differential method, ranged between 2.0 mg/100 g and 355.9 mg/100 g, expressed as cyaniding glycoside. Antioxidant activity varied from 9.8 to 19.2 μmol Trolox equivalents/g.

Keywords: aronia, polyphenols, anthocyanins, antioxidant activity, HPLS/DAD/ESI–MS analysis.

AEC 3

Characterization of phenolic compounds in honey by solid-phase extraction and HPLC-DAD-MS^n

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Phenolic compounds are widespread group of secondary plant metabolites. Flavonoids and phenolic acids are the two most important classes of phenolic compounds that are present in plants and plant derived products. As bioactive compounds their antioxidant, anti-inflammatory and antimicrobial activity has been demonstrated. Honey is a natural product with high nutritional and prophylactic-medicinal value. Polyphenols are considered as valuable honey constituents as well as compounds that can be used as chemical markers for its botanical and geographical authentication. Analysis of phenolic compounds in honey includes their extraction from the very complex sugar matrix, which is then followed by their separation and detection using reversed-phase liquid chromatography coupled to diode array detection (DAD) and mass spectrometry (MS).

The focus of this study was the identification and quantification of phenolic compounds in honey using HPLC-DAD-MS^n. Solid-phase extraction using Amberlite XAD-2 was optimized for sample preparation enabling purification and concentration of polyphenols. Separation was carried out by developing a reversed-phase HPLC method. Identification was made by comparing the obtained retention times, UV-Vis and mass spectra with standards as well as using literature data. Flavonoids, due to differences in the substitution pattern, have specific UV-Vis spectra with an absorption maxima in the range of 260-370 nm, while phenolic acids at 330 nm. In order to obtain more specific structural information for the different types of polyphenolic compounds, tandem mass spectra (MS and MS^2) were obtained using electrospray ionization in the negative ionic mode and an ion trap mass spectrometer.

Characterization of phenolic profiles was made on Macedonian and Bulgarian honey samples. Using the developed method, the following polyphenols were identified: phenolic acids (galic, caffeic, *p*-coumaric, ferulic); flavanones and flavanonols (naringenin and pinocembrin); flavones and flavonols (chrysin, galangin, quercetin, apigenin) and the glycoside rutin. Furthermore, the obtained results will be analyzed in order to be used as markers for determining the origin and authenticity of various honey samples.

Keywords: honey, polyphenols, flavonoids, SPE, HPLC-DAD-MS.

Acknowledgements: The financial support within the bilateral project between Macedonian Academy of Sciences and Arts and Bulgarian Academy of Sciences is gratefully acknowledged.

AEC 4

Development and validation of fast, simple, cost-effective and robust RP-HPLC methods for lisinopril, enalapril and perindopril determination

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New Reverse-Phase High-Performance Liquid Chromatography (RP-HPLC) methods for determination of lisinopril dihydrate (alone and in combination with calcium channel blocker amlodipine besylate), perindopril erbumine and enalapril maleate were developed and validated. These are the three most commonly prescribed and used members of the group of angiotensin converting enzyme inhibitors (ACE inhibitors), intended for treatment and prevention of cardiovascular diseases.

There are different pharmacopoeial (official) and non-pharmacopoeial chromatographic (HPLC) methods used this purpose. They often possess disadvantages, such as: long duration, long lasting gradients, use of expensive and/or harmful solvents or mobile phase additives, use of mobile phases with very low, acidic pH value, or high column temperatures that shorten column life. Such unfavorable chromatographic conditions are used to optimize the chromatographic peaks of ACE inhibitors since the peptide bond present in their structure causes formation of a mixture of two conformers in a solution resulting in a split of the main chromatographic peak due to the slow transformation of the conformers on the chromatographic column.

A few approaches during development of HPLC methods for determination of these active substances were used with the main purpose to test and suggest different chromatographic columns and conditions that will enable simple, fast and cost-effective analysis of ACE inhibitors.

Firstly, method for determination of lisinopril was developed for which alkaline mobile phases were tested with a pH value not higher than 7.5, taking into consideration the widest interval between $pKa_3 = 6.7$ and $pKa_4 = 10.1$ of lisinopril. The separation was optimized in a run time of 4 minutes, using a C18 column (end-capped, 150 mm × 4.6 mm, 5 μm) at 40 °C, a mobile phase composed of ammonium dihydrogen phosphate buffer (pH 7.2, 20 mM) and methanol (60:40, v/v) with a flow rate of 1.1 ml/min and UV detection at 214 nm. This method was then tested and adopted for analysis of combined tablets containing lisinopril and amlodipine. A mobile phase with potassium dihydrogen phosphate (pH 7.3; 20 mM) and methanol (70:30, *V*/*V*) gave good separation and symmetric peaks of lisinopril and amlodipine during a run time of only 5.5 minutes.

Then, another approach was used for development of HPLC methods for determination of perindopril and enalapril. Chromatographic peaks with optimal symmetry and short retention time were achieved using simple mobile phases with low percent of chaotropes (trifluoroacetic or perchloric acid) and several columns. The final optimized and validated method for determination of perindopril, with a run time of 2.5 minutes, is as follows: column Purospher C8e 55 mm × 4 mm, 5 μm at 30 °C, mobile phase: 0.08 % v/v TFA (pH ~ 1.95) and acetonitrile (70:30, v/v) with flow rate 1.0 ml/min, UV detection at 215 nm. An alternative was also proposed, using another column and adjusted mobile phase: Discovery C8 (150 mm x 4.6 mm, 5 μm), mobile phase with the same constituents in ratio 65:35, v/v, and same chromatographic conditions. The final optimized conditions for enalapril determination with a run time of 5 minutes are as follows: Zorbax RX C8 (250 mm x 4.6 mm, 5 μm) at 45 °C (for assay determination) or 50 °C (for dissolution determination), mobile phase composed of 0.07 % *V*/*V* $HClO_4$ (pH ~ 2.0) and acetonitrile (55:45, *V*/*V*) with flow rate 1.0 ml/min, UV detection at 215 nm.

All developed methods can be used for dissolution, assay and uniformity of dosage units testing of tablets containing these active substances. They are validated in accordance to the ICH guideline for Validation of analytical methods Q2(R1) with proven selectivity, linearity, accuracy, precision and robustness. They provide chromatograms with excellent peak symmetry and are simple, fast and cost-effective. The moderate experimental conditions make these methods favorable with regards to time and consumables consumption and consequently very useful for application in the quality control laboratories in pharmaceutical companies where a large number of analyses of this type are performed on a daily basis.

Keywords: lisinopril, enalapril, perindopril, HPLC method, development.

AEC 5

RP-HPLC-DAD method for sildenafil, vardenafil and tadalafil determination in pharmaceutical dosage forms and dietary supplements

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Sildenafil citrate, vardenafil hydrochloride and tadalafil are pharmacologically active substances, classified in the group of PDE-5 inhibitors and indicated for treatment of erectile dysfunction. There are a number of herbal formulations, classified as dietary supplements, which are used for treatment of erectile dysfunction. Rapid, simple, accurate and reproducible RP-HPLC-DAD method was developed for simultaneous of sildenafil, vardenafil and tadalafil in pharmaceutical dosage forms and dietary supplements. Chromatographic separation is achieved on a C18 column (Discovery C18, 4.6 × 150 mm, 5 µm) utilizing a mobile phase of 50 % methanol: 50 % 25 mM potassium phosphate monobasic (pH = 3.0), at a flow rate of 1.0 mL/min, column temperature 30 ºC, with UV detection at 230 nm. The method provides rapid and selective identification and quantification, with simple preparation of the sample solutions. Good linearity between response of the detector, and concentration was confirmed, over a concentration range 40-24 µg/mL for sildenafil, 30-75 µg/mL for vardenafil, 30-75 µg/mL for tadalafil, with regression coefficient better than 0.999. Linearity was also confirmed in lower concentration range 0.08-4 µg/ml for sildenafil, 0.01-5 µg/mL for vardenafil, 0.01-5 µg/mL for tadalafil, with regression coefficient better than 0.999. Accuracy of the method was confirmed with recoveries, with RSD lower than 2 %. The method is precise, confirmed by performing method repeatability and system repeatability, with low RSD values, and robust. The proposed method was validated and it can be applied in routine analysis for qualitative and quantitative determination of the target components in quality control of pharmaceutical dosage forms. The method can also be used for determination of potentially present forbidden pharmaceutically active substances in dietary supplements.

Keywords: Sildenafil citrate, vardenafil hydrochloride, tadalafil, HPLC-DAD, validation.

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AEC 6

Optimization of microwave-assisted digestion procedure for determination of target elemental impurities in pholcodine monohydrate by means of ICP-OES

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A rapid and simple method involving closed microwave digestion procedure followed by inductively coupled plasma-optical emission spectroscopy (ICP-OES) analysis was developed and further evaluated to obtain trace elements in an opioid cough suppressant active pharmaceutical ingredient (API) – pholcodine monohydrate. Solid pholcodine samples can't be introduced into the plasma directly, and initially must be dissolved by acid microwave assisted digestion. For the aim of this study, mixtures comprising different volume ratios of nitric acid and hydrochloric acid were prepared and tested for sample digestion in order to determine Class 1 and Class 2a elements according to the *Guideline for Elemental impurities Q3D* by International Conference on Harmonisation (ICH). Three digestions were carried out dissolving around 50 mg of pholcodine API under the same microwave conditions: temperature of 210 ºC (20 and 15 minutes ramping and holding time, respectively) and power of 1800 W. Among the three tested acid mixtures for pholcodine digestion, the best results were obtained by the mixture of a 6 mL concentrated nitric acid (65 %, *V*/*V*) and 4 mL concentrated hydrochloric acid (37 %, *V*/*V*). The proposed digestion procedure resulted in clear and colorless solution appropriate for ICP-OES analysis that makes the developed method suitable for routine testing of elemental impurities in pharmaceuticals.

Keywords: Elemental impurities, ICP-OES, ICH Q3D, Microwave digestion, Pharmaceutical, API, Pholcodine.

AEC 7

Forced degradation study of venlafaxine hydrochloride using HPLC/DAD

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Venlafaxine hydrochloride is a synthetic derivative of ethyl-cyclohexanol used as an antidepressant belonging to a group of drugs called selective serotonin and norepinephrine reuptake inhibitors (SSNRIs). It is metabolized to *O*-desmethylvenlafaxine, which potentiates CNS activity. Venlafaxine is used to treat major depressive disorder, anxiety and panic disorder.

A forced degradation study is an essential step in the design of a regulatory compliant stability program for both drug substances and products, in order to understand degradation pathways, to determine the stability and the shelf-life of the product, and manner of storage. The aim of this work was focused on degradation study of active substance venlafaxine hydrochloride and its product using acid and base hydrolysis, thermal degradation, photolysis and thermal + humidity degradation.

The solutions are subjected to liquid chromatographic (LC) investigations to establish the number of products formed in each condition. Chromatographic separation was optimized by isocratic HPLC method on a RP 8 column [LiChrospher 100, 250 x 4.6 mm, 5 μm] utilizing a mobile phase consisting acetonitrile and ammonium dihydrogen phosphate, pH 4.4 in the ratio of 25:75 *V*/*V* at a flow rate of 1,3 mL/min with UV detection at 225 nm.

Four degradation products were formed during the degradation study at 105 °C whereas only one was formed in 1 mol NaOH. No significant thermal + humidity, photolytic or degradation in 37 % HCl was observed in solid drug.

Besides degradation products, assay of venlafaxine hydrochloride was analyzed with optimized method.

Keywords: Venlafaxine hydrochloride, forced degradation study, degradation products, HPLC.

AEC 8

Using anthocyanin profiles as a parameter for authentication of various red juices from local markets

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Anthocyanins (ACNs) are a class of polyphenolic compounds, which are plant secondary metabolites that have been studied because of their many potential health benefits. Due to high costs of fruits, especially the ones that are rich in ACNs, food companies are tempted to increase profit by adulteration. For that reason, it is necessary to have methods for authentication of different fresh fruits and their products, e.g. fruit juices, fruit teas and fruit yogurts. The presence and pattern of specific anthocyanins can be used as markers for authentication of fruits and fruit products.

In this work HPLC/DAD/MS^n method was applied to 16 different commercial samples of fruit juices from the local markets in Macedonia. For the separation, two solvents were used: 2 % solution of formic acid in water and acetonitrile. With this method 37 different anthocyanins were identified in the analyzed samples and they were quantified using cyaniding-3-O-glucoside as external standard at 520 nm.

The obtained results suggest that 7 samples contain ACNs characteristic for the fruits from which they are derived i.e. are authentic regarding the declared fruits.

Principal component analysis (PCA) was performed for the nature and content of the different compounds and amounts to be correlated to the particular fruits.

Although these methods are very powerful, this strategy should take into account the polyphenol composition variability that depends on many factors. For that reason, we can use these compounds to verify the authenticity of fruit products, but we cannot be exact for their quantities in the processed product.

Keywords: anthocyanins, fruit juices, authentication, HPLC/DAD/MS^n.

AEC 9

How to identify authentic honey using NMR spectroscopy

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Honey is widely used in traditional and veterinary medicine, pharmacy and cosmetics, but it is also one of the most adulterated foods. A number of analytical methods have been used for authentication, determination of botanical or geographical origin and detection of adulteration. NMR spectroscopy has been widely used to identify and to quantify many components in honey, but so far no public database to distinguish different types of honey has been created.

141 honey samples and 8 syrup samples were analyzed using 1D and 2D NMR experiments. The aim was to determine the components, that allow differentiation of honey having various botanical origin and divers geographical origin. A rare tanzanian honey produced by stingless bees from genus Meliponini has also been studied. Quantitative NMR data of 35 components - carbohydrates, butane diol, proline, quercitol and other was used for statistical analysis by ANOVA, PLS-DA, Nightingale`s diagram and box-plots. Based on differences in the concentration of 16 components unambiguous discrimination of honeys from different botanical resources was achieved, while 25 substances were responsible for differentiation of the geographical origin. Most Macedonian honey samples contain quinovose – a reducing monosaccharide that has been found in plants but not yet in honey

Keywords: NMR-based metabolomics, honey, carbohydrates, chemometrics.

Organic Chemistry, Biochemistry and Pharmaceutical Chemistry (OBPC)

OBPC 1

Cytotoxicity of copper(II) complexes with S-isoalkyl derivatives of thiosalicylic acid on tumor cells of human and murine lung carcinoma *in vitro*

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Not presented.

OBPC 2

PEGylated phenothiazine derivatives as water soluble precursors for biomaterials

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Phenothiazineis a well-known fused ring heterocyclic compound possessing electron rich sulfur and nitrogen heteroatoms. It is used as a building block to design materials for high performance electronic and optoelectronic devices including light-emitting diodes, photovoltaic cells, thin film transistors, and electro-chromic cells and also in biomedicine [1,2]. Because of the low solubility of the phenothiazine based compounds in ordinary solvents, is necessary to use high polarity solvents, which are toxic for beings and environment.

In this context, the goal of the study was the synthesis of water soluble phenothiazine based building blocks for further use as in preparation of high performance semiconducting organic eco-materials and drug delivery systems. To this end, we designed three different PEG-ylated derivatives by functionalization with poly(ethyleneglycol) (**PEG)** and their synthesis was accomplished exploiting three combined synthetic strategies [3, 4, 5]. All three PEG-ylated compounds were structurally characterized by ^{1}H-NMR and FTIR spectroscopy and their optical properties were preliminary studied by UV-Vis and photoluminescence spectroscopy. As the synthetized compounds have amphiphilic structure, their nanostructuring in water was investigated by dynamic light scattering (DLS).

Keywords: phenothiazine, poly(ethyleneglycol), luminescence.

Acknowledgements: This work was supported by the Romanian National Authority for Scientific Research MEN – UEFISCDI project number PN-III-P1-1.2-PCCDI2017-0569 (10PCCDI/2018).

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OBPC 3

Urinary proteins as prognostic markers to monitor nephropathy in primary and secondary hypertension patients

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Diabetes and high blood pressure are the most common causes of end-stage renal disease (ESRD), according to recent researches of the World Health Organization. Quantitative analysis of total urine proteins and determining the type of secreted proteins are the best non-invasive markers to stage level or type of renal disease and to monitor the progression of renal disease to ensure optimal management.

Fifty adult patients from both ganders participate in this study in following adjusted model: 27 were diabetic hypertensive and 23 were non-diabetic hypertensive patients. The obtained results from serum tested parameters (urea, creatinine and uric acid) indicate impaired renal function. Qualitative analysis of the urine composition with test strips was carried out for each urine sample. The quantitative determination of total urine proteins was performed according to the Meulemans method.

Measurable concentrations of total urine proteins were observed in all samples, which can indirectly confirm the link between hypertension and nephropathy. In samples obtained from diabetic hypertensive patients, a higher urine protein concentration was determined. This indicates that there is a higher risk of developing of ESRD.

For further analysis of urine protein profile was performed sodium dodecyl-polyacrylamide gradient gel electrophoresis (SDS-PAGE). Reproducibility and repeatability of the method were examined by determining the Rf values of identical sample. The Rf values showed consistency in precision. The Rf values were also consistent and comparable in 6 independent samples run by second analyst with acceptable CV% and limit of quantification. Thus, the suggested method could be used for routine analysis of urinary proteins. Constructed electrophoregrams from SDS-PAGE gel of urine samples from both groups indicate that glomerular and tubular dysfunction are more common in diabetic hypertensive patients than in non-diabetic patients, with higher concentration of urine albumin.

Bio-analytical methods used for quantitative and qualitative determination of urine proteins allow application in diagnosis and monitoring the progression of renal diseases caused by different etiologies.

Keywords: SDS-PAGE, Meulemans, urine proteins, hypertension.

OBPC 4

First derivative spectroscopy ratio method of Bradford assay for determination of urine proteins

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The Coomassie brilliant blue (CBB) assay, known as the Bradford method, is commonly used for protein quantification in cell lysates, cellular fractions, or recombinant protein samples, because of its ease of performance, rapidity, relative sensitivity, and specifity for proteins. The method was based on reaction of formation of complex between protein and the red form of dye, which intensely absorbs light at 595 nm, so determination of microgram quantities of protein in this method is accomplished by measurement of absorbance at this wavelength. However, there is a slight nonlinearity in concentrations over 10 μg/mL, mainly caused by overlapping in the UV-VIS spectrum of the two forms of the dye in acid-base equilibrium at the usual acidic pH of the assay. Also, protein-dye binding is in equilibrium and complex formation depends on the concentration of both, the free protein and the free dye. The variable concentration produces another distortion of the linear response.

Novel and different spectrophotometric method based on first-order derivative spectrophotometry was developed to increases the accuracy and improves the sensitivity of the assay. Analyzes were performed on Varian Carry 50 UV/Visible spectrophotometer, in a 1-cm cell at wavelength range from 300 to 800 nm, with resolution 0.5 nm and scan rate of 300 nm/min. The linear calibration function was established in the concentration range 0.01 to 1 mg/mL of protein concentrations.

Significant improvement in the linearity of the method was observed with the use of the ratio of first derivative peaks at 550 nm and 425 nm ($^1D_{550/425}$), with correlation coefficient of 0.9993. The LOD of 0.035 mg/mL and LOQ of 0.0108 mg/mL were calculated.

This method was applied for estimation of total urine proteins and compared to the reference of turbidimetry method according to Meulemans. Obtained concentrations of the patient's urine proteins by both methods were compared by using correlation plots. Results indicate that protein concentrations obtained by these two methods are comparable. Developed first derivative ratio method ($^1D_{550/425}$) can be recommended for routine use due to accuracy of the results especially for lower protein concentrations.

Keywords: Bradford, urine proteins, derivative spectroscopy, ratio methods.

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OBPC 5

SDS-PAGE analysis for cerebrospinal fluid proteins

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Analysis of cerebrospinal fluid is used in the diagnosis of various neurological disorders, including multiple sclerosis and other infectious and inflammatory diseases of the brain and spinal cord. CSF analysis includes measurement of proteins, glucose, cells, pathogens and serology. Total protein, albumin and immunoglobulins in CSF are usually measured by spectrophotometric or immunometric assays in clinical laboratories, while separation and identification of different kinds of proteins are carried out by electrophoresis.

In this study, we focused the analysis on proteins with sodium dodecyl sulfate polyacrylamide gel electrophoresis (SDS-PAGE), where CSF proteins can be easily fractionated and detected without concentration of the original sample. Lumbar puncture was performed on 9 patients investigated and treated at Clinic of Neurology, Faculty of Medicine in Skopje, North Macedonia. CSF were sampled under sterile conditions and stored at -20 °C. SDS-PAGE was performed with a vertical electrophoretic apparatus on gradient gel 7-17 %. Equal volumes of CSF and the denaturing solution were heated to 95° C for 5 min, with adding reducing agent, or without it. A portion of the mixture loaded onto each well of the gel, depended of the total protein concentration in CSF. Electrophoresis was carried out at 250 mV per gel at room temperature for 180 min. After the run, gels were stained by Coomassie Brilliant Blue-R and the Mr of each protein was estimated with calibration kit (Amersham High Molecular Weight Calibration Kit for SDS-PAGE). Automated analysis, data storage and sophisticated data acquisition were carried out with Gel Pro Analyzer 3.1, which is specifically structured to analyse gels and electropherograms: complex band pattern matching (gel variation), lane relation studies, general gel analysis (accurate molecular size, quantitative determination of protein mixture etc.).

The non-reducing SDS-PAGE system was effective in clearly separating CSF proteins, particularly low molecular mass proteins. The number of bands (with Mr of 13 – 220 kDa) for patients varied and presence of Immunoglobulin G (IgG) or increased CSF albumin level were determined.

Immunoglobulin intrathecal production is an important diagnostic parameter in inflammatory conditions of the central nervous system (CNS). On the other hand, any increase of the CSF albumin level, results from an increased transudation from the blood which leads to diagnosis of dysfunction of blood-CSF barrier. Further investigation with 2D electrophoresis, or electrophoresis coupled with MS could give precise diagnosis of different inflammatory and infectious diseases of CNS.

Keywords: SDS-PAGE, CSF proteins, Electrophoregrams.

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OBPC 6

Application of Multi Wall Carbon nanotubes as drug carriers

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Biotechnology and Food Technology (BFT)

BFT 1

Effect of the molecular weight of chitosan on its edible films' properties

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Edible films has been recognized as new packaging option for food products because they prolon the shelf-life of food, while being simple to prepare, cheap and environmentally friendly. This study investigated the properties of edible films prepared as 1 % film forming solutions from low (50000-190000 Da), medium (190000-310000 Da) and high (310000-375000 Da) molecular weight chitosan. All films were plasticized by adding Tween 80 and emulsified with glycerol. Further the films were crosslinked with sodium tripolyphosphate to improve their handling and various applications. All films were characterized by their: handling abilities, thickness, water content, absorption capacity and solubility in water, their optical properties (total color change, transparency, opacity) and mechanical properties (puncture strength, Young modulus, elongation).

The results showed that the increase of the molecular weight resulted in increase of the film's thickness, but there was no change of the transperancy in the examined edible films, that was around 2.5. The opacity and the total color change were also more pronounced in the films with higher molecular weight. Their values ranged from 44 to 52 % and from 3 to 15, respectively. Total color change up to 3 is not noticable to the human eye. According to the moisture content of the samples, all edible films had similar values and were extremly dry. All edible films exhibited good mechanical properties.

In conclusion the chitosan edible films from low molecular weight showed slightly better properties compared to the others, but all films could find industrial use as coatings or packaging materials in the food industry.

Keywords: edible films, chitosan, molecular weight, mechanical properties, optical properties.

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BFT 2

Application of HPLC-DAD for phenolic evaluation of red wines during maceration

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The quality of red wines depends to great extent on their phenolic composition, the most important components which determine the colour, mouthfeel, astringency and bitterness of the wine. These compounds origin from different parts of the grape: (i) grape skins contain anthocyanins, flavan-3-ols, flavonols, dihydroflavonols, hydroxycinnamoyl tartaric acids, hydroxybenzoic acids and hydroxystilbenes, whereas (ii) flavan-3-ols and gallic acid are dominant in the seeds, and (iii) hydroxycinnamoyl tartaric acids are mainly present in the juice. In this study, phenolic compounds in Stanušina, Vranec and Cabernet Sauvignon wines were determined by HPLC-DAD and spectrophotometry. All wines were produced with different maceration time (3, 6 and 9 days) in order to study its influence on the phenolics extraction during winemaking. It was concluded that malvidin-3-glucoside and its derivatives were the major compounds, while caftaric acid was the predominant cinnamic acid derivative, followed by catechin, the main flavan-3-ol. Monitoring of winemaking showed a complex extraction pattern that vary with maceration time and grape variety, with hydroxycinnamic acids and anthocyanins were observed to be present in the highest content after 3 and 6 days of maceration, respectively, followed by a slight decrease with time. Compared to Cabernet Sauvignon and Vranec, Stanušina wines showed low level of anthocyanins, but relatively high content of hydroxycinnamic acids, such as caftaric and caffeic acids, and antioxidant activity as well.

Keywords: Anthocyanins, Autochthonous variety, HPLC, maceration, red wine.

Acknowledgments: This work was financially supported by JoinEUSEE IV, Erasmus Mundus Action 2 Partherships, which is gratefully acknowledged.

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BFT 3

Optimization and validation of capillary electrophoresis method for analysis of small-anions in red wines

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BFT 4

Production of fructo-oligosaccharides by enzymatic hydrolysis of inulin with free and immobilized inulinase

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This research concludes the profile of fructo-oligosaccharides obtained by batch hydrolysis with free and immobilized enzyme for a period of 24 h. For this purpose, three types of immobilized preparations were used: a) enzyme encapsulated in copolymer: polyacrylamide-polyethylene glycol, b) covalent bonded enzyme on magnetic nano-particles and c) adsorbed enzyme on a composite material of multiwalled nanoparticles/polypyrole /polyethylene glycol. It has been proven that short-chain fructo-oligosaccharides with DP 3-9, are found to be the most suitable carbon source for the probiotic bactiria compared to fructo-oligosaccharides with DP 2-17 and Inulin DP $\geq$ 23 [1] or according to Sanches Lopes *et al*. [2] the most appropriate length for prebiotic activity is 3 to 7. The purpose of the research is to examine the formation kinetics of fructo-oligosaccharides with different degrees of polymerization depending on the concentration of added enzyme/immobilized preparation, and the initial substrate concentration.

The distribution of fructo-oligosaccharides with different degrees of polymerization is examined with thin layer chromatography (TLC). Their concentration is calculated from standard curves for the individual fructo-oligosaccharides using Image J software. Data was obtained on the conversion rate of highly polymerized inulin and the percentage of fructo-oligosaccharides with a degree of polymerization between 3 and 6.

The highest concentration of free enzyme (16.9 U/mL) converts 36 % of 2 % (*w*/*V*) inulin solution into fructo-oligosaccharides with the degrees of polymerization 3-6 in 24 h. Similar conversions are obtained using 30 % (*w*/*V*) polyacrylamide/PEG composite and 2 % (*w*/*V*) initial concentration of inulin. When the enzyme was immobilized on multi-walled carbon nanotubes and magnetic nanoparticles, a conversion of 23 % was obtained.

Keywords: immobilization, inulinase, fructo-oligosaccharides, encapsulation, adsorption.

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BFT 5

Intelligent packaging for monitoring pH variations in food

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Many factors can influence the shelf-life of a product, such as pH, water activity, nutrient levels available, oxygen, etc. Variations in food pH could occur due to microorganism's growth which is usually connected with production of metabolites (gases) as well as chemical reactions that may impact flavour, consistency and shelf-life of products. This study focuses on development of intelligent food packaging that contains a colorimetric indicator sensible to pH changes, which will enable monitoring of the condition of the food in order to get information, to improve the safety and quality of food. Low molecular weight chitosan was used for the preparation of the edible films and also as a base for the packaging. Antocyanins, extracted from organic frozen aronia, were used as colorimetric indicators because they are sensible to pH changes and were integrated in the chitosan edible film. Three types of extracts were prepared: water, 75 % ethanol and lyofilizated solid extract. Liquid extracts were added as 20 % v/v, while solid extracts were added in three concentractions: 100 mg/100 mL, 200 mg/100 mL and 300 mg/100 mL for the preparation of the intelligent packaging. All films were characterized and immersed in buffers with pH from 3 to 11 to determine which indicator has the most visible color change.

The results of the characterization showed that all films had similar thickness of about 0.16-0.19 mm and their transparency was about 2. The films that contained the ethanol extract were the darkest and had 63 % opacity, followed by the films with the water extract that were lighter with 58 % opacity. The films prepared with the solid extract were less opaque. According to the moisture content, all films were dry, but showed good mechanical properties. When immersing the indicators in buffers with different pH, ethanol extract films showed the best results changing the colour from red in acidic to blue/green in alkaline solutions. The color change in the films with water extract was less noticeable while films with solid extract showed no visible changes.

In conclusion the films prepared with liquid extracts are better indicators because of their color changing properties and could be used for monitoring the condition of the food.

Keywords: intelligent packaging, indicators, chitosan, antocyanins, extracts, pH.

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Chemical Engineering (CE)

CE 1

Functionalization of recrystallized biosorbents as strategy for water removing in biofuel

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Worldwide petroleum-based energy resources are being depleted – onshore crude oil production peaked decades ago but our demands for petroleum are still going up. Technology is available, biodiesel texture is very similar to oil-derived diesel, and economic profitability seems sufficient thanks to the existent framework of fiscal and other financial supports. In the present work, we focused on the production of biodiesel (which is an important biofuel) from vegetable oils. With the conventional technology, vegetable oil mixed with alcohol (e.g., methanol) reacts in large-scale batch reactors and in the presence of an alkaline liquid catalyst (e.g., NaOH or KOH) to form methyl esters or biodiesel and glycerol or glycerine. The transesterification reaction can take up to 12 hours or longer to complete; and at the end of the reaction, it is necessary to use an acid to neutralize the liquid catalyst and to separate biodiesel and glycerol from the product mixture. The catalyst-neutralization and productseparation steps are timeconsuming, tedious, and costly.

The swelling behavior of absorbent system is an important parameter govering their applications specifically in pharmaceutical, chemical, petrochemical engineering. The polymer chains in absorbent interact with the solvent molecule and tend to expand to the fully solvated state, while the crosslinked structure applies a retractive force to pull the chains inside. Equilibrium is achieved when these expanding and retracting forces counter balance each other.

Keywords: process of transesterification, catalyst, biofuel, polymers, absorbents, recrystallization, hydrogels.

CE 2

Innovative methods and technology usage in natural cosmetics formulation

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The awareness regarding the safety and potential harmless of everyday products among consumers is increasing, meanwhile, nowadays trends are emphasizing the healthy lifestyle which products in accordance with the current needs.

Meaning products without preservative presence, potential mutational agents, allergens and other components with potential negative effects over one's health or the environment.
That is why in this paper the ability of natural isolates, such as essential oils and monoglycerides, was studied.

The goal was to determinate the possibility of excluding such components, as previously mentioned in cosmetics formulation, and include natural extracts that are potent enough to preserve the product and modified the product's characteristics while keeping the complete integrity of the products.

For the purposes of preserving the product, sage and thyme essential oils were used, as well as monolaurin, where it can clearly be seen the high potential of thyme essential oils and monolaurin.

Further, technologically advanced software Modde for the design of experiments was used in order to exclude the conventional agents and include natural substituents as gum acacia, xanthan gum, guar gum and tara gum.

Finally, a final formulation of cosmetic products was gained by this paper.

Keywords: Cosmetic, essential oils, antimicrobial, biopolymers.

CE 3

Developing natural cosmetics by replacement of conventional preservatives and thickeners

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The possibility of changing the standard additives in the cosmetic industry with safer, natural extracts was analyzed in this research. The replacement of conventional preservatives like benzoic and sorbic acids was done by introducing different essential oils and monolaurin. Their antimicrobial activity in real matrix, hand cream base prepared by simple emulsion of water in oil phase using emulsifier, was tested. This was done by isolating the natural contaminants of spontaneously spoiled cream and evaluate the effectiveness of the active components on these strains by Disk diffusion test - measuring the inhibition zone. The spoilage microorganisms were tentatively identified as *Aspergillus niger* and *Aspergillus flavus*.

Using the Modde software for experimental design, the ability to replace the standard thickeners by using the Thixogum product line was also examined. Spreadability, viscosity and pH were analyzed depending on the thixogum products concentration and the data was feed to the software together with the desired values. The desired values of these parameters were obtained by analyzing a commercially available cosmetic product "48 *". For the experimental design a linear model - Reduced Combinatorial was used, to create a smaller design space with a balanced distribution of all factor settings.

It was found that thyme essential oil shows the strongest antimicrobial activity followed by monolaurin and the rosemary essential oil which yielded the weakest antimicrobial effect. The software suggested a formulation that completely fitted in the desired requirements: viscosity of 41400 cP, pH 6.69 and a spreadability of 13.542 g·cm/s.

Keywords: natural cosmetic, preservatives and thickeners replacement.

Inorganic chemistry and technology, inorganic materials and metallurgy (ICTM)

ICTM 1

Mechanochemically synthesized $CoFe_2O_4$ and $CoFe_2O_4$/starch nanoparticles as efficient adsorbents for hexavalent chromium removal

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Not presented.

ICTM 2

Synthesis and characterization of new palladium(II) complex with 2-amino-5-methyl-4-phenylthiazoleY

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Thiazoles are heterocyclic compounds containing both a nitrogen atom and a sulfur atom as a part of the aromatic ring, but the term "thiazole" means a large family of derivatives. Thiazoles have found great use in medicine. Also, they represent an integral part of many compounds such as thiamine (vitamin B_1), penicillin, sulfathiazole, etc. [1]. 2-Aminothiazole derivatives are known as biologically active compounds and have found application in pharmacology. Due to the fact that they exhibit a wide range of biological activities (antibacterial, antifungal, anti-inflammatory, anti-viral, anti-analgesic, etc.), thiazoles deserve a lot of attention [2].

New palladium(II) complex with 2-Amino-5-methyl-4-phenylthiazole has been synthesized and the structure has been confirmed by elemental microanalysis, infrared (IR) and nuclear magnetic resonance (NMR) spectroscopy.

The complex was prepared by the reaction of $K_2[PdCl_4]$ with corresponding ligand in 1:2 mole ratio. Methanol solution of ligand was added to the water solution of $K_2[PdCl_4]$ and the reaction was performed at room temperature. The synthesized complex is orange colored and soluble in dimethyl sulfoxide.

Keywords: thiazole, palladium(II)-complex, biological activity.

Acknowledgement: This work is supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (project No.OI172016) and by the international scientific cooperation between the Republic of Serbia and the People's Republic of China.

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ICTM 3

Characterization of porous materials obtained under hydrothermal procedure from clayey diatomite and $Ca(OH)_2$

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The aim of this research is to obtain light porous materials, products from the hydrothermal reaction of clayey diatomite and $Ca(OH)_2$. Diatomite is a raw material with high porosity, which makes is suitable material for production of porous products. The raw material show a bulk density of 0.81 g/cm^3, water absorption 67.99 % and specific mass 1.94 g/cm^3, while the chemical composition is as follows: SiO_2 (55.80 % wt), Al_2O_2 (15.15 % wt), Fe_2O_3 (8.34 % wt), CaO (2.94 % wt.), SO_3 (0.95 % wt.), K_2O (2.01 % wt.), Na_2O (2.34 % wt.) and LOI 9.50 %. During the hydrothermal reaction of clayey diatomite with $Ca(OH)_2$new phases are formed. The probes were prepared while mixing 80 % trepel with 20 % $Ca(OH)_2$, with the help of a cylindrical mold (10 mm x 15 mm) and were pressed on a mechanical press at compressive strength from 2-10 kN. Probes obtained from the hydrothermal reaction of mixtures of diatomite and $Ca(OH)_2$ show bulk density 0.86 – 0.91 g/cm^3. The products of the hydrothermal reaction are lightweight materials, yet materials with high compressive strength ranging from 14 – 21 MPa.

Keywords: material characterization; diatomite; XRPD; compressive strength.

ICTM 4

Synthesis, structural characteristics and thin film preparation of four potential light-harvesting hybrid perovskites

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In the past decade, there has been an enormous increase in scientific works related to hybrid organic-inorganic perovskites (HOIPs). This is a result of their potential application in solar cells as light-harvesting materials. These kind of solar cells are advancing rapidly, and within 10 years (2009-2019) their efficiency has increased from 3.8 % to 25 % [1,2]. The research in this field is mainly directed towards investigation of perovskites with methylammonium and formammidinium as A-cations, more precisely the $CH_3NH_3PbI_3$ and $CH(NH_2)_2PbI_3$.

In this work the synthesis and structural characteristics of four perovskites containing methylammonium or formamidinium cation, Sb^{3+} or Bi^{3+}, Ag^+ and I^- were studied. Firstly, the possibility of obtaining of these materials in different media was investigated. From the results it can be concluded that for the antimony containing perovskites, *N*, *N*-dimethylformamide was the most appropriate solvent followed by a recrystallization in acetonitrile. For the bismuth containing perovskites 57 % hydroiodic acid proved to be the best suitable solvent. In all four cases the syntheses yielded small crimson hexagonal crystals. The powder X-ray diffraction confirmed that they have a hexagonal unit cell. In addition to this, we prepared thin films by a spin-coating method, with acetonitrile as a solvent. The determination of the band gap was performed according to the recorded UV-Vis spectra of the prepared thin films.

Keywords: hybrid perovskites, synthesis of, XRPD, UV-Vis, thin films, formamidinium, methylammonium.

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ICTM 5

Catalytic activity of mixed oxides derived from LDH in the synthesis of methylpyrazine: a comparative study

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This study is focused on selecting the most suitable mixed oxide catalyst derived from LDH for the synthesis of methylpyrazine (MP) using the cyclodehydrogenation reaction between propylene glycol and ethylenediamine. Layered double hydroxides (LDH) are part of a class having $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}[A^{n-}_{x/n}]\cdot mH_2O$ general formula [1]; in this case M^{2+} can be Zn, Co or Ni and M^{3+} is Al. Layered catalytic materials ZnAl; NiAl; CoAl with molar ratio of 3 were prepared by mechanochemical method [2] which involves directly milling in a ceramic mortar under ambient conditions of stoichiometric amounts of nitrates and alkaline compounds such as sodium carbonate and sodium hydroxide. The obtained LDH were calcinated, leading to the obtaining of the corresponding mixed oxides. Both the LDH and the mixed oxides were characterized using DRIFT and XRD analysis for confirming their structure, their textural properties by N_2 adsorption-desorption isotherms and the acidic-base character by NH_3/CO_2-TPD.

The catalytic activity of mixed oxides was tested towards the dehydration-cyclization of ethylene diamine with propylene glycol, followed by the dehydrogenation of the obtained pyperazine, yielding the MP as the main reaction product. This synthesis involves an Eley-Rideal mechanism on a bifunctional catalyst [3]. The reaction was performed in a fixed bed down flow tubular reactor, at 400 °C, using argon as carrier gas.

The influence of the reaction parameters such as reaction temperature, catalyst type, catalyst quantity and reactant flow rate on the reaction outcome has been studied. It has been observed that increasing the catalyst quantity over a certain threshold decreases the selectivity for MP. Also, an increased catalyst quantity is equivalent to a higher catalyst height, which increases contact time, causing more secondary reactions. However, a higher reactant flow rate lowers the contact time, so in order to maximize the selectivity for MP, an optimal contact time must be established. Even if in terms of conversion the three catalysts presented similar activities, regarding the selectivity in MP, the ZnAl and CoAl presented better results. The process is significantly influenced by the reaction parameters, their optimization allowing selectivities in MP up to 86 %.

Acknowledgment: Financial support PN-III-P1-1.2-PCCDI-2017-0395 and PN-III-P3-3.5-EUK-2016-0040, Executive Agency for Higher Education, Research, Development and Innovation.

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Physical, structural chemistry, spectroscopy and electrochemistry (PSSE)

PSSE 1

Influence of bismuth doping on the electrocatalytic properties of the $PrMn_{0.5}Co_{0.5}O_3$ perovskite

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In recent years, perovskite-type oxides have received great attention due to their wide range of different properties and applications. For example, they have been investigated as prospect materials that may be used in catalysis, fuel cells and electrochemical sensing of very significant biochemical molecules, such as glucose. Glucose is a metabolite that is fundamental for most living organisms and is analytically determined for monitoring a number of health conditions. Because of this, the development of efficient glucose sensors is of great importance. Enzymatic sensors are not preferred because of the problems related to enzyme stability that is greatly affected by pH, temperature and humidity, as well as to the difficulties in the immobilization of enzymes on the electrode surface. Therefore, a number of attempts for preparation of non-enzymatic glucose sensors were recently made. Some studies have shown that certain inorganic perovskite oxides, containing a rare earth metal and a 3d transition metal, can catalyze the glucose oxidation in an alkaline medium. These materials can be used for preparation of glucose sensing electrodes.

In our research, we synthesized the $PrMn_{0,5}Co_{0,5}O_3$ perovskite and investigated the possibility of substituting the Pr^{3+} cation with Bi^{3+}. All materials were synthetized using the modified Pechini method of synthesis (sol-gel method) and were then identified using powder X-ray diffraction (XRD). We determined that the limit of bismuth substitution in the A-cation position of this perovskite is 0.1. Electrocatalytical properties of the obtained perovskites were analyzed using cyclic voltammetry in solutions of KOH, CH_3OH, H_2O_2, phosphate buffer and also of glucose. It was found that $PrMn_{0,5}Co_{0,5}O_3$ does not show significant electrocatalytic activity towards glucose oxidation, but even a minor bismuth doping in the A-position of this perovskite influences the activity. Thus, bismuth doped $PrMn_{0,5}Co_{0,5}O_3$ may be considered as a prospect material for glucose sensing.

Keywords: bismuth doped perovskites; powder X-ray diffraction, cyclic voltammetry.

PSSE 2

Fast and accurate determination of important biomarkers in human blood serum

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Human blood serum is a complex matrix of biomolecules nearly impossible to analyze without a series of proper pretreatment. Nowadays, most used analytical techniques for detailed quantitative determination of compounds in human blood serum include spectrophotometry and chromatography, which include derivatization of the analyte, selection of proper solvent, etc. In our research, all results were obtained using square–wave voltammetry and without any pretreatment of the human serum. A thorough investigation on bilirubin, uric acid, total albumin and albumin fractions was made as these molecules are important indicators for development of some health deseases, susch as jaundice, Gilbert syndrome, liver congestion etc. The main goal is to develop a fast, sensitive and accurate electrochemical sensor for determination of these compounds in real samples of human blood serum, as well as studying the mechanistic nature of the electrode surface reactions. For this purpose, optimization of some square-wave parameters was made, such as frequency, accumulation time and step potential.

Keywords: square-wave voltammetry, bilirubin, uric acid, albumin, sensor.

PSSE 3

Activation and modification of multi-wall carbon nanotubes-MWCNTs for their use in obtaining composite materials: MWCNTs-perovskites

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Due to the unique behavior and their distinctive chemical properties, the carbon nanotubes - CNTs have dramatically drawn the researchers' attention. The properties of CNTs can be altered by introducing different functional groups on their surface. In this manner, one can make them polar, non-polar, or selective to different substrates. This opens a vast field of application and research. On the other hand, their composites with different materials show enhanced properties.

In this work, the attention is drawn to activation and modification of Multi-Wall Carbon Nanotubes (MWCNTs) with functional groups that are suitable for better interaction with the inorganic perovskites. For that purpose, the activated MWCNTs were functionalized using $SOCl_2$ so to obtain –COCl groups on the MWCNTs surface. Besides these groups, the surface is also saturated with –COOH, –C=O, –CHO and –OH. The modification increases the MWCNTs interaction with the perovskite materials.

The perovskites used in this work, $Ln_{0.9}Ca_{0.1}Co_{0.5}Cr_{0.5}O_3$ (Ln = Sm or Nd), were synthesized by solution combustion method. The characterization of the obtained materials as well as the composites, MWCNTs–perovskite, was conducted mainly by means of IR spectroscopy, and the results were supported by Raman spectra and XRD.

Keywords: Multi-wall Carbon Nanotubes – MWCNTs, modification, perovskite, IR spectroscopy, XRD.

PSSE 4

Preparation of composite material of organic-inorganic perovskite with multi-wall carbon nanotubes: MWCNT-$CH_3NH_3PbI_3$

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Organic-inorganic perovskites are materials that show important optical and electronic properties, since they are promising materials for solar cells fabrication. One of the most investigated materials of this type is $CH_3NH_3PbI_3$ perovskite. Recent research results have shown that they can be successfully modified with carbon nanotubes leading to even improved properties.

In this study, organic-inorganic perovskite, $CH_3NH_3PbI_3$, was synthesized in order to make composite materials with the MWCNTs. The synthesis of perovskite was performed in dimethylformamide (DMF) by dissolving the starting materials, CH_3NH_3I and PbI_2. The obtained product was found to be dihydrate which was transformed to anhydrous $CH_3NH_3PbI_3$ with perovskite structure, as was confirmed by powder XRD. MWCNTs were previously modified by introducing a silane linker, i.e. by attaching a silynazing agent. The silan acts as a linker between the MWCNTs and the perovskite. In this work 3-aminopropyltrimetoxy silane - APTMS was used as silanizing agent. Two types of composite materials were prepared, one with only activated MWCNTs ant the other with the modified one. The composite materials were investigated by IR and Raman spectroscopy as well as with powder XRD.

Keywords: Multi-wall Carbon Nanotubes – MWCNTs, modification, organic-inorganic perovskite, IR spectroscopy, XRD.

Polymers and polymer materials (POL)

POL 1

Graphen/carbon nanotube reinforced polymer composites as a UV protective coating

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In this research work, the behavior of graphene/carbon nanotubes (G/CNTs) polymer composites as UV protective coatings were investigated.

The polymer composites reinforced with 1 wt. % G/CNTs hybrids were synthetized by in situ miniemulsion. The monomer system contained methyl methacrylate (MMA), butyl acrylate (BA) and glycidyl methacrylate (GMA) in weight ratios 49.5/49.5/1, respectively. G/CNTs hybrids were prepared in several weight ratios: 10:1, 5:1, 1:1, 1:5 and 1:10. The 10:1 G/CNTs composite did not present any monomer conversion using water soluble initiator, indicating successful capturing of free radicals. In order to polymerize this system the hybrid and the initiator were physically separated using oil soluble initiator.

The photooxidative resistance of the 10:1 G/CNTs composite and the neat polymer was investigated by irradiation with UV light at 55 °C in air atmosphere, the irradiation lasted 400 hours. The changes in the chemical structure of samples were followed by FTIR spectroscopy. According to the results the 10:1 G/CNTs composite had minor changes in the chemical structure compared to the neat polymer. The tensile test measurements pointed that 10:1 G/CNTs composite had approximately five times higher Young's modulus and four times higher offset yield stress, compared to the neat polymer.

Keywords: UV protective coatings, waterborne composites, G/CNTs hybrids.

POL 2

Silver-doped reduced graphene oxide-based bimetallic nanohybrids as promising gas sensors

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Development of highly sensitive materials is an active area of research nowadays. To produce a material that is able to absorb gasses with high conductivity, sensitive to absorbed species and can be used for sensory purposes is the main goal in this research.

For the presented purpose we used dispersion of reduced graphene oxide (rGO) modified with silver particles (GOG Ag) additionally doped with platinum, palladium and ruthenium, respectively, by means of pulsed laser deposition (PLD). The obtained hybrids were characterized by means of: High-resolution transmission electron microscopy for direct imaging of the atomic structure of the samples; The surface morphology and the homogeneous distribution of the noble metal nanoparticles in the dispersion were determined and confirmed by Scanning Electron Microscopy (SEM); Raman spectroscopy was used for structural characterization of the dispersion and obtained PLD hybrids; Temperature-dependent resistivity measurements and sensor measurements towards selected organic compounds and gas sensing measurement performance towards the most common toxic gases NO_2, CO and NH_3 using Quartz crystal microbalance (QCM) were studied as well. The gas sensing examination results indicate that the obtained bimetallic nanoparticle hybrids show higher sensing response towards the considered noxious gases.

Keywords: gas sensors, toxic gases, reduced graphene oxide, bimetallic hybrids.

POL 3

Sensor, mechanical and electrical properties of graphene/MWCNTs polymer nanocomposite

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One of the most promising applications of graphene/carbon nanotubes hybrid structure is production of nanocomposites. This research work presents the sensor, mechanical and electrical properties of graphene/multi-walled carbon nanotubes (G/MWCNTs) based polymer nanocomposites.

The polymer matrix was previously synthetized by emulsion polymerization of three monomers: methyl methacrylate (MMA), butyl acrylate (BA) and acetic acid (AAc) in the following weight ratios 49.5/49.5/1, respectively. G/MWCNTs hybrids and their aqueous dispersions were prepared by sonication method in three weight ratios 5:1, 1:1 and 1:5 to obtain composites with 0.5 wt% and 1 wt% reinforcing phase.

The composites were characterized using FTIR spectroscopy. The sensor properties were analyzed on a Quartz Crystal Microbalance (QCM) sensor modified with the obtained composites and NH_3 was used as a gas pollutant. The composites 1 wt% 5:1 G/MWCNT and 0.5 wt% 1:5 G/MWCNT showed the best sensor properties. The added hybrid increased the electrical conductivity of the polymer up to 10^{-4} S/cm. As for the mechanical properties, the 1:1 1 wt% G/MWCNT and 1:5 wt1% G/MWCNT composites resulted with highest values for hardness, offset yield stress and stress at break and all the composites with 0.5 wt% reinforcement phase showed higher values for the elastic modulus.

Keywords: polymer nanocomposites; G/MWCNTs hybrids; gas sensors.

POL 4

Metal containing ionic liquids as catalyst for synthesis of polyester polyols from PET wastes

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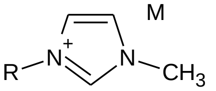
Poly(ethylene terephthalate), also known as PET, is one of the major postconsumer waste, being non-biodegradable, so the recovery of this material is needed [1]. In the absence of the catalyst, PET-glycolysis is a very slow process [2]. Currently, the common catalysts are inorganic metallic salts, or more recent, organic compounds (such as super-bases or ionic liquids). We propose the combined use of ionic liquids and inorganic salts. Glycolysis of PET wastes with different diols, using metal-containing ionic liquids $[Rmim]^+MX_3^-$ (R=*n*-butyl or *n*-lauryl) as catalysts, leads to aromatic polyester-polyols (APPs) [3]. Our aim is the obtaining such APPs useful for rigid and semi-rigid urethane foams.

In the first part, we present the synthesis and characterization of the catalyst having general formula shown in Figure 1. The synthesis scheme includes two steps: the synthesis of ionic liquids followed by their modification using an inorganic salt. The obtained catalysts were characterized by nuclear magnetic resonance spectroscopy, infrared spectroscopy and mass spectrometry.



I. R = n-C_4H_9: 1. M= $ZnCl_3^-$ 2. M= $CdCl_3^-$; 3. M= $ZnBr_3^-$
II. R = n-$C_{12}H_{25}$ M= $ZnCl_3^-$

Figure 1: General formula of the synthesized catalysts

Following up, the destruction of PET was adjusted by using ethylene glycol and, further on, it was extended to several types of diols. The discussion will be focused on the APPs structure, their properties and the efficiency of the reaction.

Acknowledgements: The financial support from UEFISCDI, Complex Projects CDI, no 70PCCDI/2018 – MAUS is gratefully acknowledged.

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POL 5

Chitosan nanofibers modified with formylphenylboronic acid. Preparation and characterization

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The aim of this paper was the preparation of chitosan based nanofibers for wound healing application. To this end, chitosan based porous nanofibers were prepared by electrospinning technique and further functionalized with formylphenylboronic acid. This design has been thought starting from the following premises: (1) Chitosan is a biocompatibile and biodegradabile polysaccharide originating from the natural chitin, which already proved antifungal and antimicrobial activity. (2) Formylphenylboronic acid is a derivative of boric acid, known for its antiseptic activity. (3) Nanofibers are materials with large area-to-volume ratio, and so a large active surface. (4) Moreover, the boric acid based derivative has been bonded to chitosan *via* imine linkage, a cleavable bond in pH acid media, which can assure the controlled release of boric acid derivative in the acidic pH media of the infected tissue [1, 2].

The targeted chitosan based nanofibers were prepared in three steps: First, a mixture of chitosan and PEG was electrospun. The water soluble PEG was used in electrospinning process, on a hand in order to improve the chitosan electrospinning ability and on the other hand to assure its easy removal towards porous chitosan fibers. Secondly, the as obtained fibers were consecutively washed with NaOH solution and water, in order to remove the acetic acid residue and PEG. Thirdly, the porous fibers were reacted with 2-formylphenylboronic acid in heterogeneous conditions, in different molar ratios of the functional groups, by imination [1]. The resulting Schiff base nanofibers were structural and morphological characterized by NMR, FTIR spectroscopy, SEM and AFM microscopy. Their antipathogenic activity was preliminary screened against *Staphylococcus aureus* – gram positive bacteria, *Escherichia coli* – gram negative bacteria, and *Candida albicans* yeast. The results proved the potential of the as obtained fibers to be used in wound healing applications.

Keywords: chitosan, nanofibers, Schiff base, electrospinning, 2-formylphenilboronic acid.

Acknowledgements: This work was supported by the Romanian National Authority for Scientific Research MEN – UEFISCDI project number PN-III-P1-1.2-PCCDI2017-0569 (10PCCDI/2018).

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POL 6

Chitosan based copolymers with enhanced solubility properties

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Chitosan (Ch) is known to be the only pseudonatural cationic polymer, presenting particular properties, such as biocompatibility, biodegradability, nontoxicity and last but not least, antimicrobial activity. Those characteristics have contributed to its applicability in numerous fields, including pharmaceutics, cosmetics, agriculture, food industry, biotechnology and wastewater treatment [1]. The limitation of chitosan is its poor solubility at neutral and basic pH, when it starts to lose its cationic nature. To diminish this drawback, researchers have focused their attention on synthesizing chitosan derivatives soluble over a wide pH range, such as quaternary ammonium salts of chitosan, carboxymethyl chitosan or chitosan-grafted copolymers [2].

The objective of this study was the synthesis and characterization of a novel chitosan derivative, by grafting a 6-membered cyclic carbonate ester, using the ring-opening graft copolymerization technique. The reactions were performed in heterogeneous system using different molar ratios between chitosan and monomer, in melt bulk or in solution, in presence of a swelling agent for chitosan [3].

The obtained copolymers were structural characterized using ^{1}H-NMR and FTIR spectroscopy. The gain information on the supramolecular changes induced by side chains grafted on chitosan backbones and the morphology of the films casted from solution was investigated using polarized light microscopy (PLM), atomic force microscopy (AFM) and fluorescence microscopy (FM).

To test the solubility of the chitosan grafted copolymers, different parameters were varied, including the solvent, pH and temperature. Some derivatives presented the property of being soluble in water, in comparison to the pristine chitosan that is soluble only in acidic media, this being the first step for the upcoming research.

Keywords: chitosan, ring-opening polymerization, solubility.

Acknowledgements: This work was supported by the Romanian National Authority for Scientific Research MEN – UEFISCDI project number PN-III-P1-1.2-PCCDI2017-0569 (10PCCDI/2018).

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POL 7

Screen printed electrodes based on polymer/CNT and polymer/G nanocomposite for advanced gas sensing application

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Future sensing applications include high-performance features, such as gas and toxin detection, real-time monitoring especially of physiological events, connected feedback. Such multi-functional sensors require advancements in sensitivity, specificity, with simultaneous delivery of multiple detection in a short time. Recent advances in 3D printing and electronics as well as in nanotechnology, have brought us closer to sensors with multiplex advantages, and additive manufacturing approaches offer a new scope for sensor fabrication. Polymer nanocomposites as an imperative domain in nanoscience and nanotechnology provide a significant breakthrough in the development of advanced materials for various sensing-application areas like electronic devices, functional electrodes, batteries and sensors. So, polymer nanocomposites of conductive polymer matrix (Polyaniline (PANI), Poly Vinilydene fluoride (PVDF)) with graphene and carbon nanotubes have gained a great interest for their application as gas sensors.

The main goal of this work will be the design of nanocomposites by using polymer matrix and carbon based nanostructures. Different techniques for the deposition of sensing layers will be compared such as drop-method, 3D printing end electro polymerization. The obtained nanocomposite sensor-electrodes will be tested for sensing of acidic and base toxic gas pollutants. Characterization will be performed by several spectroscopic techniques and electrical measurements, while morphology will be followed by SEM, TGA/DTA and SP techniques. Resistivity (i.e. conductivity) will be followed by SPE vaporization using various gases.

Keywords: carbon nanostructures, sensors, gas pollutants.

POL 8

Modification of Graphene and hybrid Graphene/MWCNT nanostructures for drug delivery applications

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In this study, two types of drug carriers, i.e. graphene (G) and hybrid graphene/multiwalled carbon nanotubes (G/MWCNT) were investigated. Carbon nanostructures were chemically modified with maleic anhydride (MAH) and polyethylene glycol (PEG 6000) in order to improve the biocompatibility and reactivity of the graphene sheets in buffers by introducing carbonyl and carboxyl groups, respectively. Doxorubicin hydrochloride (DOX·HCl) was selected as an anticancer drug to investigate its drug loading and drug release behavior. The physico-chemical properties of G, G/MWCNT, G/MWCNT-DOX and G-DOX were characterized by scanning electronic microscope (SEM), Fourier transform infrared spectroscopy (FTIR – ATR) in Attenuated transmission mode, Thermogravimetrical analysis (TGA), zeta potential and particle size distribution. The systems were characterized for their surface modificaions as welll as for drug loading efficiency and *in vitro* drug release.

The FTIR spectra indicated bonding of PEG and MAH onto the carbon nano-carriers and the loaded drug. The modification with MAH has resulted in better thermal stability compared to the pegylated carriers in both investigated systems.

The obtained results indicated a maximum drug efficiency entrapment of 24 % attributed to graphene PEG 6000. The drug release profiles showed a release of the drug over 24 hours. *In vitro* release profile was performed at 37 ºC and pH = 5.5 (endosomal pH value for cancer cells).

Keywords: Graphene, Modification, Drug Delivery System.

POL 9

Synthesis of graphene nanoribbons/polymer adsorbents for detecting toxic gases

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The atmospheric pollution with toxic gases is considered as serious environmental problem in human society. Toxic gases like CO, NH_3 and NO_2 are one of the most common air pollutants that can irritate skin, corroded lung tissue and respiratory tract and in the worst case, cause mortal danger.

Offering new materials for gas sensing performance with low cost, ambient working condition, simple preparation, high sensitivity, selectivity and reproducibility is the crucial objective of this research work. Using relatively low cost, water-borne polymer system with excellent physical and chemical properties reinforced with graphene nanoribbons as gas adsorbents was considered as most appropriate. The polymer systems was composed from methyl methacrylate (MMA), butyl acrylate (BA) and acrylamide (AAm) in weight ratio of 49.5/49.5/1, further blended with aqueous dispersion of GNRs in amount of 0.2 wt. %, and 0.8 wt. % of GNRs in relation to the polymer. The obtained hybrids were characterized by means of: tensile test measurement and dynamical mechanical thermal analysis (DMTA) for studying the mechanical, thermal and viscoelastic properties of the nanocomposites; contact angle measurements to examine the hydrophobicity/hydrophilicity and determine the surface energy of the new systems; Scanning electron microscopy (SEM) to investigate the morphology of the hybrids; gas sensing measurement performance using Quartz crystal microbalance (QCM).

Improvement of mechanical and thermal properties was noticed with higher loading of GNRs. The obtained adsorbents showed sensing response to CO and NH_3 gases.

Keywords: gas sensors, toxic gases, graphene nanoribbons, hybrid latexes p(MMA/BA/AAm).

Acknowledgements: NATO (SPS G5244) is gratefully acknowledged.

POL 10

In-depth thermal and mechanical characterization of liquid rubber composites intended for medical applications

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Silicone rubber is a widely used material in various applications, due to a large degree of flexibility, chemical stability, low surface tension, high permeability, oxidative resistance and a very good biocompatibility [1]. The poor mechanical properties of silicone rubber are the major drawback that severely hinder its practical uses [2]. The purpose of this study is to compare the improvement of mechanical and thermal properties of silicone rubber, which can be obtained by the addition of inorganic filler, such as hydrophilic nanosilica (HDK N20). The thermal and mechanical properties of the obtained composites films were studied before and after aging, such as flexural tests and immersion in Phosphate buffered saline (PBS) environment [3].

Materials and methods: Elastosil LR 3003/40 wasused as an elastomer matrix and hydrophilic nanosilica (HDK N20) as a filler. Different concentrations of nanosilica (1, 3, 5, 7%) were used. After the homogenization of the components in a laboratory mixer, the mixture was poured into metal frames of different thickness (0.6, 1 and 2 mm) and crosslinked into a laboratory press (165 °C, 50 atm, for 5 minutes). For post-crosslinking, the pressed films were placed in the oven at 200 °C for 4 hours.

The results highlighted the influence of the filler content on the thermal and mechanical behavior of the silicone rubber. Thermal analysis showed an improved thermal stability of the silicone rubber after the addition of the filler. The mechanical properties are influenced by the concentration of the added filler and by the thickness of the samples. The biocompatibility was tested by in vitro test by cytocompatibility and cells adhesion using fibroblast mouse cells, and a uniform cell proliferation on both the silicone rubber and the composite could be noticed, which demonstrates the potential use for biomedical applications.

Keywords: silicone rubber, composites, biomedical applications.

Acknowledgements: This work was supported by a grant of the Romanian National Authority for Scientific Research and Innovation, CCCDI – UEFISCDI, project number COFUND-MANUNET III-MedIn-1, within PNCDI III, contract no. 33/2018.

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Editors: Miha Bukleski and Katarina Josifovska

Publisher: Society of Chemists and Technologists of Macedonia
For the publisher: Zoran Zdravkovski

http://www.sctm.mk/kongresi.htm

ISBN 978-9989-760-17-4

CIP - Каталогизација во публикација
Национална и универзитетска библиотека „Св. Климент Охридски", Скопје

54(062)(048.3)
66(062)(048.3)

STUDENTS' Congress of SCTM (13 ; 2019 ; Skopje)
Book of abstracts / 13th Students' Congress of SCTM, 19-21 September 2019 Institute of chemistry Skopje, N. Macedonia. - Skopje :
Society of chemists and technologists of Macedonia = Скопје : Сојуз на хемичарите и технолозите на Македонија, 2019. - 51 стр. ; 21 см

Начин на пристап (URL): http://www.sctm.mk/kongresi.htm. - Регистар

ISBN 978-9989-760-17-4

а) Хемија - Собири - Апстракти б) Хемиска технологија - Собири - Апстракти COBISS.MK-ID 111204618