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TOXIC METAL IONS REMOVAL BY ADSORPTION ON NANOCARBONS FROM POLYMERS

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Keywords: adsorption; carbon; metal ions; water purification.

Introduction: The subject of this work is preparation carbon adsorbents from different polymer and biomass waste, with subsequent characterization of the samples and effective application for removal of metal ions and organic pollutants from waters.

Due to their highly porous structure and large adsorption capacity, activated carbons are widely used as adsorbents in technologies connected to pollution abatement in water and gases in chemical industry, pharmaceutical and food industries, etc. Activated carbons have often been synthesized from precursors based on expensive and depleting fossil fuels, but they can be prepared easily from cheaper biomass or agricultural by-products. In the last years appeared many reports, dedicated to the preparation of activated carbons from various cheap and alternative precursors - coal, agricultural by-products and other biomass materials, polymers, polymer waste [1-4].

Materials and methods:

Different precursor were used to prepare carbon adsorbents:

- polymers – polyolefin wax, phenol-formaldehyde resin, etc.
- agricultural wastes - coconut shells, apricot stones, almond shells, grape seeds, olive stones and pulp, cherry stones, bamboo, been pods, straw etc.

The precursor was heated up to 115°C until melting 98%. H_2SO_4 was added by drops with continuous stirring, and the mixture was heated up to 160°C. The obtained solid product was washed with water, dried at 150°C, and carbonized at 600°C. After that activation with water vapour at 800°C was performed.

Biomass carbons were prepared by hydropyrolysis procedure of biomass precursor at 800°C.

Results: Obtained carbons are distinguished with moderatel high surface area and prevailing microporous structure, detected by N_2 porosimetry.

The properties of nanocarbons determine their application as effective adsorbents for toxic metal ions (Hg, Mn, etc.).

Conclusions: The obtained carbon adsorbents are distinguished with moderately high surface area and prevailing microporous structure. Their properties determine their application as effective adsorbents for removal of metal ions from waters.

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References:

[1]. Gergova K, Petrov N, Eser S. Adsorption properties and microstructure of activated carbons produced from agricultural by-products by steam pyrolysis. Carbon 1994;32:693-702.

[2]. Bacaoui A, Yaacoubi A, Dahbi A, Bennouna C, Phan Tan Luu R, Maldonado-Hodar FJ, Rivera-Utrilla J, Moreno-Castilla C. Optimization of conditions for the preparation of activate carbon from olive waste cakes. Carbon 2001;39:425-32.

[3]. Ania CO, Parra JB, Arenillas A, Rubiera F, Bandosz TJ, Pis JJ. On the mechanism of reactive adsorption of dibenzothiophene on organic waste derived carbons. Appl Surf Sci 2007;253:5899-903.

[4]. Budinova T, Savova D, Tsyntsarski B, Ania CO, Cabal B, Parra JB, Petrov N. Biomass waste-derived activated carbon for the removal of arsenic and manganese ions from aqueous solution. Appl Surf Sci 2009;255:4650-7.

THE HEAT-TRANSFER METHOD: A VERSATILE LOW-COST, LABEL-FREE, FAST AND USER-FRIENDLY READOUT PLATFORM FOR BIOSENSOR

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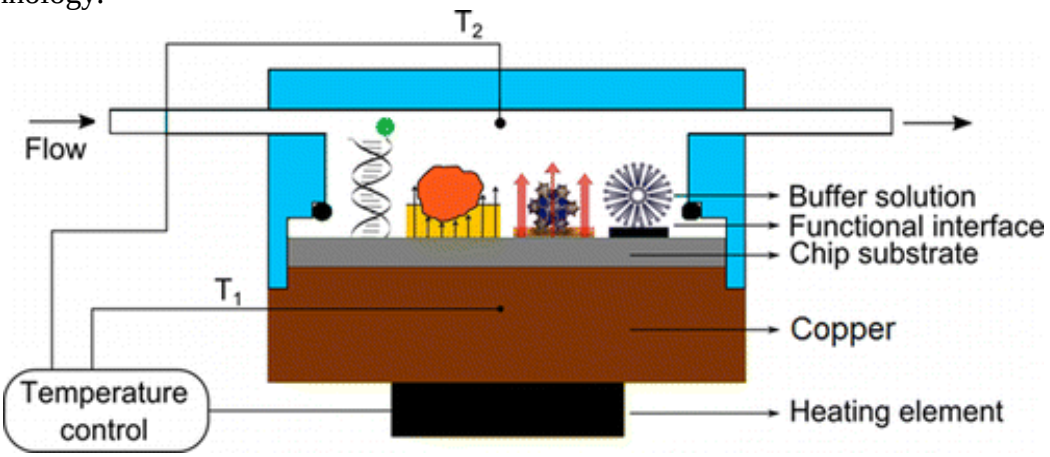
Keywords: biosensors; heat-transfer method; DNA; small molecules; bacteria.

In recent years, biosensors have become increasingly important in various scientific domains including medicine, biology, and pharmacology, resulting in an increased demand for fast and effective readout techniques. In this presentation, we will report on the recently developed heat-transfer method (HTM) and illustrate the use of the technique by zooming in on four established bio(mimetic) sensor applications: [1] mutation analysis in DNA sequences, identification of bacteria through surface-imprinted polymers, [2,3] detection of small molecules in blood samples with molecularly imprinted polymers [4,5]. The methodology is based on changes in heat-transfer resistance at a functionalized solid−liquid interface. To this extent, the device applies a temperature gradient over this interface and monitors the temperature underneath and above the functionalized chip in time. The heat-transfer resistance can be obtained by dividing this temperature gradient by the power needed to achieve a programmed temperature. The low-cost, fast, label-free and user- friendly nature of the technology in combination with a high degree of specificity, selectivity, and sensitivity makes HTM a promising sensor technology.



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References:

[1]. van Grinsven B, Vanden Bon N, Strauven H, Grieten L, Murib M, Jimenez Monroy KL, Janssens SD, Haenen K, Schöning MJ, Vermeeren V, Ameloot M, Michiels L, Thoelen R, De Ceuninck W, Wagner P. Heat-transfer resistance at solid–liquid interfaces: a tool for the detection of single-nucleotide polymorphisms in DNA. ACS Nano. 2012;6:2712-21.

[2]. van Grinsven B, Eersels K, Akkermans O, Ellermann S, Kordek A, Peeters M, Deschaume O, Bartic C, Diliёn H, Steen Redeker E, Wagner P, Cleij TJ. Label-free detection of *Escherichia coli* based on thermal transport through surface imprinted polymers. ACS Sens. 2016;1:1140–47.

[3]. Steen Redekera E, Eerselsa K, Akkermans O, Royakkers J, Dyson S, Nurekeyeva K, Ferrando B, Cornelis P, Peeters M, Wagner P, Diliën H, van Grinsven B, Cleij TJ. Biomimetic bacterial identification patform based on thermal wave transport analysis (TWTA) through surface-imprinted polymers. ACS Inf Dis. 2017;3:388–97.

[4]. Eersels K, Diliën H, Lowdon JW, Steen Redeker E, Rogosic R, Heidt B, Peeters M, Cornelis P, Lux P, Reutelingsperger CP, Schurgers LJ, Cleij TJ, van Grinsven B. A novel biomimetic tool for assessing Vitamin K status based on molecularly imprinted polymers. Nutrients. 2018;10:751.

[5]. Canfarotta F, Czulak J, Betlem K, Sachdeva A, Eersels K, van Grinsven B, Cleij TJ, Peeters M. A novel thermal detection method based on molecularly imprinted nanoparticles as recognition elements. Nanoscale. 2018;10:2081-9.

EFFECT OF COMPLEX STRUCTURE ON SELECTIVITY PROPERTIES OF ION IMPRINTED POLYMERS

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Keywords: Ion Imprinted polymers; Distribution of complexes; Isolation of complexes; Selectivity

Introduction: There is high need of highly selective materials for metals as nickel, cobalt, cadmium and copper in environmental engineering because of their toxicity and on the other hand the value and price of the metals. In the search of highly selective separation materials, ion imprinting technique leads to very attractive materials.[1] The aim of this study is to present extensive study concerning effect of complex structure on selectivity properties of ion imprinted polymers.

Materials and methods: IIPs with three different structures 1:1, 1:2 and 1:3 using nickel nitrate as a source of template were prepared by inverse suspension polymerization using ethylene glycol dimethacrylate (EDMA) as the crosslinking agent in the DMSO and DMSO/methanol (50:50, v/v).[2] Selectivity studies were made at room temperature (22-24ºC) at adjustable pH. Metal concentrations were determined by ICP-AES. Studied metal pairs were Ni/Zn, Ni/Co, Ni/Cd and Ni/Cu. Selectivity coefficients, k, for binding of specific metal ion, M_1, in presence of competing ion M_2, can be obtained from adsorption data according to Eq (1).

$$k_{M_2}^{M_1} = \frac{[M_2]_{solution} \cdot [M_1]_{adsorbent}}{[M_1]_{solution} \cdot [M_2]_{adsorbent}} \quad (1)$$

Results: The results showed that when complex structure is changing from 1:1 to 1:3 form, the selectivity coefficients, k^{Ni}_{Zn}, k^{Ni}_{Co}, k^{Ni}_{Cd}, are increasing. This is probably due to increase stability of the nickel complex formation from 1:1 to 1:3 form. New formulation for the selectivity coefficient should be based on the step-wise complex formation.[3] Nickel selectivity over copper could not be achieved.

Conclusions: Selectivity coefficient should be defined so that the variation of the coordination numbers can be taken into account.

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References:

[1]. Branger C, Meouche W, Margaillan A. Recent advances on ion-imprinted polymers. React Func Polym 2013;73:859–75.

[2]. Laatikainen K, Branger C, Coulumb B, Lenoble V. *In situ* complexation *versus* complex isolation in synthesis of ion imprinted polymers. React Funct Polym 2018;122:1-8.

[3]. Laatikainen M, Laatikainen K. Chelating adsorption with variable stoichiometry: Separation of nickel and zinc in concentrated sulfate solution. Chem Eng J 2016;287:74-82.

ACHIEVING RECOGNITION AND DETECTION OF MICROPOLLUTANTS THROUGH SMART MOLECULARLY IMPRINTED POLYMERS

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Keywords: molecularly imprinted polymers, sensor.

Molecularly Imprinted Polymers (MIPs) are synthetic polymers designed to mimic natural biological receptors like antibodies. In the classical non-covalent approach, a template molecule interacts with a functional monomer and a cross-linker in a porogen solvent. After polymerization, the removal of the template generates the recognition cavities inside the three-dimensional copolymer network. Ion Imprinted Polymers (IIPs) are prepared in a similar manner by choosing functional monomers having chelating properties with respect to a target ion. Combined with various transduction mechanisms, MIPs and IIPs are the key stones of a large panel of chemical sensors thanks to their high recognition properties, easy synthesis and high stability [1]. A significant improvement of the sensors performances can be reached when the functional monomer also acts as a sensing element [2]. This is what we intend to do by (1) incorporating a redox probe as the functional co-monomer during MIP synthesis [3,4] (Fig.1) and (2) including a fluorescent monomer inside an IIP (Fig.2).

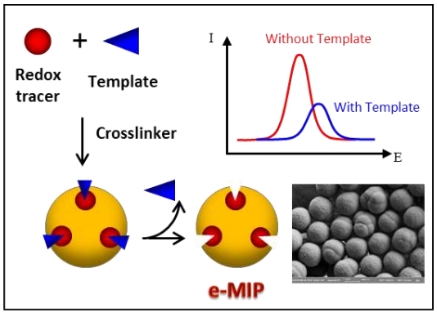

Figure 1. Concept of electrochemical MIPs

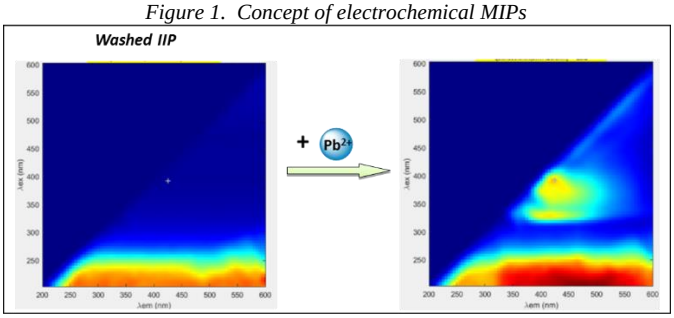

Figure 2. Impact of lead(II) addition on the IIP fluorescence signal

References:

[1]. Haupt K, Mosbach K. Molecularly Imprinted Polymers and Their Use in Biomimetic Sensors. Chem Rev 2000;100:2495–504.

[2]. Ton XA, Tse Sum Bui B, Resmini M, Bonomi P, Dika I, Soppera O, Haupt K. A Versatile Fiber‐Optic Fluorescence Sensor Based on Molecularly Imprinted Microstructures Polymerized in Situ. Angew Chem Int Ed 2013;52:8317–21.

[3]. Udomsap D, Branger C, Culioli G, Dollet P, Brisset H. A versatile electrochemical sensing receptor based on a molecularly imprinted polymer. Chem Commun 2014;50:7488-91.

[4]. Ekomo VM, Branger C, Bikanga R, Florea AM, Istamboulie G, Calas-Blanchard C, Noguer T, Sarbu A, Brisset H. Detection of Bisphenol A in aqueous medium by screen printed carbon electrodes incorporating electrochemical molecularly imprinted polymers. Biosens Bioelectron 2018;112:156-61.

LOW MOLECULAR WEIGHT (HYDRO)GELATORS BASED ON CARBOHYDRATES

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Keywords: LMWHGs; nanoparticle storage; cell culture.

Hydrogels are functional materials, used in applications from healthcare to home and personal care products. Most commercial hydrogels are polymeric, displaying polydispersity and irreversible gelation, but hydrogels can also form by self-assembly of low molecular weight hydrogelators. These have high purity, are readily modified (e.g. for alternative gelation triggers) and provide for reversible gelation. These are the unique features of these "smart" materials, which hold significant promise for tailored applications. Low molecular weight hydrogelators (LMWHGs) form viscoelastic solid-like materials by formation of a three-dimensional fibrous network derived from the non-covalent self-assembly of the gelator molecules in water (and other biologically relevant media) [1].

Our research focuses on *(i)* the design, synthesis and characterization of novel LMWHGs and their corresponding functional biomaterials and *(ii)* evaluation of potential applications, e.g. cell culture [2]. At all times, we have followed a simple strategy, amenable to scale-up, using a minimum number of synthetic steps and biocompatible building blocks with the potential to add value, e.g. biorecognition.

Our design has centred on using monosaccharide amphiphiles as LMWHGs, with our first examples being GalNHFmoc and GlcNHFmoc [3]. We have since progressed to explore alternative, more biocompatible, aromatic motifs which were food/drug-based, along with the inclusion of the phenylalanine motif. It is these compounds that will be discussed in this lecture.

We will discuss the challenges inherent in the synthesis and characterisation of the LMWHGs themselves and the soft materials prepared from them. After much optimisation, we now use a range of characterisation techniques, i.e. IR, fluorescence, NMR, SEM/TEM, XRD, rheology, CD, etc.

We will also discuss some results on the application of these soft materials, for example in the storage of nanomaterials, along with preliminary cell culture/cytotoxicity studies on selected materials [4, 5].

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References:

[1]. Du X, Zhou J, Shi J, Xu B. Supramolecular Hydrogelators and Hydrogels: From Soft Matter to Molecular Biomaterials. Chem Rev 2015;115:13165-307.

[2]. Liu J, Sun Z, Yuan Y, Tian X, Liu X, Duan G, Yang Y, Yuan L, Lin HC, Li X. Peptide Glycosylation Generates Supramolecular Assemblies from Glycopeptides as Biomimetic Scaffolds for Cell Adhesion and Proliferation. ACS Appl Mater Interfaces 2016;8:6917-24.

[3]. Birchall LS, Roy S, Jayawarna V, Hughes M, Irvine E, Okorogheye, GT, Saudi N, De Santis E, Tuttle T, Edwards AA, Ulijn RV. Exploiting CH-π interactions in supramolecular hydrogels of aromatic carbohydrate amphiphiles. Chem Sci 2011;2:1349-55.

[4]. Sitsanidis ED, Piras CD, Alexandre BD, Siligardi G, Javorfi T, Hall AJ, Edwards AA. Circular dichroism studies of low molecular weight hydrogelators: The use of SRCD and addressing practical issues. Chirality 2018;30:708-18.

[5]. Giovannini G, Kunc F, Piras CC, Stranik O, Edwards AA, Hall AJ, Gubala V. Stabilizing silica nanoparticles in hydrogels: impact on storage and polydispersity. RSC Advances 2017;7:19924-33.

IS ULTRASOUND AND MICROWAVE COUPLING A VIABLE SOLUTION FOR PROCESS INTENSIFICATION?

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Keywords: microwave; ultrasound; process intensification.

Introduction: The use of microwave energy in chemical laboratories was first described in 1986 by Gedye [1] and by Giguere [2] in organic synthesis and by Ganzler [3] in the extraction of biological matrices for the preparation of analytical samples. Because the microwave radiation is nonionized, the interaction with materials occurs by their heating. Some advantages of microwave heating over conventional systems are [4]:

- Volumetric heating: heating does not take place by transfer from a surface but to the volume of the reaction mixture;
- Selective heating - the components of a heterogeneous system can heat up differently even if the size of the components is very small;
- Rapid energy transfer-very high-power densities can be obtained which produce very high heating rates.

Because of these particularities, microwave heating is increasingly used in the synthesis and processing of materials. However, the overall process rate is often limited by mass transfer and here comes the ultrasound which can improve the mass transfer and overcome this limitation. Power ultrasound besides improving mass transfer can influence chemistry and processing, generating cavitation bubbles when passes through the liquid. There are many thousands of such bubbles in the liquid some of which are relatively stable, but others expand further to an unstable size and undergo violent collapse to generate temperatures of about 5000°K and pressures of the order of 2000 atm. If the bubble collapses occur close to a solid surface the collapse is not symmetrical and results in microjets of liquid being directed towards the surface of the material at speeds of up to 200 m/s. These jets are, of course, the underlying reason why ultrasounds are so effectives in increasing mass transfer.

The combination of these two types of irradiations – electromagnetic and mechanical – and their application to chemical reactions is of high interest, but scientific articles are quite few [4, 5].

Conclusions: Both microwave and ultrasound irradiation meet the Process Intensification guidelines for: the improvement of energy transfer; the reduction of energy consumption; the reduced volumes of reactors/plants; the improved product quality; the ease of process automation; as well as remote reaction control [6].

The main question about the combined technology is how the two separate technologies can be combined. There are two approaches:

- Use separate reactors one using ultrasound and another using MW with a recirculating pump to allow the liquid to be transferred from one reactor to another.
- Use a single reactor with both US and MW inside.

The challenges are related to the types of processes that can be intensified by applying US and MW, considering that each of these processes requires restrictive conditions to produce good results.

The paper describes the main types of equipment that make possible the simultaneously use of ultrasounds and microwaves. Some results obtained using this type of equipment are also presented.

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References:

[1]. Gedye R, Smith F, Westaway K, Ali H, Baldisera L, Laberge L, Rousell J. The use of microwave ovens for rapid organic synthesis. Tetrahedron Lett 1986;27:279-82.

[2]. Giguere R, Bray T, Duncan S. Application of comercial microwaves ovens to organic synthesis. Tetrahedron Lett 1986;27:4945-8.

[3]. Ganzler K, Szinai I. Effective sample preparation method for extracting biologically active compounds from different matrices by a microwave technique. J Chromatogr 1990;520:257-62.

[4]. Leonelli C, Mason TJ. Microwave and ultrasonic processing: Now a realistic option for industry. Chem. Eng. Process 2010;49:885-900.

[5]. Gude VG. Synergism of microwaves and ultrasound for advanced biorefineries. Res Effic Technol 2015;1:116-25.

[6]. Vinatoru M. Mason TJ, Calinescu I. Ultrasonically assisted extraction (UAE) and microwave assisted extraction (MAE) of functional compounds from plant materials. Trends Analyt Chem 2017;97:159-78.

SUSTAINABLE VALORIZATION OF LIGNIN SIDE STREAMS

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Keywords: lignin; side streams; multifunctional catalyst; microbial sequential conversion; lignohumate.

Introduction: Lignin is the most abundant renewable aromatic raw material [1]. Currently, it results as a by-product from pulp and paper industry and it is mainly used as energy source [2]. Increasing demand for (nano)cellulose from wood and development of cellulose-based biorefinery drives novel economic valorization of lignin side-stream [3]. Competitivity of lignocellulose feedstocks market is depended on the capacity to develop sustainable conversion of the aromatic side stream [2]. Biomass based biorefinery shall use not only the cellulose [3]. Lignin and silicon are the main intermediate product streams from lignocellulose based biorefinery [4]. Lignin have a potentially high added value and it should be further processed into a portfolio of bio-based products [5]. Here we present two approaches for conversion of lignin, one related to the use of multifunctional catalysts for lignin fragmentation, with further production of phenol derivatives, and the other one related to the formation of lignohumic acids by sequential fermentation with successive consortium of microorganisms.

Materials and methods: Multifunctional Fe_3O_4@Nb_2O_5@Co@Re catalysts were prepared via a multistep process [6]. The magnetic nanoparticles, obtained by coprecipitation, $Fe(NO_3)_3 \cdot xH_2O$, $FeCl_2 \cdot 4H_2O$, NH_3, were covered with a niobia, Nb_20_5, shell. Niobia was precipitated from an ammonium niobate–oxalate complex. On niobia was deposited cobalt, using a deposition/precipitation procedure. Rhenium has been finally deposited. The following methods were used: (*i*) impregnation, (*ii*) deposition (ImC) and precipitation (PP) of rhenium chloride and (*iii*) impregnation with ammonium perrhenate (ImA). The characterization of the multifunctional catalysts was realized by high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), energy-dispersive X-ray (EDX) SEM, Raman, X-ray diffraction, H_2 andNH_3 temperature-programmed desorption, X-ray photoelectron spectroscopy. A sequential lignin fermentation with *Pleurotus ostreatus* and *Trichoderma konigii – Bacillus amyloliquefaciens* was performed. The resulted lignohumate was extracted into alkali solution, precipitated with HCl and characterized by UV-VIS spectroscopy, FTIR and plant bioassay.

Results: The use of ImC and ImA methods led to more reduced catalysts, and to a decrease in cobalt content corresponded to more reduced rhenium. An inverse relation between the acidity and the degree of reduction has been found. The screening of these catalysts in the fragmentation of the lignin confirmed the role of the structural characteristics and solvent. ImC catalysts exhibited better catalytic activity, especially for low metal loadings [2%Co@3%Re, 85% yield of LF, 15.5% yield of LR in tetrahydrofuran (THF), and 14.5% yield of insoluble LR in THF]. Although the extent was smaller, the PP catalysts allowed a more advanced fragmentation of the lignin to fragments with molecular weights between 200 and 400 Da. The catalysts were totally recovered by application of a magnetic

field and recycled six times without any loss of activity or selectivity. The sequential lignin fermentation lead to a formation of lignohumate, which demonstrate plant biostimulant effect.

Conclusions: Sustainable alternatives for lignin valorization were developed. It was developed a total recoverable multifunctional catalyst, based on Fe_3O_4@Nb_2O_5 on which rhenium and cobalt was deposited. This recoverable catalyst was proven to fragmentate lignin. A biomimetic fermentation process was developed, leading to the formation of a lignohumate, with plant biostimulant characteristics.

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References:

[1]. Calvo‐Flores FG, Dobado JA. Lignin as renewable raw material. ChemSusChem, 2010;3(11):1227-1235.

[2]. Renders T, Van den Bosch S, Koelewijn SF, Schutyser W, Sels BF. Lignin-first biomass fractionation: the advent of active stabilisation strategies. Energy & Environmental Science, 2017;10(7):1551-1557.

[3]. Cao L, Iris KM, Liu Y, Ruan X, Tsang DC, Hunt AJ, Zhang S. Lignin valorization for the production of renewable chemicals: State-of-the-art review and future prospects. Bioresource technology, 2018;268(12):465-475.

[4]. Khaleghian H, Molaverdi M, Karimi K. Silica removal from rice straw to improve its hydrolysis and ethanol production. Industrial & Engineering Chemistry Research, 2017;56(35):9793-9798.

[5]. Kim KH, Kim CS. Recent efforts to prevent undesirable reactions from fractionation to depolymerization of lignin: Towards maximizing the value from lignin. Frontiers in Energy Research, 2018;6:92.

[6]. Opris C, Cojocaru B, Gheorghe N, Tudorache M, Coman SM, Parvulescu VI, van Bokhoven JA. Lignin fragmentation onto multifunctional Fe3O4@ Nb2O5@ Co@ Re catalysts: the role of the composition and deposition route of rhenium. ACS Catalysis, 2017;7(5):3257-3267.

STOCHASTIC MODELLING IN CHEMICAL ENGINEERING

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Keywords: mathematical modeling; stochastic models; cellulose hydrolysis; deep bed filtration.

Introduction: The practical applications of stochastic processes theory are multiple. This fact is a consequence of the capacity of this theory that can predict the future of a dynamic system by use of its history and its actual state [1]. The prediction of the future by history and actual state is possible for processes where as vehicle of their dynamics it identifies one or more systems with complete random links (SCRL). *The state of a system at time **n** is a random variable* An *with values in a finite space (measurable)* (A **A**). *The state evolution at time n+1 results from the appearance of a* Bn+1 *result which is also a random variable with values in a finite space (measurable)* (B **B**). *The appearance of a result signaling the state evolution could be represented considering a* **u** *application of* AxB *in* A *and introducing the following statement*: An+1=**u**(An, Bn+1) *for all* n>=0 . *The* Bn+1 *probability distribution conditioned by* Bn, An, Bn-1, An-1,….B1, A1, A0, *and symbolized as* P(Bn+1/Bn,An,…A_0), *depends only on the state* An. *The group* [(A,**A**),(B,**B**), **u:**AxB→A,P] *defines a SCRL*. The space A represent the **process component** and the space B is the **process connection**. In the case of cellular stochastic models, a phenomena results by different structures formation and the passage from one structure to another is made randomly; in this case the structure formation is the "process component" and the passing steps are the "connection process". Two cases are analysed here by mean of cellular stochastic models.

Cellulose hydrolysis. The first case refers to acidic cellulose (biomass) hydrolysis. The breakage of the β-1,4-glycosidic bonds by acids leads to the hydrolysis of cellulose polymers, resulting in the sugar molecule glucose or oligosaccharides. Mineral acids, such as HCl and H_2SO_4, have been used in the hydrolysis of cellulose [2,3]. Here the process component is represented by all fragments with molecular mass under initial cellulose molecular mass, which appear in breaking of molecular structure; the process connection is a Markov type, represented by distribution of the breaking probabilities for all fragments from process component. The effect of temperature and acid concentration in acidic cellulose hydrolysis is very well considered by effect of this parameters on transition frequency in Markov chain connection. The model description, the model mathematical expression, the procedure of model implementation was given in detail. The use of several types of matrix of transition probabilities is also found in the paper. Uniform distribution for breaking probabilities of cellulose chain was selected in matrix of transition probabilities, which has been used in treatment of hydrolysis evolution for cellulose with low molecular mass. The emphasis in the matrix of the transition probabilities of temperature and environment acidity effect on dynamic evolution of hydrolysis, allowed of model to be expanded and compared with data generated by formal kinetic models.

Deep bed filtration. The second case focuses on dynamics deep bed filtration when it is possible to obtain an analytical solution of model. Two elementary processes can be identified for particle evolution in the filtrating granular bed *i.e.*, a first one (1) considering that the particle moves with the velocity v determined by the fluid flowing over the filter grains and a second one (2) taking into account the particle deposition (v=0). The case of deep filtration of some radioactive waste waters is used as data source for model parameters identification. The exploitation of model is also presented

References:

[1]. Dobre T, Sanchez JM. Chemical Engineering Modelling Simulation and Simimitude, Chapter 4, Wiley VCH, 2007.

[2]. Torget RW. Fundamental aspects of dilute acid hydrolysis/fractionation kinetics of hardwood carbohydrates. 1.Cellulose hydrolysis. Ind Eng Chem Res 2000;39:2817-2825.

[3]. Jacobsen ES, Wyman EC. Cellulose and hemicellulose hydrolysis models for application to current and novel pretreatment processes. Appl Biochem Biotechnol 2000;84-86:81-96.

[4]. Dobre T, Zicman LR, Pârvulescu OC, Neacşu E, Ciobanu C, Drăgolici FN. Species removal from aqueous radioactive waste by deep-bed filtration. Environ Pollut 2018;241:303-310

A FAVORED CYCLIZATION ACCORDING TO BALDWIN'S RULES (5-EXO-TRIG) OF SOME ISONIAZID ANALOGUES IN ACID CATALYSIS

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Keywords: isoniazid analogues; tautomerism; NMR; enant. pure γ-lactols; 2-HOO-THF; 2-HO-THF; X-ray analysis

Introduction: Tetrahydrofurane is oxidized in time to peroxides, the first and the most important peroxide being 2-HOO-THF. This is decomposed to other peroxides, and to 2-HO-THF at a limited extent, even when it is kept on sodium wire. Different procedures are used to destroy the peroxides, in goal to use THF, but usually, when the peroxides content exceed ~ 0.05% peroxides, a careful use is required. In the same time, isoniazid analogues are mainly used for tuberculosis treatment, but recently are also studied and new biological activities of these hydrazone type compounds: anticonvulsant, antidepressant, antimicrobial, antimalarial, antiplatelet, vasodilator, antiviral, antitumoral, etc. were found.[1,2] This paper combined our interest to obtain new isoniazid analogues using lactoles like 2-HO-THF and enantiomerically pure lactols from the sequence of prostaglandin synthesis which favored, according to Badwin's rules (5-exso-trig)[3] the cyclization to the tautomer with a tetrahydrofurane ring in acid catalysis.

Materials and methods:

2-HO-THF from old epoxidized THF, and/or prepared from 2-HOO-THF (from peroxides or synthesized) by reduction withPh_3P, and by oxidation of 1,4-butandiol; enantiomeric pure γ-lactols from the sequence of prostaglandin synthesis; isoniazid (INH). The lactols were reacted with isoniazid in an adequate solvent.

Results: An isoniazid analogue was synthesized from 2-HO-THF in different synthetic strategies. Other isoniazid analogs were obtained from enantiomerically pure γ-lactols from the total stereocontrolled prostaglandin synthesis. NMR Spectroscopy in DMSO and $CDCl_3$ put in evidence a tautomerism of the isoniazid compounds between the linear Schiff base and cyclic N,O-aminals (favored according to Baldwin's rules); *such a tautomerization was never mentioned in the literature for an isoniazid analogue.* X-Ray crystallography confirmed the linear Schiff tautomer in the crystal of an analogue. Antimicrobial screening study: the inhibition of growth was measured against 5 bacteria: *Escherichia coli*, *Klebsiella pneumoniae*, *Acinetobacter baumannii*, *Pseudomonas aeruginosa* and *Staphylococcus aureus*, and 2 fungi: *Candida albicans* and *Cryptococcus neoformans* (ESI, Table 3S). The isoniazid analogues and INH were found to be inactive

Conclusions: A number of isoniazid analogues were synthesized, fully characterized by IR, NMR, X-ray analysis and evaluated for antimicrobial and antifungal activity.

The study put in evidence a long range tautomerism for isoniazid analogues, not mention in the literature for an isoniazid compound.

Acknowledgements*: We thank CO-ADD Community for Open Antimicrobial Drug Discovery (Institute for Molecular Biosciences, The University of Queensland, 4072 St Lucia QLD Australia**) for free antibacterial and antifungal screening of the the isoniazid analogues.*

References:

[5]. S. Rollas, S. G. Küçükgüzel, Biological Activities of Hydrazone Derivatives, Molecules, 2007, 12, 1910-1939.
[6]. Narang, B. Narasimhan, S. Sharma, A Review on Biological Activities and Chemical Synthesis of Hydrazide Derivatives *Current Medicinal Chemistry*, **2012**, *19*, 569-612.
[7]. J.E. Baldwin, "Rules for Ring Closure" J. Chem. Soc., Chem. Commun.,734 (1976).; K. Gilmore, I. Alabugin, R.Mohamed, WIREs Comput. Mol. Sci., 2016, doi 10.1002/wcms.1

MOLECULAR DOCKING STUDIES OF SOME NOVEL QUINOLONE COMPOUNDS

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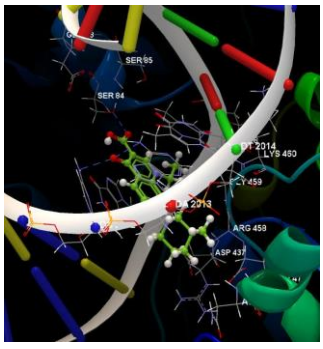
Keywords: molecular docking; fluoroquinolones; quinolones; antimicrobials.

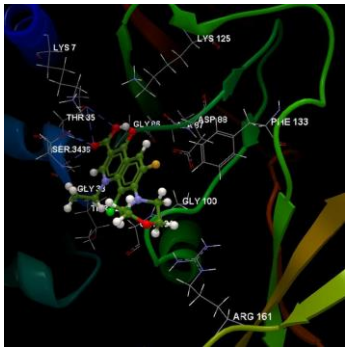
Introduction: An important parameter in the development of a new drug is the drug's affinity to the identified target (protein/enzyme). Predicting the ligand binding to the target (protein/enzyme) by molecular simulation would allow the synthesis to be restricted to the most promising compounds [1,2].

Materials and methods: A restricted hybrid HF-DFT calculation was performed in order to obtain the most stable conformer of each ligand and a series of DFT calculations using the B3LYP levels with 6-31G* basis set has been conducted. The docking studies of the quinolone compounds will be performed with the CLC Drug Discovery Workbench to identify and visualize the ligand-receptor interaction mode.

Results: A series of quinolones have been designed. For these compounds there have been performed calculations of characteristics and molecular properties and molecular docking studies to identify and visualize the most likely interaction ligand (quinolone) with the receptor protein. The protein-ligand complex has been realized based structure of Moxifloxacin with *St.aureus* DNA gyrase and DNA which was available through the Protein Data Bank (PDB entry 5CDQ).The result of molecular docking study, as shown in Fig. 1a for quinolone FPQ 30, the compound with the better activity *"in vitro"* against *St. Aureus* ATCC 6538 (MIC=0.125 µg/ml), reveals docking score -37.47 (RMSD=0.07 Å). The protein-ligand complex has been also realized based ccrystal structure of Ribose-5-phosphate isomerase A from *Pseudomonas aeruginosa* which was available through the Protein Data Bank (PDB entry 4X84). The result of molecular docking study, as shown in Fig. 1b for quinolone FPQ 30, the compound with the better activity *"in vitro"* against *Ps. Aeruginosa* ATCC 9027 (MIC=1.28 µg/ml), reveals docking score -37.88 (RMSD=0.05 Å).



1a



1b

Figure 1.Docking pose of the FPQ 30 interacting with residues in the binding site of 5CDQ (1a) and Docking pose of the FPQ 30 interacting with residues in the binding site of 4X84 (1b)

Conclusions: A restricted hybrid HF-DFT calculation was performed in order to obtain the most stable conformer of each ligand and a series of DFT calculations using the B3LYP levels with 6-31G* basis set has been conducted. The docking studies have been carried out using CLC Drug Discovery Workbench Software in order to predict the most possible type of interaction, the binding affinities and the orientation of the docked ligand at the active site of *St. aureus* (PDB: 5CDQ), *E. coli* (PDB: 1S14), *Ps. Aeruginosa* (PDB: 4X84) and *Streptococcus pneumoniae* (PDB: 3FOE).

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References:

[1]. Meng X-Y, Zhang H-X, Mezei M and Cui M., Molecular Docking: A powerful approach for structure-based drug discovery. Curr Comput Aided Drug Des. 2011; 7: 146–57.

[2]. Ferreira FG, dos Santo RNs, Oliva G and Andricopulo AD. Molecular Docking and Structure-Based Drug Design Strategie. Molecules 2015, 20, 13384-421; doi:10.3390/molecules20071338

CARBAZOLIC POLYMERS FUNCTIONALIZED WITH ZINC MONOHYDROXIFTALOCIANINE FOR THE PHOTOSENSIBLE CLEARING

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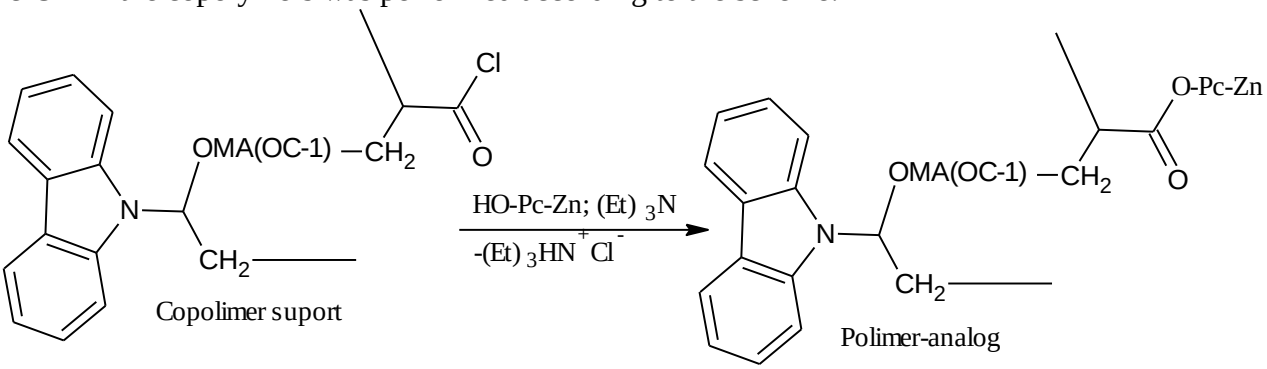
Key words: support copolymers; polymer-like; zinc phthalocyanine; triethylamine; 2,4,7-trinitrofluorenone

Introduction: The problem of photosensitive layers development from carbazole polymers is also present at the contemporary stage, especially for electronics, optoelectronics and other fields of modern technic[1,2]. A special role is played by the carbazole-metalophthalocyanine polymer systems in photovoltaic cells [3].

Materials and Methods: The paper is dedicated to the synthesis and research of photosensitive polymeric materials from N-vinylcarbazole (N-VC) ternary copolymers with octyl methacrylate (OMA) or octa-1-ene (OC-1), then functionalized with zinc monohydroxyphthalocyanine (Zn-Pc-OH). Synthesis of the support copolymers was carried out by the method of radical polymerization in the presence of the azo-bis-isobutyro- nitrile initiator (AIBN) at 70°C for 4 hours. The N-VC content was constant, equal to 60 mol%, and Cl-AC ranged from 10 to 20 mol%. The support copolymers were sedimented from MeOH. The characteristic viscosity is 0.10-0.14 Dl/g. The functionalization of Zn-Pc-OH in the copolymers was performed according to the scheme:



Results: The functionalized copolymers with Zn-Pc-OH were purified by sedimentation from hexane, then dried in vacuo at 50°C. They later served to make photosensitive layers. Their structure was confirmed by FTIR spectroscopy by the disappearance of vibrations ν= 3400-3550 cm^{-1} and ν= 1000-1050 cm^{-1} characteristic of the -OH groups, as well as the emergence of several vibrations of new valency. From the copolymer solution with Zn-Pc-OH and 15% of 2,4,7-trinitrofluorenone were made thin layers with a thickness of 3-6 μm that exhibiting real photosensitivity of 10^{-15} -10^{-6} J/cm^2 in the field visible spectrum of λ = 400-800 nm and in the near-infrared reign.

Conclusions: Several N-vinylcarbazole functionalized with zinc monohydroxyphthalocyanine copolymers was obtained. Structures of copolymers from N-VC: OMA (OC-1):Cl-AC were confirmed by FTIR spectroscopy (Brucker ALPHA). The stratums of N-VC: OMA (OC-1):Cl-AC, sensitized with 2,4,7-trinitrofluorenone, possesses good photosensitivity in the visible and near infrared spectrum of the diapason.

References:

[8]. J.V.Grazulevicius, P.Strohriegl, J.Pielichowski, K.Pielichowski. Carbazole-containing polymers: synthesis, properties and applications. In: Progress in Polymer Science, 2003 Volume 28, Issue 9, p. 1297-1353. Doi:10.1016/S0079-6700(03)00036-4 (*Journal article)*.

[9]. S. Robu, T. Potlog, G. Dragalina, A. Popuşoi, I. Lungu, N. Nasedchina, A. Chirita. Photosensitive layers from carbazole copolymers sensibilized with metalophtalocyanines. The International Symposium "Priorities of Chemistry for a Sustainable Development" PRIOCHEM Romania - Bucharest October 25 - 27, 2017, XIII-th Edition, p. 9. http://www.icechim.ro/priochem/editia14/volumrezumate2017.pdf. Accessed 12 July 2018 (*On-line resource*).

[10].Tamara Potlog, Vadim Furtuna, Cornel Rotaru, Roman Rusnac, Ştefan Robu, Tomoaki Masuzawa, Hidenori Mimura. Material properties of zinc phthalocyanine from fa solution and application in organic solar cell. In: International Journal of Industrial Electronics and Electrical Engineering, 2018 Volume-6, Issue-1, p.40-46. ISSN(p): 2347-6982, ISSN(e): 2349-204X (*Journal article)*.

ANION-DEPENDENT SELF-ASSEMBLY OF COPPER(II) COORDINATION POLYMERS

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Keywords: coordination polymers; bidentate ligands; self-assembly; anion influence.

Introduction: Self-assembled coordination polymers have received great attention in recent years due to their structural diversities and also to their wide array of potential applications in many fields including gas storage, catalysis, magnetism, luminescence, and ion exchange [1].

Materials and methods: Various Cu(II) salts, such as $Cu(NO_3)_2 \cdot 3H_2O$, $Cu(ClO_4)_2 \cdot 6H_2O$, $Cu(CF_3SO_3)_2$, $Cu(BF_4)_2 \cdot 6H_2O$, have been reacted with sodium azide, 1,2-bis(4-pyridyl)ethane (bpa), and 1,3-bis(4-pyridyl)propane (bpp). All the synthesized compounds have been characterized by elemental analysis, standard spectroscopic techniques (FTIR, UV-Vis-NIR), as well as by single crystal and powder X-ray diffraction. The elemental analysis was performed using the Euro EA Elemental Analyzer (Euro Vector) and Callidus software. Molecular structures were determined by single-crystal X-ray diffraction with a STOE IPDS II diffractometer using the SHELX-97 and Diamond 3 softwares for calculations and graphical representations. A XRD Benchtop Powder Diffraction system was used to aquire the powder diffraction data, which were processed with NIST software. IR spectra were recorded on a Bruker Fourier Transformance Tensor V-37 spectrophotometer, using OPUS software. Solid-state electronic spectra were recorded using the UV-Vis-NIR Jasco V670 spectrophotometer, equiped with Spectra Manager software.

Results: The self-assembly of polymeric networks from different Cu(II) salts and the N-donor ligands: azide, bpa, and bpp as bidentate spacers, has been systematically investigated in order to obtain some basic information useful for the crystal engineering of coordination frames upon variation of the counterions. The crystal structures of the resulting assemblies have been determined and the intermolecular interactions of the compounds in the crystalline phase have been investigated. The structural diversity of the new compounds depends on the starting Cu(II) salts, conducting to 1-D, 2-D, and 3-D extended structures. The chain-like structure of compound $^1{}_\infty[Cu(bpa)_2(H_2O)_2](NO_3)_2$ is depicted in Figure 1. The data obtained from X-ray diffraction reveals a significant influence of the nature of anions on the self-assembly of the coordination frameworks. The anion exchange properties of the obtained coordination polymers have been studied.

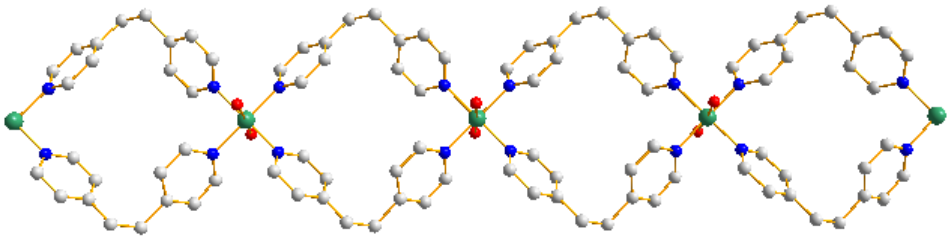

Figure 1. The chain-like structure of compound $^1{}_\infty[Cu(bpa)_2(H_2O)_2](NO_3)_2$, where copper atoms are in green, oxygen atoms in red and nitrogen atoms in blue (Hydrogen atoms were omitted for clarity).

Conclusion: New polymeric 1-D, 2-D, and 3-D networks with different Cu(II) subunits as nodes and N-donor bridging ligands as linkers were prepared. A systematic investigation of the effects of the counterions on the dimensionality of the obtained coordination polymers was conducted.

Acknowledgements*: This work was supported by the Romanian Executive Agency for Higher Education, Research, Development and Innovation - UEFISCDI (project PN-II-RU-PD-2012-3-0528) and University of Bucharest (project 154/22.01.2014).*

References:

[1] Chin T.C., Kenneth S. One dimensional coordination polymers: Applications to materials science. Coord. Chem. Rev., 1993, 128(1-2): 293-322; Sareeya B., Satoru J., Susumu K., Chemistry and application of flexible coordination polymers. Sci. Technol. Adv. Mat., 2008, 9(1).

SYNTHESIS AND STUDY OF SOME CHEMISTRY POLYMERIC ANTIOXIDANTS DOUBLE FUNCTIONALISED WITH MALIC ANHYDRIDIDE, QUERCETINE AND OTHER ANTIOXIDANTS

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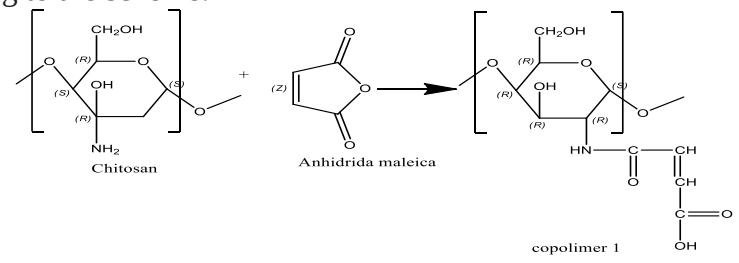
Keywords: Chitosan; maleic anhydride; functionalised polymer; quercetine; antioxidants.

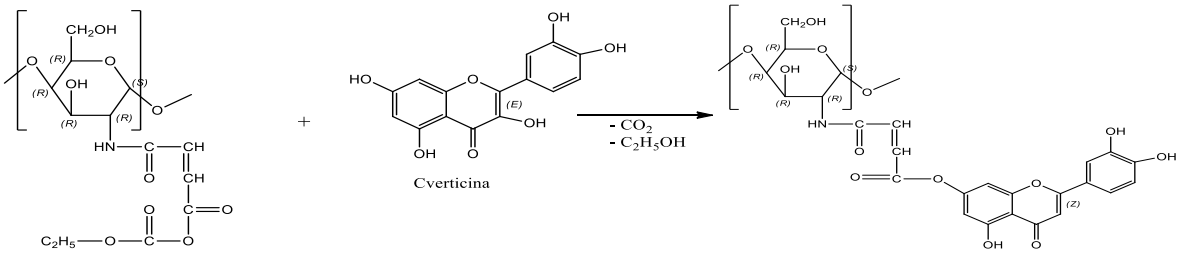
Introduction: Nowdays, special attention is given to natural polymers with antibacterial and antioxidant properties [1,2]. The fixation of the biologically active compounds on the macromolecular compound chain contributes to the prolongation effect, the reduction of the toxicity of the obtained compound, and in some cases the increase of the biological activity. For these reasons, the authors in the present paper investigate the possibility of chitosan functionalization of antioxidant compounds such as quercetin, ascorbic acid and others.

Materials and methods: The functionalisation of maleic anhydride to chitosan was performed in the first step according to the scheme:



PA-1

The synthesis was carried out at room temperature for 24 hours. After purification, by PA-1 sedimentation was dissolved in dimethylformamide, it was subjected to quercetin grafting according to the scheme:



PA-2

Results: The chemical structure of PA-1 and PA-2 has been confirmed with IR spectra by the emergence of new vibrations. It has been found that functionalized chitosan has a stronger antioxidant activity than pure querticine with the same concentration of querticine.

Conclusions: Analyzing the obtained data, we can mention that it was obtained new polymeric compounds, with antioxidant properties stronger antioxidant properties than pure antioxidants.

***Acknowledgements**: The researches were carried out within the project STCU 6377.*

References:

[11].Jun Liu, Xiao-Yuan Wen, Jian-Feng Lu, Juan Kan, Chang-Hai Jin. Free radical mediated grafting of chitosan with fumaric and ferulic acids: Structures and antioxidant activity. in: International Journal of Biological Macromolecules. Vol. 65, 97–106, 2014.

[12]. M.A. Abd El-Ghaffar, M.S. Hashem. Chitosan and its amino acids condensation adducts as reactive natural polymer supports for cellulase immobilization. in: Carbohydrate Polymers. Vol. 81, 507–516, 2010.

DEVELOPMENT OF RECIPES BASED ON PHYTOSYNTHESIZED NANOPARTICLES FOR THE PROTECTION OF CROPS

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Keywords: phytosynthesized nanoparticles; vineyard; apple culture; fungal diseases.

Introduction: In recent decades, the nanotechnology research area has shown a high interest in obtaining and characterizing nanomaterials through "*green chemistry*", in order to reduce or eliminate the use and generation of hazardous substances for human health and the environment. The project *Development of vegetal extracts and innovative phytosynthesized nanostructured mixtures with phytotherapeutic applications to reduce biocenotic stress in horticultural crops* represents the Research Project no. 3, part of the Complex Project *Increasing the institutional capacity of bioeconomic research for the innovative exploitation of indigenous vegetal resources in order to obtain horticultural products with high added value* (BIOHORTINOV).

Materials and methods: The project proposes the use of natural extracts (obtained from indigenous species of ferns) for the phytosynthesis of metallic nanoparticles, following recipes previously developed [1-4] and optimized in the present works.

Results: The obtained results support the use of fern extracts for obtaining noble metal nanoparticles [5]. The nanomaterials were analytically characterized using modern techniques (X-ray Diffraction, X-ray Fluorescence, Transmission Electron Microscopy etc.), confirming the successful synthesis of the nanoparticles.

Conclusions: The mixtures natural extracts/phytosynthesized nanoparticles proved to have very good antimicrobial properties, the tests being especially conducted on microorganisms responsible for the main fungal diseases that affect the vineyard culture and the apple culture.

Acknowledgements: *This work was supported by a grant of the Romanian National Authority for Scientific Research and Innovation, CNCS/CCCDI – UEFISCDI, Complex project PN-III-P1-1.2-PCCDI2017-0332; Contract: 6PCCDI/2018, within PNCDI III.*

References:

[1]. Fierascu RC, Ion RM, Fierascu I. Noble metals nanoparticles synthesis in plant extracts. Optoelectron Adv Mat - Rapid Comm. 2010;4(9):1297-1300.

[2]. Ortan A, Fierascu I, Ungureanu C, Fierascu RC, Avramescu SM, Dumitrescu O, Dinu-Pirvu CE. Innovative phytosynthesized silver nanoarchitectures with enhanced antifungal and antioxidant properties. Appl Surf Sci. 2015; 358:540-8.

[3]. Bunghez IR, Fierascu RC, Dumitrescu O, Fierascu I, Ion RM. Characterization of silver nanoparticles obtained by *Lavandula angustifolia* extract. Rev Roum Chem. 2015;60(5-6):515-9.

[4]. Fierascu I, Georgiev MI, Ortan A, Fierascu RC, Avramescu SM, Ionescu D, Sutan A, Brinzan A, Ditu LM. Phyto-mediated metallic nanoarchitectures via *Melissa officinalis* L.: synthesis, characterization and biological properties. Sci Rep. 2017; 7:12428.

[5]. Sutan NA, Fierascu I, Fierascu RC, Manolescu DS, Soare LC. Comparative analytical characterization and in vitro citogenotoxic activity evaluation of *Asplenium scolopendrium* L. leaves and rhizome extracts prior to and after Ag nanoparticles phytosynthesis. Ind Crop Prod. 2016; 83C:379-86.

EFFECT OF ACTIVATED CARBON DERIVED FROM APRICOT STONES AND $Mg_2Ni_{0.9}V_{0.1}$ ADDITIVES ON HYDROGEN STORAGE PROPERTIES OF Mg

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Keywords: activated carbon; hydrogen storage; metal hydrides.

Introduction: Magnesium is attractive material for hydrogen storage because of its high hydrogen absorption capacity (7.6 wt%), low price and abundance. However, some disadvantages like slow hydrogen sorption kinetics and high sorption temperatures, makes its practical application difficult. In order to improve the hydrogen sorption characteristics of Mg a lot of investigations with the use of different additives were done. The absorption-desorption characteristics towards hydrogen of composite 90wt.% Mg- 5wt.% activated carbon (synthesized from apricot stones- ACA)- 5wt% $Mg_2Ni_{0.9}V_{0.1}$, obtained by ball milling under Ar atmosphere are investigated [1-3].

Materials and methods: Detailed preparation procedure and characterization methods of activated carbon can be found in [1-3]. The intermetallic $Mg_2Ni_{0.9}V_{0.1}$ is synthesized from powdery magnesium, nickel and vanadium of 99.9% purity. Stoichiometric mixtures of the corresponding metals were pelleted and heated in an argon atmosphere at 823K for 120 h. The phase composition of the alloys obtained was controlled by X-ray phase analysis using CuKα radiation. The Mg_2Ni sample is almost single-phase and contained traces of $MgNi_2$.

The hydrogen absorption- desorption properties of the composites were determined by volumetric or Sievert's type apparatus. The mixture with composition of powder Mg (with purity 99.8 %, -325 mesh or 44 μm by Strem Chemicals), 5 wt.% activated carbon ACA and 5 wt% $Mg_2Ni_{0.9}V_{0.1}$, is obtained by ball milling under Ar in planetary mono mill Fritsch Pulverisette 6.

Results: The kinetics curves of hydriding at 623 K and 573 K show faster reaction at lower temperature, but the obtained capacity after 60 min of hydridng is higher at higher temperature. Both additives have positive effect on hydrogen sorption characteristics of magnesium and the obtained hydrogen absorption capacity is 4.5 wt. % at 573 K and 5.5 wt% at 623 K. Some desoprtion at 573 K is detected but with very slow reaction rate and after 60 min less than 1 wt % is desorbed. The X-ray diffraction patterns of the 90wt.% Mg- 5wt.% ACA- 5wt% $Mg_2Ni_{0.9}V_{0.1}$ shows the presence of main phase of MgH_2 and also Mg_2NiH_4 type phase, Mg and MgO.

Conclusions: The combination of these two additives e. g. activated carbon derived from apricot stones and $Mg_2Ni_{0.9}V_{0.1}$ to magnesium leads to faster hydriding reaction at 573K and some desorption at lower temperature, even with slow rate. Our investigations clearly show that they have favorable effect on the sorption kinetics of magnesium. The activated carbon object of this study can be used as suitable additive for magnesium based hydrogen storage materials.

References:

[1]. Gergova K., Petrov N. and Eser S., Carbon, 1994; 32: 693-702.
[2]. Cabal B., Budinova T., Ania C. O., Tsyntsarski B., Parra J. B., Petrova B., J. Hazard. Mater. 2009; 161: 1150-1156.
[3]. Conchi O. A., Petrov N., Tsyntsarkski B., Budinova T., Parra J. B., Mladenov M., Raicheff R., Proc. Annual World Conference Carbon 2009, Biarritz, France 249 (P3-20, ID100).

RECYCLING OF POLYURETHANE FOAMS BY SYNTHESIS OF POLYMERIC COMPOSITES WITH THERMOPLASTIC ELASTOMERS

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Keywords: composites; polyurethane foams; thermoplastic elastomers; styrene-diene block-copolymers.

Introduction: The objective of the study was the synthesis and characterization of some polymer composites based on polyurethane foam waste and thermoplastic elastomers [1-4].

Materials and methods: Waste recycling of polyurethane foams has been prepared by grinding and blending by varying the amounts of styrene-isoprene block-copolymers. The polymer composites based on polyurethane foam waste and styrene-isoprene block-copolymers were obtained by pressing at high temperature and pressure.

Results: The new polymer composites have been characterized by Differential Scanning Calorimetry (DSC), Thermo-gravimetric Analysis (TGA) and Dynamic mechanical analysis (DMA).

Conclusions: Polymer composites based on polyurethane foam waste and styrene-isoprene block-copolymers have properties that could recommend them for the production of thermo-insulating materials (sandwich panels) for home building or similar ones.

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References:

[1]. S.L. Cooper, J. Guan, Advances in Polyurethane Biomaterials, Woodhead Publishing 2016, ISBN: 978-0-08-100614-6 (print) ISBN: 978-0-08-100622-1 (online)

[2]. T.E. Odetoye, Recycling of Polyurethane Foams _A Strategy in Waste Management and Control, Nigerian Journal of Technological Development, volume 8(2), 2011, 140-151.

[3]. G. Behrendt, B.W. Naber, The Chemical Recycling of Polyurethanes, Journal of the University of Chemical Technology and Metallurgy, 44, 1, 2009, 3-23

[4]. Gebreselassie et al., Method of recycling Polyurethane foam components - US patent 6,299,811, 2001.

BIODEGRADABLE COMPOSITES BASED ON WHEAT BRAN AND POLYLACTIC ACID

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Keywords: polymer composites; wheat bran; polylactic acid; tableware; biodegradable materials.

Introduction: The objective of the study was synthesis and characterization of biodegradable composites based on wheat bran and polylactic acid, obtained by melt alloying [1-5].

Materials and methods: Biodegradable composites based on wheat bran were obtained by mixing in melt in a Brabender plastograph with polylactic acid. After mixing, the biodegradable composites based on wheat bran were and polylactic acid were processed by pressing at high temperature and pressure.

Results: The biodegradable composites based on wheat bran were and polylactic acid were characterized by Differential Scanning Calorimetry (DSC), Thermo-gravimetric Analysis (TGA) and Dynamic mechanical analysis (DMA).

Conclusions: Biodegradable composites based on wheat bran and polylactic acid have properties that they recommend as an alternative to plastic materials, for the manufacture of tableware, plates and bowls.

Acknowledgements: *This work was supported by a NUCLEU Program, conducted with MCI support, project number* ***PN.18.22.04.01/2018, contract 21N/2018.***

References:

[1]. Greg Ganczewski, BIOTREM – Compostable tableware from wheat bran – development and LCA, COST Action FP1405 Meeting: "Existing technologies and current developments in active and intelligent packaging", Aveiro, Portugal, 15-16 September 2015.

[2]. S. Heikkinen et al., Comparison of two wheat bran extracts in the sheet extrusion process, Industrial Crops and Products, 91, 2016, 1–5.

[3]. M. Pruckler et al., Wheat bran-based biorefinery 1: Composition of wheat bran and strategies of functionalization, LWT - Food Science and Technology, 56, 2014, 211-221.

[4]. K. Madhavan Nampoothiri et al, An overview of the recent developments in polylactide (PLA) research, Bioresource Technology, 101, 2010, 8493–8501.

[5]. KARGER-KOCSIS J., Polypropylene: Structure, Blends and Composites, Chapman & Hall, 1995.

THE MECHANICAL AND THERMAL PROPERTIES OF SBS AND SIS FILMS OBTAINED BY SPIN CASTING FROM DIFFERENT SOLVENTS

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Keywords: SBS; SIS; separation degree; mechanical and thermal properties.

Introduction: The different effect of solvents on the separation degree and dispersion of the minority polystyrene (PSt) phase into the polydiene continuous phase was studied.

Materials and methods: The styrene-butadiene block-copolymer (SBS) and styrene-isoprene block-copolymer (SIS) were synthetized by sequential anionic polymerization of monomers in cyclohexane solution initiated with n-butyl-lithium. From toluene, cyclohexane, dioxane, dichloroethane and tetrahydrofuran solutions (20 wt%) of these SBS and SIS block-copolymers were obtained films by spin-casting (3h, 50-60°C) which were characterized by mechanic, dynamic mechanical (DMA) and thermal (DSC) analysis.

Results: It was observed that the block-copolymer films presented significant distinctive mechanical (tensile properties), dynamic mechanical and thermal properties depending on the used solvent. This behavior is due to the different morphology of the polystyrene phase, lamellar structure or discrete dispersed nanodomains ordered in various networks.

Conclusions: The phases (PSt and polydiene) separation degree significantly increases when the solvent is more adequate for one of these phase (Tg increases for PSt and decreases for polydiene). The storage modulus increases with the PSt separation degree confirming its reinforcing effect, properly modifying the tensile properties.

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EFFICIENCY EVALUATION OF OXIDIZED CARBON NANOTUBES LOADED WITH CISPLATIN IN THE TREATMENT OF TRIPLE NEGATIVE BREAST CANCER

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Keywords: carbon nanotubes; cisplatin; functionalization; breast cancer; oxidative stress.

Introduction: Defined by the absence of estrogen and progesterone receptors and the absence of HER2 overexpression, triple negative breast cancer is a heterogeneous disease that cannot be treated with usual biological or hormonal therapies [1]. Consequently, other ways of treatment are studied, drug delivery with carbon nanotubes (CNTs) nanoparticles as anticancer drug carriers being investigated as the main future cancer therapy in the field of medicine [2,3]. Thus, the aim of the present study was to evaluate the anti-tumoral effects of oxidized single and multi-walled CNTs loaded with cisplatin (CisPt) on breast cancer cells.

Materials and methods: Covalent functionalized oxidized CNTs (single and multi-walled carbon nanotubes) with CisPt were obtained through two main steps: firstly, the functionalization was carried out through chemical oxidation of CNTs with a mixture of sulfuric acid and nitric acid (3:1 molar ratio). Then, the oxidized CNTs were conjugated with CisPt. Mammary adenocarcinoma cells (MDA-MB-231 cell line) were exposed to varying concentrations of conjugated and non-conjugated oxidized CNTs (0.5 – 4 μg/mL) and CisPt (0.3 – 2.5 μg/mL) for 24 and 48 hours. Untreated cells were used as control. Plasma membrane damage was evaluated through the analysis of lactate dehydrogenase (LDH) level released in cell culture medium. Also, cellular viability was assessed using MTT assay. Anti-tumoral activity of CNTs and CisPt was also estimated through evaluation of NF-kB protein expression and oxidative stress markers (reactive oxygen species – ROS production and Nrf2 protein expression). Cellular morphology, cytoskeleton actin integrity and internalization of nanoparticles were also examined using optical and fluorescence microscopy.

Results: The results highlighted a significant decrease of viability induced by oxidized single-walled CNTs conjugated with CisPt starting with 24 hours of incubation in correlation with the increase of LDH level at 48 hours, compared to non-conjugated oxidized CNTs and CisPt. Moreover, oxidative stress was induced by the elevated ROS levels in a concentration-dependent manner for all treatments with more pronounced effects for conjugated oxidized single and multi-walled CNTs. Also, an activation of Nrf2 and a decrease of NF-kB protein expressions were observed for the same types of nanoparticles after 48 hours of exposure. Optical microscopy revealed the aggregation of nanoparticles and their attachment to cellular membrane starting with 24 hours. After 48 hours, some slight morphological changes were found at high concentrations of CisPt, non-conjugated oxidized multi-walled CNTs and conjugated oxidized single and multi-walled CNTs compared to non-conjugated oxidized single-walled CNTs, probably due to their better dispersion in culture medium. In correlation with cells' morphology, local changes in organization of F-actin filaments were observed after 48 hours of incubation with high concentrations of CisPt (1.2 μg/mL) and CNTs (2 μg/mL).

Conclusions: Overall, our results, defined by viability modifications and induction of oxidative stress, showed a more pronounced cytotoxic condition for CNTs conjugated with CisPt compared to the non-conjugated ones or CisPt, suggesting their efficiency in the treatment of breast cancer.

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References:

[1]. Collignon J., Lousberg L., Schroeder H., Jerusalem G. Triple-negative breast cancer: treatment challenges and solutions. Breast Cancer (Dove Med. Press). 2016;8:93-107.

[2]. Rastogi V., Yadav P., Bhattacharya SS., Mishra AK., Verma N., Verma A., Pandit JK. Carbon nanotubes: an emerging drug carrier for targeting cancer cells. J. Drug Deliv. 2014;2014:670815.

[3]. Madani SY., Naderi N., Dissanayake O., Tan A., Seifalian AM. A new era of cancer treatment: carbon nanotubes as drug delivery tools. Int. J. Nanomedicine. 2011;6:2963-2979.

OPTICAL PROPERTIES OF SOME TEXTILES DYED WITH CURCUMINOID HYBRID SYSTEMS

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Keywords: curcumin derivatives; hybrid materials; nanosol; fluorescence; textile fibers.

Introduction: The development of eco-friendly dyeing procedures for textile fibers has brought to the attention of researchers the natural dyes, which are biodegradable, do not produce allergies and have UV protective, antioxidant and antibacterial properties. However, there are some drawbacks regarding the usage of natural dyes for dyeing of textile materials, especially because of their poor fastness to light. Therefore, in order to compensate for this deficiency, dyeing is performed using mordants, metal salts, nanosols, depending on the type of the fiber. These treatments increase the dyestuffs resistance to light, but unfortunately in the case of curcumin derivatives, complexation with metal ions leads to fluorescence quenching. One of the most important factors for applying nanosols on textile fibers is the adhesion between the substrate and the coating material. Until now, there are various studies on the usage of the silica matrices as hosting materials, for the immobilization of anionic dyes and coating of polyester or viscose, as well as for dyeing of natural textile fibers with direct or disperse dyes in sol-gel systems [1-4].

Materials and methods: In this study are presented experimental data regarding the manufacture of some compositions using sol-gel processes by appropriate selection of the chromogens and silane components. Compositions were applied onto the surface of textile materials by pad-dry method and properties of coated textile fibers were analyzed.

The host matrix was obtained by generating of modified silica networks with aromatic groups by the hydrolysis/condensation of TEOS:organosilanes precursors in molar ratio 1: 0.1-1: 2, in acid catalysis. The curcumin derivatives have been immobilized in silica matrices by sol-gel processes and deposited on textile materials by the impregnation-thermopixing method.

Results: The dyeing of the textile fibers in the sol-gel system provided intense and uniformly colored materials. The coated textiles have been characterized from the structural, morphological and tinctorial properties. The spectrophotometric measurements revealed that colored textiles preserve the original properties of chromophores and are influenced by interactions between the dye and the host matrix.

Conclusions: Following the functionalization process of textile materials with curcuminoid hybrid systems, were obtained coatings having improved tinctorial and optical properties.

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References:

[1].Hasan M., Hossain M. B., Azim A. Y. M. A.,, Ghosh N. C., Reza S., IJET-IJENS, 2014, 14(5), 17-23
[2].Hasan M., Nayem K. A., Azim A. Y. M. A., IJRRSET, 2014, 3(7), 838-844
[3].Raditoiu A., Raditoiu V., Amariutei V., Purcar V., Ghiurea M., Raduly M., Wagner L., Mat. Plast. 2015, 52(4), 442-448.
[4].Berendjchi A., Khajavi R., Yazdanshenas M. E., Int. J. Green Nanotechnol., 2013, 1:1-7

COMPOSITE NANOGELS FOR CONTROLLED DRUG DELIVERY

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Keywords: composite nanogels; polyethyleneglycol diacrylate; zeolite; controlled release systems.

Introduction: With 16 milion people suffering from it worldwide, and nearly 1.5 milion new cases emerging yearly, cancer poses a real challenge for both medicine and engineering. Solving this issue does not imply finding a unique solution, but rather, proposing a series of alternatives that increase the efficiency of existing treatment plans. A promising approach is the encapsulation of drug into nanoparticles that are engulfed by tumors tissue and circulate long enough to expose it to the medicine [1,2].

Materials and methods: This study was mainly aimed at developing a sustained system based on the passive targeting of tumors. The design consists in the obtaining of cross-linked polyethyleneglycol diacrylate (PEGDA) nanogels (NGs) that will contain 5-fluorouracil (5-FU) - loaded zeolite nanoparticles (NZ) in their polymer structure. Final products were characterized in terms of: particle size and size distribution by means of Dynamic Light Scattering (DLS); morphology of composite NGs using Transmission Electron Microscopy (TEM); chemical structure by Fourier Transform Infrared Spectroscopy (FTIR). Moreover, preliminary incorporation and release behavior were studied using 5-FU as model-drug.

Results: The development of composite NGs for the slow-release of drug was successful. Composite NGs were obtained starting from 3 different zeolite weight percentages. Up to 3% content in zeolite, the composites remained in the range of 100-200 nm average-diameters, being well-suited for the envisioned application. All compounds are able to achieve a slow-release of the drug, the composites standing out due to a higher relative amount of 5-FU released by the end of the 7 days-study (Fig. 1.).

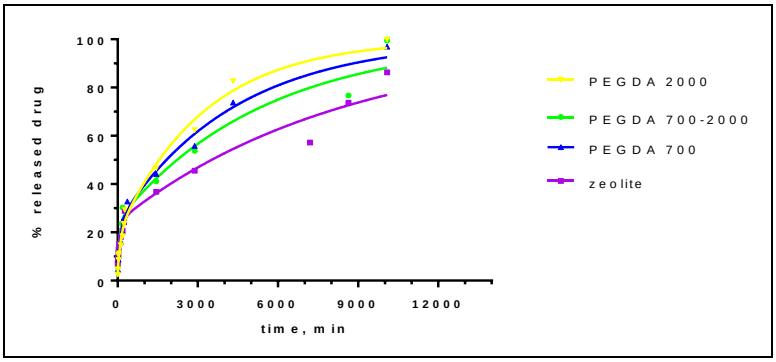

Fig. 1. *Release curves for composite nanogels - 3% NZ.*

Conclusions: Based on these results, PEGDA – NZ composite NGs show potential for the controlled drug delivery. These results, together with the composite size, are favorable characteristics for passive targeting treatment of tumor tissue.

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References:

[1].Pérez-Herrero E. and Fernández-Medarde A. Advanced targeted therapies in cancer: Drug nanocarriers, the future of chemotherapy. Eur J Pharm Biopharm. 2015; 52–79.

[2].Yallapu M.M., Jaggi M. and Chauhan S. Design and engineering of nanogels for cancer treatment. Drug Discov Today, 2011; 457–463.

WATER-IN-OIL MICROEMULSIONS AS ALTERNATIVE FUELS FOR INTERNAL COMBUSTION ENGINES

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Keywords: microemulsion; alternative fuel; internal combustion engine.

Introduction: Nowadays the increased demand for fuel, the indiscriminate extraction together with the depletion of crude oil reservoirs, as well as the mounting pollution and the rapid degradation of the environment are matters of serious worldwide concern. The pollution and environmental degradation are mainly due to the exhaust gases of the internal combustion engine (ICE) that contain carbon dioxide (CO_2) and nitrogen oxides (NO_x). CO_2 is dangerous because gives rise to global warming through greenhouse effect, whereas NO_x turns into smog of fine particulate matter (PM) causing severe diseases of lung and heart. Those pieces of evidence are a good reasoning to seek 'green' fuels for replacing diesel totally or at least in part, and neat vegetable oils or their microemulsions are suitable candidates for this purpose. The work presents innovative results on microemulsion alternative fuels prepared with ecofriendly chemicals.

Materials: Rapeseed oil (RSO), diesel (D) or mixtures thereof, Synperonic A9C (AS9C – anionic surfactant) , Brij 30 (B30 – nonionic surfactant, NS), Igepal CO-520 ($NPEO_5$ – NS), Tween 65 (T65 – NS), Tween 85 (T85 – NS), and *i*-butanol (B) as the cosurfactant.

Methods: Pseudo-ternary phase (PTP) and Winsor (W) diagrams, oil/water interfacial tension (σ_{ow}), solubilization parameter of oil (SP_o) and water and (SP_w) and the particle size (PS).

Results: The water solubilization capacity of oil/surfactant/cosurfactant systems evaluated by pseudo-ternary phase and Winsor diagrams unveiled that the extent of the single-phase microemulsion area (SPMA) depends on the nonionic surfactant (NS). The anionic surfactant alone does not make microemulsions. Addition of AS9C to NS decreases the SPMA. However, SPMA increases by cosurfactant addition. For D/RSO blends, the SPMA does not change as compared to diesel. In the PTP diagrams, addition of electrolyte decreases the SPMA. The tests of oil/water interfacial tension, solubilization parameter of oil and water and and the particle size show that the WIII microemulsions have minimal σ_{ow}, and maximal SP_o, SP_w and PS values.

Conclusions: The work unveils the relationships between the phase behavior and the microemulsions properties and emphasizes the best way of developing novel, optimal and eco-friendly fuels.

PRELIMINARY *IN VITRO* BIOLOGICAL EVALUATION OF SMALL PRISTINE AND FUNCTIONALIZED MESOPOROUS SILICA NANOPARTICLES

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Keywords: mesoporous silica nanoparticles, functionalization, biocompatibility, antiproliferative activity

Introduction: Mesoporous silica nanoparticles (MSN) show a great interest for biomedical applications i.e. the clinical use as drug carriers due to a good biocompatibility and controlled biologically active molecules delivery in different pathologies [1,2]. In this study we aimed to evaluate the biocompatibility, as well as the anti-proliferative activity of pristine and functionalized MCM-41-type MSN on two different human cell types.

Materials and methods: Pristine MCM-41-type nanoparticles were obtained by sol-gel method using tetraethyl orthosilicate as silica source, cetyltrimethylammonium bromide or tetradecyltrimethylammonium bromide as structure directing agents and triethanolamine that ensures both MSN dispersion and base catalysis for the hydrolysis and condensation reactions of silica precursor. The functionalized MCM-41 nanoparticles with methyl, mercaptopropyl, vinyl and cyanopropyl moieties were synthesized by co-condensation approach. All the samples were characterized by small-angle X-RD, nitrogen adsorption-desorption isotherms, and TEM. In order to evaluate cell toxicity, two pristine (MCM-PEG 550 and MCM-PEG C14) and four functionalized MCM-41 samples were evaluated on HaCat (normal human keratinocyte cell line) by the indirect method, according to ISO 10993-5-2009. Three concentrations (50, 100, 150 µg/mL) from each sample suspension in triplicates were used. After 24h of cultivation in a humid atmosphere (5% CO_2) at 37°C, cell viability was quantified by MTT method. Antiproliferative activity evaluation was performed on Mel-Juso (human melanocytes cell line) by using the same time point and methods in correlation with the cell viability tests.

Results: All samples exhibited an ordered hexagonal pore array and high porosity having specific surface area values in the range of 916-1222 m^2/g. MCM-PEG 550, MCM-CH3, MCM-vinyl and MCM-SH consist of spherical nanoparticles in the range of 50-70 nm, while MCM-C14 and MCM-CN present larger particles of around 200 nm. *In vitro* cytotoxicity tests showed that cell viability was dependent on concentration, particle size and type of organic groups grafted on the silica pore walls. After 24h of cultivation in the MSN presence, HaCat cells showed a good proliferation rate in the case of MCM-CH3, MCM-CN at 50 and 100 µg/mL and MCM-PEG550 for all tested concentrations. MCM-PEG C14, MCM-SH and MCM-vinyl samples induced a moderate cytotoxicity (55-70%) at all the studied concentrations. Concerning the antiproliferative potential, the samples exhibited an anti-tumoral activity, in direct correlation with the organic groups introduced via functionalization. Among the investigated nanoparticles suspensions, MCM-SH and MCM-vinyl presented the highest anti-proliferative effect. Cell proliferation percentage was $\leq 45\%$ for the MCM-SH suspension and $\leq 50\%$ for the MCM-vinyl suspension. Morphological observations were correlated with the cell viability values.

Conclusions: Pristine MSN having nanoparticles with an average size of 62 nm and methyl or cyanopropyl functionalized MCM-41 exhibited a higher biocompatibility when compared with samples functionalized with mercaptopropyl, vinyl or pristine MCM C14 with about 200 nm diameter. Antiproliferative effect of the studied silica samples was dependent on the concentration as well as on the functional groups. MCM-SH sample induced the strongest anti-tumoral effect on the human malignant melanocytes.

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References:

[1].Slowing II, Vivero-Escoto JL, WuCW, Lin VSY. Mesoporous silica nanoparticles as controlled release drug delivery and gene transfection carriers. Adv Drug Del Rev. 2008; 60:1278–88.

[2].Bajenaru L, Berger D, Miclea L, Matei C, Nastase S, Andronescu C, Moisescu MG, Savopol T. Correlation of the intracellular reactive oxygen species levels with textural properties of functionalized mesostructured silica. J Biomed Mater Res Part A 2014:102A: 4435-42.

SYNTHESIS AND CHARACTERIZATION OF Pr-SO_3H FUNCTIONALIZED ORDERED MESOPOROUS SILICA

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Keywords: heterogeneous catalysts; mesoporous silica; organosilane; inorganic-organic hybrid materials.

Introduction: In the last years, a significant number of works have been devoted to the development of inorganic-organic hybrid materials based solid acid catalysts for different applications in heterogeneou catalysis. These mesoporous materials have unique properties consisting of regular pore system, large specific surface area, high pore volume, narrow pore size distribution and hgh thermal and chemical stability. The properties of mesoporous silica can be adjusted by incorporation of different heteroatoms such as Al, Fe, B, Ti, Zr, etc., or functional groups such as sulfonic or amino groups in their structure [1-3].

The objective of this work was to modify the surface of inorganic mesoporous silica materials (MCM-41 and SBA-15) with propylsulfonic acid functional groups to be used in different organic reactions.

Materials and methods: The mesoporous silica materials used in this study were prepared using cationic surfactant (CTAB) assisted synthesis in alkaline medium (MCM-41) and non-ionic surfactant (triblock-copolymer Pluronic P_{123}) assisted synthesis in acidic medium (SBA-15), respectively. The two mesoporous silica materials have been investigated comparatively as supports in order to check the influence of the organic functionalities loading in the range: 2.5 – 10 mmol/g.

The functionalization of mesoporous silica supports with Pr-SO_3H groups was performed by a post-synthesis grafting route with 3-mercaptopropyltrimethoxysilane (MPTMS) as propyl-thiol (Pr-SH) precursor and toluene as solvent. The reactions were carried out in a close-system at 90^{o}C for 4h under continuous stirring. The oxidation of thiol groups (-SH) to sulfonic groups (-SO_3H) was carried out with hydrogen peroxide.

The structural and textural properties of the parent mesoporous silica (supports) and organically-modified materials were evaluated by XRD, FTIR and N_2 adsorption/desorption measurements. The amount of loaded organic functional groups was checked by thermogravimetric measurements.

Results: The XRD and N_2 sorption analyses evidenced that support materials exhibit well-ordered 2-D hexagonal mesostructure and IV type adsorption/desorption isotherms, characteristic to MCM-41 and SBA-15, respectively. The support materials have high surface area (800-1000 m^2/g), high pore volume (1.0-1.2 cc/g) and mesopores diameter of 3 nm (MCM-41) and 7.3 nm (SBA-15). The functionalization of the MCM-41 is accompanied by an important decrease of surface area and pore volume, which is dependent of the organic concentration and can indicate that the pore accessibility is affected by the presence of functional groups on the material surface. The effect of the functionalization is less significant in the case of SBA-15. The decrease of surface area, pore volume and pore diameter is an argument of the presence of organic functional groups grafted on the external surface as well as inside the mesopores. This result can be explained taking into account the particular structure of SBA-15 mesoporous silica with thicker pore walls and consequently, higher hydrothermal stability as compared to MCM-41 mesoporous silica.

Conclusions: The structural and textural properties of MCM-41 and SBA-15 mesoporous silica materials can be modified by incorporation of propyl-sulfonic acid groups using a post-synthesis grafting method. The effect of Pr-SO_3 H functionalization is dependent on the particularities of the mesoporous support structure.

Acknowledgements*: This work was supported by PN III Program, PN-III-P1-1.2-PCCDI-2017; Program 1 - Development of national CD system; Subprogram 1.2 - Institutional performance, complex projects developed in CDI consortia, Contract 32PCCDI/2018*

References:

[1].Duarte P, Ferreira DP, Lopes TF, Pinto JV, Fonseca M, Machado IF. Microporous Mesoporous Mater. 2012; 161: 139-147.

[2].Brás A, Merino E, Neves P, Fonseca I, Dionisio M, Schönhals A, Correia N. J. Phys. Chem. C 2011; 105:4616-4621.

[3].Dalla Costa BO, Legnoverde MS, Lago C, Decolatti HP, Querini CA. Microporous Mesoporous Mater. 2016; 230: 66-75.

ANTIBACTERIAL POLYMERIC MATERIALS BASED ON STYRENE-BUTADIENE BLOCK-COPOLYMERS GRAFTED WITH IZOFURAL

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Keywords: antibacterial materials; antibacterial tests; styrene-butadiene block-copolymers.

Introduction: In the last years, polymeric materials with antibacterial properties have received a special attention [1, 2]. These materials are used both in clinical applications in hospital and in home care. This paper presents the synthesis by polymer-analogous reactions of new Izofural grafted styrene-butadiene block-copolymers with antibacterial properties.

Materials and methods: Styrene-butadiene block-copolymers (SBS) were obtained by anionic polymerization in cyclohexane solution initiated with n-butyl lithium. SBS elastomers were maleinized in toluene solution using as initiator AIBN. Izofural was grafted on maleic groups from the modified SBS, according to the scheme:

Figure 1. Grafting reaction of Izofural on maleic groups of the modified SBS.

Results: Maleinized block-copolymers grafted with 3, 6 and 10 % mole Izofural which presented antibacterial properties (tested at USMF N. Testemitanu, Chisinau) were obtained by the presented method, their structure and composition being confirmed by IR spectroscopy and elemental analysis.

Conclusions: The results have demonstrated an increased bacterial activity depending on the Izofural content and low toxicity, properties suitable for their use in medical applications.

References:

[1].Plată N. A., Vasiliev E. A. Polimeri fiziologic activi. Moscova, Știința, 1987, pp. 456.
[2].Ghioca P., Robu Ș., Prisacari V., Filip V., Spurcaciu B., Iancu L., Grigorescu R. M. Materiale Plastice. 2014. Vol. 51. No 1. pp. 94-96.

NOVEL MATERIALS BASED ON ZINC OXIDE, DEPOSITED ON METALLIC SURFACES HAVING ANTI-ICING PROPERTIES

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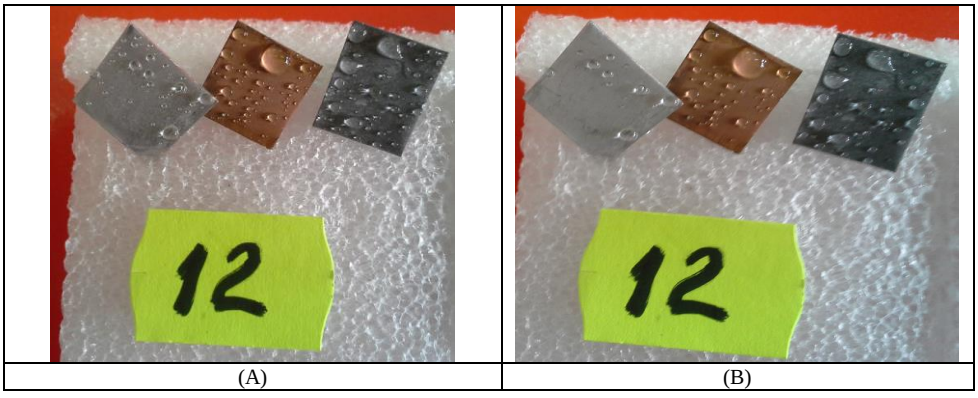
Keywords: anti-icing, zinc oxide nanoparticles, metallic surfaces

Introduction: In recent years, the wetting behaviors of nanostructures of ZnO materials have been study. By changing the surface morphology (or) by chemical modification, a superhydrophobic ZnO surface will be prepared [1]. The superhydrophobic surface has been proven to be helpful in improving anti-icing properties by delaying ice formation, enhancing the dynamic anti-icing behavior of water droplets impacting the superhydrophobic surface, reducing the ice adhesion strength, and so forth [2]. These superhydrophobic nanostructured surfaces may lead to important applications such as coatings for cables, insulators, aircraft wings, ship hulls, glass structures, windshields, etc. [3]. In our study, three types of metallic surfaces will be tested: zinc, copper and aluminum.

Materials and methods: Zinc Oxide nanoparticles were modified through sol-gel procedure at room temperature: commercial ZnO powder was well dispersed in a mixture of ethanol, deionized water and ammonia concentrated solution. Tetraethylorthosilicate (TEOS) and modifying agents N9 (octyltriethoxysilane - OTES), N11 ((3-glycidyloxypropyl)trimethoxysilane - GPTMS) and N12 (octadecyltrimethoxysilane - ODTES) were added in order to obtain the final materials, which were analysed with FTIR spectroscopy. Contact angle measurements and anti-icing properties were realized after materials deposition on mettalic surfaces.

Results: Preliminary visual evaluation (Fig. 1) showed that obtained materials deposited on metallic supports formed films with varying degrees of opacity, depending on the amount of product deposited. The films exhibit nano / micrometric roughness.



(A) (B)

Fig. 1. Sample 12 at -20° C: (A) after half on hour; (B) after an hour

Conclusions: Comparing all samples tests results, (N12) coating material had a better anti-icing property, due to the presence of the octadecyl group from ODTES.

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References:

[1].Barshilia Harish C., Selvakumar N., Pillai N., Mayura Devi L., Rajam K. S., Wettability of ZnO: A comparison of reactively sputtered; thermally oxidized and vacuum annealed coatings, Applied Surface Science, 257, 2011, 4410-4417.

[2].Zuo Z., Liao R., Song X., Zhao X., Yuan Yuan, Improving the anti-icing/frosting property of a nanostructured superhydrophobic surface by the optimum selection of a surface modifier, RSC Adv. 8 (2018) 19906-19916.

[3].Sarkar D. K., Farzaneh M., Superhydrophobic Coatings with Reduced Ice Adhesion, J. Adhes. Sci. Technol. 23 (2009) 1215–1237.

MECHANICAL PROPERTIES OF POLYPROPYLENE/HEMP FIBERS COMPOSITES

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Keywords: hemp fibers; polymer composites; tensile properties.

Introduction: Polypropylene (PP) reinforced with natural fibers has been intensively studied to replace glass fibers (GF) reinforced polymers in automotive applications [1-3]. The impact of weight reduction in auto parts is high in terms of fuel economy and reduced environmental impact. Hemp fibers (HF) have approximately two times lower density than GF and their use as reinforcement in PP may give important benefits. However, both increased stiffness and toughness are requested by most of auto parts, for example for the side door, which is a very difficult task.
In this work, an easy processable PP/block copolymer blend was reinforced with HF in different proportion and the influence of melt processing conditions and HF concentration on the mechanical properties of composites was studied.
Materials and methods: PP/block copolymer/HF mixtures were extruded using a twin-screw extruder and the resulted composites were characterized by scanning electron microscopy, tensile tests and dynamic mechanical analysis.
Results: Better dispersion of HF and higher increase of static and dynamic mechanical properties were observed in PP composites containing block copolymer and maleic anhydride-modified polypropylene. The HF increased the stiffness and the block copolymer has as effect an increase of toughness so that the PP composites modified with block copolymer and HF showed balanced mechanical properties.
Conclusions: The composites based on polypropylene modified with block copolymer and HF showed good mechanical properties and can be considered as an alternative to PP/GF composites in auto parts fabrication.

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References:

[1].Väisänen T., Batello P., Lappalainen R., Tomppo L. Modification of hemp fibers (Cannabis Sativa L.) for composite applications. Ind. Crops Prod., 2018; 111: 422-429.
[2].Panaitescu D.M., Vuluga Z., Ghiurea M., Iorga M., Nicolae C., Gabor, R. Influence of compatibilizing system on morphology, thermal and mechanical properties of high flow polypropylene reinforced with short hemp fibers. Composites Part B, 2015; 69:286-295.
[3].Sepe R., Bollino F., Boccarusso L., Caputo F. Influence of chemical treatments on mechanical properties of hemp fiber reinforced composites. Composites Part B, 2018, 133:210-217.

PHOTOCATALYTIC ACTIVITY OF TIO_2 SENSITIZED WITH AZOMETHIN – PHTHALOCYANINE METAL COMPLEXES

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Keywords: photocatalysis; TiO_2; phthalocyanine; azomethine, mixt cromophore.

Introduction: The photocatalytic processes are currently receiving the most attention because they represent some of the most promising technologies involving renewable energy sources. The treatment of pollutants in wastewater is an area of interest in most research laboratories. Titanium dioxide is one of the most important photocatalytic materials targeted for environmental cleanup, as it is cheap, available in large quantities, is environmentally safe and its energy band is identical to the water redox level. In addition to these advantages, TiO_2 also has a number of inconveniences such as the high rate of recombination of electrons and holes, low quantum yields in photocatalytic reactions in aqueous solutions and the high value of the bandgap which can only be satisfied with UV radiation. An important area of research is to reduce the size of th bandgap which can be assured by sensitizing with organic dyes to allow the use of visible light sources for the activation of photocatalytic processes.
In the paper we present the use of azomethin-phthalocyanine dyes as sensitizers for TiO_2 and their testing for the photocatalytic degradation of organic dyes in wastewater.

Materials and methods: The azomethin-phthalocyanine dyes were synthesized by reaction of 4-amino phthalonitrile and 2-hydroxy naphthaldehyde followed by obtaining the phthalocyanine ring by heating to reflux in the presence of various metal salts. A series of novel compounds of original design, containing two chromophore systems, azomethine and phthalocyanine, complexes of Zn, Co, Mn, and Ni were synthesized and characterized. The anchoring of the dye on the TiO_2 substrate was accomplished by dissolving it in N, N-dimethylformamide solution (10^{-3} mol / L) followed by the addition of TiO_2 and stirring for 24 hours at room temperature, then centrifuged, washed with ethanol and acetone and dried. TiO_2 sensitized with organic dyes were dispersed in the printing paste and applied to cotton supports. The testing of photocatalytic activity was performed in a glass vessel equipped with a magnetic stirrer and illuminated with various illumination sources emitting in the UV-VIS domain. The processes of photocatalytic degradation of methyl orange were studied by measuring the absorbance at 20 min intervals using a Jasco V550 spectrometer.

Results: The study was conducted to identify the efficiency of catalytic activity of the four new synthesized compounds, as well as the optimization of working conditions for different lighting sources, different concentrations of pollutants, pH, and temperature. The experiments have also been carried out on the type of degradation mechanism using different scavengers to see what the active species is causing degradation. The resulting experimental data show that the uses of azomethine-phthalocyanine compounds as sensitizers is beneficial in all cases leading to increased degradation efficiency and allowing the use of visible illumination sources. At the same time, TiO_2 sensitization and the efficiency of degradation processes is dependent on the metal ion present in the phthalocyanine ring, with the best results obtained in the case of the Co complex. The optimum working conditions involve a weak acidic environment (pH = 4-5), temperatures of 20-25^{0}C, and methyl-orange concentrations of 10^{-4} mol/L. The mechanism of reaction occurs predominantly by superoxide radicals.

Conclusions: The sensitization of TiO_2 with novel compounds, of original design, containing two chromophore systems, azomethine and phtalocyanine is a viable alternative to increasing its photocatalytic activity.

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References:

[1].Vallejo W, Diaz C, Cantillo A. Methylene blue photocatalytic degradation under visible irradiation on TiO2 thin films sensitized with Cu and Zn tetracarboxy-phthalocyanines, Journal of Photochemistry and Photobiology A: Chemistry 299 (2015) 80–86.
[2].Ebrahimian A, Zanjanchi M. A, Noei H, ArvandM,Wang Y. TiO2 nanoparticles containingsulphonated cobalt phthalocyanine: preparation, characterization and photocatalytic performance. Journal of Environmental Chemical Engineering. 2 (2014) 484–494.

PREPARATION AND CHARACTERIZATION OF ZnO NANOPARTICLES FOR MULTIFUNCTIONAL TEXTILES WITH ANTIBACTERIAL PROPERTIES

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Keywords: ZnO nanoparticles; multifunctional textiles; in situ synthesis; antibacterial activity.

Introduction: The use of functional textiles with antibacterial properties is rapidly growing, due to the high demand in protection of sensitive social groups, such as children or hospitalized elderly people[1]. Metallic or metal oxide nanoparticles are considered as potential replacement of classic antibiotics in the treatment of infections with multidrug resistant pathogens[2]. Many methods were reported for the fabrication of functional textiles with antibacterial activity, most of them based on the deposition of nanopowders in various dispersion media, followed by specific finishing treatments. An alternative way is to obtain the functionalization by "in situ" synthesis of nanoparticles on the textile material[3]. Thus, the fabric network act as template for the growth of nanoparticles.In the present work synthesis and characterization of nanoparticulated zinc oxide powders have been studied for the fabrication of functional textiles with antibacterial activity and protection against UV radiation.

Materials and methods: The ZnO nanopowders were obtained using hydrothermal or solvothermal methods and the deposition onto the textiles was achieved by in situ synthesis of nanoparticles on pretreated fabric. The shape and size of nanoparticles was tuned by changing the reaction conditions (solvents, temperature and additives). The nanomaterials were characterized in term of composition, crystallinity size and shape, using dynamic light scattering, FTIR spectroscopy, X-ray powder diffractometry and SEM microscopy. Cotton was used as model textile material, since it is widely used in antibacterial functional clothing. The presence of the nanoparticles on the textile fiber surface was confirmed by SEM analysis. The effectiveness of the functionalization is measured using UV-Vis spectrophotometry in order to assess the ultraviolet protection capacity of the treated samples. The antibacterial activity was tested against common strains Gram-negative bacterium Escherichia coli, Gram-positive bacterium Staphylococcus aureus.

Results: ZnO spherical and flower-like nanoparticles were obtained, with size ranging from 100 to 1000 nm and directly deposited onto cotton fibers through simple synthesis on pretreated textile.
Funtionalized materials exhibit good protective efficiency against UV radiation and remarkable antibacterial activity against both Gram-negative and Gram-positive tested bacteria.

Conclusions: The ZnO nanopowder synthesized with the "in situ" method proposed allow a facile functionalization of cotton textiles. The performance of ZnO nanoparticles as antibacterial and UV-absorbing agent can be efficiently transferred to textile materials through a simple finishing procedure. The functionalized textiles exhibit promising properties as materials with superior UV absorbing and antibacterial activity.

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References:

[1].D. S. Morais, R. M. Guedes, and M. A. Lopes, "Antimicrobial Approaches for Textiles: From Research to Market," *Mater. Basel Switz.*, 2016, 9 (6), Jun.

[2].L. Wang, C. Hu, and L. Shao, "The antimicrobial activity of nanoparticles: present situation and prospects for the future," *Int. J. Nanomedicine*, 2017, 12, 1227–1249.

[3].M. Rehan, A. Barhoum, G. Van Assche, A. Dufresne, L. Gätjen, and R. Wilken, "Towards multifunctional cellulosic fabric: UV photo-reduction and in-situ synthesis of silver nanoparticles into cellulose fabrics," *Int. J. Biol. Macromol.*, 2017, 98, 877–886

MODIFIED ELECTRODES WITH POLY(3,4-ETHYLENEDIOXYTHIOPHENE)-COPPER NANOCOMPOSITE: SYNTHESIS AND APPLICATIONS FOR THE NITRATE DETECTION

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Keywords: PEDOT; copper nanocomposites; nitrate ion detection; cyclic voltammetry; electrochemical sensor.

Introduction: Nitrate pollution of water sources is a huge problem for the society. Excess nitrates present in food, fertilizers and industrial wastes affect both human health and the surrounding environment [1]. Cu-based nanomaterials are efficient electrochemical catalysts for nitrate reduction due to their superior electrical conductivity that promote the transfer of charge and their high specific surface that can provide more active centers for NO_3^- adsorption [2]. Poly(3,4-ethylenedioxythiophene) (PEDOT) is a remarkable conductive polymer with low oxidation potential, high electrical conductivity, good electrochemical activity and high stability. In the present work, we have combined the unique electronic properties of copper nanomaterials with the excellent sensing properties of PEDOT films for the determination of nitrate from water.

Materials and methods: The copper nanoparticles (CuNPs) have been synthesized by alkaline polyol method. Cu nanowires (CuNWs) were obtained following a two-step treatment. Firstly, $Cu(OH)_2$ was synthesized by wet chemical route followed by reducing with hydrazine in a concentrated NaOH solution containing ethylene diamine at 70^{o}C. The as prepared Cu nanomaterials have been thermally treated under Ar atmosphere at 600^{o}C in order to obtain CuNWs.

Electrochemical measurements were performed with an Autolab PGSTAT 302N (Ecochemie) controlled by GPES 4.9 electrochemical software from Eco-Chemie (The Netherlands) and connected to a three-electrode cell. All experiments were carried out at room temperature. Gold and platinum disk electrodes (Metrohm) with a 2-mm diameter were used as working electrodes, while a glassy carbon rod was used as a counter electrode. As reference it was employed a saturated calomel electrode. The modified electrodes with poly(3,4-ethylenedioxythiophene)-copper nanocomposite were characterized by Cyclic Voltammetry (CV) and linear sweep voltammetry (LSV).

Results: The poly(3,4-ethylenedioxythiophene) - CuNPs based sensor showed a linear response on concentration range between 0.4 and 2 mM with a LOD of 112.8 µM and poly(3,4-ethylenedioxythiophene)-copper NWs based sensor showed a linear response on the concentration range between 0.4 and 2 mM with a LOD of 85 µM.

Conclusions: This work demonstrates that the new modified electrodes based on poly(3,4-ethylenedioxythiophene)-copper nanocomposite show electrocatalytic activity for the nitrate detection.

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References:

[1]. Bagheri H , Hajian A., Rezaei M., Shirzadmehr A. Composite of Cu metal nanoparticles-multiwall carbon nanotubes-reduced graphene oxide as a novel and high performance platform of the electrochemical sensor for simultaneous determination of nitrite and nitrate . J Hazard Mater. 2017;324:762-772

[2]. Mott D, Galkowski J,Wang L, Luo J, Zhong CJ. Synthesis of Size-Controlled and Shaped Copper Nanoparticles Langmuir. 2007; 23:5740-5745

PLA/PHB BIOMATERIALS MODIFIED BY CELLULOSE FIBERS

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Keywords: polylactic acid; polyhydroxybutirate; cellulose; thermal analysis; mechanical properties.

Introduction: The strictness of the environmental legislation caused a major interest in using natural materials as resources for the production of biomaterials for medical applications. Green polymers such as polylactic acid (PLA) and polyhydroxybutirate (PHB) received major interest from both industrial and research sectors for the replacement of commodity plastics [1,2]. Both PLA and PHB have limitations related to their brittleness, mechanical and thermal properties compared to synthetic polymers. Different micro- and nano-fillers were tested to overcome these shortcomings PLA and PHB can be processed using common technologies for thermoplastics (melt mixing, thermoforming, injection molding, extrusion blow molding, film extrusion) which is a very important issue for biomedical industry.

This paper in focused on the investigation of the influence of cellulose micro- and nanofibers upon the characteristics of PLA/PHB biomaterials intended for biomedical applications. This study provides a comparison of morphological, thermal and mechanical characteristics (static and dynamic) of PLA/PHB/micro-nanocellulose biomaterials developed by applying two different processing methods: solution casting and melt-processing.

Materials and methods: Peak force QNM (Quantitative Nanomechanical Analysis-QNM) was used for the morphological characterization, differential thermal analysis (DSC) and thermogravimetric analysis (TGA) for assessing the thermal behavior and dynamic mechanical analysis (DMA) and tensile tests for the mechanical characterization.

Results: Stronger cellulose fiber - PLA/PHB matrix interactions were obtained through melt-mixing technique as compared with solution casting method. An increase in stiffness of the matrix was observed when cellulose fibers were incorporated through melt-mixing technique: storage modulus increased both below and above the glass transition temperature, same behavior being observed also for the tensile modulus and strength.

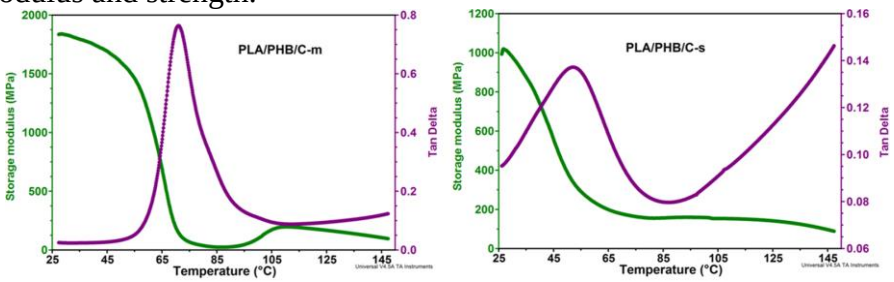

Figure 1. Dynamic mechanical properies of PLA/PHB biomaterials

Conclusions: QNM emphasized the influence of cellulose reinforcement type upon crystalline structure of PLA/PHB blends. A good distribution of cellulose fibers into resulted biomaterials was found regardless the obtaining method. According to DSC results, the incorporation of cellulose fibers induced an enhancement in crystallinity of the PLA/PHB. The important improvements in the mechanical behavior of PLA/PHB biomaterials highlighted the reinforcing capability of the cellulose fibers.

Acknowledgements:*This work was supported by two grants of Ministry of Research and Innovation, CNCS - UEFISCDI, PN-III-P1-1.1-TE-2016-2164, no. 94/2018, Biocompatible multilayer polymer membranes with tuned mechanical and antiadherent properties (BIOMULTIPOL) and PN-III-P4-ID-PCE-2016-0431, no. 148/2017, Nanocellulose 3D structures for regenerative medicine (CELL-3D) within PNCDI III.*

References:

[1].De Castro DO., Bras J, Gandini A, Belgacem N. Surface grafting of cellulose nanocrystals with natural antimicrobial rosin mixture using a green process. Carbohydr. Polym. 2016;137;1-8.

[2].Song Z., Xiao H., Zhao Y. Hydrophobic-modified nano-cellulose fiber/PLA biodegradable composites for lowering water vapor transmission rate (WVTR) of paper. Carbohydr Polym 2014 111:442-8

THE PROCESS OF OBTAINING AND STUDY OF RESORCINOL FUNCTIONALIZED CHITOSAN

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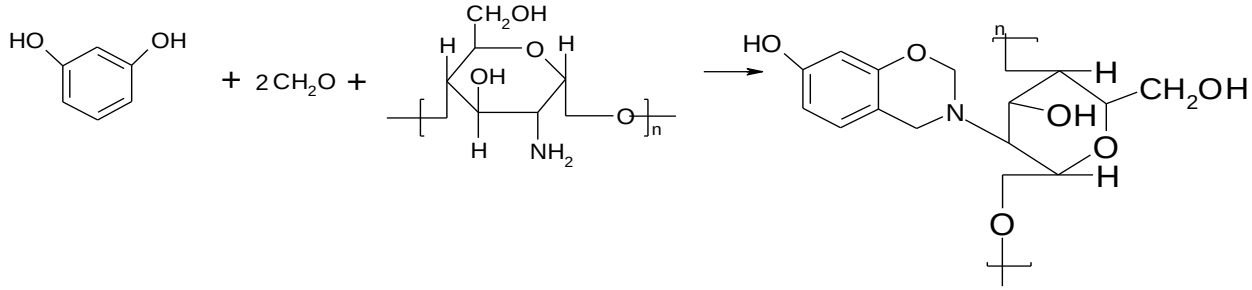
Keywords: Chitosan; resorcinol; functionalisation; polimerisation; functionalised chitosan.

Introduction: Chitosan, which is a copolymer consisting of β-(1-4)-2-acetamido-D-glucose and β-(1-4)-2-amino-D-glucose units, is derived from chitin by deacetylation in the alkali condition. Compared with chitosan, functionalisation chitosan has better water solubility and chemical properties. Recently antioxidant activity of chitosan and its derivatives has attracted much attention due to their nontoxic nature and natural abundance [1].

The process of chitosan functionalisation with different antioxidants represents an important modification method to prepare chitosan derivatives with good water solubility, biocompatibility and unique bioactivities [2].

Materials and methods: The functionalisated chitosan was performed by anionic polimerisation according to the scheme:



Results: Analyzing the chitosan and resorcinol spectra, comparing with the IR spectra of the obtained compound, we observe a change in the chitosan spectrum band to the $–NH_2$ group; in this domain there are two peaks characteristic of the $–NH_2$ linked group, which create 2 middle bands symmetric ν and asymmetric ν which is less pronounced in the spectrum of the obtained compound, instead there is a pronounced band in the 1200 cm^{-1} region specific for the -CN group. C-C aromatic groups are present in the compound obtained at 1500 and 1600 cm^{-1}, the bands given in the IR spectrum of chitosan are less pronounced. The absorbance of the C-O-C group is shown by a strong peak at 1200 cm^{-1}. The aromatic structure of the resorcinol shows the presence of the -OH vibration bands in the 3240 cm^{-1} region, and in the functionalized compound, this spectrum is modified due to changes in the -OH group. The chitosan and resorcinol structural changes were confirmed by IR spectroscopy.

The solubility of the obtained compound was verified in various organic and inorganic solvents. It has been determined that the only solvent which dissolves the given compound of those studied is dimethylformamide.

The anti-oxidant activity of the functionalized with resorcinol chitosan was determined by the DPPH test. By performing the appropriate operations we can mention that the DPPH solution changes its coloration more intensively at higher concentrations of antioxidant.

Conclusions: By performing the appropriate operations we can mention that the DPPH solution changes its coloration more intensively at higher concentrations of antioxidant.

***Acknowledgements**: The researches were carried out within the project STCU 6377.*

References:

[1]. Shyan Bob Shen, Hatsuo Ishida. Synthesis and Characterization of Polyfunctional Naphthoxazines and Related Polymers. In: Journal of Applied Polymer Science. Journal of Applied Polymer Science, Vol. 61, 1595-1605,1996.
[2]. Tao Sun, Yun Zhu, Jing Xie, Xuhong Yin. Antioxidant activity of N-acyl chitosan oligosaccharide with same substituting degree. Bioorganic & Medicinal Chemistry Letters, Vol. 21, 798–800, 2011.

STUDY OF MORPHOLOGY OF SOME RENEWABLE MODIFIED POLYMERS AS METHOD TO SPLIT THE NUCLEATION AND REINFORCEMENT EFFECTS

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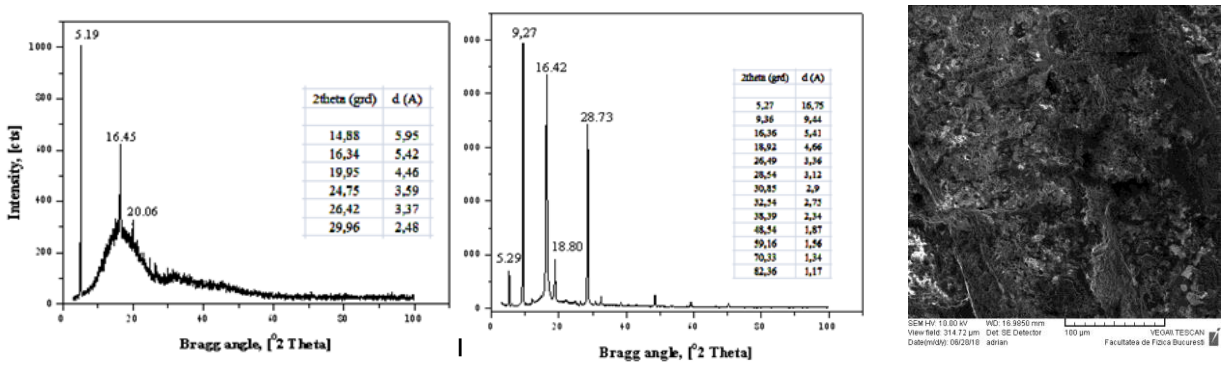
Keywords: nucleation; reinforcement; renewable; durability; polymers.

Introduction: To increase the durability of renewable polymers several methods have been used, including nucleation and/or reinforcement [1]. Because the increasing of durability in both cases is due to morphological changes, the paper aim was to identify the differences between the morphologies of the PLA modified both with nucleation and reinforcing agents for 3D and 4D targeted applications.

Materials and methods: PLA was physically modified by melt compounding with nucleation and reinforcing agents and the resulted materials were shaped as 3D filaments with diameter of +/-0.035 mm. The morphology of the new blends and its composition dependence was simultaneous studied through XRD and SEM. The new materials characterization included also the mechanical properties measurements.

Results: The obtained materials had various morphologies (fig.1) and mechanical properties, depending on the ratio between the two agents.



a) b) c)

Conclusions: The low ratio between the nucleation agent and the reinforcement led to new materials, with controlled mechanical properties and amorphous morphology. For a ratio almost equal with 1 between the two agents, materials with brittle fracture and semicrystalline morphology were generated. Both categories were shaped as filaments for 3D printing with diameter tolerance of +/-.035 mm for targeted applications.

***Acknowledgements**: This work has been funded by the Ministry of Research and Innovation through project no. 40/2018–5/3D-LONG LIFE.*

References:

[1] Y. Wang, S. M. Chiao, T.-F. Hung, S.-Y. Yang, Improvement in Toughness and Heat Resistance of Poly(lactic acid)/Polycarbonate Blend Through Twin-Screw Blending: Influence of Compatibilizer Type, Journal of Applied Polymer Science DOI 10.1002/app

COATED MAGNETIC PARTICLES FOR DYES ADSORPTION

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Keywords: Magnetic particles; chitosan-polyglycidol mixture; coated nanoparticles; methylene blue adsorption.

Introduction: Residual dyes and pigments from various industries are known as environmental pollutants. Their removal from wastewater is done by different techniques such as photocatalytic oxidation, sonochemical or electrochemical treatment, coagulation, flocculation and last but not least, adsorption. Adsorption of dyes on coated magnetic nanoparticles is an effective technique with a high adsorption capacity. In this work, we synthesize and characterize magnetic nanoparticles, coated with biocompatible layers, for the adsorption of methylene blue (MB).

Materials and methods: We investigate iron oxide nanoparticles (MAG) coated or not with sodium dodecylsulfate (SDS) and/or a mixture of chitosan and polyglycidol (Complex C). The studied particles, having from one to three electrostatically deposited layers, are respectively denoted: MS (MAG with SDS), MSC (MS with Complex C) and MSCS (MSC with SDS). Surface tension, DLS, Zeta potential, SEM and magnetometric determinations are performed to characterize the investigated systems. The adsorption properties of the coated particles, toward MB, are revealed by UV-Vis spectroscopy.

Results: The successive covering of magnetic nanoparticles with oppositely charged layers (SDS respectively, Complex C) provides particles with a good colloidal stability in time. The multi-layer deposition is confirmed by DLS, Zeta potential and SEM. The obtained particles are superparamagnetic, and the MSCS system is effective in MB adsorption.

Conclusions: The present work opens the way toward the application of magnetic particles covered with Complex C and SDS in removing the pollutant dyes from wastewaters.

***Acknowledgements**: This paper was carried out within the Polish-Romanian joint research project for years 2016-2018 entitled: 'Synthesis and characterization of magnetic core - hydrophilic polymer shell particles for biomedical and environmental applications'. It has been financially supported by Polish Academy of Sciences and Romanian Academy within the research program 'Colloids and dispersed systems' of the 'Ilie Murgulescu' Institute of Physical Chemistry. The support of EU (ERDF) and Romanian Government under POS-CCE O2.2.1 project INFRANANOCHEM, No. 19/2009.03.01 is gratefully acknowledged.*

DSC STUDY OF THERMAL BEHAVIOR OF SOME RENEWABLE POLYMERS MODIFIED FOR USING AS 3D PRINTED DURABLE APPLICATION

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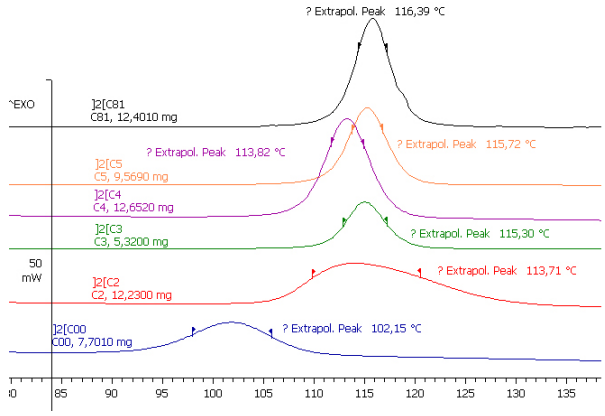
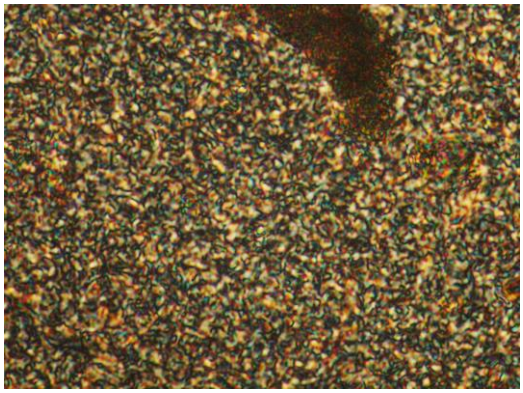
Keywords: renewable polymers; PLA; DSC; POM.

Introduction: The properties of renewable polymers can be controlled to be use as materials for 3D printing of durable applications considering different paths [1]. The paper's goal was to study the thermal behavior of reinforced PLA for estimation the possibility of its shaping as filaments with required diameter for 3D printing of durable applications.

Materials and methods: The PLA reinforcing was made through melt compounding of the filler with the PLA with selected chemical structure. The thermal behavior was estimated through DSC measurements, at different rate heating, before and after removing the thermal history of each new compound. Also it were measured the impact resistance of each new materials and through polarized optical microscopy (POM) the morphology structure.



a)



b)

Figure1. Influence of the filler on the crystallization (a) and morphology of the modified renewable polymers (b)

Conclusions: Depending on the compositions and obtaining conditions the crystallization of new materials take place in shorter time with almost 10 – 15 min. and at high temperature with more than 10^0C– 35^0C as in case of unmodified renewable polymers. Due to the reinforcement the impact resistance is almost twice greater and, depending on the filler content, the morphology contains or not bigger or smaller crystals.

***Acknowledgements**: This work has been funded by the Ministry of Research and Innovation through project no. 40/2018–5 / 3D-LONG LIFE and 59CI.*

References:

[1].Nagarajan V., Mohanty A. K., Misra M. Perspective on Polylactic Acid (PLA) based Sustainable Materials for Durable Applications: Focus on Toughness and Heat Resistance. ACS Sustainable Chem. Eng. 2016

STUDY OF PHOTOCATALYTIC DESTRUCTION OF PERSISTENT ORGANIC POLLUTANTS IN WATER

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Keywords: photocatalysis; bensothiasols; destruction; heterogeneous and homogeneous processes.

Introduction: Specifics and advantages of homogeneous and heterogeneous processes of persistent organic pollutants destruction in water are presented, considering the practical application of the proposed methods for the environmental protection purposes [1].

Materials and methods: ABT (2-aminobenzothiazol) – a persistent pollutant in environment, weakly subjected to degradation under natural conditions, was used for the studies. Its adsorption spectrum has two maxima $\varepsilon_{1=}$ 5677 and $\varepsilon_{1\ =}$2166 $M^{-1}\cdot cm^{-1}$. As photoinductor in heterogeneous medium, TiO_2 (anatas) was used with following crystalline lattice parameters, Å: a = 3.782, c = 9.509, particle size 10-25 nm, specific surface 24.7 m^3/g, in concentrations 0.5-1.0 g/l. For homogeneous catalysis, Fenton's reagent was used on the base of potassium trioxalate $K_3[Fe(C_2O_4)_3]$ •$3H_2O$ (PTO)/H_2O_2. Pollutant destruction and formation of intermediates was controlled with HPLC method.

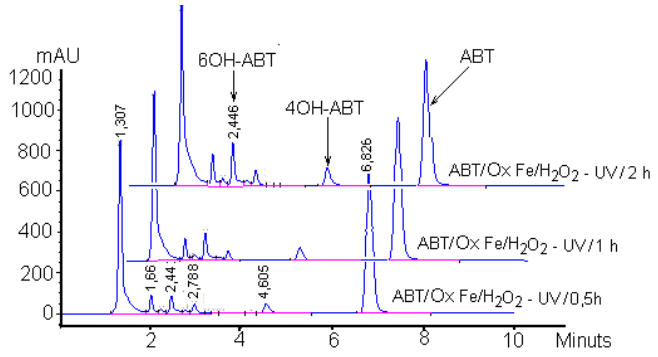

Fig.1. Chromatograms of ABT photo-degradation

Results: The studies of homogeneous processes of water pollutants destruction have shown that Fe-containing photoinductor, introduced in ABT-contining water in the amount of 0.3-3.0 Mmol, is capable to ensure the ABT decomposition by 7-10% even without UV-irradiation, whereas with the prolonged irradiation within 100 hours and more – by 80-100%. It was shown that the intermediate formed as a result of ABT decomposition is 2-amino-6-hydroxybenzothiazol OH-ABT (Fig.1). Its destruction kinetics was similar to that of the ABT. In case of hydrogen peroxide introduction in homoheneous process it accelerates the destruction processes, however, if the microorganisms are additionally used to assimilate the pollutants, H_2O_2 may reduce their activity.

Heterogeneous destruction processes were studied using TiO_2. Photocatalytic activity of TiO_2 is explained with processes, running under the UV-irradiation with the formation of electron hopes (h^+) and free electrone (e^-) by the reaction: $TiO_2 + h\nu \rightarrow e^- + h^+$, which in their turn promote the formation of $^{\bullet}O^{2-}$ radical: $e^- + O_2 \rightarrow {}^{\bullet}O_2^-$, and $TiO_2(h^+) + H_2O_{adc.} \rightarrow TiO_2 + {}^{\bullet}OH_{adc.} + H^+$. As a result, similarly with Fenton reagent introduction, a series of redox-processes run, with the formation of free radicals ($OH^{\bullet}$, HO_2^-, $O_2^{\bullet-}$ etc.).

Conclusion: Using of Fenton's reagent in photochemical processes is inevitably resulted in its graduate destruction, which provokes the treated water compartments pollution with its decomposition products, containing iron compounds which are difficult to remove. When the photoinductor based on the system TiO_2/H_2O_2 is applied, similar ABT destruction effect is provided. In this case, solid photoinductor particles can be easily removed by the filtration.

References:

[1].Ajuboury D., Feroz S. Performance of different photocatalytic oxidation processes in petroleum wastewater treatment: A comparative study. Global Nest Journal, March 2017. https://www.researchgate.net/publication/312032094.

[2].Covaliov V., Covaliova O., Cinclei A., Mailhot G., Besse P., Delort A.-M., Bolte M., Dragalin I. Complex approach to the problem persistent organic pollutants degradation in water environment. In: Environmental Engineering and Management Journal. Iaşi, Gh.Asachi Tehnical University, Romania. 2004, vol.3(4), p.603-610.

PHOTOSTABILIZATION OF RIBOFLAVINE BY ITS ENCAPSULATION IN NATURAL AND SYNTHETIC ZEOLITES

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Keywords: riboflavin; zeolites; hydrogen bonds; encapsulation.

Introduction: Riboflavin/vitamin B_2 (RB) is known as one of the most important vitamins used in maintaining cellular balance, muscular and nervous equilibrium in humans and animals. RB has the maximum absorption at 222, 268, 374 and 444 nm in water and has a yellow color. When aqueous solutions containing RB are exposed to sunlight, RB is converted into lumichrome (LC) under neutral conditions, and to lumiflavin (LF) in alkaline solutions. For the photostabilization of RB, natural (clinoptilolite) and synthetic (AX) zeolites were used in this encapsulation study [1].

Materials and methods: RB (10^{-4} M) was prepared by heating a mixture of phosphate buffered saline (PBS) solution and an excess of RB at 55^0C. The solution was then sterile filtered (0.22 µm) and the optical density was measured at 446 nm for a sample diluted 10 times. Knowing the molar extinction coefficient of the aqueous solution of RB (ε_{446nm} = 11,400) the concentration of the diluted solution (750 µM) was calculated and the RB stock solution was further diluted with PBS to a final concentration of 400 µM. Irradiation was performed with an Ar laser (Applied Photophysics Ltd., UK) [emission at 488 nm] corresponding to the wavelength of RB. Also, for the photodegradation reaction a high pressure 125 W Hg lamp (Romlux) has been used [emission at 405 and 436 nm], corresponding to the wavelength of RB.

Results: The variation of RB's fluorescence spectrum was recorded before and after the encapsulation in the zeolite, as shown in fig. 1. The excitation wavelength was 390 nm in both cases, for the initial aqueous solution a higher intensity being recorded (wavelength = 530 nm, I = 127) than in the case of the encapsulated riboflavin (wavelength = 525nm, I = 91).

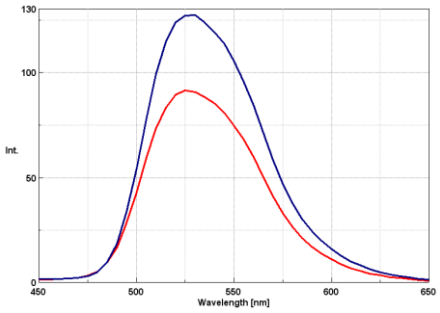

Figure 1. Fluorescence spectrum of RB before (blue) and after (red) encapsulation.

In addition, the hipsochromic movement of the emission band reappears (towards smaller wavelengths), specific to the hydrogen bond formation. These new experiments have reinforced the belief that riboflavin was encapsulated in zeolites, that is photo-chemically stabilized (in the case of the riboflavin solution a dramatic decrease in riboflavin bands appears) and, in addition, the stabilization is mainly due to the hydrogen bonds between the two components.

A vital role in the process of encapsulation is played by water molecules, responsible for the formation and stabilization of the nano – tubular structures by hydrogen bonds that occur between groups bearing nonparticipating electrons. Π-π interactions occurring at over – stacking, with an average π-π distance of 4.9 Å, are most responsible for this sequence of molecules.

Conclusions: Riboflavin was encapsulated in zeolites, it was photo-chemically stabilized (in the case of the riboflavin solution a dramatic decrease in riboflavin bands appears) and, in addition, the stabilization is mainly due to the hydrogen bonds between the two components.

References:

[1] Sheraz MA, Kazi SH, Ahmed S, Anwar Z, Ahmad I, Photo, thermal and chemical degradation of riboflavin. Beilstein J. Org. Chem. 2014;10:1999–2012. doi:10.3762/bjoc.10.208.

THE INFLUENCE OF THE STEREOISOMERY ON THE PROPERTIES OF SOME MODIFIED RENEWABLE POLYMERS DESIGNED FOR DURABLE 3D PRINTING

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Keywords: 3D printing; stereoisomers; renewable; durability; polymers.

Introduction:

Because of the two asymmetric carbon atoms in the molecule, lactide possesses three optical isomers or stereo-isomers, namely, L-, D-, and meso-lactides. Different PLAs were prepared from these isomers one of them even at industrial scale [1]. The aim of the paper was to study the influence of the D-isomer content of some PLAs with different molecular weight on the properties of PLLA to obtain materials for 3D printed durable applications.

Materials and methods:

The new materials were obtained by melt compounding in classical conditions, of some PLAs with different D-isomer content (PDLA) and different molecular weight. Thermal behavior of the new compounds was investigated by differential scanning calorimetry and the morphology by polarized optical microscopy. The impact properties were measured in line with the polymer characterization practice.

Results:

The properties of the new obtained materials depend on the studied parameters (fig.1-2)

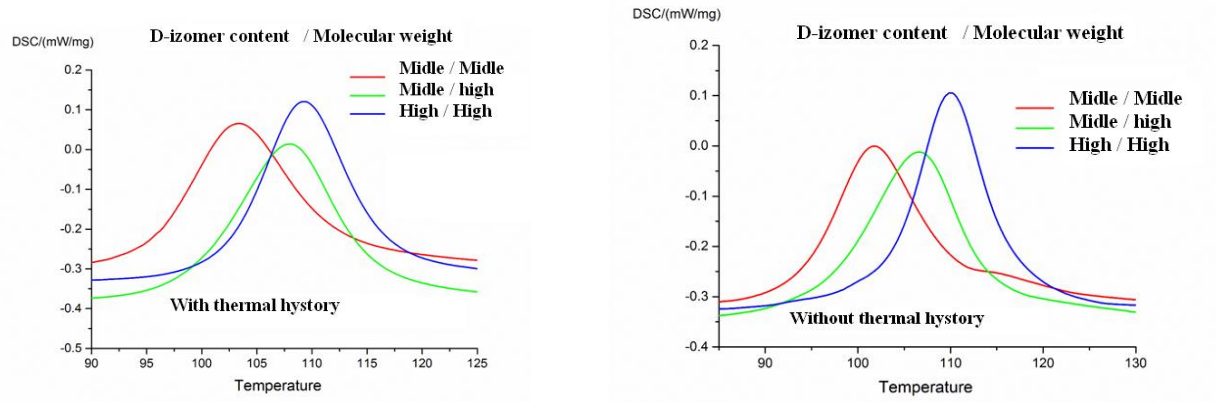

Fig.1-2. The influence of the D-isomer content and of the molecular weight of some PLAs on the crystallization of PLLA–extrusion grade

Conclusions:

Because of stereo-complexation the crystallinity, heat resistance and impact behavior of PLLA was improved which means enhanced durability of the new materials. The greater the D-isomer content and the molecular weight of the PDLA the more important are the improving of the properties of the new materials.

Acknowledgements: *This work was supported by a grant of the Ministery of Research and Innovation, CCDI-UEFISCDI, project number PN-III-P1-1.2-PCCDI-2017-0428, 40/2018–5 / 3D-LONG LIFE within PNCDI III.*

References:

[1] Idong Feng, Bao Zhang, Xinchao Bian, Gao Li, Zhiming Chen, and Xuesi Chen Thermal properties of polylactides with different stereoisomers of lactides used as comonomers. Macromolecules 2017; 50(16):6064–6073.

CHANGES IN THE BIOCHEMICAL COMPOSITION OF SELECTED *TETRASELMIS* SPECIES, CULTURED SEMI-CONTINUOUSLY UNDER DISTINCT RENEWAL RATES

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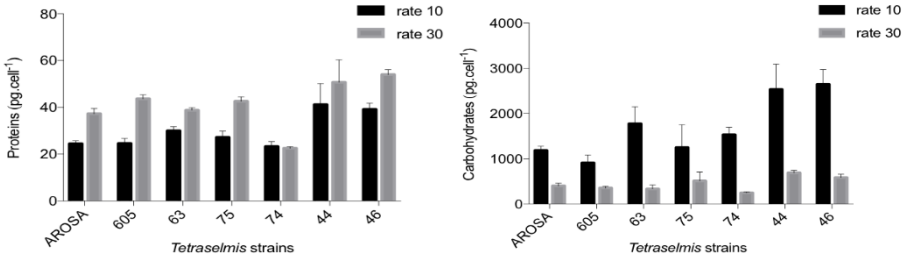
Keywords: Microalgae; Tetraselmis; Semi-continuous culture; Biochemical composition

Introduction: Several strains of *Tetraselmis suecica* (UW 605 and AROSA) and of *Tetraselmis sp.* that were characterized as lipogenic (RG 63, RG 75 and RG 74) and non-lipogenic (RG 44 and RG 46) through the flotation method were cultured semi-continuously using two different daily renewal rates, 10 % and 30 % of the volume of the cultures, in attempts to ascertain the changes in production rates of proteins, carbohydrates and lipids.

Materials and methods: The strains were cultured in 80 mL test tubes, with filtered sea water (35 ‰ salinity), sterilized and enriched with nutrients and vitamins, according to Fabregas et al. [1] with a final concentration of nitrogen in the culture medium of 8 mM. They were submitted to 12 h light: 12 h dark photoperiod, with a light intensity of 152 μmol photons m^{-2} s^{-1}. Cells were inoculated at a density of 0.5 x 10^6 cell. mL^{-1}, and subjected to aeration of 250 mL/min supplemented with CO_2, in order to keep the pH below 8 at a temperature of 20 °C. As soon as cultures reached the early stationary phase of growth, the semi-continuous growth regime was initiated with daily renewal of 10 % or 30 % of the culture medium, in the first hour of the light period. Fresh biomass was used for all biochemical analyses – lipids, proteins and carbohydrates. All analyses were carried out in triplicate. Carbohydrates were measured by the phenol-sulphuric acid method [2], lipids by the charring method [3] and proteins by the Folin-phenol method [4].

Results: As expected, an increase in renewal rate produced an increase in protein content of the biomass but a decrease in carbohydrate content in all strains. Lipid content decreased for RG 63 and RG 74 strains (lipogenic) with a renewal rate of 30 % and increased for RG 44 and RG 46 strains (non-lipogenic).

Conclusion: Our results prove the influence of cultivation mode upon the biochemical composition of microalgae.



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References:

[1]. Fabregas J, Herrero C, Cabezas B, Abalde J. Mass culture and biochemical variability of the marine microalga Tetraselmis suecica Kylin (Butch) with high nutrient concentrations. Aquaculture. 1985;49:231–44.

[2]. Kochert G. Carbohydrate determination by the phenol-sulfuric acid method. In: Hellebust JA, Craigie JS, editors. Handbook of Phycological Methods. London: Cambridge Univ. Press; 1978:95–7.

[3]. Marsh JB, Weinstein DB. Simple charring method for determination of lipids. J Lipid Res. 1966;7:574–6.

[4]. Lowry OH, Rosebrough NJ, Farr AL, Randall RJ. Protein measurement with the Folin phenol reagent. J Biol Chem. 1951;193:265–75.

POSSIBILITIES OF BIOMETHANE PRODUCING AS ALTERNATIVE TO THE FOSSIL GAS

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Keywords: biogas; bio-methane; purification; compressing; register

Introduction: The Biogas significantly developed in the last 2-3 decades over the world, especially into the countries where the residual bio-resources are available. The action is sustained in Europe also by the requirements of E.U. Directives till 2020 or 2050, regarding renewable versus fossil fuels to produce energy. Although Romania had in the past over 400 biogas running plants, today there exist only o few (about 25, based only on outside technologies), medium power, which may not cover the current requirements on energy saving and environmental protection.

Taking in account the achievements and experience in this domain, based only on autochthon technologies [1],[2], still existing to owner or collaborators, the paper proposes to revamp these opportunities for the sector.

Also, the authors underline that such developing may reduce the dependency of imported natural gas fuel.

Materials and methods: The content of presentation is based both on previous Romanian achievements and on current world/European practice and development in the domain.

The way to turning in account of biogas is versatile and depend on local conditions and management. As basis, the biogas may be directly used on home gas cookers, as fuel of motors producing warm water and electricity (cogeneration), or simply by purification and compressing. In this last alternative, the obtained gas is called bio-methane and may be used as motor fuel, captured into pressure charging car recipients, or delivered into national gas network [3]

The data regarding the actual situation in Romania on energy supply upon Romanian villages is documented.

For future cases, Romania may develop, parallel with biogas producing, the technologies for biogas purification [4]. The available literature data were used to convince on the opportunity to apply proper methods for this aim.

In this moment, 16 European countries joined to an organization dealing with registering of bio-methane, as suppliers or consumers, and any new country will be sustained and considered following a proper methodology.

Results: The work put on the table the current situation in Romania regarding biogas production and perspective for next decades, in case the farmers, local or central authorities are interested to develop such technologies, based on Romanian patents (already tested).

Also, the methods to purify the biogas to bio-methane are developed and compared.

Finally, the attending of country and European bodies, dealing with evidence of all bio-methane quantities delivered into or extracted out from national network will be achieved [5].

Conclusions: Ordaining of such delicate problems, regarding on management of biogas/bio-methane may arise independency from imported fossil gas resources, parallel with reduction of global uncontrolled spillage of dangerous matters or gaseous emissions into environment.

***Acknowledgements**:*

References:

[13].Nikolic V. Instalatie de producer a biogazului, Mai 2010, (technological project).
[14].Craiu C. Digestia anaeroba a namolurilor biodegradabile 16.07.2011, (P.P.Show).
[15].Sdrula N, Stefan DS. The biogas –a promising biofuel –able to improve the energy demand and reduction of green house effects, Priochem Ed. XII, Oct. 2016 (P.P.Show.).
[16].Biomethane advantages-desavantages, https://www.biomethane.org.uk (On line resource).
[17].European Renewable Gas Registry, http://www.ergar.org/downloads/. (On line resource).

EXTRACTION OF BIOACTIVE COMPOUNDS FROM MICROALGAE CULTIVATED ON LIQUID DIGESTATE FROM BIOGAS PRODUCTION FOR USE IN FERTILIZER FORMULATIONS

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Keywords: Chlorella vulgaris; Microalgae; Bioactive compounds; Liquid digestate; Fertilizer; Tomato plants

Introduction: Microalgae has the ability to remove organic compounds from the liquid digestate, especially phosphorus and nitrogen with the added advantage that it recycles these nutrients with lower costs than usual procedures of treatment. Another advantage is that the microalgae grown in these conditions is a source of valuable bioactive components, with potential use as bio-components in fertilizers. Processing of the digestate is a serious environmental problem for biogas production plants, due to the high content of undigested organic substrate, microbial biomass and large amounts of nitrogen and phosphorus [1,2]. This work focuses on the growth of microalgae biomass (*Chlorella vulgaris* strain) for the extraction of crude bioactive extract for use in fertilizer formulations. The microalgae biomass is cultivated using liquid digestate from biogas production as a nutrient source. The crude extract was added in different concentrations to an NPK fertilizer (19:8:8+2MgO). The fertilizer formulations prepared with different concentrations of obtained crude extract were tested on tomato plants, to measure the effects they have on plant development and management of water and nutrients from the soil: plant height, plant weight, stem width, root length, leaf number, leaf width, branch number and dry biomass. It was shown that the development of the tomato plants was best using the fertilizer formulation with NPK + 5% (w/w) bioactive extract, visible mainly on the root and the stem of the tomato plants, thicker than the other formulations.

Materials and methods: The *Chlorella vulgaris* culture is performed in a photobioreactor with the growth medium liquid digestate resulted from biogas production, diluted until the nutrient composition is similar to the microalgae strain standard culture medium (BBM). The crude extract, obtained by ultrasound assisted extraction, was tested in an NPK fertilizer formulation on tomato plants. The fertilizer formulation was applied near the root of the tomato plants and it was diffused into the soil by watering. After 34 days of growth, the plants are investigated and measured.

Results: The crude extract obtained from Chlorella vulgaris grown in liquid digestate (8% w/w dry microalgae biomass) was found to be comprised mainly out of pigments (7.68% Chlorophyll α, 1.91% Chlorophyll β and 3.15% Carotenoids) and algal oil fraction (37.89%). The crude bioactive extract was found to be most effective in stimulating plant development when included in an NPK fertilizer formulation at 5% (w/w), offering the best results regarding the plant strength. Plants treated with 5% (w/w) extract in NPK fertilizer presented the highest weight of dry biomass (average of 1.47g compared with 1.21g reference), the longest and fullest root (double the length compared with the reference) and the thickest stem (2.72 mm compared with 2 mm reference).

Conclusions: The crude extract obtained from *Chlorella vulgaris* biomass is rich in pigments and algal oil, bioactive compounds that facilitate plant growth and strong development by addition to fertilizer formulations. The best results were obtained when adding 5% (w/w) bioactive extract to the NPK fertilizer formulation. The bioactive compounds present in the crude extract provide the plant with a better management of the nutrients, thus increasing its development.

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References:

[1]. European Biogas Association, Biomethane & Biogas Report 2015, http://european-biogas.eu/2015/12/16/biogasreport2015/ - accessed august 2017.

[2]. Ge S, Champagne P. Nutrient removal, microalgal biomass growth, harvesting and lipid yield in response to centrate wastewater loadings, Water Research, 2016;88:604-612.

EFFECTS OF MICROWAVE EXPOSURE ON CELL VIABILITY OF *SACCHAROMYCES CEREVISIAE* DURING GLUCOSE FERMENTATION

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Keywords: microwave irradiation; yeast; cell viability

Introduction: The aim of this paper was to study the effects of microwave exposure during batch fermentation processes of glucose by *Saccharomyces cerevisiae*, on cell viability in comparison to conventional batch fermentation processes. Overall microwave effects might be classified as thermal, corresponding to augmentation of reaction rates based on a temperature increase, specific, thermal effects which can't be obtained when using convention heating and non-thermal. Thermal effects are directly proportional to the radiation intensity while non-thermal effects occur in certain frequency regions only, and depend on the interaction between the exposed sample and microwaves [1, 2].

Materials and methods: Experiments were carried out using Red Ethanol yeast, glucose as the substrate and the fermentation broth was prepared using distilled water and the following nutrients: $(NH_4)_2SO_4$, KH_2PO_4, $MgSO_4 \cdot 7H_2O$, Citric acid, Na_2HPO_4, the concentrations of which were maintained for all carried out experiments. Cell viability was estimated using Trypan Blue to stain dead cells, pictures of which were taken using an optical microscope coupled with a digital camera. SEM, flow cytometry and GC analysis were also carried out.

Results: In the experimental setup which was used an optimum Specific Absorption Rate domain was determined, with higher fermentation rates being achieved through microwave irradiation without the prolonged exposure being detrimental towards cell viability. Through both SEM analysis and optical microscopy of the exposed and control samples, no significant stress was observed on either cell wall integrity or on cell viability. Experiments were carried out at different substrate levels, yeast concentrations and different temperatures, and in all cases microwaves exposure didn't lead to an increase in number of death cells, yet in some cases microwave exposure proved to be beneficial towards increasing fermentation rates [3].

Conclusions

Based on gas chromatography analysis couple with SEM and optical microscopy analysis, microwave exposure was proved to be useful during the fermentation process by increasing fermentation without having a significant negative effect on either cell viability, cell morphology or number of cells.

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References:

[1]. Kappe O, Stadler AM, Dallinger D. Microwaves in Organic and Medicinal Chemistry. Second ed. 2012: Wiley-VCH Verlag GmbH & Co.

[2]. Loupy A. Ed. Microwaves in Organic Synthesis. 2006, WILEY-VCH Verlag GmbH & Co: Weinheim.

[3]. Calinescu I, Vlaicu A, Chipurici P, Ighigeanu D, Lavric V. Alcoholic fermentation in the presence of microwaves, Chemical Engineering and Processing - Process Intensification 2018;126:16-22.

INFLUENCE OF NUTRIENTS AND PHYTO-STIMULATORS ON THE METHANOGENESIS PROCESSES

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Keywords: biogas technology; methanogenesis; phyto-stimulators; nutrients; organic substrate

Introduction: A complex approach in the biogas technology has been proposed, in view to ensure the increasing of kinetic indicators of methanogenesis and the yield of biomethane, as a result of the anaerobic digestion of biomass, including the dosing in the biochemical process of the micro-amounts of biologically active additives. Effects of nutrients and phyto-additives on biochemical process were studied. Modified advance treatment method to remove P and N from waters was elaborated.

Materials and methods: For wastewater treatment, phyto-additives were used. For the advanced treatment, the polluted water was tested containing 1440 mg/l N(NH_4) and 350 mg/l PO_4^{3-} ions. Especially elaborated bioreactor and integrated chemical reactor were used for the experiments.

Results: It was shown that introduction of the elaborated phyto-stimulators into the process of biochemical digestion of biomass is a advantageous approach, enabling to essentially increase the biomass digestion degree (by about 12-15%), and at the same time to reduce the lag-phase of methangenesis process, and thus to enhance the biogas formation rate. Biomethane contents in biogas is also increasing from 55-60% to 92-97%, in dependence on phyto-stimulator nature and its concentration [1].

Presence of nutrients (N and P compounds) in the treated biomass and water with high organic load composition exerts the effect on the biomass digestion, increasing the biomass digestion coefficient. At the same time, nutrients concentration in the digested liquid is reduced by 20-30% with time, as compared to its initial contents. The remaining 80% of nutrients remaining in water composition, once entered the natural waters, can provoke their euthrofication Therefore, the additional/advanced water treatment is necessary prior to the water discharge into the natural water bodies.

To provide the efficient advanced treatment of waste waters with the removal of N and P compounds, a modified chemical method has been proposed [2]. The specifics of this process allow to obtain the complex compound $MgNH_4PO_4$, which is a prolonged action effective soil fertilizer. To save the materials, it was proposed to use the eluates/wastes from ion-exchange processes, which contain up to 15-17% $MgCl_2$. Magnesium suspension was introduced in treated water to ensure the ratio $[Mg^{2+}]$: $[NH_4^+]$: $[PO_4^{3-}]$ = 5 : 2 : 1. pH value was 8,5. Sludge was dewatered by centrifugation. The treated water contained: NH_4^+ - 2 mg/l, PO_4^{3-} - 0,5 mg/l, COD – 25 mg O_2/l.

Conclusion: Both phyto-catalysts and nutrients contained in the digested biomass can ensure the intensive methanogenic process and efficient wastewater treatment. For the advanced water treatment with the removal of N and P compounds, the resource-saving efficient method was proposed, which allow to reach the limited admissible concentrations of pollutants prior to the water discharges into the natural water bodies.

References:

[1]. Covaliov V, Duca Gh, Covaliova O. “Green Energy: Innovative ecobiotechnologies and integrated bioreactors”. USM: CEP, 2017, 504 p. ISBN 978-9975-71-902-5.

[2]. Covaliova O, Covaliov V, Ungureanu D. Brevet MD Nr.165. Procedeu de epurare a apelor reziduale de la complexele zootehnice de azot amoniacal şi fosfaţi. BOPI, Nr. 3, 2010.

EFFECTS OF NEW THIOUREA DERIVATIVES ON ANIMAL AND PLANT CELLS

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Keywords: thiourea derivatives; cytotoxicity; Triticum; Artemia

Introduction: We hereby report on the preliminary toxicity assessment of four thiourea derivatives on plant and animal cells. The four substances are: (4d) N-(3,5-dimethoxyphenyl)-N'-(2-thienyl)-thiourea, (4e) N-(3,4-dimethoxyphenyl)-N'-(2-thienyl)-thiourea, (4f), N-(2,4-dimethoxyphenyl)-N'-(2-thienyl)-thiourea, (4g), N-(2,5-dimethoxyphenyl)-N'-(2-thienyl)-thiourea previously obtained from 2-thiopheneacetic acid [1].

Materials and methods: The cytotoxicity of aqueous suspensions (prepared with Tween 80, was assessed by: the Constantinescu method (*Triticum* test) (10^{-3} -10^{-6}M) and the *Artemia franciscana* bioassay (10^{-3} -10^{-7}M) [2, 3]. Experiments were performed in duplicate for the *Triticum* test and in triplicate for the *Artemia* bioassay. The statistical analyses for *Triticum* were carried out on the measurements performed after 72 hours, using conventional and robust multiple regression to assess the statistical differences among the substances and concentrations tested.

Results:

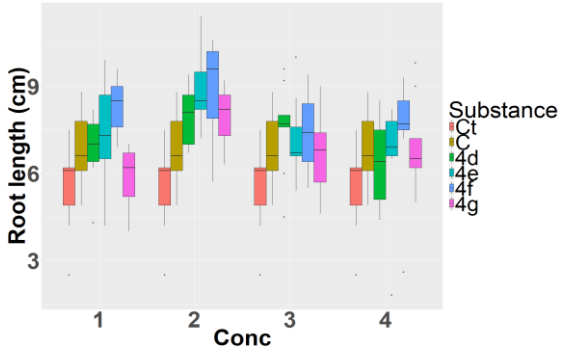

Figure 1. Boxplot representation of the variation of *Triticum* root length

The four substances had little toxicity on the *Triticum* rootlets, they tended to slightly stimulate the growth as compared with the control group in one replica of the study, whereas they inhibited slightly the growth in a second replica. The stimulatory effect was statistically significant ($p<0.0001$) in the first experiment, but not significant or only marginally significant in the second (p varying between 0.045 and 0.84). The absence of a consistent effect and of a concentration dependence is coherent with a lack of effects of the substances tested on the root growth. The toxicity on the nauplii of *Artemia franciscana* Kelogg was also very limited. Lethality was generally seen only at the milimolar levels (first concentration evaluated) and in a small proportion (in most cases under 10%); an IC_{50} value could not be computed.

Conclusions: The four thiourea derivatives have little acute toxicity and may be further explored for their potential therapeutic activities.

References:
[1]. Bădiceanu CD, Nuță DC, Missir AV, Hrubaru M, Delcaru C, Dițu LM, Chifiriuc MC, Limban C. Farmacia. 2018;66(1):149-156.
[2]. Bădiceanu CD, Dimcevici Poesina N, Missir AV, Stecoza CE, Dinu M. Farmacia. 2014;62(1):23-33.
[3]. Kellogg VL. Science. New Series. 1906;24(619):594-596.

STABILIZATION OF THE BIOGAS DIGESTATE SUSPENSION FOR OPTIMAL PROCESSING

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Keywords: biogas plant; digestate; biochar; fuel

Introduction: Biogas production by anaerobic fermentation is a promising method of producing an energy carrier from renewable resources [1]. A common biogas plant with a power of 500 kW emits more than 10,000t of digestate per year with a dry matter of about 10% [2]. The utilization of biogas digestate offers the possibility for production of bioenergy. The objective of this study was to investigate the stabilization of the biogas digestate suspension for optimal processing in order to obtain biochar and bio-oil products.

Materials and methods: The distribution of particle sizes was measured with a particle size measurement by dynamic light scattering (Zetasizer Nano ZS).The particle morphology was recorded by Axiovert 40CFL Inverted Microscop and the physico-chemical stability was studied by optical dispersion analysis (Turbiscan Lab Expert).

Results: The effect of two stabilizers agents concentration (wt. %) on biogas digestate suspension stabilization have been evaluated. The results showed that the viscosity of suspension decrease due to the addition of stabilizer, resulting in an improved fluidity. Moreover, the addition of low amounts of stabilizers agents produced suspensions with small and uniformly distributed particle sizes and longer sedimentation times.

Conclusions: The experimental data reported suggest that addition of low concentration of stabilizer agent produce suspension with lower viscosity, smaller particle size and with longer sedimentation time.

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References:

[1]. Rehl T, Mülle J. Conservation and Recycling. 2011:56:92–104.
[2]. Kratzeisen M, Starcevic N, Martinov M, Maurer C, Müller J. Fuel. 2010:89:2544–2548.

OPTIMIZATION OF THE IMMUNOASSAY SYSTEM FOR ELECTROCHEMICAL DETECTION OF AFLATOXIN M1

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Keywords: Aflatoxin M1; immunoassay; electrochemical detection

Introduction: Contamination with AFM_1 occur in human breast milk, milk and dairy products, being of real concern for public health, especially for infant and young children. Due to its high toxic potential and high stability towards milk processing technologies, such as pasteurization and ultra-high temperature heating (UHT), this mycotoxin can be found usually at higher concentration than that found in raw milk [1, 2]. To minimize its occurrence in commercialized milk and dairy products it is necessary to use fast, sensitive, selective and cheap assays for detection of this metabolite.
Materials and methods: An electrochemical platform has been developed and integrated into an on-line flow injection immunoassay system for sensitive detection of AFM_1. the principle of detection is based on the direct competition between AFM1 and its conjugate with horseradish peroxidase (AFM1-HRP) for the specific monoclonal antibody of AFM1.
Results: Using 3,3`,5,5`-tetramethylbenzidine (TMB) as substrate for the peroxidase at a screen-printed gold electrode modified with a co-polymeric film was possible to determined by electrochemical measurements the amount of the conjugate captured by the monoclonal antibody.
Characterizations and optimization of the experimental conditions were performed through cyclic voltammetry and amperometry studies, using the enzyme HRP. The working potential has been optimized and decided to be +0.1 V vs Ag/AgCl, while the optimum concentrations of TMB and respectively H_2O_2, were set at 0.5 mM and respectively 10 mM. The electrochemical active compound was possible to be determined by chronoamperometric measurements at the optimum applied potential, and further the AFM1 concentration.
Conclusions: The developed immunoassay system enables electrochemical detection of AFM1 with good reproducibility and operational stability.

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References:
[1]. European Food Safety Authority (EFSA). Opinion of the Scientific Panelon Contaminants in the FoodChainon a Request from the Commission Related to the Potential Increase of Consumer Health Risk by a Possibleincrease of the Existing Maximum Levels for Aflatoxins in Almonds, Hazelnuts and Pistachios and Derived; EFSA: Parma, Italy, 2007; pp. 1–127.
[2]. Jalili M, Scotter M. A review of aflatoxin M1 in liquid milk. Iran. J. Health Saf. Environ. 2015;2:283–295.

EXTRACTION AND BIOLOGICAL ACTIVITIES OF CHITIN/CHITOSAN FROM BY-PRODUCTS OF *GANODERMA LUCIDUM* MUSHROOM

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Keywords: Ganoderma lucidum; chitin; extraction; characterization; biological activity

Introduction: *Ganoderma lucidum* is a woody Basidiomycota mushroom from the Ganodermataceae family, used in traditional oriental medicine, an accepted remedy in the American Pharmacopoeia of Plants and Therapeutic Compendium. Chitin, which is an N-acetylglucosamine polymer, is a structural component found in the exoskeleton of invertebrates such as crustacean and insects, and also exist within the structure of cell wall of mushrooms. Chitin is extracted for a wide range of applications: medical, pharmaceutical, dietary, food, technical, etc. The main objective of this research was to obtain chitin/chitosan isolated from the by-products of Ganoderma lucidum mushroom (which is obtained through biotechnological culture) and to evaluate its biological activity.

Materials and methods: By-products of Ganoderma samples were washed and dried in an owen at 50 °C for 10 days. Chitin extraction may be performed using enzymatic and chemical methods. Samples were ground into powder in a mixer before chitin extraction. The homogenized suspension of Ganoderma (in deionized water), was centrifugated, deproteinized with NaOH 4M and washed four times. The chemical extraction with NaOH was performed twice. Enzymatic extraction of chitin was performed with specific commercial enzymes. Chitosan was produced by chitin deacetylation. The antioxidant capacity was determined by the inhibition of ABTS cationic radical and the scavenging of the stable radical DPPH. *In vitro* biocompatibility of obtained chitin was tested in NCTC fibroblast cell line and the anti-proliferative effect in HEP2 tumoral cell line, according to the standard SR EN ISO 10993-5 using the MTT assay.

Results: The optimum chitin/chitosan extraction method was selected according to the obtained yield. The enzymatic method for chitin extraction was most efficient than the chemical method. Our results showed that the chitin extracted from Ganoderma by-products has a significant antioxidant capacity. The results of MTT assay demonstrated that the chitin extracts did not affect the cell viability at 100-750 µg/mL, therefore it is not cytotoxic. The obtained chitin samples had a stronger anti-tumoral effect at concentration of 100-750 µg/mL when tested on HEP2 tumoral cell line.

Conclusions: The Ganoderma by-products are a promising source of chitin. The chitin used in our experiments was obtained by the enzymatic method. The antioxidant capacity of Ganoderma extracted chitin is comparable with those of chitin obtained from other sources [1]. The results of MTT assay concerning cell viability were confirmed by cell morphology observations. All tested chitin/chitosan samples were noncytotoxic in NCTC fibroblast cell culture, at concentrations ranging between 100-750 µg/mL and induced an anti-proliferative effect on tumoral cell line (HEP-2) in the same range.

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References:

[1]. Jianjun Zhanga, Guangyuan Mengb, et. al. Extraction, characterization and antioxidant activity of polysaccharides of spent mushroom compost of Ganoderma lucidum. International Journal of Biological Macromolecules. 2016;(82):432–439.

COMPARATIVE STUDY ON METHODS OF EXTRACTING PECTIN FROM BY-PRODUCTS OF VEGETABLES AND FRUITS

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Key words: pectin; galacturonic acid; methylation; emulsion; cytotoxicity

Introduction: By-products derived from the industrialization of vegetables and fruits (pomace, peels) are a reusable source for pectin production. Pectin is a highly safe food additive and, therefore, it is used in industry. Pectin is a galacturonic acid polymer with gelling, thickening and stabilizing properties [1]. The purpose of this study was the comparative analysis of pectin extraction methods from by-products of vegetables and fruits industrialization, in order to obtain a useful product for the food, pharmaceutical or cosmetic industry.

Materials and methods: Pectin was extracted by the thermal, ultrasonic and enzymatic methods. Preliminary characterization of pectin extracts was carried out by determining the moisture content, ash and dry matter content. The content in uronic acids was determined by orcinol method [2]. The degree of methylation was analyzed by the titrimetric method with some modifications [3]. Emulsion activity and emulsion stability were investigated using the method described by Dalev and Simeonova (1995) with a slight modification [4]. The biocompatibility of pectin extracts was assessed by the indirect method in human epithelial cell lines, according to ISO 10993-5. After 24 h of cell cultivation in the presence of pectin extracts, the cell viability was determined using CCK-8 kit. Cell morphology was observed at a Nikon inverted phase contrast microscope [4].

Results: The yield of pectin extraction using various methods was calculated and compared, in order to select the optimal protocol. Analysis of uronic acids allowed the identification of pectin extracts that contain at least 65% galacturonic acid (indicated by FAO as necessary for any pectin utilized in food industry) and the best extraction method for the selected sources. *In vitro* cytotoxicity tests showed that all pectin extracts were biocompatible. Optical microscopy observations were correlated with cell viability values determined by CCK-8 method.

Conclusions: All these results have shown that it is possible to obtain from by-products of vegetable and fruit industry, a useful pectin extract for the food industry with its high content of galacturonic acid and biocompatibility with human epithelial cells.

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References:

[1]. May CD. Industrial Pectins: Sources, Production and Applications, Carbohydrate Polymers. 1990;12:79-99.

[2]. Moldovan L, Craciunescu O, Balan M, Gaspar A, Gherghina E. The Purification, Physico-chemical Characterization and Bioactivity of Polysaccharides from *Viscum album*, Revista de Chimie (Bucuresti). 2008;59:1022-1025.

[3]. Liew SQ, Chin NL, Yusof YA. Extraction and Characterization of Pectin from Passion Fruit Peels, Agriculture and Agricultural Science Procedia. 2014;2:231-236.

[4]. Craciunescu O, Gaspar A, Trif M, Moisei M, Oancea A, Moldovan L. Preparation and Characterization of a Collagen-Liposome-Chondroitin Sulfate Matrix with Potential Application for Inflammatory Disorders Treatment, Journal of Nanomaterials. 2014. Article ID 903691. 9 pages.

SELECTED PEPTIDES FROM BOVINE COLOSTRUM FERMENTED WITH KEFIR GRAINS EXHIBITED ENHANCED BIOACTIVITY *IN VITRO*

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Keywords: colostrum; biopeptides; antioxidant activity; antihypertensive; cytotoxicity

Introduction: Kefir grains represent a consortium of lactic acid bacteria and yeasts associated in symbiosis on complex of polysaccharides and proteins matrix, and are usually used for milk/colostrum fermentation [1]. Still, the extent of milk proteins hydrolysis and the differences from milk bioactive peptides are not clearly defined. The aim of this study was to analyze the bioactivity of isolated peptides from samples of bovine colostrum fermented with enhanced kefir consortia, in order to identify those with application in developing new nutraceutical and cosmeceutical functional products.

Materials and methods: Colostrum powder (Axyar, Belgium), provided by Medica Laboratories, was solubilized in water, in a concentration of 10% (w/w) and sterilized at 105^0C, for 10 min. Then, colostrum was inoculated with 2.8 g artisanal Romanian kefir grain supplemented with 10^6 ufc/mL inoculum of two *Candida lipolytica* yeast strains (MIUG D99 and MIUG D67). Fermentation was conducted in stationary conditions, at 28 ^{0}C, for 96 h and 144 h, respectively. Lyophilized fermented products (C1 and C2) were extracted in water, at 4 ºC, overnight and centrifuged at 9000g. The supernatant was passed through ultrafiltration membrane YM10, in order to collect the fractions of peptides with molecular weight lower than 10 kDa (PMW<10). SDS-polyacrylamide gel electrophoresis was performed on samples of unfermented and fermented colostrum and isolated peptides. The antioxidant activity was determined by ABTS assay [2] and the antihypertensive action was evaluated as inhibitory activity of angiotensin-converting enzyme (ACE) [3]. Peptides cyto-modulatory activity was assessed in a culture of fibroblast-type cells using MTT test for cell proliferation evaluation and Live/Dead assay for cell viability observations.

Results: Used kefir grains enhanced with yeast strains for colostrum fermentation allowed to obtain a mixture of bioactive peptides. Protein identification according to molecular weight and the variation of hydrolysis degree in C1/C2 fermented samples were revealed by gel electrophoresis. Peptide fractions PMW<10 isolated by ultrafiltration exhibited antioxidant activity higher than that of unfermented and fermented colostrum (used as controls), and ACE inhibitory activity *in vitro*, which indicated their possible application in mitigating hypertension development. MTT test results revealed good proliferation of fibroblast cells after 48 h of cultivation in the presence of PMW<10 peptide fractions. Cell viability test showed high proportion of viable cells that appeared in bright green fluorescence, after 48 h of cultivation in the presence of tested peptides, similar to those in control culture.

Conclusions: The selected microorganism consortia had the capacity to release bioactive peptides during bovine colostrum fermentation. Isolated peptides PMW<10 exhibited enhanced bioactivity *in vitro*, compared to unfermented and fermented colostrum. These studies open new perspectives for optimization of colostrum fermentation biotechnology with adjuvant probiotics and selected yeasts with proteolytic activity, as well as the standardization of the fermented product in bioactive peptides content.

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References:

[1]. Mohanty DP, Mohapatra S, Misra S, Sahu PS. Milk derived bioactive peptides and their impact on human health – a review. Saudi J Biol Sci. 2016;23:577-83.

[2]. Dallas DC, Citerne F, Tian T, Silva VLM, Kalanetra KM, Frese SA, Robinson RC, Mills DA, Barile D. Peptidomic analysis reveals proteolytic activity of kefir microorganisms on bovine milk proteins. Food Chem. 2016;197:273-84.

[3]. Moldovan L, Gaspar A, Toma L, Craciunescu O, Saviuc C. Comparison of polyphenolic content and antioxidant capacity of five Romanian traditional medicinal plants. Rev Chim. 2011;62:299-303.

[4]. Ahmad I, Yanuar A, Mulia K, Mun'im A. Review of angiotensin-converting enzyme inhibitory assay: rapid method in drug discovery of herbal plants. Pharmacogn Rev. 2017;11:1-7.

GELATIN EXTRACTION FROM MARINE SNAIL *RAPANA VENOSA*: PHYSIOCHEMICAL AND BIOCOMPATIBILITY PROPERTIES

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Keywords: collagen; acid/enzymatic extraction; biocompatibility; electrophoresis

Introduction: *Rapana* spp. are abundant marine snails belonging to the *Muricidae* family with nutritional benefits and rich in proteins with unexploited potential in research applications [1,2]. This study aimed to optimize the extraction process of gelatin from *Rapana venosa* collected from Black Sea, in order to obtain valuable proteic extracts for use in the pharmaceutical/cosmetic field.

Materials and methods: We have used acid and enzymatic methods for gelatin extraction from eviscerated snail mass. The obtained extracts were analysed in terms of total protein and collagen content by biuret and Sircol methods [3]. The molecular weight profile was investigated by SDS-polyacrylamide gel electrophoresis. In addition, *in vitro* biocompatibility studies were conducted on mouse fibroblast cell line NCTC clone L929 using the MTT assay and cell morphology observations [4].

Results: We obtained a higher yield of gelatin using acid hydrolysis (with acetic acid) rather than enzymatic treatment (pepsin in acetic acid). The acid soluble extract of gelatin exhibited higher collagen content compared to the enzymatic extract, whereas the protein content was significantly higher for the enzymatic extract. Electrophoretic profile of gelatin extract obtained in acidic conditions was similar to that of commercial porcine gelatin, used as standard. Instead, enzymatic extract presented a high degree of hydrolysis and peptides with molecular weight below 36 kDa. *In vitro* studies showed no cytotoxic effect of acid extract of gelatin within the concentration range of 500 μg/ml – 5 mg/ml after 72 h of cell exposure, whereas the pepsin extract exhibited a lower biocompatibility, with values of cell viability above 80 % (non-cytotoxic) up to the concentration of 500 μg/ml. Furthermore, the quantitative results obtained by the MTT assay correlated well with cell morphology observations based on optical microscopy.

Conclusions: Gelatin extract from marine snail obtained by acid hydrolysis method had a high content in collagen and a molecular weight similar to that of commercial gelatin. Its *in vitro* biocompatibility was high and allowed fibroblast cells proliferation, as supported by both quantitative and qualitative assays. Our results are promising, suggesting the potential use of marine gelatin in pharmaceutical and skin care products.

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References:

[1]. Luo F, Xing R, Wang X, Peng Q, Pengcheng L . Proximate composition, amino acid and fatty acid profiles of marine snail *Rapana venosa* meat, visceral mass and operculum. J Sci Food Agric. 2017;97:5361–8.

[2]. Badiu DL, Luque R, Dumitrescu E, Craciun A, Dinca D. Amino acids from *Mytilus galloprovincialis* (L.) and *Rapana venosa* molluscs accelerate skin wounds healing via enhancement of dermal and epidermal neoformation. Protein J. 2010;29:81-92.

[3]. Zhou P, Regenstein JM. Determination of total protein content in gelatin solutions with the Lowry or biuret assay. J Food Sci. 2006;71:C474-79.

[4]. Craciunescu O, Gaspar A, Trif M, Moisei M, Oancea A, Moldovan L, Zarnescu O. Preparation and characterization of a collagen-liposome-chondroitin sulfate matrix with potential application for inflammatory disorders treatment. J Nanomater. 2014;ID903691.

CHEMICAL COMPOSITION AND ANTIOXIDANT ACTIVITY OF *TAMARILLO* AND *CARAMBOLA* EXOTIC FRUITS

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Keywords: anthocyanins; phenolic content; antioxidant capacity; fruits; nutritional value

Introduction: Fruits intake has a major effect upon human health, due to their complex chemical composition. It is well known that exotic fruits have become popular among Romanian consumers and are widely used for their nutritional value. Tamarillo (*Solanum betaceum* Cav.) and carambola (*Averrhoa carambola* L.) are two exotic fruits native to South America and China/India respectively. They are an important source of anthocyanins, carotenoids, vitamin C, minerals (magnesium, calcium, selenium, zinc), condensed tannins, saponins, polysaccharides and fatty acids [1-3]. Both fruits have shown anti-inflammatory, antioxidant, prebiotic, hypoglycaemic, hypocholesterolemic and antimicrobial properties [4, 5]. **The aim** of our work was the phytochemical screening and evaluation of antioxidant activity of Tamarillo and Carambola fruits sold in Romanian supermarkets.

Materials and methods: Fruits were purchased from a local supermarket (Bucharest) in October 2016. For phytochemical screening, qualitative (specific chemical reactions) and quantitative assays have been used. Specific chemical reactions were performed using different extraction solvents (diethyl ether, methanol and water). Total phenolic (expressed as tannic acid equivalents) and anthocyanins (expressed as cyanidin chloride equivalents) contents was determined by means of spectrophotometric methods. Antioxidant capacity was evaluated using ABTS (2,2'-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid) and ferric reducing power assays. The antioxidant activity was expressed as ascorbic acid equivalents.

Results: Qualitative analysis revealed the presence of carotenoids, polysaccharides, phenolcarboxylic acids, tannins and flavones (for both fruits), sterols, anthocyanins, saponins (for tamarillo fruits). Regarding fresh squeezed juices, tamarillo had a higher phenolic content (0,1 g/100 mL fresh juice) compared to carambola (0,09 g/100 mL fresh juice). Moreover, tamarillo juice had a modest anthocyanins content (4,5 mg/100 mL fresh juice). The highest antioxidant capacity was found for tamarillo fresh juice (69,30 mg ascorbic acid/100 mL freh juice – ferric reducing power assay and 2118 mg ascorbic acid/100 mL fresh juice – ABTS assay).

Conclusions: Analysed fruits are a source of natural compounds with antioxidant activity and can be used as an adjuvant for diseases in which oxidative stress is a key factor.

References:

[1]. Osorio C, Hurtado N, David C, Hofmann T, Heredia-Mira FJ, Morales AL. Chemical Characterisation of anthocians in tamarillo (Solanum betaceum Cav.) and Andes berry (Rubus glaucus Benth.) fruits. Food chemistry. 2012;132:1915-1921.

[2]. Wei SH, Chen H, Yan T, Lin YM, Zhou HC. Identification of antioxidant components and fatty acid profiles of the leaves and fruits from Averrhoa carambola. LWT Food Science and Technology. 2014;55:278-285.

[3]. Zainudin MAM, Hamid AA, Anwar F, Osman A, Saari N. Variation of bioactive compounds and antioxidant activity of Carambola (Averrhoa carambola L.) fruit at different ripening stages. Scientia Horticulturae. 2014;172:325-331.

[4]. Nascimento EG, Corso RC, Werner PFM, Baggio HC, Iacomini M, Cordeiro MCL. Structure of an arabinogalactan from the edible tropical fruit tamarillo (Solanum betaceum0 and its antinociceeptive activity. Carbohydrate Polymers. 2015;116:300-306.

[5]. Thomas R, Jebin N, Saha R, Sarma DK. Antioxidant and antimicrobial effects of Kordoi (Averrhoa carambola) fruit juice and bamboo (Bambusa polymorpha) shoot extract in pork nuggets. Food Chemistry. 2016;190:41-49.

PRELIMINARY RESEARCH ON FORMULATION OF A PHYTOPREPARATION WITH ANTIOXIDANT AND HEPATOPROTECTIVE EFFECTS

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Keywords: hepatoprotective; natural compounds; antioxidant; fatty liver; hepatoregenerative

Introduction: Hepatopathy is a real health problem, non-alcoholic fatty liver disease becoming the most common liver disease. It is expected that non-alcoholic liver steatosis will be the most important cause of liver transplant in the near future [1]. Starting from all these aspects, the purpose of the present work is the development of a database, but also the phytochemical analysis of some vegetal raw materials with hepatoprotective, hepatoregenerative and antiradical effects, quoted by the literature [3], [4].

Materials and methods: For this study we used *Carduui mariani fructus*, *Cynarae folium*, *Cichorii herba*, *Schizandrae chinensis fructus*, purchased from the pharmaceutical market in 2017. Pharmacognostical analysis was applied in order to determine the quality of vegetal raw materials (qualitative and quantitative chemical analyses) and establish the operational extraction parameters (type of solvent, extraction time, type of extractive method) for obtaining dried vegetal extracts enriched in active compounds at the level of damaged liver cells [2].

Results: Phenolic compounds (flavones, AFCs, proanthocyanidins) were identified in all the raw materials. *Carduui mariani fructus* sample contains 59.807 mg% flavones expressed as rutoside and 0.860 g% AFCs expressed as caffeic acid, *Cynarae folium* sample contains 0.547 g% caffeic acid and 63.75 mg rutoside and *Cichorii herba* sample contains 1.086 g% caffeic acid and 57.060 mg rutoside. The determinations were made in extractive alcoholic solutions, 96^{c} and 50^{c}. In dried extracts, the concentration of active principles is variable: in *Carduui mariani* extract we have 0,327 g% flavones expressed as rutoside, in *Cynarae folium* extract 1,402 g% AFCs expressed as caffeic acid and in *Cichorii herba* extract 13,45 g % AFCs expressed as caffeic acid.

Conclusions: The selected raw materials can be used in the preparation of enriched vegetal extracts in compounds with hapatoprotective, hepatoregenerative and antihepatotoxic effects.

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References:

[1]. Begriche K, Massart J, Robin M, Borgne-Sanchez A, Fromenty B. Drug-induced toxicity on mitochondria and lipid metabolism: Mechanistic diversity and deleterious consequences for the liver, Journal of Hepatology, 2011;54(4):773–794.

[2]. Colak E, Ustuner MC, Tekin N, Colak E, Burukoglu D, Degirmenci I, Gunes HV. The hepatocurative effects of *Cynara scolymus L*. leaf extract on carbon tetrachloride-induced oxidative stress and hepatic injury in rats, Springerplus, 2016;29(5):216.

[3]. Ruan X, Shen C, Meng Q. Establishment of a methology for investigating protectants against ethanol-induced hepatotoxicity, Food and Chemical Toxicology, 2010;48(5):1145-51.

[4]. Wellington K, Jarvis B. Sylymarin: a review of its clinical proprieties in the management of hepatic disorders, Biodrugs, 2001;15(7):465-89.

ANALYSIS OF LIPIDIC FRACTION IN FLOWERS AND LEAVES OF VERBASCI SPECIOSI

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Keywords: lipidic fraction; Verbasci speciosi folium et flores

Introduction: *Verbasci speciosi flores* are used in therapy for their anti-inflammatory, expectorating, demulcent and moisturising effect given by the phytocomplex represented by iridoid glycosides , flavonoids, triterpenic saponins, polysaccharides, phytosterols and fatty acids [1,2,3]. Being given that on the species of *Verbascum* from the spontaneous flora of Romania there have not been carried out any studies with regard to the lipidic fraction and knowing cardioprotective, anti-inflammatory and hypocholesteromiant effect of the essential fatty acids, the work presents the researches carried out for this purpose.

Materials and methods: *Verbasci speciosi flores* et *folium* picked up in Ilfov County, Romania (June 2017); the lipidic fraction obtained by extraction in cyclohexane at room temperature; the method used to establish the content of fatty acids is based on the conversion of acids and triglycerides in methyl esters of fatty acids and their chromatographic analysis, gas chromatography method, FID (flame ionisation detector) detector.

Results: from the flowers of 50 g vegetal material it was obtained 0,43 g lipidic fraction, and from 30 g leaves it was obtained 0,17 g of lipidic fraction. In the lipidic fraction obtained from flowers the highest rate is represented by the linoleic acid (7,05%), followed by the oleic acid (2,65%) and the palmitic acid (2,19%); in the lipidic fraction obtained from Leaves the highest rate belongs to the alpha-linolenic acid (30,53%), followed by the palmitic acid (10,67%) and the oleic acid (6,80%).

Conclusions: the flowers and leaves of Verbasci speciosi can be used as a source of essential fatty acids with cardioprotective, anti-inflammatory, hypocholesteromiant and anti-radicallary action.

References:

[1]. Skaltsounis Al, Tsitsa-Tzardis E, Demetzos C, Harvala C. Unduloside, a new iridoid glycoside from Verbascum undulatum. J Nat Prod. 1996;59:673-675.

[2]. Seifert KH, Jahne S, Hesse M. Verbascenine, ein macrocyclische spermin alkoloid aus Verbascum. Helv Chim Acta. 1982;65:2540-2547.

[3]. Mayank A. Panchal, Krishna Murti, Vijay Lambole. Pharmacological properties of Verbascum thapsus-a review, Volume 5, Issue 2, November December 2010, article-015, ISSN 0976-044X.

[4]. Makhatova BG, Datkhayev UM, Burda NYe, Kyslychenko VS. Fatty Acids from Verbascum songaricum Herb, RJPBCS, ISSN 0975-8585, Nov-Dec. 2015, pp. 278-279.

EFFECTS OF $CdSO_4$, Na_2SeO_3, AND SELENIUM POLYOXOMETALATES ON THE GROWTH OF *BRASSICA NAPUS* L.

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Keywords: plants; Cadmium; Selenium; polyoxometalates; toxicity

Introduction: Cadmium (Cd) presents high toxicity to humans, animals and plants, being harmful to living cells at very low concentrations. In plants it stunts development by diminishing water and nutrient uptake and reducing photosynthesis [1]. Cd also causes visible symptoms such as browning of roots, chlorosis and growth inhibition [2]. Selenium (Se) is an essential element for animals and humans, being included in selenoproteins (oxidoreductases, redox signals regulators or for thyroid hormone activation), but it has a very narrow dose window between beneficial effects and toxicity. In plants, Se is not considered an essential element, but it was found to have a protective role, by increasing the defense capacity against Cd induced oxidative-stress [3]. The aim of this study was to test the effects of Cd and Se on the growth and fresh weight of *Brassica napus* L.

Materials and methods: The *Brassica napus* seeds var. PT264 (S.O.C France) were grown in an Economic Lux climate chamber with Imago 500 controller (Model ECD01E, Snijders Labs, Tilburg, The Netherlands). *Brassica napus L.* seeds were sterilized with ethanol and sodium perchlorate and subjected to cold stratification at 4°C until the next day. The seeds were transferred into Berzelius beakers and placed on Knopp medium including 0.4 % agar, pH 6.0 (control) and on Knopp media with different concentrations of $CdSO_4$, Na_2SeO_3 and/or a new polyoxoselenium molibdate ($K_{3,3}(NH_4)_{0,7}\cdot[Se_2Mo_5O_{21}]\cdot 2H_2O$) compound. Two concentrations of $CdSO_4$ (50 µM and 100 µM) were tested for their toxicity. Two concentrations for Na_2SeO_3 (2 µM and 5 µM) and polyoxometalates (1 µM and 2.5 µM) were tested, as well as combinations of cadmium and selenium salts. The beakers were covered with aluminium foil. The fresh weight and length of plants were measured after 2 weeks cultivation in the climate chamber at 24°C day and 20°C night, with photoperiod 10000 Lux (135 $\mu mol\cdot m^{-2}\cdot s^{-1}$) 16 h day and 8 h night, with a relative humidity (RH) of ≈ 55% during day and ≈ 80% during night.

Results: The Selenium treated plants (2 µM Na_2SeO_3, 1 and 2,5 µM polyoxometalates) showed slightly better development of the upper parts, with fully grown cotyledons, and one or two true–leaves, along with a properly branched out root system while higher concentration of sodium selenite (5 µM) was toxic to plants. Cadmium salts were toxic to plants at all concentrations, the effects being easily observed, such as a lack of roots or lack of branches and poorly developed upper parts. Cadmium toxicity was partially inhibited by Selenium, plants showing better development (weight and length) than those grown in the presence of only cadmium salts, but the effects were highly dependent on both Cd and Se concentrations.

Conclusions: Our results indicate that there is a thin equilibrium between the concentration/dose and the effects of Cd and Se compounds. Depending on both Cd and Se concentrations, the effects seem to be either antagonistic or synergic. More studies are needed in order to get an in depth understanding of the conditions and parameters necessary for alleviating the Cd toxicity using Se. The effect of molibdenum (Mo) will be also tested in further studies.

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References:

[1]. Krupa Z, Oquist G, Huner NPA. The effect of cadmium on photosynthesis of *Phaseolus vulgaris* – a fluorescence analysis. Physiol Plant. 1993;88:626–30.

[2]. Kahle H. Response of roots of trees to heavy metals. Environ Exp Bot. 1993;33:99–119.

[3]. Sharma P, Dubey RS. Involvement of oxidative stress and role of antioxidative defense system in growing rice seedlings exposed to toxic levels of aluminium. Plant Cell Rep. 2007; 26:2027–2038.

SIMULTANEOUS SPECTROMETRIC DETERMINATION OF NARINGIN AND NARINGENIN IN CITRUS JUICE

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Keywords: naringin; naringenin; absorbencies additivity; derivative spectrometry; citrus juice

Introduction: Naringin (NG) (4,5,7-trihydroxyflavanone-7-rhamnoglucoside) and its aglycone and enzymatic hydrolysis product, naringenin (NGN), are flavonoids commonly present in citrus fruits, especially grapefruit, NG being responsible for its bitter taste, whereas NGN is almost tasteless. These flavonoids exhibit, among others, anti-ulcer, anti-inflammatory and antioxidant effects having thus protective action against some degenerative diseases [1]. Due to the similarity of these compounds structures only chromatographic techniques are able to detect the individual components from a mixture [2]. Based on the observation that, at certain pH-values, NG and NGN show quite well separated UV absorbtion maxima, the present work describes the simultaneous quantitative determination of NG and NGN from sintetic mixtures and citrus juices using both the absorbencies additivity and the zero crossing methods in the second order derivative spectrometry.

Materials and methods: NG and NGN working solutions were obtained by succesive dilution with Britton-Robinson buffer of the daily prepared ethanolic 10^{-3} M stock solutions. Molecular absorption spectra were recorded using an ultraviolet-visible (UV-VIS) spectrometer (V-530 Jasco-Japan) connected to a PC running the Spectra Manager software. All measurements were carried out in 1.00 cm quartz cuvettes.

Results: Studies on the pH influence on NG and NGN UV absorption spectra, performed in Britton Robinson buffer (BRB), revealed that at pH 9.15 the UV absorption maxima of the two analytes are well-separated, (λ_{NGN} = 322.5 nm and λ_{NG} = 282.5 nm). Starting from this observation, both the absorbencies additivity and the zero crossing methods for the second order derivative spectra were applied on different synthetic NG and NGN mixtures (equimolar and mixtures with different NG and NGN concentrations in the range 2×10^{-6} M to 6×10^{-5} M of each component) in BRB pH 9.15, in order to quantitatively determine each component of the mixture. The recoveries obtained by the zero-crossing method varied between 99.96 and 117.59 % for NG and 107.31 and 115.85 % for NGN, being higher in the situation were NG was kept constant and NGN concentration was more than 3 times higher. Similar results were obtained using the absorbencies additivity method. The NG content (g/L) of white grapefruit, pink grapefruit, orange and lemon juice was found to be 0.296, 0.2893, 0.1067 and0.076, respectively. The NGN content (g/L) of white grapefruit, pink grapefruit, lemon and orange juice was found to be 0.049, 0.038, 0.0186and 0.0187, respectively.

Conclusions: According to our results, obtained by the zero-crossing method, NGN interferes in NG determination if its concentration is three times higher. Nevertheless this is not a very big problem due to the fact that most citrus juices have higher contents of NG than NGN and in this situation the interferences are small. Thus, the developed method was used to estimate the NG and NGN content in freshly pressed white and pink grapefruit, orange and lemon juices as well as in commercially available grapefruit juice.

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References:

[1]. Bacanli M, Basaran AA, Basaran N. The antioxidant and antigenotoxic properties of citrus phenolics limonene and naringin. Food Chem Technol. 2015;81:160-170.

[2]. Ribeiro AI, Ribeiro HLM, Naringin and naringenin determination and control in grapefruit juice by a validated HPLC method. Food Control. 2008;19:432-8.

DETERMINATION OF TOMATOES PHENOLIC COMPOUNDS ANTIOXIDANT ACTIVITY BY A SIMPLE VOLTAMMETRIC METHOD

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Keywords: antioxidant activity; voltammetry; trolox; blended tomato samples

Introduction: Antioxidant species are synthetic or natural substances, which in the recent decades have attracted a considerable interest because of their broad pharmacological activity, anti-aging properties and their use in various healthy products. The consumption of plant-foods, which are natural antioxidant sources, is associated with reduced risk of chronic diseases related to the oxidative stress (cancer, cardiolovascular, neurodegenerative, inflammatory illnesses) [1]. Tomato, one of the most consumed fresh and processed vegetables, contains a huge number of compounds (like lycopene; phenolic species; flavonoids; vitamins A, C and E) mainly responsible for its antioxidative properties [2,3]. This work reports a simple and sensitive voltammetric method for evaluation of blended fresh tomato antioxidant activity.

Materials and methods: All the reagents used were of analytical grade and all solutions were prepared in bidistilled water. A Trolox (*TX*) stock solution of 10^{-2} M in 50% ethanol was employed as reference antioxidant and an acetate buffer solution (pH=3.5) as supporting electrolyte. The voltammetric experiments were performed at room temperature using an AUTOLAB PGSTAT12 and an electrochemical cell with three electrodes: glassy-carbon working (GCE), a Pt wire counter and an Ag/AgCl (3 M KCl) reference electrode, respectively. Two replicates of blended tomatoes (*BT*) were obtained from commercial Romanian fresh fruits using a domestic blender. The obtained puree was diluted with 80 % ethanol in 1% HCl solution, mixed vigorously, filtered and then a certain volume of filtrate was added to acetate buffer solution and analyzed.

Results: In order to obtain the best results for voltammetric determination of *TX* (antioxidant, soluble substitute of vitamin E), the influence of some important experimental parameters on GCE response was investigated, such as working electrode activation and its behavior towards *TX*; buffer solution pH and composition; potential sweep rate. Under the optimized working conditions, the performances of the proposed voltammetric method were: linear calibration curve in the concentration range of 0.4 – 45 μM *TX*; detection limit of 0.17×10^{-7} M; a good precision, RSD ~ 4.7 % (n=10). The estimation of *BT* antioxidant activity was carried out by the evaluation of the differential pulse voltammetry signals registered for certain volumes of processed puree both as such and after adding known concentration of *TX* and the final results were expressed as *mg TX echivalent / 100 g BT*.

Conclusions: This electrochemical method is simple, sensitive, rapid, reliable to determine the antioxidant activity of fresh fruit or vegetabels as *TX equivalent* and can be considered an alternative to the conventional methods that usually are time and reagent consuming.

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References:

[1]. Garcia-Alonso FJ, Navaro-Gonzales I, Ros G, Periago MJ. Assesments of antioxidant properties of tomato extracts: A synergistic approach using in vitro chemical tests and cell-based assays. Acta Aliment. 2015;44:297–3.

[2]. Galhardo-Borguini R, Markowicz Bastos DH, Machado Moita-Nato J, Sobral Capasso F, Ferraz sa Silva Torres EA. Antioxidant potential of tomatoes cultivated in organic and conventional systems. Braz. Arch. Biol. Technol. 2013;56:521–9.

[3]. Domenech-Carbo A, Gavara R, Hernandez-Munoz P, Dominguez I. Contact probe voltammetry for in situ monitoring of the reactivity of phenolic tomato (*Solanum Lycopersicum* L.) compounds with ROS. Talanta. 2015;144:1207–5.

GREEN ACETALIZATION OF GLYCEROL WITH FORMALDEHYDE OVER HIGHLY EFFICIENT SUPPORTED TUNGSTOPHOSPHOROUS ACID

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Keywords: glycerol acetalization; glycerol formal; phosphotungstic acid

Introduction: Glycerol acetals and ketals are extensively used as additives, bases, scents, and flavors in several industries [1]. Glycerol formal properties, recommend it as a potential substitute for most organic solvents used on an industrial scale, such as methyl-isobutyl ketone, cyclohexanone, terpenes and butyl-diglycol ether. Glycerol formal is a mixture of 4-hydroxymethyl-1,3-dioxolane (5-membered cyclic ketal) and 5-hydroxy-1,3-dioxane (6-membered cyclic ketal) and the main methods used at industrial level are based on glycerol condensation with formaldehyde in the presence of acid catalyst [2]. Heteropolyacids (HPAs) are highly active heterogeneous catalysts in acid type reactions and to overcome disadvantages such as low thermal stability and surface area or separation problem from reaction mixtures and solubility, great variety of supports have been used as support to immobilize HPAs [3-4]. The main objective of this research is to study the catalytic properties of tungstophosphorous acid (PW) supported on mesoporous silicas (HMS and MCM41) in the solventless condensation reaction of glycerol with formaldehyde.

Materials and methods: Glycerol was converted to glycerol formal through a solventless acetalization reaction with formaldehyde catalyzed by tungstophosphorous acid (PW) supported on two type of mesoporous silica MCM41 and HMS. The general drawback of glycerol acetals synthesis is the formation of water in the process that favores the occurrence of the reverse reaction and also weakens the acid strength of the catalysts. In our work p-formaldehyde has been choosen as a formaldehyde source to avoid using more water in the system.

The catalyst supports were obtained by conventional hydrothermal synthesis and the catalysts were prepared by impregnation of the mesoporous silica supports, in the form of calcinated powder, with a solution of tungstophosphorous acid. The catalysts were characterized by determining their textural properties and total acidity and by SEM, Raman and XRD techniques. They were tested in the reaction of glycerol with p-formaldehyde in a batch reactor.

Results: Under the reaction conditions molar ratio glycerol:formaldehyde of 1:1, reaction temperature of 120°C, reaction time of 3 h and catalyst amount of 2%, glycerol formal yield was over 99% on 30%PW/HMS and 40%PW/HMS catalysts.

Conclusions: Mesoporous silica supported tungstophosphoric acid has good prospects for the synthesis of glycerol formal. Using p-formaldehyde as a source of formaldehyde, avoided the additional introduction of the water in the system.

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References:

[1]. Mallesham B, Sudarsanam P, Rajua G, Reddy BM. Design of highly efficient Mo and W-promoted SnO2 solid acids for heterogeneous catalysis: acetalization of bio-glycerol, Green Chem. 2013;15(2):478.
[2]. Trifoi AR, AgachI PŞ, Pap T. Glycerol acetals and ketals as possible diesel additives. A review of their synthesis protocols. Renew. Sust. Energ. Rev. 2016:62;804-814.
[3]. Garcia JI, Garcia-Marin H, Pires E. Glycerol based solvents: synthesis, properties and applications. Green Chem. 2014;16(3):1007-1033.

CHARACTERISATION OF SOME INNOVATIVE BIOPRODUCTS WITH LARGE ADDED VALUE RESULTED FROM THE SIDE FLOWS OF THE AGRO-FOOD INDUSTRY

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Keywords: resveratrol; chinchonine; grape seed oil; extraction and separation

Introduction: The main objective of this work was the extraction and purification of biologically active compounds from materials resulted from the lateral flows of agro-food and bio-pharmaceuticals industry and is part of the EU strategy for a bioeconomy for Europe in the direction of the bioconversion of high added value by-products and the efficient and sustainable use of bioresources. Resveratrol, cinchonine and grape seed oil from waste resulting from wine production were extracted. Resveratrol can be used in cardiovascular diseases, carcinogens, diabetic diseases. It can be extracted from the red grapes from the resulting by-product to their squeezing, from the skin of the grapes and even from the seeds. The cinchonin alkaloids can be extracted from the quinine by-product of the quinine tree bark and can be used in the cardiovascular disease drug industry, in organic synthesis for the separation of optically active enantiomers and for the separation of markers in oncology. Grape seed oil is a powerful antioxidant, emollient and nutritious, has antibacterial and regenerative effect.

Materials and methods: The raw material used to obtain resveratrol is the grape waste resulting from its vinification. This is the pressing cake from the wine - the vineyard or the boas - consisting of the grains of the grapes, their trunks, which remain after the deciphering of the grapes or the clumps of bunches, respectively of the grapes. The raw materials involved in the fabrication process are: vegetal material - marc, demineralized water, denatured ethyl alcohol, acid for pH correction, hydrochloric acid, sulfuric acid, ethyl acetate, active charcoal, sodium bicarbonate, tonsil, chitosan, acetic acid. The enzymatic extraction method was used. We present the comparison between enzimatic and non-enzimatic extraction of active substances from the marc, determined by HPLC spectra.

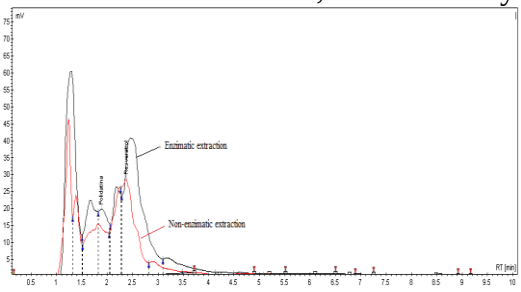

Figure 1. HPLC spectra of the enzymatic and non-enzymatic extraction

Results: The optimal ratio between resveratrol and ethanol is 0.063; the optimal desolubilization temperature is 10 ° C; the ratio of V_{total}/ V_{etanol} is 50; ethyl acetate behaves similarly to ethanol. After reflux, however, no difference was observed between the enzyme treated sample and the non-enzymatic treatment. The introduction of the cellulase enzyme in the hydrolysis step to replace the initial hydrochloric acid resulted in an enzymatic hydrolysis yield of 40% higher after 72 hours of treatment at a temperature of 45-50 ° C (pH = 5).

Conclusions: In conclusion, the use of the cellulose enzyme in the hydrolysis step can successfully replace the hydrochloric acid.

***Acknowledgements**: Competitiveness Operational Program, Project 127/23.09.2016.*

References:

[1]. Cai Y. Studies on extracting of resveratrol and its biological activities, Bejing. Master degree thesis of Beijing University of Chemical Technology. 2010.
[2]. Yang J. Development status and suggestions of peanut industry in China. Food Nutr. China. 2009;1:17–19.
[3]. Ma D. Studies on the Extraction and Separation technology of Emodin and Resveratrol from Polygonum Cuspidatum. Tianjin. Master degree thesis of Tianjin University. 2006.
[4]. Cao Y. Studies on the extraction and purification of resveratrol from Polygonum Cuspidatum, Changsha. Master degree thesis of Hunan Agricultural University. 2001.

RESEARCH ON VARIOUS SOURCES OF WILLOW BARK IN ORDER TO OBTAIN PLANT EXTRACTS RICH IN SALICYLIC DERIVATIVES

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Keywords: salicin; willow; rosmarin; oregano

Introduction: Salicin is a natural compound found in the bark of some trees, among which the best known source is willow (*Salix alba).* Over time, it has been shown that salicilin - a compound belonging to the class of glycosides - is a precursor of acetylsalicylic acid (aspirin), which diminishes the production of prostaglandins and thromboxanes due to its anti-inflammatory, analgesic and antipyretic effects[1]. Unlike synthetic analogues, natural salicylates do not have side effects and are very well tolerated by the body. The authors have researched several types of willow bark (depending on their age, age, season), selecting the richest source of salicylic derivatives. It has been used in combination with other plant extracts in a phyto-therapeutic product for external use that intervenes locally in reducing the inflammatory process, muscle contraction and pain [2].

Materials and methods: Willow bark (*Salix alba*) represents the main source of salicin and other salicylic derivatives (salicortin, 2'-O-acetylsalicortin and tremulacin), compounds that have a similar structure to aspirin (acetylsalicylic acid). In order to select the willow bark with high content of salicylic derivatives we studied several samples of willow bark from different geographical areas of the country, young (2-3years old) and mature, harvested in the spring and summer seasons. (Figure 1).

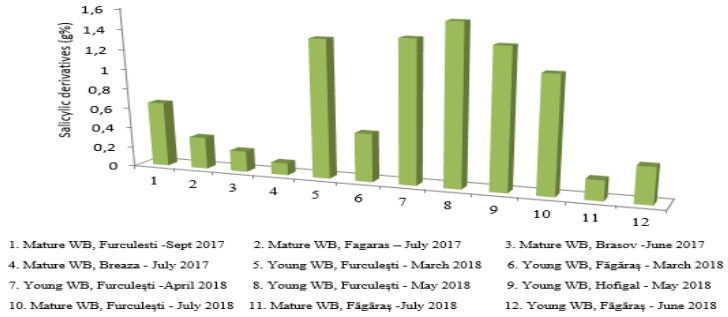

Figure 1. Variation in the percentage content of salicylic derivatives, in different samples of white willow bark

Results: From the presented data, it is observed that the best corresponding vegetal material is young willow bark (2-3 years old), from the southern part of the country (Furculești -Teleorman) harvested in the spring, with a minimum of 1.58% salicylic derivatives.

Using willow bark with high content of salicylic derivatives (Fig.1) in combination with aerial parts of rosmarin and oregano led to the obtaining of an active phytocomplex in the form of an improved concentrated liquid extract with a minimum of 1.35% salicylic derivatives.

Conclusions: Therefore we created a new product called SALICILOL GEL, using this active phytocomplex with anti-inflammatory and analgesic action which was tested in the "Alexandra" Breaza Natural Therapy Complex, with outstanding results for relieving the discomfort of the joints, muscles and skin, with anti-inflammatory effects, stimulating peripheral circulation and alleviating rheumatic and muscular pain.

References:

[1]. Dannhardt G, Kiefer W. Cyclooxygenase inhibitors - current status and future prospects. Eur J Med Chem. 2001;36(2):109-26.

[2]. European Medicines Agency. Assessment Report on Salicis Cortex (Willow Bark) and Herbal Preparation(S) thereof with Well-Established Use and Traditional Use. Doc. Ref.: EMEA/HMPC/295337/2007. 26 September 2009.

RECOVERY OF SILYMARIN FROM THE BY-PRODUCT RESULTED IN PROCESSING OF MILK THISTLE OIL BY COLD-PRESSING

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Keywords: Milk thistle; silymarin; recovery; by-products

Introduction: Milk thistle (*Silybum marianum* (L.) Gaertneri) fruits are used in alternative and conventional medicine, largely for treatment of liver disorders. The main active component of this plant fruits is silymarin, a mixture of lignano-flavonoids including: silychristin, silydianin, silybin A, silybin B, isosilybin A and isosilybin B. From milk thistle fruits it is obtained a precious oil by cold-pressing and a by-product reach in silymarin (1.5 - 4.0 %). The aim of this work was to develop a method for recovery of silymarin from the by-product resulted from processing of milk thistle oil by cold-pressing of fruits.

Materials and methods: For the study of the extraction of silymarin from the by-product it were used different extraction methods: maceration, Soxhlet, accelerated extraction based on the use of cavitation phenomena (ultrasound or microwave assisted) and different solvents: ethanol, methanol, ethyl acetate, acetone, water and mixture of them. It was performed the study of the temperature influence on the extraction. The main extraction conditions were studied. Silymarin content of the by-product, of the extracts and of the obtained silymarin concentrates were evaluated by different HPLC methods. The obtained extracts and silymarin concentrates were characterized also in terms of total phenols and antioxidant capacity.

Results: It was settled an extraction technology for the extraction of silymarin from by-product based on the use of non-flammable solvent (or with reduced flammability) and mild working conditions, as technology agreed by trader. Good results were obtained by extraction of silymarin from the by-product with ethanol 85%.

Conclusions: The by product resulted by cold-pressing the Milk thistle fruits has an important content of silymarin and others antioxidant phenolic compounds and can be used with good results for recovery of silymarin with an yield greater than 80%. It was obtained a concentrate of silymarin with a content higher than 60%. The obtained silymarin concentrate will be used by HOFIGAL in phyto-drugs formulation and food supplements.

Acknowledgements: *Financial support from the UEFISCDI, PN-III-P2-2.1.-BG 2016-0119, project no 13BG/2016 is gratefully acknowledged.*

MUSTARD TOTAL EXTRACT CONVERSION INTO BIOACTIVE PRODUCTS FOR CONSERVATIVE ORGANIC FARMING

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Keywords: mustard oil; bioassisted Soxhlet extraction; bioactive product

Introduction: Mustard oil extracted in our previous experimental research from yellow Indian mustard oilseeds should be considered inedible oil due to the high content in erucic acid (35.63-39.30%) as the main fatty acid constituent. Present study evidenced the possibility of complete valorization of inedible oilseeds for agricultural biotechnology using an innovative experimental model for obtaining an original bioactive product for nutrition and protection of cultivated plants in organic conservative farming systems.

Materials and methods: Ground yellow Indian mustard seeds commercially available (Solaris), n-hexane 96%, ethanol 96%, Cellulase from *Trichoderma reesei* ATTCC 26921, Protease from *Aspergillus oryzae* (Sigma), KOH and $CuSO_4$ were used. Mustard total extract was obtained by an azeotrope solvent extraction coupled with enzyme hydrolysis posttreatment of degreased meal into a Soxhlet laboratory system operating without intermediary compounds separation and captured in a rapeseed potassium soap previously prepared in the Soxhlet bottle. Double decomposition reaction with copper sulphate was used to convert the alkaline emulsion into a mixture of bioactive compounds encapsulated in copper soaps.

Results: GS-MS evidenced that mustard total extract was rich in organic silicon phytocompounds, linoleic acid (76.44%) and proteic nitrogen (1.01%), glycerol derivatives of fatty acids (15.10%), xylopyranoside (29.64%) and proteic nitrogen (30.18%). All these bioactive compounds captured in the *in situ* neutralized extracted oil produced an emulsion, treated with copper sulphate to obtain a stable gel oleoderivate product.

Conclusions: The main advantages of the proposed bioassisted technology were: the reflux low temperature of solvent azeotropic mixture protected thermolabile phytochemicals and enzymes activity; bioactive compounds remained in the final product, alkaline emulsion being also obtained in mild conditions; hazardous solvent traces were completely removed directly from the system. The potassium and copper soap formed a stable bioactive emulsion rich in natural silicon phytocompounds with antifungal potential, nutraceutic oligosaccharides and hydrolysates with protein origin useful for biostimulation of cultivated plant growth, also to form protective films against freeze, pests and diseases. The final product could be used as a biodegradable matrix for the (micro) encapsulation of insect-fungicidal natural compounds into formulated bioproducts with agronomical applications. The experimental results obtained in this research work demonstrated that our bioassisted extractive conversion technology of oilseeds could become one of the most environmentally safe biotechnologies for obtaining vegetable oil bio-based products for nutrition and protection of plants cultivated in organic conservative agrosystems.

Acknowledgements*: This research work was sustained by PN18.22.01.01 and Converst_Si "Conversion of phytogenic silica rich food industry by-products into value added products" funded by Romanian Ministry of Research and Innovation.*

References:

[1]. Popescu M, Oancea F, Radu E, Deșliu-Avram M, Cornea CP. Bioconversion of oilseeds into bioproducts for cultivated plants nutrition and protection. Agriculture for Life, Life for Agriculture Conference Proceedings. 2018;1(1):572-578, ISSN (Online) 2601-6222, DOI: https://doi.org/10.2478/alife-2018-0090.

[2]. Popescu M, Deșliu-Avram M, Oancea F, Lupu C, Cornea CP. Bioassisted azeotropic Soxhlet extraction of mustard oilseeds. Journal of Biotechnology Supplement. 2017;256:101S.

[3]. Popescu M, Deșliu-Avram M, Radu E, Capra L, Somoghi R, Oancea F. Complete valorization of mustard oilseeds by using bioassisted Soxhlet azeotropic extraction. Proceedings of the 13th edition of PRIOCHEM International Symposium. 2017. 25-27 october, Bucharest.

[4]. Popescu M, Oancea F, Deșliu-Avram M. Vegetable oil conversion into core-shell bioproducts for stored grain protection. Scientific Bulletin Series F. Biotechnologies. 2016;20:210-213.

[5]. Popescu M, Oancea F, Deșliu-Avram M. Ecological products for stored grain protection and process for obtaining the same. Patent application A00817/2015.

ENVIRONMENTALLY FRIENDLY METHODS FOR OBTAINING PECTIN FROM APPLE POMACE

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Keywords: pectin; apple pomace; extraction methods

Introduction: The pectin is obtained industrially from apple pomace and citrus peels by conventional extraction methods with strong acids (oxalic, sulfuric, hydrochloric and nitric) which are economically and efficiently but insecurely in handling and with negative impact on the environment. The modern processes of pectin extraction, such as enzymatic, microwave, ultrasonic extraction, are expensive. In order to obtain the pectin from apple pomace, two environmentally friendly methods were used: autoclaving and extraction with organic acids.

Materials and methods: The working method involves two steps: pretreatment of the apple pomace with the purpose of neutralizing pectolytic enzymes and removing water-soluble substances and pectin extraction itself using autoclaving and extraction with organic acids. Extraction of pectin by autoclaving consists of rehydrating the pomace flour with distilled water in different ratios, homogenization and autoclaving at 121^0C for 30-60 minutes. For pectin extraction with organic acids a solution of citric acid is added to the rehydrated pomace flour, pH extraction 2-4.5 and heated to a temperature between 70^0C-95^0C for 30-90 minutes. Pectin is recovered from the supernatant by precipitation with 96% ethanol.

Results: The yield of pectin extraction by autoclaving varied between 7.41% and 16.4%. The yield of pectin obtained from apple pomace by treatment with organic acids varies between 5.8% and 14.5%. Increasing pectin yield is directly proportional to increasing time and extraction temperature. Also, extraction pH is another very important parameter influencing yield.

Conclusions: The method of pectin extraction by autoclaving was more efficient, but this process is not commercially used for extraction of pectin from apple pomace.

Acknowledgements: *This work was supported by a grant of the Romanian National Authority for Scientific Research and Innovation, CCCDI – UEFISCDI, project number PN-III-P3-3.5-EUK-2016-0015.*

NEW MODELS FOR RAPE SEEDS PELLETING

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Keywords: seed pelleting; rapeseed crops; seed germination

Introduction: Seed coating and pelleting methods has become the mainstay for many of the horticulture and crop industries worldwide. Growth and yield of any plant or crop depends on quality of seeds. From 2013, the use of the neonicotinoids in European agriculture, especially on rapeseed crops, has been banned by the European Commission. The new seed treatment technologies are focused on the hydration, coating and pelleting of the seeds. Some of these can be used to improved performance on the resistance to drought and to pests during germination of seeds and emergence of seedlings. This paper presents the innovative process to obtain new models of bioactive compositions for rape seeds pelleting, to improve the stimulation of the germination, protection against fungi and insects and conservation of the treatments.

Materials and methods: The raw material, subjected to chemical and enzymatic hydrolysis, came from waste by-products of leather and other industries. The new products were analyzed by HPLC and ICP-OES methods.

Results: The germination of the rape seeds with modified surface was studied. The experimental results and the optimal formula to modify the surface of the rape seed was evaluated.

Conclusions: The new models of bioactive compositions for rape seeds pelleting, improved the stimulation of the germination, protection against fungi and insects and conservation of the treatments. A higher concentration of gibberellic acid has been extracted and quantified from the germinated seeds treated with the new compositions in comparison with untreated seeds.

***Acknowledgements**: The authors gratefully acknowledge the financial support of the UEFISCDI, Romania, in the framework of National Partnership Program, financing contract no. 93EUK/2017.*

EXPERIMENTALS RESEARCH ON ENZYMATIC HYDROLYSIS OF BIOMASS FROM DIFFERENT VEGETABLE SOURCES

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Keywords: vegetable biomass; cellulases; enzymatic hydrolysis

Introduction: In this twenty-first century, due to excessive technology, our planet is drastically threatened by pollution by the accumulation of various wastes with harmful effects on health.
Waste is a very important aspect of sustainable development, all the more so as the reuse of all materials has become a primary objective for every society. Thus, the Waste Framework Directive 2008/98 / EC contains provisions on prevention and recycling so that by 2020 Member States recycle at least 50% of the total mass for domestic and similar waste. Romania, as a Member State, has developed at Government level a series of laws and decisions on the National Strategy and the Waste Management Plan at national, regional and county level.
As a main objective in this paper we have studied the enzymatic hydrolysis of biomass from different vegetal sources under the action of cellulases [1, 2, 3].
Materials and methods: In this twenty-first century, due to excessive technology, our planet is drastically threatened by pollution by the accumulation of various wastes with harmful effects on health.
Waste is a very important aspect of sustainable development, all the more so as the reuse of all materials has become a primary objective for every society. Thus, the Waste Framework Directive 2008/98/EC contains provisions on prevention and recycling so that by 2020 Member States recycle at least 50% of the total mass for domestic and similar waste. Romania, as a Member State, has developed at Government level a series of laws and decisions on the National Strategy and the Waste Management Plan at national, regional and county level.
As a main objective in this paper we have studied the enzymatic hydrolysis of biomass from different vegetal sources under the action of cellulases.
Results: Enzymatic hydrolysis with cellulase obtained from *Aspergillus niger* depends on the nature of the substrate, the duration of the hydrolysis, and the previous treatments. By comparison, considering that all samples were performed at the same reaction parameters, the best results on the yield of enzymatic hydrolysis were obtained with the biomass of Three Stem Breeds of 10, 35% and 11, 14% at 10 minutes and 20 minutes respectively of hydrolysis, also confirmed by the result obtained in the gravimetric determination of the total conversion. Although fan and straw samples required a longer reaction time (120 minutes), the enzymatic hydrolysis yield is lower, probably due to high lignin and cutin content involving additional treatments.
Conclusions: The obtained results demonstrate that the biomass from the studied vegetable sources has a high potential for recovery, both by infusion and by enzymatic hydrolysis, thus opening up the prospect of obtaining new useful biomaterials.

***Acknowledgements**: This work was supported by the National Authority for Scientific Research and Innovation Project PN-16190106.04.*

References:

[1]. Wilson DB. Three microbial strategies for plant cell wall degradation. Ann. N. Y. Acad. Sci. 2008;1125:289–297.
[2]. Xiao-Zhou Z, Yi-Heng PZ. Cellulases: characteristics, sources, production, and applications (131-146), Bioprocessing Technologies in Biorefinery for Sustainable Production of Fuels, Chemicals, and Polymers, First Edition. Edited by Shang - Tian Yang, Hesham A. El-Enshasy, Nuttha Thongchul. Published 2013 by John Wiley & Sons, Inc.
[3]. Berteanu E, Paraschiv M, Manole C, Zuav AL, Tcacenco L. Plant extacts with therapeuitic value, existing in the Danube-Danube Delta basin. Priorichem XIII. pp. 87. 2017. Section 2. Bio-resources and biotechnologies.

FLAVORS DETECTION IN FOODS WITH A BI-ENZYMATIC BIOSENSOR BASED ON A STABLE PB-CU FILM/ CARBON PAPER ELECTRODE

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Keywords: Prussian blue; carbon paper electrode; bienzymatic biosensor; odorants; food

Introduction: The recent studies were concentrated to identify and quantify different compounds used as flavors in the food service industry to flavor, improve, and generally increase the appeal of their products. These compounds have a major contribution to the quality of final product and their use should be ensure the consumer safety. Various analytical methods were developed to accurately quantify the volatile constituents [1, 2]. In this work, a stable and reproducible layer of Prussian blue (PB) modified with copper was electrodeposited on carbon paper electrodes for the amperometrically detection of H_2O_2 at -50 mV. Carbon fiber composite paper were used as low-cost alternative substrates for screen-printed sensor manufacturing. Carboxyl esterase (CaE) catalyses the hydrolysis of a carboxylic ester with production of alcohol that is detected with a second enzyme- alcohol oxidase (AOx). Starting from this principle, a bi-enzymatic sensor was developed and applied to the detection of several used as sweeteners in beverages (like: aspartame) and odorants in food esters (like: methyl cinnamate, methyl butyrate, ethyl cinnamate and ethyl butyrate) (Figure 1).

Materials and methods: The electrochemical measurements were performed with a galvanostat/potentiostat Autolab PGSTAT302N (Metrohm-Autolab) controlled by a PC with the software Nova 1.11. The Toray carbon paper (Alfa Aesar) was used as working electrode and a DropSens screen-printed electrode as the reference electrode and counter-electrode. The amperometric measurements were made with a 0.1 M phosphate buffer solution (PBS) pH 7.4 supplemented with 0.1 M potassium chloride.

Results: Several enzymatic ratios were tested and optimal ratio 1: 3 (AOX: CaE) was chosen. In the optimum condition, linear calibration plots between 0-1 mM of odorants concentrations were obtained (Figure 2). The reproducibility of the measurements ranged between 3.64-6.65%.

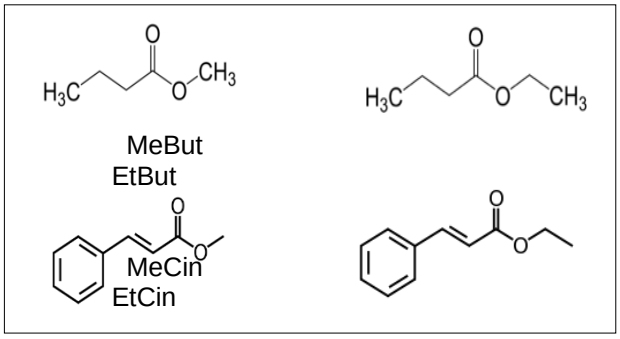

Figure 1. Chemical structure of analytes.

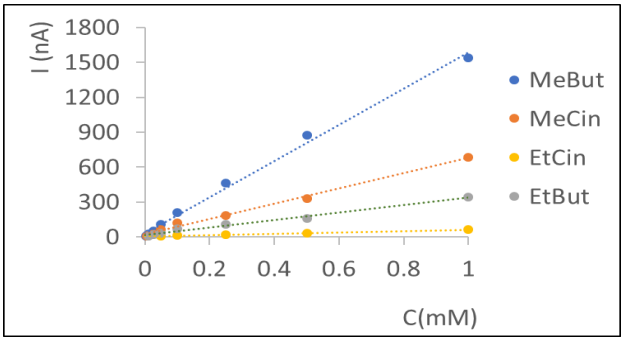

Figure 2. Calibration plots obtained with the bi-enzymatic

Conclusions: A stable PB-Cu film was electrodeposited on the carbon paper electrodes for the detection of H_2O_2 at low potentials with low interferences. Alcohol oxidase and carboxyl esterase were immobilized by cross-linking with glutaraldehyde and bovine serum albumin on the modified electrode. The resulted biosensor was successfully employed for *in vivo* measurements.

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References:

[1]. Lu Y, Huang Y, Li S, Zhang Q, Wu J, Xiong Z, Xiong L, Wan Q, Liu Q. Fast taste detection with odorant-binding proteins (OBPs) on screen-printed electrodes modified by reduced graphene oxide. Sens and Actuators B. 2017;252:973-982.

[2]. Niu Y, Yao Z, Xiao Q, Xiao Z, Ma N, Zhu J. Characterization of the key aroma compounds in different light aroma type Chinese liquours by GC-olfactory, GC-FPD, quantitative measurements, and aroma recombination. Foo Chem. 2017;233:204-215.

ENHANCEMENT OF NANOSILICA BIOSOLUBILITY BY KOMBUCHA FERMENTATION

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Keywords: Nanosilica; solubility; fermentation; Kombucha - symbiotic colony of bacteria and yeast

Introduction: Nanosilica phytolith $SiO_2.nH_2O$, resulted after orthosilicic acid polycondensation and precipitation into plant cell wall are the main source of soluble silicon species [1]. Soluble silicon species, and especially orthosilicic acid, H_4SiO_4, have been proved to exert several beneficial effects on humans, as maintenance of the optimal connective tissue function, including osteoporosis prevention, stimulation of the immune system and Alzheimer's disease prevention [2, 3].
Materials and methods: We used a liquid fermentation by a symbiotic colony of bacteria and yeast (SCOBY) to enhance biosilica solubility. SCOBY is traditionally used to produce Kombucha, an Asia traditional beverage, produced traditionally from sweetened *Camelia sinensis* leaf tea by fermentation with SCOBY. We used rice husk, horsetail and honey bee collected pollen as biomaterial rich in biosilica. We monitored the evolution of soluble silicon species by the silicomolybdic acid spectrophotometric method [4].
Results: SCOBY fermentation increase the soluble silicon significantly, by 180%, 225% and, respectively, 280% on rice husk, horsetail aerial part powder and honey bee collected pollen. The plant nanosilica solubilization was more significant after 18 days of Kombucha fermentation. Such solubilization it is probably a result of the accumulation of organic acids.
Conclusions: The fermentation of pollen with Kombucha releases important amounts of soluble silicon from nanobiosilica embedded into siliceous plant material. The resulted products represent a new source to produce dietary supplements, wherein highly available soluble silicon is combined with Kombucha phytonutrients.

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References:
[1]. Farooq MA, Dietz KJ. Silicon as versatile player in plant and human biology: overlooked and poorly understood. Frontiers in plant science. 2015;6:994.
[2]. Price CT, Koval KJ, Langford JR. Silicon: a review of its potential role in the prevention and treatment of postmenopausal osteoporosis. International journal of endocrinology. 2013. Article ID 316783. 6 pages.
[3]. Nielsen FH. Update on the possible nutritional importance of silicon. Journal of Trace Elements in Medicine and Biology, 2014;28(4):379-382.
[4]. Coradin T, Eglin D, Livage J. The silicomolybdic acid spectrophotometric method and its application to silicate/biopolymer interaction studies. Spectroscopy, 2004;18(4):567-576.

OPTIMIZATION OF THE REACTION CONDITIONS FOR THE SYNTHESIS OF NEW STRIGOLACTONE MIMIC (SL-6)

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Keywords: eco-efficiency; strigolactone mimic; optimization; Design-Expert

Introduction: We describe the optimization reaction condition for the new SL-6 strigolactone mimic. First identified and characterized as plant secondary metabolites used as cue for parasitic plants seeds[1], nowadays strigolactones (SLs) analogs and mimics are known best for their positive role on field crops, as a tool to control parasitic weed, through early stage ”suicidal” seed germination [2-5] and also for their function as exo-signal involved inti increased exogenous mycorrhizal symbiosis [6-9]. Recent research showed that SL-6 mimics SLs functions such as induced germination stimulant for parasitic weed seed in the rhizosphere of *Orobanche*, *Phelipanche* and *Striga spp.* and biological activities on plant pathogenic fungi [10]. Improving the eco-efficiency of the SL-6 production, a maximum yields percentage is required for the synthesis reaction conditions.

Materials and methods: The synthesis required reaction conditions was optimized by a design experiment, based on a surface response methodology based on the previously analyzed results [10], with several synthesis reaction conditions modified. These conditions were: K_2CO_3 and Bromo-furanone (both expressed in mmole); solvent (acetone/DMF); temperature (^oC); and the reaction time (hour). The experiments were set-up and the data were analyzed using Design-Expert® v10.0 software (Stat-Ease, Minneapolis, MN, USA).

Results: SL mimics were obtained by treating commercially available cyclic hydroxy ketones in DMF solvent, with 5-bromo-3-methyl-5H-furan-2-one, in presence of K_2CO_3. This leads to the formation of SL bearing a naphthalimide core. N-substituted phthalimide nucleus have been demonstrated to have a growth plant regulating activity [10].

The relationship between yield, reaction time and temperature are represented in figure 1. The optimal reaction conditions for the SL-6 synthesis, resulted after experimental data analysis with Design-Expert® v10.0 (Stat-Ease, Minneapolis, MN, USA), was: 3 mmole K_2CO_3, 2.6 mmole 5-bromo-3-methyl-5H-furan-2-one; DMF solvent; 50°C and 24 hours.

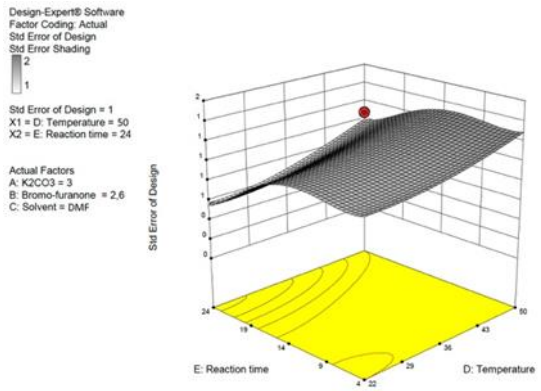

Figure 1. The relationship between SL mimics yield, reaction time and temperature

Conclusion: Optimal condition were established for the synthesis of SL-6 srigolactone mimic.

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References:

[1]. Cook CE, et al. Germination stimulants. II. Structure of strigol, a potent seed germination stimulant for witchweed (Striga lutea). Journal of the American Chemical Society. 1972;94(17):6198-6199.

[2]. Yoneyama K, et al. Strigolactones: structures and biological activities. Pest Manag Sci. 2009;65(5):467-70.

[3]. Xie X, Yoneyama K, Yoneyama K. The strigolactone story. Annu Rev Phytopathol. 2010;48:93-117.

[4]. Akiyama K, Hayashi H. Strigolactones: Chemical Signals for Fungal Symbionts and Parasitic Weeds in Plant Roots. Annals of Botany. 2006;97(6):925-931.

[5]. Matusova R, et al. The strigolactone germination stimulants of the plant-parasitic Striga and Orobanche spp. are derived from the carotenoid pathway. Plant Physiol. 2005;139(2): 920-34.

[6]. Akiyama K, Matsuzaki K, Hayashi H. Plant sesquiterpenes induce hyphal branching in arbuscular mycorrhizal fungi. Nature. 2005;435(7043):824-7.

[7]. Akiyama K, et al. Structural requirements of strigolactones for hyphal branching in AM fungi. Plant Cell Physiol. 2010;51(7):1104-17.

[8]. Bouwmeester HJ, et al. Rhizosphere communication of plants, parasitic plants and AM fungi. Trends in Plant Science. 2007;12(5):224-230.

[9]. Gomez-Roldan V, et al. Strigolactone inhibition of shoot branching. Nature. 2008;455(7210):189-94.

[10]. Oancea F, et al. New Strigolactone Mimics as Exogenous Signals for Rhizosphere Organisms. Molecules. 2017;22(6).

HEAT OF SOME PLANT SPECIES FOR BIOFUELS PRODUCTION

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Keywords: solid biofuel; pellets; heating value; ash; moisture content

Introduction: Heat is one of the most important types of energy. Combustion is responsible for over 97% of the world's bio-energy production [1]. Biomass is considered one of the main renewable energy resources of the future due to its large potential, economic viability and various social and environmental benefits [2-3].The heating systems can function on plant or other organic material, for example, wood chips, agricultural residues, etc. Using local biomass resources it is possible to reduce the pollution of atmosphere caused by greenhouse gas emissions. The aim of the research was to evaluate some plant biomass qualitative properties for production of solid fuel. By choosing suitable plants, high dry matter biomass solid fuel products can be obtained.

Materials and methods: The selected species of herbs were: thorn (xanthium spinosum), burdock (bardanae radix), thistle (silybi mariani) and eryngo (eryngium planum). Biomass samples were collect from local areas, were characterized in the form of pellets, and kept before in oven at 105°C for overnight. The heating value was determined using a Parr Instruments 6200 microprocessor controlled isoperibol oxygen bomb calorimeter.

Results: The following aspects were determined during the research: higher heating value, moisture and ash content, nitrogen, density for the selected species. It was determined and compared the heating value of the studied samples.Heating value is given in two types, as higher heating value (HHV) and as higher heating value of ash free material (HHVf). The later was calculated after substraction of ash from the weight of the HHVdetermination biomass samples. Below is presented the variation of HHV versus ash content (Figure 1) and moisture content (Figure 2). Nitrogen content varied from 0.088% to 0.56% and was the highest in thistle.Densities (Kg/m^3) varied from 0.24 to 0.76%.

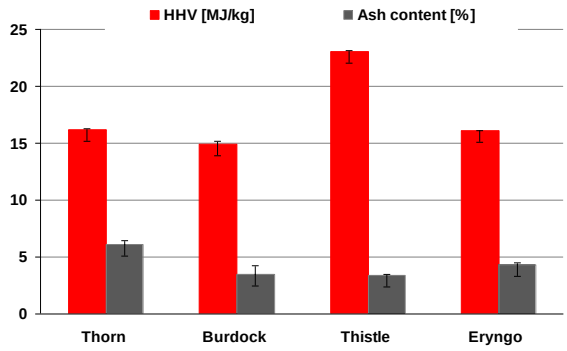

Figure 1. Variation of higher heating value (HHV, MJ/kg) versus ash (%)

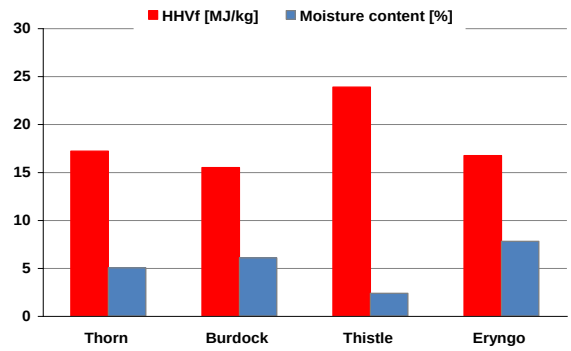

Figure 2. Variation of higher heating value (HHVf, MJ/kg) versus moisture content (%)

Conclusions: Based on the obtained results it was stated, that, from among the investigated species, Thistle (silybi mariani) is the most perspective energy crop among the tested plants, having the highest heating value of 23.87 MJ/Kg and lowest ash content (3.35%). The determined parameters indicates thistle to be a good material for domestic pellets production and other energy usages.

Acknowledgements: *This contribution was carried out within the research programme - Chemical Thermodynamics of the "Ilie Murgulescu" Institute of Physical Chemistry, financed by the Romanian Academy. Support of the EU (ERDF) and Romanian Government, that allowed for acquisition of the research infrastructure under POS-CCE O 2.2.1 project INFRANANOCHEM - Nr. 19/01.03.2009, is gratefully acknowledged.*

References:

[1]. Demirbas A. Progress in Energy and Combustion Science. 2004;30:219-230.

[2]. Demirbas A. Biomass resources for energy and chemical industry, Energy Edu Sci Technol. 2000;5:21-45.

[3]. Patel B, Gami B, Biomass Characterization and its use as solid fuel for combustion, Iranica Journal of Energy and Environment. 2012;123-128.

MICROALGAE STRAINS SELECTION FOR EFFICIENT REDUCTION OF CARBON, NITROGEN AND PHOSPHORUS FROM LIQUID DIGESTATE RESULTED FROM BIOGAS PRODUCTION

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Keywords: Anaerobic digestion; Chlorella vulgaris; Arthrospira platensis; Microalgae; Liquid digestate

Introduction: The aim of this study was to compare the growth of microalgae (growth rate, biomass concentration and lipid content) in mineral medium and in liquid digestate obtained from anaerobic digestion. Of the 9 strains of microalgae that were tested, *Chlorella vulgaris* and *Arthrospira platensis* proved to be the most suitable for this process. The possibility of growing microalgae in liquid digestate medium offers the great advantage of minimizing the costs necessary for growth of microalgae, as it is being done by consuming the nutrients (treatment) in a side-product obtained from biogas production through anaerobic digestion.

Anaerobic digestion (AD) is a biological process by which, in the absence of oxygen, organic matter is transformed into biogas, principally consisting of methane (50–80 vol.%) and carbon dioxide. Also, from the anaerobic digestion process results a biologically stable and partially hygienic organic product: the digestate that has a high mineral load, mainly nitrogen (N) and phosphorus (P). Digestate may be separated into solid (10–20% by mass) and liquid (80–90% by mass) fractions by screw press or decanter centrifuge. Solid digestate contains less water and is more stable; it can be easily transported and stored. Solid digestate can either be used as agricultural biofertiliser or be further converted to heat and/or value-added products via thermal processes. By contrast, liquid digestate processing is more difficult. The most simple treatment method is to directly spread on agricultural land, but it may cause chemical, biological or physical contamination. Also, the digestate is continuously produced and the land application is depend on the crop growth stage, soil type and time of years [1]. Study of microalgae-based digestate treatment has become a topic of much interest in the past few years. Microalgae can efficiently remove various nutrients from digestate, particularly nitrogen and phosphorus. The mineral medium necessary for microalgae growth contain manly nutrients like nitrogen and phosphorus, thus the combining of liquid digestate treatment and microalgae cultivation can reduce the growth medium cost.

Materials and methods: The experiments were made using 9 strains of microalgae from ICECHIM culture collection, inoculated each in its specific growth medium, *Scenedesmus acutus* (AICB 121) – BBM medium, *Scenedesmus acutus* (AICB 340) – BBM medium, *Chlorella sacharophyla* (AICB 396) – BBM medium, *Chlorella vulgaris* (AICB 329) – BBM medium, *Chlorella vulgaris* (AICB 311) – BBM medium, and *Arthrospira platensis* (AICB 49) – Z medium, *Arthrospira fusiformis* (AICB 606) – Z medium, *Nannochloris sp*. (AICB 424) – Z medium and *Chroococcum minutus* (AICB 1013) – BG11 medium. The liquid digestate was analized for C, N and P and diluted until a composition similar to the specific growth medium for each microalgae strain. The inoculums of the 9 strains of microalgae was added to the diluted liquid digestate and monitored for growth process. These microalgae strains have grown in the presence of different microbial phyla found in the digestate, whose community configuration changes continuously during the development of microalgae. Within these consortia the microalgal population is much better developed than the population of microorganisms.

Results: From the 9 strains of microalgae tested, 2 strains, *Chlorella Vulgaris* and *Arthrospira Platensis* were chosen for the best results obtained at cultivation on liquid digestate, as they were the most resilient ones and presented the best growth rate in this environment.

Conclusions: In this study, it was demonstrated that microalgae such as *Chlorella Vulgaris* and *Arthrospira Platensis* can efficiently remove C, N and P from liquid digestate, using these nutrients for microalgae biomass growth, showing the possibility of combining liquid digestate treatment and microalgae cultivation in order to reduce the growth medium cost.

***Acknowledgements**: This work was supported by PN III Program, PN-III-P1-1.2-PCCDI-2017; Program 1 - Development of national CD system; Subprogram 1.2 - Institutional performance, complex projects developed in CDI consortia, Contract 32PCCDI/2018.*

References:

[1]. Xia A, Murphy JD. Microalgal Cultivation in Treating Liquid Digestate from Biogas Systems. Trends in Biotechnology. 2016;34(4):264-275. http://dx.doi.org/10.1016/j.tibtech.2015.12.010.

ANIMAL KERATIN SUBSTRATES DEGRADED BY GEOPHILIC KERATINOLYTIC FUNGI

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Keywords: keratin; keratinases; keratinolytic fungi; keratin degradation

Introduction: Leather industry, one of the high polluting industries, involves many steps in the process of transformation of hide leather (putrescible) into commercial leather (non putrescible): unhairing, tanning, bating, dyeing, and degreasing. The process implies the use of large quantities of toxic chemicals such as sulfide, resulting in the accumulation of effluents with a negative impact on the environment [1, 2]. Over the past decades, there are many attempts to replace the conventional methods with biotechnological approaches, the use of specialized microorganisms and their hydrolytic enzymes representing a viable alternative [3-5]. The aim of the work was to evaluate the activity of two geophilic fungal isolates on keratin substrates, samples of animal skins.

Materials and methods: The microbial cultures were carried out in agitated flasks containing a mineral basal medium and samples of animal skins. The keratinases activity in culture supernatants was determined using keratin azure. The morphological and structural aspects were observed by light microscopy (Olympus BX51) and Scanning Electron Microscopy (SEM*)* on a FEI-QUANTA 200 microscope.

Results: The activity of fungal strains on keratin substrates determined different levels of biodegradation, depending of samples characteristics. Microscopic observations revealed hyphae network attached on hair strand or stretching between hair strands, lifting of cuticles, several broken hair strands. *Fusarium* sp. has produced more broken hair strands as compared with *Cladosporium* sp., indicating a better activity for dehairing process.

Conclusions. Furthermore, the selected *Fusarium* sp. strain will be tested for the collagenase activity in order to allow their use in leather processing.

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References:

[1]. Pradeep MR, Narasimha G. Effect of leather industry effluents on soil microbial and protease activity. J Environ Biol. 2012;33: 39-42.
[2]. Bhavan S, Rao JR, Nair BU. A potential new commercial method for processing leather to reduce environmental impact. Environ Sci Pollut Res. 2008;15: 293-295.
[3]. de Souza FR, Gutterre M. Application of enzymes in leather processing: a comparison between chemical and coenzymatic processes. Braz J Chem Eng. 2012;29: 473-481.
[4]. Dettmer A, Ayub Maaz, Gutterres M. Hide unhairing and characterization of commercial enzymes used in leather manufacture, Braz J Chem Eng. 2011;28: 373-380.
[5]. Zerdani I, Faid M, Malki A. Digestion of solid tannery wastes by strains of *Bacillus* sp. isolated from compost in Morocco, Inter J Agr Biol. 2004;6:758–761.

DIGESTION OF KERATINOUS WASTE SUBSTRATES UNDER MICROSCOPIC OBSERVATION

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Keywords: keratin; keratinolytic fungi; keratin digestion; SEM

Introduction. Keratinous wastes are solids from agro-industrial processing which accumulate and pollute the environment. New concepts of recycling and energy conserving include the valorization of keratin –rich wastes as carbon and nitrogen sources and stimulate the attempts to convert them into valuable products [1, 2]. Keratinous waste degradation by biological methods has been increasingly interested because of environmental awareness [3]. The aim of this study is to highlight the biodegradation of keratinous wastes by efficient keratinolytic fungi using Scanning Electron Microscopy (SEM) investigation.

Materials and Methods. The keratinolytic fungi were incubated with different keratin waste substrates. The morphological and structural aspects of samples before and after microbial contact were observed by SEM analysis on a FEI-QUANTA 200 microscope.

Results. The biodegradation of keratin by keratinolytic fungi occurs in two phases, surface erosion followed by radial penetration. The effect of keratinolytic activity depends on the features of fungal species tested. Relevant images of keratin digestion by keratinolytic fungi were obtained.

Conclusions. These results indicate that SEM is a very powerful tool to study, offering information on interactions between microorganism and structural elements of keratin samples. It can be conclued that the microscopic approaches have contributed to a better understanding of the biodegradative process of keratin substrates.

Acknowledgements: *This research was financially supported by ANCSI in the frame of the project PN.16.31.01.03, NUCLEU Program.*

References

[1]. Zhang H, Carrillo F, López-Mesas M, Palet C. Valorization of keratin biofibers for removing heavy metals from aqueous solutions.Textile Res J. 201;.doi.org/10.1177/0040517518764008.
[2]. Tesfaye T, Sithole B, Ramjugernath D. Valorisation of chicken feathers: recycling and recovery routes. Proceedings Sardinia 2017 Sixteenth International Waste Management and Landfill Symposium, 2 -6 October 2017, Cagliari, Italy, CISA Publisher, Italy.
[3]. Korniłłowicz-Kowalska T, Bohacz I, Biodegradation of keratin waste: Theory and practical aspects. Waste Manag. 2011;31(8):1689-701.

OIL EXTRACTION OPTIMIZATION WITH BBD FROM *NIGELLA* SEEDS

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Keywords: Nigella seeds oil; optimization; Box-Behnken Design

Introduction: *Nigella* (*N. sativa* L.) oil has primarily a high content of omega-6 (linoleic acid), then omega-9 (oleic acid) and last palmitic acid, thus constitutes a market niche especially due to its pharmacological properties [1]. The extraction of oil from *nigella* seeds, using an experimental Box-Behnken Design (BBD) in accordance with response surface methodology (RSM), was studied in order to find and establish the variables which could maximize the relative extraction efficiency [2]. The objectives of this paper is finding optimal process parameters for the solvent extraction of *nigella* oil with three variables and three levels BBD using RSM.

Materials and methods: *Nigella* seeds were purchased from R&D Station for Agriculture, Neamt district. The seeds were grinded and sieved in order to obtain particles with diameters of about 600 μm. n-Hexane (for analysis) purchased from Sigma-Aldrich was used as extraction solvent. Laboratory Soxhlet extraction with hexane was used to determine the initial *nigella* oil content. The average of the *nigella* oil content was 38% [3].

Results: All experiments were performed to determine the optimal extraction conditions corresponding to a maximum oil content extracted from *nigella* seeds. Analyzing the data obtained, the achievement of a wide range of extraction yield variation is observed in between 72.87% and 90.96%, where the minimum value obtained is for X_1 = 25°C, X_2 = 4 mL/g and X_3 = 2 hours, and the maximum for X_1 = 55°C, X_2 = 8 mL/g and X_3 = 2 hours. The second-order polynomial equation corresponding coefficients were determined by applying the multiple regression analysis using the Statistica software [4].

Conclusions: The optimum extraction yield was at: 55°C extraction temperature, 8 mL/g liquid/solid ratio and an extraction time of 2 hours. Following the experiments, a positive influence was observed on the *nigella* oil extraction at (X_1) temperature and (X_2) liquid/solid ratio. Adequacy of the regression model was evaluated using the ANOVA analysis of variance. This paper could represent a starting point in developing processes to a higher valorization of *nigella* oil.

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References:

[1]. Kooti W. Hasanzadeh-Noohi Z. Sharafi-Ahvazi N. Asadi-Samani M. Ashtary-Larky D. Phytochemistry, pharmacology, and therapeutic uses of black seed (*Nigella sativa*), Chin. J. Nat. Med. 2016;14(10):732-745.

[2]. Avram M. Stroescu M. Stoica-Guzun A. Floarea O. Optimization of the oil extraction from Camelina (*Camelina sativa*) seeds using response surface methodology. Rev. Chim. 2015;66(3):417–421.

[3]. Desliu-Avram M. Popescu M. *Nigella sativa* seed oil extraction for bioactive compounds exploration. Proceedings of the 12th edition of PRIOCHEM International Symposium. 2016, 27-28th October. Bucharest.

[4]. Avram M. PhD thesis: Modern technologies of oils extraction from vegetable materials. Bucharest. 2015.

STUDY REGARDING THE DETERMINATION OF ENDOTOXINS IN ^{18}F-RADIOPHARMACEUTICALS

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Keywords: bacterial endotoxins; radiopharmaceuticals; quality control; validation

Introduction: The aim of this work was to validate the Bacterial Endotoxin testing for ^{18}F-radiopharmaceuticals formulated in a physiological saline solution. Radiopharmaceuticals are radioactive preparations used in nuclear medicine as tracers in diagnostic imaging. The radiopharmaceuticals must be sterile and apyrogenic. The absence of bacterial endotoxins implies the absence of a pyrogenic component. Endotoxins are potentially natural compounds of the cell wall of gram negative bacteria.

Materials and methods: The bacterial endotoxin test was performed using Endosafe-PTS equipment (Charles River Laboratories, USA). Interfering factors should not be present and all the equipment used which comes in contact with the sample should be depyrogenised. Tests were carried on PTS cartridges with sensitivity of 0.05-5.0 EU/mL.

Results: Dilution of ^{18}F-radiopharmaceuticals was prepared to determine the optimal dilution to avoid the interference with the test. To validate the optimum dilution 3 batches for each radiopharmaceutical was run on the Endosafe PTS. The recommended dilution to quantify endotoxins of gram-negative bacterial origin using amoebocyte lysate from horseshoe crab is calculated from the recommenced limit and the sensitivity of the assay.

The results for the optimal dilution for ^{18}F-radiopharmaceuticals manufactured in Radiopharmaceuticals Research Centre show that 1:50 is the minimum dilution volume to carry out the test and therefore the recommended dilution volume.

Conclusions: The validated dilution for each radiopharmaceutical show results with recoveries close to 100% (acceptance criteria for spike recovery value: 50-200%). The endosafe test is fast and sensitive method for the quantitation of pyrogens in ^{18}F-radiopharmaceuticals. No inhibition of the product positive control was found in the recommended dilution range.

***Acknowledgements**: This work was supported under Research Programme Partnership in Priority Areas PNII MEN-UEFISCDI, contract PN 18 09 0203.*

References

[1]. European Pharmacopoeia, 9.0 Edition 2017. 2.6.14. Bacterial Endotoxins.
[2]. Endosafe-PTS System User's Guide Version 7 (PIPTS101-10).

REVERSE MICELLES WITH ENTRAPPED ADDITIVES ACTING AS NANOREACTORS FOR LIPASE-CATALYZED PRODUCTION OF FATTY ACIDS

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Keywords: Enzyme catalysis; Kinetic Modeling; Lipase; reverse micelles; fatty acids; olive oil

Introduction: Nowadays, the enzyme stability is an important task of research. Naturally occurring osmolytes can be used as proteins stabilizers [1]. This study is focused on the effect of trehalose, myo-inositol and phytic acid on the structural stability and activity of Candida rugosa Lipase entrapped in reverse micelles [2].

Materials and methods: The materials used were: Lipase from Candida Rugosa, sodium dioctyl sulfocuccinate, isooctane, n-buthanol, trehalose, phytic acid sodium salt hydrate phytic acid, myo-inositol, cupric acetate, pyridine and acetonitrile, extra virgin olive oil. The methods used were: DLS, surface tension, Circular dichroism spectroscopy, Static fluorescence spectroscopy, UV-Vis.

Results: Enzymatic activity was measured in the presence and absence of modulators. Modification of enzyme activity, correlated with changes in the enzyme structure, led to the conclusion that trehalose and myo-inositol improve the enzyme activity and stability, while phytic acid lowers the reaction rate through changes in the enzyme secondary structure (see Figure 1). The kinetics of the enzyme encapsulated in reverse micelles in the presence of trehalose, myo-inositol and phytic acid differ from those when none of the additives were present (see Figure 2).

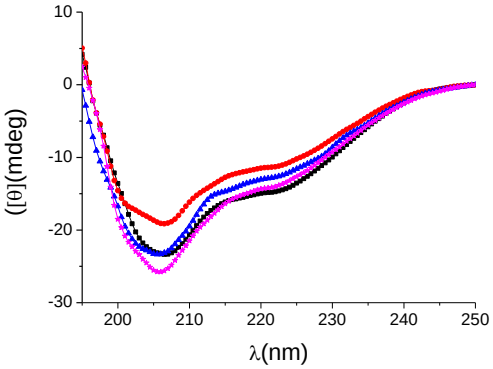

Figure 1. Circular dichroic spectra of aqueous lipase in the presence of trehalose (★) , myo-inositol (▲), water (■) and phytic acid (●)

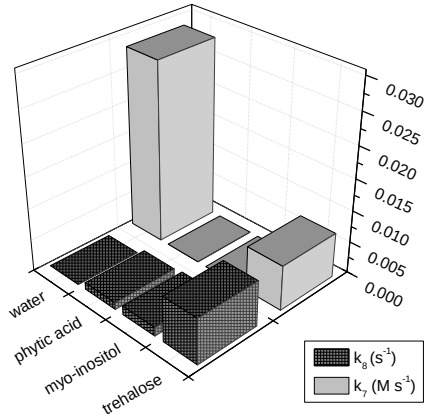

Figure 2. Inactivation constants for olive oil hydrolysis in the presence of lipase.

Conclusions: Lipase exhibits "superactivity" in reverse micelles when trehalose and myo-inositol are present and the activity is significantly lowered in the presence of phytic acid. Results of this study could give further insights about the enzyme stabilization mechanism.

References:

[1]. Koh MY, Mohd. Ghazi T. I Renewable and Sustainable Energy Reviews. 2011;15:2240-2251.
[2]. Carvalho CML, Cabral JMS. Biochimie. 2000;82:1063-1085.

SNAIL MUCUS, A NATURAL BIOMATERIAL WITH THERAPEUTIC ACTION - THEORETICAL APPROACH

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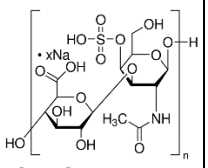
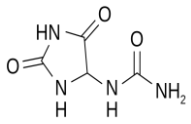
Keywords: snail mucus; mucins; mucoproteins; allantoin; antibiotic peptides

Introduction: Since ancient times, the snails were recommended in medicine and prepared under different pharmaceutical forms. Gasteropod species such as snail-Helix and slug–Arion, wich have a hydrogel-like mucus, are increasingly being exploited for cosmetic and cosmeceutical, bioengineering, medical and pharmaceuticals applications. The mucus of land sanils and slugs is produced by the foot of the gasteropod or has evolved to coat the external parts of the gasteopds body.The main constituent of gasteropod mucus is a complex of proteins and polysaccharides. Mucus is a viscous gel layer produced from goblet cells, mucus secretory cells or submucosal glands found on various mucous membranes. Mucus, an exopolymer, has a gelatinous consistency and lubricant due largely to specific proteins called mucoprotein-heavy and heavy proteins, many of which are glycoproteins and mucopolysaccharides [hyaluronic acid], such as mucin.

The mucus isolated from snails contain bioactive compounds as glycans, peptides, glycopeptides, proteins, amio acids, antimicrobial peptides, with antitumore properties and antimicrobial activities.

					
Snail -Helix	Mucus is produced by lining tissues	Muller-One equipment for mucus exaction	Chondroitin sulphate	Allantoin	Achacin enzyme

The potentials of snails mucus ad theirs components

Research confirmed that snail slime was naturally rich in vitamins, proteins and substances such as glycolic acid, allantoin, collagen and elastin - all of which are popular ingredients in cosmetics.

Mucins are the major macromolecular constituent of the mucous secretions and play a key role in the pharmaceutical industry as a drug delivery agent and as a pharmaceutical excipient if properly harnessed. They are also negatively charged. This makes mucin a good candidate for drug delivery as they can be conjugated to positively charged drug molecules and targeted to the respective tissues. Mucins are often used for modelling of mucoadhesive and bioadhesive systems.

The macromolecular antibacterial glycoprotein from edible snail could be useful as a harmless food additive to prevent bacterial growth. An antibacterial factor named achacin that acts on both Gram-negative and Gram-positive bacteria was found in the body surface mucus of the giant African snail, Achacina fulica. Achacin has been characterized as a glycoprotein, which shows a bactericidal efect against Escherichia coli and Staphylococcus aureus.

In cosmetics, snail slime, rich in proteins of high and low molecular weight hyaluronic acid and antioxidants, are supposedly has a double function when applied to human skin: on one hand it is claimed to stimulate the formation of collagen, elastin and dermal components that repair the signs of photoaging and, on the other hand, is claimed to minimize the damage generated by free radicals that are responsible for premature skin aging.

Conclusions: The snail, always keeping a part of the mystery, may have other properties useful for future medicine. The recent discoveries on this small animal show at least that they deserve the full attention of the researchers.

Acknowlegements: *This paper was developed during the master course Advanced Processing of Protein Materials IASI 2017-2019.*

References:

[1]. Bonnemain B. Helices et medicaments: l'escargot au service de la sante depuis l'Antiquite jusqu a nos jours. Revue d'Histoire de la Pharmacie. 2003;338:211-218.

[2]. Swapna P, Ravinder RT. Quantification of mucoproteins (glycoproteins) from slugs mucus, Arion Hortensis and Arion ater. Inernational Journal of Pharmaceutical Research and Bio-Science. 2015;4(2):242-250.

EVALUATION OF SOME DERIVATIVES WITH NITROBENZOFURAZAN MOIETIES

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Keywords: nitrobenzofurazan derivatives; UV-vis; fluorescence; hydrophobicity; biological properties

Introduction: Starting from 4-chloro-7-nitrobenzofurazan **1** and thiolic nucleophiles **2a** – **2e** (2-pyridinethiol-1-oxide **2a**; 2-pyridinethiol **2b**; 4-pyridinethiol **2c**; N-acetylcysteamine **2d** and N-acetylcysteine **2e**), five compounds **3a-3e** were synthesized and characterized by ^{1}H- and ^{13}C-NMR, IR, electronic absoption spectrometry, fluorescence and reverse-phase thin-layer chromatography. Some of their biological properties were evaluated.

Materials and methods: **Cell Culture**

The eukaryotic cell culture used, human ileocecal adenocarcinoma HCT-8 cells (ATCC CCL244^{TM}), were maintained as an adherent culture in Dulbecco's Modified Essential Medium (DMEM) (Sigma, USA) supplemented with 10% heat-inactivated fetal bovine serum (Sigma, USA) at 37^{0}C, 5% CO_2, in a humid atmosphere. For biological tests the tested compounds were initially dissolved into DMF to prepare concentrated stock solutions (10mg/mL). Following, additional dilutions were prepared in culture medium.

Results: The synthesis and the physisco-chemical properties of the compounds **3a-3e** have been reported by us in a previous paper [1].

For derivatives **3a** – **3e** the cytotoxic effect was tested on cell cultures. In order to determine the toxic effect of the NBD thioethers **3a** – **3e** on eukaryotic cells, we evaluated their influence on cell cycle.

The cytotoxic effect of tested compounds **3a-3e** was also evaluated at molecular level by analyzing the expression levels of some genes implicated in apoptosis (Figure 1).

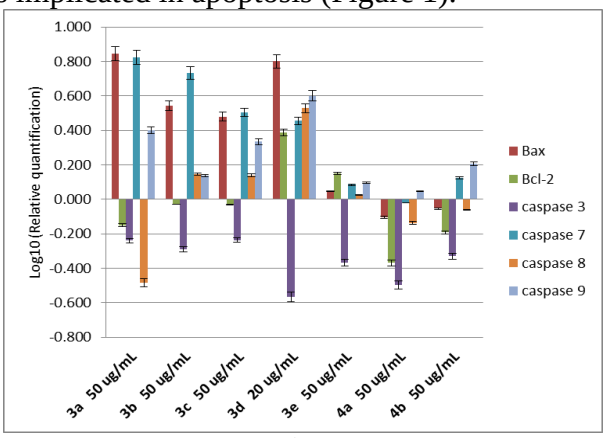

Figure 1. The influence of tested compounds on the expression of genes implicated in apoptosis induction in HCT-8 cells

Conclusions: Five thioethers **3a-3e** were synthesized from the electrophile 4-chloro-7-nitrobenzofurazan and thiolic nucleophiles by S_NAr process. The strong bathochromic shift, irrespective of the solvent, was observed in the case of compound **3e** while, for the compounds **3a** – **3d** no significant changes in the absorption wavelenghts are observed. The fluorescence emission spectra in solution of compounds **3a – 3e** exibit a single maximum λ_{em} ~ 530 nm. Depending on the R_{M0} values the hydrophobicity decreases in order of compounds **3c** > **3b** > **3d** > **3a**. The cytotoxic effect of the compounds **3a** – **3e** on eukaryotic cells was determined. The most toxic compound proved to be **3d**.

Acknowledgements: *Financial support from Project PCE 2016 - 0187 is gratefully acknowledged.*

References:

[1]. Bem M, Radutiu AC, Voicescu M, Caproiu MT, Draghici C, Maganu M, Enache C, Constantinescu T, Balaban AT. Rev. Roum. Chim. 2018;63:149-155.

ISOLATION OF *Venturia inaequalis* FROM IDARED APPLE VARIETY

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Keywords: Venturia inaequalis, apple scab, fungi isolation, Idared variety, apple leaves

Introduction: In order to test some bio fungicides, the isolation of *Venturia inaequalis* was carried out. *Venturia inaequalis* is an fungus that causes the Apple scab disease [1-3].
Materials and methods: The fungus strain was cultivated onto potato-dextrose agar (abbreviated "PDA") from Sigma-Aldrich with next composition: agar, 15 g/L, dextrose, 20 g/L and potato extract, 4 g/L. Chloramphenicol antibiotic was used to avoid the bacterial contamination. Experiences were effectuated with samples (fruits and leaves, IDARED apple variety) from Research Institute for Fruit Growing Pitesti – Mărăcineni.
Results: Morphological observations were taken based on colony, conidia and conidiophore morphology and other morphological characters [4, 5].

Figure 1. Apple scab isolation (a), Conidia of *Venturia inaequalis* (microscope view) (b)

Conclusions: *Venturia inaequalis* was isolated from infected apples (leaves and fruits) and grown on the potato-dextrose agar culture medium with the goal to test some bio fungicides.

Acknowledgements: *"This work was supported by a grant of the Romanian Ministery of Research and Innovation, CCCDI-UEFISCDI, project number PN-III-P1-1.2-PCCDI-2017-0332"/Project 3, contract 6PCCDI/2018, within PNCDI II.*

References:
[1]. Didelot F, Caffier V, Orain G, Lemarquand A, Parisi L, Sustainable management of scab control through the integration of apple resistant cultivars in a low-fungicide input system. Agriculture, Ecosystems and Environment. 2016;217:41-48.
[2]. González-Domínguez E, Armengol J, Rossi V, Biology and epidemiology of venturia species affecting fruit crops: A review. Frontiers in Plant Science. 2017.
[3]. Bowen JK, Mesarich C H, Bus V G M, Beresford R M, Plummer KM, Templeton MD. Venturia inaequalis: The causal agent of apple scab. Molecular Plant Pathology. 2011;12(2):105-122.
[4]. Simmons EG. Alternaria an identification manual. CBS Fungal Biodiversity Center Utrercht the Netherlands. 2007; pp. 775.
[5]. Leslie JF, Summerell BA. The Fusarium Laboratory Manual. Blackwell Publishing. First edition. 2006; pp. 388.

BIOLOGICAL EFFECTS OF HYDROALCOHOLIC EXTRACT OF *LYCOPODIUM ANNOTINUM* L. (*LYCOPODIACEAE, PTERIDOPHYTA*)

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Keywords: Lycopodium annotinum; extract; Cucumis sativus; phytototoxicity

Introduction: The *Lycopodiaceae* species contain a series of bioactive compounds of the alkaloids class such as huperzine A and B, 8-B phlegmariurine, cernuine, lycocernuine, lycopodine, dihydroxycernuine (Cambie and Ash, 1994, Ma and collab., 2007, Zangara 2003, Zhang and collab., 2002 and 2008), which give them neuroprotective, antifungal, antithermal, etc. properties. The extracts obtained from spores of *Lycopodium clavatum* have hepatoprotective and anticarcinogenic effects (Pathak et al., 2009). The lycopodine obtained from *L. clavatum* inhibits the growth of HeLa cells (Mandal et al., 2010). A series of synthetic derivatives was included in different formulations that are now tested for their effect against Alzheimer's disease. Considering the therapeutic importance of *Lycopodiaceae,* the aim of this study was to test the phytotoxic, cytotoxic and genotoxic effects of the extracts obtained from *Lycopodium* native sources.

Materials and methods: The plant material represented by the aerial parts (stems and leaves) of the species *Lycopodium annotinum* L. was collected from the Vâlsan Valley. The solvent used for the extract was made of a mixture of ethyl alcohol 96º and distilled water, in 1:1 proportion, and the proportion of plant material to solvent was 1:10 (weight:volume). The time necessary for obtaining the extract was 48 hours, the extraction being undertaken at room temperature (18-20ºC). After extraction, the material was filtered using Whatman no. 1 filter paper. For the phytotocicity tests we used *Cucumis sativus* L. as a test plant, while for emphasizing the cytotoxic and genotoxic effects we used the *Allium cepa* L. test. The raw hydroalcoholic extracts were used in concentrations of 10%, 20% and 30%.

Results: The hydroalcoholic extracts of *L. annotinum* affect the germination process of seeds, the growth in length of rootlets and stemlets of *Cucumis sativus* seedlings, as well as their fresh biomass. These effects were dependent on the tested concentrations. In the meristematic tips of *A. cepa* incubated in extracts of *L. annotinum,* the mitotic division was inhibited and the frequency of chromosomal aberrations was lower as compared with the control sample. The mitoinhibitory and genoprotective effects of the extracts tested were dependent on the concentrations.

Conclusion: The hydroalcoholic extracts of *L. annotinum* had phytotoxic effects, influencing seed germination as well as the growth process of *C. sativus* seedlings and biomass accumulation. In addition, the tested extracts had mitoinhibitory and genoprotective effects on the onion meristematic cells. The mitoinhibitory effect emphasized by the *Allium* test explains the impaired growth in *C. sativus* seedlings.

Acknowledgements*: "This work was supported by a grant of the Romanian Ministery of Research and Innovation, CCCDI-UEFISCDI, project number PN-III-P1-1.2-PCCDI-2017-0332"/Project 3, contract 6PCCDI/2018, within PNCDI III.*

References:

[1]. Cambie RC, Ash J. Fijian medicinal plant. Melbourne, CSIRO; 1994.

[2]. Ma X, Tan C, Zhu D, Gang DR, Xiao P. Huperzine A from *Huperzia* species - An ethnopharmacological review. J ethnopharmacol. 2007;113:15-24.

[3]. Zangara A. The psychopharmacology of huperzine A: an alkaloid with cognitive enhancing and neuroprotective properties of interest in the treatment of Alzheimer's disease. Pharmacol Biochem Behav. 2003;75:675-686.

[4]. Zhang Z, ElSohly HN, Jacob MR, Pasco DS, Walker LA, Clark AM. Natural product inhibiting *Candida albicans* secreted aspratic proteases from *Lycopodium cernuum*. J Nat Prod. 2002;65:979-985.

[5]. Zhang HY, Zheng CY, Yan H, Wang ZF, Tang LL, Gao X, Tang XC. Potential therapeutic targets of huperzine A for Alzheimer's disease and vascular dementia. Chemico-Biological Inter. 2008;175:396-402.

[6]. Pathak S, Banerjee A, Paul S, Khuda-Bukhsh AR. Protective potentials of a plant extract (*Lycopodium clavatum*) on mice chronically fed hepato-carcinogens. Indian J Exp Biol. 2009;47(7):602-7.

[7]. Mandal SK, Biswas R, Bhattacharyya SS, Paul S, Dutta S, Pathak S, Khuda-Bukhsh AR. Lycopodine from *Lycopodium clavatum* extract inhibits proliferation of HeLa cells through induction of apoptosis via caspase-3 activation. Eur J Pharmacol. 2010;626(2-3):115-122.

NOVEL CONSERVATION TREATMENTS FOR HISTORICAL LEATHER

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Keywords: leather, HNTs, long-term protection.

Introduction: Historical leathers, in a huge variety of items as footwear and garments, bookbinding, wall tapestry, upholstery, harnesses, armours, storage vessels, household tools, cases, musical instruments, toys, ritual objects are regarded as important testimonials of our cultural heritage. It is vital therefore that these objects remain well preserved along with all the knowledge involved, from their material aspects and value use to historical, cultural and artistic values. One of the most difficult challenges in leather conservation concern with consolidation and pH control. To set up a novel green protocol for the long-term protection of historical and archaeological leather we have investigated the filling and stabilisation process of vegetable-tanned and alum-tawed leathers treated with various mixtures based on halloysite nanotubes (HNTs).

Materials and methods: The following mixtures were tested: HNTs/PEG200 composite, HNTs/1-chlor buthane–beeswax (2%) composite, HNTs/hydro-alcoholic solution of urea (2%), HNTs/keratin hydrolysate. Both the selected solutions and beeswax are commonly used in various conservation formulations for treating aged and deteriorated collagen-based materials [1-3]. All treatments with HNTs were tested on new vegetable-tanned and alum-tawed leather as well as on a heavily deteriorated historical vegetable tanned leather bookbinding given by the History Museum of Vaslui City following the book restoration and substitution of the old binding with a new one.

A comprehensive characterization of leather before and after the treatment with HNTs formulations was carried out through morphology (SEM), wettability (contact angle measurements), thermal stability (thermal microscopy and standard method SR EN ISO 3380-2003), chemical stability (FTIR-ATR) and flame-retardant properties (standard method EN ISO 6940:2004).

Results: The treatment with halloysite nanotubes formulations generated varied responses depending on both the nature of the tanning agent (condensed tannin, hydrolysable tannin, alum) and formulation type, but did not alter the chemical and thermal properties. In terms of chemical stabilization, the most efficient was the HNTs/hydro-alcoholic solution of urea (2%) formulation, while the less efficient was HNTs/PEG200.

Conclusions: This work proposes the use of various halloysite formulations in a new green protocol for the long-term protection of vegetable-tanned and alum-tawed leather and represents a starting point to develop, with a biocompatible approach, smart composite materials in which the nanotube cavity is filled with active species for leather protection (such improvement of softeness, fulness, confering antimicrobial activity, pH control or active response to external stimuli i.e. UV light).

Acknowledgements: *This work has been financially supported by the Romanian Ministry of Research and Innovation through the projects Inovative methods for the preservation of collagen-based artworks (KOLLART), PED 168/2017 and Eco-friendly leather manufacturing process for art and heritage bindery (PRO-ART), contract no.160/2017.*

References:

[18]. Ershad-Langroudi A, Mirmontahai A. Thermal analysis on historical leather bookbinding treated with PEG and hydroxyapatite nanoparticles. J Therm Anal Calorim. 2015;120:1119-27.

[19]. Badea E, Miu L, Carsote C, Petroviciu I, Granziero R, Perona S, Cacchia V, Pittari B, Laurora C, Della Gatta G, Cucos A, Budrugeac P, Vitale Brovarone A. Validazione di interventi di recupero conservativo di manufatti in pergamena. In Lo Stato dell'Arte 12. Florence. Nardini Editore; 2014. pp. 463-470.

[20]. Crudu M, Miu L. Produs de conservare activa si preventiva a pieilor de patrimoniu (Product for the active and preventive conservation of heritage leather). Patent No. 127958/2009 (issuing date 26.020.2016).

THE EFFECT OF MESOPOROUS SBA-15 SUPPORT MODIFICATION ON THE ACTIVITY OF Pt-BASED CATALYSTS IN CO AND VOCs OXIDATION

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Keywords: PtTi-SBA-15 catalysts; CO; CH_4; C_6H_{12}; total oxidation.

Introduction: CO and volatile organic compounds (VOC's) from air, emitted during industrial processes are recognized as pollutants and are considered to be dangerous to human health. In this work we present catalytic oxidation reactions of these compounds performed with PtTi-SBA-15 catalysts with various compositions.

Materials and methods: SBA-15 mesoporous support, with different TiO_2 mass percent (n=1, 5, 10, 30 %), were obtained by direct synthesis and impregnation (samples TnS and iTnS). The morphology and dispersion of Ti-SBA-15 mesoporous support, with 5% TiO_2, were modified by using of butyl alcohol in direct synthesis (samples T5Sb) process. PtTi-SBA-15 catalysts were obtained by impregnation of Ti-SBA-15 supports with aqueous H_2PtCl_4 solution. The percent of Pt in the samples with different titania content was 0.25% (samples PTnS). In samples with 5% titania and modified SBA-15 support the percent of Pt was 0.25, 0.5 and 1% (samples PxT5Sb) The obtained samples were characterized by SEM, TEM, XRD, XPS, TPR. Catalytic properties were tested in oxidation of CO, methane and n-hexane from air.

Results: XRD at low angle showed ordered mesoporous structure, typically for SBA-15 support, for all the samples except PT30S sample. Titania crystalline phases (anatase, rutile) were detected by XRD at wide angle, in the samples with higher titania concentration (10 and 30%). SEM microscopy evidenced the variation of morphology of T5S and T5Sb samples. Catalytic performances were correlated with TPR results and Pt dispersion evidenced by H_2 chemisorption. The effect of noble metal interaction with supported titania was observed on Pt/PtO_x variation and Pt atomic concentration on catalyst surface. XPS evidenced finely dispersed TiO_2 species for all the samples except T30S sample. The presence of Pt^0 and Pt^{2+} was evidenced in all the samples. Their concentration varied with titania content, the synthesis method and after catalytic reaction. A significant decreasing of Pt and Ti content on surface was observed for samples obtained in presence of butyl alcohol.

Conclusions: New catalysts with ordered hexagonal porous structure and activity in catalytic oxidation of CO and VOCs were obtained. The best results were obtained for PT5S and PT30S samples. In case of PxT5Sb samples the activity increased with Pt content.

CONTRIBUTIONS TO THE INTERPRETATION OF MASS SPECTRUM OF TETRA-ETHOXYSILANE. PART III: ACCURATE MASS AND M+1, M+2 ISOTOPIC EFFECTS

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Keywords: tetraethoxysilane; mass spectrum; accurate mass; M+1; M+2 isotopic effects.

Introduction: The aim of this article in continuation of Parts I and II is the study of the fragmentation reactions of tetraethoxysilane (TEOS) as a precursor in the sol-gel process. In Part I [1] the primary fragmentation ions at masses 207, 193, 179 and 163 were obtained experimentally by B/E linked scan. In Part II [2] eliminations of neutral fragments from the primary ions and the obtained ions by consecutive elimination reactions were evidenced experimentally by the B/E and $B/E(1-E)^{1/2}$ linked scans. In this third and final Part of interpretation of the TEOS mass spectrum, the separation of ions by mass spectrometry at high resolutions of 5000 and 6600, compared to standard resolution 1000, and measurements of the M+1 and M+2 isotopic effects at the resolution of 5000 are presented.

Materials and methods: The experimental data for this paper were obtained on a GC-MS tandem produced by VG-Analytical, England. Working conditions for 70-SE, VG Analytical double focusing mass spectrometer. Excitation source with electronic impact at 70 eV; response time: 0.03 ms; accelerating voltage: 8 kV; temperature in the ion source: 180^{o}C; electronic amplifier: 250.

Results: For this work has been achieved a library of the mass spectra obtained for TEOS in the different sol-gel reaction mixtures [3], analyzed by GC-MS at a resolution of R=1000. It shows the TEOS mass spectrum containing the molecular ion at m/e 208 together with 84 fragmentation ions (Figure 1).

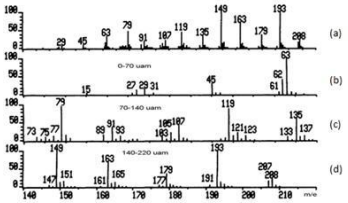

Figure 1. Mass spectrum of TEOS as an average of 12 mass spectra at resolution R=1000; (a) full, (b) 0-70 amu (c) 70-140 amu and (d) 140-220 amu.

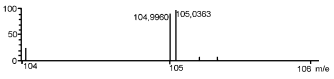

Figure 2. The separation of the fragmentation ions with nominal mass 105 at high resolution (R=5000) with preset error of ± 10 mmu.

Increased numbers (95) of TEOS fragmentation ions by mass spectrometry at high resolutions of 5000 and 6600, compared to standard resolution 1000 are presented in this work. An example of separation at high resolution is that of the ions with nominal mass 105. The separation of the fragmentation ions $C_3H_9O_2\ ^{28}Si^+$ with mass 105.0372 and $C_2H_5O_3\ ^{28}Si^+$ with mass 105.0008 are presented. (Figure 2). According to the isotopic distributions of the atoms that compose an silicon alkoxide as TEOS, the strongest M+1 and M+2 isotopic effects are due to silicon atom (4.67 and 3.10%) [3]. The measurements of M+1 and M+2 isotopic effects of 22 ions at optimal resolution (R=5000) are presented.

Conclusions: In this third and final Part, the arguments for the existence of 95 ions in TEOS mass spectrum are presented by experimental accurate mass measurements at high resolutions (5000 and 6600). A thorough example is presented: The separation of the ion $C_3H_9O_2\ ^{28}Si^+$ with mass 105.0372 and the ion $C_2H_5O_3\ ^{28}Si^+$ with mass 105.0008 at high resolution (R=5000).

There are also presented experimental measurements of the M+1 and M+2 isotopic effects at high resolution (5000) for the most intense 22 ions of TEOS mass spectrum.

References:

[1]. Badescu V. Contribution to the interpretation of mass spectrum of tetraethoxysilane (TEOS). Part I. The molecular ion. Primary events. Rev Roum Chim 2014;59:875-82.

[2]. Badescu V. Contributions to the interpretation of mass spectrum of tetraethoxysilane (TEOS). Part II: charge induced reactions. Eliminations of neutral fragments. Rev Roum Chim 2015;60:1107-15.

[3]. Badescu V., The alkoxide reactivity studied by ionic processes in the gas phase (Ph. D. Thesis), Roumanian Academy, Bucharest, Inst. Phys. Chem., 1998.

OBTAINING A COLLAGEN BASED FERTILIZER - SMART HYDROGEL

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Keywords: leather waste; collagen; hydrogel.

Introduction: The leather processing industry has made significant efforts in recent years on the improved efficiency in using energy and materials, as well as in discarding the use of hazardous materials in production phases. Solid waste (from raw hide and tanned leather, residual wool and sludge from wastewater treatment) is a significant issue of the leather sector[1].

The originality and innovative contribution of the scientific paper consists in re-evaluation of tanned leather waste from the leather sector by turning them into raw materials with added value and using in construction materials industry, by developing new production concepts for new biocomposite materials[2].

Materials and methods: In this study, was used limed hide waste from fleshing and trimmimg cattle hides (weight category 35 kg) from SC Pielorex Jilava tannery, Romania.

An innovative process has been proposed, namely a direct hydrolysis of pelt waste in an acid medium, enrichment with dipotassium phosphate (to improve the nutritional properties by the addition of phosphorus and potassium required for plant growth and development) and compounding with polymers (corn starch, maleic copolymers, urea etc.) resulting in new complex products called multicomponent hydrogels (Figure 1).

The hydrogel structure was preferred due to its capacity of swelling by absorbing large amounts of water which could be further released into the soil together with the nutrients needed for plant growth.

Results: The IR optical microscopy and chemical analysis have proved the obtaining of new hydrogels with collagen structure with microencapsulated nutrients which may be used as smart biofertilizers, particularly as foliar fertilizer (Figure 2).

Figure 1. Installation for waste conversion

Figure 2. The Smart hydrogel

Figure 3. Tests on degraded soils

*Obtaining hydrogels with collagen structure by hydrolyzing pelt waste for applications in agriculture is a novelty, given that the collagen structure is mainly used in the composition of hydrogels used in medicine. In support of this are the most recent scientific reports in this area related to the interest of researchers in interdisciplinary fields concerning the preparation of hydrogels with collagen structure.

*This scientific paper is based on a new concept, that of performing direct hydrolysis, using a polymer and nutritional multicomponent system required to obtain hydrogel for agriculture.

*Optical microscopy and IR analysis confirmed that the protein source can be transformed by direct hydrolysis into a multicomponent system - hydrogels with collagen structure and encapsulated micronutrients.

Acknowledgements: *This work was financially supported by UEFISCDI, in the frame of ERANET INCOMERA 2017-2019 Agro-Smartgel "Collagen - based composites obtained by pelt waste processing for smart biofertilizers structure for obtaining smart multifunctional products", contract 11/ 2018.*

References:

[1]. Zainescu G, Constantinescu R, Sirbu C. Smart hydrogels with collagen structure made of pelt waste. Rev Chim. 2017; 68:393-5.

[2]. Angelucci DM, Stazi V, Daugulis AJ, Tomei MC. Treatment of synthetic tannery wastewater in a continuous two-phase partitioning bioreactor: Biodegradation of the organic fraction and chromium separation. J Clean Prod. 2017;152:321-9.

NANOTECHNOLOGY – TOWARDS NEW APPLICATIONS IN THE FIELD OF CULTURAL HERITAGE PRESERVATION

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Keywords: nanomaterials; paper artifacts; ceramic artifacts; conservation.

Introduction: Developing under the impetus of short-term interests may be a threat to cultural heritage. Cultural heritage can have value well-being and quality of community life, can help prevent cultural globalization, support cultural diversity and positively affect economic development. The project *Nanotechnology - an innovative approach with development of materials and techniques for safeguarding the cultural heritage* represents the Research Project no. 2, part of the Complex Project *Multidisciplinary complex project for monitoring, preservation, protection and promotion of the Romanian cultural heritage* (RO-CHER).

Materials and methods: The project proposes the use of well-established nanomaterials [1, 2] for the development of innovative recipes for the restoration and conservation of paper and ceramic artifacts.

Figure 1. Paper (up) and ceramic artifacts (down) considered for the study

Results: Application of nanomaterials in the field cultural heritage artifacts was previously proven by our group as a successful alternative to classical methods [1, 2]. The developed recipes will be adapted to the specific of each support material, following extensive archaeometry studies [3, 4].

Conclusions: Development of new recipes for the restoration/conservation of cultural heritage artifacts will provide modern alternative for specialist from museums working in the area of cultural heritage preservation.

Acknowledgements: *This work was supported by a grant of the Romanian National Authority for Scientific Research and Innovation, CNCS/CCCDI – UEFISCDI, Complex project PN-III-P1-1.2-PCCDI-2017-0413, Contract 50PCCDI/2018, within PNCDI III.*

References:

[1]. Fierascu I, Dima R, Ion RM, Fierascu RC. A new approach for the remediation of biodeteriorated mobile and immobile cultural artefacts. Europ J Sci Technol. 2013;9(2):161-8.

[2]. Fierascu I, Fierascu RC, Somoghi R, Ion RM, Moanta A, Avramescu SM, Damian CM, Ditu LM. Tuned apatitic materials: synthesis, characterization and potential antimicrobial applications. Appl Surf Sci. 2018;438:127-35.

[3]. Fierascu I, Avramescu SM, Fierascu RC, Ortan A, Vasilievici G, Cimpeanu C, Ditu LM. Micro-analytical and microbiological investigation of selected book papers from the nineteenth century. J Therm Anal Calorim. 2017;129(3):1377-87.

[4]. Fierascu RC, Fierascu I, Ortan A, Constantin F, Mirea DA, Statescu M. Complex archaeometallurgical investigation of silver coins from the XVIth-XVIIIth century. Nuclear Inst. Methods Phys Res B. 2017;401:18-24.

DEVELOPMENT OF METHODOLOGIES FOR TRANSDISCIPLINARY STUDIES OF CULTURAL HERITAGE ARTIFACTS

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Keywords: transdisciplinary studies; analytical techniques; microbial deterioration.

Introduction: Application of various modern analytical techniques in the study of cultural heritage artifacts represents an emerging field of research, with a tremendous quantity of results being obtained for each such study [1, 2]. *Transdisciplinary studies for the valorization of the national cultural heritage* represents one of the three demonstrative scientific experiments of the project *Techniques for storing and capitalization the results of advanced scientific research* (SoVaReX), combining knowledge of archaeometry, IT&C and history.

Materials and methods: The demonstrative experiment aims to develop and implement new methodologies (using X-ray diffraction, X-ray fluorescence, Particle induced X-ray emission, thermal analyses, FTIR, microscopy techniques, microbiological evaluation etc.) for the study of cultural heritage artifacts (focusing on metallic artifacts, historical textiles and wood artifacts) and, in the same time, to validate the functionality of the computer system for the acquisition, processing, storage, modelling and analysis of advanced scientific experiments, developed by the project coordinator, IFIN-HH.

Results: The methodologies developed in the project were applied on a series of cultural heritage artifacts, subject of several published works [3, 4]. In the same time, the obtained results were deposited in the database developed by the coordinator (Figure 1).

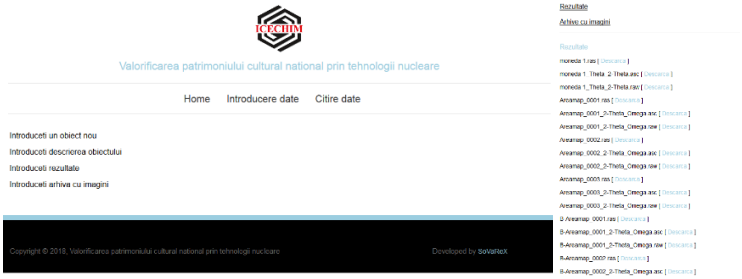

Figure 1. Images of the database and (some) of the contained results

Conclusions: The demonstrative experiment managed to offer not only the proposed methodologies, but also the confirmation of the appropriateness of the database for such results. Supplementary information are available on the web-page of the project (http://sovarex.nipne.ro/) and of the demonstrative experiment (http://sovarex-patrimoniu.nipne.ro/).

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References:

[1]. Fierascu I, Avramescu SM, Fierascu RC, Ortan A, Vasilievici G, Cimpeanu C, Ditu LM. Micro-analytical and microbiological investigation of selected book papers from the nineteenth century. J Therm Anal Calorim. 2017;129(3):1377-87.

[2]. Fierascu RC, Fierascu I, Ortan A, Constantin F, Mirea DA, Statescu M. Complex archaeometallurgical investigation of silver coins from the XVIth-XVIIIth century. Nuclear Inst. Methods Phys Res B. 2017;401:18-24.

[3]. Raditoiu V, Chican IE, Raditoiu A, Fierascu I, Fierascu RC, Fotea P. Application of Fourier-Transform Infrared Spectroscopy (FTIR) for the study of cultural heritage artifacts. 1st International Conference on VR Technologies in Cultural Heritage (VRTCH'18) – Springer. *In press*.

[3]. Fierascu RC, Fierascu I, Doni M. Valorization of cultural heritage through archaeometry studies using nuclear techniques and other scientific methods. General considerations and short literature survey. 2018. ISBN: 978-973-0-27114-0.

PHOTOCATALYTIC DEGRADATION OF CYTOSTATICS UNDER LIGHT IRRADIATION

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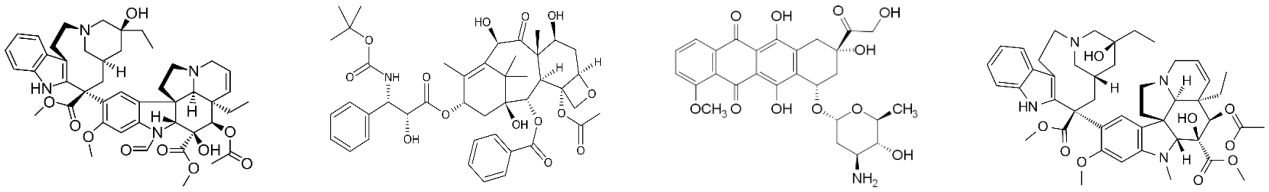
Keywords: cytostatics; photocatalytic degradation; drug waste; emerging pollutants.

Introduction: Pharmaceuticals, especially cytostatics have become a major group of emerging contaminants as widespread pollutants of surface water, groundwater and drinking water. These cytostatics are of great importance, owing to their cytotoxicity, mutagenesis and genotoxicity[1]. Therefore, it is crucial to monitor their presence in the environment and to destroy this drug waste. This study aims to investigate the photocatalytic degradation of vincristine (an antitumor vinca

alkaloid), vinblastine (a vinca alkaloid antineoplastic agent), docetaxel (an antineoplastic agent) and epirubicin (an antineoplastic agent derived from doxorubicin) under light irradiation (figure 1).

Materials and methods: The irradiation experiments were carried out in quartz cuvette, filled with 3ml of drug solution at different concentration. Samples were subjected to different irradiation times (ranging from 0.5 sec to 45 min) depending on their degradation behavior, using a medium pressure Hg polychromatic lamp. After illumination, the entire content of each cuvette was analyzed using a spectrophotometer.

Results: It was observed decreases of UV-Vis absorption bands in the case of all the cytostatics. Also, by FTIR spectrum it was determined that degradative photo-oxidation processes occur from modification of specific absorption bands in region between 1600 cm^{-1} and 1800 cm^{-1}. Figure 2 shows that the degradation rate depends on the structure of the compound, the type of functional groups.



Vincristine Docetaxel Epirubicine Vinblastine

Fig. 1. Chemical structures of the cytostatics studied.

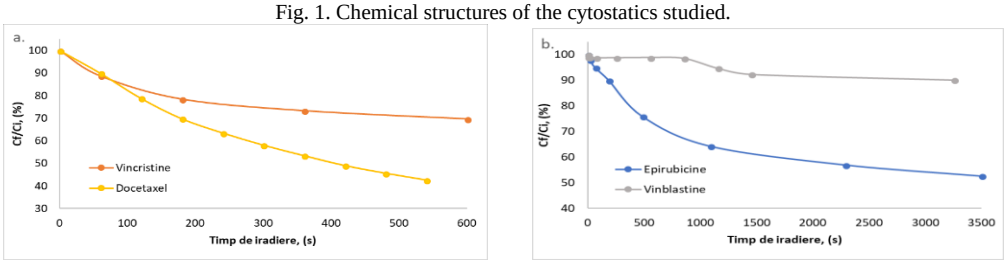


Fig. 2. Kinetic curves of vincristine, docetaxel (*a*) and epirubicine, vinblastine (*b*) under different irradiation times.

Conclusions: This study evidences that the degradation rate depends on the structure of the compound and the type of functional groups, which confirmed that the photocatalytic process is able to play a key role in the degradation of cytostatics.

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References:

[1.] Calza P. Medana C, Sarro M, Rosato V, Aigotti R, Baiocchi C, Minero C. Photocatalytic degradation of selected anticancer drugs and identification of their transformation products in water by liquid chromatography–high resolution mass spectrometry. J Chromatogr A. 2014; 1362:135-44.

POLYMERS IDENTIFICATION IN WASTE ELECTRIC AND ELECTRONIC EQUIPMENT (WEEE) PLASTICS

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Keywords: WEEE; recycling; identification methods.

Introduction: The reintroduction into the economic circuit of recovered plastic materials from waste electric and electronic equipment (WEEE) is an important social concern, being an effective and innovative process in line with the new European directions on materials recovery and waste recycling, contributing to reduction of EEE plastics from landfill [1, 2, 3]. So, WEEE plastics can be processed as high-performance polymer composites for the production of non-food packaging containers, transport vessels, technical landmarks, pavements, etc.

Materials and methods: The materials used in the study were collected from unused computer casing, internal plastic parts and accessories. The plastics identification was achieved by: density determination, burning test, infrared spectroscopy (FTIR), differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).

Results: The plastics were separated into marked items and unmarked unmetallic parts that were sorted by form, color and by components parts of the same type. The initial components determination was performed by density and combustion tests and specific domains of the waste composition were obtained. The absorption bands resulted from IR spectroscopy were compared to the base polymers and then the waste composition was confirmed by thermal analysis. The results showed a majority styrenic multi-component polymer system.

Conclusions: The considered identification methods indicated the presence of a majority of styrenic polymers in the EEE waste and the proper compounding process can be thus selected in order to obtain high-performance composited.

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References:

[1]. Tostar S. Mechanical and Thermal Properties of Recycled WEEE Plastic Blends. Thesis for the Degree of Doctor in Philosophy, Chalmers University of Technology, Gothenburg, Sweden, 2016.

[2]. Florea D, Paven H, Vuluga Z, Vuluga DM. Identification, Sorting and Characterization of Plastics from WEEE. Mater Plast. 2011;48:176-82.

[3]. Ragert K, Delva L, Van Geem K. Mechanical and chemical recycling of solid plastic waste. Waste Manag. 2017; 69:24-58.

NANOEMULSION SYNTHESIS AND CHARACTERIZATION OF CARBONATED HYDROXYAPATITE

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Keywords: carbonated hydroxyapatite; nanoemulsion.

Introduction: Hydroxyapatite (HA) and related metallic derivatives with silver, gold, platinum, have been widely studied for different applications, including the conservation/preservation of cultural heritage [1]. Except of these, carbonated hydroxyapatite (CAH) powder can be obtained by different methods, nanoemulsion method being the most recent being able to produce nano size CAH particles [2].

Materials and methods: Carbonated hydroxyapatite, as powder in very fine and uniform droplet sizes, has been obtained by a nanoemulsion technique adopted from Zhou et al. [3]. CHA

nanoparticles were synthesized from $Ca(NO_3)_2 \cdot 4H_2O$, $(NH_4)_2HPO_4$ and NH_4HCO_3, under magnetic stirring. The aqueous solution pH was adjusted to 11 using sodium hydroxide 1 M prior to mixing. The reaction was carried out at room temperature [3]. The carbonated hydroxyapatite was characterized by Fourier Transforms Infrared (FT-IR) and Raman Spectroscopy, X-ray Diffraction (XRD), Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM-EDS).

Results: CAH has a pure crystalline structure in majority characterized by XRD peaks, by FTIR (phosphate bands at 590–610 cm^{-1} and 1000 cm^{-1}, CO_3^{2-} at 870 cm^{-1} and 1467–1412 cm^{-1}), by Raman through the bands from 570, 960, 1046 and 1069 cm^{-1}) and a relatively spherical shape (visible by SEM-EDS), Figure 1.

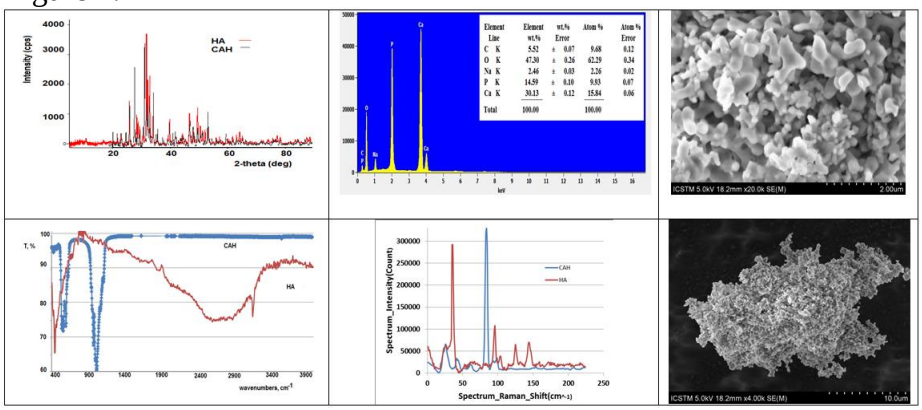

Figure 1. Analytical investigations of CAH and HA (from top to down and from left to right: XRD, EDS, FTIR, Raman and SEM)

Conclusions: In this paper, the research was focused on the synthesis and characterization of CHA through nanoemulsion method revealing the success of this method from further applications.

Acknowledgements: *This work was supported by a grant of the Romanian Ministery of Research and Innovation, CCCDI – UEFISCDI, project number PN-III-P1-1.2-PCCDI-2017-0476 / 51PCCDI/2018, within PNCDI III.*

References:

[1]. Ion RM, Nyokong T, Nwahara N, Suica-Bunghez IR, Iancu L, Teodorescu S, Dulama ID, Stirbescu IR, Gheboianu A, Grigorescu RM. Wood preservation with gold hydroxyapatite system. Herit Sci. 2018;6:37-49.

[2]. Wong WY, Mohd Noor AF. Synthesis and sintering-wet carbonation of nano-sized carbonated hydroxyapatite. Proc. Chem. 2016;19:98-105.

[3]. Zhou WY, Wang M, Cheung WL, Guo BC, Jia DM. Synthesis of carbonated hydroxyapatite nanospheres through nanoemulsion. J Mater Sci Mater Med. 2008;19:103-10.

NANOTECHNOLOGIES AND NANOMATERIALS: APPLICATIONS AT CORVINS'CASTLE

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Keywords: Cultural Heritage; Corvins'Castle; nanomaterials; nanotechnology.

Introduction: Nanotechnology is now recognized as a new technological revolution useful for conservation and restoration of mobile and immobile objects of cultural heritage. Our research group, with a solid experience recognized at many cultural heritage objectives during the last 15 years, promotes nanotechnologies, suitable consolidating and protecting nanomaterials and adequate techniques for different structures. The diagnosis of the degradation stage of different materials such as natural stone, mortars, artistic components (painted surfaces, Matia-fresco Loggia, stone) from the

Corvins' Castle, Hunedoara, have been investigated by using advanced investigative techniques proper for recommendations on restoration and preservation operations.

Materials and methods: Modern high-fidelity portable and laboratory equipments have been used for analyzes: Scanning Electronic Microscopy (SEM-EDS), Optical Microscopy (OM), X-ray Diffraction (XRD), Fourier Transformed Infrared (FT-IR) and Raman spectroscopy, polychromy analysis (by chromatic parameters), UV analyzes, bacterial and fungal tests, detection of infections, species, genre, are the other main points of this paper.

Results:

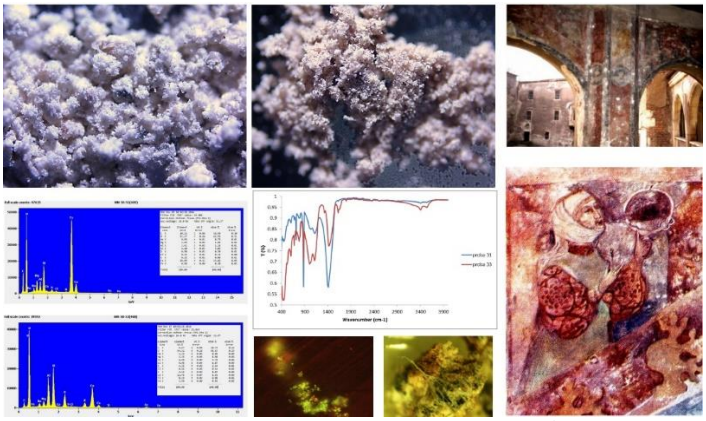

Figure 1. Analytical investigations and some analytical results for Loggia Matia

Conclusions: As a preliminary conclusion, the Corvins' Castle was constructed from dolomite-limestone blocks from the natural local resources, crenellated to the upper part. XRD indicates mostly the presence of dolomite, calcite and quartz, with small amount of illite, muscovite, paragonite, montmorillonite, wonesite, feldspars, chlorite and some clays as raw material: whitmoreite, kornelite, micas and other heavy minerals. Incompatibilities between traditional materials and the new ones observed after restorations over time with effects on the walls and painted surfaces.

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References:

[1]. Ion RM, Nyokong T, Nwahara N, Suica-Bunghez IR, Iancu L, Teodorescu S, Dulama ID, Stirbescu IR, Gheboianu A, Grigorescu RM. Wood preservation with gold hydroxyapatite system. Herit Sci. 2018;6:37-49.

STABILITY ASSESSMENT OF ADDITIVATED FORMULATIONS CONTAINING SURFACTANTS AND OXIDIZING AGENTS

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Keywords: surfactants; sodium hypochlorite; hydrogen peroxide; stability; decontamination.

Introduction: The purpose of the present study was to assess the effect of surfactants over time on the stability of sodium hypochlorite or hydrogen peroxide formulations. The oxidizing agents are used in chemical decontamination of chemical warfare agents with the aim to neutralize them completely into non-toxic compounds. Surfactants have the role to solubilise sparingly soluble chemical warfare agents and catalyse their detoxification [1, 2].

Materials and methods: Different classes of surfactants were used in the study, such as ethoxylated alcohols (alcohol C_{12}-C_{15} 10 OE, alcohol C_{12}-C_{14} 9 OE), sulfated alcohols (sodium dodecyl sulfate), sulfated ethoxyated alcohols (sodium laureth sulfate 2,5 OE), sulfonated alkylbenzene (sodium dodecylbenzenesulfonate), quaternary ammonium compounds (didecyldimethylammonium chloride), acylated amino acids (sodium lauroyl glycinate), amino oxides (lauryldimethylamine oxide). The formulations where made with same concentration of surfactant (5%). Sodium hypochlorite or hydrogen peroxide was added in known concentrations (4% active chlorine and 4% active oxygen)

and specific additives were used in order to stabilize the formulations. In the experiments was tested also a product made by REGO COM.

Results: The stability of additivated formulations were compared with non-additivated formulations and the active chlorine/active oxygen, pH and foaming power were determined in time. Blank solutions of sodium hypochlorite (4% active chlorine) and hydrogen peroxide (4% active oxygen) were used in order to evaluate the effect of surfactants on the stability of formulations. Certain surfactants were not compatible with oxidizing agents, such as sodium dodecylbenzenesulfonate or sodium lauroyl glycinate. A good stability over time was found for the product made by REGO COM and formulations containing ethoxylated alcohols, sulfated ethoxylated alcohols, lauryldimethylamine oxide or didecyldimethylammonium chloride.

Conclusions: Stabilization of the formulations containing surfactants and oxidizing agents requires specific additives, since surfactants reduce sodium hypochlorite or hydrogen peroxide activity in variable proportions. Based on the amount of active chlorine or active oxygen found in the formulations at the end of testing period, we can conclude that ethoxylated alcohols, sulfated ethoxylated alcohols, lauryldimethylamine oxide or didecyldimethylammonium chloride can be used in foaming formulations which will be developed for the decontamination of chemical warfare agents.

Acknowledgements: *This work was financially supported by the Romanian National Authority for Scientific Research and Innovation – UEFISCDI, Contract No. 70PCCDI/2018.*

References:

[1]. Yang YC, Baker JA, Ward JR. Decontamination of chemical warfare agents. Chem. Rev. 1992;92(8):1729-43;

[2]. Khan AW, Sharma RK, Ali J, Ansari SH, Kotta S. Recent advances in decontamination of chemical warfare agents. Def. Sci. J. 2013;63(5):487-96.

AN INNOVATIVE PLATFORM FOR SAFEGUARDING, PROMOTING AND VALUING CULTURAL HERITAGE

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Keywords: Earth Observation; nanotechnology; cultural heritage safeguarding and promoting; integrated platform.

Introduction: An exhaustive approach for cultural heritage sustainable management implies contributions from several scientific disciplines. Following this concept, the "Multidisciplinary complex project for the monitoring, conservation, protection and promotion of the Romanian cultural heritage" (RO-CHER) aims at benefiting from state-of-the-art technologies in order to develop innovative products tailored for different cultural heritage sites. The products will be integrated in an online multi-layered geospatial platform that will serve both as technical information hub for site managers and decision makers and straightforward information point for general public and cultural centres.

Materials and methods: Using various remote sensing methods (for example, change detection, supervised/ unsupervised classification, optical and radar data fusion, synthetic aperture radar interferometry, etc.), a large number of products can be generated based on satellite images, such as reference maps, multitemporal maps, land use/land cover change maps, risk analysis maps, disaster maps, ground and buildings displacement maps [1-3]. Nanotechnology will be used for developing

innovative materials for cultural heritage conservation [4]. LiDAR remote sensing will be applied for 3D reconstruction and modelling [5].

Results: Considering the relatively large number of scientific disciplines the project deals with, the estimated results consist of different outputs that will be integrated in a single geospatial platform. For each selected cultural heritage site, the platform will offer information derived from satellite data for the monitoring and assessment of the conservation state, nanotechnology-based materials and methods for restoration, as well as advanced digital products for the cultural heritage promotion and advertising.

Conclusions: The integrated platform that will be developed within the RO-CHER project will enable a more effective governance of the cultural heritage. By providing essential information for the public and private managers, the platform will represent a robust tool for safeguarding, promoting and valuing cultural heritage. Apart from the results that are targeting the scientific community, the project also envisages the development of innovative digital 3D products that are appropriate for museums, cultural and centres and tourism offices.

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References:

[1]. Cuca B. The contribution of Earth Observation technologies to monitoring strategies of cultural landscapes and sites. 26th International CIPA Symposium, 28 August–01 September 2017, Ottawa, Canada.

[2]. Tapete D, Cigna F. Rapid mapping and deformation analysis over cultural heritage and rural sites based on persistent scatterer interferometry. Int J Geophys. 2012:618609, DOI: 10.1155/2012/ 618609.

[3]. Zhou W, Chen F, Guo H. Differential radar interferometry for structural and ground deformation monitoring: a new tool for the conservation and sustainability of cultural heritage sites. Sustainability 2015;7:1712-29.

[4]. Fierascu I, Fierascu RC, Somoghi R, Ion RM, Moanta A, Avramescu SM, Damian CM, Ditu LM. Tuned apatitic materials: synthesis, characterization and potential antimicrobial applications. Appl Surf Sci 2018;438:127-35.

[5]. Dong P, Chen Q. LiDAR remote sensing and applications. CRC Press Taylor & Francis Group; 2018.

REMOVAL OF ORGANIC POLLUTANTS FROM WATER BY ADSORPTION ON NANOCARBONS FROM POLYMERS

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Keywords: adsorption; carbon; organic pollutants; water purification.

Introduction: Due to their highly porous structure and large adsorption capacity, activated carbons are widely used as adsorbents in technologies connected to pollution abatement in water and gases in chemical industry, pharmaceutical and food industries, etc. Activated carbons have often been synthesized from precursors based on expensive and depleting fossil fuels, but they can be prepared easily from less expensive biomass or agricultural by-products.

Materials and methods: Preparation of synthetic carbons. The precursor (polyolefin wax, phenol-formaldehyde resin, etc.) was heated up to 115°C until melting 98%. H2SO4 was added by drops with continuous stirring, and the mixture was heated up to 160°C. The obtained solid product was washed with water, dried at 150°C, and carbonized at 600°C.

Biomass (coconut shells, apricot stones, almond shells, grape seeds, olive stones and pulp, cherry stones, bamboo, been pods, straw etc.) and synthetic carbons were subjected to hydropyrolysis procedure at 800^{o}C.

Chemical activation. The initial material was ground to 0.5mm particle size. The activation process involved mixing of the initial material and the activating agent (K_2CO_3) in water, with ratio agent vs precursor 4:6. The mixing was performed at room temperature under stirring for 12 h. After mixing, the slurry was subjected to drying at 110◦C overnight. Carbonization was carried out at 950◦C in N_2 atmosphere, and then heated at this temperature for 10 min. The carbonized product was washed and dried at 110°C.

Results: Data form N_2 adsorption isotherms demonstrate that obtained carbon adsorbents are distinguished with moderately high surface area and prevailing microporous structure.

By using IR spectroscopy and Boehm method, different oxygen-containing surface groups were detected on the carbon surface

The properties of nanocarbons determine their application as effective adsorbents for removal of organic (phenols, naphthalene, etc.).

Conclusions: Nanocarbons synthesized by different methods from various precursors have high surface area and microporous structure, which determine their application as adsorbents for effective removal of organic compounds from water. The high adsorption capacities of nanocarbons depend on their porous parameters and presence oxygen surface groups.

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References:

[1]. Savova, D.; Apak, E.; Ekinci, E.; Ferhat Yardim, M.; Petrov N.; Budinova, T.; Razvigorova, M.; Minkova, V.; Biomass conversion to carbon adsorbents and gas. Biomass Bioen. 2001, 21, 133-142.

[2]. Ryu, Z.; Rong, H.; Zheng, J.; Wang, M.; Zhang, B. Microstructure and chemical analysis of PAN-based activated carbon fibers prepared by different activation methods. Carbon 2002, 40, 1144-1147.

[3]. Park, S.-J.; Jung, W.-Y. Preparation and structural characterization of activated carbons based on polymer resin. J. Colloid Interface Sci. 2002, 250, 196-200.

[4]. San Miguel, G.; Fowler, G. D.; Sollars, C. J. A study of the characteristics of activated carbons produced by stream and carbon dioxide activation of waste tyre rubber. Carbon 2003, 41, 1009-1016.

EFFECT OF COMPOSITION AND PROPERTIES OF PRECURSOR DURING THE PREPARATION OF CARBON COMPOSITES

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Keywords: carbon composites; coal tar pitch; petroleum coke; baking criterion.

Introduction: The influence of composition and properties of the initial materials on the interaction of coal tar pitch and petroleum coke in carbon composites is studied.

The interaction between binder and filler particles during the process of preparation of the carbon material depends on the physico-chemical properties of the binder, the nature and surface properties of the filler, the condition of the baking process, etc. [1–3].

Materials and methods: The softening point of pitches was determined by the ring and ball method. Baking criterion was determined by mixing filler (petroleum coke) and binder (coal tar pitch) at a temperatures above the softening point of the pitch, subsequent pressing the mixture, and heating in nitrogen atmosphere at 900°C. FTIR spectra of the samples were obtained using KBr pellets on a Bruker IFS 113 V spectrometer. The EPR measurements were performed using EPR spectrometer type Bruker ER 200 spectrometer.

Results: Baking ability of the pitches, obtained after different oxidation treatments of commercial coal tar pitch (Figure 1), was studied. It is determined that physico-chemical properties of the obtained pitches influence the baking ability.

The investigations show processed of recombination of paramagnetic centers and interaction of oxygen-containing functional during the preparation of the composite.

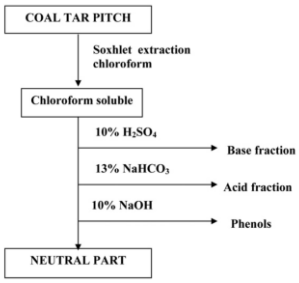

Figure 1. Scheme of separation of coal tar pitch.

Conclusions: The physico-chemical properties of pitch influence the baking ability. The data indicate that polar compounds of the pitches are concentrated in the adsorption layer as a result of interaction with petroleum coke surface. This suggests that chemical interactions take place between these structures during the preparation of the composite. The oxidation treatment increases the ‘‘baking criterion’’ of the coal tar pitch, due to the changes in the composition and properties of the resultant pitches.

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References:

[1]. Fitzer E, Huttner W. Structure and strength of carbon/carbon composites. J Phys D Appl Phys 1981;14:347–71.

[2]. Figueiras A, Fernandez JJ, Granda M, Bermejo J, Casal E, Menendez R. Influence of matrix precursors on the microstructure and mechanical properties of C/C composites. J Microscopy 1995;177:218–29.

[3]. Blanco C, Casal E, Granda M, Menendez R. Influence of fibre-matrix interface on the fracture behaviour of carbon–carbon composites. J Eur Ceramic Soc 2003;23:2857–66.

STUDIES REGARDING EFFECT OF ORGANIC SALTS IN WOOD PROTECTION AGAINST SOME MICROBIOLOGICAL AGENTS, WITH APPLICATIONS IN CONSERVATION OF CULTURAL HERITAGE

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Keywords: microorganisms; wood protection; cultural heritage.

Introduction: Conservation of historic wood objects is a complex process, as factors such as wood type, storage and biological agents involved in the deterioration. In the case of old, historically valuable wood, the impact of chemicals on the material is extremely important, as it can lead to a change in color [1-4]. The purpose of the study was to evaluate (1) the effect of organic salts which contain tertiary ammonium salt and quaternary ammonium salts on microbiological agents involved in biodegradation processes and (2) the impact of the application of these compounds on wood surfaces.

Materials and methods: As microbiological agents implied in wood degradation were used the bacteria and fungi from the genus *Alternaria* sp. and *Pseudomonas* sp.; as biocidal materials were used organic salts which contain tertiary and / or quaternary nitrogen.

The efficacy of salts tested was evaluated by measurements of inhibition diameter. The assessment of the impact on wood surfaces treated with afore mentioned organic salts was determined by luminance and color determinations.

Results: Laboratory studies have shown that the most effective are organic salts containing a quaternary nitrogen atom followed by organic salts containing a tertiary nitrogen atom. Regarding the

impact of treatments with organic salts on wooden surfaces, the determinations made showed that these did not undergo any color changes and the protective effect of the selected substances could last up to 3 months under laboratory conditions.

Conclusions: Laboratory studies conducted on wood samples (no historical value) showed that organic salts containing a quaternary or tertiary nitrogen atom may be used to protect wood objects against microbiological agents of the Alteranaria sp. or Psudomonas sp. type, without appearance changes of wooden material

References:

[1]. Carr JM, Duggan PJ, Humphrey DG, Platts JA, Tyndall EM. Quaternary Ammonium Arylspiroborate Esters as Organo-Soluble, Environmentally Benign Wood Protectants. Aust J Chem 2005;58:901-11.

[2]. Carr JM, Duggan PJ, Humphrey DG, Platts JA, Tyndall EM. Wood Protection Properties of Quaternary Ammonium Arylspiroborate Esters Derived from Naphthalene 2,3-diol, 2,2'-Biphenol and 3-Hydroxy-2-naphthoic acid. Aust J Chem 2010;63:1423-9.

[3]. Ashori A, Behzad HM, Tarmian A. Effects of chemical preservative treatments on durability of wood flour/HDPE composites. Composites B 2013; 47:308-13.

[4]. Singh T, Singh AP. A review on natural products as wood protectant. Wood Sci Technol 2012;46:851-70.

SOLUTION MOLAR ENTHALPIES FOR 1-BUTYL-3-METHYLIMIDAZOLIUM CHLORIDE + 1-PROPANOL SYSTEM AT (303.56 AND 318.68) K

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Keywords: 1-Butyl-3-methylimidazolium chloride; 1-Propanol; Solution; Enthalpy; Infinite dilution.

Introduction: Ionic liquids (ILs), a new class of green solvents with low melting point (< 373 K), exhibit unique physicochemical properties. Due to their negligible vapor pressures, they have been suggested as replacements for volatile organic compounds (VOC) (which are flammable and toxic) and in a growing number of applications. 1-Butyl-3-methylimidazolium chloride ([bmim]Cl) is known as prototype IL, used for the synthesis of other more complicated ILs. To date, for the 1-propanolic system of [bmim]Cl, a number of two papers only have reported some of these properties [1]: vapor-liquid equilibria and activity coefficients at infinite dilution (pure solvents). In the available literature [1] for the [bmim]Cl + 1-propanol system no data on solution and excess molar enthalpies have been found. The ILs and electrolyte systems and the infinite dilution concentration range are very important for industry from both experimental and modeling viewpoints [2]. There is an increasing need for enthalpic properties and experimentally based improved electrolyte models in a wide range of industries [2]. The molar enthalpies of solution at infinite dilution, the apparent relative molar enthalpies for the solutes and relative molar enthalpies for the mixtures were determined in this work.

Materials and methods: Pure IL was dried till constant mass under high vacuum and stored afterwards under the same conditions. Pure 1-propanol was dried and stored on molecular sieves. The calorimetric measurements were carried out in a SETARAM C80 3D computer-controlled calorimeter using reversal mixing cells. Details on the calibration and heat measuring procedure have been reported recently [3]. The uncertainties are: 0.6% for $\Delta_s H_{m,IL}^{\infty}$ and 0.1% for $\Delta_s H_{m,mix}$ for heats, ± 0.0001 mol kg^{-1} for molality, and ±0.05K for temperature. The data have been correlated with Archer and Rard (1998) [4] model.

Results: Enthalpies of solution for 1-butyl-3-methylimidazolium chloride ([bmim]Cl) + 1-propanol system have been measured over the composition range from m = 0.0048 to 2.6224 mol kg^{-1}of [bmim]Cl at temperatures of 303.56 K and 318.68 K and atmospheric pressure. The data have been

correlated adequately with Archer and Rard (1998) model for electrolyte systems. The absolute mean relative deviations obtained in molar enthalpy of solution correlation were situated between 5.9 % and 11.2 %. The molar enthalpies of solution at infinite dilution (both negative decreasing with increasing temperature), the apparent relative molar enthalpies for the solutes, and relative molar enthalpies for the mixtures were determined according to this model. The later thermodynamic property is endothermic in the whole composition range of studied homogenous mixtures and at constant mole fraction decreases with increasing temperature.

Conclusions: It is confirmed that within low concentration range of the IL the interactions which appear at mixing of the two compounds are strongly attractive and they are most likely dominated by the packing of unlike molecules.

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References:

[1]. DDBST (Software and Separation Technology) GmbH, The Dortmund Data Bank (DDB), Oldenburg, Germany, http://www.ddbst.com/ , accessed September 2018.

[2]. Hendriks E, Kontogeorgis GM, Dohrn R, de Hemptinne JC, Economou IG, Zilnik LF, Vesovic V. Industrial requirements for thermodynamics and transport properties. Ind Eng Chem Res 2010;49:11131–11141.

[3]. Teodorescu M, Popa VT. Solution and excess molar enthalpies for 1-butyl-3-methylimidazolium chloride + water system at (303.15 and 318.15) K. Rev Roum Chim 2016;61(6-7):525-530.

[4]. Archer DG, Rard JA. Isopiestic investigation of the osmotic and activity coefficients of aqueous $MgSO_4$ and the solubility of $MgSO_4 \cdot 7H_2O$(cr) at 298.15 K: thermodynamic properties of the $MgSO_4 + H_2O$ system to 440 K. J Chem Eng Data 1998:43:791-806.

BEHAVIOR OF HUMAN MSC CELLS ON PEPTIDE-COATED TITANIUM SURFACES

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Keywords: biomaterial; titanium surface; peptide coating; mesenchymal stem cells; bone implant

Introduction: Implant surface properties are important factors for creating stable interfaces between implant and bone tissue. For bone implant, topography and chemical surface of the biomaterial are important cues that can alter protein adsorption of biological fluids or of those synthesized by cells, thus affecting cellular and tissue response [1,2,3]. Following the bone differentiation steps, the synergistic effect of topography and peptide coating with the ability to self-assemble on Ti surfaces was examined *in vitro* on the behavior of osteoprogenitor MSC mesenchymal stem cells. **Materials and methods**: Coated micro and nanostructured surfaces were created by excimer laser processing technique, followed by Ti magnetron sputtering and peptide matrix deposition. Cell morphology, proliferation and viability were analyzed in the initial steps of cell differentiation, using colorimetric and enzymatic-imagistic methods, immunofluorescence and scanning electron microscopy (SEM) techniques. Subsequently, the ability of MSC cells to differentiate into osteoblasts on analyzed surfaces was investigated in long-term experiments, assessing the presence of specific mineralization markers by Alizarin Red staining, EDS-Energy Dispersive X-ray Spectroscopy and osteocalcin expression by immunofluorescence microscopy inspection. **Results**: Fibrilar structures addition to surface materials had led to a significant decrease in the contact angle and thus to the increase of the hydrophilic character. MSC viability and proliferation on topographically modified materials coated with peptide structures increased compared with uncovered surfaces as *in vitro* tests revealed. Live/Dead assay showed no cellular death on all materials. An increased number of actin filaments displaying focal point intensity were observed on fibrilar peptide coated materials thus suggesting a

favorable cell adherence, spreading and cellular interaction with the surface material. Generally, the cells cover several topographic elements with the nucleus located inside the cavities with the highest depth. These observations are also supported by the SEM microscopy investigations which allowed the visualization of cellular morphology and the appearance of some filopodial structures distributed according to the topographic structures. Biological tests indicated a rapid mineralization of nano and microstructured materials coated with peptide structures beginning even from 14 days of culture and continuing with an intensification of mineralization up to 21 days. These results highlight the tendency of MSC cells to differentiate themselves towards the osteoblastic pathway more quickly and efficiently on materials with similar bone structure and functionalized with peptides in osteogenic medium as compared to unstimulated osteogenic medium. EDS confirmed the uniform distribution and presence of calcium and phosphorus on surface materials with normal Ca/P ratio values similar to those seen at human bone. Peptide-coated surfaces significantly increased osteocalcin expression when compared to uncoated substrates. **Conclusions**: The in vitro results indicate that fibrilar peptide coating on topographically modified materials support and sustain adhesion and proliferation and osteogenic differentiation of MSC cells was better expressed on this type of material. Biocompatibility and osteogenic abilities of these materials recommends them as a potential support for bone implants.

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References:

[21].Dalby MJ, Gadegaard N, Tare R, Andar A, Riehle MO, Herzyk P, Wilkinson CDW, Oferro OC. The control of human mesenchymal cell differentiation using nanoscale symmetry and disorder. Nature Materials. 2007; 6(12):997-1003.

[22].Mathews S, Mathew SA, Gupta PK, Bhonde R, Totey S. Glycosaminoglycans enhance osteoblast differentiation of bone marrow derived human mesenchymal stem cells. J Tissue Eng Regen Med. 2014; 8(2):143-152

[23].Leach JK, Whitehead J. Material-directed differentiation of mesenchymal stem cells for tissue engineering and regeneration. ACS Biomat Sci Eng. 2018; 4(4):1115-1127

OXI-(CO)POLYMERIZATION OF MONOLIGNOLS ASSISTED BY PEROXIDASE ENZYME IN ONE-POT APPROACH

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Keywords: lignin; biocatalysis; peroxidase; oxi-(co)polymerization.

Introduction: Lignin represents a very important component of biomass due to its polymeric complexity which provides the structural integrity (rigidity and resistance) to the cell walls [1]. Although major achievements were obtained in the past decade, the structural intricacy of lignin still represents an important factor for its use in different applications [2]. Based on this, we propose a new pathway to control the properties of lignin using enzyme biocatalytic process.

Materials and methods: The oxi-copolymerization process of building block was performed using 2 mg/mL monolignol (SA/CA), 1.295 U mL^{-1} 2-1B peroxidase mutant [3] in PBS buffer (10 mM, pH = 7.4), 0.6% H_2O_2, 20 mg/mL functionalized support ,40°C, 24 h and 1000 rpm. Different methods such as spectrophotometry, Folin-Ciocalteu analysis, TGA, FTIR, contact angle, SEM, TPD-NH_3 were used to demonstrate the changes in the properties, structure and morphology of the artificial lignin [4].

Results: Oxi-(co)polymerization process of two monomeric structures from natural lignin (e.g. coniferyl alcohol, CA and sinapyl alcohol, SA) have been developed. Resulted polymer will be directly attached to a functionalized support in one-pot approach. Firstly, caffeic acid was bound to a

solid support (SC2–amino C2 methacrylate, ECR8309F and SC6–amino C6 methacrylate, ECR8409F) to provide phenolic structures on the particles surface, followed by the production of the polymer directly on the support surface.

Lignin-based composites had been produced via a green route starting from CA or SA monomers as monolignols. The results indicated that SA allowed to develop more efficient polymerization of monolignols compared CA. The polymeric product had higher acidity and lower hydrophobicity for SA than CA monolignols. Additionally, CA-based polymer was produced as thinner polymeric layers.

Conclusions: This study provides an efficient one-pot system for the production of artificial lignin-composites starting from monolignols. The new polymer produced has an important advantages, such as low heterogeneity and controlled properties of the polymeric mixture. One of the applications of lignin-composites is as support for biomolecules (e.g. enzyme) immobilization.

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References:

[1]. Boerjan W, Ralph J. Lignin biosynthesis,Annu. Rev. Plant Biol. 2003;54:519-546.

[2]. Buono P, Duval A, Verge P, Averous L, Habibi Y. New Insights on the Chemical Modification of Lignin: Acetylation versus Silylation, ACS Sustainable Chem. Eng. 2016;4,10:5212-5222.

[3]. Garcia-Ruiz E, Gonzalez-Perez D, Ruiz- Dueñas F, Martínez A, Alcalde M. Directed evolution of a temperature, peroxide and alkaline pH tolerant versatile peroxidase Biochemical Journal 2012;44 (1):487-498.

[4] Ion S, Opris C, Cojocaru B, Tudorache M, Zgura I, Galca AC, Bodescu AM, Enache M, Maria G-M, Parvulescu VI, One-Pot Enzymatic Production of Lignin-Composites, Front. Chem. 2018;6:124.

SOLUBILITY ENHANCEMENT OF RESVERATROL BY ENCAPSULATION INTO MESOPOROUS SILICA

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Keywords: mesoporous silica; solubility enhancement; drug delivery; resveratrol; encapsulation

Introduction: Resveratrol is a natural phenol with antioxidant properties. However, it has poor-water solubility, which limits its bioavailability. A promising strategy for increasing the solubility of biological active molecules is their encapsulation into mesoporous silica nanoparticles (MSN) [1]. Encapsulated compounds are usually amorphous, having increased dissolution rate and solubility. To date, only MSN with small pore size (<3-4 nm) were investigated as carriers for resveratrol [2]. Herein, the encapsulation and release of Resveratrol from MSN with larger pores (6-24 nm) was investigated. The effect of functionalization with organic groups was also studied.

Materials and methods: Mesocellular foam silica (MCF) and SBA-15 were prepared by sol-gel method [3]. Both MSN were also functionalized with organic groups. Resveratrol was loaded at 20% wt. final concentration in composite materials by incipient wetness impregnation. The resveratrol release profiles were obtained in phosphate buffer solution pH 7.4 and compared with the solubility curve of the pure compound.

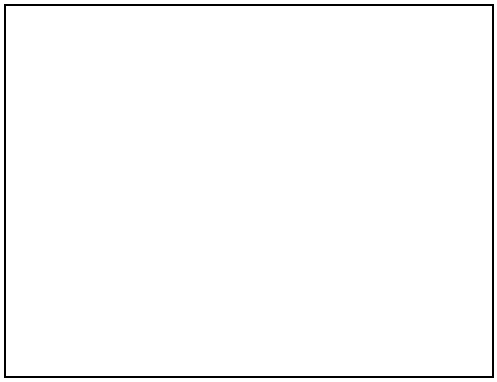

Fig. 1. Solubility enhancement of mesoporous silica encapsulated resveratrol

Results: The silica matrices and resveratrol-loaded composites were characterized by N_2 adsorption-desorption isotherms, FT-IR spectroscopy, X-ray diffraction, differential scanning calorimetry and scanning electron microscopy. The results show that the biological active compound is successfully encapsulated into the inorganic carrier mesopores, as a nanocrystalline phase. The release profiles show a significant increase in the resveratrol solubility with respect to the pure compound (Fig. 1). The resveratrol release profiles were fitted with a kinetic model based on several first order processes.

Conclusions: Mesoporous silica with average pore diameters of 6-24 nm can act as matrices for the resveratrol encapsulation. All composite materials show increased solubility of the biological active compound, up to 48 h. The solubility enhancement effect can be explained by the presence of the resveratrol molecules as nanocrystalline phases inside the carrier mesopores, having large specific surface area.

***Acknowledgements**: The financial support of the Romanian project nr. 85/2018 PCCDI is greatly appreciated.*

References:

[1] Y. Zhang, Z. Zhi, T. Jiang, J. Zhang, Z. Wang, S. Wang. Spherical mesoporous silica nanoparticles for loading and release of the poorly water-soluble drug telmisartan, Journal of Controlled Release. 2010;145:257-263.

[2] N. Summerlin, Z. Qu, N. Pujara, Y. Sheng, S. Jambhrunkar, M. McGuckin, A. Popat. Colloidal mesoporous silica nanoparticles enhance the biological activity of resveratrol, Colloids and Surfaces B: Biointerfaces. 2016;144:1-7.

[3] R.A. Mitran, D. Berger, C. Munteanu, C. Matei. Evaluation of Different Mesoporous Silica Supports for Energy Storage in Shape-Stabilized Phase Change Materials with Dual Thermal Responses, The Journal of Physical Chemistry C, 2015; 119:15177-15184.

HIGH DISPERSED Fe_2O_3-TiO_2 SUPPORTED OXIDES AS PHOTOCATALYSTS IN DEGRADATION OF AMOXICILLIN

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Keywords: antibiotic degradation, amoxicillin, supported Fe_2O_3-TiO_2, hierarchical zeolite, SBA-15

Introduction: Antibiotics are pollutants with low biodegradability and selective pressure to environmental bacteria causing the formation of antibiotic resistence genes. The present work reports the synthesis of active photocatalysts in degradation of amoxicillin from water based on supported Fe_2O_3-TiO_2 mixed oxides. Ti and Fe oxides were supported on hierarchical zeolites, possessing secondary porosity at mesoscale imposed on primary microporous structure, and on SBA-15 mesoporous silica. It was studied the effects of support and metal immobilization method on photocatalytic properties.

Materials and methods: The mesoporous supports (hierarchical Y zeolites and SBA-15 silica) were obtained by hydrothermal synthesis and mesoporous structure was obtained in the presence of cationic (CTAB) and nonionic (P123) surfactants. In the first step Ti (5% TiO_2) was supported by direct synthesis or post synthesis (impregnation) and in the second step, iron was supported by impregnation (TiO_2:Fe_2O_3 molar ratio 1:4). In order to compare the results was obtained and tested unsupported Fe_2O_3-TiO_2 mixed oxide. These materials were characterized by XRD, SEM electron microscopy, N_2 sorption, UV-Vis and Raman spectroscopy. Photocatalytic degradation of amoxicillin (AMX) from aqueous solution (30mg|L) was performed under UV and visible irradiation

Results: The obtained results confirmed the ordered porous structure for silica support, the characteristic peaks which are typical for Y zeolite, its high crystallinity and specific textural properties. XRD at low angle evidenced the ordered hexagonal porous structure typical for SBA-15 silica. The isotherm of N_2 adsorption-desorption for hierarchical zeolites highlighted the successful formation of mesopores in the system. UV–Vis absorption spectrum exhibited the presence of this narrow band gap semiconductor, as well as the reduced TiO_2 band gap, greatly ameliorated the light absorption properties, and enabled the absorption of visible light. Photocatalytic activity of materials varies depending on the synthesis route, the support and the method of metals immobilization.

Conclusions: New activie photocatalysts were obtained by dispersion of Ti and Fe mixed oxides on supports with micro and/or mesoporosity and crystalline and/or amorphous structure. The synthesis method and support properties influenced dispersion and metal oxides interaction, these being determinant parameters for the photocatalytic properties.

SYNTHESIS OF BIOLOGICALLY ACTIVE PIRAZOLONES THROUGH MULTICOMPONENT REACTIONS

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Keywords: pirazolones, multicomponent reactions, antibacterial activity, antibiofilm activity

Introduction: Recent literature mentions several "one pot" methods for the synthesis of several heterocyclic compounds, as pyrazolones, in particular [1]. We have proposed to optimize the synthesis through multicomponent reactions of substituted pyrazolones.

Materials and methods: Synthesis of pyrazolones was started from four components: phenylhydrazine, ethyl acetylacetate, β-naphthol and various aldehydes. All reagents were purchased from Sigma Aldrich. Synthetic method use the classic refluxing of the four-component with magnetic stirring and monitoring the reaction through thin layer chromatography. The NMR spectra were performed on a Varian Inova-400 (500 MHz), in deuterated chloroform or dimethyl sulfoxide (DMSO-d_6). All synthesized pirazolones are evaluated by qualitative and quantitative methods against 4 bacterial strains [2].

Results: By optimizing the syntheses (method, reaction time, solvent, catalyst) we obtained the compounds in good yields (50-60%). All pyrazolones have shown good and very good antimicrobial activity, on all microbial strains tested, as can be seen in Fig 1 (on *Pseudomonas aeruginosa*). The antimicrobial activity of pyrazolones 1-5 was better than the strains considered as standard, M+ and M-.

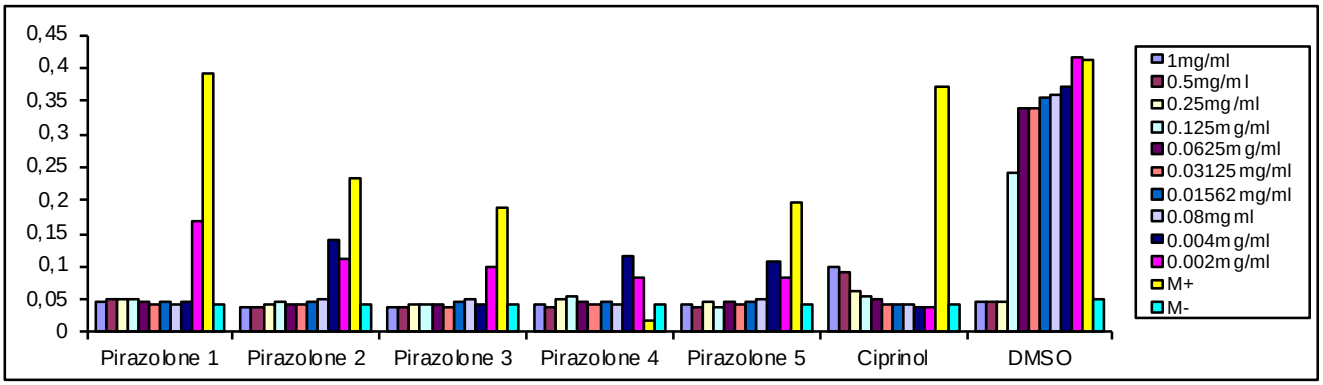

Fig. 1 Antimicrobial activity of the pirazolones **1-5** against *Pseudomonas aeruginosa*

The compounds exhibited excellent antimicrobial activity in both MIC determinations, showing better antifungal activity than antibacterial activity, the best activity on *Escherichia coli.* In the biofilm, the pyrozolones showed very good antimicrobial activity on two of the strains tested: *Streptococcus aureus* and *Pseudomonas aeruginosa*.

Conclusions: In the present study, the synthesis of 5 biologically active substituted pyrazolones was optimized using tetra-component reactions. All compounds exhibited microbicidal and antibiofilm features, both in planktonic and adherent state, therefore they can be used as antimicrobial and antibiofilm agents.

References:

[1] Marinescu M, Emandi A, Marton G, Cinteza LO, Constantinescu C, Structural studies and optical nonlinear response of some pyrazole-5-ones, Nanosci Nanotechnol Lett. 2015; 7: 846-854.
[2] Marinescu M, Tudorache DG, Marton G, Zalaru C, Popa M, Chifiriuc CM, Stavarache C, Synthesis, DFT study and antimicrobial features of some benzimidazole derivatives, J Mol Struct. 2017, 1130:463-471.

THE INFLUENCE OF FILLERS AND FLAME-RETARDANT AGENTS UPON LOW-SMOKE AND FLAME-RETARDATION PROPERTIES OF PVC-BASED COMPOSITES

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Keywords: flame-retardant agent, thermal and mechanical properties

Introduction: PVC is the world's third largest plastic in terms of sales volume. This polymer is relatively low cost, chemical resistant, has stability to weathering and versatility. It is a very durable and long-lasting construction material which can be used in a variety of applications, rigid or flexible, white or black and a wide range of colors in between. These properties lead it being used for a wide variety of applications: building, transport, packaging, electrical/electronic and healthcare. Polyvinyl chloride compounds are intensively used for cable jackets and primary electrical insulation. Such compounds can also be used for the relatively demanding plenum applications, and they must meet the requirements of the NFPA 262 test (Standard Method of Test for Flame Travel and Smoke of Wires and Cables for Use in Air-Handling Spaces). Neat PVC, rigid or unplasticized polyvinyl chloride, is difficult to ignite, but it has 56.8 % chlorine content and an oxygen index of about 47, compared to most non-halogen polymers, which have oxygen index ranging from 17.4 (polypropylene or polymethyl methacrylate) to 26 (polycarbonate). PVC is a brittle material and it is never used as an uncompounded polymer. Hence, it must be mixed with different additives, especially stabilizers. The decomposition temperature of the polymer is close to the processing temperature and for that reason stabilizers are needed. Fillers can increase stiffness and strength, improve impact performance, can also be used to add color, opacity, and conductivity to a compound. Plus, fillers can be incorporated at low extra-cost. The PVC formulator needs to select fillers that will process well, while providing the required physical performance at the lowest possible formulation cost. A good understanding of the role of fillers can lead to significant savings in material costs. Therefore, in this paper is presented the influence of the fillers and the flame-retardant agents upon flexible polyvinyl chloride systems.

Materials and methods: The studied compounds were reinforced with calcium carbonate, aluminum trihydrate (ATH) and Ultracarb (natural hydromagnesite and huntite). Calcium carbonate is the most used filler; it is usually viewed as filler rather than as a flame retardant. When heated to 1150^{o}C, it yields CO_2 endothermically, but this action takes place at a very high temperature and cannot help retarding the burning of the polymer. Yet, calcium carbonate does act as a diluent non-flammable. Through burning, calcium carbonate (especially the fine grades types) can also capture hydrogen chloride emitted during combustion and, thus, can reduce the corrosivity of the smoke, as well as provide some stabilizing action. On the surface of the polymer a protective layer, made up of aluminum oxide and the products of carbonization, is formed, which further turns off the combustion. This protective layer also reduces smoke density by adsorbing soot particles. Ultracarb is a natural halogen-free mineral that can be used as fire-retardant filler suitable for plastics and rubbers. It is produced from a deposit of hydromagnesite and huntite. For this study, Ultracarb LH15C with stearate treated surface was used.

Results: The influence of the inorganic flame-retardant fillers upon the flexible polyvinyl chloride (PVC) compounds have been systematically investigated in this paper, in terms of structure and thermal and mechanical properties, by FTIR, TGA, DMA, DSC, and tensile strength tests.

Acknowledgements:

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A NEW NANOCOMPOSITE HYDROGEL VEHICLE FOR THE TREATMENT OF GASTROINTESTINAL CANCER

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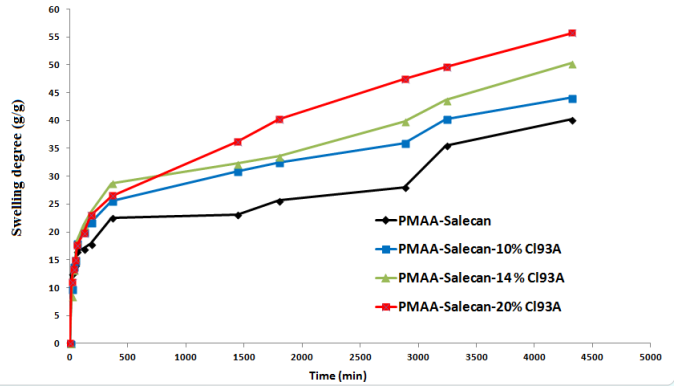
Keywords: hydrogels, nanocomposites, drug delivery

Introduction: Controlled release of drugs is a largely investigated biomedical field where hydrogels have found important applications. A drug-hydrogel system designed for controlled drug delivery displays many advantages such as: reduced toxicity in the human organism, i.e. the sides effects induced by the toxic drug attacking both healthy and target cells are minimized; improved pharmacokinetic profile by increasing the release time of the drug; the ability to carry adequate amounts of drug; selective delivery of the drug adapted to structural changes in response to various physical or chemical triggers (ex. pH variation).

The aim of the present study was to obtain novel semi-interpenetrated poly (methacrylic acid)/biopolymer hydrogel networks-clay nanocomposites by using different amounts of Salecan [1], as the biopolymer and different concentrations of Montmorillonite as the clay.

Materials and methods: The syntheses were conducted via free radical copolymerization in the presence of ammonium persulfate as initiator and N, N'-methylenebisacrylamide as crosslinking agent. In order to evidence the structural and morphological modifications as a consequence of the various clay concentrations and different amounts of Salecan, used in the synthesis process, the obtained materials were characterized by several techniques, as follows: FT-IR, TGA, X-ray diffraction and microscopy analyses (SEM, TEM), DMA and swelling studies.

Results: Influence of MMT concentration on swelling degree after 3 days.



Conclusions: Newly synthesized hydrogel nanocomposites based on different concentrations of montmorillonite and different amounts of Salecan were prepared and their properties were tested. We found that the swelling properties of the vehicle can be nicely adjusted by simply tuning the Salecan and montmorillonite concentration in hydrogel composition. FTIR spectra, confirmed the incorporation of layered silicates but also the entrapment of Salecan into the PMAA hydrogel matrix. TGA isotherms proved that the Salecan and clay presence influenced the thermal behavior of the nanocomposites hydrogels. XRD proved mainly intercalated composites were obtained. All hydrogels demonstrated spectacular porous architectures, as observed by SEM pictures. Future studies will follow the drug loading of these new hydrogel-clay nanocomposites for the treatment of gastrointestinal cancer.

***Acknowledgements**: This work was supported by a grant of the Romanian National Authority for Scientific Research and Innovation, CNCS/CCCDI-UEFISCDI, project number PN-III-P2-2.1-PED-2016-1896, within PNCDI III. The research was financially supported by MCI Core Programme in the frame of the project Nano-Bio-Sel, PN.18.22.01.01.*

References:

[1] Qi X., Wei W., Li J., Liu Y., Hu X., Zhang J., Bi L., Dong W., Fabrication and Characterization of a Novel Anticancer Drug Delivery System: Salecan/Poly(methacrylic acid) Semi-Interpenetrating Polymer Network Hydrogel ACS Biomater Sci Eng, 2015, 1, 1287–1299.

INTENSIFICATION OF MICROALGAL GROWTH DETERMINED BY MICROWAVE TREATMENT

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Keywords: microalgal oil; microwaves; biofuel

Introduction: We outline the main results obtained by using microwave treatment, applied in discontinuous mode and continuous mode on microalgal cultures. This type of treatment is new, its investigation being justified by the ever-increasing demand for alternative sources of energy, especially for biofuel. Our studies addressed this demand by developing new methods of microalgal growth, which aimed to capitalize on some of the beneficial effects that microwaves have on biological systems. The selection of microalgae was due to their significant potential to produce oil for biofuel synthesis. As compared to oil crops, the microalgae metabolic flexibility represents an advantage, as it can assure desired biochemical compositions by varying the growth conditions. In addition, photobioreactors used for microalgal growth may be installed on non-arable land, no competition ensuing with classical crops. Moreover, the production of microalgal biomass is possible throughout the whole year (e.g., [1]). Based on the results obtained so far, we also propose an original system for microwave treatment in continuous mode. The proposed system is relevant by novelty, as the current methods are using systems for microwave treatment in discontinuos mode (e.g., [2]; [3]).

Materials and methods: The microwave treatments were applied in both discontinuous and continuous mode on microalgal cultures of *Nannochloris sp.* ([4]), by varying different parameters controlling their growth conditions (e.g., treatment time and microwave power). The next main steps of the work consisted in the ultrasound-assisted extraction of microalgal biomass lipid fraction and the determination of the percentage of oil existing in the lipid fraction.

Results: The treatment in discontinuous mode with the microwave power of 220 W and the treatment time of 10 s resulted in the highest increase of the microalgal dry biomass concentration (41%), while the treatment in continuous mode with microwave powers of 5 W and 10 W and 2 to 4 days treatment time resulted in up to 11% increase of the dry biomass concentration, as compared to the respective control samples (i.e., non-irradiated with microwaves). For the continuous mode, the microwave power was determined in order to produce a significant increase (almost 40%) of the oil content compared to the control sample. In this case, we noticed that with the increase of the oil content, the degree of unsaturation also greatly increased.

Conclusions: According to the results, the use of both types of microwave treatment leads to increases in the concentration of microalgal dry biomass, thus this study will continue addressing the demand for biofuel production from microalgae. The relevance of the new system for microwave treatment in continuous mode consists in paving the way for growing microalgae in photobioreactors, by its potential to ensure proper experimental data, as well as process knowledge, to scale-up from the laboratory phase to pilot.

Acknowledgements: *The work has been funded by the Project 32PCCDI/2018.*

References:

[1]. Schlagermann, P. et al. Composition of algal oil and its potential as biofuel. Journal of Combustion, 2012; Article ID:285185:1-14.

[2]. Asadi, A. *et al*. Physiological variability in cyanobacterium *Phormidium sp*. Kützing ISC31 (Oscillatoriales) as response to varied microwave intensities. Journal of Agricultural Technology, 2011; 7(3): 665-677.

[3]. Scharff, C. et al. The use of high-frequency electromagnetic radiation for an increased productivity of microalgae in closed systems- A concept; In: International Symposium on Soilless Cultivation 1004; 2012; pp. 93:99.

[4]. Oancea, F., S. Velea, L. Ilie, E. Stepan (2015). Nannochloris sp. stain for obtainment of bio-based aviation fuel. WO 072873.

BIO - NANOPARTICLES GENERATED FROM LEAVES OF PALE-GREEN KOHLRABI

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Keywords: biosynthesis, metal nanoparticles, pale-green kohlrabi, aqueous extract

Introduction: Bio – synthesized metallic nanoparticles are constantly gaining importance since more and more plants or plant parts are used to prepare them [1,2]. Kohlrabi (*Brassica oleracea* Gongylodes Group) is a versatile vegetable with important health benefits [3]: fights cancer, improves heart health, lowers blood pressure, etc. This paper presents the biosynthesis of different metallic nanoparticles, namely silver nanoparticles (AgNPs), gold nanoparticles (AuNPs) and iron oxide (magnetite – Fe_3O_4) nanoparticles (FeONPs) from aqueous extract of Kohlrabi leaves and their potential use to retain cytostatic drugs on different functionalized polymeric membranes. **Materials and methods**: Pale-green kohlrabi was bought from the local market and its leaves were thoroughly washed, dried at room temperature for 10 days, grinded and further used to prepare the aqueous extract. A qualitative and quantitative screening of phytochemicals was performed using standard analytical methods and the aqueous extract was used for the biosynthesis of the metallic nanoparticles at 50^0C, under continuous stirring, for 4 hours. In order to confirm the formation of the metallic nanoparticles, UV-Vis, FTIR, DLS and SEM spectra were recorded, and their antioxidant activity was also determined. **Results**: The qualitative screening of phytochemicals from the aqueous extracts of pale-green kohlrabi leaves showed a positive response for saponins, carbohydrates, alkaloids, etc. thus making it a perfect raw-material for the biosynthesis of AgNPs, AuNPs and FeONPs. The UV-Vis spectra were recorded at different time intervals for all the metallic nanoparticles and exhibited peaks at 435 nm for AgNPs, 525 nm for AuNPs and 410 nm for FeNPs respectively and compared to that recorded for the aqueous extract. Using FTIR measurements we were able to determine the major functional groups present in the structure of the metallic nanoparticles (e.g.: C=C, C=O, C-H, etc.).

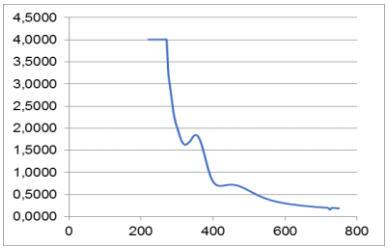

Figure 1. UV-Vis spectra of AgNPs

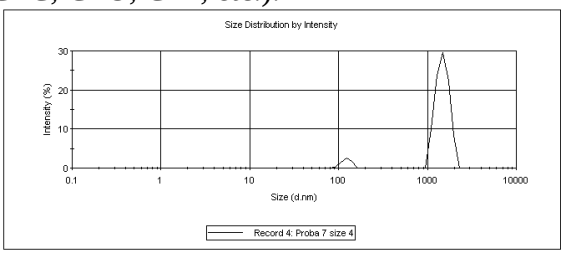

Figure 2. DLS spectra of AgNPs

Conclusions: This paper present the biosynthesis, using aqueous extract from pale-green kohlrabi leaves, of three metallic nanoparticles: AgNPs, AuNPs and FeNPs and their physical – chemical characterization using UV-Vis, FTIR, DLS and SEM. Also, preliminary studies were carried out to determine the ability of these metallic nanoparticles to retain certain cytostatic drugs once combined with polymeric membranes.

***Acknowledgements**: This research paper was prepared with the financial support of the project PN 18.22.04.01.02.*

References:

[1] Sorescu A.A., Nuta A., Ion R. M., Suica-Bunghez I. R., *"Green synthesis of silver nanoparticles using plant extracts"*, Proceedings of The 4th International Virtual Conference on Advanced Scientific Results – SCIECONF, pp. 188-193, June 6 - 10 2016, Slovakia

[2] Sorescu A.A., Ion R. M., Nuta A., Suica-Bunghez I. R., *"A review on the synthesis of silver nanoparticles. Green vs. conventional method"*, Proceedings of The 4th International Global Virtual Conference - GV-CONF 2016, pp. 211-216, 18-22 April 2016, Zilina, Slovakia

[3] Pasko P., Sulkowska-Ziaja K., Muszynska B., Zagrodzki P., *"Serotonin, melatonin, and certain indole derivatives profiles in rutabaga and kohlrabi seeds, sprouts, bulbs, and roots*", LWT – Food Science and Technology, vol. 59, 2014, pp. 740-745.

BIOBUTANOL RECOVERY FROM ABE MIXTURE USING DISTILLATION COLUMNS

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Keywords: biobutanol, ABE mixture, distillation, biofuel

Introduction: Biobutanol is obtained by fermenting biomass from a variety of sources (corn, sugar cane, wood, household and agricultural waste, etc.), in the presence of microorganisms from the Clostridium genus. The resulted mix contains three solvents that are of a great importance for the chemical industry – acetone, ethanol and butanol. The importance of recovering biobutanol consists in the possibility of it being a great replacement for fossil fuel, having similar qualities to the ones of gasoline. Moreover, biobutanol has a caloric power that is net superior to the one of alcohol, having a higher octane number, and its introduction does not require modifying the installations currently present on automobiles.

Materials and methods: The objective is to describe the technological design process of an equipment that handles the separation of the ABE mix coming from a ferment reactor with solvent recovery. The process is executed using nitrogen stripping, leading to a more concentrated ABE mix, with the purpose of recovering and purifying Biobutanol. In order to obtain pure biobutanol from the ABE mix, two installations have been modeled and studied using the Aspen Plus V9 ® simulator. The purifying of the solvents is performed in distillation columns, operated at atmospheric pressure, the separation occurring in the same order as their boiling points.

Results: The installations have been analyzed from an economical and dimensional point of view, and a comparison between the two possibilities of separations has been made.

Conclusions: Both plants provide butanol with similar quality and purity, the notable differences consist in the number of machines used and the energy consumed to obtain the same amount of butanol.

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RELEASE KINETICS OF AMLODIPINE BESYLATE AND VALSARTAN FROM PLGA-BASED NANOPARTICLES

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Keywords: nanoparticles, amlodipine, valsartan, drug release, kinetics

Introduction: The aim of this study was to investigate the release behaviour of a combination of two drugs (amlodipine besylate -AML, valsartan - VAL) from poly (D,L-lactide-co-glycolide) (PLGA).

Materials and methods: Three formulations were investigated with different ratios of AML:VAL:PLGA (1:16:5, 1:16:7.5, and 1:16:10). The drugs release from the PLGA nanoparticles was determined by a dialysis membrane method under sink conditions [1-3]. The whole system was kept under stirring at 100 rpm, using sodium phosphate buffer, *p*H 7.4 as release medium. Samples were taken at predetermined intervals (15', 30', 45', 60', 120', 180', 240', 300', 360', 420' and 24 h) from the receiver solution. The released drugs in each time point were determined by spectrophotometry using a UV-VIS spectrophotometer.

Results: In order to evaluate the *in vitro* drug release data, four kinetics models were used to describe AML and VAL release kinetics from PLGA nanoparticles. Zero-order, First order, Higuchi and Hixson-Crowell, kinetics models were applied and, on the basis of best fit with the highest correlation value (R^2), it was concluded that AML and VAL release from all samples follows the Higuchi model (R^2>0.91). *In vitro* release data showed that all formulations had a biphasic profile characterized by an initial "burst effect" of both drugs during the first half hour followed by a slower release reaching a maximum after 24h.

Conclusions: The *in vitro* release study showed a slow release for both drugs under the physiological condition (*p*H = 7.4). These data reveal that amlodipine besylate and valsartan encapsulated in PLGA nanoparticles could represent a feasible strategy for hypertension's treatment. However, further *in vitro* studies on various cell lines are needed to demonstrate the therapeutic effect.

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References:

[24].Avgoustakis K, Beletsi A, Panagi Z, Klepetsanis P, Karydas AG and Ithakissios DS. PLGA-mPEG nanoparticles of cisplatin: in vitro nanoparticle degradation, in vitro drug release and in vivo drug residence in blood properties. J Control Release. 2002; 79(1-3): 123-135.

[25].Lara MG, Bentley MV and Collett JH. In vitro drug release mechanism and drug loading studies of cubic phase gels. Int J Pharm. 2005; 293(1-2): 241-250.

[26].Nimesh S, Manchanda R, Kumar R, Saxena A, Chaudhary P, Yadav V, Mozumdar S and Chandra R. Preparation, characterization and in vitro drug release studies of novel polymeric nanoparticles. Int J Pharm. 2006; 323(1-2): 146-152.

SYNTHESIS AND EVALUATION OF PLGA NANOPARTICLES COATED WITH A LIPID LAYER FOR BIOMEDICAL APPLICATIONS

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Keywords: lipid coated polymer nanoparticles, valsartan, biomedical applications

Introduction: Nowadays intensive efforts are focused on developing drug carriers, which can provide a more efficient delivery of therapeutics. Lipid coated polymer nanoparticles represent a new and interesting class of drug carriers combining advantages of both polymeric nanoparticles, like: high stability, high carrier capacity, nanometric size that promotes effective permeation through cell membranes [1,2], and lipids, like excellent biocompatibility [3]. Therefore the objective of this study was the synthesis of polymeric nanoparticles coated with a lipid layer (L-NPs) and their evaluation for drug release.

Materials and methods: L-NPs and uncoated NPs were prepared via nanoprecipitation method using a biodegradable polymeric matrix - poly (D,L-lactide-co-glycolide) (PLGA), an amphiphilic block copolymer stabilizer (Pluronic F127) and phosphatidylcholine for coating. Valsartan, an angiotensin II receptor antagonist used in cardiovascular disease treatment, was chosen as model drug. Coated and uncoated NPs were assessed in terms of entrapment efficiency and size. Also, *in vitro* drug release studies were performed by using a dialysis membrane method under sink conditions and four models (Zero-order, First order, Higuchi and Hixson-Crowell) were applied to evaluate the *in vitro* drug release data.

Results: The designed nanoformulations presented good entrapment efficiency, small sizes and the *in vitro* release study showed a slow release of valsartan.

Conclusions: The obtained results suggest that nanoparticles coated with a lipid layer could be exploited as drug carriers for pharmaceutical and biomedical applications. However, further studies are needed to demonstrate the therapeutic effect.

Acknowledgements: This work was supported by Ministery of Research and Innovation CNCS-UEFISCDI, projects PN-III-P1-1.1-PD-2016-1756, contract no 74/2018 and 6N/ 2016-PN-16-27-02-01.

References:

[1]. Gelperina S, Kisich K, Iseman MD, Heifets L. The Potential Advantages of Nanoparticle Drug Delivery Systems in Chemotherapy of Tuberculosis. American J Resp Critical Care Med. 2005; 172(12): 1487–1490.

[2]. Grottkau BE, Cai X, Wang J, Yang X, Lin Y. Polymeric nanoparticles for a drug delivery system. Curr Drug Metab. 2013; 14(8): 840-6.

[3]. Li J, Wang X, Zhang T, Wang C, Huang Z, Luo X, Deng Y. A review on phospholipids and their main applications in drug delivery systems. Asian J Pharm Sci. 2015; 10 (2): 81–98.

STRUCTURAL DIVERSITY OF NEW COORDINATION COMPOUNDS OBTAINED FROM DIVALENT METALS AND $(PH_2PO)_2NH$ BIDENTATE LIGAND

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Keywords: divalent metal complexes, $(Ph_2PO)_2NH$ bidentate ligand, structural diversity

Introduction: The coordination chemistry of tetraorganodichalcogenoimidodiphosphinato ligands, $[(XPR_2)(YPR_2)N]^-$, raised considerable interest in last years due to the high flexibility of the XPNPY skeleton which allows easy accommodation of the ligand unit to different coordination requirements related to a particular metal atom [1], as well as to the potential applications of the corresponding metal complexes, *e.g.* NMR shift reagents, selective metal extractants, industrial uses as optical devices or catalytic systems [2].

Materials and methods: The following reagents were used in the syntheses of new coordination compounds: $Zn(ClO_4)_2\cdot 6H_2O$, $Cu(ClO_4)_2\cdot 6H_2O$, $Co(ClO_4)_2\cdot 6H_2O$, and the bidentate ligand $(Ph_2PO)_2NH$. All obtained compounds have been characterized by elemental analysis using the Euro EA Elemental Analyzer and Callidus software. Solid-state electronic spectra were recorded using the UV-Vis-NIR Jasco V670 spectrophotometer, equiped with Spectra Manager software, and MgO as reference. Vibrational spectra were recorded on a Tensor 27 spectrophotometer from Bruker with OPUS software. The FTIR spectra were recorded on pellets, using KBr as reference. Their crystal structures were determined by single-crystal X-ray diffraction using the STOE IPDS II diffractometer. ShelX software was used for structural characterization of the synthesized compounds, while the graphic representations were made using Diamond 3 program.

Results: New coordination compounds with the bidentate ligand $(Ph_2PO)_2NH$ were obtained from three different divalent metal ions: Zn(II), Cu(II), and Co(II). In all compounds, $(Ph_2PO)_2NH$ is deprotonated and coordinated as chelating bidentate ligand. The molecular structure of compound **1** was established by X-ray diffraction studies which revealed its mononuclear nature $Zn[(Ph_2PO)_2N]_2$. Zinc(II) atom is four-coordinated with tetrahedral geometry. Compound **2** is a dinuclear Copper(II) complex in which the two metal atoms are bridged by two methoxy groups. It has the molecular formula $[((Ph_2PO)_2N)Cu(\mu_2\text{-}CH_3O)]_2$. Both Cu(II) atoms are four-coordinated with square-planar geometry as seen in Figure 1. Starting from Cobalt(II) salt was obtained compound **3** which has a cubane-like $\{Co_4O_4\}$ core with metal atoms and oxygen atoms occupying alternating vertices.

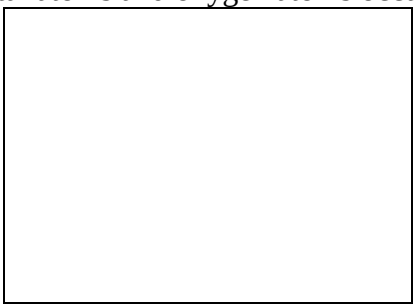

Figure 1. Molecular structure of compound 2
(Hydrogen atoms were omitted for clarity).

Conclusion: The use of the bidentate ligand, $(Ph_2PO)_2NH$, along with various metal salts, such as $Zn(ClO_4)_2\cdot 6H_2O$, $Cu(ClO_4)_2\cdot 6H_2O$ and $Co(ClO_4)_2\cdot 6H_2O$, leads to the synthesis of three new coordination compounds with different nuclearities.

***Acknowledgements**: This work was supported by the Romanian Executive Agency for Higher Education, Research, Development and Innovation - UEFISCDI (project PN-II-RU-PD-2012-3-0528) and University of Bucharest (project 154/22.01.2014).*

References:

[1]. M. Nema, M. Jönsson, R.A. Varga, A. Silvestru, C. Silvestru, Rev. Roum. Chim., 2007, 52(1-2), 51-58.
[2]. W.-M. Cheung, H.Y. Ng, I.D. Williams, W.-H. Leung, Inorg. Chem., 2008, Vol. 47(10), 4383-4391.

NEW POLYMERIC COMPOSITE FOR 3D PRINTING

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Keywords: ABS, $CaCO_3$, filament, 3D printing

Introduction: New composite polymeric filaments for 3D printing are desired [1]. They should fulfil different criteria such as ecological requirements (eco-friendly), antibacterial properties [2], and functional characteristics of mechanical strength, shape, melting behavior, and others. The filament should also consider the final requirements of the 3D printed product, e.g. its electromagnetic, optical, biomedical properties [3], esthetical details, etc. In our work we fabricated a new composite filament by mixing ABS with $CaCO_3$, targeting the ecological aspects of reducing the quantity of the polymer.

Materials and methods: Commercial ABS was dissolved in acetone, mixed with 10 % $CaCO_3$ powder, and dried by evaporation. The solid mixture was cut in small pieces and extruded at 200-215^{o}C into a filament of about 1.6 mm diameter, and 3 m length. The obtained filament was used for printing a bulk sample.

Results: We obtained a composite filament of ABS+$CaCO_3$ (Fig. 1). The first filament shows a high porosity due to strong evaporation of remnant acetone. The filament was cut in small cylinders and extruded again. The new filament was compact, dense and the powder was uniformly distributed. The 3D printing parameters were selected as for standard ABS. The printed sample had some flaws on the horizontal (top) surface, but excellent quality on the vertical walls.

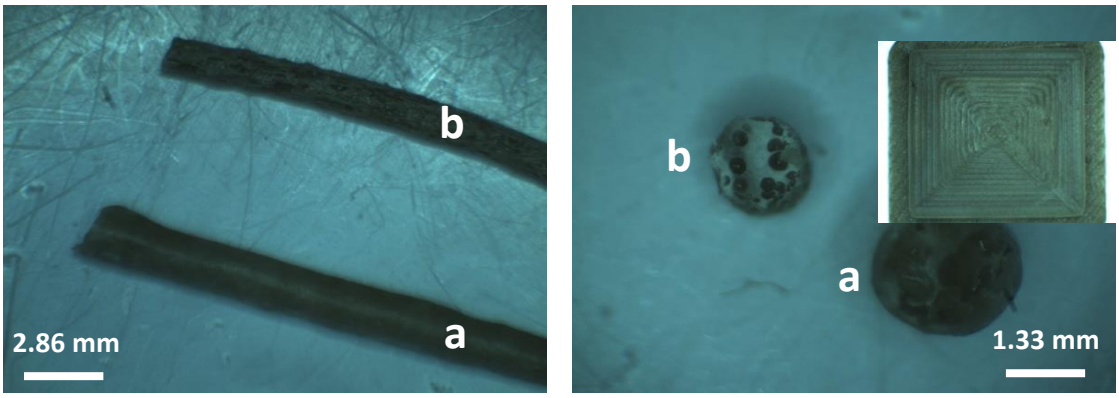

Figure 1. Optical microscopy of ABS+10 wt% $CaCO_3$ filament depending on the extrusion parameters: (a) 1st extrusion at 200°C, (b) 2nd extrusion at 215°C (left picture - longitudinal view, right picture - transversal section). The inset, 3D printed sample.

Conclusions: In our work we produced a composite filament of ABS+$CaCO_3$. The resulted filament was demonstrated to be useful for 3D printing. The decrease of the polymer amount is a promising solution for production of eco-friendly products. Extrusion temperature has strong influence on the filament quality. Further 3D printing tests are required for finding the optimal parameters (temperature, speed) towards high surface quality and layer deposition.

Acknowledgements: This work was supported by a grant of the Romanian National Authority for Scientific Research and Innovation, CCCDI-UEFISCDI, project number 74/2017 COFUND-M-ERA.NET II-BIOMB, within PNCDI III.

References:

[1]. Wang X., Jiang M., Zhou Z., Gou J., Hui D. 3D printing of polymer matrix composites: A review and prospective. Composites B 2017; 110:442-58.

[2]. Guo R., Wen J., Gao Y., Li T., Yan H., Wang H., Niu B., Jiang K. Effect of the adhesion of Ag on the effectiveness and durability of antibacterial properties. J Mater Sci 2018; 53:4759-67.

[3]. Abdul Hamid Z.A., Tham C.Y., Ahmad Z. Preparation and optimization of surface-engineered poly(lactic acid) microspheres as a drug delivery device. J Mater Sci 2018; 53:4745-58.

A FLUORESCENCE STUDY ON SOME AMINOGLYCOSIDES

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Keywords: amino-glycosides derivatization, fluorescence, molecular imprinted polymers

Introduction: Aminoglycosides are compounds belonging to a medicinal and bacteriologic category of traditional Gram-negative [1] antibacterial therapeutic agents that inhibit protein synthesis and contain as a portion of their molecules an amino-modified glycoside [2]. Examples of common aminoglycosides are gentamicin, streptomycin, kanamycin, tobramycin, and neomycin. The difficulty of their spectrometric determination from various samples is given by the lack of chromophores [3].

Materials and methods: One possibility of improving aminoglycosides detectability is the derivatization with reagents in order to induce absorbing or emitting properties. From these possibilities, the derivatisation with *o*-phtalaldehyde (OPA) to obtain fluorescent compounds was performed. Because of aminoglycosedes similar behavior in the derivatization reaction, gentamicin (GNT) was chosen as a model compound to develop a fluorimetric method for their determination. The GNT derivatization reaction with OPA was carried out at room temperature, in the presence of a sulfhydryl compound and in alkaline media and the substituted isoindole formed was detected at 445 nm using an excitation wavelenght of 356 nm.

Results: This study aims to present some results concerning the influence of some important experimental parameters on this analytical method, such as reagent concentration, pH value of the aqueous solution, and reaction time. The calibration graph was liniar from 0,1 ppm up to 10 ppm with a good precision, RSD < 5%).

Conclusions: This methods was applied to the determination of gentamicin from samples obtained by solid-phase extraction using molecular imprinted polymers.

***Acknowledgements**: This work was supported by University of Bucharest, research grand number 1490/2018.*

References:

[1]. Izquierdo P., Pavon P., Gomez-Hens A., Perez-Bendito D., Kinetic fluorimetric determination of aminoglycoside antibiotics by use of OPA and N-acetylcysteine as reagents, Fresenius J. Anal. Chem., 349, 1994, pgs. 820-823.

[2]. Omar A. M., Nagy D. M., Hammad M., Aly A. A., Highly sensitive spectrofluorimetric method for determination of certain aminoglycosides in parmaceutical formulations and human plasma, AAPS PharmSciTech., 14, 2013, pgs. 37-828.

[3]. Omar M.A., Ahmed H.M., Hammad M.A., Derayea S.M., Validated spectrofluorimetric method for determination of selected aminoglycosides, Spectrochim. Acta, 135, 2015, pgs. 472–478.

SYNTHESIS, CHARACTERIZATION AND THERMAL BEHAVIOR OF POLYNUCLEAR COORDINATION COMPOUNDS WITH ORGANOSTANNIC KNOTS

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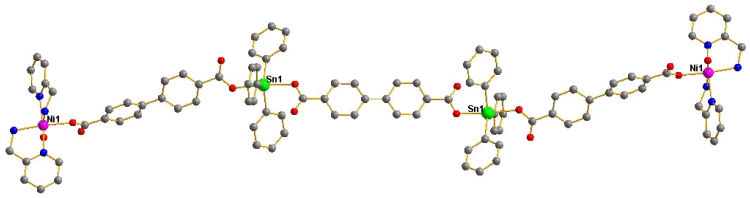
Keywords: organostannic knots, building blocks, polynuclear complexes, thermal analysis, TG-FTIR

Introduction: Organostannic compounds are of great interest due to various fields of use, especially in industry, agriculture, and medicine [1]. Over time, it has been observed that the activity of organostannic compounds and coordination compounds containing organostannic knots varies according to the nature of the organic radical, coordination number of metal atom, and structure of the compounds. The properties of polynuclear compounds with organostannic knots are influenced by the coordinating ligands used as spacers. Thermogravimetric analysis (TGA) can be used to determine the stability of a compound and to evaluate the degradation pathways under thermal stress in both inert and oxidative atmosphere [2].

Materials and methods: Three new polynuclear complexes with triphenyltin(IV) as building blocks have been synthesized. The following reagents were used in the syntheses: triphenyltin(IV) chloride (Ph_3SnCl), 4-aminopyridine (4-ampH), trimesic acid (tma), biphenyl-4,4'-dicarboxylic acid (BPDC), *trans*-$[Ni(ampy)_2(NO_3)_2]$. The single-crystal X-ray diffraction was performed using the STOE IPDS II diffractometer. The TG/DTG/DTA + FTIR measurements were performed on a Netzsch STA 409 PC thermal analyzer coupled to a Bruker Tensor 27 FTIR spectrometer equipped with a TG-IR gas cell.

Results: One of the compounds is a tetranuclear complex with a {Ni-Sn-Sn-Ni} metal sequence, in which two $Ni(ampy)_2$ and two Ph_3Sn moieties are united by three biphenyl-4,4`-dicarboxylate linker (Figure 1). The Sn(IV) atoms are pentacoordinated, with trigonal bypiramidal geometry, while the Ni(II) atoms are hexacoordinated with distorted octahedral geometry. Following the TG-FTIR analysis of the tetranuclear complex, it was observed that the material is stable up to 195 °C, and then it will lose weight in three stages, all of which are endothermic processes (Figure 2). The other two compounds are monodimensional coordination polymers formed by coordination of completely deprotonated trimesate anion to Ph_3Sn units. In both polymers, tin atoms have two different geometries: tetrahedral and trigonal bypiramidal. As a result of TG-FTIR analysis of the other two compounds are stable up to 175 °C, respectively up to 90 °C.

Conclusions: Correlation between the structure of the newly obtained compounds and their thermal behavior have been made and discussed.



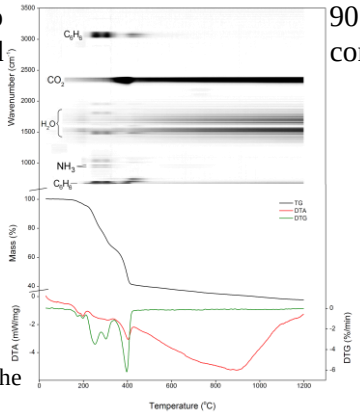


Fig. 1. Molecular structure of the tetranuclear complex. **Fig. 2** TG-FTIR analysis of the tetranuclear complex recorded in N_2.

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References:

[1]. Kimbrough, R.D., Toxicity and Health Effects of Selected Organotin Compounds: A Review. Environ Health Persp., 1976, 14, 51-56.

[2]. Chilwal, A., Malhotra, P., Narula, A.K., Synthesis, Characterization, Thermal, and Antibacterial Studies of Organotin (IV) Complexes of Indole-3-Butyric Acid and Indole-3-Propionic Acid. Phosphorus, Sulfur, and Silicon and the Related Elements, 2014, 3, 410-421.

BIO-BASED POLYAMIDE MELT-PROCESSING WITH 2D EMERGING MATERIALS

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Keywords: bio-based polyamide, thermoplastic materials, 2D materials, extrusion, injection moulding

Introduction: Bio-based plastic alternative, for a wider application spectrum involving raw products, requires several improvements in terms of processing ability (with eco-process without solvent like melt extrusion and injection moulding). Next to a high productivity and eco-process, properties improvements very often reduce the applications at industrial scale for these emerging plastics. In this work we try to prove that combining two paradigm (emerging materials like: bio-plastic and 2D materials graphene or non-graphene origin) several problems can be solved by one pot approach. In another context the automotive sector was proven a viable environment for the application of the emerging technologies and materials. In this area the weight reduction of the cars has large benefits in CO_2 reduction and fuel consumption for conventional, hybrid and electric vehicles. Therefore, the best solution is to provide viable materials based on greener technologies and from bio-renewable resources.

Materials and methods: The materials and methods used for this study in brief consisted in one matrix of bio-based polyamide, b-PA, obtained at industrial scale from decamethylene diamine and sebacic acid. Two types of graphene nanoplatelets were used, with particles distribution in different grades. One graphene nanoplatelets grade had particles with diameters approximately around 5 microns (G1) and another grade with particles bellow one micron (G2). Another 2 D material used for composite obtaining consisted in a non-graphene origin, layered structures, like hydrotalcite in a commercial grade (HT). The final polymer materials were obtained using extrusion process (using either single screw or twin screw equipment), followed by injection moulding process. Samples were analysed for the general mechanical profile by a Universal Testing Machine Instron 3382 (INSTRON, USA). Impact behaviour was tested by a HIT 5.5P Pendulum Impact Tester (ZWICK-ROELL, Germany).

Results: The initial b-PA was found quite ductile and not very promising concerning the dimensional stability. The main results highlighted the influence of the 2D filler nature on the compound processing ability. Polar 2D fillers like HT were found to be less accessible for the homogenization with b-PA matrix. This behaviour was highlighted during the processing event for the use of either single screw or twin screw extruder, before the injection moulding. The high shear force needed for the homogenization was a consequence of the strong interaction generated by carbonyl counter ion found in-between HT layers. Once the shear force was attained by using intensive extrusion (with the twin screw geometry) the level of dispersion was reflected in a notable improvement of the mechanical properties. Graphene origin 2D structures having a polarity closer to b-PA required a less intensive energy in the extrusion process and have proved a spectacular increase in the mechanical properties in terms of automatic modulus of elasticity, reducing the axial strain and improving the impact properties.

Conclusions: Mechanical properties of b-PA were improved on several directions, for both 2D structures. Axial strain of the neat b-PA was reduced by one order of magnitude in the presence of graphene nanoplatelets. Bio-based polyamide reinforced with 2D structures either graphene nanoplatelets or eco-friendly hydrotalcite were found as new materials and viable alternatives for automotive applications in what concerns the mechanical properties profile.

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THERMAL PROPERTIES OF BIO-BASED POLYAMIDE NANOCOMPOSITES WITH LAYERED STRUCTURES

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Keywords: bio-based polyamide, thermogravimetric analysis, 2D materials, differential scanning calorimetry

Introduction: Thermal analysis was proven as a viable tool to assess structural behaviour of a new bio-based polyamide. The limitation of such polymers in comparison with other polyamide fossil grade solutions can be expressed by the low glass transition temperature (close to room temperature), structural behaviour of the macromolecular chains and their associated orientation. In automotive application thermal stability is a critical parameter as well as for the processing stage during the material obtaining. Using different reinforcing layered structures like graphene particles or double layered hydroxides, some thermal properties can be negatively affected. For example, for untreated graphene particles (possessing a high thermal conductivity) the thermal inertia effect is reduced and the polymer matrix can be degraded faster and even at much lower temperatures. This behaviour can restrict not only the application area but also the processing condition parameters. In this context our goal was to find the thermal application spectra and structural involvement for a new type of 2D materials based on full bio-based polyamide and layered structures. The effects of fillers in polymer chains entanglement and orientation, phase crystallization, glass transition, melting temperature and thermal degradation behavior were investigated.

Materials and methods: The materials used for this study consisted in a bio-based polyamide PA 1010; one commercial grade graphene nanoplatelets (GnP) with an average particles size distribution under one micron; a double layered hydroxide (LDH), hydrotalcite (Sigma-Aldrich) in the carbonate form. Several composites were obtained using PA and different concentration of GnP (0-6 wt. % to polymer). The final materials were obtained with a single screw extruder, then cooled, dried and granulated. The samples were analyzed by thermogravimetric analysis (TGA) using a TGA Q5000IR equipment (TA INSTRUMENTS USA) and differential scanning calorimetry (DSC) using a DSC Q2000 equipment (TA INSTRUMENTS USA).

Results: The initial PA was found in good thermal behaviour profile for the industrial polymer processing requirements and potential automotive parts application. After using the 2D reinforcing structures only marginal decrease of the thermal stability were found. The decomposition temperature of PA 1010 was slightly decreased in the presence of different GnP concentration. The same behaviour was registered for the PA 1010 LDH nanocomposites. The influence of GnP filler concentration was reflected in the glass transition (Tg) value changes. The higher the dispersion and reinforcing effect the higher the Tg value. GnP tends to reduce the amount of free PA 1010 and the melting enthalpy has been reduced inversely proportional with GnP concentration. In the case of LDH, a strong influence on PA 1010 phase melting was registered. Small amounts of LDH (5%) also increase the PA 1010 Tg value process with clear projection also on melting-crystallization stage.

Conclusions: Thermal decomposition of PA 1010 was not much influenced by the reinforcing fillers. Polymer chains entanglement can be reduced by the presence of the different 2D fillers type and concentration. GnP and LDH affect the melting temperature and reduce the PA 1010 free phase.

***Acknowledgements**: This work was supported by a grant of the Romanian Ministery of Research and Innovation, CCCDI - UEFISCDI, project number PN-III-P1-1.2-PCCDI-2017-0387 / 80PCCDI Tehnologii emergente pentru valorificarea industriala a structurilor 2 D (grafenice si nongrafenice) Acronym EMERG2Ind, within PNCDI III.*

THE NANOMECHANICAL AND TRIBOLOGICAL PROPERTIES OF BIO-POLYAMIDE/GRAPHENE NANOCOMPOSITES

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Keywords: Bio-PA nanocomposites, Graphene, Nanoindentation, Nanoscratching

Introduction: In recent years, the interest for composites based on bio-polymers has grown, as they are a successful alternative to petroleum based plastics. Furthermore, bio-polymers reinforced with fillers have found widespread applications in many fields of industry due to their high properties. The addition of graphene to bio-polyamide provides a composite material with high mechanical properties for lightweight structures used in automotive industry. Many applications in the automotive industry require polymeric nanocomposites with improved surface properties (hardness, elasticity, wear and scratch resistance). In this paper, the effects of graphene on the nanomechanical and tribological properties of bio-polyamide were investigated.

Materials and methods: Two types of commercial graphene nanoplatelets (with different nanoparticle sizes) and a bio-polyamide (PA 1010) were used. In dynamical conditions by melt processing method, PA nanocomposites with 4 wt. % graphene nanoplatelets were obtained. The nanoindentation and nanoscratch behaviour of PA and its nanocomposites based on Graphene was examined. The nanoindentation and nanoscratch tests have been performed at room temperature on a TI Premier system (Hysitron Inc., USA) using a three-side pyramidal Berkovich tip. The nanomechanical properties were obtained by the values of hardness (H) and reduced modulus (Er). After scratching, the coefficient of friction, the surface roughness and the depth of scratch were analysed.

Results: The addition of 4 wt. % graphene nanoplatelets in bio-PA has led to changes of both Er and H, compared to neat bio-PA. The nanocomposite obtained with larger nanoplatelets had higher values than those with the smaller ones. This bio-PA nanocomposite had a lower coefficient of friction and lower scratch penetration depth than bio-PA nanocomposite obtained with smaller nanoplatelets.

Conclusions: The results showed that the two types of graphene studied influence differently the PA properties. The larger nanoplatelets grade showed a better nanoreinforcement effect than the submicron nanoplatelets grade.

***Acknowledgements**: This work was supported by a grant of the Romanian Ministery of Research and Innovation, CCCDI - UEFISCDI, project number PN-III-P1-1.2-PCCDI-2017-0387 / 80PCCDI Tehnologii emergente pentru valorificarea industriala a structurilor 2 D (grafenice si nongrafenice) Acronym EMERG2Ind, within PNCDI III.*

OBTAINING PROTEIN HYDROLYSATES FROM ORGANIC WASTE

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Keywords: soy protein, hydrolysates, organic waste

Introduction: Many plant foods possess biological properties that make them to be considered as potential functional or health promoting foods. Some of these properties are attributed to biologically active peptides and proteins [1].The purpose of this study was the complexation of amino acids obtained by alkaline hydrolysis of the soy protein isolate with zinc.

Materials and methods: The alkaline hydrolysis reactions of the soy protein isolate and the amino acid complexation were realized using an installation consisting of an Erlenmayer glass, a magnetic plate and a condensar. All experiments were performed at reflux temperature. The degree of hydrolysis was determined by UV-VIS spectrophotometry.

Results: The products obtained after the complexation reaction of amino acids obtained by alkaline hydrolysis of the soy protein isolate with zinc salt were analyzed. The Fourier transform infrared (FT-IR) analysis was used to investigate the spectral changes between complexed and uncomplexed protein hydrolyzate. The FT-IR spectra shows proves of zinc complexed protein hydrolyzate formation by displacements of peak from 1600 cm^{-1} to 1714 cm^{-1} which indicates changes in the tensile vibration of the C=O bond and the bands from the region of 1500 cm^{-1}-1600 cm^{-1} which are attributed to the symmetrical and asymmetric bending of the N─H bond indicating metal involvement in complexation.

Conclusions: The experimental data indicated that zinc complexed protein hydrolyzate were synthetized with a zinc content of 4.84%.

***Acknowledgements**: This work was supported by a grant of the Romanian Ministery of Research and Innovation, CCCDI - UEFISCDI, project number 39PCCDI/2018.*

References:

[1]. M.C. Garcı´a n , P. Puchalska, C. Esteve, M.L. Marina, Talanta 2013:106:328–349.

THE STUDY OF OXIDANT-ANTIOXIDANT STATUS IN TYPE 2 DIABETES MELLITUS

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Keywords: Type 2 diabetes mellitus, oxidant-antioxidant balance, MDA, GSH

Introduction: Hyperglycemia is considered a major initiator of oxidative stress which leads to the formation of free radicals and consequently lipid peroxidation occurs, which leads to tissue damage and diabetes mellitus development. Free radicals have been defined as intermediates of some biological redox reactions necessary for the maintenance of life. In presence of a free radical initiator and oxygen they may be oxidized this leading to lipid peroxidation, as it was suggested, might be associated with running out of hydrogen. In particular lipid peroxidation measured as levels of malondialdehyde (MDA). Glutathione (GSH), an intracellular thiol causes the eradication of free radicals or reduction in hydrogen peroxide level on state of oxidative stress. Decrease in the reduced GSH level has been reported in the erythrocyte of diabetics. Decrease in the level of GSH occurs both due to the competition between aldose reductase and glutathione reductase for NADPH, a cofactor, and increased oxidative stress (increased ratio of NADH/NAD).

Materials and methods: Thirty normal healthy subjects with fasting plasma glucose (FPG) < 5.50 mmol/L were a control group. The ages ranged from 18 to 50 years. Thirty Type 2-diabetic subjects were selected from the special center of the endocrine glands and diabetes in Thi-Qar. Glucose was determined by an enzymatic colorimetric test on basis of Trinder-Reaction. MDA was performed as described by Fong et al., while the Levels of GSH in all subjects were measured by the enzymatic recycling method.

Results: The results show a significant elevation ($P \leq 0.05$) in levels of glucose and MDA of type 2-diabetic patients in comparison with healthy subjects, which reached to 16.30 ± 0.50 mmol/L and 0.87 ± 0.19 nmol/mL for the type 2- diabetic patients, and 4.60 ± 0.15mmol L and 0.29 ± 0.5 nmol/mL for the control group, respectively. Also, it has been found a significant decrease ($P \leq 0.05$) in GSH levels in type 2- diabetic patients, which reached to 3.43 ± 0.90 µM/mL in comparison with the control group which reached to 6.13±0.21 µM/mL.

Conclusions: In conclusion we can observe that the increase in glucose levels leads to free radical formation by auto-oxidation and increase in lipid peroxidation (MDA levels), and inadequate antioxidant defense can occur during DM. In addition, GSH deficiency will make the present state worse by increasing the oxidative stress, since GSH is an important antioxidant.

***Acknowledgements**: This work supported by the Iraqi government*.

References:

[1]. Fong KL, McCay PB, Poyer, JL. Evidence that Peroxidation of Lysosomal Membranes Is Initiated by Hydroxyl Free Radicals Produced during Flavin Enzyme Activity J. Biol. Chem. 1973:248(22):7792-7. 7792

[2]. Trinder P. Ann. Clin Biochem.1989: 6: 24-33.

[3]. Kalkan IH, Suher M. The relationship between the level of glutathione, impairment of glucose metabolism and complications of diabetes mellitus. Pak J Med Sci 2013; 29(4):938-942.

[4]. Vanderjagt DJ, Harrison JM, Ratliff DM, Hunsaker LA, Vanderjagt DL. Oxidative stress indices in IDDM subjects with and without long-term diabetic complications. Clin Biochem. 2001; 34:265-270.

[5]. Greiling H, Gressner AM., Lehrbuch D. Klinischen Chemie und Pathobiochemie. 3rd ed. Stuttgart New York: Schattauer Verlag; 1995.

POLY(2-ISOPROPENYL-2-OXAZOLINE) BASED HYDROGELS FOR DRUG RELEASE SYSTEMS

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Keywords: poly(2-isopropenyl-2-oxazoline), hydrogels, biomaterials, drug release

Introduction:

Poly(2-isopropenyl-2-oxazoline) (PiPOx) is a water soluble, biocompatible and functional polymer having a 2-oxazoline heterocycle unit as a pendant group.[1,2] The reactive 2-oxazoline pendant units in the polymer side chain allow crosslinking with functional compounds such as dicarboxylic acids. Herein we report the synthesis of new hydrogels based on PiPOx using different functional dicarboxylic acids. Further on we determined the drug release kinetics for the synthesized hydrogels using diclofenac sodium (DCFNa).

Materials and methods:

Poly(2-isopropenyl-2-oxazoline), azelaic, succinic, malic, tartric acids, and L-cysteine hydrochloride monohydrate.

Results:

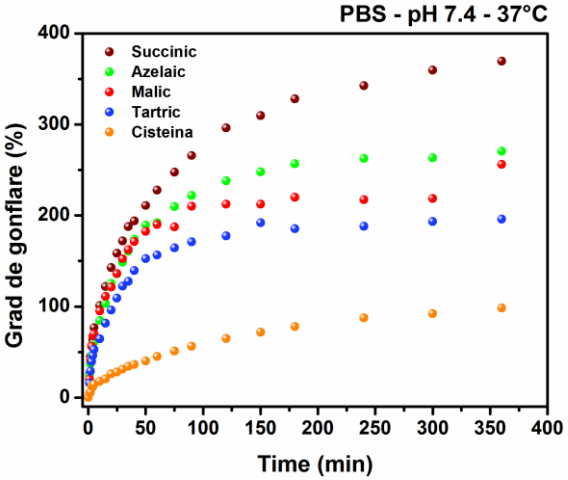

Figure 1. Swelling degree–time plots for the hydrogels in PBS

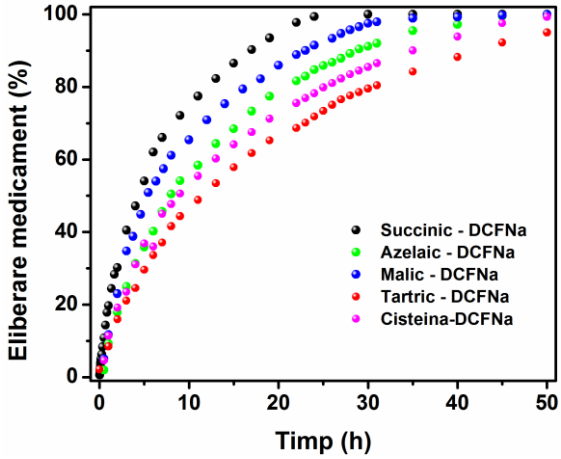

Figure 2. Dependence of DCFNa release rate on the crosslinker nature

Conclusions:

New PiPOx based hydrogels were synthesized for controlled drug released application. The equilibrium swelling degree was influenced by the nature of the crosslinker used. Controlled release experiments were conducted, and positive results were obtained working with sodium diclofenac. Hydrogel matrix interactions with different drugs will to be further investigated.

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References:

[1]. F. A. Jerca, V. V. Jerca, A. M. Anghelache, D. M. Vuluga, R. Hoogenboom, *Polymer Chemistry* **2018,** doi:10.1039/C8PY00612A.

[2]. V. V. Jerca, F. A. Nicolescu, A. Baran, D. F. Anghel, D. S. Vasilescu, D. M. Vuluga, *Reactive and Functional Polymers* **2010**, *70*, 827-835.

THE COMPOSITE PENCIL GRAPHITE ELECTRODES AS DISPOSABLE VOLTAMMETRIC SENSORS FOR DRUGS ANALYSIS

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Keywords: composite, pencil graphite electrode, dipyridamole, propranolol, metamizole

Introduction: Pencil graphite leads are composite materials consisting of graphite (~60%), clay (~30%) and a binder (e.g. high polymer) [1]. When used in voltammetric determinations, they are known as pencil graphite electrodes (PGE), which are disposable, affordable and easy to use working electrodes having also good electrochemical properties. In recent years, PGEs have been extensively used for the voltammetric analysis of different compounds among them being also some drugs [2, 3]. The present work describes the voltammetric behavior and new developed voltammetric methods using a PGE for the determination of the analgesic metamizole (MTZ) and two drugs used for the treatment of cardiovascular disease, dipyridamole (DYP) and propranolol (PRO).

Materials and methods: The drugs working solutions were obtained by succesive dilution with the corresponding supporting electrolyte of the $5 \cdot 10^{-3}$ M ethanolic DYP and of the daily prepared $1 \cdot 10^{-2}$ M aqueous PRO and MTZ stock solutions. Voltammetric recordings were carried out on an Autolab PGSTAT 12 electrochemical system equipped with a three electrodes measurement cell (working electrode: PGE) [3] and a PC running GPES 4.9 software.

Results: The influence of the electrode material, the pencil lead type (regarding hardness and bare / electrochemically pretreated surface), the nature and pH of the supporting electrolyte on the voltammetric response of the three above mentioned drugs was studied by both cyclic (CV) and differential pulse voltammetry (DPV). The optimized determination conditions were found to be: bare HB pencil leads for all three analytes, phosphate buffer solution (PBS) pH 7.00 for DYP, Britton Robinson buffer (BRB) pH 6.80 for PRO and BRB pH 1.81 for MTZ. The three drugs presented irreversible, pH-dependent oxidation peaks which are diffusion limited for PRO and MTZ and whereas DYP oxidation is both diffusion and adsorption controlled. Under optimized conditions the developed DPV on PGE methods presented wide linear ranges of more than 3 orders of magnitude, namely $7.5 \cdot 10^{-7} – 2.5 \cdot 10^{-3}$ mol L^{-1} DYP, $2 \cdot 10^{-7} – 1 \cdot 10^{-4}$ mol L^{-1} PRO and $1 \cdot 10^{-6} – 2 \cdot 10^{-3}$ mol L^{-1} MTZ, respectively. The repeatability of the electrode response for each of the three analyzed drugs, expressed as percentage relative standard deviation, was evaluated at three concentration levels. The obtained values were within the accepted limits for the respective concentration levels. The standard addition method was applied with good results to determine the active principle content of some pharmaceutical preparations of the corresponding drugs.

Conclusions: The analyzed drugs are electroactive giving well-defined oxidation DPV peaks on PGE. Based on this fact, new simple and fast DPV methods have been developed for DYP, PRO and MTZ quantification using a cheap, commonly available and disposable working electrode. The applicability of the new DPV methods was tested by successful determination of the drugs contents in pharmaceuticals.

***Acknowledgements**: This work was supported by University of Bucharest, research grand number 20045/2018.*

References

[1]. Cousta Sousa M., Buchanan JW. Observational Models of Graphite Pencil Materials. Comput. Graph. Forum, 2000; 19: 27:49.

[2]. David IG., Popa DE., Buleandra M. Pencil graphite electrodes: a versatile tool in electroanalysis. J. Anal. Meth. Chem. 2017; Article ID 1905968: 22 pages.

[3]. David IG., Florea MA., Cracea OG., Popa DE., Buleandră M., Iorgulescu EE., David V., Badea IA., Ciucu AA., Voltammetric determination of B_1 and B_6 vitamins using a pencil graphite electrode. Chem. Pap., 2015;69: 901-10.

SOLUBILITY STUDIES OF TRICLOCARBAN IN VARIOUS AQUEOUS SOLUTIONS

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Keywords: triclocarban, solubility, endocrine disruptors

Introduction: Triclocarban (TCC) or 3,4,4'-trichlorocarbanilide, $C_{13}H_9C_{l3}N_2O$ is widely used as an antimicrobial agent in disinfectants, deodorant, soaps and detergents.[1] Its large consumption led to is presence in the environment, because it is not completely removed by several water treatments.[1] This organic contaminant was recently considered a new type of endocrine disruptor which might modify the transcription of genes [2] and it bioaccumulates in algae.[3] It can be found in wastewaters from cosmetics and detergents, or even in natural waters at concentrations between 0,4-50 µg/L.[4]

The data presented in this study refers to the influence of the synthetic or natural aqueous solutions composition on TCC solubility, taking into account that data over the solubility of TCC in different solvents, or in solutions with various matrices, especially regarding inorganic ions and organic matter are not present in the literature.

Materials and methods: Triclocarban (TCC), (minimum purity 99 %) was from Fluka/Sigma-Aldrich Chemical, Germany; humic acid of technical purity was from Sigma-Aldrich and acetonitrile of HPLC grade purity was purchased from Merck. The chromatographic method (HPLC) applied was described in [5].

Results: The solubility of the TCC is influenced by the chemical composition of the aqueous solution and by the temperature. The experiments of TCC solubility were performed in ultrapure water, in humic acid aqueous solutions of 10 and 50 ppm and in NaCl aqueous solutions of 0.01 M and 0.05 M at two temperatures, 25°C and 5°C. The results indicated the following values in certain conditions: TCC solubility in ultrapure water was 0.12 g/L (at 25°C) and 0.092 g/L (at 5°C),; TCC solubility in 10 ppm humic acid solution was 0.071 g/L (at 25°C) and 0.071 g/L (at 5°C); TCC solubility in 0.01 M NaCl solution was 0.041 g/L (at 25°C) and 0.022 g/L (at 5°C); TCC solubility in 0.05 M NaCl solution was 0.028 g/L (at 25°C) and 0.019 g/L (at 5°C).

Conclusions: The organic hydrophobic compound TCC shows higher values of the solubility in ultrapure water, in comparison with those in aqueous solutions with different salinities. Solubility of TCC decreases by decreasing temperature, but it increases by increasing the concentration of humic acid in the solution. Fulvic acid present in aqueous solutions also leads to higher values of the TCC solubility, in comparison with those determined in the presence of humic acid.

References:

[1]. Ding S.L., Wang X.K., Jiang W.Q., ZhaoR.S., Shen T.T., Wang C.,Wang X. Influence of pH, inorganic anions and dissolved organic matter on the photolysis of antimicrobial triclocarban in aqueous systems under simulated sunlight irradiation. Environ. Sci. Pollut. Res.2015, 22, 52014-5211.

[2]. Hynther A., Bromba C.M., Wulff J.E., Helbing C.C. Effects of triclocarban, triclosan and methyl triclosan on thyroid hormone action and stress in frog and mammalian culture systems. Environ. Sci. Technol., 2011, 45, 5395-5402.

[3]. Schebb N.H., Inceoglu B., Morisseau C., Ahn K.C., Gee S.J., Hammock B.D. Investigation of human exposure to triclocarban after showering and preliminary evaluation of its biological effects, Environ. Sci. Technol., 2011, 45, 3109-3115.

[4]. Snyder E. H., O'Connor G. A., McAvoy D. C. Measured physicochemical characteristics and biosolids-borne concentrations of the antimicrobial Triclocarban (TCC). Sci. Total Environ.2010,408, 2667–2673.

[5]. Senin, R. M., Ion, I., Oprea, O., Vasile B., Stoica, R., Ganea, R., Ion, A.C.(2018) Soprtion of bisphenol A in aqueous solutions of fullerene C60, *Rev. Chim*., 69(6), in press.

CONSTRUCTION OF MONOLIGNOL-BASED COMPOSITES USEFUL FOR ENZYME IMMOBILIZATION

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Keywords: Lignin; Oxi-(co)polymerization; Co-solvent; Immobilized lipase.

Introduction: Processed lignin finds applications as stabilizer in colloidal suspensions, dispersing agent, binder for drilling agents, glue, surfactant, adhesive and cement additive, component of animal feed, pesticide etc. [1]. At industrial scale, the use of lignin finds many limitations, mostly due to its variety in composition, which is influenced by the source of extraction (hardwood, softwood, different species of plants), as much as by the method of extraction (kraft process, soda process, oragnosolv etc.) [2]. An alternative to limit the lignin drawbacks is to construct lignin polymer with predictable structure and properties. Such a product is called artificial lignin. In this study, artificial lignin has been synthesized based on biocatalysis starting from coniferyl alcohol (CA), as strategic monomer.

Materials and methods: The materials and methods used for this study are: amino-activated resins particles (amino C2/C6 methacrylate), 4-phenylenediamine, 4-amino-2-hydroxybenzoic acid, glutaraldehyde, coniferyl alcohol, aniline, lipase from *Candida antarctica*, MeOH, EtOH, THF. To evaluate the activity of the immobilized lipase the p-nitrophenol method has been used.

Results: Biocatalytic system for CA polymerization has been developed. The polymer was produced directly on a solid support previously functionalized with cross-linker (e.g. 4-phenylenediamine and 4-amino-2-hydroxybenzoic acid). The solid support used consisted of amino-activated resins particles (amino C2/C6 methacrylate). First, the support was functionalized by the attachment of 4-phenylenediamine and 4-amino-2-hydroxybenzoic acid, respectively. Then, oxi-(co)polymerization process of CA/CA and aniline using peroxidase enzyme as bio-catalyst and H_2O_2 for initiating the oxidation process has been performed. The preparation approach is described in details in our published study [3]. As an application for the monolignols-based composites, they have been tested as a solid support for lipase immobilization. Lipase from *Candida antarctica* has been covalently immobilized. The activity of the bio-catalytic materials was evaluated based on p-nitrophenol method. Using the absorbance of blank solutions prepared in the same conditions, the conversion rates of the oxi-(co)polymerization process were calculated and presented comparatively (Figure 1).

Figure 1. Comparative results for the conversion rate of the oxi-(co)polymerization process of coniferyl alcohol with aniline (P2) and without aniline (P1) on solid support

Conclusions: Biocatalytic alternative for valorization of lignin has been developed. Prepared lignin-based composites exhibited a good alternative as support for lipase immobilization due to their physico-chemical properties.

References:

[1]. Vishtal A, Kraslawski A. Challenges in Industrial Applications of Technical Lignins. BioResources. 2011; 6: 3547-68.

[2]. Ahvazi B, Cloutier E, Wojciechowicz O, Ngo TD. Lignin Profiling: A Guide for Selecting Appropriate Lignins as Precursors in Biomaterials Development. ACS Sustainable Chem. Eng. 2016; 4: 5090-105.

[3]. Ion S, Opris C, Cojocaru B, Tudorache M, Zgura I, Galca AG, Bodescu AM, Enache M, Maria GM, Parvulescu VI. One-Pot Enzymatic Production of Lignin-Composites. Front. Chem. 2018; 6:124.

A GUIDE WITH THE MOST COMMON PLASTICS

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Keywords: plastics, Polyethylene terephthalate, Polyamides, Polyethene, recycling

Introduction: Plastic is material consisting of any of a wide range of synthetic or semi-synthetic organic compounds that are malleable and so can be molded into solid objects. In developed economies, about a third of plastic is used in packaging and roughly the same in buildings in applications such as piping, plumbing or vinyl siding. Other uses include automobiles (up to 20% plastic), furniture, and toys. In the developing world, the applications of plastic may differ. This category includes both commodity plastics, or standard plastics, and engineering plastics. The most common plastics are: Polyamides, Polyester, Polyethylene Polyethylene terephthalate, etc. They are used every day due to their widespread applications such as bottles, packaging, clothes and more. Most plastics are durable and degrade very slowly, as their chemical structure renders them resistant to many natural processes of degradation. However, microbial species capable of degrading plastics are known to science, and some are potentially useful for the disposal of certain classes of plastic waste.

Polyamides (PA) or nylon is part of the family of polymers. It was originally intended as a synthetic silk replacement, for military applications such as parachutes. Today, it is used in clothing, guitar strings and fishing lines.

Polyethylene terephthalate (PET) is a lightweight polymer and comes in forms of varying rigidity. It's commonly used for plastics drink bottles and also for clothing fibers. Additionally, it's used in ready meal packing and tapes.

Polyethene is the most produced plastic and comes in a number of different forms, including high density polyethene and low density polyethene. It is used in plastic bags, bottles, plastic films and toys. It is not biodegradable.

Plastic recycling is the process of recovering scrap or waste plastic and reprocessing the material into useful products. Since the vast majority of plastic is non-biodegradable, recycling is a part of global efforts to reduce plastic in the waste stream, especially the approximately 8 million tons of waste plastic that enters the Earth's ocean every year.

Materials and methods: The poster will present the main plastic materials and how they can be recycled and what they can get from recycling.

Conclusions: Plastic polymers must be recycled because they are toxic to the environment.

Acknowledgements*: This work was supported by a grant of the Romanian Ministery of Research and Innovation, CCCDI - UEFISCDI, project number 40PCCDI/2018.*

References:

[1] Vert, Michel; Doi, Yoshiharu; Hellwich, Karl-Heinz; Hess, Michael; Hodge, Philip; Kubisa, Przemyslaw; Rinaudo, Marguerite; Schué, François (2012). "Terminology for biorelated polymers and applications (IUPAC Recommendations 202)" . Pure and Applied Chemistry. *Pag. 377–410.*

[2] Life cycle of a plastic product. Americanchemistry.com. Retrieved on 2017-09-15

[3] Yutaka Tokiwa; Buenaventurada P. Calabia; Seiichi Aiba (September 2009). "Biodegradability of Plastics". International Journal of Molecular Sciences.

[4] Chetna Sharon; Madhuri Sharon (2012). "Studies on Biodegradation of Polyethylene terephthalate: A synthetic polymer" Journal of Microbiology and Biotechnology Pag. 248–257.

NANOPARTICLE-MEDIATED DELIVERY OF ANTIMICROBIAL PEPTIDE FOR ENHANCED PERFORMANCE OF MEDICAL IMPLANTS

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Keywords: nanoparticles, drug delivery, coatings, laser, antimicrobial

Introduction: As the incidence of microbial resistance continues to increase in the world, the search for new alternatives to antibiotics, with novel action mechanisms, has become of utmost importance. Herein, we report on the laser fabrication of thin films containing antimicrobial peptides-based nanoparticles.

Materials and methods: The nanovectors have been delivered to surfaces as coatings using Matrix Assisted Pulsed Laser Evaporation (MAPLE) that allowed for accurate and precise thickness control, preservation of the chemical integrity of antimicrobial function, physicochemical integrity, and compatibility with non-contact masking techniques. Preliminary characterization of coatings included SEM, TEM, and XRD, in order to check the coating uniformity, nanoparticle shape and crystallinity. The comparative chemical investigation of the target and coatings was performed by FTIR to verify functional group and bonding, and adherence tests at the substrate-nanocoatings interface. The antimicrobial activity has been assessed on planktonic and biofilm embedded Gram-negative bacilli resistant strains and the inhibitory activity was quantified by measuring the density of liquid cultures or number of viable biofilm cells. Furthermore, the biocompatibility of obtained nanovectors will be reported.

Results: We obtained biocompatible thin films with remarkable antimicrobial properties.

Conclusions: Our studies indicate that antimicrobial peptides-based nanoparticles prepared by MAPLE may be used to impart antimicrobial activity to implants, medical devices, and other contact surfaces. All tests recommend our thin films as new strategies against biofilm formation and removal.

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THE INFLUENCE OF THE STEREOISOMERY ON THE PROPERTIES OF SOME MODIFIED RENEWABLE POLYMERS DESIGNED FOR DURABLE 3D PRINTING

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Keywords: 3D printing, stereoisomers, renewable, durability, polymers

Introduction:

Because of the two asymmetric carbon atoms in the molecule, lactide possesses three optical isomers or stereo-isomers, namely, L-, D-, and meso-lactides. Different PLAs were prepared from these isomers one of them even at industrial scale [1]. The aim of the paper was to study the influence of the D-isomer content of some PLAs with different molecular weight on the properties of PLLA to obtain materials for 3D printed durable applications.

Materials and methods:

The new materials were obtained by melt compounding in classical conditions, of some PLAs with different D-isomer content (PDLA) and different molecular weight. Thermal behaviour of the new compounds was investigated by differential scanning calorimetry and the morphology by polarized optical microscopy. The impact properties were measured in line with the polymer characterization practice.

Results:

The properties of the new obtained materials depend on the studied parameters (fig.1-2)

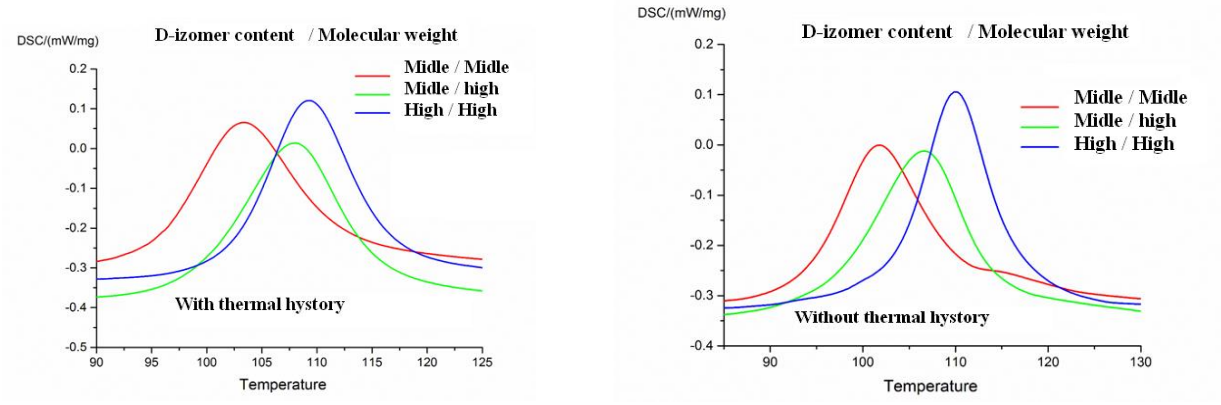

Fig.1-2. The influence of the D-isomer content and of the molecular weight of some PLAs on the crystallization of PLLA–extrusion grade

Conclusions:

Because of stereo-complexation the crystallinity, heat resistance and impact behavior of PLLA was improved which means enhanced durability of the new materials. The greater the D-isomer content and the molecular weight of the PDLA the more important are the improving of the properties of the new materials.

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References:

[1] Idong Feng, Bao Zhang, Xinchao Bian, Gao Li, Zhiming Chen, and Xuesi Chen Thermal properties of polylactides with different stereoisomers of lactides used as comonomers. Macromolecules 2017;50(16):6064–6073.

APPLICATION OF NATURAL FRUIT EXTRACTS AS GREEN CORROSION INHIBITORS FOR STEEL IN NATURAL WATER

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Keywords: natural fruit extracts, corrosion, steel, natural water

Introduction: Corrosion of metals and alloys particularly in different media is an enormous economic problem. Among the various methods to avoid or prevent destruction or degradation of metal surface, the corrosion inhibitor is one of the best knowing methods of corrosion protection and is the most useful on the industry. The corrosion inhibitors has prompted the search for green corrosion inhibitors because are biodegradable in nature, do not contain heavy metals or other toxic compounds [1-3]. Corrosion inhibitors may be inorganic or organic substances (i.e. chromates, nitrites, alkanolamine, mercaptobenzothiazole, benzotriazole). These have been widely used as effective and good metal corrosion inhibitors in various corrosive environments to reduce the corrosion rate of metals (i.e. iron, steel, aluminum) [2,3]. In addition to being environmentally friendly and ecologically acceptable and inexpensive, extracts from different parts of plant (fruits, leaves, seeds, flowers, peel) could efficiently replace and eliminate the negative impact caused by conventional anticorrosive products because get adsorbed on the metal surface and can decelerate the corrosion rate [2-4].

The main objective of the present study was to evaluate the corrosion inhibition efficiency of different natural fruit extracts on steel in the natural water.

Materials and methods: The small rectangular coupons of steel were used for corrosion tests. The coupons was weighed and then suspended in glass bottles what contain small amount of natural water, without and with different natural fruit extracts (cowberry and bilberry). After 5 days, the coupons were taken out and the corrosion products were removed using a solution of ammonium citrate. Afterwards the coupons were dried using the filter paper and weighed accurately using an analytical balance. The corrosion tests were performed at room temperature without any other aeration or agitation. The corrosion rate was examined by gravimetric method. In order to evaluate the corrosion of steel, corrosion rate and corrosion inhibitor efficiency (percentage) were calculated.

Results: The obtained results shows that the corrosion rate of metal decreases after specified period of time, when extracts of natural fruit were used.

Conclusions: The best value of corrosion inhibition efficiency for steel was over 60%, when cowberry extract was used. The natural fruit extracts reduces the corrosion rate of steel in the natural water.

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References:

[1]. Khan G, Newaz KMdS., Basirun WJ, Mohd Ali HB, Faraj FL, Khan GM. Application of Natural Product Extracts as Green Corrosion Inhibitors for Metals and Alloys in Acid Pickling Processes- A review, Int J Electrochem Sci. 2015;10:6120-4.

[2]. Al-Otaibi MS, Al-Mayouf AM, Khan M, Mousa AA, Al-Mazroa SA, Alkhathlan H Z. Corrosion inhibitory action of some plant extracts on the corrosion of mild steel in acidic media. Arab J Chem. 2012;1-7.

[3]. Bribri El A, Tabyaoui M, Tabyaoui B, Attari El H, Bentiss F. The use of Euphorbia falcata extract as eco-friendly corrosion inhibitor of carbon steel in hydrochloric acid solution. Mater Chem Phys. 2013;141(1):240-7.

[4]. Faustin M, Maciuk A, Salvin P, Roos, C, Lebrini M. Corrosion inhibition of C38 steel by alkaloids extract of Geissospermum leave in 1 M hydrochloric acid: Electrochemical and phytochemical studies. Corros. Sci. 2015; 92:287-0.

COMPARATIVE STUDY FOR OBTAINING INULINASE AND INVERTASE BY YEASTS

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Keywords: inulin, inulinase, invertase, yeasts, bioprocess,

Introduction: Inulinases (EC 3.2.1.7) are enzymes that catalyze the hydrolysis of inulin to fructose and fructooligosaccharides. Invertases (EC 3.2.1.26), also called beta-fructofuranosidases break the terminal non-reducing beta-fructofuranosides residues. These enzymes have important applications in the food and pharmaceutical industry.

Microorganisms are important sources for obtaining enzymes [1]. Among the producing microorganisms are bacteria (e.g., *Bacillus* sp., *Pseudomonas* sp., *Streptomyces* sp.), yeasts (*Saccharomyces* sp., *Candida* sp., *Hansenula* sp.) and fungi (*Aspergillus* sp., *Penicillium* sp.) [2].

Our goal was to obtain inulinases and invertases in submerged cultivation with strains of yeasts.

Materials and methods: Yeast strains used in bioprocesses belong to the microbial culture collection of INCDFC-ICCF and are from species *Saccharomyces*, *Candida* and *Hansenula*. Media used in bioproceses contained preponderant inulin, and yeast extract. For enzymatic activity determination was used the method described by Miller [3].

Results: Although all strains of yeast used in bioprocesses produced both inulinases and invertases, for *Candida arborea* ICCF 193 were obtained the best results.

Conclusions: Based on the performed studies, it was observed that the bioprocessing media induced predominantly the production of invertase, according to enzymatic activities obtained.

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References:

[1]. Periasamy Anbu, Subash C. B. Gopinath, Arzu Coleri Cihan, and Bidur Prasad Chaulagain, "Microbial Enzymes and Their Applications in Industries and Medicine," BioMed Research International, 2013, vol. 2013.

[2]. Habibullah Nadeem, Muhammad Hamid Rashid, Muhammad Hussnain Siddique, Farrukh Azeem, Saima Muzammil, Muhammad Rizwan Javed, Muhammad Amjad Ali, Ijaz Rasul, Muhammad Riaz, Microbial invertases: a review on kinetics, thermodynamics, physiochemical properties, Process Biochemistry, 2015, 50 (8), 1202-1210.

[3]. Miller GL, Use of dinitrosalicylic acid reagent for determination of reducing sugar. Anal Chem, 1959, 31:426–428.

STUDY ON ANTIBACTERIAL ACTIVITY OF SILVER NANOPARTICLES AGAINST BACTERIA FROM *PSEUDOMONAS* SP. AND *BACILLUS* SP.

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Keywords: antibacterial activity, silver nanoparticles, Pseudomonas sp., Bacillus sp.

Introduction: Silver nanoparticles (AgNPs) are used in many applications because of their biocidal action against viruses, bacteria and fungi [1]. Our goal was to investigate antibacterial activity of AgNPs against some strains from *Pseudomonas* sp. and *Bacillus* sp..

Materials and methods: *Pseudomonas* sp. and *Bacillus* sp. strains used in experiments belong to the microbial culture collection of INCDFC-ICCF. For AgNPs synthesis, silver ions were treated with plant aqueous extracts by a method described by Singhal et al. [2]. Plant aqueous extracts from *Ocimum basilicum* L. and *Menta piperita* L. were obtained by solid-liquid extraction in a Soxhlet installation.

The qualitative biochemical fingerprint of aqueous extracts from *Ocimum basilicum* L. and *Menta piperita* L. was investigated by UV-VIS spectroscopy.

Results: Best results in terms of antimicrobial activity were obtained for AgNPs synthesized by bioreduction with plant aqueous extracts from *Ocimum basilicum* L.

Conclusions: Silver nanoparticles demonstrated a powerful antibacterial activity against all four strains from *Pseudomonas* sp. and *Bacillus* sp.; the inhibition zones remained unchanged for more than one week.

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References:

[1]. Navindra Kumari PalanisamyEmail author, Nas Ferina, Athirah Nur Amirulhusni, Zaini Mohd-Zain, Jamal Hussaini, Liew Jian Ping, Rajkumar Durairaj, Antibiofilm properties of chemically synthesized silver nanoparticles found against *Pseudomonas aeruginosa*, Journal of Nanobiotechnology, 2014, 12:2.

[2]. Garima Singhal, Riju Bhavesh, Kunal Kasariya, Ashish Ranjan Sharma, Rajendra Pal Singh, Biosynthesis of silver nanoparticles using *Ocimum sanctum* (Tulsi) leaf extract and screening its antimicrobial activity, J Nanopart Res, 2011, 13: 2981.

NEW METHOD FOR PRODUCTION OF VERBENOL AND VERBENONE USING PEROXIDASE-LACCASE BIENZYMATIC BIOCATALYTIC SYSTEM

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Keywords: (+)-α-pinene; peroxidase; laccase; allylic oxidation.

Introduction: α-pinene, a bicyclical hydrocarbon ($C_{10}H_{16}$) with a monoterpenoidic structure is present in high concentrations in essential oils from pine trees and rosemary plant [1]. Moreover, α-pinene is a very important component of turpentine as waste materials of paper and pulp industry. Chemically, α-pinene is a versatil molecule. Following only the oxidative route, α-pinene leads to formation of important compounds like campholenic aldehyde, verbenol, verbenone and α-pinene oxide with important contributions in fields like pharmaceutical, cosmetic, chemical and food industries [1]. While verbenone is an important intermediate of taxol synthesis (therapeutic drug used for treating cancer), verbenol is used in food industry as a flavoring component in soups, meats, soft drinks or ice-cream [1].We propose a biocatalytic route to synthesize verbenol and verbenone via allylic oxidation of α-pinene using peroxidase-laccase cocktail as biocatalyst and H_2O_2 as oxidation reagent.

Materials and methods: The enzymes CPO (Chloroperoxidase from Caldariomyces fumago), HRP (Horseradish peroxidase), PaDa-I (mutant of UPO from Agrocybe aegerita expressed in Saccharomyces cerevisiae), BB8 and 2-1B (mutants of VPO from Pleurotus eryngii expressed in Saccharomyces cerevisiae), EP004, EP010 and EP013 from EUCODIS Bioscience) were dissolved in aqueous Acetate Buffer solution 0,01M (pH=5,02), followed by adding the laccase type enzyme (Laccase M120), the substrate ((+)-α-pinene) and the oxidation reagent (H_2O_2 30%). The solution was shacked at 25-40°C, followed by freezing and extracting the products with acetonitrile, centrifuged and filtrated using a syringe filter. The samples were analyzed using HPLC.

Results: Set up and optimization of the biocatalytic system for allylic oxidation of α-pinene had been developed. (+)-α-pinene was oxidized using H_2O_2 assisted by peroxidase and laccase. Optimum parameters of the process have been set up as 40°C Therefore, the biocatalytic system allowed to transform α-pinene with a conversion of 87% and selectivity of 77%.

Conclusions: A biocatalytic system for selective synthesis of verbenol and verbenone via allylic oxidation had been developed. The composition of the produced mixture verbenol-verbenone can be varied according with the experimental conditions. The developed system is a good alternative for green production of verbenol and verbenone interesting for flavor and fragrances industry.

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References:

[1]. Negoi A, Parvulescu V, Tudorache M. Peroxidase based biocatalysis in a two phase system for allylic oxidation of α-pinene . Catal. Today 2018;306:199–206.

THE ASSESSMENT OF TAXODIUM DISTICHUM VOLATILE OIL: CHEMICAL COMPOUNDS AND ACUTE TOXICITY

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Keywords: bald cypress tree; volatile oil; toxicity; TLC; GC-MS

Introduction:

Taxodiaceae family includes 10 genera, of which very well known is *Taxodium*. By some authors, this genus is monotypic and the *T. distichium* species has 3 subspecies [1]. The leaves and the seeds have been traditionally used as antimalarials and in treating liver disease. The research of the past decade has revealed antitumour, antimicrobial, antihelmintic, and antiinflammatory properties [2].

In this research we are looking to obtain, characterize and evaluate the toxicity of the volatile oil from bald cypress cultivated in Romania.

Materials and Methods:

The volatile oil has been obtained from leaves and female cones by steam distillation and the major chemical compounds have been studied by TLC and GC-MS [3]. The acute toxicity has been investigated on the *Daphnia magna* crustacean comparative to thujone reference.

Results:

The volatile oil was extracted with a yield of 0.115% from leaves and with a yield of 1.165% from female cones. The main compounds identified by TLC and GC-MS were: α-pinene, caryophyllene oxide, caryophyllene, camphene, terpinen-4-ol, α-thujone and β-thujone. The biological testing has pointed out a high toxicity of the volatile oil compared to the thujone reference.

Conclusions:

The research undertaken has lead to preliminary results useful for pharmaco-botanical research of T*axodium distichum* cultivated in Romania.

References:

[1]. Miller, D. H., Bacchus, S. T., & Miller, H. A. (1993). Chemical differences between stressed and unstressed individuals of bald-cypress (Taxodium Distichum).Florida Scientist, 178-184.

[2]. Su, Z., Yuan, W., Wang, P., & Li, S. (2013). Ethnobotany, phytochemistry, and biological activitiesof Taxodium Rich.Pharm. Crop,4, 1-14.

[3]. El Tantawy, M. E., El Sakhawy, F. S., El Sohly, M. A., & Ross, S. A. (1999). Chemical composition and biological activity of the essential oil of the fruit of Taxodium distichum L. Rich growing in Egypt. Journal of Essential Oil Research,11(3), 386-392.

NEW FUMARATE POLYNUCLEAR SYSTEMS WITH ORGANOTIN NODES

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Keywords: Organotin nodes, fumarate linker, polynuclear systems

Introduction: Organotin(IV) compounds have been intensively investigated because of their outstanding structural diversity, as well as catalytic and biological properties [1]. A new series of coordination compounds with different organotin(IV) subunits as nodes and fumarate anions as spacers were prepared. The influence of the nature of organotin(IV) nodes on the structural properties of the new systems obtained was investigated.

Materials and methods: Three organotin(IV) halides - Ph_3SnCl, Me_3SnCl, Bu_3SnCl - have been used, along with fumarate anions, to synthesize new polynuclear coordination compounds. The elemental analysis of the obtained compounds was performed using the Euro EA Elemental Analyzer (Euro Vector) using a Callidus software. Molecular structures were determined by single-crystal X-ray diffraction with a STOE IPDS II diffractometer using the SHELX-97 and Diamond 3 softwares for calculations and graphical representations. IR spectra of all samples were recorded in the range of 4000-400 cm^{-1} using a Bruker Fourier Transformance Tensor V-37 spectrophotometer, using OPUS software and KBr as reference.

Results: A new series of 0-D, 1-D, 2-D, and 3-D coordination compounds with triorganotin(IV) nodes and fumarate anion as *spacer* has been synthesized. All compounds have been characterized by elemental analysis, IR spectroscopy, and single crystal X-ray diffraction. Compound **1**, $[(Ph_3SnCl)_2(\mu_4\text{-fumarate})[(Ph_3Sn\text{-bipy})_2]$, a 0-D complex, contains a tetranuclear triphenyltin(IV) fumarato-cluster. The tin atoms have trigonal bipyramidal geometry, with the phenyl groups in equatorial positions and an oxygen atom from the fumarate ligand in one axial position. The second axial position is occupied at two opposing tin atoms by the monodentate 4,4'-bipyridyl ligand, and at the other two tin atoms by chlorine atoms maintained from the starting reagent. Complex **2**,$\{[Ph_3Sn(CH_3OH)]_2(\mu_4\text{-fumarate})[(Ph_3Sn)_2(\mu_2\text{-fumarate})]\cdot CH_3OH\}_n$, is a 1-D coordination polymer in which the tetranuclear triphenyltin(IV) fumarato-clusters from compound **1** are linked by bidentate fumarate *linker*s. Replacing the starting reagent Ph_3SnCl with Me_3SnCl and Bu_3SnCl, respectively, two new compounds have been obtained. Single crystal X-ray diffraction studies revealed a 2-D framework with a parquet-like network topology for compound **3**. The 3-D extended structures of compounds **3** and **4** are depicted in Figure 1 and Figure 2, respectively.

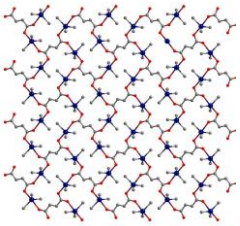

Figure 1. Molecular structure of compound **3**

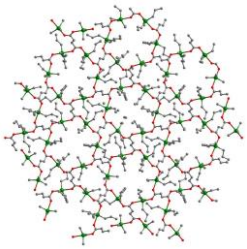

Figure 2. Molecular structure of compound **4**

Conclusion: The influence of organotin(IV) nodes on the dimensionality of the obtained coordination polymers with fumarate anions as linkers was investigated. The biological activity of all obtained compounds is under investigation.

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References:

[1] Pruchnik, H., Lis, T., Latocha, M., Zielinska, A., Prunchnik, P., J. Organomet. Chem., 2015, 777, 81-87.