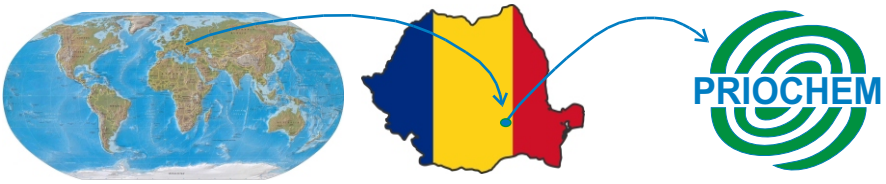
The International Symposium

PRIORITIES OF CHEMISTRY FOR A SUSTAINABLE DEVELOPMENT

Volume of summaries

www.icechim.ro



The International Symposium "PRIORITIES OF CHEMISTRY FOR A SUSTAINABLE DEVELOPMENT" PRIOCHEM

XIII-th Edition

ROMANIA - Bucharest

October 25 - 27, 2017

Volume appearing with support:

Partner:

Societatea de Chimie din ROMÂNIA

Media Partner

Radio România Cultural

Exhibitors:

EPI SISTEM BRAȘOV – ROMÂNIA

NANOTEAM

ABL&E–JASCO România S.R.L.

IGISIGN member of iNES GROUP

Technical Page for Summaries Volume

Coordinators of the edition:
Dr. Biochem. Mihaela DONI - General Manager ICECHIM
Mat. Octavian FRANGU - Technical Director ICECHIM
Dr. Eng. Raluca IANCHIS - Responsible for Section 1
Dr. Eng. Malina AVRAM - Responsible for Section 2
Dr. Chem. Radu FIERASCU - Responsible for Section 3
Dr. Eng. Emilia OPRESCU - Responsible for Section 4
Dr. Eng. Tanta IORDACHE - Responsible for Section 5

Cover, graphics and conception of the edition:
Master-MK Ec. Consuela MIHALEA - Specialist Marketing ICECHIM

The International Symposium
"PRIORITIES OF CHEMISTRY FOR A SUSTAINABLE DEVELOPMENT"
PRIOCHEM

XIII-th Edition, ICECHIM - Bucharest - ROMANIA
October 25 - 27, 2017

The original title (in Romanian): Simpozionul international „PRIOCHEM”
Edited by: ICECHIM Bucharest, Romania
ISSN 2285 - 8334
ISSN-L 2285 - 8334

MIP BUILDING: DO BETTER BRICKS MAKE BETTER STRUCTURES?

Andrew J. Hall*

Medway School of Pharmacy, Universities of Greenwich & Kent, Anson Building, Central Avenue, Chatham Maritime, Chatham, Kent, ME4 4TB

**Corresponding author: A.Hall@kent.ac.uk*

In principle, molecular imprinting is a simple, yet effective, way to create biomimetic materials with recognition sites for virtually any target species we choose. While lacking the elegance and refinement of their biological counterparts, these materials offer different attractive features, not least their ease and low cost of manufacture and their robust nature.

The non-covalent approach, first described over 40 years ago, is now established as the method of choice and many of the building blocks from those early days remain favourites to this day. Indeed, a survey of the literature shows that the vast majority of imprinted polymers are random copolymers of methacrylic (MAA) acid and ethylene glycol dimethacrylate (EDMA). This combination does lead to success, but the quality/quantity of the recognition sites created within these polymers has long been debated.

We believe that the MAA-EDMA axis cannot and will not be suitable on every occasion and have long been designing and synthesising novel, bespoke building block solutions for imprinting, taking inspiration from Nature and supramolecular chemistry.

In this lecture, we will discuss our work on the introduction of new molecules from which to build our imprinted materials. Starting with our contributions to the recognition (functional) monomer arsenal, we will move on to "dummy" templates, before ending with a description of our recent research into new generations of cross-linking monomers from renewable resources.

We aim to show the opportunities that can be realised by allowing space for synthetic creativity and side-stepping the conventional approaches, thus allowing for imprinted materials with enhanced function.

INJECTABLE THERMOSENSITIVE HYDROGELS FROM N-ISOPROPYLACRYLAMIDE HOMO- AND BLOCK CO-POLYMERS

Mircea Teodorescu*

Department of Bioresources and Polymer Science, Faculty of Applied Chemistry and Materials Science, Polytechnic University of Bucharest, 1-7 Polizu Str., 011061, Bucharest, Romania

**Corresponding author: mirceat@tsocm.pub.ro*

Keywords: poly(N-isopropylacrylamide); injectable hydrogels; thermosensitive polymers

Injectable hydrogels are low-viscosity aqueous polymer solutions that gel very rapidly after injection into the body as a consequence of either a chemical crosslinking reaction or a physical sol-gel transition induced usually by a temperature or pH change. Injectable hydrogels are very attractive for biomedical applications, like for example drug delivery and tissue engineering, because, among others, they are easy to be placed inside the body without requiring a surgical procedure, the therapeutic agent can be easily incorporated, and the resulting gel matches very well the irregular-shape body cavity to be filled.

Among the polymers employed for injectable hydrogels, poly(N-isopropylacrylamide) (PNIPAM) is one of the most studied because of its thermosensitive character with a lower critical solution temperature (LCST ≈ 32°C) below the human body temperature and an abrupt thermal response. However, PNIPAM has two important drawbacks which seriously limit its biomedical applications: a) it is difficult to be removed from the body because of its non-biodegradable character, and b) it undergoes demixing/syneresis, i.e. conversion to a shrunken gel and an aqueous layer, right after the gel formation. Several methods have been described in literature as solutions for these deficiencies, like for example manipulating the gelation temperature of the hydrogel or the synthesis of PNIPAM with hydrolysable ester groups within the main chain, in the first case, and statistical copolymerization of NIPAM with hydrophilic monomers, attaching the PNIPAM chain to a polymer block with permanent water solubility, or by mixing hydrophilic biopolymers, in the latter case.

The present work shows our studies concerning the improvement of the water retention/syneresis resistance and degradability of PNIPAM-based injectable thermosensitive hydrogels by some of the methods indicated above.

Acknowledgements: *Financial support from the Ministry of National Education,CNCS-UEFISCD, through the PN II-ID_12_2007 and PN-II-ID-PCE-2012-4-0082 grants is gratefully acknowledged.*

INTERPHASES AND DURABILITY IN POLYMER BASED COMPOSITE MATERIALS: CHARACTERIZATION AND MODELIZATION

Jean-François Chailan*, Lénaïk Belec, Yoan Joliff, Ahmad Fahs

Laboratoire MAPIEM – EA 4323 – Université de Toulon - CS 60584 – 83041 Toulon Cedex 9, France

**Corresponding author: chailan@univ-tln.fr*

For several years now, our research group focuses his attention on interphases in polymer based composite materials or polymer films deposited on inorganic surfaces. We have developed original experimental protocols in order to finely characterize accurately macromolecular organization and behavior close to inorganic inert materials as well as metallic surfaces or glass fiber, notably in thermoset/fibers systems. More recently, numerical models based on the finite element method have been developed in the laboratory to complement the understanding of phenomena and to quantify the evolution of the properties of composites.

Our global approach consists in compiling results from micrometer scale using thermo-mechanical technics (Dynamic Mechanical or Thermal Analysis), nanometer scale throughout observation techniques (SEM) and mechanical and/or topological responses obtained by Atomic Force Microscopy (AFM), as well as molecular scale using spectroscopy (FTIR).

Such multiscale/multitechniques methods allows us to characterize more precisely polymer structure, organization and properties (thermal, mechanical) in the interphase as the initial state, i.e. before any ageing.

Knowing that composite material durability is strongly related to the interphase one, we applied our interphase characterization protocols to the monitoring of interphase loss of properties during ageing. Notably in the case of hydrothermal ageing which is of a great interest in composite applications such as marine or aircraft building or wind turbine offshore plants.

Finally, our mechanical and/or thermal data obtained at micro/nanoscale can be used as input data in order to improve numerical models taking into account the interphase properties (size, specific mechanical properties), and to predict the composite loss of properties during ageing.

References:

[1]. Belec L, Joliff Y. Mechanically affected zone in AFM force measurements — Focus on actual probe tip geometry. Mater. Design. 2016;104:217-226.

[2]. Belec L, Nguyen TH, Nguyen DL, Chailan JF. Comparative effects of humid tropical weathering and artificial ageing on a model composite properties from nano- to micro-scale. Composites Part A. 2015;68:235-341.

[3]. Joliff Y, Rekik W, Belec L, Chailan JF. Study of the moisture/stress effects on glass fibre/epoxy composite and the impact of the interphase area. Compos. Struct. 2014;108:876-885.

THE USE OF CHEMICAL ENGINEERING RESEARCH AND MODELING IN FOOD PROCESSING INDUSTRY

Tanase Dobre[1,2*]

[1]*Faculty of Applied Chemistry and Materials Science, Polytechnic University of Bucharest, 1-7 Polizu Str., 011061, Bucharest, Romania*

Academy of Technical Sciences of Romania, 26 Dacia Blvd., 010413, Bucharest, Romania

**Corresponding author: tghdobre@gmail.com*

Keywords: mathematical modeling; shrinking core; oil seeds extraction; sensitivity analysis; parameters identification

The actual scientific literature makes a clear increasingly of the fact that what was classic and what is the latest in chemical engineering research and modeling comes and is being implemented more and more over the classical methods of research in the field of food processing. Here we present the case of oil extraction from various sorts of seeds with particularization of Camelina seeds.

The oil extraction from a spherical particle in an adequate solvent is analyzed by a dynamic model. The oil extraction occurs by moving the unsolubilized solid/solute-free phase interface towards the center of the particle. We assume that the transport of solute molecules has three resistances: 1) the resistance due to oil core dissolving; 2) the resistance due to the solute-free portion of the particle; 3) the resistance due to a surface layer near solid-liquid interface. Generally, the equation governing the dynamic behavior of oil extraction is numerically solved. However, sometimes analytical expressions for the time dynamics of the size of the unsolubilized oil portion can be obtained in some special cases. The present analysis on oil process extraction takes into account the effect of variable bulk solute concentration and of seed internal characteristics such as particle porosity, particle tortuosity and core oil dissolving kinetics. Result consists in a general mathematical model whose particularization is given for the case of Camelina seeds oil extraction. For Camelina seeds the oil hexane extraction has been characterized by particularization of the general modified shrinking core model. It has obtained that the particle dimensionless porosity is set to 0.08, while the constant of kinetic process from the shrinking core surface is strongly dependent on core position and on the temperature after relation $k_d = k_{d0}(t)\left(r_c / R\right)^n$ with $n = 4$ and $k_{d0}(t)$ in the range 4.3 – 8.3 10^{-8} m/s.

References:

[1]. Stroescu M, Stoica A, Parvulescu OC, Avram M, Dobre T. A shrinking core model for seeds oil extractionwith particularization to Camelina oil separation. Chem. Eng. Res. Des. 2015;97:1–8.

[2]. Crisan C, Calinescu I, Dobre T, Zalaru C. Calculation of separation processes used for extraction of active principles from fruits of *Coreopsis tinctoria* Nutt. Rev. Chim. 2013;64(4):366–371.

CARBON MATERIALS FROM POLYMER WASTES

B. Tsyntsarski[1*], M. Todorova[1], N. Petrov[1], T. Budinova[1], B. Petrova[1], I. Stoycheva[1], A. Sarbu[2], A.L. Radu[2], E.B. Georgescu[2], T. Sandu[2]

[1]*Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Acad. G. Bonchev str., BL.9, 1113, Sofia, Bulgaria*

[2]*INCDCP-ICECHIM, 202 Spl. Independentei, 060021, Bucuresti, Romania*

**Corresponding author: boyko.tsyntsarski@abv.bg*

Keywords: porous carbon; activated carbon; carbon foam; polymer waste

Introduction: The object of this investigation is synthesis of porous carbon materials from different polymers and wastes.

Materials and methods: Two stage procedure, including preliminary thermo-oxidation treatment with mineral acids at 200 ^{o}C and subsequent carbonization at 600 ^{o}C, was applied to produce porous carbon materials. Hydropyrolisis at 800 ^{o}C was used as additional procedure to obtain activated carbon. The structure and properties of obtained carbon materials were studied by SEM, XRD, BET, etc.

Results: Carbon foams wiht high mechanical strength were produced using precursors obtained after thermo-oxidation treatment of polymer precursors with mineral acids.The composition and properties of the modified pitches allow foam formation without using pressure and stabilization step.

The chemical composition of the initial mixture significantly affects the physicochemical properties of the obtained activated carbon. Increasing oxigen content leads to formation of nanoporous carbons with large surface area and oxygen functionalities of basic nature.

The investigation of the relation between the properties of the precursor and the structure of the obtained porous carbons indicate, that the composition of the precursor affects the synthesis procedure, and consequently, the final characteristics and structure of the carbon products.

Conclusions: The results show that porous carbons synthesized from polyethylene wax and phenol-formaldehyde resin are characterized by high surface area and high mechanical strenght, which imply their possible application as adsorbents, constructive materials, etc.

Acknowledgements*: The authors appreciate the funding by WAPUMECA project in the frame of collaboration between Romanian Academy Sciences and Bulgarian Academy of Sciences, and by Project DFNI-E02-2 with Bulgarian National Science Fund.*

INORGANIC CONSOLIDANTS AND PROTECTIVE TREATMENTS FOR ROMANIAN MONUMENTS

Rodica Mariana Ion[1,2*]

[1]*INCDCP-ICECHIM, 202 Spl. Independentei, 060021, Bucuresti, Romania*

[2]*Valahia University, Materials Engineering Dept., 18-24 Unirii Blvd, 130082, Targoviste, Dambovita, Romania*

**Corresponding author: rodica_ion2000@yahoo.co.uk*

Keywords: consolidant; calcareous material; hydroxyapatite; conservation; restoration

Introduction: The nanotechnologies, as a new and revolutionary area in Cultural Heritage, can improve the conservation and restoration by diagnosis and identifying the surfaces damaging type, cleaning and treatment of the surfaces affected by polluting substances and black crusts. With a smaller size and a higher penetrability, nanomaterials can contribute to solving of the problems that could be quantified as new products for consolidation and protection of natural and artificial stones, wood, paper and mural paints [1,2]. In this review, some diagnosis, digitization, preservation and restoration procedures of stone or wood surfaces from different monuments: Churches Ensemble - Basarabi-Murfatlar, Potlogi Palace, Nanu Muscel house-Bucuresti [3], Fîntineanu house- Slatina, Cioflea house-Targoviste, Rezii Churches-Braila, wood churches from Buzau County, will be discussed.

Materials and methods: Some nanomaterials as hydroxyapatite (HAp) or its composition with a mineral clay or with TiO_2, prepared in our lab, have been characterized by appropriate analytical techniques, patina/polychromy analysis and mechanical resistence/compatibility of the treated surface.

Results: HAp is one of the main consolidant product in highly porous limestones (stone or wood) with a higher consolidant activity. HAp jointed with calcium oxalate trihydrate (caoxite) concluded that the caoxite induced the stabilization of HAp and their mixed composition produced an important reinforcement of the treated support after accelerated weathering tests. Similar results have been obtained for hydroxyapatite joined with TiO_2.

Conclusions: The study of the effectiveness, compatibility and durability of these new nanomaterials are necessary in order to avoid the use of inadequate treatments, which modify the aesthetic, physical and chemical properties of stone or wood materials, causing new pathologies. This knowledge is crucial when designing and implementing the interventions and materials for the safeguard of cultural heritage.

Acknowlegements: This study was supported by the grants PNII 222/2012, 11BM/2016, PNII 261/2014, PN 16.31.02.04.04 from UEFISCDI-MEN.

Reference:

[1] Ion RM, Turcanu-Caruțiu D, Fierăscu RC, Fierăscu I, Bunghez IR, Ion ML, Teodorescu S, Vasilievici G, Rădițoiu V. Caoxite-hydroxyapatite composition as consolidating material for the chalk stone from Basarabi–Murfatlar churches ensemble. Appl Surf Sci. 2015;358:612-618.

[2] Ion RM, Doncea SM, Composition for paper deacidification, process to obtain it and method for its application. EP 2017; 2626464 B1

[3] Ion RM, Gurgu V, Bucurica IA, Teodorescu S, Ion ML, Postolache D, Darida I. 3D-Reconstruction of the Complex Stuccoes from Patrimony Buildings, Digital Presentation and Preservation of Cultural and Scientific Heritage. Conference Proceedings. 2017;7:107-112.

IMPROVEMENT FOR ION IMPRINTING TECHNIQUE

Katri Laatikainen[1*], Catherine Branger[2], Bruno Coulomb[3], Véronique Lenoble[4], Tuomo Sainio[5]

[1]*Laboratory of Chemical Metrology, Lappeenranta University of Technology, P.O. Box 20, FI-53851 Lappeenranta, Finland*

[2]*Laboratoire MAPIEM, EA 4323, Université de Toulon, 83957 La Garde, France*

[3]*CNRS, LCE, Aix-Marseille Université, Marseille, France*

[4]*Laboratoire PROTEE, EA 3819, Université de Toulon, 83957 La Garde, France*

[5]*Laboratory of Separation Technology, Lappeenranta University of Technology, P.O. Box 20, FI-53851 Lappeenranta, Finland*

**Corresponding author: katri.laatikainen@lut.fi*

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

Introduction: In the search for highly selective separation sorbents, ion imprinting technique leads to very attractive materials.[1,2] The aim of this study is to propose *In situ* complexation method as a simple way to control the stoichiometry of metal/ligand complexes.

Materials and methods: In this method, absorption spectra at different metal/ligand ratio are first measured by UV/vis spectrophotometer in water or specific solvent mixture Then stability and extinction coefficients are calculated by commercial HypSpec program based on the least-squares minimization scheme.[3] Stoichiometry of metal/ligand complexes can be calculated at different metal/ligand ratios and under some conditions (solution, temperature) different complex structures can be isolated. Finally IIP can be synthesized via normal procedures. In this study, 1-(pyridin-2-yl)-N-(4-vinylbenzyl)methanamine (Vbamp) monomer[4] was used as chelating ligand and nickel as the template ion. Relative amounts of 1:1, 1:2, and 1:3 complexes in the prepolymerization medium were adjusted by changing the Ni/Vbamp ratio, the counter-anion and the solvent composition at the polymerization temperature. After characterization of the complex distribution by UV/vis spectroscopy, IIPs were synthesized by inverse suspension polymerization with EDMA as the crosslinking agent. For the sake of comparison, 1:2 and 1:3 Ni/Vbamp complexes were also isolated using precipitation method and used for the preparation of control IIPs.

Results: The results showed that using this new approach (control of the complex stoichiometry in the prepolymerization medium), selectivity of IIPs for nickel was as high as by isolating the complexes using precipitation method.

Conclusions: The improvement is one step further in the development of ion imprinted polymers.

Acknowledgements: *This work was financially supported by the Academy of Finland, the Research Foundation of the Lappeenranta University of Technology, the Magnus Ehrnrooth Foundation, and the Finnish Cultural Foundation. South Karelia Regional funds are gratefully acknowledged. The authors are thankful to D.Sc. Tuomas Sihvonen and Ms. Anne Hyrkkänen for assistance with the experimental and analytical work.*

References:

1. C. Branger W. Meouche, A. Margaillan, React Func Polym 2013, 73, 859–875.
2. T. P. Rao, S. Daniel, J. Mary Gladis, TrAC Trends Anal. Chem. 2004, 23, 28–35.
3. P. Gans, A. Sabatini, A. Vacca SUPERQUAD: J. Chem. Soc. Dalton Trans. 1985, 1195-1200.
4. K.Laatikainen, D.Udomsap, H.Siren, H.Brisset, T.Sainio, C.Branger, Talanta 2015, 134, 538-545.

IN SITU' SERS EFFECT STUDIES WITH SCREEN-PRINTED ELECTRODES AND A COMPACT RAMAN SPECTROELECTROCHEMICAL INSTRUMENT

D.M.-Yerga, A. Pérez-Junquera, D.H. Santos, P.F. Bolado*

DropSens, S.L.,Edificio CEEI, Parque Tecnológico de Asturias, 33428 Llanera, Asturias, Spain

**Corresponding author: pfanjul@dropsens.com*

Keywords: Raman Spectroelectrochemistry; screen printed electrodes; SERS substrates

Introduction: UV-VIS, NIR and Raman Spectroelectrochemistry techniques can be used as 'in situ' and real time characterization and quantification techniques. These are powerful techniques since more complete and specific information is obtained with optical and electrochemical signals recorded simultaneously. However, the main current disadvantages are related to complex experimental setup where two analytical instruments (spectrometer and potentiostat) controlled by two different software should be triggered and usually a home-made spectroelectrochemical cell is used [1, 2]. The purpose of this study is to introduce a new compact and portable Raman spectroelectrochemical instrument controlled by one software in combination with screen printed electrodes.

Materials and methods: The new instrument integrates a 785 nm laser, a Raman spectrometer and a potentiostat/galvanostat fully synchronized in the same box. A Raman probe and a Raman spectroelectrochemical cell are used under optimized conditions together with Screen Printed Electrodes (SPEs). These miniaturized strips where the three electrodes of the electrochemical cell are printed together in the same alumina substrate are easy to handle, do not need to be pretreated previously to be used and require a low volume of solution (around 40 µl) [3, 4].

Results: Time resolved and quantitative measurements were developed on SPEs using different molecules such as ferricyanide, ruthenium bipyridine, thionine or the active pharmaceutical ingredient called naratriptan. On the other hand, silver, gold and copper based SPEs are shown as cost effective Surface Enhanced Raman Spectroscopy (SERS) substrates. The complete experimental setup is demonstrated to be easy to handle in comparison to the use of conventional electrodes and allows fast, in situ, real time and time resolved Raman Spectroelectrochemical measurements.

Conclusions: Metallic screen printed electrodes (silver, gold and copper) are shown as disposable and low cost SERS substrates in combination with a new compact Raman-Electrochemistry instrument. Electrochemical pretreatment of the electrodic surface is shown as a simple procedure to increase the SERS enhancement factor and diferent anlytes were sensitively detected.

References:

[1] C.Zong, C-J.Chen, M.Zheng, D-Y.Wu, B.Ren (2015), Transient Electrochemical Surface Enhanced Raman Spectroscopy: a millisecond time resolved study of an electrochemical redox process, JACS, 137, 11768-11774

[2] L.Zhao, J.Blackburn, C.L.Brosseau (2014), Quantitative detection of uric acid by electrochemical-surface enhanced raman spectroscopy using a multilayered Au/Ag substrate, Anal.Chem., 87, 441-447**.**

[3] P.Fanjul-Bolado, D.Hernández Santos, P.J.Lamas-Ardisana, A.Martín Pernía, A-Costa García (2008), Electrochemical characterization of screen-printed and conventional carbon paste electrodes, Electrochimica Acta, 53(10), 3635-3642.

[4] P.Fanjul Bolado, P.Queipo, P.J.Lamas Ardisana, A.Costa García (2007), Manufacture and evaluation of carbon nanotube modified screen-printed electrodes as electrochemical tools, Talanta, 74, 427-433.

PHOTOSENSITIVE LAYERS FROM CARBAZOLE COPOLYMERS SENSIBILIZED WITH METALOPHTALOCYANINES

S. Robu, T. Potlog, G. Dragalina, A. Popușoi, I. Lungu, N. Nasedchina, A. Chirita

Moldova State University, Chisinau

**Corresponding author: stefan_robu@yahoo.com*

Keywords: Carbazole copolymers; metalophtalo-cyanines; photosensitive; photovoltaic cells; 2,4,7-thrinitrofluorenone

Introduction: Organic semiconductors based on carbazole polymers, for example, poly-N-epoxy-propilcarbazole, copolymers of N-vinylcarbazole, 9-carbazolyletylmethacrylat [1] and others are applied for elaboration of optical registration systems, optoelectronic and photovoltaic elements.

Materials and methods: In this paper the possibility of sensibilized some carbazole polymers, for example, copolymers of N-vinylcarbazole with 1-octen, poly-N-epoxi- propylcarbazole and others using phtalocyanines of copper (Pc-Cu) or zinc (Pc-Zn) was investigated. The method for obtaining nanocomposites from carbazole polymers with metalophtalo- cyanines and deposition of these thin layers (d=2-5 μm) was developed. The sensibilization of the organic semiconductors was obtained by 2,4,7-thrinitrofluorenone (TNF) which had been supplemented with 3-50%mas of homogeneous metalophtalocyanine and obtained thin films had transparence over 90%.

Results: Spectral analysis shows that the photoconductivity band increases up to λ>800 nm in the presence of zinc phtalocyanine in concentrations of 5-25%mas (Fig. 1).

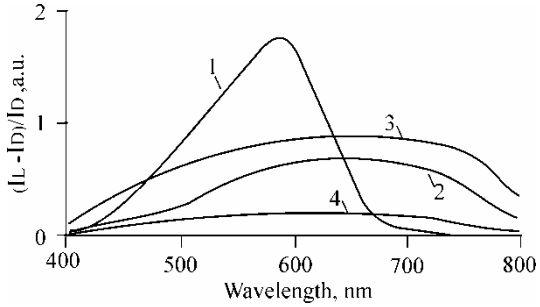


Fig.1. Spectral dependence of photosensitivity of the photopolymer layers sensitized with Pc-Zn: 1- 0%; 2 - 5%; 3 - 10%;4-25%

Obtained samples from carbazole polymer with metalophtalocyanines were additionally tested by the electrophotographical method [2]. The results showed that at the wavelengths λ > 700 nm sensitized photopolymer layers with 2,4,7-TNF have no photosensitivity, but the layers supplied with 10%mas Pc-Zn have photosensitivity and can be used for registration of optical information.

Conclusions: The sensibilized layers of carbazole polymer with 2,4,7-thrinitrofluorenone supplemented with phthalocyanine of zinc have extended spectral photosensitivity and can be recommended for the elaboration of electrophotographical carriers and other photonic devices.

Refrences: [1] G.Dragalina, C.Dragutan, S.Robu, I.Andries, L.Iancu, P.Gioca. Synthesis of Some Carbozole Monomers Designed to Obtain Materials with Photosensitive Properties. Materiale plastic .52.№4.2015, p.449-451.

[2] N.Barbă, I.Dementiev, S.Robu. Elaborarea mediilor fotosensibile din fotopolimeri carbazolici. Lucrare metodică, CEP USM, Chisinau, 2009, p. 18-26.

NEW OH-PROTECTED OPTICALLY ACTIVE INTERMEDIATES FOR SYNTHESIS OF CONSTRAINED CARBOCYCLIC NUCLEOSIDES

C. Tănase[1*], C. Draghici[2], L Pintilie[1], C. Negut[1], M. Maganu[2]

[1]*National Institute for Chemical-Pharmaceutical Research and Development, 112 Vitan Av., Bucharest 031299, ROMANIA*

[2]*Organic Chemistry Center "C.D.Nenițescu, 202 B Splaiul Independentei, Bucharest 060023, ROMANIA*

**Corresponding author: cvtanase@gmail.com*

Keywords: selective $NaBH_4$ reduction; SN2 mesyl substitution; azides; azide reduction; amines

Introduction: The synthesis of new constrained carbocyclic nucleoside analogues request key optically active intermediates for linking to the heterocyclic purine or pyrimidine bases or for building the purine or pyrimidine bases on a functionalized intermediate with a structure maintained in the sugar moiety. In a continuation of our studies,[1-3] the paper presents the synthesis of a few optically active key functionalized compounds with the structure required for sugar miety of the new nucleoside analogues. The paper deals mainly with the obtaining of the key intermediates protected at the hydroxyl with ether-protecting groups to easy the work-up of the reaction mixture and increasing the yields.

Materials and methods: The starting compound is an optically active by-product from the earlier stages of prostaglandin synthesis, and its transforming into kew intermediates is performed in 2 to 6 steps, by known reactions.

Results: Starting from the above mentioned intermediate, we obtained a library of key intermediates for synthesis of nucleoside analogues by Mitsubobu reaction, by building of the heterocyclic base on a functionalized fragment required for wanted sugar moiety, for clik chemistry and as synthons for fine organic chemistry.

The compounds were characterized by optical rotation, IR and ^{1}H- and ^{13}C-NMR

Conclusions: We obtained key intermediates protected at the hydroxyl group with ether-protecting grups in optically active form for obtaining constrained carbocyclic nucleosides, for clik chemistry and as synthons for fine organic chemistry.

References:

[1]. Tănase, C, Cocu FG, Căproiu MT, Neagu M, Manda G, "New bicyclo[2.2.1]heptane nucleoside analogues as antitumor agents", *Rev. Chim.(Bucuresti),*60(2), **2009**, 147-151.

[2]. Tănase CI, Drăghici C, Căproiu MT, Shova S, Mathe C, Cocu FG, Enache C, Maganu M, New carbocyclic nucleoside analogues with a bicyclo[2.2.1]heptane fragment as sugar moiety; synthesis, X-ray crystallography and anticancer activity, *Bioorg. Med. Chem., 22 (1),* **2014**, 513-522.

[3]. Tănase CI, Drăghici C, Cojocaru A, Galochkina AV, Orshanskaya JR, Zarubaev VV, Shova S, Enache C, Maganu M, New carbocyclic N^6-substituted adenine and pyrimidine nucleoside analogues with a bicyclo[2.2.1]heptane fragment as sugar moiety; synthesis, antiviral, anticancer activity and X-ray crystallography, *Bioorg. Med. Chem., 23 (19),* **2015**, 6346-6354.

PHYSICO-CHEMICAL PROPERTIES OF HYDROXYAPATITE/TITANIA NANOCOMPOSITES AND THE MECHANISM OF FORMATION REACTION

C. Marinescu[1*], A. Sofronia[1], S. Tanasescu[1], C. Teisanu[2]

[1]*Institute of Physical Chemistry Ilie Murgulescu of the Romanian Academy, 060021 Bucharest, Romania*

[2]*University of Craiova, Faculty of Mechanics, 200512, Craiova, Romania*

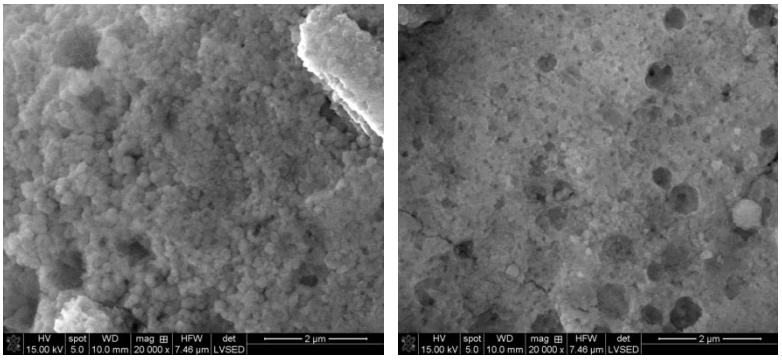
**Corresponding author:alcorina@chimfiz.icf.ro*

Keywords: titania-hydroxyapatite; nanocomposite; TSS

Introduction: Hydroxyapatite (HAP), ($Ca_{10}(PO_4)_6(OH)_2$), is the main inorganic component of bone. HAP – based biomaterials are used as medical implants for bone tissue and teeth reconstitution [1]. High temperature processing of HAP-based materials is essential for biomedical applications. Thus, it is important to understand the thermal transitions on heating. The goal of this work was to develop new TiO_2-HAP based biocomposites starting from titanium hydride (TiH_2) and commercial HAP (Aldrich) (HAP : TiH_2 = 3 :1 ratio) for further applications in engineered tissue implants.

Materials and methods: A two-step sintering (TSS) method [2] was used to obtain high density nanocomposites. X-ray diffraction (XRD), scanning electron microscopy (SEM) and Fourier Transform Infrared Analysis techniques were employed for the nanocomposites characterization. The reactions between HA and TiH_2 at sintering were investigated by simultaneous high temperature thermogravimetry coupled with differential scanning calorimetry (TG-DSC) in order to study the reaction mechanism of the TiO_2-HAP formation.

Results: Study of the thermal behavior of TiH_2-HAP mixture led to obtaining the reaction path of the biocomposites formation. SEM images of the etched samples (etched in HF 2% for 2 minutes) show that the appropriate holding time increase in the second sintering stage leads to homogenization of the particle size and pore distribution.



Conclusions: Using a nonconventional sinterization process at high temperatures as TSS method proved to be suitable for obtaining a composite of stable microstructure with matching mechanical and thermophysical characteristics of the constitutive phases.

***Acknowledgements*:** *This work was supported by the EU (ERDF) INFRANANOCHEM (No. 19/01.03.2009) and BONY PN-II-PT-PCCA-2013-4-2094 (No. 244/2014). The authors thank Dr. Simona Petrescu for SEM micrographs.*

References:

[1] C.V.M. Rodrigues et all Biomaterials 2003; 24:4987–97

[2] O. Gingu et all Proc. ImechE Part E: J. Process Mechanical Engineering., 2011; 225:62.

STUDIES ON THE STABILITY OF MESOPOROUS SILICA IN BIOLOGICAL FLUIDS

M. Deaconu[1*], D. Constantin[2], C. Goldmann[2], R.A. Mitran[1,3], C. Matei[1], D. Berger[1]

[1]*University „Politehnica" Bucharest, Department of Inorganic Chemistry, Physical-Chemistry and Electrochemistry, Polizu Street no. 1-7, Bucharest 011061, Romania*

[2] *Laboratoire de Physique des Solides, Université Paris-Sud XI, CNRS, F-91405 Orsay Cedex, France*

[3] *"Ilie Murgulescu" Institute of Physical-Chemistry, Romanian Academy, 202 Splaiul Independentei, Bucharest 060021, Romania*

**Corresponding author: mihaela_deaconu@yahoo.com*

Keywords: mesoporous silica; biodegradation; functionalization

Introduction: Ordered mesoporus silica is a promising carrier in drug delivery systems [1], however their efficiency depends on support stability in biological fluids. Among the important factors in degradation of mesoporous silica [2], surface modification and physiological environment were investigated in order to determine the effect of functionalization on the stability of mesoporous silica.

Materials and methods: The biodegradation of mesoporous silica materials was determined in phosphate buffer solutions pH 5.7 and 7.4, at 37^{o}C, at different time intervals. The materials were characterized before and after biodegradation by small-angle X-ray diffraction, FTIR spectroscopy, nitrogen adsorption/desorption isotherms, thermogravimetric analysis, dynamic light scattering, scanning electron microscopy and transmission electron microscopy.

Results: The functionalized mesoporous silica materials were successfully obtained by co-condensation approach. Pristine and organically-modified silica particles were coated with poly(ethylene glycol) (PEG) and their biodegradability was studied in different biological fluids.

Conclusions: The biodegradation degree of samples depends on the surface functionalization and also on the pH value of the studied environment.

Acknowledgements: *The authors are grateful for the financial support of the UEFISCDI program PN III no. 73BM/2017.*

References:

[1]. Vallet-Regi M, Ramila A, del Real RP, Perez-pariente J. A new property of MCM-41: drug delivery systems. Chem Mater. 2001;13:308-11

[2]. Paris JL, Colilla M, Izquierdo-Barba I, Manzano M, Vallet-Regi M. Tunning mesoporous silica dissolution in physiological environments: a review. J Mater Sci. 2017;52:8761-71

STYRENE-DIENE BLOCK-COPOLYMERS REINFORCED WITH POLYSTYRENE

P. Ghioca*, R.M.Grigorescu, L. Iancu, B. Spurcaciu, C.A.Nicolae, A.R. Gabor

INCDCP-ICECHIM, 202 Spl. Independentei, Sector 6, 060021 Bucharest, Romania

**Corresponding author: pghioca@yahoo.com*

Keywords: styrene-diene block-copolymers; polystyrene; composites

Introduction: The paper presents the polystyrene reinforcing effect of some styrene-diene block-copolymers on the physical-mechanical characteristics and thermal degradation stability of the associated composites. One of these composites applications can be considered the obtaining of electrical cables insulation.

Materials and methods: The linear styrene-isoprene block-copolymers were synthesized via anionic three stages sequential polymerization of monomers in cyclohexane solution initiated with n-butyllithium, by adding the next monomer only after the total consumption of the previous one. The star styrene-butadiene block-copolymers were synthesized via anionic polymerization of monomers in cyclohexane solution initiated with n-butyllithium, by coupling the diblock polystyrene-polybutadienyl lithium with silicium tetrachloride. At the end of each reaction step, samples were removed from the polymerization reactor in order to determine the monomer conversion and the molecular mass of the constituent blocks. The block copolymers molecular weight was determined by gel permeation chromatography (GPC) and was characterizated by Fourier Transform Infrared Spectroscopy (FT-IR). **The** reinforcement of block copolymers was performed with polystyrene Polystyrol 143 (BASF) in toluene solution. The physical - mechanical, dynamic mechanical properties (DMA) and TGA of elastomer composites were determined on films with a thickness of about 1 mm. obtained by centrifugal casting at temperatures not exceeding 60^0 C from toluene solution.

Results: Please provide here the principal results. Here can also be inserted figures (max. 2 figures); please use the figure template bellow (max. 3.5 cm×7cm). Do not use tables.

Conclusions: The study has highlighted the reinforcement effect of polystyrene SBS and SIS block copolymers due to the distribution of polystyrene only in the polydiene phase. The reinforcing mechanism is influenced by both biphasic morphology of block copolymers and different degrees of polystyrene adhesion at polybutadiene and polyisoprene phase.

Acknowledgements: *This work was financed by The Romanian National Authority for Scientific Research, UEFISCDI, project no. PN.16.31.03.01.*

LOMEFLOXACIN DELIVERY SYSTEMS BASED ON MCM-41-TYPE CARRIERS

A.M. Brezoiu*, M. Deaconu, D. Berger, C. Matei

University "Politehnica" of Bucharest, Faculty of Applied Chemistry and Materials Science

**Corresponding author: anamaria_brezoiu@yahoo.com*

Keywords: fluoroquinolone antibiotic; drug delivery systems; mesoporous silica; Lomefloxacin

Introduction: A major concern of our days medicine consists in the drug resistance of the microorganisms that occur mostly because of antibiotic overuse. To overcome this, one strategy is the development of new formulations for the pre-existing drug molecules with enhanced efficiency, a less expensive and time-consuming procedure than the synthesis of novel therapeutics [1]. Therefore, our research was focused on the obtaining of new drug delivery systems with controlled released kinetics. The study presents the obtaining and characterization of new formulations based on heteroatom modified mesoporous MCM-41 silica and a fluoroquinolone antibiotic, lomefloxacin.

Materials and methods: The pristine and drug-loaded materials were characterized using various techniques: small- and wide-angle X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), nitrogen adsorption–desorption isotherms. The electron microscopy (SEM and TEM) images were obtained for mesoporous carriers. The antimicrobial activity of antibiotic-loaded materials was assessed against *E. coli* strain and compared with the effect of the drug alone.

Results: The mesoporous carriers obtained by heteroatom introduction (Al, Mg, Fe, Ce and Zn) into the silica framework present high specific surface area ranging from 510 to 831 cm^2/g and total pore volume values between 0.49 and 0.96 cm^3/g, as well as tuneable average pore size (2.38-2.82 nm). The heteroatom introduction was achieved through ionic exchange methods and as it was expected enhanced interactions between modified-MCM-41 silica-type carrier and drug molecules was achieved either through increased Lewis acidity or by the possibility of donor-acceptor bonds formation. The heteroatom modification of MCM-41 materials led either to the formation of crystalline oxide phases (CeO_2 and Fe_2O_3) on the silica surface in the case of cerium and iron ions, or amorphous mesophases for Mg, Zn and Al doping. Further, the synthesized mesoporous materials were employed in lomefloxacin delivery systems with 20 % (wt.) antibiotic content. The drug release experiments were performed in simulated body fluid pH 7.4 [2], at 37 °C, under constant magnetic stirring, in duplicate. All drug-loaded samples present good bactericide activity against *E. coli* strain similar with that of the drug alone in the same quantity, but exhibiting a sustained drug release.

Conclusions: The synthesized mesoporous MCM-41-type silica carriers with different heteroatom content (Si/heteroatom molar ratio=5-115) presented very good adsorption properties and narrow pore size distribution curves. Slower delivery kinetics were obtained for drug-loaded carriers containing Zn, Al and Mg into silica matrix, while faster ones were determined for samples containing Ce or Fe ions.

References: [1] Robert A. *et al. Med. Mal. Infect.* 2017;47(2):142–151.
[2] Marques M. R. C. *et al. Dis. Tech.* 2011;18:15-21.

CONTROLLING DRUG DELIVERY KINETICS FROM MESOPOROUS SILICA CARRIERS THROUGH DRUG-SILICA INTERACTIONS

R.A. Mitran[1,2], C. Matei[2], D. Berger[2]

[1] *"Ilie Murgulescu" Institute of Physical Chemistry, Romanian Academy, 202 Splaiul Indepedentei, Bucharest, 060021, Romania*

[2] *University "Politehnica" of Bucharest, Faculty of Applied Chemistry and Material Science, 1-7 Polizu street, Bucharest, 011061, Romania*

**Corresponding author: raul.mitran@gmail.com*

Keywords: mesoporous silica; drug delivery; kinetics; controlled release

Introduction: Mesoporous silica nanomaterials are promising drug delivery carriers because of their excellent adsorption properties, high ability to tailor their morpho-textural properties through synthesis and biosafety. [1] The drug delivery process from mesoporous silica materials or from other nanocarriers is complex, being influenced by both the nature and properties of the carrier and drug molecules, but also by the supramolecular interactions between the two as well as by diffusion constraints. Moreover, the empirical models used to explain the drug release kinetics often do not provide sufficient information to correlate the properties of the carriers and drugs to the release kinetics profile. We explore the application of a three-parameter theoretical kinetic model to the drug release process from various mesoporous silica carriers. The model consists of an equilibrium between drug adsorption and desorption from the mesopore surface, followed by the diffusion of desorbed drug through the mesochannels. [2] Even under the assumption that all three processes follow first order kinetics, this model is powerful enough to provide quantitative information of the drug release process.

Materials and methods: Mesoporous carriers with different pore sizes and geometries (MCM-41, SBA-15, MCM-48) have been investigated. The influence of grafting organic groups with hydrophilic/hydrophobic and acid-basic properties on the release kinetics has also been studied. Due to the importance of electrostatic interactions between the silica pore surface and drug molecules, mesoporous aluminosilicate of AlMCM-41 and AlSBA-15 type were prepared and investigated. The carriers and drug-loaded samples were characterized by small- and wide-angle diffraction, IR spectroscopy, TGA, SEM, X-ray fluorescence spectroscopy and N_2 porosimetry. Drug release studies were carried out *in vitro*, at 37°C. The influence of the mesoporous carriers properties on the release kinetics were correlated.

Results: Here we explore the application of a three-parameter theoretical kinetic model to the drug release process from various mesoporous silica carriers. The model consists of an equilibrium between drug adsorption and desorption from the mesopore surface, followed by the diffusion of desorbed drug through the mesochannels. [2] Even under the assumption that all three processes follow first order kinetics, this model is powerful enough to provide quantitative information of the drug release process**.**

Conclusions: It was found that the release process can be precisely controlled by changing the mesoporous materials properties or the supramolecular interactions inside the mesochannels.

References:

[1]. M.Vallet-Regi, A.Rámila, R.P.del Real, J. A Pérez-Pariente, Chem. Mater. 2001, 13, 308-311

[2]. R.-A. Mitran, C. Matei, D. Berger, J. Phys. Chem. C, 120, 29202-29209, 2016.

New Poly(ethylene glycol) Composite Hydrogels with Nanozeolite as the Filler for Controlled Delivery Applications

B. Cursaru[1*], A. Zaharia[1], A.-L. Radu[1], A. Sarbu[1], T.-V. Iordache[1], A.-M. Florea[1], R. Ianchis[1], C.-M. Damian[2], T. Sandu[1], F.-X. Perrin[3], M. Teodorescu[2]

[1]*The National Institute for Research & Development in Chemistry and Petrochemistry -ICECHIM, Advanced Polymer Materials and Polymer Recycling Group, 202 Spl. Independentei, 060021, Bucharest, Romania*

[2]*University POLITEHNICA of Bucharest, Faculty of Applied Chemistry and Materials Science, Department of Bioresources and Polymer Science, 1-7 Polizu Street, 011061, Bucharest, Romania*

[3]*Laboratoire MAPIEM EA 4323 SeaTech-Ecole d'ingénieurs, Université de Toulon BP 20132, 83957 La Garde, Cedex, France*

**Corresponding author: bogdancursaru@yahoo.com*

Keywords: hydrogels; poly(ethylene glycol); nanozeolite; rosehip extract; composite

Introduction: The hydrogels unique properties recommend them for applications in drug delivery [1].

Materials and methods: New Poly(ethylene glycol)s composite hydrogels were obtained by cross-linking PEG_{700} with diacrylate terminal groups in the presence of nanozeolite as a filler and of rose hip extract (activating in the same time an active substance and reaction medium) at 25ºC using potassium persulfate and tetramethylethylenediamine as initiating system. The influence of the nanozeolite content upon the controlled release properties of the *in situ* loaded hydrogel was investigated.

Results: The slowest release rate was obtained by adding 3% of nanozeolite into hydrogel (Fig.1). At a 7% content of nanozeolite, the extract release rate slightly increased as compared with 3% nanozeolite, due to the formation of the some agglomerates of the nanosized zeolite [2], which were revealed by the SEM micrographs (Fig.2), together with the porosity of the hydrogels.

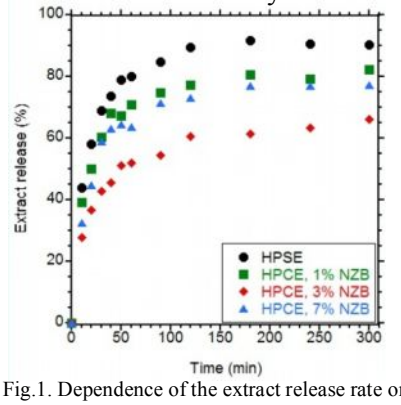


Fig.1. Dependence of the extract release rate on nanozeolite content of the composite hydrogel

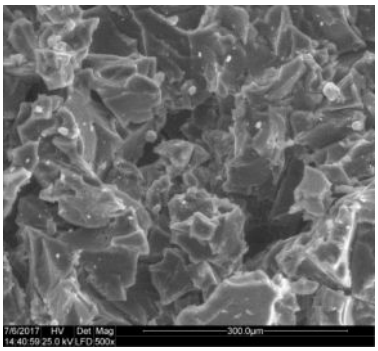


Fig.2. SEM micrograph of the hydrogel with 7% nanozeolite

Conclusions: The extract release rate slightly decreased at a higher amount of nanozeolite into the composite hydrogel, due to some physical aggregation of the nanozeolite particles.

Acknowledgements: *This project was funded by the Romanian Research Project PN-II-RU-TE-2014-4-0953, no. 44/2015 and ERA-NET WATERWORKS- 2015, ProWsper no. 39/2017.*

References: [1]. Hoare TR, Kohane DS, Hydrogels in drug delivery: Progress and challenges, Polymer 2008;49:1993-2007.
[2] Sotoudeh S, Barati A, Davarnejad R, Farahani MA, Antibiotic release process from hydrogel nano zeolite composites, Middle-East Journal of Scientific Research 2012;12(3):392-6.

IN VITRO BIOCOMPATIBILITY INVESTIGATION OF MONTMORILLONITE CLAY-BASED PARTICLE AS POTENTIAL DRUG CARRIER SYSTEMS

M. Icriverzi[1*], P. Florian[1], M. Trif[1],
I.C. Gifu[2], R. Ianchis[2], A. Roseanu[1]

[1]*Institute of Biochemistry of the Romanian Academy, Bucharest, Romania*
[2]*National R-D Institute for Chemistry and Petrochemistry ICECHIM, Bucharest, Romania*
**radu_mada@yahoo.co.uk*

Keywords: Cloisite; polymeric nanocomposite; drug carrier; anticancer therapy

Introduction: Encapsulation of nanoclays - such as montmorillonite clays - into polymers to generate complex networks may create promising systems with improved capacity of retaining and releasing therapeutic drugs [1]. In the present study, natural montmorillonite, Cloisite®Na^+ and the organically modified ones, Cloisite®30B and Cloisite®93A were evaluated *in vitro* for their cytotoxicity. Cloisite®93A was further selected for creating modified cloisite/polymeric nanocomposite constructs. Its influence on cellular viability and morphological feature over time was tested *in vitro* on two different mammalian cell lines.

Materials and methods: Polydispersity index (PDI) and diameter size of cloisite solutions (Southern Clay Products Inc.) were determined by DLS using a ZetaPlus instrument. Cytotoxic effects of different cloisite concentrations and polymeric PMMA-modified Cloisite®93A systems were evaluated by MTS reduction assay at 24 and 48 h on two *in vitro* model cellular lines, normal MDBK (Madin Darby Bovine Kidney) and human colon adenocarcinoma HT29 cells. Cell morphology was examined under the automated TissueFAXSiPlus imaging system at two different time points.

Results: DLS graphs showed polydispersity of clay solution and a z-average mean between 2000-3000 nm for all cloisite types. MTS cell proliferation assay demonstrated a decrease of cell viability, irespective of cell line, after cloisite exposure for 24 and 48 hours with increase of different clay concentration (31.25µg/ml- 500µg/ml). Cloisite®93A at 31.25µg/ml concentration showed the highest cell viability and normal morphology compared to control (untreated cells). Metabolic activity of normal and tumoral cells after two days of direct treatment with biopolymer-modified clays was not affected. Bright-field miscoscopy scanning of the probes revealed no morphological changes in any of the cell line tested.

Conclusions: Based on morphological and viability cellular changes, our *in vitro* results present the possibility of using Cloisite®93A-PMMA network for tumoral chemotherapeutic drug carrier-delivery system.

Acknowledgements: *This work is supported by a Grant of the Romanian National Authority Scientific Research an Innovation, CNCS/CCCDI-UEFISCFI, project number PN-III-P2.1-PED-2016-1896 and project number 4/2017 of the Institute od Biochemistry-Romanina Academy Research Program.*

References:

[4]. Nagahama K., Kawano D., Oyama N., Takemoto A., Kumano T., Kawakami J. Self-assembling polymer micelle/clay nanodisk/doxorubicin hybrid injectable gel for safe and efficient focal treatment of cancer. Biomacromolecules. 2015; 16(3): 880-889.

LIGNIN POLYMER ANALOGUES WITH BACTERICIDE PROPERTIES

M. Grinco[1], A. Barbă[1], V. Kulcitki[1*], A. Dizdari[2], V. Prisăcari[2], S. Robu[3]

[1]*Institute of Chemistry of the Academy of Sciences of Moldova*

[2]*State University of Medicine and Pharmacy „N.Testemițanu"*

[3] *State University of Moldova*

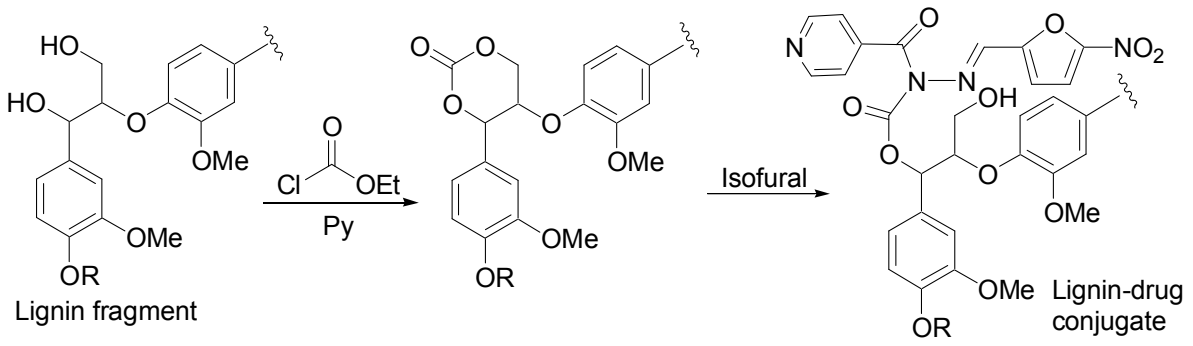
**Corresponding author: kulcitki@yahoo.com*

Keywords: lignin; isofural; conjugation; bactericide; polymer analogues

Introduction: Lignin is one of the most abundant natural polymers on Earth and identification of new application of this material represents a relevant priority. We report in the current communication our results on the investigation of polymer analogous transformations of lignin, aimed to the synthesis of new conjugates with antibacterial properties, basing on the known drug isofural ((*E*)-N´-[(5-nitrofuran-2-yl) methylene] isonicotinylhydrazide).

Materials and methods: The synthesis of the polymer analogue has been performed according to the known procedure [1] with the use of ethyl chloroformate as a linker. Commercial intact or degraded Kraft lignin were used as polymeric substrate. A lignin-isofural mass ratio of 1:1 and 2:1 was applied. The excess unreacted drug was removed by sedimenting the polymeric fraction with an antisolvent.

Results: The structure of the obtained polymer analogues and the drug incorporation degree have been confirmed basing on the IR spectroscopy and elemental analysis.



The results of bioactivity testing have been positive for a series of strains (*E. faecalis*, *E. coli*, *Pr. vulgaris*), in particular for *S. aureus*, for which the minimum inhibition concentration constitutes 12 mkg/ml, which is only slightly higher then the similar value of pure isofural (9.37 mkg/ml).

Conclusions: A successfull application of intact and degraded commercial lignin as efficient vehicle for an active pharmaceutical ingredient with antibacterial properties has been demonstrated. The polymeric product resulting on the chemical conjugation of isofural can be recomended as a pharmaceutical form with broad aplications.

Acknowledgements: *The presented work was performed within the project "Non conventional green procedures for renewable raw materials processing" supported financially by STCU (Ukraine) and ASM (Moldova, project No. 5894).*

References:

[1] Groves ES, Aldwin L, Winkelhake JL, Nitecki DE, Gauney S, Rudolph AA. USA Patent WO 90/15628, 27.12.90.

OBTAINIG AND CHARACTERISATION OF STARCH-BASED EDIBLE FILMS INCORPORATING NATURAL GREEN COLORANTS

M. Mironescu*, I.D. Mironescu

Department of Agricultural Sciences and Food Engineering, Faculty of Agricultural Sciences Food Industry and Environmental Protection, University „Lucian Blaga" of Sibiu, Romania

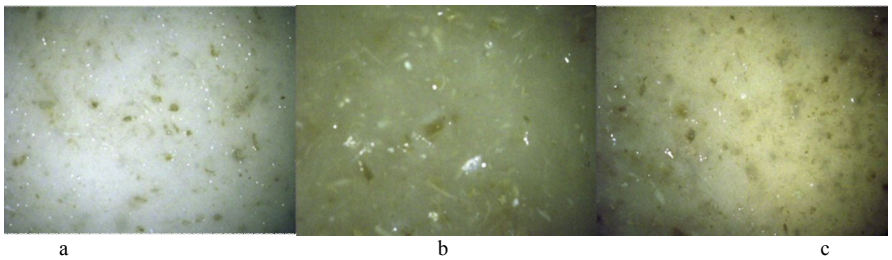
**Corresponding author: monica.mironescu@ulbsibiu.ro*

Keywords: starch edible film; spinach; nettle; parsley

Introduction: Great emphasis is put nowadays on finding solutions for using biodegradable materials as films or coatings, to replace conventional synthetic plastics. Starch, as cheap, readily available and highly safe raw material, is the most used biopolymer in producing films or coatings [1]. This research investigates the production and characterisation of an edible film from starch, which incorporates natural green colourants extracted from spinach, nettle and parsley. The film was applied on cheese and the evolution of cheese humidity was monitored.

Materials and methods: The solvent used for producing the film was obtained by fine blending of water and plant leaves (added in percentage of 5%, 10% and 15%). The solvent was mixed with corn starch:glycerol:acetic acid 1N:solvent in the ratio 1:1:1:100, then heated for 1 hour at 90^{o}C with continuous mixing. In order to be coated, small fermented cheese pieces were immersed directly into the gel and then the gel was casted in forms and dried at 40^{o}C for 20-24 h to remove the solvent and to form the film. The structure of the film was analysed microscopically. Water activity of film was also determined, together with the water content in cheese during one month of maintaining at 20^{o}C.

Results: The method used in this research allowed the obtaining of an edible film based on modified starch (acetylated starch) incorporating natural colorants from plants (figure 1).The optimal quantity of leaves is 10% for all plants tested; a higher leaves content gives film too dark in colour and 5% leaves are not enough to colour the films significantly. The film has very low water activity a_w (0.4) and this low value is maintained in during one month of monitoring. Cheese loses water in the ratio 1 week:2 weeks: 3 weeks: 4 weeks= 3:5:7:10%.



a b c

Figure 1. Starch-based films with different concentrations of parsley: a-5%; b-10%; c-15%

Conclusions: Spinach, nettle and parsley leaves can be successfully incorporated into the edible film based on acetylated starch, the optimal percentage being 10%. The film applied on cheese determines a loss of humidity until 10% in one month of preserving.

References:

[1]. Vieira MGA, Altenhofen da Silva M, Oliveira dos Santos L, Beppu MM, Natural-based plasticizers and biopolymer films: A review. Eur. Polymer J. 2011; 47(3):254–263.

RADIATION INDUCED SYNTHESIS AND CHARACTERIZATION OF SILVER NANOPARTICLES

E.M. Lungulescu[1], I. Ion[1], N.O. Butoi[1], A-M. Luchian[1], R. Ducu[1], V. Marinescu[1]

[1] *R & D Institute for Electrical Engineering (ICPE-CA) 313 Splaiul Unirii, Sector 3, Bucharest, Romania*

**Corresponding author: ion.ioana@icpe-ca.ro*

Keywords: γ – irradiation; metal nanoparticles; biocidal effect; fungus

Introduction: The radiation induced synthesis of metal nanoparticles presents some important advantages as compared to conventional chemical and physical methods: the process is simple and clean, can be carried out in very mild conditions (ambient pressure and room temperature), provides metal nanoparticles in fully reduced, highly pure and highly stable state, no disturbing impurities like metal oxide are introduced

Materials and methods: Silver nanoparticles were successfully prepared in one-step by γ-irradiation technique using 15, respectively 25 mM of AgNO3 in a water-ethanol-polyvinylpyrolidone (PVP, used as stabilizer) system at room temperature and under ambient pressure. The gamma irradiation was carried-out in a Co-60 laboratory irradiator (Ob-Servo Sanguis, Institute of Isotopes, Hu), in the dose range between 2-100 kGy (Dose rate: 1.2 kGy/h). The optical properties of irradiated solutions with various weight of the EtOH were investigated by UV-Vis spectroscopy, DLS (Dynamic Light Scattering), SEM (Scanning Electron Microscopy), FTIR (Infrared spectroscopy). Microbiological examination of the biocidal effect of the obtained nanosilver against Aspergillus Niger sp. and Trichoderma sp. was performed.

Results: All spectra exhibit a Plasmon Resonance Absorption (PRA) band specific to silver nanoparticles ranging between 399 nm to 497 nm, related to silver nanoparticle size. Red shift in the plasmon absorption peak were found for all solutions, for all doses, except the samples with high amount of ethanol (only in the dose range of 2-10 kGy), where a blue shift was observed. Red shift in the plasmon absorption peak reveals that the size of the silver nanoparticles increases with the integrated irradiation dose.

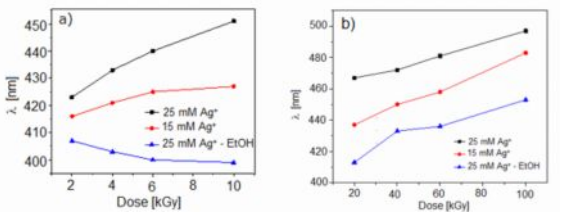


Fig. 1 – Influence of irradiation dose on the PRA peak: a) 2-10 kGy; b) 20-100 kGy

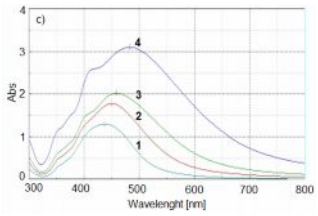


Fig. 2 -UV-Vis spectra of 25 mM of $AgNO_3$ in Water-Ethanol-PVP system: 1-20 kGy, 2- 40 kGy, 3-60 kGy; 4 -100 kGy

Conclusions: The size of synthetized particles can be tailored by irradiation dose or amount of added ethanol and this make from γ-irradiation an effective technique for preparing silver nanoparticles. The biocidal effect depends on the size and the shape of the radio-synthetized silver nanoparticles.

LUMINOPHORE HYBRID COATINGS FOR TEXTILE MATERIALS

M. Raduly, V. Raditoiu, A. Raditoiu, V. Amariutei, L. Wagner

Research and Development National Institute for Chemistry and Petrochemistry – ICECHIM, 202 Splaiul Independentei, 060021, Bucharest, Romania

**Corresponding author: radulymonica@yahoo.com*

Keywords: curcumin derivatives; β-diketone; fluorescence; hybrid materials; luminescent materials

Introduction: Textile materials used in signaling-related applications (road equipments, sports equipment, specialty materials, advertising, etc.) are usually dyed with fluorescent dyes as highlighting coloring materials. In order to increase the performances (color properties, fluorescence life, and resistance to photodegradation) of this type of colored textile materials, a series of research experiments were performed to obtain suitable nanosols compatible with different types of textiles. Several works reported the usage of sol-gel processes to generate functional coatings (repellent, fireproof, electrically conductive, antimicrobial, catalytic, UV-shielding) on textiles surface [1-4].

Materials and methods: The study presents experimental data regarding the selection of the components (dyes, auxiliary components, solvents and co-solvents, film-forming materials) and the properties of textile fibers after functionalization.

Some derivatives of acetylacetone were immobilized in hybrid silica matrices by sol-gel processes and nanosols were deposited on textile materials by the pad-drying method. Hybrid silica film-forming materials are obtained by the hydrolysis / condensation of some mixtures of alkoxysilane precursors with aromatic/aliphatic group, in the presence of acetylacetone luminophores, and in acid catalysis.

Results: Textile materials coated with luminescent film-forming materials of the type studied in our work are uniformly and fairly intense colored materials with yellow to red fluorescent colors. Determination of color and luminescence parameters revealed that the colored textiles present enhanced fluorescence characteristics comparatively to the original chromophores.

Conclusions: As a result of the experimental work, different textile substrates colored with fluorescent film-forming hybrid materials were obtained, some of them presenting outstanding signaling properties, high visibility and good washing and rubbing (wet and dry) fastness.

Acknowledgements: *This work was supported by the National Authority for Scientific Research and Innovation [Project PN 16.31.03.03.].*

References:

[1]. Mahltig B., Haufe H., Böttcher H., J. Mater. Chem., **2005**, 15, 4385-4398
[2]. Nedelcev T., Krupa I., Lath D., Spirkova M., *J. Sol-Gel Sci. Techn.*, **2008**, 46, 47-56.
[3]. Raditoiu A., Amariutei V., Raditoiu V., Ghiurea M., Nicolae C., Wagner L., Rev. Chim., **2012**, 63(6), 612-617.
[4]. Raditoiu A., Raditoiu V., Amariutei V., Purcar V., Ghiurea M., Raduly M., Wagner L., Mat. Plas., **2015**, 52(4), 442-448.

Preparation of 5-Fluorouracil loaded zeolite nanoparticles as drug delivery systems

A. Zaharia[1*], C-P. Spatarelu[1], A.-L. Radu[1], B. Cursaru[1], T.-V. Iordache[1], A.-M. Florea[1], T. Sandu[1], S. Apostol[1] , A. Sarbu[1], M. Teodorescu[2], F.-X. Perrin[3]

[1]The National Institute for Research & Development in Chemistry and Petrochemistry -ICECHIM, Advanced Polymer Materials and Polymer Recycling Group, 202 Spl. Independentei, 060021, Bucharest, Romania

[2]University POLITEHNICA of Bucharest, Faculty of Applied Chemistry and Materials Science, Department of Bioresources and Polymer Science, 1-7 Polizu Street, 011061, Bucharest, Romania

3University of South Toulon-Var, Laboratoire Matériaux Polymères Interfaces et Environnement Marin, BP 132, 83957 La Garde Cedex, France

**Corresponding author: anamaria.lungu1984@gmail.com*

Keywords: 5-Fluorouracil; nanozeolite; slow- release; cytotoxicity

Introduction: A natural nanozeolite loaded with bioactive substances was used to develop a slow-release system [1].

Materials and methods: The 5-fluorouracil (5-FU) loaded nanozeolite (NZ) particles were prepared by immersing the NZ particles in a DMSO solution of 5-FU. The solution was subsequently ultrasounded, and subjected to a continuously magnetic stirring. The drug was encapsulated in the NZ particles, creating a barrier for the release of SBA, yielding a slow-release profile of the active substances. The loading of the nanozeolite was confirmed through UV-Vis spectroscopy and by TGA technique. The results were correlated with those provided by the release and cytotoxicity determinations, allowing a more accurate assessment of the 5-FU content and a potential cytotoxic activity [2].

Results: The product exhibits a slow-release profile of the drug, at the end of the study. Cytotoxicity test on the L929 cell line indicated a reduction in cell viability. The value was lower compared to the 5-FU neat solution of an equivalent concentration, indicating a possible potentiation of its cytotoxic effect in the encapsulated form.

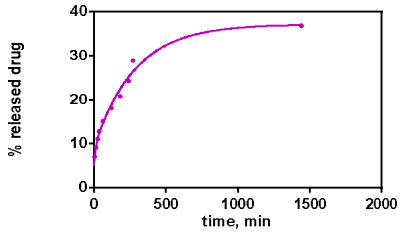


Fig.1. In vivo release of 5-FU from NZ particles in PBS medium

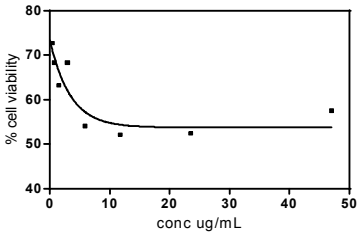


Fig.2. Cell viability variation of the L929 cell line, incubated in a range of 5-FU concentration

Conclusions: Therefore, the nanozeolite particles show great potential for the application as 5-Fluorouracil carriers for a possible cytotoxic activity.

Acknowledgements: *This project was funded by the Romanian Research Project PN-II-RU-TE-2014-4-0953, no. 44/2015 and M ERA-NET 2 Cofund, TANDEM no. 71/2017.*

References: [1]. Datt, Ashish, "Applications of mesoporous silica and zeolites for drug delivery", PhD (Doctor of Philosophy) thesis, University of Iowa, 2012.

[2]. Daniel B. Longley, D. Paul Harkin and Patrick G. Johnston, „5-Fluorouracil: mechanisms of action and clinical strategies", Nature Publishing Group; May 2003, volume 3, 330-338.

CRYSTAL STRUCTURE, MAGNETIC PROPERTIES AND CORROSION BEHAVIOUR OF THE MODIFIED SPECIAL STEELS IN IONIC LIQUIDS

A.M. Popescu[1], O. Demidenko[2], K. Yanushkevich[2], E.I. Neacşu[1*], C. Donath[1], A. Galyas[2], A. Zhyvulka[2], V. Constantin[1]

[1] *Affiliation "Ilie Murgulescu" Institute of Physical Chemistry of the Romanian Academy, Laboratory of Electrochemistry and Corrosion, Splaiul Independentei 202, Bucharest-006021, Romania*

[2] *Scientific – Practical Materials Research Centre NAS, P. Brovki 19 str., 220072 Minsk, Belarus*

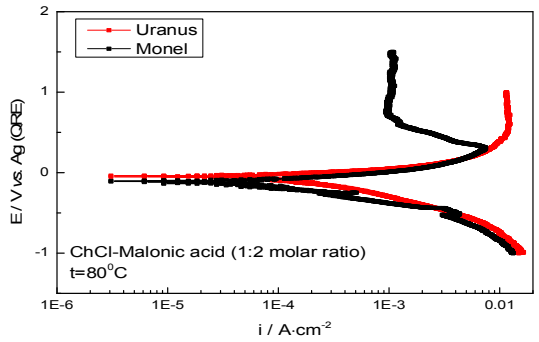
**Corresponding author: neac_elena@yahoo.com*

Keywords: special steel; XRD; magnetic properties; ionic liquids; corrosion

Introduction: The influence of the corrosion processes in different ionic liquids media on the surface morphology, crystal structure and magnetic characteristics of some modified special steels (Uranus-B6 and Monel-400) was studied. Corrosion studies were carried out in different ionic liquids based on 2 hydroxy-ethyl-trimethyl-ammonium chloride (ChCl) and the corresponding corrosion parameters were calculated.The structure modification after the corrosion process was observed by metallographic microscopy.

Materials and methods: The crystal structure was studied by using an X-ray diffraction method. The specific magnetization was investigated by the ponderomotive method. Corrosion experiments were performed with a potentiostat PARSTAT-2273 with a special soft for data achizition Power Corr.The micrographic images were obtained with a metallurgical microscope (USA) with camera aquisition.

Results: The structure and magnetic properties of Uranus-B6 and Monel-400 were determined. Corrosion process was found to be biger in ChCl-Malonic acid than in ChCl-Oxalic acid for both steels used.



The lower corrosion rate 0.72 μm/year was obtained for MONEL-400 in the ChCl-Oxalic acid (1:1)M ionic liquid. The micrography confirms these results.

Conclusions: This is the first study on corrosion of Uranus and Monel in ionic liquids based on choline chloride. Also the magentic properties were for the fisrt time determined on these steels.

Acknowledgements: *The financial support of the Romanian Academy and the Research Fund of NAS of Republic Belarus (bilateral project 2016-2017) is acknowledged.*

SURFACE FUNCTIONALIZATION OF NANOCELLULOSE FOR BIOMEDICAL APPLICATIONS

D. M. Panaitescu*, A. N. Frone, I. Chiulan, R. A. Gabor, C.A. Nicolae, M. Ghiurea, B. Trica, D. Florea

National Institute of R&D for Chemistry and Petrochemistry

**Corresponding author: panaitescu@icf.ro*

Keywords: nanocellulose; surface treatment; AFM

Introduction: Nanocellulose is a research topic of increased interest because it has attractive properties [1]. For the successful application of nanocellulose in the biomedical field and in other domains, the modification of the surface properties of nanocellulose is mandatory [2]. Chemical functionalization of nanocellulose is undertaken with the aim of tuning the surface energy of nanocellulose to improve its compatibility with hydrophobic matrices or to introduce electrostatic charges on its surface for better dispersion in different environments. Several attempts have been undertaken to chemically modify nanocellulose, such as silanization, esterification with organic acids or anhydrides, grafting of polymers on cellulose by free radical polymerization or ring-opening polymerization [3,4]. However, the chemical functionalization of nanocellulose must be done in such a way as to preserve its valuable properties and should be located on its surface. In our work we tried to modify the surface of nanocellulose in a controlled manner providing increased hydrophobicity, good thermal stability and crystallinity.

Materials and methods: Nanocellulose obtained from different sources (wood, plant, bacterial synthesis) was surface treated to provide amino, sulfate, carboxylic, ester and vinyl groups on its surface.

Results: Improved hydrophobicity was obtained for all applied treatments but the degree of improvement was different depending on the added functionality. The thermal stability as well as the crystallinity were also affected by the treatments.

Conclusions: The results of this study have shown that the careful choice of the agents and reaction conditions may lead to the desired hydrophobicity level and improved thermal stability, keeping the crystallinity practically unchanged.

Acknowledgements: *This research was supported by the Romanian National Authority for Scientific Research and Innovation, CNCS/CCCDI – UEFISCDI, project number PN-III-P4-ID-PCE-2016-0431, Contract 148/2017 (CELL-3D)*

References:

[1]. Panaitescu DM, Frone AN, Chiulan I. Green composites with cellulose nano-reinforcements. In: Thakur VK, Thakur MK, Kessler M, editors. Handbook of Composites from Renewable Materials, Volume 7. Scrivener Publishing LLC; 2017. pp. 299–338.

[2]. Cherian BM, Leao AL, de Souza SF, Thomas S, Pothan L, Kottaisamy M. Cellulose Nanocomposites for High-Performance Applications. In: S. Kalia et al. editors. Cellulose Fibers: Bio- and Nano-Polymer Composites, Chapter 21. Springer-Verlag Berlin Heidelberg; 2011 pp. 540-587.

[3]. Taokaew S, Phisalaphong M, Newby BZ. Modification of bacterial cellulose with organosilanes to improve attachment and spreading of human fibroblasts, Cellulose 2015; 22: 2311–2324.

[4]. Missoum K, Bras J, Belgacem MN, Organization of aliphatic chains grafted on nanofibrillated cellulose and influence on final properties, Cellulose 2012;19:1957–1973.

VOLTAMMETRIC INVESTIGATION OF FERULIC ACID USING A DISPOSABLE PENCIL GRAPHITE ELECTRODE

L. Iordache, I.G. David, M.C. Cheregi, D.E. Popa, M. Buleandra

[1]*University of Bucharest, Faculty of Chemistry, Department of Analytical Chemistry, 4-12 Regina Elisabeta Av., 030018, Bucharest 3, Romania*

**Corresponding author: mihaela.cheregi@g.unibuc.ro*

Keywords: ferrulic acid; disposable pencil graphite electrode; voltammetric investigation; beverage analysis

Introduction: Ferulic acid (3-methoxy-4-hydroxycinnamic acid) (AF) is one of the most important bioactive phenylpropionic acids existing in the plant cellular wall being responsible to the protection against diseases and the plant growth [1]. AF is present in whole grains, vegetables, olive oil, coffee, red wine, etc. The antioxidant action of this cinnamic compound is due to its ability to capture different oxidizing species (e.g. superoxide anion, hydroxyl radicals, peroxyl), thus contributing to the human organism protection against free radicals and UV radiation. Due to the fact that hydroxycinnamic acids possess native electroactivity, electrochemical methods can be used as modern tools for studying the electron-transfer reaction mechanisms and for obtaining additional analytical information. The present work describes the development of a new voltammetric method for the AF determination using a pencil graphite electrode (PGE).

Materials and methods: AF working solutions were obtained by successive dilution of the freshly prepared ethanolic $2 \cdot 10^{-2}$ M AF stock solution with Britton-Robinson buffer. An electrochemical system Autolab PGSTAT 12, equipped with a three electrodes measurement cell (PGE as working electrode) [2] and a PC running GPES4.9 software, was used for the analytical studies.

Results: The AF voltammetric behavior on PGE was studied through the influence of the following parameters on the analytic signal: the pencil graphite lead type, the pH of the supporting electrolyte, the potential scan rate and the analyte concentration. The AF first oxidation peak is a 2 electrons, pH-dependent, diffusion-controlled redox process [3]. Its peak current varies linearly with the concentration in the range $4 \cdot 10^{-7} – 1.8 \cdot 10^{-3}$ M.

Conclusions: The developed voltammetric method for the AF quantification using a cheap, easily available and disposable electrode is simple and fast. It was applied to determine the *total medium-activity antioxidants content* in beer, expressed as *mg Equivalent AF/L*.

Acknowledgements: *This work was supported by the following grants: Romanian National Authority for Scientific Research and Innovation CNCS/CCCDI-UEFISCDI, project number* ***PN-III-P2-2.1-PED-2016-0477****, within PNCDI III and University of Bucharest project,* ***UB 1490/2017.***

References:

[1] Galato, D., Ckless, K., Susin, M. F., Giacomelli, C., Ribeiro-do-Valle, R. M., Spinelli, A., Antioxidant capacity of phenolic and related compounds: correlation among electrochemical, visible spectroscopy methods and structure–antioxidant activity. Redox Rep., 2001; 6:244-50

[2] David, I. G., Florea, M. A., Cracea, O. G., Popa, D. E., Buleandră, M., Iorgulescu, E. E., David, V., Badea, I. A., Ciucu, A. A., Voltammetric determination of B_1 and B_6 vitamins using a pencil graphite electrode. Chem. Pap., 2015; 69: 901-10.

[3] Liu, L., Gao, X., Zhang, P., Feng, S., Hu, F., Li, Y., Wang, C., Ultrasensitive detection of ferulic acid using poly(diallyldimethylammonium chloride) functionalized graphene-based electrochemical sensor. J. Anal. Methods Chem., 2014, 2014:1-9

SYNTHESIS, SPECTRAL AND THERMAL CHARACTERIZATION OF NEW COPPER (II) AND IRON (III) COMPLEXES

M. Marinescu[1*], I. Stanculescu[2], G. Marton[3]

[1]*University of Bucharest, Faculty of Chemistry, Department of Organic Chemistry, Biochemistry and Catalysis, RO - 010184, Bucharest, Romania*

[2]*University of Bucharest, Faculty of Chemistry, Department of Chemistry Physics, RO – 010184, Bucharest, Romania*

[3]*University Polytechnic of Bucharest, Faculty of Applied Chemistry and Applied Science, 1-7 Polizu, 011061, Bucharest, Romania*

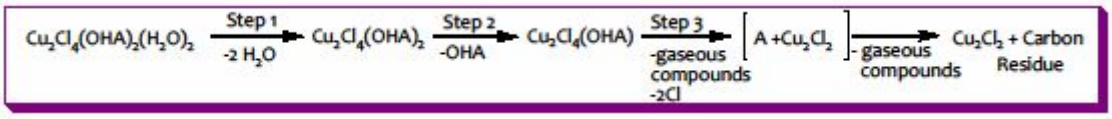
**Corresponding author: (maria.marinescu@chimie.unibuc.ro; maria7marinescu@yahoo.com)*

Keywords: metal complexes; 1,2,3,4,5,6,7,8-octahydroacridine; FTIR, TG-DTA, DFT theory

Introduction: Eco-friendly synthesis of 4 complexes with monodentate ligands: $[Cu(L_1)Cl_2(H_2O)]_2$, $[Cu(L_2)Cl_2(H_2O)]_2$, $[Fe(L_1)Cl_3]_2$ and $[Fe(L_2)Cl_3(H_2O)]_2$ (L_1 = 1,2,3,4,5,6,7,8-octahydroacridine; L_2 = 1,2,3,4,5,6,7,8-octahydroacridine-10-oxide) are reported. The complexes were characterized by FTIR and UV-VIS spectroscopy, elemental and TG-DTA analysis. All complexes structures were further optimized using DFT theory and the first hyperpolarizability was calculated for all compounds [1].

Materials and methods: L_1 and L_2 previously synthesized [2] were used for synthesis of complexes. DFT at M11/ktzvp level of theory was used for geometry optimization of the complexes [3].

Results: Both copper and iron complexes have different geometries. Generally, heating of the compounds first results in the release of water molecules (Scheme 1). The nonlinear optical (NLO) response of Fe (III) and Cu (II) complexes is investigated by the static hyperpolarizability coefficients (β), calculated **using the semi-empirical quantum chemistry algorithms (MOPAC software).**



Scheme 1. The sequence of thermal degradation of the compound $[Cu(L_1)Cl_2(H_2O)]_2$ (L_1 = OHA)

Conclusions: We expect that all four synthesized complexes to be very stable. For all complexes, we expect good non linear properties because of theirs structures with bridged chlorine atoms and also because of the very good values of the hyperpolarizabilities calculated.

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;6:846–54.

[2]. Potmischil F, Marinescu M, Loloiu T. Hydroacridines XXVIII. Syntheses of New 9-Substituted 1,2,3,4,5,6,7,8-octahydroacridine Derivatives and their N(10)-Oxides. Rev Chim (Bucharest). 2007;58;795-8.

[3]. Marinescu M, Tudorache DG, Marton G, Zalaru CM, Popa M, Chifiriuc MC, Stavarache C, Constantinescu C. Density functional theory molecular modeling, chemical synthesis, and antimicrobial behaviour of selected benzimidazole derivatives. J Mol Struct. 2017;1130:463-71.

BIOMASS AND POLYMER BASED CARBONS FOR ELECTROCHEMICAL APPLICATIONS

M. Todorova[1], B. Tsyntsarski[1], N. Petrov[1], T. Budinova[1], B. Petrova[1], I. Stoycheva[1], A. Stoyanova[2], A.L Radu[3], E.B. Georgescu[3], S. Apostol[3], T. Sandu[3], A. Sarbu[3]

[1]Institute of Org. Chem. with Centre of Phytochem., Bulg. Acad. Sci., Acad. G. Bonchev str., BL.9, BULGARIA

[2] Institute of Electrochemistry and Energy Systems, Bulg. Acad. Sci., Acad. G. Bonchev str., BL.10, BULGARIA

[3] INCDCP-ICECHIM, Spl. Independentei 202, sector 6, Bucuresti, ROMANIA

**Corresponding author: boyko.tsyntsarski@abv.bg*

Keywords: porous carbon; supercapacitors; biomass; polymer waste

Introduction: This study is dedicated to synthesis and electrochemical application of porous carbon materials from different biomass and polymer by-products.

Materials and methods: Activated carbon was synthesized from mixtures (1:1) of tar from steam pyrolysis of varios biomass (cherry stones, grape stones, olive stones) and furfural are treated with H_2SO_4 at 160 ^oC upon continuous stirring. The obtained solid product is heated to 600 ^oC in a covered silica crucible with a heating rate of 10 ^oC/min under nitrogen atmosphere. Steam activation with water vapour at 800 ^oC for 1 h is used to obtain activated carbon with alkaline surface. Tar from various biomass waste (cherry stones, grape stones, olive stones) was obtained by collecting the liquid products from carbonization at 600 ^oC. Two-stage procedure, including preliminary thermo-oxidation treatment with mineral acids at 200 ^oC and subsequent carbonization at 600 ^oC, was applied to produce carbon from polymer waste; hydropyrolisis at 800 ^oC was used as additional procedure. The structure and properties of obtained carbon materials were studied by SEM, XRD, BET, etc.

Results: The chemical composition of the initial mixture significantly affects the physicochemical properties of the obtained activated carbon. Lignin and cellulose content in biomass precursors determine formation of nanoporous carbons with high surface area and surface oxygen functionalities. The investigation of the relation between the properties of the precursor and the structure of the obtained porous carbons indicate, that the composition of the precursor affects the synthesis procedure, and consequently, the final characteristics and structure of the carbon products. It was shown that carbon-based electrode material demonstrates very good capacitive characteristics.

Conclusions: The results show that porous carbons synthesized from polymers and different biomass are characterized by moderately high surface area and presence of surface oxygen functionalities, which imply their possible use for different applications. It was shown that carbon-based electrode material demonstrates very good capacitive characteristics.

Acknowledgements: *The authors appreciate the funding by WAPUMECA project in the frame of collaboration between Romanian Academy Sciences and Bulgarian Academy of Sciences, and by Project DFNI-E02-18 with Bulgarian National Science Fund.*

BIODEGRADABLE POLYMERIC COMPOSITE BASED ON PBAT

E. Grosu[1], C. Opran[2], M. Enachescu[2], M. Rapa[1], A. Turcanu, A. Andras[1], A. Trifoi[1]

[1]S.C. ICPAO S.A., Medias, Sibiu county, 8, Carpati, 551022, Romania

[2]University POLITEHNICA Bucharest, 313, Splaiul Independntei, 060042

**Corresponding author: elena_grosu@yahoo.com*

Keywords: biodegradable polymers; PBAT; PLA; mechanical properties; SEM

Introduction: Thermoplastic polymers based on petrochemical resources exhibit good mechanical properties as tensile strength, good barrier to gases and are relative low cost. For this reason polymers as polyethylene terephthalate (PET), polyethylene (PE), polypropylene (PP) and polyamide (PA) are used extensive to process into packaging. The inconvenient of the packaging is generation of large quantities of wastes. An alternative for these polymers is the use of polymers from renewable resources, that biodegrade when are exposed in the soil, producing water, carbon dioxide and inorganic compounds. We present some investigations on mechanical properties and morfologic feature of biodegradable polymeric recipes based on PBAT, in order to be used in packaging industry.

Materials and methods: The materials used were PBAT Ecoflex FBX 7011 from BASF, PLA 4032D from Nature Works Company and mineral fillers Imeris Talc Luzenac A20. The materials were melt blended into reactive extruder with corotating screw. The physical-mechanical test and morphology analysis by SEM (figure 1 and 2) were performed on some polymeric recipes containing PBAT, PLA and mineral fillers, in order to evidence the influence of the each material content.

Results: The tensile properties of recipe with higher content of PLA exhibit the optimal values. SEM investigations reveal a good compatibility between the components and uniform morphology (figure 1 and 2).

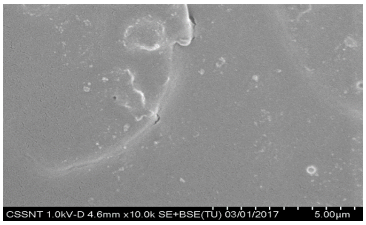


Figure 1. SEM micrography of polymeric recipe with 30% PLA

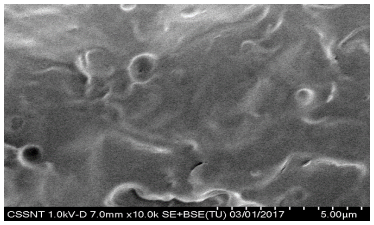


Figure 2. SEM micrography of polymeric recipe with 60% PLA

Conclusions: Results obtained for physical/mechanical tests of polymeric recipes based on PBAT, PLA and mineral fillers were finded optimal for use theses materials in biodegradable packaging.

References:

[1]. Arvanitoyannis, I. S. Totally and partially biodegradable polymer blends based on natural synthetic macromolecules: preparation, physical properties, and potential as food packaging materials. Journal of Macromolecular Science, Reviews in Macromolecular Chemistry and Physics, 1999, C39(2), 205-271.

[2]. Rotzinger B., Talc-filled PP: A new concept to maintain long term heat stability. Polymer Degradation and Stability. 2006, 91, 2884-2887.

[3]. Petersen, K., Nielsen, P. V., Bertelsen, G., Lawther, M., Olsen, M. B., Nilssonk, N. H., et al. Potential of biobased materials for food packaging. Trends in Food Science & Technology, 1999, 10, 52-68.

FATTY ACID AMIDE ANALOGUES WITH POTENTIAL BIOLOGICAL EFFECTS

C. Negut[1*], C. Tanase[1], L. Pintilie[1], D. I. Udeanu[2*], E. Morosan[2], C. Draghici[3], M. Maganu[3]

[1]*National Institute for Chemical - Pharmaceutical Research and Development ICCF, Bucharest, Romania*

[2]*Faculty of Pharmacy, University of Medicine and Pharmacy "Carol Davila", Bucharest, Romania*

[3]*Organic Chemistry Center "C.D.Nenițescu", 202B Splaiul Independentei, 060023, Bucharest, Romania*

** Corresponding authors: negutcatalina79@gmail.com, denisaudeanu@gmail.com*

Keywords: Fatty acid amide analogues; food-intake; body weight regulation

Introduction: Obesity and overweight are considered two of the most important medical problems of current day, due to the effect on general health of population and the diseases associated or further developing like metabolic syndrome, cardiovascular disease, type II diabetes mellitus (T2D) [1] and some forms of cancer. Obesity is a condition that can be very well prevented, and compared to applying treatment, prevention strategies are more effective and not expensive [2, 3].

It is known that fatty acid amides are not only important for industrial applications [4] and even as ingredient of foods. Due to increased knowledge of their important mediator effect as endogenous molecules for many biological activities in different tissue types, the biochemical, pharmacological [5] studies are extended to new analogues of fatty acid amides.

Materials and methods: Albino swiss (NMRI) male mice weighing 18±2g were purchased from the Animal Biobase of the University of Medicine and Pharmacy "Carol Davila", Bucharest. Animals were kept in standard laboratory conditions and were fed twice a day and received water ad libitum. The experiment was performed in compliance with European Communities Council Directive 2010/63 and Ordinance No. 37 of the Romanian Government from 2nd February, 2002.

Results: Fatty acid amide analogues were synthesized from oleic acid, activated by 1,1'-carbonildiimidazole to oleoylimidazole and amines, and characterized by IR, MS, ^{1}H- and ^{13}C-NMR spectra. The compounds were investigated for their influence on body weight and food-intake effects on an obesity-induced mouse model.

Conclusions: The fatty acid amide analogues demonstrate the potential use of these molecules in obesity treatment.

Acknowledgements: *This paper has been financed through the NUCLEU Program, which is implemented with the support of ANCSI, project no. PN 16-27 01 06.*

References:

[1]. Naughton S.S., Mathai M.L., Hryciw D.H., McAinch A.J., Int. J. Endocrinology, 2013, p. 1-11.
[2]. King L., Gill T., Allender S., Swinburn B., Best practice principles for community-based obesity prevention: development, content and application, Obes Rev 12, 2011, p. 329-338.
[3]. Wang Y.C., McPherson K., Marsh T., Gortmaker S.L., Brown M., Health and economic burden of the projected obesity trends in the USA and the UK, The Lancet. 378, 2011, p. 815-825.
[4]. Khare S.K., Kumar A., Kuo T.M., Bioresour. Technol. 100, 2009, p. 1482-1485.
[5]. Farrell E.K., Merkler D.J., Drug Discovery Today 13, 2008, p. 558-568.

SILVER DOPING ENHANCES THE INTERACTION OF ZEIN NANOPARTICLES WITH GRAM-NEGATIVE BACTERIA LIPOPOLYSACCHARIDES

K.H. Jaberi, M. Mernea, O. Calborean, L. Petrescu,
I. Gheorhe, D.F. Mihailescu, G. Stoian

University of Bucharest, Faculty of Biology, Splaiul Independentei, No 91-95, 050095, Sector 5, Bucharest, Romania

**Corresponding author: maria.mernea@bio.unibuc.ro*

Keywords: Gram-negative bacteria; zein; lipopolysaccharides; metal ions; THz spectroscopy

Introduction: The misuse of antibiotics has led to the emergence of multidrug resistant bacterial strains. Most of the antibiotic resistance mechanisms are ineffective against nanoparticles (NPs) because their mode of action involves direct contact with the bacterial cell wall. Therefore, the attention was been focused on new and powerful NP-based materials with antibacterial activity and NPs in particular have demonstrated broad-spectrum antibacterial properties against both Gram-positive and Gram-negative bacteria.

A series of studies have shown that many NPs can inhibit bacterial growth and biofilm formation, including Au-based NPs, Ag-based NPs, ZnO NPs, CuO NPs and the biochemical machanism involves the prompt neutralization of the surface electric charge of the bacterial membrane and change its penetrability, ultimately leading to bacterial death. Protein capping agents were used for the stabilization of the nanoparticles. Although the antibacterial properties of metal ions are well established, there are various hypotheses regarding the mechanism of action. In this context, the aim of our study was to analyze the interaction between nanoparticles based on zein doped with a series of metal ions (Ag^{+}, Cu^{2+}, Zn^{2+}) and membrane lipopolysaccharides (LPS) present in the wall of gram-negative bacteria.

Materials and methods: NP were synthesized following the method described in (1), using a different zein:soy lecithin ratio. Zein-lecithin NPs were doped with different metal ions metal ions (Ag^{+}, Cu^{2+}, Zn^{2+}). NPs were mixed with increasing concentrations of *Escherichia coli* and *Pseudomonas aeruginosa* LPS molecules and were analysed with TeraHertz (THz) and Fourier Transformed Infrared (FTIR) spectroscopies. The antimicrobian effect of synthesized NPs was assessed by agar diffusion test.

Results: Performed assays have shown significant differences between the antimicrobial activity and the interaction of NPs doped with different metal ions and *E. coli* or *P. aeruginosa* LPS molecules.

Conclusions: Our results demonstrate that Ag Zein NPs has stronger antimicrobian activity in comparison with Zein NPs doped with other ions.

Acknowledgements: *Research was supported by UEFISCDI PNII Grants PCCA-198/2014. The authors thank Prof. Gabi Drochioiu, Univ. Al. I. Cuza Iaşi, Romania, for kindly spplying us with a pure zein sample.*

References: [1] Dai L, Sun C., Wang D., Gao Y. The Interaction between Zein and Lecithin in Ethanol-Water Solution and Characterization of Zein–Lecithin Composite Colloidal Nanoparticles. PLOS ONE 2016; 11(11): e0167172.

PHYSICO-CHEMICAL, MORPHOSTRUCTURAL AND COLORISTICAL CHARACTERIZATION OF MODIFIED PIGMENTS FOR LEATHER DYEING

M. Deaconu*, A.A. Athanasiu, S. Doncea, R. Senin, M. Mateescu

National Research and Development Institute for Chemical and Petrochemical –ICECHIM, Splaiul Independentei , no 202, sector 6 , Bucharest, Romania;

**Corresponding author: deaconu319@yahoo.com and aathanasiu@yahoo.com*

Keywords: modified pigments; physico-chemical; morphostructural and coloristical characterization

Introduction: The research activities performed to achieve a new process for dyeing natural leather using non-specific coloring materials namely pigments: PBlk 7 (Carbon Black), PBl 15:3 (Blue Phthalocyanine) and PR 122 (Quinacridone Red). The pigments are totally insoluble substances in water and organic solvents and so they can not be used as such to dye leather in aqueous media. In this project, the our team aims to research a process for synthesis by functionalization of pigment particles and their conditioning to be brought into a form of coloidall solution or nano-dispersion which can be used to dye leather in aqueous medium.

Materials and methods: The pigments modified by synthesis [1], [2] were characterized physico-chemically, morphostructurally and coloristical. Identification and characterization of phisico-chemical and morpho-structural characteristics of the functionalized pigments compared to the original powder product, using FT-IR, TEM, TGA, elemental analysis and the average particle diameter distribution. The methods used for the study are generally known except for the morphostructural characterization method that used *"the negative color technique"* to highlight the particles on a colored background.

Results: -Fourier Transformed (FT-IR) spectroscopy analyzes indicated the degree of modification/ functionalization of the pigment particles, namely the chemical attachment of some ionic functional groups : $-SO_3^-$; $-COO^-$; $C_6H_4SO_3^-$ obtained by sulphonation; sulphonation +oxidation or „diazotation". -Coloristical characterization was performed by Absorption Spectra in VIS domain.

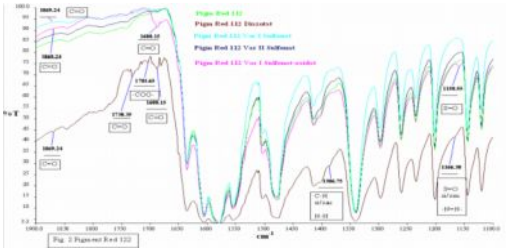


Fig 1-The FT-IR spectrum for PR 122)

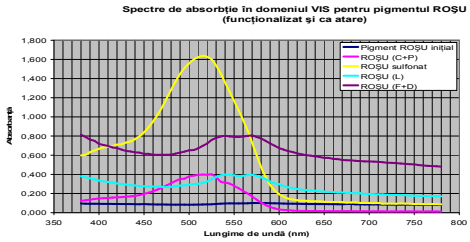


Fig.2-The absorption spectrum in VIS domain for PR 122

Conclusions: Through the characterizations performed on the final color materials it was found that the results obtained were good and reproducible at laboratory and for industrial level.

Acknowledgements: *This work was financially supported by MECS-UEFISCDI, in the frame of Romanian PN II-Partnership -Joint Applied Research Projects Program - Contract No. 216/2014, stage 4/ 2017*

References:

[1]Bv US 6,699,319 /2004, *Process for preparing modified pigments*

[2]Sujeeth; Puthalath K. (Ballwin, MO), Kane; John P. (Ellisville, MO), Ouellette; Daniel A. (St. Peters, MO), Ulrich; Mark (Florissant, MO), Bv US 9,221,986/2015 *„Self-dispersing particles and methods for making and using the same"*

THE EFFECT OF STYRENE-ISOPRENE BLOCK-COPOLYMERS AND CLAYS ON POLYMER COMPOSITES BASED ON POLYPROPYLENE

B. Spurcaciu[1], L. Iancu[1*], P. Ghioca, R. Grigorescu[1], C. Nicolae[1], R. Gabor[1], I. Bujanca[1], M. Rapa[2], E. Grosu[2], M. Matei[3]

[1] The National Institute of Research and Development for Chemistry and Petrochemistry ICECHIM Bucharest.
[2] S.C. ICPAO S.A., Medias.
[3] Politehnica University of Bucharest, Center of Research and Eco-Metallurgical Expertise

**Corresponding author: lorena.iancu@icechim.ro*

Keywords: polymer composites; polypropylene; styrene-isoprene block-copolymers; clays

Introduction: The study aimed the improvement of thermal and mechanical properties of recycled polypropylene by achieving polymeric composites with styrene-isoprene block-copolymers and nanoclay silicates.

Materials and methods: Styrene-isoprene block-copolymers (SIS) were obtained by anionic sequential polymerization. The reactions were carried out in cyclohexane solution through a three-stage process and were initiated with n-butyl lithium.

Polymer composites based on recycled polypropylene were obtained by melt mixing in a Brabender plastograph with styrene-isoprene block-copolymers and nanoclay silicates.

Results: The polymer composites based on recycled polypropylene with styrene-isoprene block-copolymers and nanoclay silicates were characterized by Differential Scanning Calorimetry (DSC), Thermo-gravimetric Analysis (TGA), Dynamic mechanical analysis (DMA), physical-mechanical analysis, and X-ray Diffraction (XRD).

Conclusions: The results indicated an improvement of thermal and mechanical properties of synthesized composites materials compared to recycled polypropylene.

Acknowledgements: *This* work *was supported by the Romanian National Authority for Scientific Research Core Program, under Grant PN.16.31.03.01*

References:

[1]. Paul Ghioca, Lorena Iancu, Ramona Marina Grigorescu, Bogdan Spurcaciu, Maria Rapa, Cornel Cincu, Alexandra Pica, Ecaterina Matei **"**Recovered Polypropylene Composites with High Impact Strength" *Mater. Plast.*,1, 2017, 18-22.

[2]. Ghioca P., Iancu L., Vuluga Z., Spurcaciu B., Grigorescu R., Iorga M., Florea D., The Morphology Influence of Styrene-Diene Block Copolymers Reinforced with Bentonite, *Mater. Plast.*, 2016; **53**:34-37.

[3]. Messori M., Recent Advances in Elastomeric Nanocomposites, Advances Structured Materials, edited by Mittal V, et all, Springler-Verlag, 2011, p. 57.

MORPHOLOGICAL AND STRUCTURAL PROPERTIES OF ALKYL-MODIFIED SILICA PARTICLES OBTAINED FROM SODIUM SILICATE

C.L. Nistor[1*], S.G. Nițu[1], E. Alexandrescu[1], C. Petcu[1], R. Ianchiş[1], R. Şomoghi[1], I.C. Gîfu[1], B. Trică[1], C.M. Ninciuleanu[1]

[1]National Research & Development Institute for Chemistry and Petrochemistry – ICECHIM, Splaiul Independentei no.202, 6th district, P.O. 35-174, 060021, Bucharest, Romania

**Corresponding author: lc_nistor@yahoo.com*

Keywords: alkyl-silica particles; thyme oil encapsulation; sodium silicate; oleic acid; mesoporous silica

Introduction: Different alkyl-silica hybrid particles were synthesized by a sol-gel process, in an aqueous medium, using oleic acid - sodium oleate complex as stabilizing system. The alkyl silanes (RTES) / sodium silicate (Na_2SiO_3) molar ratio was 1/5. The purpose of this study was to evaluate the effect of various alkyl functions *(C1-C18)*, *in situ* grafted by sol-gel technique, on the morphological and structural properties of the resulted hybrid particles, as well as on their potential use as carriers for thyme oil encapsulation. We also investigated the effect of thyme oil addition to the reaction mixture on the particle's final properties.

Materials and methods: The main source silica particles preparation was sodium silicate. Along with it, various silica co-precursors (RTES), carrying different alkyl functionality (methyl triethoxysilane (MeTES), n-propyl triethoxysilane (PrTES), isobutyl triethoxysilane), isobutyl triethoxysilane (iBuTES), octyl triethoxysilane (OTSO), dodecyl triethoxysilane (DOTEOS) and octadecyl triethoxysilane (ODTES)), have been added. The resulted alkyl-functionalized particles were evaluated for size, polydispersity index, zeta potential and surface morphology. After washing, drying and calcining, they were also investigated by N_2 adsorption-desorption analyses.

Results: Studying the effect of the organic functions from the different alkyl-silane co-precursors on the morpho-structural properties of the alkyl-silica particles, gave us valuable information for obtaining stable and homogeneous dispersions and about their potential use as carriers for bioactive volatile oils.

Conclusions: Optimized silica particles dispersions, encapsulating thyme-oil, were obtained due to the use of the adequate amount of surfactant and essential oil. All the used alkyl-silane co-precursors led to mesoporous silica particles, able to effectively encapsulate the active substance.

Acknowledgements: *This work was supported by the grant funded by the Romanian National Authority for Scientific Research, project number PN 16.31.03.04.04 and by a grant of the Romanian National Authority for Scientific Research and Innovation, CNCS/CCCDI-UEFISCDI, project number 19BG/2016 (PN-III-P2-2.1-BG-2016-0157), within PNCDI III.*

ZIRCONIUM MODIFIED SBA-15 MESOPOROUS SILICA

R. Ganea[1*], S. Velea[1], G. Vasilievici[1], D. Bombos[2]

[1]*National Research and Development Institute of Chemistry and Petrochemistry ICECHIM 060021 Bucharest, Romania*

[2]*Petroleum - Gas University of Ploiesti, 39 Calea Bucuresti,100520, Ploiesti, Romania*

**Corresponding author: rganea@gmail.com*

Keywords: mesoporous silica; zirconium modification; heterogeneous catalyst; acidity; nitrogen sorption

Introduction: Zirconium-containing mesoporous materials can find applications in many important reactions as hydrocarbon isomerization, alkylation and etherification. SBA-15 mesoporous silica of 2D hexagonal ordered structure is an attractive catalytic support due to its large pores (2-10 nm) and high hydrothermal stability [1-2]. In this paper, zirconium - containing SBA-15 mesoporous silica samples have been synthesized and characterized by N_2 sorption and acidity measurements.

Materials and methods: Zirconium oxynitrate-$ZrO(NO_3)_2 \cdot xH_2O$ was used as Zr^{4+} precursor to prepare zirconium-containing SBA-15 by direct synthesis. The syntheses of SBA-15 and Zr-SBA-15 were performed in acidic medium by neutral templating route using triblock- copolymer-Pluronic P_{123} as surfactant and tetraethylorthosilicate as silica source. An appropriate amount of zirconium precursor was added to the synthesis mixture to yield a Si/Zr molar ratio of 20 and 10, respectively. The syntheses of SBA-15 and Zr-SBA-15 samples were carried out in the following conditions: (i) stirring at room temperature for 24 hrs and (ii) ageing at 90^{o}C for 48 hrs in static conditions. The as-synthesized samples were calcined in air at 550^{o}C for 48 hrs to remove the organic molecules.

The textural properties were determined by nitrogen adsorption-desorption measurements using a Quantachrome Nova 2200e sorption analyzer and the acidity of the synthesized samples was evaluated by the temperature programmed desorption of diethyl amine using a thermogravimetric equipment.

Results: All the samples exhibited type IV adsorption-desorption isotherms with H_1 hysteresis loop, characteristic of SBA-15 mesoporous silica [3]. A correlation between textural properties and synthesis parameters of Zr-SBA-15 has been established. The total acid strength of Zr-SBA-15 samples increased with zirconium loading in the synthesis mixture of mesoporous silica.

Conclusions: SBA-15 and Zr-SBA-15 mesoporous materials have been synthesized by neutral surfactant (Pluronic P_{123} triblock-copolymer) assisted route. The preparation of Zr-SBA-15 by direct synthesis is to be taken into account to develop a good solid acid catalyst for esterification reactions.

Acknowledgements: *The authors gratefully acknowledge the financial support of the UEFISCDI, Romania, financing contract no. 80BG/2016 (GLYCESTER)*

References: :

[1]. Yang L, Yang X. Tian E. Vattipalli V. Fan W. Lin H. J. Catal. 2016; 333: 207–216 (*Journal article)*.

[2]. Garg S. Soni K. Kumaran M. Bal R. Gora-Marek K. Gupta J. K. Charma L. D. Dhar G. M. Catal. Today. 2009; 141: 125–129 (*Journal article)*.

[3]. Malero J. A. Bautista L. F. Iglesias J. Morales G. Snachez-Vasquez R. Catal. Today. 2012; 195: 44–53 (*Journal article)*.

INCREASE THE PERFORMANCE OF THE CUMULATIVE FABRICATION TECHNIQUE BY CONTROLLING THE ADHESION BETWEEN THE LAYERS VIA MELT RHEOLOGY

M.E. Grigore[1], M. Ghiurea[1], R. Trusca[2], R. Stoica[1], C.M. Ninciuleanu[1], R. Ianchis[1], R.M. Grigorescu[1], M. Ladaniuc[1], D. Dimonie[1]

[1] The National Research and Development Institute for Chemistry and Petrochemistry – ICECHIM, Spl. Independentei, 202, Bucharest, Romania
[2]Politehnica University of Bucharest, Spl. Independentei, 313, Bucharest, Romania

**Corresponding author: grigore.madalina10@gmail.com*

Keywords: additive / cumulative /3D printing technique; adhesion; layers; melt rheology; renewable material

Introduction: The application of the additive / cumulative / 3D printing technique[1] compared to the subtractive ones is particularly cost-effective because it allows for rapid manufacturing of objects, better suited to market requirements, with any form and geometry, robust, compact, sometimes even with layered structure. Unfortunately occasionally, after a couple of well bond layers, follow others that do not stick to each other. The goal of the paper was to find a method to increase the adhesion between the 3D printed layers.

Methods and materials: The 3D printing of some renewable materials based on PLA was simulated by depositing the extrudates from an indexer as layer over layer (fig.1a). The dependence of the adhesion between the resulted layers, on the melt flow conditions it was studied.

Results: It was found that, depending on the melt flow conditions, after deposition, the adhesion between the layers occurs or not. If, at overlaying, the polymer extrudate is rather viscous then, there is no adherence between the resulted solid layers. If the extrudate viscosity is too small, then the polymeric material cannot be overlayed because it become a compact mass, sometimes yellow due to degradation. The differences between the described situations are related to the melt properties (mainly viscozity) in different flowing conditions (fig.1b).

Fig.1

a) **b)**

Conclusions: Melt flow conditions which allow the controlling of the melt viscosity and so the necessary overlaying of the polymeric material and adhesion between layers to ensure the integrity at impact of the resulted piece have been selected.

Acknowledgements: *The researches were supported by the project no. PN.16.31.03.02.*

References: SR/ISO/ASTM 52900:2016 – Fabricatie aditiva. Principii generale. Terminologie, ASRO-Standard Roman, Septembrie 2016

BIODEGRADATION OF SOME RENEWABLE ITEMS ACHIEVED BY COMPARATIVE TECHNIQUES: 3D PRINTING AND CLASSIC MELT FLOWING

M.E. Grigore[1], M. Ghiurea[1], M. L. Jecu[1], I. Raut[1], M. Calin[1], S. Doncea[1], R. Trusca[2], R. Stoica[1], C.M. Ninciuleanu[1], R. Ianchis[1], R.M. Grigorescu[1], M. Ladaniuc[1], D. Dimonie[1]

[1] The National Research and Development Institute for Chemistry and Petrochemistry – ICECHIM, Spl. Independentei, 202, Bucharest, Romania
[2]Politehnica University of Bucharest, Spl. Independentei, 313, Bucharest, Romania
**Corresponding author: grigore.madalina10@gmail.com*
Keywords: 3D printing; classical melt flow techniques; renewable; biodegradation; Aspergillus Niger

Introduction: Biodegradation of renewable polymeric materials is one of their main advantages over non-renewable those. Takeing into consideration that the 3D printing is looked as the possible third industrial revolution[1], the goal of the paper was to compare the biodegradation behavior of the same item, obtained from the same renewable polymeric materials, but using two different routes: 3D printing and classical melt flowing.

Methods and materials: The same samples (20x20x1 mm plates) were realized from the same renewable material based on PLA, both through 3D printing with horizontally and vertically overlaying and by pressing. The biodegradation with *Aspergillus Niger* was followed by periodic characterization (10 days, 90 days) via SEM, DSC, DTA-TGA and comparing the measured properties with initial those.

Results: After 90 days of biodegradation, in all cases, the Aspergillus *Niger* has developed predominantly in morphological areas with defects both on the surface and fracture, regardless the obtaining procedure of the studied plates. The more the structural defects, the bigger is the biodistruction.

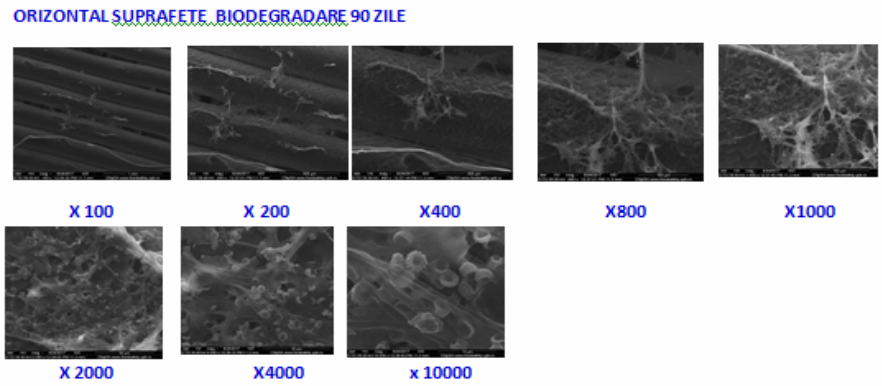


Fig.1 Biodegradation, after 90 days of plates obtained from the same renewable materials through 3D printing

Conclusions:

Differences depending on the obtaining procedure of the analyzed plates, regarding the biodistruction mechanism (initiation and evolution) it was observed. The rigorous controlling of the morphological defects can diminish the biodistruction in both situations. The biodistruction is continued until obtaining evidence one each mechanism and its dependence on the achieving procedure of analyzed samples.

Acknowledgement: *The researches were supported by the project no. PN.16.31.03.02.*
References: [1]Aaron Council at all., 3D Printing: Rise of the Third Industrial Revolution (Gyges 3D Presents), https://www.amazon.com/3D-Printing-Industrial-Revolution-Presents-ebook/dp/B00IPO42F2

MORPHOLOGICAL DEPENDENCIES ON THE OBTAINING PROCEDURE OF RENEWABLE PLASTIC ITEMS: 3D PRINTING AND CLASSIC MELT FLOWING

M.E. Grigore[1], R. Stoica[1], R. Trusca[2], M. Ghiurea[1], C.M. Ninciuleanu[1], R. Ianchis[1], R.M. Grigorescu[1], M. Ladaniuc[1], D. Dimonie[1]

[1] The National Research and Development Institute for Chemistry and Petrochemistry – ICECHIM, Spl. Independentei, 202, Bucharest, Romania
[2]Politehnica University of Bucharest, Spl. Independentei, 313, Bucharest, Romania
**Corresponding author: grigore.madalina10@gmail.com*

Keywords: morphology; plates; surface and fracture defects; 3D printing; classical melt flowing technique

Introduction: It is known that there are opinions according to which the 3D printing can become the future three industrial revolution. The purpose of the paper was to identify the dependence of morphological defects (meaning according to [1]) of some renewable plastics products on the obtaining technique: 3D printing and classical melt flowing (press).

Methods and Materials: The same samples (20x20x1 mm plates) were achieved from the same renewable material based on PLA, both through 3D printing, with horizontally and vertically overlaying , and by pressing. The 3D printing conditions were selected considering the variation of the surface aspects of the extrudates obtained at a melt flow indexer in different conditions. The morphological defects have been identified by SEM, DSC, TGA-DTA, others.

Results: Although the 3D printing conditions were identical with those in which, at indexer, extrudates without defects have been obtained, the 3D printed plates had several defects. It was observed that the number of defects depends not only on the printing conditions and the polymeric material deposition methods, but also on the formulation.

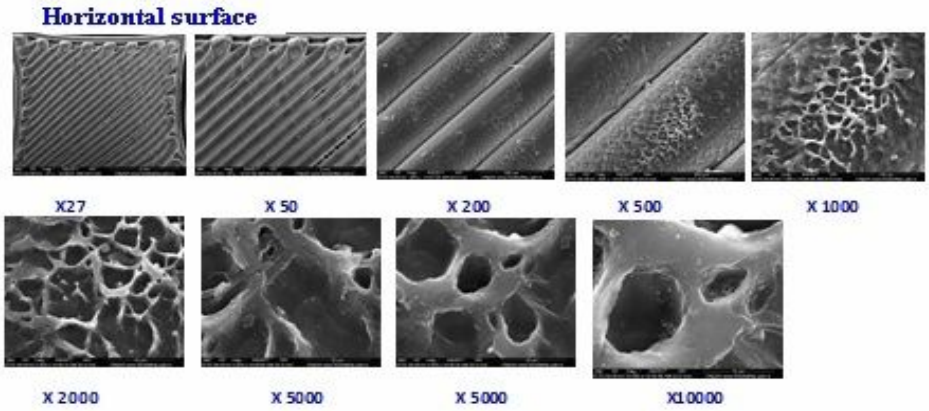


Fig.1 The surface defects of 3D printed plates obtained by horizontal deposition of the renewable material layers

Conclusions: The formulation of the renewable material designed for 3D printing is not the same with those needed for classical melt processing techniques. In 3D printing the melt flow is carried out according to its own laws, other than those of the known classical melt flowing procedures. If the melt processing is not well conducted than, even plates obtined by pressing may have also many defects. The diminishing of the morphological defects must consider mainly the melt rheology path.

Acknowledgement: *The researches were supported by the projects no. PN.16.31.03.02 and PN-III-P2-2.1-CI-2017-0569.*

References:

[1] Linda Sawyer,David Grubb,Gregory F. Meyers, Polymer Microscopy, Library of Congress, 1987, ISBN 978-0-387-72627-4,E-

POLYMER COMPOSITES BASED ON POLYPROPYLENE WITH STYRENE-BUTADIENE BLOCK-COPOLYMERS AND CLAYS

B. Spurcaciu[1], R. Grigorescu[1]*, P. Ghioca[1], L. Iancu[1], N. Nicolae[1], R. Gabor[1], I. Bujanca[1], M. Rapa[2], E. Grosu[2], E. Matei[3]

[1] The National Institute of Research and Development for Chemistry and Petrochemistry ICECHIM Bucharest
[2] S.C. ICPAO S.A., Medias
[3] Politehnica University of Bucharest, Center of Research and Eco-Metallurgical Expertise

**Corresponding author: rmgrigorescu@gmail.com*

Keywords: polymer composites, polypropylene, thermoplastic elastomers, clays

Introduction: The study aim was the improvement of thermal and mechanical properties of recycled polypropylene composites with thermoplastic elastomers and nanoclay silicates obtained by melt alloying.

Materials and methods: Styrene-butadiene block-copolymers (SBS) were obtained by anionic sequential polymerization. The reactions were carried out in cyclohexane solution through a three-stage process and were initiated with n-butyl lithium.

Polymer composites based on recycled polypropylene were obtained by melt compounding in a Brabender plastograph with styrene-butadiene block-copolymers and nanoclay silicates.

Results: The polymer composites based on recycled polypropylene with styrene-butadiene block-copolymers and nanoclay silicates were characterized by Differential Scanning Calorimetry (DSC), Thermo-gravimetric Analysis (TGA), Dynamic mechanical analysis (DMA), physical-mechanical analysis, and X-ray Diffraction (XRD).

Conclusions: The results indicated an improvement of thermal and mechanical properties of composites compared to recycled polypropylene.

Acknowledgements: *This work was supported by Program 2 - Creşterea competitivităţii economiei româneşti prin cercetare, dezvoltare şi inovare, Project : Cecuri de inovare,* ***NR. 122CI / 2017*** *"COMPOZITE ANTISOC PE BAZA DE POLIPROPILENA RECUPERATA CU ANDURANTA RIDICATA"*

References:

[1]. Ghioca P., Iancu L., Vuluga Z., Spurcaciu B., Grigorescu R., Iorga M., Florea D., The Morphology Influence of Styrene-Diene Block Copolymers Reinforced with Bentonite, *Mater. Plast.*, 2016; **53**:34-37.

[2]. Utracki L.A., Wilkie C.A., Polymer Blends Handbook, Springer, 2014.

[3]. Chen W-C, Lai S-M, Chen C-M, Preparation and properties of styrene-ethylene-butylene-styrene block copolymer/ clay nanocomposites: I. Effect of clay content and compatibilizer types, *Polym Int, 2008;* **57**: 515–522.

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

NEW ELECTROCHEMICAL SENSOR DEVELOPED FOR N-ACETYL-5-METHOXYTRYPTAMIN DETECTION

D. López-Iglesias[1], J. J. García-Guzmán[1], J. M. Palacios-Santander[1], L. Cubillana-Aguilera[1], M. Marin[2], S. Lupu[3], C. Lete[2,*]

[1]Institute of Research on Electron Microscopy and Materials (IMEYMAT), Department of Analytical Chemistry, Faculty of Sciences, Campus de Excelencia Internacional del Mar (CEIMAR), University of Cadiz, República Saharaui, S/N. 11510 Puerto Real, Cadiz, Spain

[2] Institute of Physical Chemistry "Ilie Murgulescu" of the Romanian Academy, Bucharest, Romania

[3] Faculty of Applied Chemistry and Materials Science, University Politehnica of Bucharest, Romania

**Corresponding author: cecilia_lete@yahoo.com*

Keywords: melatonin; carbon sonogel; electrochemical sensor

Introduction: The outstanding properties of Sonogel-Carbon materials as wide operational potential window, renewable surface, high conductivity, good mechanical properties, easily to be modified with chemical or biological modifiers, and ~~a~~ quite good stability in different solvents, made them very attractive in electrochemical applications field. The synthesis is based on sonocatalysis that involves the application of high-energy ultrasound directly to the precursors. In this manner the ultrasonic cavitation is achieved, promoting hydrolysis with acidic water in the absence of any additional solvent. Melatonin (N-acetyl-5-methoxytryptamin), the molecule of darkness, is a lipophilic hormone secreted by the pineal gland and this is produced during night. This hormone is synthesized by the pineal parenchymal cells from serotonin by N-acetylation and O-methylation, and secreted by them into the blood and the cerebrospinal fluid, being a strong antioxidant~~,~~ with inhibitory activity for some cancer forms, and also has good effects in neuronal disorders.

Materials and methods: Electrochemical experiments were performed with an Autolab PGSTAT 302 N potentiostat, controlled by GPES 4.9 electrochemical software from Eco-Chemie (The Netherlands). Sonogel-Carbon (SNGCE), Sonogel-Carbon composite material based on conducting polymers as PEDOT (SNGCE/PEDOT), Sonogel-Carbon modified with gold nanoparticles (SNGCE/AuNPs) electrodes were synthesized and characterized by Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS).

Results: Assessment of the analytical performance in terms of limits of detection and quantification, linear response range, sensitivity and repeatability of the electrochemical sensors based on Sonogel-Carbon material was achieved. The obtained sensitivity was 4.3×10^{-3}A/**M.** The lower Melatonin concentration that could be measured in optimal conditions established within this study is 160 nM. The linear response was in the concentration range from 160 nM to 10 μM.

Conclusions: This work demonstrates that Sonogel-Carbon electrodes, provide an easy, fast and reliable analytical tool for the detection and determination of melatonin.

ELECTROCHEMICAL BIOSENSORS BASED ON COMPOSITE MATERIALS FOR CATECHOLAMINES AND POLYPHENOLS ANALYSIS

J.J. Garcia-Guzmán[1], L. Cubilana Aguilera[1], D. Bellido-Milla[1], C. Lete[2], M. Marin[2], J.M. Palacios Santander[1], S. Lupu[3*]

[1]*Institute of Research on Electron Microscopy and Materials (IMEYMAT), Department of Analytical Chemistry, Faculty of Sciences, Campus de Excelencia Internacional del Mar (CEIMAR), University of Cadiz, República Saharaui, S/N. 11510 Puerto Real, Cadiz, Spain*

[2]*Institute of Physical Chemistry "Ilie Murgulescu" of the Romanian Academy, 202 Splaiul Independentei, 060021 Bucharest, Romania*

[3]*Department of Analytical Chemistry and Environmental Engineering, Faculty of Applied Chemistry and Materials Science, University Politehnica of Bucharest, 1-7 Gh. Polizu Street, 011061 Bucharest, Romania*

**Corresponding author: stelianl@yahoo.com*

Keywords: electrochemical biosensors; tyrosinase; dopamine, caffeic acid; beers

Introduction: New electrochemical biosensors based on Sonogel-Carbon electrodes (SNGCEs) modified with composite materials consisting of a conducting polymer, poly[3,4-ethylenedioxythiophene], (PEDOT), and enzyme (tyrosinase, Tyr), have been developed. The fabrication of these biosensors has been achieved via original sinusoidal voltages (SV) and sinusoidal currents (SC) preparation methods [1]. The obtained biosensors have been applied in the electroanalysis of dopamine and caffeic acid, as well as in real samples analysis, i.e. beers and wines.

Materials and methods: The PEDOT-Tyr composite coatings have been electrodeposited onto SNGCEs using the SV and SC procedures. The SV procedure consists in the application of a sinusoidal voltage with fixed frequency and amplitude over a selected d.c. potential. The SC procedure lies in the use of a sinusoidal current of fixed frequency and amplitude, superimposed on a d.c. current. The modified SNGCEs have been characterized by electrochemical methods.

Results: A comparison of the analytical performances of SV- and SC-based biosensors has been perfomed. It was observed that the SC-based sensor showed better analytical performance for dopamine electroanalysis, with a linear response range from 20 to 300 μM. The SC-based biosensor has been applied in the dopamine determination in pharmaceutical products (Zentiva, Romania) with good recoveries comprised between 96 and 110%. This biosensor was also used in the polyphenols index assessment, expressed as caffeic acid content, in several kinds of beers, and good repeatability and reproducibility values, comprised between 5 and 15%, have been obtained.

Conclusions: The SC-based biosensor has displayed better analytical performance in terms of linear response range, repeatability, reproducibility, and limit of detection, for dopamine and beers analysis.

Acknowledgements: *This work was supported by a grant from the Romanian National Authority for Scientific Research, CNCS–UEFISCDI, Project number PN-II-ID-PCE-2011-3-0271. J.J. Garcia-Guzmán greatly acknowledges the PhD scholarship from EDUCA for supporting a research stage at the University Politehnica of Bucharest.*

References:

[1]. Garcia Guzman JJ, Cubilana Aguilera L, Bellido Mila D, Rodriguez NI, Lete C, Palacios Santander JM, Lupu S, Development of Sonogel-Carbon based biosensors using sinusoidal voltages and currents methods. Sens. Actuators B: Chem. 2017; https://doi.org/10.1016/j.snb.2017.08.161.

SYNTHESIS AND CHARACTERIZATION OF MICROCAPSULES BASED ON NATURAL BIOPOLYMERS AND LAUREL ESSENTIAL OIL

C. Chelaru, M. Ignat

INCDTP - Division Leather and Footwear Research Institute, 93 Minulescu Ion Str., 031215, Bucharest, Romania

**Corresponding author: cchelaru_cciprian@yahoo.com*

Keywords: natural polymers; Laurel essential oil; microencapsulation

Introduction: The objective of this paper is to use the microencapsulation [1] technique for obtaining microcapsules that can improve the properties of leather products. The products were characterized by instrumental technique as optical microscopy, FT-IR (ATR) spectroscopy, dynamic light scattering (DLS) and by microbiological tests [2].

Materials and methods: The materials used for this study are natural products. Microcapsules were made from natural polymer, sodium alginate [3] and Laurel essential oil [2]. In order to test the antibacterial properties of the new synthesized microcapsules, they have been dispersed on a natural bovine leather support and tested against *E. coli.*

Results: The main results are the new obtained microcapsules based on natural polymer and leather with improved antibacterial properties that can be used for various applications in many fields.

Conclusions: The results confirm the obtaining of microcapsules with spherical shape (optical microscopy), sizes around 40-60 microns and a good stability (DLS). Microbiological tests showed the efficiency of the new synthesized microcapsules dispersed on the leather support against *E coli*.

Acknowledgements: *This study was funded by ANCSI in the frame of Nucleu Program 2016-2017, project code PN 16 34 04* 03.

References:

[1] Devi, N., Hazarika, D., Deka, C. *et al.* (2012), "Study of Complex Coacervation of Gelatin A and Sodium Alginate for Microencapsulation of Olive Oil", *J. Macromol. Sci., Part A: Pure Appl. Chem.* 49, 936-945.

[2] Kaya, D.A., Ferdes, M., Badea, N. *et al.* (2012), "The effect of Laurel and Thymbra essential oils on antioxidant and antimicrobial properties of collagen hydrolysate", *Rom. Biotech. Lett.*, 17(5), 7694-7701.

[3] Martins, I.M., Barrerio, M.F., Coelho, M. *et al.* (2014), "Microencapsulation of essential oils whit biodegradable polymeric carriers for cosmetic application", *Chem. Eng. J.*, 245 (1), 191-200.

IMPACT OF SURFACTANTS ON POLYGLYCIDOL IN WATER. A SURVEY BY SURFACE TENSION, FLUORESCENCE, DLS AND FTIR

A. Băran[1], A. Iovescu[1], M. Gosecka[2], G. Stîngă[1], S. Peretz[1,†], T. Basinska[2], S. Slomkowski[2], M.E. Maxim[1], D.F. Anghel[1,*]

[1] *'Ilie Murgulescu' Institute of Physical Chemistry of the Romanian Academy, Colloid Laboratory, 202 Spl. Independentei, 060021 Bucharest, Romania*

[2]*Department of Engineering of Polymer Materials, Center of Molecular and Macromolecular Studies, Polish Academy of Sciences, H. Sienkiewicza 112, 90-363 Lodz, Poland*

**Corresponding author: danflorin.anghel@gmail.com, adan@icf.ro*

Keywords: Linear and hyperbranched polyglycidols; surfactants; fluorescence; ST; DLS; FTIR; ζ-potential

Introduction: Polyglycidol (PGL) is a highly flexible and hydrophilic polyether with a broad spectrum of pharmaceutical and biomedical applications. Depending on the route of synthesis; one may obtain linear (LPGL) or hyperbranched polyglycidol (HPGL), the latter having a globular structure, which hampers the interaction with biomolecules. On the other hand, the surfactants are biomimetic species as they well-mimics the cellular membranes. This work investigates the effect of nonionic, cationic, and anionic surfactants on linear and hyperbranched polyglycidols. The acquired data are useful for designing products with better drug delivery than those currently available on market.

Materials and methods: Linear polyglycidols of M_w 3250 (LPGL32) and 9610 (LPGL96) and a hyper-branched polyglycidol of M_w 4040 (HPGL40) are investigated. $C_{12}E_6$, CTAB and SDS are the surfactants used. Measurements of surface tension, FTIR, fluorescence, DLS and ζ-potential are carried out.

Results: The study reveals that LPGL is more favorable to surfactant interaction than HPGL. Among the surfactants, only SDS interacted with both LPGL and HPGL. The pyrene probe and SDS were able to access the holes in the HPGL4040.

Conclusions: The study unveils that linear polyglycidols form stable colloidal aggregates with SDS. They depend on surfactant concentration and recommend these systems for drug delivery. The HPGL40 is less affected by SDS than the linear polymers. Therefore, HPGL40 is suitable for medical implants, in particular for modification of their surface.

***Acknowledgements**: This paper was carried out within the Polish - Romanian joint research project for years 2013-2015 entitled: 'Studies of thermo-sensitivity of particles interfacial layer by fluorescent methods'. It has been financially supported by the Polish Academy of Sciences and the Romanian Academy within the research program 'Colloids and dispersed systems' of the 'Ilie Murgulescu' Institute of Physical Chemistry. The Romanian authors gratefully acknowledge the support of EU (ERDF) and Romanian Government allowing for acquisition of the research infrastructure under POS-CCE O2.2.1 project INFRANANOCHEM, No. 19/2009.03.01 and the support from PN-II-ID-PCE-2011-3-0916 grant. †This paper is dedicated to our colleague Dr. Sandu Peretz who passed away during the elaboration of this work.*

INNOVATIVE HYBRID POLYMER MEMBRANES WITH CARBON POWDERS CONTENT: PREPARATION AND CHARACTERIZATION

T. Sandu[1], A. Sarbu[1,*], B. Tsyntsarski[2], T. Budinova[2], C. M. Damian[3], A.-L. Radu[1], T.-V. Iordache[1], A.-M. Florea[1], A. Zaharia[1], S. Apostol[1]

[1]The National Institute for Research & Development in Chemistry and Petrochemistry -ICECHIM, Advanced Polymer Materials and Polymer Recycling Group, 202 Spl. Independentei, 060021, Bucharest, Romania

[2]Bulgarian Academy of Sciences, Institute of Organic Chemistry, Acad. G. Bonchev str., 1113 Sofia, Bulgaria

[3]University POLITEHNICA of Bucharest, Faculty of Applied Chemistry and Materials Science, Department of Bioresources and Polymer Science, 1-7 Polizu Street, 011061, Bucharest, Romania

**Corresponding author: andr.sarbu@gmail.com*

Keywords: polyacrylonitrile; copolymer; membranes; inorganic powders; hybrids

Introduction: Membranes are widely used in separations, as they are able to act as selective barrier due to their inherent porosity [1]. Polyacrylonitrile is widely used for membranes production [2], while Activated Carbon is a well known adsorbent [3]. Based on this, the work tried to obtain new materials.

Materials and methods: For an advanced study, 5 membranes were prepared (using acrylonitrile-vinyl acetate copolymer in mixture with polyvinyl alcohol): 1 using neat polymer blend; 4 using polymer blend and carbon powders (2 with BAC1; 2 with SC2). The effect of inorganic powders (nature and/or amount) on the final properties of membranes was evaluated by FTIR and TGA. For proper asignment, FTIR spectra were, also, recorded for raw materials.

Results: Membranes exhibit characteristic peaks of raw materials; certain differences corresponding to preparation conditions. TGA furthur confirms the importance of using carbon powders on the membrane characteristics.

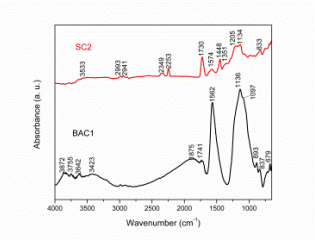


Fig.1. FTIR spectra for inorganic powders

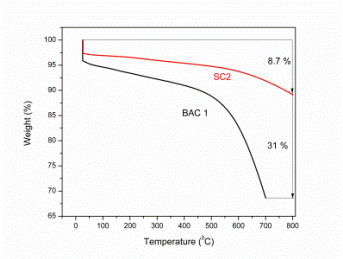


Fig.2. TGA curves for inorganic powders

Conclusions: The aimed objective of getting hybrid polymer membranes bearing carbon powders were acheieved. Final membranes features may be adjusted by modifying preparation conditions.

Acknowledgements: *This work was funded by the WAPUMECA project and PN 16.31.02.01.*

References: [1]. M. Ulbricht, "Advanced functional polymer membranes", Polymer, 2006, 47, 2217-2262.

[2]. Jung B., „Preparation of hydrophilic polyacrylonitrile blend membranes for ultrafiltration", J. Membr. Sci., 2004, 229, 129-136.

[3] Tsyntsarski B, Petrova B, Budinova T, Petrov N, Sarbu A, Sandu T, Yardim MF, Sirkecioglu A, Removal of detergents by zeolites and membranes Bulg. Chem. Co., 2014, 46, 157-164

THE EFFECT OF HALLOYSITE NANOTUBE FUNCTIONALIZATION ON PMMA-HALLOYSITE NANOTUBE NANOCOMPOSITES PROPERTIES

Z. Vuluga*, M. C. Corobea, M. Iorga, D. Florea, C. A. Nicolae, V. Raditoiu, M. Ghiurea, R. Somoghi, B. Trica

National Research and Development Institute for Chemistry and Petrochemistry-ICECHIM Bucharest

**Corresponding author: zvuluga@icechim.ro*

Keywords: Hallosyite nanotubes; functionalization; PMMA nanocomposites

Introduction: The interest for polymer nanocomposites containing Halloysite nanotubes (HNT) increased, due to the advantageous combination of low cost with improved properties and easy processing [1]. The properties of polymer nanocomposites with HNT depend on the interface between the nanotube and the polymer. A high adhesion at the polymeric matrix/filler interface leads to the uniform dispersion of the nanotube and improved load transfer between the nanotubes and surrounding polymer chains. Therefore, the functionalization of HNT is very important for processing and enhancing the properties of polymer nanocomposites [2].

Materials and methods: As polymer matrix PMMA black was used. The surface of HNT was modified with N,N'-ethylenebis(stearamide) (EBS). Modification was done in dynamical conditions, using a Brabender Plastograph. PMMA nanocomposites with 2% modified HNT (HNT-EBS) were prepared in dynamical conditions using a co-rotating twin screw extruder type Brabender. The effect of HNT-EBS on the morphological/structural (XRD, TEM, FTIR), thermal stability (TGA), rheological (MFI), aesthetic (colour and gloss), tribological (friction and wear) and mechanical (Young Modulus, Tensile Strength and Impact Strength) characteristics was examined.

Results: EBS interacts with HNT through hydrogen bonding established by amide groups with silanolic and siloxane residues (Fig. 1). HNT-EBS has an uniform orientation and dispersion in the polymer matrix (Fig. 2), which is reflected in a slight increase in strength and stiffness of PMMA/HNT-EBS nanocomposite in comparison with PMMA/ HNT nanocomposite.

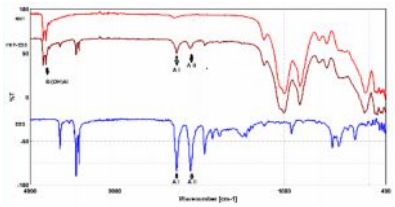


Fig. 1 FTIR spectra of HNT, EBS and HNT-EBS

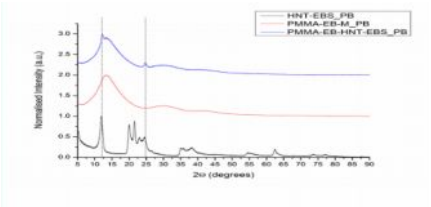


Fig. 2 XRD patterns of HNT-EBS, PMMA and PMMA/HNT-EBS

Conclusions: HNT-EBS disperses easily and uniformly into PMMA. PMMA/HNT-EBS nanocomposite exhibits improved thermal stability and higher gloss in comparison with PMMA/HNT nanocomposite.

Acknowledgements: *Financial support by the EU Commission through Project H2020-686165-IZADI-NANO2INDUSTRY is gratefully acknowledged.*

References: [1]. Sinha Ray S, Okamoto M. Polymer/layered silicate nanocomposites: a review from preparation to processing. Prog Polym Sci 2003; 28:1539–641. [2]. Liu M, Jia Z, Jia D, Zhou C, Recent advance in research on halloysite nanotubes-polymer nanocomposite, Progress in Polymer Science 39 (2014) 1498–1525.

CHITOSAN AND PVA POROUS TRIDIMENSIONAL STRUCTURES WITH HIGH AFFINITY FOR FLUIDS

A. I. Subtirica[1*], M.G. Albu Kaya[2], A.A.-M. Chivu[3]

[1, 3]NationalR&D Institute for Textiles and Leather (INCDTP) – Textile Division

[2]NationalR&D Institute for Textiles and Leather (INCDTP) – Leather Division

**Corresponding author: adriana.subtirica@certex.ro*

Keywords: chitosan; poly (vinyl alcohol); chemical crosslinking; lyophilization

Introduction: In this work Chitosan and PVA hydrogels were prepared by crosslinking using glutaraldehyde. The hydrogels were freeze-dried, in order to conduct to a porous sponge – like structure. The degrees of swelling of PVA and chitosan matrix were evaluated in distilled water. The lyophilized hydrogels presented characteristics that allow them to have wide application range, such as parts of super-absorbent hygine products, water stabilization systems for agriculture, slow release systems, etc. Due to the biocompatibility and biodegradability known character of both used polymers, the sponges could find applications in medical area, such as potential wound dressings, due to their ability to mantain a moist environment, that is well known to contribute to a quicker healing process.

Materials and methods: Chitosan and PVA were purchased from Sigma, Glutaraldehyde solution was purchased from Merck. The lyophilization process was made in a laboratory scale equipment.

Results: Depending on the used polymer concentration and crosslinking density, for PVA it was obtained water retention up to 6090% and for chitosan water retention up to 13100%, after reaching equilibrium.

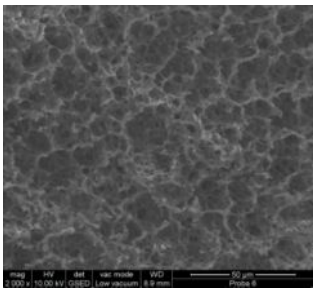


Figure 1: SEM image of PVA matrix

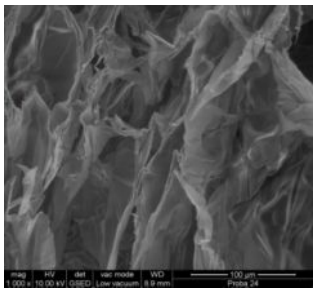


Figure 2: SEM image of Chitosan matrix

Conclusions: The capacity of the matrix to retain fluids depends on the content of glutaraldehyde. The highest capacity of swelling and absorption has been obtained for the smallest content of reticulant.

Acknowledgements: *This paper was conducted with the financial support of ANCSI, project PN 16 34 02 04.*

References:

[1]. Mulchandani N, Shah N, Mehta T, Synthesis of Chitosan-Polyvinyl Alcohol Copolymers for Smart Drug Delivery Application, Polymers & Polymer Composites, Vol. 25, No. 3, 2017, http://www.polymerjournals.com/pdfdownload/1252585.pdf Accesed: august 2017 (*On-line resource*).

[2]. Caló E, Khutoryanskiy V, Biomedical applications of hydrogels: A review of patents and commercial products, European Polymer Journal 65, 2015, http://www.sciencedirect.com/science/article/pii/S0014305714004091 Accesed: august 2017 (*On-line resource*).

[3]. Li Liua, Qi Gaob, Xuemin Lua, In situ forming hydrogels based on chitosan for drug delivery and tissue regeneration, Asian Journal of Pharmaceutical Sciences, Volume 11, Issue 6, December 2016, http://www.sciencedirect.com/science/article/pii/S1818087616300502 Accesed: august 2017 (*On-line resource*).

GRAPHENE QUANTUM DOTS AS FLUORESCENT PROBES FOR BIOMOLECULES: EXPLORING THEIR POTENTIAL AS A TURN-ON SENSOR FOR TRYPSIN-EDTA

R. Nkhahle, T. Nyokong*

Department of Chemistry, Rhodes University, Grahamstown 6139, South Africa

**Corresponding author: t.nyokong@ru.ac.za*

Keywords: Quantum dots; sensing; fluorescence; quenching; trypsin-EDTA

Introduction: Graphene quantum dots (GQDs) possess excellent optical and electronic properties that can be altered in a controlled manner due to the fact that they adhere to the quantum mechanics' particle in a box model [1, 2].

Materials and methods: The approach taken was the bottom-up approach with the synthesis being that of a hydrothermal nature. Citric acid served as the source of carbon and NaOH being the base in the synthesis of the pristine GQDs. In synthesizing the doped quantum dots, urea and thiourea were used in place of NaOH to produce the nitrogen-doped GQDs and the sulphur/nitrogen co-doped GQDs.

Results

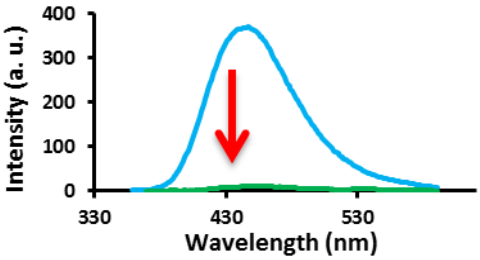


Figure 1: Emission spectra illustrating the quenching of the fluorescence by cytochrome C.

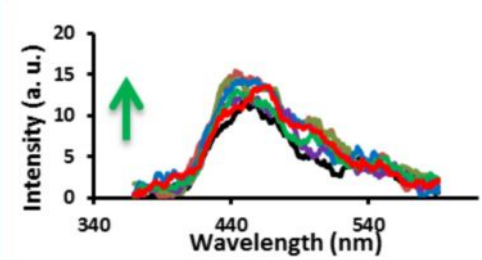


Figure 2: Emission spectra illustrating an attempt at "turning on" of the fluorescence through the addition of the trypsin-EDTA.

Conclusions: Quantum dots synthesized and characterized successfully; cytochrome C is an effective quencher of graphene quantum dots however; restoration of fluorescence unsuccessful upon addition of analyte.

Acknowledgements: *This work was supported by the Department of Science and Technology (DST) and National Research Foundation (NRF), South Africa through DST/NRF South African Research Chairs Initiative for Professor of Medicinal Chemistry and Nanotechnology as well as Rhodes University.*

References

[1]. Wang F, Gu Z, Lei W, Wang W, Xia X and Hao Q. Graphene quantum dots as a fluorescent sensing platform for highly efficient detection of copper (II) ions. Sensors and Actuators B 2014; 190: 516 – 522.

[2]. Dey S, Govindaraj A, Biswas K and Rao CNR. Luminescence properties of boron and nitrogen doped graphene quantum dots prepared from arc-discharge-generated doped graphene samples. Chemical Physics Letters 2014; 595–596: 203 – 208.

STRIGOLACTONE MIMICS AND BIOACTIVATED PLANT RESIDUES INTEGRATION INTO CONSERVATION AGRICULTURE SYSTEMS

F. Oancea[1,2*], E. Georgescu[3], T.-E. Şesan[1,4], F. Georgescu[3], I. Răut[1], A. Cociu[5]

[1]*National R&D Institute in Chemistry & Petrochemistry, 202 Spl. Independentei, 060022, Bucharest, Romania*

[2]*University of Agronomic Sciences & Veterinary Medicine, 59 Mărăşti Blvd., 011464 Bucharest, Romania*

[3]*Teso Spec Srl, R&D Department, 53 Muncii Str., 915200 Fundulea, Călăraşicounty, Romania*

[4]*University of Bucharest, Faculty of Biology, 91-95 Spl. Independentei, 050095, Bucharest, Romania*

[5]*National Agricultural R&D Institute, 1, Nicolae Titulescu Str., 915200 Fundulea, Călăraşicounty, Romania*

**Corresponding author: florino@ping.ro*

Keywords: strigolactone mimics; bioactivated plant residues; polyamines; conservationagriculture

Introduction: Application of strigolactone represents one of the solutions to several issues which limit conservation agriculture (CA) development. CA systems provide more environmental services compared to the traditional ones, and reduce the necessary inputs for the same level of yield. However, the CA systems have also negative impacts: reduced availability of the nutrients, development of soil borne plant pathogen agents, less aerated structure on heavy soil, weed infestation, lower soil temperature and delaying on the initial development of the cultivated plants.

Materials and methods: We developed a conservation agriculture (CA) system, which includes plant residues bioactivation by a treatment with plant beneficial microorganisms (PBMs). *Trichoderma asperellum* Td36 and *Brevibacillusparabrevis* B50, selected for their antagonism against soil-borne plant pathogens and for their ability to release polyamines from plant residues mulch. We combined this approach of bioactivated with the use of synthetic strigolactones. We synthesized strigolactones mimicsby treatingcommerciallyavailablecyclichydroxyl-ketones in DMF with 5-bromo-3-methyl-5*H*-furan-2-one in the presence of K_2CO_3. The SL mimic 3-methyl-5-(benzo[de]isoquinoline-1,3-dione-2-yloxy)-5*H*-furan-2-one presents the main characteristics of strigolactones as exo-signals: stimulation of the germination of the parasitic plant seeds; induction of hyphal branching on mycorrhizae spores; modification of the pattern of plant pathogenic fungi.

Results: On a field trial done on conservation agriculture platform from NARDI Fundulea we tested our hypothesis regarding the positive interaction between microbially released polyamines and strigolactones. Regulatory effects of both polyamines and strigolactones, on beneficial rhizomicrobiome and cultivated plant growth and developmentcompensate the drawbacks of CA systems.Stimulation of arbuscular mycorrhiza (AM) and of others beneficial microorganisms improve nutrient availability.Plant beneficial microorganisms reduces the impact of soil borne pathogens, due to the activation of cultivated plant defensemechanisms. AM fine fungal network and glomalin deposited by AM symbiosis aggregated soil particles and promote an aerated soil structure, more resistant to erosion. Strigolactones action on cultivated plant architecture creates better conditions for using plant residues as a tool for weed control. Stimulation by microbially released polyamines on plantsdevelopment and their response to abiotic stress influences plant growth and development, reducing the impact of lower soil temperature on plant cultivated on CA systems.

Conclusions: Strigolactone application increase the yield of corn by 11.4% and positively interact with polyamine releasing microorganism treatment, increasing significantly their effects on corn yield.

Acknowledgements: *This work is supported by the Ministry of Research and Innovation, UEFISCDI, Project PN-II-PT-PCCA-2013-4-0846 - CERES, contract 159/2014.*

FLAVONOIDS, POLYPHENOLS AND MINERALS FROM *ACORUS CALAMUS* L. (ACORACEAE)

A. I. Anghel[1], M. V. Hovaneț[1], R. Ancuceanu[1*], M. Dinu[1], C.S. Stoicescu[1], O. T. Olaru[1], A. Dune[2],M. Ciolea[2], C. V. Popescu[2,3]

[1] *"Carol Davila" University of Medicine and Pharmacy, Bucharest, Faculty of Pharmacy*

[2] *S.C. HOFIGAL Export Import S.A., Bucharest, Romania*

[3] *"Vasile Goldiș" Western University, Arad, Faculty of Pharmacy*

**Corresponding author: robert.ancuceanu@umfcd.ro*

Keywords: Acorus calamus L.; Acoraceae; flavonoids; polyphenols; minerals

Introduction: *Acorus calamus* L. (Acoraceae)has a long history of traditional medicinal use in different geographic regions, being used for a variety of indications,as well as in the food and perfume industries [1, 2]. Its chemical constituents include, besides primary metabolites,sesquiterpenes, alkaloids, and flavones . Little is known on the quantitative contents in flavonoids, polyphenols and minerals in different parts of this species, especially for the plants cultivated in Romania and we investigated it.

Materials and methods: The plants were cultivated on two preluvosols with different characteristics (□PR□ and □PC□) and a chernozem soil (□C□). Flavonoids and polyphenols were assayed spectrophotometrically, and minerals by AAS.

Results: The flavonoid levels were close to the limit of cuantification in the subterraneous organs and significanly higher in leaves. The amount of polyphenols (gallic acid equivalents (GAE), mg/g) was about twice in leaves than in the subterraneous organs (Fig. 1). Instead, iron and other minerals tended to be higher in root and rhizomes than in leaves.

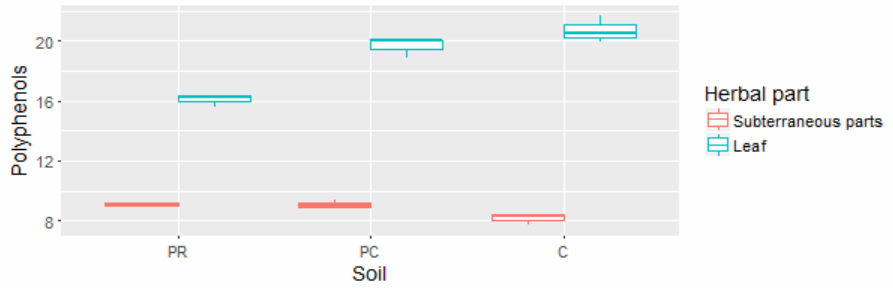


Figure 1. Boxplot graph showing the variation of polyphenol contents in *Acorus calamus* L. by herbal part

Conclusions: The influence of soil on flavonoid, polyphenol and mineral contents is very limited, more important is the herbal part analyzed.

Acknowledgements: *This work has been carried out within the programme "Parteneriate in domenii prioritare – PN II (Partnerships in priority sectors – PN II), with the financial support of the Romanian Ministry of National Education–UEFISCDI, Research Grant (Project) no. PN-II-PT-PCCA-2013-4-1572.*

References:

[1]. Li J, Li ZX, Zhao J, Wang W, Zhao XF, Xu B, Li L, Zhang L, Ren J, Khan IA, Li SX. A novel tropoloisoquinoline alkaloid, neotatarine, from Acorus calamus L.Chem Biodivers. 2017 Jul 11. doi: 10.1002/cbdv.201700201. [Epub ahead of print].

[2]. Rahamooz Haghighi S, Asadi MH, Akrami H, Baghizadeh A. Anti-carcinogenic and anti-angiogenic properties of the extracts of Acorus calamus on gastric cancer cells. Avicenna J Phytomed. 2017; 7(2):145-156.

GRAPHENE- AND SYRINGALDAZINE-BASED ELECTROCHEMICAL MICROSENSOR FOR MONITORING THE EXTRACELLULAR pH OF LIVING CELLS

S. Gáspár[1*], L. Stănică[1], M. Gheorghiu[1]

[1]*International Centre of Biodynamics, 1B Intrarea Portocalelor, 060101 – Bucharest, Romania*

**Corresponding author: sgaspar@biodyn.ro*

Keywords: pH microsensor; graphene; syringaldazine; Scanning Electrochemical Microscope; pH regulation

Introduction: In this work, we set out to develop an electrochemical microsensor, which is suitable to monitor the extracellular pH of living cellswith high spatiotemporal resolution. To accomplish this goal, we used graphene to improve a previously described electrochemicalpH sensor [1].

Materials and methods: Carbon fiber (φ =30 µm) was used to build needle-type, carbon fiber microelectrodes (CFMEs). The resulting CFMEs were subsequently modified with graphene and syringaldazine in order to make them pH sensitive. Such pH microsensors were positioned to controlled distances from adherently growing HT-29 tumor cells using a Scanning Electrochemical Microscope (SECM). The way these cells acidify their extracellular space was investigated.

Results: In cyclic voltammetry, the syringaldazine-modified CFMEs presented two nicely-shaped peaks due to the oxidation and reduction of syringaldazine. The formal potential, calculated from the peak potentials of these two current peaks, shifted with ~ 60 mV per pH unit. Calibration curves built using solutions with known pH, and the integration of the pH microsensors into SECM allowed the determination of pH at different distances from adherently growing HT-29 cells. Our measurements show that pH changes induced by cells extend as far as 100 µm from cells(see Figure 1).

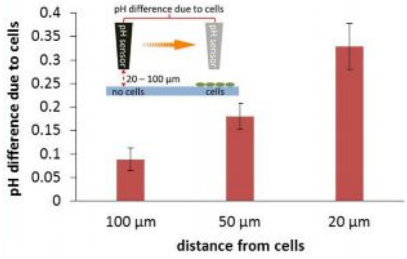


Figure 1. pH changes induced by cellular metabolism as measured with a syringaldazine-modified CFME. pH differences observed relative to an area without cells are shown.

Conclusions: The simplicity, robustness, good pH sensitivity, and small size of the developed microsensors recommend such microsensors for comparative studies on the pH regulation of normal and tumor cells. Such studies are underway in our laboratory.

Acknowledgements: *The authors thank the Romanian Executive Unit for Higher Education, Research, Development and Innovation Funding for funding through grants PN-III-P2-2.1-PED-2016-1106 and Flag-ERA-Graphtivity.*

References:

[1]. Michalak M, Kurel M, Jedraszko J, Toczydlowska D, Wittstock G, Opallo M, Nogala W. Voltammetric pH Nanosensor. Anal. Chem. 2015;87(23):11641–11645.

PROCESSING AND CHARACTERIZATION OF POLYMER BIODEGRADABILITY

A. M. Musuc[1*], L. Jecu[2], M. Doni[2], V. T. Popa[1]

[1]*Romanian Academy, "IlieMurgulescu" Institute of Physical Chemistry, 202 Spl. Independentei, 060021 Bucharest, Romania*

[2]*National Research and Development Institute for Chemistry and Petrochemistry – ICECHIM, 202 Spl. Independentei, 060021 Bucharest, Romania*

**Corresponding author: amusuc@icf.ro; musucadina@yahoo.com*

Keywords: biodegradability; crystallization; differential scanning calorimetry

Introduction: The use of plastic is growing day by day. Over 300 million tons of synthetic plastics are produced annually in the world and every year 25 million tons are being accumulated in the environment [1, 2]. One of the major environmental threat is the slow rate of degradation or non-biodegradability of the organic materials under natural conditions. Polyethylene finds a wide range of applications in daily use because of its easy processing for various products used for carrying food articles, for packaging textiles, for manufacturing laboratory instruments and automotive components [3].

Materials and methods: Commercial grade low-density polyethylene (PE) from Sigma, Germany, was used for the preparation of films, without further treatment of purification.The biodegradability studies were carried out by incubating the unmodified and modified polyethylene films (with 1%rosemary, *Rosmarinus officinalis,* extract) with *Aspegillus Niger*, *Penicillum sp*., *Bacillus licheniformis*, *Candida lipolytica*. The thermal runs were performed on a SETARAM microDSC 7 evo within the 50–120^{o}C temperature range, with thermal cycling at heating rates of 0.3, 0.4, 0.5, 0.6 and 1^{o}C min^{-1}, in nitrogen atmosphere with a flow rate of 50 mL min^{-1}.

Results:µDSC thermograms reveala slight melting signal splitting manifested as a shoulder in LDPE with 1%RM samples; this is clearly manifested only within the first heating of the temperature program. The small increase in the crystallinity degree after microbial attack can be caused by consumption of amorphous part of polymer by microorganisms.Peak melting temperatures are practically unaltered within experimental errors.

Conclusions: Based on experimental results it can be concluded that rosemary extract can be used for ehancing the biodegradation of polyethylene films.

Acknowledgements: *This paper was done within the „Green Chemistry" research program of the "IlieMurgulescu" Institute of Physical Chemistry of the Romanian Academy. Support of the EU (ERDF) and Romanian Government that allowed for acquisition of the research infrastructure under POS-CCEO 2.2.1 project INFRANANOCHEM – Nr. 19/01.03.2009 is gratefully acknowledged.*

References:

[1]. North EJ, Halden RU. Plastics and Environmental Health: The Road Ahead. Reviews on environmental health. 2013;28(1):1-8.

[2]. Mohan SK, Suresh B. Indo Am. J. Pharm. Sci. 2015;2(12):1636-1639.

[3]. NoorunnishaKhanam P, Al Ali AlMaadeed M. AdvManufPolym Compos Sci. 2015;1:63-79.

NOVEL 3D METAL COMPLEXES OF THIO SCHIFF BASES

G. Zamfir[1*], N. Stanica[2], C. Draghici[3], M. V. Neacsu[2], M. Silion[4], E. Rusu[4], L. Moisa[5]

[1]TechnicalCollegium"Mircea cel Batrin", 52 Feroviarilor Street, 012207, Bucharest, Romania

[2]Institute of Physical Chemistry of Romanian Academy, 202 Splaiul Independentei,060021, Bucharest, Romania

[3]Institute of Organic Chemistry of Romanian Academy, 202 Splaiul Independentei,060023, Bucharest, Romania

[4]Institute of Macromolecular Chemistry ,"Petru Poni", 41A, Aleea Grigore Ghica 700487, Iasi, Romania

[5]Districtual Emergency Hospital Bacau, Romania

**Corresponding author: georgeta.zamfir@yahoo.com*

Keywords: thio Schiff bases;complexes; template synthesis; spectroscopic methods

Introduction: Complexes of 3d metal with thio Schiff base (L=p.dimetilaminobenzilidene-2-mercaptoaniline), were synthesized and analised with ^{1}H and ^{13}C- NMR, IR, UV-Vis,ESI-MS, EPR.

Materials and methods: Synthesis of complexes were realised by analytical purity of substances. A relative new method were utilised from all complexes named "template synthesis", that avoids direct synthesis of complexes without corresponding Schiff base synthesis. Thus disappears a number of synthesis phase as: synthesis, purification and dissolution of Schiff base, that means energy, solvent and time economy. Complexes were obtained by reflux of ethanolic solutions of raw materials [1-5].

Results: Complexes are coloured powder, stable at high temperatures.Molar conductance value (10^{3-} M, 20, DMF),suggests nonelectrolitic nature of compounds. Complexes are soluble only in DMF and DMSO. The analytical data show that M:L stoechiometry is: 1:1 from Cu(II) and Zn(II) complexes, 1:2 from Ni(II) complex and 1:3 from Co(III) complex. IR data reveals that in all complexes ligand coordinates throu azometinic nitrogen and thiphenolic sulphur. Magnetic moment value of 2.82 MB of Ni(II) complex sustains octahedral geometry in accord with UV-Vis absorbtions bands and color of complex. Absorbtion bands in UV-Vis range of Cu(II)complex, at 755 and 920 nm, assigned to $^{2}T_{2g} \rightarrow 2E$ transitions , suggests tetrahedral geometry of complex, structure that is confirmed from ESI-MS and EPR spectra [2, 4, 6]. According to this data, the general formulaes of complexes are proposed: $[Co(L)_3](NO_3)_3$, $[Ni(L)_2Cl_2]$, $[Cu(L)(NO_3)]2H_2O$ and $[Zn(L)(NO_3)]$ [1-4]. Complexes were tested against some bacteria as Stafilococus aureus, by discs method, using medicaments as ciprofloxacin as control and presented medium antibacterial activity [7].

Conclusions: Four new complexesof Co(III),Ni(II), Cu(II) and Zn(II) ions with L= p.dimetilaminobenzilidene-2-mercaptoaniline by template synthesis were obtained. Ligand acts as bidentate NS monoanionic in all complexes. Cu(II)and Zn(II) complexes present tetrahedral geometry and Co(III) and Ni(II) complexes show octahedral environments[2,4,6].

Acknowledgements: *Bucharest University, Anorganic Chemistry Department.*

References:

[1]. Lindoy F. Livingstone S. E., Inorg. Chim. Acta, 1967,365.
[2]. Lever ABP. Inorganic Electronic Spectroscopy, Pergamon Press. N.Y.,1984.
[3]. Conry RR. Copper Inorganic&Coordination Chemistry. DOI:10 1002/0470 862, 2015.
[4]. Zamfir G, Stanica N, Draghici C, Rusu E, Kriza A. Rev. Chim. Vol 63, No 11, 2012, 1176.
[5]. Senyuz N, Ylmaz B, Buyukgunggor O. Spectrochimica Acta Part A: Mol.and Biomol. Spectr. 101(2013), 167.
[6]. Patel RN, Patel DK, Sukla KK, Singh Y. J. Coord. Chem. 2013, Vol 66, No 23, 4131.
[7]. Mishra AP, Kumar K. J. Indian Chem. Soc. vol. 86, 2009, 1150.

INTEGRATED SET-UP FOR SELECTIVE EXTRACTION OF CO_2 FROM BIOGAS FOR MICROALGAE CULTIVATION

V.Covaliov[1], O.Covaliova[1*], V.Bobeica[1], Iu. Morari[2]

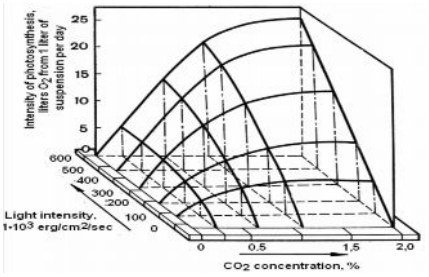
[1]State University of Moldova, Institute of Research and Innovation, Republic of Moldova, Chisinau, MD 2009, 60 Mateevici Str.
[2]Agromodvita" SRL, Republic of Moldova
**Corresponding author: covaleva.olga@yahoo.com*

Keywords: microalgae; wastewater treatment; bioreactor; biogas; carbon dioxide separation

Introduction: To elaborate intensified biogas technology, application of phyto-catalysts was proposed, as well as development of CO_2separation system for micro-algae cultivation.

Materials and methods: New equipment was developed and tested, including biogas purification system from CO_2based on new principle [1, 2], the set-up for micro-algae cultivation, collectionand thickening of microalgae [3,4].Dosing of nutrients for micro-algae growth was envisaged and standard LED lamps were used.

Results: Carbon dioxidewas separated from biomethane and introduced into the micto-algae cultivation basin.Microalgae consume from the aquatic medium 94% of CO_2per biomass unit, and only 6% are obtained from water and other dissolved substances. For formation of 1 kg of dry biomass from microalgae, 1.83 kg of $CO_2$is absorbed and 2 kg of oxygen gas (O_2) is generated which is released into the atmosphere. This reduces the release of anthropogenic CO_2into the atmosphere, and the purified biomethane can be more efficiently used as a source of heat and electrical energy.The Fig. 1 shows diagram of O_2 yield in dependence of CO_2 introduced into the basin, and illumination degree of water suspension with micro-algae.



Conclusions: The modified equipment was elaborated for the intensification of microalgae cultivation, through the selective extraction of CO_2 from purified biogas. Effectiveness of the microalgae cultivation is provided by the continuous supply of carbon dioxide, with creating a high mass transfer conditions in the facility.The compact equipment proposed allows the continuous year-round exploitation of facility in a production and technological cycle.

Acknowledgement: *This research was carried out under the Moldo-Romanian Research Project "Microalgal systems used for the reduction of CO_2 emissions from the biomass digestion" Nr. 16.80013.5807.11/Ro.*

References:

[5]. Patent Application #2014-0117 MD.Biogas cleaning plant. Covaliov V., Covaliova O., Ungureanu D., Nenno V. Publ. BOPI nr. 3/2016.

[6]. Patent # 4130 MD. Biogas-cleaning equipment. Covaliov V., Covaliova O., Ungureanu D., Nenno V. Publ.BOPI nr. 10/2011.

[7]. Patent # 4418 MD. Combined plant for selective extraction of CO_2 from biogas and cultivation of microalgae. Covaliov V., Covaliova O., Timofte N., Morari Iu. Publ. nr. BOPI 5/2016.

[8]. Patent # 4372 MD. Equipment for cultivation of microalgae. Covaliov V., Morari Iu., Covaliova O., Sliusarenco V., Nenno V., Bobeică V. Publ. BOPI nr. 9/2015.

NEW STRATEGY FOR VALORIZATION OF LIGNIN RESIDUES BASED ON BIOCATALYTIC OXI-POLYMERIZATION OF MONOLIGNOLS

C. Opris, S. Ion, V.I. Parvulescu, M. Tudorache*

University of Bucharest, Bucharest, 030016, Romania

**Corresponding author:madalina.sandulescu@g.unibuc.ro*

Keywords: lignin residues; biocatalysis; enzyme; oxi-polymerization

Introduction: Lignin, the second most abundant natural polymer after cellulose of terrestrial sources plays a negative role in pulp and paper industry, *i.e.*over 70 million tons of lignin residues are produced annually in the world.

In this context, we developed a biocatalytic system based on the oxi-polymerization of lignin waste-units (e.g. monolignols such as sinapyl alcohol SA and coniferyl alcohol CA) via peroxide-based oxidation assisted by the enzyme (e.g. peroxidase enzyme).

Materials and methods: Oxi-polymerization of SA and CA monolignols had beed performed using 2 mg mL^{-1} lignin monomer, 0.6 % H_2O_2 and 2.582 U mL^{-1} enzyme shacked (100 rpm) for 2 h.

Results: Different peroxidase enzymes (e.g. unspecific peroxidase PADA-I, and versatile peroxidase 2-1B and R4) were tested exhibiting similar catalytic activity for the same monolignol (Table 1). As a general remark, SA was easier recognized and transformed by peroxidase compared to CA. Fast kinetic of the biocatalytic process allowed to achieve maximum conversion of the lignin fragments (around 90 % for couple of 4R and SA) in only 2 hours (Table 1). Also, large polymer structure was produced with 4R peroxidase enzyme (MW=3188 Da and PD=3).

Table 1. Peroxidase screening for oxy-polymerization of monolignols.

	SA				CA			
	HRP	**PaDa-I**	**2-1B**	**4R**	**HRP**	**PaDa-I**	**2-1B**	**4R**
C (%)	30	84	89	90	35	50	53	49
Mw	555	226	721	3188	2130	586	677	859
Mn	446	214	582	1115	1889	575	670	733
PD	1.24	1.06	1.24	2.86	1.13	1.02	1.01	1.17

Conclusions: This study offers new perspective on the valorization of the lignin residues (mono-/oligo-lignols). Controlled architecture of the prepared polymers has been done using specific type/ratio of monolignols. Additionally, well-known monomers following always the same reaction route give the opportunity for diminishing the heterogeneity of ligno-polymeric products, which is an important advantage.

Acknowledgements: *This work was financially supported by PN III TE program, contract no. 103/2015, 27BG/2016 and 8PED/2017 from MEN-UEFISCDI, Romania.*

MINIATURIZED BIOANALYTICAL SYSTEMS FOR SENSITIVE DETECTION OF SOME TOXIC COMPOUNDS AND THEIR METABOLITES

A.-M. Gurban[1*],T. Noguer[2], K. Y. Goud[2], M. Badea Doni[1],J.-L. Marty[2], C. Bala[3,4]

[1]National Research & Development Institute for Chemistry &Petrochemistry — ICECHIM, Biotechnology Department, 202 Spl. Independentei, 060021 Bucharest, Romania

[2]BAE Laboratory, Universite de Perpignan Via Domitia, Perpignan 66860, France

[3]LaborQ

[4]Department of Analytical Chemistry, University of Bucharest, 4-12 Regina Elisabeta Blvd., 03001 Bucharest, Romania

**Corresponding author: amgurban@yahoo.com*

Keywords: dithiocarbamate fungicides; mycotoxins; endocrine disrupters; aptasensors

Introduction: In the last decades, there have been an increasing need and request for development of fast, portable and cheap analytical methods for environmental and food monitoring.Classical methods such as gas chromatography and high-pressure liquid chromatography usually allows a specifically identification of a wide spectrum of pollutants, while biosensors allow the detection of one class of compounds having a common biological target [1]. A great variety of enzyme,microbial, antibody and aptamer based biosensors have been developed and reported for the detection of some commonly used pesticides, industrial chemicals and toxins.

Materials and methods: Disposable biosensors based on dehydrogenases, oxidases, antibody or aptamers have been developed for sensitive detection of dithiocarbamate fungicides, endocrine disruptor compounds, mycotoxins and tumor biomarkers. The screen-printed carbon paste electrodes were modified with appropriate mediators and nanocomposite materials prior biocomponent immobilization [2-4].

Results: Discrimination betweenmetham-sodium and itsmetabolitemethyl-isothiocyanate (MITC) was possible to be performed using an aldehyde dehydrogenases (AlDH) based biosensor. Sincemetham-sodiumdid not inhibit AIDH, MITCcould be detected at ppb levels. Further,new nanocomposites were developed by combination ofPrussian blue mediator with carbon nanotubes and ionic liquids for detection of estrogenic compounds and tumor biomarker. The developed nanocomposite materials exhibited synergistic electrocatalytic effect toward hydrogen peroxide reduction. Aflatoxin B_1 was determined in wine and beer samples using aptamer based fluorescenceassay, while its metabolite, aflatoxin M_1 was determined in milk samples using an off-line flow immunoassay system with electrochemical detection.

Conclusions: Thedeveloped electrochemical biosensors enable the sensitive detection of target analytes, with low detection limits, exhibiting good reproducibility and operationalstabilities.

Acknowledgements: *This work was supported by a grant of the Romanian National Authority for Scientific Research and Innovation, CCCDI – UEFISCDI, project number ERANET-MANUNET II -TOX-HAZ-ASSESS.*

References:

[1].Sonnenschein C., Soto A. M., J. Steroid Biochem. Mol. Biol.1998; 65: 143.
[2]. Gurban A.-M., Rotariu L., Marinescu V. E., Bala C., Electroanalysis 2012; 24 (12): 2371-2379.
[3]. Goud K. Y., Sharma A, Hayat A., Catanante G., Gobi K. V., Gurban A.-M., Marty J. - L., Analytical Biochemistry 2016; 508: 19-24.
[4]. Noguer T., Balasoiu A.-M., Avramescu A., Marty J.-L., Analytical Letters 2001; 34 (4): 513-5.

POLYPHENOLS, FLAVONES CONTENT AND TOXICITY ASSESSMENT OF THE VARIETY PERPETU ® EVERESTE APPLE LEAVES

A. I. Anghel[1], M. Dinu[1], M. V. Hovaneț[1], R. Ancuceanu[1*], D. M. Morărescu[1], C. Munteanu[2], C. S. Stoicescu[1,2]

[1]*Carol Davila University of Medicine and Pharmacy, Traian Vuia 6, Bucharest, Romania Bucharest, Romania*

[2]*Ilie Murgulescu Institute of Physical Chemistry of the Romanian Academy, 202 Splaiul Independentei, Bucharest, Romania*

**Corresponding author: robert.ancuceanu@umfcd.ro*

Keywords: Malus Perpetu ® Evereste;polyphenols; flavones; toxicity

Introduction: *Malus* Perpetu® Evereste (Rosaceae) is an apple variety resistant to apple scab (a disease caused by the ascomycete fungus *Venturia inaequalis*) [1]. The content of dihydrochalcones from young leaves and immature fruits (the main polyphenol classes of *Malus*) is correlated with a reduced susceptibility to fire blight and scab [2]. Dihydrochalcones have been reported to have antitumor effects on human cancer cell lines [3]. In Romania the *Malus* Perpetu® Evereste is known as an ornamental species. The purpose of this research was to investigate the polyphenol and flavone content of its leaf plant extracts, as well as to verify their cytotoxicity.

Materials and methods: The extracts from young leaves were prepared by extraction under reflux with methanol 50% and water. The polyphenolic and flavonoid content was evaluated spectrophotometrically. Toxicity tests were performed on plant and animal organisms with hydroalcoholic and aqueous extracts from leaves (5 %, w/v), on plant (*Triticum vulgare* L.) and animal cells (lethality test on *Artemia franciscana* Kellog). In these tests diluted solutions of 1.5–0.125% and 0.067–1.0% (w/v), respectively, were used.

Results: A higher flavonecontent was obtained in the aqueous solution,whereas the polyphenols were in higher amounts in the hydroalcoholic solution. In the *Triticum* test the aqueous extraction solution had a more potent inhibitory effect than the hydroalcoholic one, but the differences were small. In the *Artemia franciscana* bioassay, the $LC_{50}$was 4644 ppm for the hydroalcoholic solution and 3210 ppm for the aqueous one.

Conclusions: The extracts have some toxicity on plant cells, but they have little toxicity to invertebrate animals like *Artemia sp*.

Acknowledgements: *The authors acknowledge to Mrs. CSIII Cătălina Tudora- INMA for support in identifying the species*

References:

[1]. Duron M. In vitro propagation of the ornamental INRA *Malus*×Perpetu®Evereste. Scientia Horticulturea. 1984; 22:133-137.

[2]. Hutabarat OS, Flachowsky H, Regos I et al. Transgenic apple plants overexpressing the chalcone 3-hydroxylase gene of Cosmos sulphureus show increased levels of 3-hydroxyphloridzin and reduced susceptibility to apple scab and fire blight. Planta 2016; 243:1213–1224.

[3]. Qin X. Xing, YF, Zhou, Z, Yao Y. Dihydrochalcone Compounds Isolated from Crabapple Leaves Showed Anticancer Effects on Human Cancer Cell Lines. Molecules 2015; *20:* 21193-21203.

STUDIES ON THE LIPID CONTENT OF WATERMELON SEEDS AS SECONDARY PRODUCT TO ADD ECONOMIC VALUE TO THEIR COSMETIC USE

V. Tamas*, M. Neagu, G. Ivopol

S.C HOFIGAL EXPORT-IMPORT S.A., Intrarea Serelor, No. 2, Bucharest, Romania

**Corresponding author: cercetarehofigal2013@yahoo.com*

Keywords: watermelon seeds; oil; Soxhlet method; carotenes

Introduction: The extensive and rich watermelon crops in Romania stimulate the initiation of some researches to add economic value to the products resulting as waste.

The present paper aims to evaluate the lipid content of the watermelon seeds for their use in cosmetic formulations.

Materials and methods: Watermelon seeds come from ripe watermelon harvested from the southern areas of Romania and were manually separated from the pulp.

The study investigates the lipid content and its composition for its potential use in cosmetic formulations.

Subsequently, fatty oil was extracted for analytical purpose by the Soxhlet method using n-hexane as a solvent, while the fatty acid profile was analyzed by GC.

Results: Watermelon seeds contain between 25 and 29% fatty oil with a rich composition of unsaturated fatty acids, mostly linoleic acid (>65%).

The oil also contains significant quantities of other important compounds like carotenes (β-carotene) and phytosterols.

Conclusions: Watermelon seeds prove a considerable content of oil with a high nutritional value, suited for cosmetic use.

References::

[1]. Duduyemi, Oladejo, Adebanjo S.A, Oluti Kehnide, Extraction And Determination of Physico-Chemical Properties Of Watermelon Seed Oil (*Citrullus Lanatus* L.) For Relevant Uses, International Journal Of Scientific& Technology Research Volume 2, Issue 8, August 2013, pp. 66-67.

[2]. Basil S. Kamel, H. Dawson, Y. Kakuda, Characteristics and Composition of Melon and Grape Seed Oils and Cakes, JAOCS, Volume 62, No.5, May 1985.

COMPARATIVE STUDIES CONCERNING BIOACTIVE COMPOUNDS CONTENT IN *M. CHARANTIA* L. LEAVES AND FRUITS EXTRACTS

A. Oancea*, S. Savin, A. Toma, R. Tatia, O. Craciunescu, L. Moldovan

National Institute R&D for Biological Sciences, 296, Splaiul Independentei, Bucharest

**Corresponding author: oancea.anca@gmail.com*

Keywords: Momordica leaves and fruits; phytochemical screening; biocompatibility; anti-tumoral capacity

Introduction: *Momordica charantia*L. is a popular plant used for treating of diabetes-related conditions amongst the indigenous populations of Asia, South America, India and East Africa[1]. The aim of this study was to compare the phytochemical screening of alcoholic extracts of *M. charantia* L. leaves and fruits (cultivated in Roamania) treated with multifunctional products and also to test and compare the biocompatibility and anti – tumoral effect of the leaves and fruits extracts.

Materials and methods: *M. charantia* L. plants were treated with multifunctional products (*Trichoderma* consortium, thyme oil, different nutrients and ceramics - V2-V6; V1 control). The quantitative determination was performed by measuring total polyphenols and flavonoids content. The antioxidant capacity was determined by the inhibition of ABTS cationic radical and the scavenging of the stable radical DPPH [2]. *In vitro* biocompatibility of plants extracts was tested on NCTC fibroblast cell line and the anti –proliferative activity was tested on HEP2 tumoral cell line, using the NR assay [3].

Results: The fruits extracts of treated *M.charantia* L. contain significant amounts of antioxidants, polyphenols and flavonoids comparative with the untreated plant. Leaves of plants treated with V4A, V4B contain a higher amount of flavonoids and polyphenols than the other analyzed plant leaves. The results of NR assay demonstrated that the extracts of plants treated with V2, V3, V4A, V4B and the control V1 (leaves and fruits) did not affect the cell viability at 50-150 µg/mL after 72 h of cultivation. Leaves extract of V4A treated plants had a strong anti-tumoral effect at concentration of 100-150 µg/mL on HEP2 cell line being also biocompatible in this concentration range. The morphological test confirmed the results of NR assay.

Conclusions: The content of phenolic compounds in *Momordica* fruits is higher than that of leaves, while the antioxidant activity is higher in leaves than in the fruit, meaning that this activity did not depend only on the content in polyphenols but also on other types of compounds. V4A is the treatment that induced in *M. charantia* L. plant leaves both a non-cytotoxic effect on normal cells and an anti-proliferative effect on tumoral cells. *Momordica* leaves induced a higer anti-proliferative effect on tumoral cells than this plant fruits.

Acknowledgements:*This research was financially supported by the project PN-II-PT-PCCA-2013-4-0995-160/2014(MAIA).*

References:

[1]. Cefalu WT, Ye J, Wang ZQ. Efficacy of dietary supplementation with botanicals on carbohydrate metabolism in humans. PubMed, Endocr Metab Immune Disord Drug Targets.2008;8:78–81.

[2].Oancea A, et al. Phytochemical screening of the bioactive compounds in the most widespread medicinal plants from Calarasi-Silistra cross-border area.Buletin of Transilvania University of Brasov. 2013;6(55):133–136.

[3]. Borenfreund E, Puerner JA. A simple quantitative procedure using monolayer cultures for cytotoxicity assays. J Tiss Culture Meth. 1984;9:7–9.

INCREASING DENITRIFICATION CAPACITY OF MICROBIAL POPULATIONS, TO BE FURTHER USED IN RAS, BY SELECTIVE CULTIVATION

C. Moisescu[1], M. Iordan[1,2], M. Cîrnu[1], I.I. Ardelean[1*]

[1]Institute of Biology Bucharest , Romanian Academy, Splaiul Independenei 296, Bucharest 060031
[2]RAJA Strada Răscoalei 1907, 5, Constanța 900178
**Corresponding author: ioan.ardelean57@yahoo.com*

Keywords: biofiltration; denitrification; selective cultivation;recirculating aquaculture system

Introduction: Recirculating aquaculture system (RAS) is a modern technology in which spent water can be reused. The core of RAS is the biofiltration/ cleaning of spent water mainly with respect to organic substances, nitrate, ammonia and phosphorus[1-4]. In this paper we focus on improving the denitrification activity of filtering microbiota mainly by selective cultivation, because nitrate can limit the number of water recirculating cycles.

Materials and methods: The starting biological populations to be enriched in (micro)aerophilic denitrifying bacteria are: activated sludge from a municipal waste water treatment plant and microbiota from a fish farm biofilter. The strategy to increase the cell density of denitrifyingbacteria is focused on growing microbial consortia, in either batch or discontinuous conditions, on synthetic media with acetate or ethanol as sole carbon source and nitrate as the main final electron acceptor [3,4], in the presence of *p*H indicators (bromthymol blue or cresol red).

Results: In liquid synthetic media, thedenitrification activity doubled after one month whereas on solid media macro-colonies of denitrifying bacteria were obtained having red color, as a consequence of proton consumption during denitrification [3,4]. Interestingly for RAS, the final nitrate concentrations reach low levels (2-4 mg/L).

Conclusions: Selective cultivation of microbial populations on synthetic media increases the capacity of denitrification by a factor of 2, arguing that ongoing experiments will further improve the activity and density of denitrifying bacteria. The isolation of macrocolonies of denitrifying bacteria argues the capacity to purify these bacteria and grow them in axenic cultures. The enriched populations together with purified strains could be further used to increase the cleaning/filtration capacities in fish farms (one task of ABAWARE Project) and (municipal) waste water plants, as well.

Acknowledgements: *This work is funded by ABAWARE Project. Thanks are also due to Prof. Dr. Crăciun Nicolae (AQUATERRA), partner in ABAWARE project, for kindly providing microbiota from fish farm biofilter (Plutonița).*

References:

[1]. Dalsgaard, J., Lund, I., Thorarinsdottir, R., Drengstig, A., Arvonen, K., Pedersen, P.B., Farming different species in RAS in Nordic countries: Current status and future perspectives, Aqua. Engin.2010 ,doi:10.1016/j.aquaeng.2012.11.008.

[2]. Chen R, Deng M, He X and Hou J Enhancing Nitrate Removal from Freshwater Pond by Regulating Carbon/Nitrogen Ratio. Front. Microbiol. 2017; 8:1712 doi: 10.3389/fmicb.2017.01712.

[3]. Crab, R., Avnimelech, Y., Defoirdt, T., Bossier, P., Verstraete, W.,. Nitrogen removal techniques in aquaculture for a sustainable production. Aquaculture 2007 ; 270: 1–14.

[4]. Takaya N, Catalan-Sakairi MAB, Sakaguchi Y, Kato I, Zhou Z, Shoun H. Aerobic denitrifying bacteria that produce low levels of nitrous oxide. Appl Environ Microbiol. 2003; 69:3152-3157.

NANOSTRUCTURED REVERSE MICELLES: FROM BIOSEPARATION TOOL TO INORGANIC SYNTHESIS TEMPLATE

M.L. Arsene*, L. Jecu, M. Badea-Doni, I. Răut, M. Călin, G. Vasilescu, D. Constantinescu Aruxandei, A.M.Gurban

INCDCP-ICECHIM, Spl. Independentei 202, 060021, Bucharest, Romania

**Corresponding author: melania_arsene@yahoo.com*

Keywords: reverse micelles; enzymes; nonotubes; nanowires;nanorods

Introduction: In order to possibly open up new practical perspectives of the reverse micelles (RMs) as nanostructured medium, we aim to highlight their potentialities and multifunctionality in different scientific fields, from downstream processing of biomolecules to templatesfor synthesis of many types of nanoparticles.The major developments in strategies for RMs applications both in the improving of the recovery of bioactive compounds and in the controlled synthesis of nanoparticles are summarized.

Materials and methods: Herein, we evaluate the potential of different RM systems, consisting of various surfactants in apolar solvents, in terms of both biocatalytic and inorganic synthesis performance versus modulated parameters of the nanostructured medium.

Results: Bioseparation process mediated by RMs combines the step of extraction, concentration and purification of enzymes, antibiotics and various other bioproductsin chemical, biotechnological and pharmaceutical industries.Reverse micellar technique of lipase production, including the main steps and parameters, is discussed in detail.On the other hand, reverse micelles are becoming more recognized as good nanoreactors for obtaining spherical nanoparticles of a variety of inorganic materials, such as metals, chalcogenides, oxides, and other precipitates, as well for non-spherical nanostructures and their assemblies, like core–shell nanostructures.The proposed mechanisms for RM-based synthesis of inorganic nanowires/nanorods, as well for nanotubes, are presented.

Conclusions: While bioproducts extraction/purification mediated by RM is already considered as a viable alternative for the other available conventional downstream processing techniques, RMs have recently received attention as reaction and templating media,proving to be a versatile nanostructured reaction media for the bio-inspired synthesis of a huge variety of inorganic nanostructures.

Acknowledgments: *This research was financially supported by the project PN-16.31.02.01-NUCLEU Program.*

References:

[1]. Saran Chaurasiya, R., Umesh Hebbar, H., Raghavarao, K.S.M.S., Recent Developments in Nanoparticulate Based Reverse Micellar Extraction for Downstream Processing of Biomolecules, Cur Biochem Eng 2015; 2: 118-134.
[2]. Eastoe, J.; Hollamby, M. J.; Hudson, L. Adv. Colloid Interface Sci.2006, *128-130*, 5-15.
[3]. Limin Qi, Encyclopedia of Surface and Colloid Science DOI: 10.1081/E-ESCS-120023694.

CONTROLLABLE BIO-MIMETIC MEDIUM FOR BIOCATALYSIS PERFORMING

M.L. Arsene*, L. Jecu, M. Badea-Doni, I. Răut, M. Călin, G. Vasilescu, D. Aruxandei Constantinescu, A.M.Gurban

INCDCP-ICECHIM, Spl. Independentei 202, 060021, Bucharest, Romania

** Corresponding author: melania_arsene@yahoo.com*

Keywords: reverse micelles; stabilization; biocatalysis; crowding agents

Introduction: Due to their structures, reverse micelles (RMs) simulate in a great extent the biological microenvironment conditions and therefore are useful models for confinement over proteins entrapped inside them.In contrast with most of the studies focused on the biophysical properties of protein in RMs, we have undertaken this study to explore the effects of protein crowding and confinement on the structure and stability of enzymes in RM expressed this time as enzymatic activity in order to improve the performance of biocatalytic reactions.

Materials and methods: The coupled system AOX/PER, widely used for analytical applications, is the experimental model selected because involves enzymes differentiated by folds and sizes, but at the same time relate one to another.

Results: Enzymatic oxidation of methanol was study in a cell-like RM environment with a high concentration of macromolecules which are naturally accompanying components of alcohol oxidase in brute extract. Therefore, in our experiments we used a partial purified alcohol oxidase from*Hansenula polymorpha*from which have been removed only the contaminants which interfered either with optical transparency of RMs (cellular debris, insoluble compounds) or with the enzymatic assay (selective removal of catalase to obtain a catalase-free enzyme).A controlled increasing/ decreasing of protein crowding/ concentration was obtained by changing the ratio between the surfactant concentration and the water content from inside pools of the reverse micelles.

Conclusions: Simultaneous crowding/concentration created by the presence of natural crowders solubilized inside the water-pool of RM has an effect of global stabilization on the system enzyme-RM, concomitant with improving of the biocatalytic performance.

Acknowledgments: *This research was financially supported by the project PN-16.31.02.01-NUCLEU Program.*

CHARACTERISATION OF THE ESSENTIAL OILS OF SOME AROMATIC PLANTS

C. Georgescu[1*], M. Mironescu[1], E.Radu[2]

[1]*"Lucian Blaga" University of Sibiu, Sibiu, Romania*

[2]*The National Institute for Research & Development in Chemistry and Petrochemistry – Bucharest, Romania*

**Corresponding author: cecilia.georgescu@ulbsibiu.ro*

Keywords: essential oils; GC-MS; microbial activity; antioxidant propreties

Introduction: Essential oils are natural products which have special characteristics and many interesting applications in food industry, medicine and cosmetics. Aromatic plants are important in the food not only for their use as flavouring but also for their antioxidant properties [1].The objective of this study was to obtain, characterise and evaluate the ability for mould spores inhibition of anessential oil extracted from fennel seeds (*Foeniculum vulgare*), lovageherba (*Levisticumofficinale*) and yarrowherba (*Achilleamillefolium*) harvested in Transylvania County, Romania.The present study investigated also the antioxidant activity of the essential oil from same species.

Materials and methods: The essential oil was obtained by hydrodistillation in a neo-Clevenger apparatus and a detailed chemical analysis was conducted by gas chromatography–mass spectrometry (GC-MS). The essential oil was screened for antimicrobial activity against pathogenic bacteria and fungi by using the disk diffusion test. The method applied to measure the antioxidant activity was the free radical scavenging by using DPPH [2].

Results: Results showed that the fennel seeds contain 1.5% volatile oil, lovageherba contain 0.8% and yarrow herba contain 0.17%. From lovageherba22 volatile components were separated and identified. The main component was terpineolacetat, 67.3%.From yarrow herba16 volatile components were separated and identified. The mains components were estragol 23.15% and chamazulene 19.03% which give the dark blue colour of essential oil. From fennel seeds 7 volatile components were separated and identified. The main component was estragol, 88.65%. About antioxidant properties, essential oil from lovageherba, has the highest antioxidant actitivity.

The essential oils showed differentiated antimicrobial activity against pathogenic microorganisms. The general order was: Fungi (*Penicillium*sp. *>Candida albicans>Aspergillus niger)*>Pathogenic bacteria *(Salmonella anatum≥Staphylococcus aureus ≥ Escherichia coli ≥Bacillus cereus.*

Conclusions:

- from fennel seed we obtained the highest extraction yield;
- all essential oils analyzed have antioxidant properties and antimicrobial activity;
- yarrow showed the highest antimicrobial action.

References:

[1]. Hall C., Cuppett S., Wheeler d., Fu X. Effects of bleached and unbleached rosemary oleoresin and rosmariquinone on light-sensitized oxidation of soybean oil. J.Am.Oil Chem. Soc.1994;71:533-5.

[2]. Popovici C., Saykova I, Tylkowski, B. Evaluation de l'activite antioxydant des composes phenoliques par la reactivite avec le radical libre DPPH. Revue de Genie Industriel. 2009;4:25-39.

GREENVET- ANTIVIRAL EFFECTOF CERTAIN PLANT DERIVATIVESAND PRODUCTS CONTAINING SUCH DERIVATIVES

C. Chiurciu*, V. Chiurciu, E. Lupu, I. Ionescu, F. Mitroi,
D. Ciobanu, L. Diaconu, G. Oltean, I. Nicolae

ROMVAC Company S.A., şos. Centurii nr. 7, Voluntari., jud. Ilfov, Romania

**Corresponding author:chiurciu@romvac.ro*

Keywords: plant derivatives; VERO cells; paramyxovirus; antiviral

Introduction: The purpose of the research was to testthe antiviral effect of certain active principles - plant derivatives and medicinal products containing such derivatives -Ugeroclin-S and Mastitrat gel.

Materials and methods: a) plant derivatives (licorice-oak tree tincture, licorice-plantain-valerian decoct, green tea decoct andbrotherwort essential oil); b) MASTITRAT GEL and UGEROCLIN-S products;c) CDV/WHO-134 paramyxovirus, VERO cell line;d)culture media, buffers, solutions, specific laboratory facilities and materials.

Testing of plant derivatives-cell linecompatibility: a 24-hour culture was inoculated with eachsubstance separatelyto binary and decimal dilutions (up to 10^{-6}), monitoring cytotoxicity for 1 week. The working dilution to which the respective derivative is compatible with the cell line causing nocell damage was determined at the end of procedure.

Antiviral effect of tested materials: decimal dilutions of virus were carried out in EMEM, each dilution being mixed with an equal part of the testing materialand inoculated on a 24-hour cell monolayer. Cultures were monitored for 7 days, recording any occurring phenomenon.

Results: The specificvirus-induced cytopathic effect and the cytotoxic effectinduced bythe green tea decoct and MASTITRAT GEL were present, beingrepresentative for the relevantaspects. The viral suspension titerassessed after 7 days was between $10^{5,6}$ and $10^{5,8}CPID_{50}$/ml. The contact between viral suspension and active principlesdefinitely revealed an antiviral effect, with titer reduced up to 1000 times.

Conclusions: The tested plant derivatives and medicinal productshave a clear antiviral effect.

Acknowledgements:We are grateful to UEFISCDI Institute (Ministry of National Education) for the good collaboration on the accomplishment of PN-II-PT-PCCA-2013-4-0415 project (GREENVET- contract: 155/2014) within the PARTNERSHIP Program.

References:

[1]. Astani A, Reichling J, Schnitzler P. Comparative study on the antiviral activity of selected monoterpenes derived from essential oils. Phytother Res. 2010;24(5):673-679.
[2]. Muhammad Ovais Omer, Waleed Hassan AlMalki, Imran Shahid Shahzada Khuram, Imran Altaf, Saeed Imran.Comparative study to evaluate the anti-viral efficacy of Glycyrrhiza glabra extract and ribavirin against the Newcastle disease virus. Pharmacognosy Res. 2014;6(1):6–11.
[3]. Shin WJ, Kim YK, Lee KH, Seong BL. Evaluation of the antiviral activity of a green tea solution as a hand-wash disinfectant.Biosci Biotechnol Biochem. 2012;76(3):581-584.
[4]. Wellenberg GJ, WHM van der Poel, JT Van Oirschot. Viral infections and bovine mastitis: a review.Vet Microbiol. 2002;88(1):27-45.
[5]. Antiviral Essential Oils:Why They Work and How We Use Them-https://www.anandaapothecary.com/essential-oil-science/antiviral-essential-oils. 21 Oct. 2013.

NEW PHYTO-OPO-THERAPIC PRODUCT WITH OPTIMUM CONTENT IN DIGESTIVE ENZYMES

A. Cozea*, V. Tamas, S. Manea, M. Neagu

S.C.HOFIGAL EXPORT IMPORT S.A. Intrarea Serelor 2, sector 4, Bucharest, Romania

ResearchandDevelopmentDepartment

**Corresponding author: andreea.cozea@yahoo.com*

Keywords:enzymatic product; phyto-opo-therapy; digestive enzymes

Introduction: The importance of the main digestive enzymes: amylase, lipase, and protease and the role in digestion process is well known, and the many suffering caused by imbalances or deficiencies.In this context, Hofigal researchers have developed a new product that contains digestive enzymes of the phyto-opo-therapeutical nature along with digestive enzymes, along with other interest phytotherapeutical compounds of the entire digestive system as well as the entire human organism.

MaterialsandMethods: The product, accordingtothe formula, contains digestive enzymesfromthecuticle of chickengizzardand digestive enzymesfromparsley/cabbageleaves, processedappropriately, alongwithothercompounds of interest in theskimmed-extractof theseeds of thearmorandwiththeconcentratedartichoke extract. The methodsusedto determine themain digestive enzymesin thementioned vegetal andopo-therapeutic material as well as in thefinished product (amylase, lipase, protease) andpepsin (theenzyme specific tothechickengizzard) are methods specific tothoseenzymesexpressed in α-Amylaseexpressed in maltose; U/g/min/37˚C, min, Lipase, expressed in fattyacids U/g/min/37˚C, min.; Protease, expressed in casein U/g/min/37˚C, min, Pepsin, expressed in L-tyrosine (Tyr), U/g/min/37˚C, min.

Results:A new product hasbeendevelopedtoimprovethe digestive enzymedigestion of thecuticle of thechickengizzardand of theplant material with a convenient digestive enzyme content as well as colagog-choleretic and hepatic regenerationproperties. This natural combinationis a digestive complex with a balancedintake of digestive enzymes (amylase, protease, lipaseandpepsin) for theenzymaticrebalancing of the digestive system.

Conclusions: Enzymatic complex is a product with an increased efficiency in stimulation of the digestive process both by enzymatic activity and by the contribution of important phytotherapeutical compounds with which it acts synergistically, ensuring the prevention and regulation of digestive dysfunctions of the entire digestive system.

References:

[1]. DumitruIF, Iordachescu D. Determination of the enzymatic activity of α-amylase, spectrophotometric method described by Hostettler, Ed. Typography of the University of Bucharest- "Practical biochemistry, proteins and enzymes (Part I)", 1986, pp. 133-135.

[2]. Cojocaru DC. Determination of lipase activity, spectrophotometric method described by Willstatter, Ed. TEHNOPRESS IASI - "Practical Enzymology", 2005, pp. 201-203.

[3]. LorandL. Methods in Enzymology, Protease from Staphylococcus aureus, Determination of Protease Activity, spectrophotometric method described by G. Drapeau, Ed. Academic Press, NY, Vol. 45B, 1978, pp. 469.

[4]. Cojocaru DC. Determination of Pepsin Activity, spectrophotometric method described by ANSON, Ed. TEHNOPRESS, IASI, Practical Enzymology, 2005, pp. 280-282.

THE EFFECT OF THE OLIGOLAC ANIMAL PREMIX ON THE MORFO-PHYSIOLOGICAL PERFORMANCES OF BROILERS AND LAYING HENS

G. Oltean[1*], I. Nicolae[1], C. Chiurciu[1], V. Chiurciu[1], E. Lupu[1], B. Frunzareanu[2], S. Stanculescu[1], I. Calin[1], L. Diaconu[1], C. Uluitu[1], V. Filip[1], G. Mustatea[3], S. Gusita[1], A. Nica[1], P. Chitonu[1]

[1]S.C. ROMVAC Company S.A., Voluntari, Ilfov, Romania

[2]Institute for Control of Biological Products and Veterinary Medicines, Bucharest, Romania

[3]National Instituteof Research & Developmentfor Food Bioresources, Bucharest, Romania

**Corresponding author: gabriel_oltean@yahoo.com*

Keywords: OLIGOLAC ANIMAL PREMIX;Kluyveromyces marxianus; selenium; broilers; laying hens

Introduction: OLIGOLAC ANIMAL PREMIX is a feed additive consisting of selenium lactic yeasts (Kluyveromyces marxianus NRRLY 1195 R), brewer's yeast, lactose, glucomannose protein, kaolin and sodium carbonate and is intended to be administered in feeds at a rate of 1%. Its effectiveness was tested based on the effect on weight gain of broilers, hen's laying curve, egg weights, fertility and the presence in the egg of the selenium, akey component in the premix formulation.

Materials and methods: We used broiler chickens and laying hens from the Leghorn Lohaman breed, raised under SPF conditions, ROMVAC SPF recipe R1 feed (broilers), ROMVAC SPF recipe R5 (laying hens). Control batches were established, receiving only base feed, test lot, with 1% premix in the base feed (according to the package leaflet) and control group with modified formula (supraconcentration - 5% premix - in chicken, respectively subconcentration - 0.5% premix - in laying hens). The chickens were weighed at the initial time, 20 days, 50 days and at the end of the experiment (80 days); the mean body weight of each batch was calculated. At the laying hens, the experiment was initiated 30 days before the laying began and continued for 75 days from the beginning of the laying. We haverecordedthe number of eggs harvested daily, the weight of the egg, the fertility and the hatching of eggs, the egg presence of selenium and its distribution in the birds' organs.

Results: The average body weight in the group fed with 1% premix was 27% higher than the control group, representing a 5.4% increase. Selenium content in eggs was 22.5% higher in feed with 1% Oligolac. Analysis of selenium content in organ samples showed an increase in selenium accumulations, especially in the kidneys and spleen of laying hens. Also, fertility increased from 75% to 83% as a result of administration of the premix.

Conclusions: OLIGOLAC ANIMAL PREMIX determines increases in body weight in broiler chickens, increases in selenium concentration in eggs and poultry organs, positively influences fecundity and hatchability. The number and weight of the eggs were not influenced by the administration of the premix.

Acknowledgements: *OLIGOLAC ANIMAL PREMIX was developed under UEFISCDI - INOVARE Program - Eureka-Eurostars European Cooperatioan Subprogram.*

MONITORIZATION OF AFLATOXIN M_1 IN MILK USING AN OFF-LINE IMMUNOASSAY SYSTEM

A.-M. Gurban[1],P. Epure[2], D. Constantinescu-Aruxandei[1], F.Oancea[1], M.-L. Jecu[1], M.-L. Arsene[1], M. Badea Doni[1*]

[1]National Research & Development Institute for Chemistry &Petrochemistry — ICECHIM, Biotechnology Department, 202 Spl. Independentei, 060021Bucharest, Romania

[2]EPI-SISTEM SRL, Bvd. Brasovului 145, Sacele, Brasov, Romania

**Corresponding author:mihaela.doni@icechim.ro*

Keywords: Aflatoxin M1; off-line system; immunoassay; electrochemical detection

Introduction: Aflatoxins are the most toxic compounds from mycotoxins, exerting mutagenic and cytogenic toxicity and inducing human primary liver cancer [1]. Aflatoxin M_1 (AFM_1) represents the hydroxylated metabolite of aflatoxin B_1 (AFB_1), contaminating the milk of female mammals after ingestion of contaminated food or feed with AFB_1. Contamination with AFM_1 occur not only in raw milk, but also in the dairy products, usually at higher concentrations than those found in raw milk [2].Due to the high toxic potential of AFM_1, 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 off-line flow injection immunoassay system has been designed for the electrochemical detection of AFM_1in milk. In this regard, an indirect competitive assay was carried out, the mixture containing the antigen, the labelled antigen and a monoclonal specific antibody being incubated off-line. As labelled antigen was used AFM_1 labelled with horseradish peroxidase (HRP). After equilibrium was reached, this mixture was introduced into a flow-injection system, where the complex antigen-antibody is trapped onto a Protein G column.The labeled antigen was eluted.

Results: AProtein G column was used for trapping the formed complexes (antibody-antigen or antibody-labelled antigen), while 3,3`,5,5`-tetramethylbenzidine (TMB) was used as substrate for amperometric determination of HRP activity. A screen-printed carbon electrode (DropSens) was used for electrochemical detection of AFM_1 in milk. This system allowed the quantification of AFM_1 in a range of 20 to 500 ppt, with a detection limit of 20 ppt.

Conclusions: This off-line immunoassay system showed a good precision for the determination of AFM_1 in milk samples, with a satisfactory detection limit according to the actual regulations set for this aflatoxin in milk. The sample preparation was simple and fast comparing with chromatographic and ELISA techniques.

Acknowledgements: *This work was supported by a grant of the Romanian National Authority for Scientific Research and Innovation, CCCDI – UEFISCDI, project number ERANET-MANUNET II -TOX-HAZ-ASSESS.*

References:

[1]. Zain M. E., Impact of mycotoxins on humans and animals, Journal of Saudi Chemical Society 2011; 15(2):129-144.

[2]. Prandini A., Tansini G., Sigolo S., Filippi L., Laporta M., Piva G., On the occurrence of aflatoxin M1 in milk and dairy products, Food and Chemical Toxicology 2009; 47(5):984-991.

DEVELOPMENT OF AN APTAMER-BASED FLUORESCENCE ASSAY FOR DETECTION OF AFLATOXIN B_1

K. Y. Goud[1], M. Badea Doni[2], J. L. Marty[1], A.-M. Gurban[1,2*]

[1]BAE Laboratory, Universite de Perpignan Via Domitia, Perpignan 66860, France

[2]National Research & Development Institute for Chemistry & Petrochemistry — ICECHIM, Biotechnology Department, 202 Spl. Independentei, 060021 Bucharest, Romania

**Corresponding author: amgurban@yahoo.com*

Keywords: Aflatoxin B1; fluorescence assay; FAM-labelled aptamer; TAMRA-labelled DNA

Introduction: Besides the adverse effects of the alcoholic beverages, these also could be a source of contamination with several toxins and pollutants transmitted from grains during the production process. The mainely used agricultural products for alcoholic beverage production are wheat, barley and maize, products which can be contaminated by mycotoxins such as aflatoxins [1].Aflatoxin B_1 (AFB_1) represents the most commonly found highly toxic compound in agriculture crops. Due to its high toxicity, inducing mutagenic and carcinogenic effects in humans and animals, it has been classified as group 1 human carcinogen by the International Agency for Research on Cancer [2].

Materials and methods: An aptamer-based fluorescence assay has been developed for sensitive detection of AFB_1. Aptamers are single-stranded nucleic acids having high affinity and specificity to a wide range of targets. The detection of AFB_1 is based on the quenching – based aptamer assay using TAMRA (tetramethyl-6-carboxyrhodamine) – FAM (carboxyfluorescein) quenching system. The FAM-labelled aptamer was used as fluorophore, while TAMRA-labelled DNA single strand as a quencher for recognition of target analyte molecule.

Results: The FAM-modified aptamer has been characterized with a good fluorescence output signal. In the presence of TAMRA-DNA strand, the fluorescence response was quenched with a decrease in the fluorescence intensity. The aptamer assay showed a good linear calibrationfor AFB_1, with a wide linear range from 0.25 to 32 ng/mL and a detection limit of 0.2 ng/mL.

Conclusions: The aptamer-based fluorescence assay showed good interaction between AFB_1 and FAM-aptamer, inducing significant recovery in fluorescence response. The aptamer assay is suitable for designing of a simple and rapid aptasensing platform for sensitive and selective detection of AFB_1.

Acknowledgements: *This work was supported by a grant of the Romanian National Authority for Scientific Research and Innovation, CCCDI – UEFISCDI, project number ERANET-MANUNET II -TOX-HAZ-ASSESS.*

References:

[1]. Hwang J., Lee K. Reduction of aflatoxin B1 contamination in wheat by various cooking treatments, Food Chem. 2006; 98:71-5.

[2]. YuL., Zhang Y., Hu C., Wu H., Yang Y., Huang C., et al., Highly sensitive electrochemical impedance spectroscopy immunosensor for the detection of AFB1 in olive oil, Food Chem. 2015;176: 22-6.

ULTRASTRUCTURAL AND MORPHOLOGICAL CHANGES DURING KOMBUCHA POLLEN FERMENTATION

I. Moraru[1], E. Utoiu[2,3], V. S. Manoiu[3], L. Ionita[3], A. Oancea[3*], F. Oancea[4]

[1]*S.C. Laboratoarele Medica SRL, 11 Frasinului Street, Otopeni, Ilfov County, Romania*

[2]*University of Agronomic Sciences and Veterinary Medicine of Bucharest, 59 Mărăşti Blvd, District 1, Bucharest, Romania*

[3]*National Institute of Research and Development for Biological Sciences, 296 Splaiul Independenței, 060031, Bucharest, Romania*

[4]*The National Institute for Research & Development in Chemistry and Petrochemistry-ICECHIM, 202 Spl. Independenței 060021, Bucharest, Romania 3*

**Corresponding author: oancea.anca@gmail.com*

Keywords: pollen; fermentation; kombucha; electron microscopy; ultrastructure

Introduction: Polen is recognized for its nutritional value and its high content of bioactive compounds, but due to its external structure it has a low bioavailability for human consumption. Sporopolenin is a biopolymer with extremely high stability and very high resistance to biodegradation, including to the action of digestive enzymes and it is present in exine composition (the rigid outer layer of pollen) [1]. The aim of the present work was to observe the modifications at ultrastructural level of pollen grains under fermentation conditions in presence of SCOBY / Kombucha consortia.

Materials and methods: For ultrastructural analysis fermented pollen and kombucha samples were investigated using a Philips EM 208S electronic transmission microscope equipped with the OlympusSoft Imaging System iTEM video camera and the 80 kV Acceleration Voltage system. Samples were prepared according to Liu., T. (2012) [2]. Morphological analysis were performed by scaning electron microscopy using an SEM-HITACHI SU-1510 microscope.

Results: The SEM images highlighted the adhesion of the SCOBY / Kombucha consortium to pollen grains forming a relatively compact structure. Also, after the fermentation process, morphological changes of the pollen grains (swelling, breaking, deformation) could be observed. TEM investigations showed differences between the structure of control pollen grains and those undergoing fermentation in kombucha. We observed the outer layer modification, the emptying of the germination pores, the breaking of the exine layer and the release of the grains contents in their environmental media.

Conclusions: This morphological and ultrastructural analysis demonstrated that, through the pollen fermentation process in presence of SCOBY / Kombucha consortia, morphological modifications of external membrane and a release of polen grains content, increasing their content bioavailability.

Acknowledgements: *This work was supported by a grant of the Romanian Ministry for Research and Innovation. CNCDI – UEFISCDI, project, PN-III-P2-2.1-BG-2016-0051 3-Biotic.*

References:

[1]. WiermannR, Ahlers F, Schmitz-Thom I. In Biopolymers Online, Wiley-VCH Verlag GmbH & Co. KGaA, 2005.

[2]. Liu T. Plastic Embedding and Sectioning of Plant Tissues. Bio-protocol. 2012;2(23):296.

DETERMINATION OF METABOLIC PREBIOTICS FROM KOMBUCHA FERMENTED BEE POLLEN PRODUCTS

E. Utoiu[1,2], A. Toma[2],A.Oancea[2*], A.Gaspar-Pintiliescu[2],F. Oancea[1,3]

[1]University of Agronomic Sciences and Veterinary Medicine of Bucharest, 59 Mărăști Blvd, District 1, Bucharest, Romania

[2]National Institute of Research and Development for Biological Sciences, 296, Splaiul Independenței, 060031, Bucharest, Romania

[3]The National Institute for Research & Development in Chemistry and Petrochemistry-ICECHIM, 202 Spl. Independenței 060021, Bucharest, Romania 3

**Corresponding author: oancea.anca@gmail.com*

Keywords: Kombucha; polyphenols; pollen; prebiotic; fermentation

Introduction: Pollen has a high content of bioactive compounds - vitamins, minerals, essential fatty acids, carotenoids, flavonoids.However,their bioavailability is limited by the extremely complex structure of the pollen wall. We tested the effect of fermentation with Kombucha consortia on the bioavailability of pollen compounds and on enrichment withantioxidant polyphenols of final product produced by Kombucha symbiotic culture of bacteria and yeast (SCOBY). Such antioxidant polyphenols are acting as metabolic prebiotic, stimulating development of probiotic bacteria[1].

Materials and methods: Determination of total phenols was made with Folin-Ciocâlteu reagent [2], using known concentration of caffeic acid for the calibration curve, while flavonoid content is measured as quercetin equivalent [3]. Total antioxidant capacity was evaluated through DPPH and ABTS methods. Determination of polyphenols and flavonoids by HPLC was performed on an Agilent 1100 series with a DAD detector and a C18 ZORBAX Eclipse XDB column.

Results: Our data demonstrated a slow release of bioactive compounds from pollen to Kombucha fermentation broth, suggesting a permeabilization of the pollen exine. Pollen have a high content of polyphenols and biosilica. Continuous increasing level of polyphenols and soluble silicon on samples taken from Kombucha fermenting on black tea and pollen mixtures could be explained by a slow release of the bioactives from pollen under the SCOBY action.

Conclusions: Kombucha consortium, which are developing on clusters on the surface of pollen exine, most probably promote the formation of small pores, by oxidative degradation of sporopollenin matrix. Further studies are necessary for a better substantiation of the theory regarding exine degradation and slow release of the pollen bioactives.

Acknowledgements: *This work was supported by a grant of the Romanian Ministry for Research and Innovation. CNCDI – UEFISCDI, project, PN-III-P2-2.1-BG-2016-0051 3-Biotic.*

References:

[1]. Etxeberria, U., Fernández-Quintela, A., Milagro, F. I., Aguirre, L., Martínez, J. A., &Portillo, M. P, Impact of polyphenols and polyphenol-richdietarysources on gutmicrobiotacomposition. *Journal of agricultural and food chemistry*, 2013, *61*(40), 9517-9533.

[2]. Singleton, V.L., Orthofer, R., Lamuela-Raventos, R.M., Meth. Enzymol., 299, Academic Press, Abelson J.N., Simon M.I., eds., San Diego, 1999, p. 152.

[3]. Alexandru, V., Balan, M., Gaspar, A., Craciunescu, O., Moldovan, L., Studies on the antioxidant activity, phenol and flavonoid contents of some selected Romanian medicinal plants used for wound healing, Rom. Biotech. Lett., 2007, 12, (6), 3467-3472.

CHEMICAL COMPOSITION, CYTOTOXIC EFFECTS OF INDIGENOUS HERBAL PRODUCTS DRY EXTRACTS WITH POTENTIAL ANTITUMOR ACTIVITY

C. E. Gîrd, T. Costea*, L. E. Duțu, I. Nencu, M. L. Popescu, O. T. Olaru

''Carol Davila'' University of Medicine and Pharmacy, Faculty of Pharmacy, Bucharest, Romania

**Corresponding author: teodoracostea85@yahoo.com*

Keywords: berberine; phenols; cytotoxic activity; Daphnia magna

Introduction: Cancer is a multifactorial disease, with high indicence and mortality.Resistance to chemotherapy is the major cause of failure in cancer treatment [1]. The role of plants natural compounds in chemoprevention represents an area of great interest. Taking into consideration the scientific data [2-4] the aim of our research was the determinaion of chemical composition and cytotoxic properties of selective dry extracts from indigenous greater celandine (*Chelidonium majus* L.) aerial parts, alfalfa (*Medicago sativa* L.) aerial parts and common barberry (*Berberis vulgaris* L.) bark, that might be used for obtaining a phytomedicine with antitumor activity.

Materials and methods: Herbal products were harvested from an ecological crop (Hunedoara county), Romania. Hydroalcoholic (50% ethanol) dry extracts were obtained by means of freeze-drying method. Qualitative (HPLC) and quantitative assays (spectrophotometric and HPLC determinations) have been used for dry extracts phytochemical screening. Total phenolic content (expressed as tannic acid equivalents), flavones (expressed as rutin equivalents) and phenolcarboxylic acids (expressed as chlorogenic acid equivalents) were determined by means of spectrophotometric methods. The cytotoxic effects of dry extracts were assessed using *Daphnia magna* bioassay.

Results: Common barberry dry extract has the highest content of total polyphenols (14.95 g/100 g dry extract),while greater celandine and alfalfa aerial parts dry extracts are a rich source of flavones. HPLC analysis revealed the presence of berberine in all analysed extracts, the highest content was found for common barberry dry extract. Phenolcarboxylic acids (caffeic acid and chlorogenic acid) were also identified in greater celandine and common barberry dry extracts. Cytotoxic properties towards *Daphnia magna* intervertebrate decreased as follows: common barberry dry extract > greater celandine dry extract > alfalfa dry extract; however, they were lower compared to berberine hydrochloride, used as standard reference.

Conclusions: Analysed dry extracts are a source of bioactive compounds with cytotoxic properties.

Acknowledgements: *This research received funding from UEFISCIDI, Romanian-R.P China bilateral research project no. 59/BM/2016.*

References:

[1]. Omran Z., Scaife P., Stewart S., Rauch C. Physical and biological characteristics of multi drug resistance (MDR): an integral approach considering pH and drug resistance in cancer. Seminars in Cancer Biology. 2017; 43: 42-48.

[2]. Arora D., Sharma A. A review on phytochemical and pharmacological potential of genus *Chelidonium*. Pharmacognosy Journal. 2013; 5: 184-190.

[3].Rafinska K. et al. *Medicago sativa* as a source of secondary metabolites for agriculture and pharmaceutical industry. Phytochemistry Letters. 2017; 20: 520-539.

[4]. Patil J.B., Kim J., Jayaprasha G.K. Berberine induces apoptosis in breast cancer cells (MCF-7) through mitochondrial dependent pathway. Eur. J. Pharmacol. 2010; 645:75-80.

EVALUATION OF POLYPHENOL CONTENT AND TOXICITY OF *MORUS ALBA* FRACTIONATED PLANT EXTRACTS

M. Dinu[1], C. Popescu[2,3], O.T. Olaru[1*], A. Dunè[2], N. Băbeanu[4], O. Popa[4], G.M. Nitulescu[1], R.V. Ancuceanu[1]

[1] *"Carol Davila" University of Medicine and Pharmacy, Bucharest, Faculty of Pharmacy*

[2] *S.C. HOFIGAL Export Import S.A., Bucharest, Romania*

[3] *"Vasile Goldiş" Western University, Arad, Faculty of Pharmacy*

[4] *University of Agricultural Sciences and Veterinary Medicine, Bucharest, Romania*

**Corresponding author: octav_olaru2002@yahoo.com*

Keywords: polyphenols; plant extracts fingerprinting; toxicity evaluation

Introduction: Polyphenols are widely distributed compounds in plants which act as antioxidants and could exert anti-allergic activities. In the search of new active plant extracts with anti-dermatitis activity we studied some fractionated extracts from *Morus alba* species. In this study we assessed their total phenolic content and cytotoxicity. Their IR spectra was also evaluated in order to obtain the corresponding fingerprints.

Materials and methods: Total phenolic content was assessed using Folin Ciocalteu spectrophotometric method and the fingerprinting by recording attenuated total reflectance IR spectra on a spectral range of 4000-400 cm^{-1} and by using HPLC. The toxicity was evaluated using two tests, one on plants - *Triticum aestivum* - and one on invertebrate organisms - *Daphnia magna*.

Results: Thefingerprint of the extracts showed specific IR bands and HPLC peaks which can be used to the identification of the fractionated extracts. The main polyphenols identified by HPLC were epicatechin, kaempferol, rutin, p-coumaric acid, chlorogenic acid and caffeic acid. The total polyphenolic content, expressed in gallic acid equivalents was between 2.6 and 7.3 g%. Both methods, *Triticum aestivum* and *Daphnia magna* bioassays, revealed that the extracts exhibited moderate to low toxicity.

Conclusions: The research resulted in chemically characterized fractionated extracts which are good sources of polyphenols.The study identified several extracts with low toxicity and will be further analyzed for the development of anti-dermatitis new agents.

Acknowledgements: *The authors acknowledge the financial support offered by Romanian National Authority for Scientific Research, UEFISCDI, through grant PN-II-PT-PCCA-2013-4-1953, no. 199/2014.*

References:

[1]. Mukherjee PK., Maity N., Nema NK., Sarkar BK. Bioactive compounds from natural resources against skin aging. *Phytomedicine*, 2011; *19*(1): 64-73.

[2]. Yamamoto T., Yoshimura M., Yamaguchi F., Kouchi T., Tsuji R., Saito M., Kikuchi M. Anti-allergic activity of naringenin chalcone from a tomato skin extract. *Bioscience, biotechnology, and biochemistry*, 2004; 68(8): 1706-1711.

STUDY OF THE ANTI-INFLAMMATORYPROPERTIES OFANTHRISCUS SYLVESTRIS EXTRACTS

B. Ş. Velescu[1], O. T. Olaru[1], A. Orţan[2], N. Băbeanu[2], O. Popa[2],G. M. Nițulescu[1], C. E. Dinu-Pîrvu[1*]

[1]Carol Davila University of Medicine and Pharmacy, Traian Vuia 6, Bucharest, Romania

[2]University of Agricultural Sciences and Veterinary Medicine, Romania

**Corresponding author: ecristinaparvu@yahoo.com*

Keywords: polyphenols;anti-inflammatory activity; natural compounds

Introduction: Thewild chervil(*Anthriscussylvestris*Hoffm., *Apiaceae* family) is a wild plant common in most of the temperate regions, and is most characteristic of hedgerows, road verges, neglected pastures and hay meadows. The plant is used in human nutrition, and the root being intensively studied in anticancer therapy due to the presence of various lignans, of which deoxypodophyllotoxin is prevalent [1, 2].

Materials and methods: The anti-inflammatory potential of the wild chervil was investigated using several extraction methods. The obtained extracts were chemically analyzed in order to obtain the chemical fingerprint by IR and HPTLC, and standardized in total polyphenols using Folin Ciocalteu method. The pharmacological effect was determined in rats, using the plethysmometer procedure.

Results: Thechemical fingerprint of the extracts showed specific IR bands. The main polyphenols identified by HPTLC were isoquercitrin, quercetin, myricetin, luteolin and caffeic acid. For all extracts, the total polyphenolic content, expressed in gallic acid equivalens was measured. The extracts showed good anti-inflammatory effect compared to diclofenac, used as positive control.

Conclusions: In our research we obtained and characterized extracts from *Anthriscussylvestris*. Furthermore, we investigate their anti-inflammatory properties. The good anti-inflammatory effect showed by the extracts is a starting point in the development of promising formulations for dermal administration for human or veterinary use.

Acknowledgements: *This work received financial support from UEFISCDI through the project PN-II-PT-PCCA-2013-4-0953 No. 176/07.01.2014.*

References:

[1]. Olaru OT., Nițulescu GM., Orţan A., Dinu-Pîrvu CE. Ethnomedicinal, phytochemical and pharmacological profile of *Anthriscussylvestris* as an alternative source for anticancer lignans. Molecules.2015;20(8): 15003-15022.

[2]. Olaru OT., Nițulescu GM., Orţan A., Băbeanu N., Popa O., Ionescu D.,Dinu-Pirvu CE. Polyphenolic content and toxicity assessment of AnthriscussylyestrisHoffm. Romanian Biotechnological Letters, 2016; 21(6): 12054-12061.

STRUCTURAL ANALYSIS OF JANUS KINASES INHIBITORS TARGETING TRIPLE NEGATIVE BREAST CANCER

G. M. Nițulescu[1*], G. Iancu[2], G. Nițulescu[1], R. C. Iancu[2], O. T. Olaru[1], D. Vasile[2]

[1]*Carol Davila University of Medicine and Pharmacy, Faculty of Pharmacy, Traian Vuia 6, Bucharest, Romania,*

[2]*Carol Davila University of Medicine and Pharmacy, Faculty of Medicine, Bulevardul Eroilor Sanitari 8, Bucharest, Romania,*

**Corresponding author: nitulescu_mihai@yahoo.com*

Keywords:Bemis Murcko; computational studies; QSAR

Introduction: Recentresearch revealed that inhibition of the Janus kinases (JAK) protein can shrink triple-negative breast cancer, which lacks expression of the estrogen, progesterone receptor, and human epidermal growth factor receptor. This cancer is the most lethal form of breast cancer and still lacks a targeted treatment. In order to perform a screening for new JAK inhibitors we analyzed the structural descriptors and the shape profile required for a potent inhibition.

Materials and methods: A large library of JAK inhibitors was generated using PubChem and specific filters.The obtained collection of over 2200 compounds was analysed using DataWarrior software to calculate chemical descriptors encoding various aspects, like the chemical graph, chemical functionality, pharmacophore features. The compounds were clustered in diverse subsets based on the JAK inhibition potency and also on their chemical diversity.Scaffold abstraction based on the Bemis and Murcko approach was performed and structural activity patterns were developed.

Results: A large collection of JAK inhibitors was obtained and their structural profile was analyzed obtaining a set of thumb-up rules for the design of new chemical entities. The structure activity relationships can provide a simple pattern for future developments.

Conclusions: The structure activity relationships can provide a simple pattern for future developments of new JAK inhibitors. The biological assessment of the anti-proliferative effect will provide the framework for new potential triple negative breast cancer agents.

Acknowledgements: *This work was supported by a grant of the Romanian National Authority for Scientific Research andInnovation, CCCDI – UEFISCDI, project number 46 BM/2016 Code PN3-P3-246.*

References:

[1]. Hampton T. Targeted therapy blocks growth of triple-negative breast cancer in mice. 2016;315(21):2267.

[2]. Nitulescu GM, Iancu G, Nitulescu G, Iancu RC, Bogdanici C, Vasile D. Brave new hope for breast cancer: Aminopyrazole derivates between rational design and clinical efficacy. Rev Chim. 2017;68(4):754–7.

SCREENING NATURAL SCAFFOLDS AS ANTIVIRULENCE AGENTS

G. Nițulescu, A. Ungurianu, G. M. Nițulescu*,I. M. Nicorescu, O. T. Olaru, D. Margină

Carol Davila University of Medicine and Pharmacy, Traian Vuia 6, Bucharest, Romania

**Corresponding author: nitulescu_mihai@yahoo.com*

Keywords: sortase; natural compounds; flavonoids

Introduction: Sortases are transpeptidases that occur in almost all Gram-positive bacteria attaching the surface proteins to the cell wall. Sortases play an important roles in virulence and infection being promising targets for the development of antivirulence agents.

Materials and methods: The inhibitory activity of various natural compounds was determined by quantifying the increase in fluorescence intensity upon cleavage of the 5-FAM/QXL® FRET substrate using SensoLyte® 520 Sortase A Activity Assay Kit. According to kit protocol, reactions were performed in a 96-well plate. All compounds were dissolved in dimethyl sulfoxide and diluted with sterilized distilled water.Reactions were carried out at room temperature and analyzed fluorometrically. We used as the positive control p-hydroxymercuribenzoic acid.

Results: Chemically, the tested compounds belong to the flavonoid, coumarins, cinnamic acid derivatives, alkaloids, anthraquinones, and the terpene families.The best inhibitory effects on sortase A enzyme were obtained for the flavonoid and anthraquinone scaffold.

Conclusions: In our search focused on in finding some new antibacterial solutions targeted on virulence mechanisms, we screened a chemical diverse set of natural compounds and found significant Srt A inhibitors.Because their potential and accessibility these bioresoursescan become an important solution for future therapies.

Acknowledgements: *The authors acknowledge the financial support offered by Romanian National Authority for Scientific Research UEFISCDI through grant PN-II-RU-TE-2014-4-1670, no. 342/2015.*

References:

[1]. Marraffini LA, Dedent AC, Schneewind O. Sortases and the art of anchoring proteins to the envelopes of gram-positive bacteria. Microbiol Mol Biol Rev. American Society for Microbiology. 2006;70(1):192–221.

[2]. Nitulescu G, Zanfirescu A, Olaru TO, Nicorescu MI, Nitulescu MG, Margina D. Structural Analysis of Sortase A Inhibitors, Molecules. 2016; 21(11), 1591.

PHARMACOGNOSTICAL RESEARCH CONCERNING *LOPHANTUS ANISATUS* LEAVES, FLOWER AND WHOLE AERIAL PARTS

I. Nencu*, C. E. Gîrd, L. E. Duțu, T. Costea, M. L. Popescu

Department of Pharmacognosy, Phytochemistry and Phytotherapy, Faculty of Pharmacy, University of Medicine and Pharmacy, "Carol Davila", 6 Traian Vuia street, Bucharest, Romania

**Corresponding author: ioanaitudor@gmail.com*

Keywords: giant hyssop; polyphenols;volatile oil

Introduction: *Lophantus anisatus (giant hyssop, anise hyssop)* is one of the fourth melliferous plant, worldwide known for it's medicinal plant, aromatic and ornamental properties. Because of its genetic capacity to adapt to environmental conditions and due to economical importance, the plant drawn attention of Romanian biologist, and nowadays it is studied at Laboratory of Genetics Breeding and Biodiversity Conservation from VRDS Buzau**.**

The aim of the study is the evaluation of the chemical composition of the leaves, flower and whole aerial parts of *Lophantus anisatus* by qualitative and quantitative means, in order to select the raw material with highest content of active principles, for further obtaining pharmacologically active dry extracts.

Materials and methods: The raw materials (leaves, flower and aerial parts) were detached from specimes harvested in June, 2017, from crops of the VRDS Buzau. The anatomical elements of the vegetal products were determined using microscopic exam (powder preparation clarified using chloral hydrate 80%, Carl Zeiss Microscope, ob10x.). The identity of the main active principles was established by phytochemical screening and thin-layer chromatography. Using spectrophotometric methods was assessed the content of total polyphenolic compounds, flavonoidic and phenolcarboxilic acids. Also, the mucilage content for all vegetal products was established using gravimetric method. The content of volatile oil was assessed using Neo Clevenger apparatus.

Results: The phytochemical screening shows the presence, in all three raw materials, of mucilages, flavonoids, phenolcarboxilic acids, tannins and saponins. Carotenoids and proanthocyanidins were found only in the flowers of giant hyssop. The content of volatile oil is 0.8 mL/100 g raw material. Quantification of the phenolic compounds show that the leaves of Lophantus anisatus has the highest content of total phenolic compounds, flavonoids and phenolcarboxilic acids. Regarding mucilages content, the flower are the richest compared to the other two raw materials. The chemical exam results show minor differences between the content of active principles of aerial parts against leaves and flower. Therefore, we choose the whole aerial parts for further research.

Conclusions:*Lophantus anisatus* are a valuable sources of phenolic compounds and mucilages. The whole aerial part was selected for further work.

References:

[1].Vînătoru C., Zamfir B., Bratu C., Peticila A., *Lophanthus Anisatus*, A Multi – Purpose Plant, acclimatized and improved at VRDS Buzau. Horti - B. 2015;LIX : 277-280.

CHEMICAL COMPOSITION AND ANTIOXIDANT ACTIVITY OF INDIGENOUS *TRAMETES BIFORMIS* (Fr.) PILAT

T. Costea*, C. E. Gîrd, L. E. Duțu, I. Nencu, M. L. Popescu

''Carol Davila'' University of Medicine and Pharmacy, Faculty of Pharmacy, Department of Pharmacognosy, Phytochemistry, Phytotherapy, Bucharest, Romania

**Corresponding author: teodoracostea85@yahoo.com*

Keywords: mushrooms; sterols; phenolic compounds; scavenger capacity

Introduction: Mushrooms have been long used for both nutritional purposes and therapeutic effects (anticancer, immunomodulatory, hypoglycaemic and hypolipidaemic properties). It is well known, that they are an important source of bioactive compounds (proteins, phenols, aminoacids, polysaccharides, vitamins, steroids) [1]. Nearly 60 *Trametes* species are known in the world, the most famous of the genus is *Trametes versicolor* (L. Fr.) [2]. However, others, such as *Trametes biformis* (Fr.) Pilat, also known as *Coriolus biformis* (Fr.) Pat. or *Trichaptum biforme* (Fr.) Ryvarden are less studied. The aim of our research was the phytochemical screening and evaluation of antioxidant activity of violet toothed polypore mushroom (*Trametes biformis*).

Materials and methods: The mushroom was collected in October, 2016 from Moraresti (Argeș county, Romania). Qualitative (specific chemical reactions, thin layer chromatography - TLC) and quantitative assays were performed on hydroalcoholic (70% ethanol) and aqueous dry extracts, in order to determine the influence of solvent type upon chemical composition and antioxidant capacity. Total phenolic (expressed as tannic acid equivalents) and sterol contents (expressed as ergosterol equivalents) were assed using spectrophotometric methods. Scavenger activity towards DPPH and ABTS free radicals was used for antioxidant capacity evaluation, which was expressed as ascorbic acid equivalents (mg vitamin C/g dry extract).

Results: Analysed dry extracts are a source of phenolic compounds, sterols and polysaccharides. TLC analysis revealed the presence of ergosterol in both samples. The aqueous dry extract has a higher content of phenolic compounds (2.50 g polyphenols/100 g dry extract), compared to the 70% ethanolic one (1.41 g polyphenols/100 g dry extract). The antioxidant capacity is strongly correlated with the total phenolic content, since the best free radical scavenger activity was found for the aqueous dry extract (91.57 mg ascorbic acid/g dry extract – ABTS method; 45.72 mg ascorbic acid/dry extract – DPPH assay).

Conclusions: Analysed dry extracts are a source ofbioactive compounds. The best antioxidant activity was found for *Trametes biformis* aqueous dry extract.

References:

[1]. Wasser SP. Medicinal mushrooms science, current perspectives, advances, evidences and chalenges. Biomed J.2014; 37:345-356.

[2]. Barros AB, Ferrao J, Fernandes T. A safety assessment of *Coriolus versicolor* biomass as food supplement. Food and Nutrition Research. 2016; 60(1): 29953.

ANTITUMOR AND TOXICOLOGICAL RESEARCH ON EXTRACTS FROM *CORYDALIS* SPECIES

O. T. Olaru[1*], M. van de Venter[2], G. Nitulescu[1], L. Spies[2], O. C. Seremet[1], T. Koekemoer[2], C. M. Gutu[1], B. Swanepoel[2], G. M. Nitulescu[1]

[1] *"Carol Davila" University of Medicine and Pharmacy, Bucharest, Romania*

[2] *"Nelson Mandela" Metropolitan University, Port Elizabeth, South Africa*

**Corresponding author: octav_olaru2002@yahoo.com*

Keywords: Corydalis species; plant extracts; antitumor; toxicity evaluation

Introduction:*Corydalis*DC. genus (Fumariaceae family) has about 12 species of annual and perennial herbaceous plants spread mainly in the northern hemisphere. The species contain as active compounds alkaloids, mainly isoquinoline derivatives. In the present work we obtained several extracts from the aerial parts from two *Corydalis* species and evaluate their anticancer properties against three human cancerous cell lines. Their acute toxicity was evaluated using a method on invertebrate organisms - *Daphnia magna*bioassay.

Materials and methods: *Corydalis cava* and *Corydalis solida* were harvested from GiurgiuCounty, from the spontaneous flora, during blooming period. The aerial parts were extracted with water. After extraction and concentration using a rotary evaporator, the extractive solutions were dried using a freeze dryer. The cytotoxicity screening was performed using the MTT assay against human tumour cancer cell lines MCF7, Caco-2 and HeLa. The extracts were used in the concentration range of 3 to 300 µg/mL. The bioassay was performed according to the method described in the literature [1, 2]. The test was performed on concentration in the range of 62.5 to 500 µg/mL and the results were calculated using GraphPad Prism version 5.0 software (USA).

Results: The extracts induced moderate cytotoxicity on HeLa cell line. The results on MCF7 and CaCo-2 cell lines were similar. The lethal concentrations which causes the death of 50% of organisms (LC50) were determined by interpolating on lethality - logarithm of concentration curves, using the least squares fit method. 95% confidence intervals of LC50 (CI95%) and the correlation coefficient (r^2) of the curves, were also calculated.

Conclusions: The extracts exhibited a moderate toxicity and promising anti-proliferative effect on all three cell lines. Further studies are in progress to establish the mechanism and the compounds responsible of the two effects.

Acknowledgements: *The authors acknowledge the financial support offered by UEFISCDI (Romania - grant no.8BM/2016) and NRF (South Africa), through Romania - South Africa Joint Collaboration.*

References:

[1]. Olaru OT., Venables L., van de Venter M., Nitulescu,GM., Margina D., Spandidos DA., Tsatsakis AM. Anticancer potential of selected Fallopia Adans species. *Oncology letters*, 2015; 10(3): 1323-1332.

[2]. Nitulescu GM., Draghici C., Olaru OT. New potential antitumor pyrazole derivatives: Synthesis and cytotoxic evaluation. *International journal of molecular sciences*, 2013; 14(11): 21805-21818.

COMPLETE VALORIZATION OF MUSTARD OILSEEDS BY USING BIOASSISTED SOXHLET AZEOTROPIC EXTRACTION

M. Popescu*, M. Desliu-Avram, E. Radu, L. Capra, R. Somoghi, F. Oancea

INCDCP-ICECHIM, 202 Spl. Independentei, 060021, Bucharest, Romania

**Corresponding author: mariana280259@yahoo.com*

Keywords: Soxhlet extraction; mustard oilseed; enzyme

Introduction: Vegetable oils had been obtained at industrial scale for many years from botanical tissues using conventional extraction methods: mechanical cold pressing, solvent extraction and supercritical fluid extraction. Soxhlet extraction was the most applied method for vegetable oil recovering after low yield mechanical cold pressing of oilseeds. Some disadvantages such as the toxicity of organic solvents contaminating final products, high temperatures and pressure of accelerated solvent extraction destroying the integrity of bioactive phytochemicals and expensive equipments for supercritical fluid methods required the development of mild and cleaner effective technological alternatives. Present study proposed a technical solution for toxic solvent traces removal from oils extracted using Soxhlet method and isolation of valuable compounds from mustard oilseeds[1].

Materials and methods: Indian yellow mustard oilseeds were ground and extracted into a Soxhlet laboratory device with an azeotropic mixture of ethanol: n-hexane. The optimal parameters of solvent extraction were 8 hours of reflux at the azeotrope boiling point. Two experiments used a cellulase and protease cocktail to break cellular walls. All the extraction steps were performed without intermediary discharge of biomass from the cartridge usinga single batch Soxhlet extraction. Final products were assayed, after solvents removal and centrifugation, by GC-MS method comparing to mass spectral libraries (NIST08) and Kjeldahl nitrogen analysis for protein. Transmission Electron Microscopy (TEM) of integral and spent biomass was performed to identify the oil presence in the samples.

Results: Oil content of yellow mustard was 27.9%, comparable with hexane Soxhlet extraction but completely free of hexane. TEM images showed the advanced disruption of cellular walls by enzymatic treatment. Bioactive compounds such as fatty acids, phytosterols and lignocerate were identified in the oily fraction after dry azeotropic extraction. Aqueous and enzymatic pretreatments reduced oil yields, and increased polar compounds. The supernatant contained trilinolein, xylopyranoside and proteic nitrogen, with concentrations depending on the inputs order in the process.

Conclusions: Enzyme assisted aqueous extraction of vegetable oils coupled with an azeotropic solvent system for Soxhlet extraction have been proposed in this study for further research development and experimental validation as an effective environmentally safe technology for extraction of vegetable oils and compounds with agri-food applications as a potential valuable tool for biotechnology.

Acknowledgements: *This work was funded by the Project PN 16.31.01.01.04, financially supported by UEFISCDI-MRI.*

Reference:

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

THE INFLUENCE OF VARIOUS PARAMETERS ON THE FORMATION OF PROBIOTIC MICROCAPSULES

D. Pasarin,C. Rovinaru*

The National Institute of Research and Development in Chemistry and Petrochemistry

**Corresponding author:rovinarucamelia@yahoo.com*

Keywords: microencapsulation; sodium alginate; probiotic

Introduction: Probiotic microencapsulation process has many applications in food, feed and pharmaceutical sectors. The microencapsulation methods can be classified in chemical, physical-mechanical and physicochemical and use a wide range of encapsulated materials**.** Extrusion method is very used at lab level and sodium alginate is one of the most studied materials for microencapsulation. The aim of the work was to study influence of different parameters such as sodium alginate and $CaCl_2$ solutions concentration, distance between needle and $CaCl_2$ solution, needle diameter and flow rate on the alginate microcapsules formation and size by extrusion.

Materials and methods: Probiotic strains (*L.acidophilus* and *L.plantarum*) were microencapsulated by extrusion method, using different sodium alginate solution concentrations (1.5-3.5%) with flow rates between 1 and 3mL/min, $CaCl_2$ solution concentrations (1 – 5.5%). These solutions were prepared separately and autoclaved for 15 min. at 121^0C. The $CaCl_2$ solution was magnetically stirred at 350 rpm and it was kept constant in all experiments. Some distances between syringe and $CaCl_2$ solution (10-20 cm) and needle syringe diameters (0.19 – 0.15 mm) were tested.

Results: The optimum conditions for microencapsulated of both probiotic strainswere: sodium alginate solution concentration 3.5% and $CaCl_2$ solution concentration 2.5%. The smaller microcapsules were achieved when the distance between syringe needle and $CaCl_2$ solution was 10 cm and needle syringe diameter 0.15 mm.

Conclusions: This method can be applied only at lab level and the most important factors whichinfluence the microencapsulation are needle syringe diameter, sodium alginate solution concentration and $CaCl_2$ solution concentration. For the generation of microcapsules smaller than 0.15 mm, another microencapsulation method is indicated.

Acknowledgements: The authors would like to thanks the UEFISCDI that have supported PROBEV Eureka 92/2016 research project.

ACCUMULATION OF INORGANIC ZINC SALTS BY CAROTENOGENIC YEASTS

C. Rovinaru, D. Pasarin*, L. Capra

The National Institute of Research and Development in Chemistry and Petrochemistry
**Corresponding author: diana.pasarin@gmail.com*

Keywords: Sporobolomyces sp; zinc salts; zinc enriched biomass

Introduction: Some species of *Sporobolomyces sp.* yeasts are the main carotenoid producing microorganisms [1]. Yeasts require mineral nutrients for cellular growth and metabolism. Zinc is an essential trace element in biological systems and it participates in various pathways of metabolism. Zinc optimal concentration in growth medium depends on strain and culture conditions, and its uptake by yeast is metabolism-independent and metabolism-dependent, with most of the available zinc transferred very quickly into the vacuole [2].

The aim of this work was to evaluate the ability of *Sporobolomyces sp.* yeast to accumulate zinc from solid substrate and the influence of Zn^{2+} trace element from different salts sources on yield of biomass and organic Zn content in biomass.

Materials and methods: Experiments were carried out with the yeast *Sporobolomyces sp.* maintained on YPD medium. The culture medium was supplemented with two inorganic Zn salts, i.e. zinc sulfate heptahydrate and zinc oxide in concentrations of 0.025% and 0.1%, respectively, in aerobic conditions, in dark, at 28°C, for 72 hours. The control culture had no zinc added to the medium. The content of Zn^{2+} in yeast cell biomass was analyzed by ICP-OES.

Results: The results showed that the addition of different inorganic Zn sources, in concentration of 0.025% and 0.1% did not influence the yield of dry yeast biomass, which reached 1.88-1.99 g/L culture medium. The amount of yeast biomass has decreased at concentration of 1% Zn salt solutions. Zn content present in the biomass was higher than that in the yeast biomass without Zn treatment (control), namely 0.850% (w/w) and 0.0079% (w/w), respectively, according to amount of zinc addition into the cultivation medium.

Conclusions: Different zinc salts added to the growth media in concentrations from 0.025% and 0.1%do not affect the biomass formation. Zinc uptake by the yeast*Sporobolomyces sp.* dependson zinc salts concentration in growth medium.No major differences were found in terms of zinc uptake using different zinc salts. Zinc sulphate heptahydrate is an economically source of supplementary zinc.

Acknowledgements: *The authors would like to thanks the UEFISCDI that have supported BIOCAROMIN 57PTE/2016 research project.*

References:

[1]. Marova I.Production of enriched biomass by red yeasts of *Sporobolomyces sp.* grown on waste substrates.Journal of Microbiology, Biotechnology and Food Sciences, 2012, 1-4, 534-551.
[2]. Walker G. Metals in Yeast Fermentation Processes. Advances in Applied Microbiology, 2004; 197-229.

ULTRASOUND FIELD EXTRACTION INTENSIFICATION AND THE MORPHOLOGY OF *CAMELINA SATIVA* GROUND SEED

M. Desliu-Avram*, M. Popescu

INCDCP-ICECHIM, 202 Spl. Independentei, 060021, Bucharest, Romania

**Corresponding author:malinaavram@yahoo.com*

Keywords: seed oil; Camelina sativa; extraction; ultrasound field

Introduction: Camelina oil is considered to be a high quality edible oil, due to its relatively high content (>50%) in omega-3 and -6 fatty acids and low saturated fatty acids [1]. The aim of this research is to improve the liquid-solid extraction yield of *Camelina sativa*oil, or improve the selectivity of the extractive process, using ultrasound influence.

Materials and methods: An ultrasound bath with the frequency of 40kHz was used as an intensification technique for the extraction of *Camelina sativa* seed oil, in order to test the extractive process in the ultrasound field, with adjustable power between 50-150W, indicated in percent between 0-100, where n-hexane was used as extraction solvent. Ground camelina seeds of 0.63mm particle size were used, at the optimal liquid/solid ratio of 6mL/g set for batch extraction,determined using a statistical method(Box-Behnken Design) based on Response Surface Methdology (RSM) [1], at a power of 100W and a temperature of 30±2°C.The oil yieldswere determined at different periods ofextraction time.The microstructure of particle size fraction of camelina seed before and after batch extraction, respectively in the ultrasound field, was observed using Scanning Electron Microscopy (SEM) [2].

Results: The extraction yields obtained over 30-40 minutes in the ultrasonic field are approaching the values obtained by batch extraction at 40°C in 2 hours, conditions corresponding to the optimal conditions determined for batch extraction.SEM images showed that ultrasounds caused visible structural changes at the surface and inside the particle, causing the appearance of spaces and voids from which cellular contents have been released.

Conclusions: The research results demonstrated the possibility of tissue and cell membrane damage by ultrasounds which intensifyedmass transfer and allowed the solvent to penetrate the plant structure and accelerate the vegetable oil solubilization.This work sustained the development of new procedures for camelina oil obtaining, rich in polyunsaturated fatty acids and tocopherols (vitamin E) useful for somefeed, food products, industrial applications, jet fuel and biofuels [3].

Acknowledgements: *This work was funded by the Project PN 16.31.01.01.04, financially supported by UEFISCDI, Ministry of Research and Innovation.*

References:

[1]. 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;66:417–421.

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

[3]. Zanetti F. Eynck C. Christou M. Krzyżaniak M. Righini D. Alexopoulou E. Stolarski MJ. Van Loo EN. Puttick D. Monti A. Agronomic performance and seed quality attributes of Camelina (*Camelina sativa* L. crantz) in multi-environment trials across Europe and Canada. Industrial Crops & Products. 2017. Article in press.

THE DEVELOPMENT OF MICRO-TOM TOMATOES AFTER ADMINISTRATION OF A FOLIAR BIOSTIMULANT

M. Ghiurea, M. Deşliu-Avram*, V.A.Faraon, Ş.O. Dima, C. Neamțu, V. Zamfiropol-Cristea, F. Oancea*

INCDCP-ICECHIM, 202 Spl. Independentei, 060021Bucharest, Romania

**Corresponding author: malinaavram@yahoo.com, florino@ping.ro*

Keywords: Micro-Tom tomato; phenolic compounds; biostimulant; climate chamber

Introduction:A great challenge in organic crops is the resistance of plants to biotic and abiotic stresses. In the present study, we evaluated the influence of a foliar plant biostimulant of several characteristics (morpho-physiological, biological activity and phytochemicals) of Micro-Tom tomatoes. Plant biostimulants are enhancing plant resitance to biotic and abiotic stress and increase accumulation of the bioactive compounds into plant leaves. The objectives of the present work are, firstly, to evaluate the physiological parameters and, secondly, to characterize the phytochemical profiles of the vegetative organs (leaves, stems and roots) of tomatoes plants. The phytochemical profiles is improtant for both valorizationof the side stream from tomatoes crop in the defence of tomato plants against biotic and abiotic agents.

Materials and methods: The plants were grown in a climate chamber (Micro Clima-Series™ – Model ECD01E), in which temperature (18-27°C) and light (4300-10000 Lux) are controlled by a programmable controller. The night/day cycle was set to: only day or 12h day/12h night, with a humidityof about 54-84%. Tomato Micro-Tom seeds were sterilized and germinated a few days [1, 2] before planting in Arasystem. The number of applications with commercial foliar biostimulant was halved, and the dose of biostimulant solution was doubled.

Results: The plants development was compared with the growth of standard untreated tomatoes.The evaluation of physiological parameters is done in connection with shoot system lenght, stem thickness, number of vegetatives shoots, lenght and volume of root system and leaf area. The biological activity of Micro-Tom plants is assesed regarding the effective photochemical quantum yield of photosystem II and the stomatal conductance. The phytochemical profiles are determined and characterized by HPLC, FT-IR and XRD.

Conclusions: It has been established the evaluation scale of Micro-Tom tomatoes in connexion with morpho-physiological parametersand values of phytochemical compounds analized by different methods. Further experimental setup adjustments will be made to optimize the growth method.

Acknowledgements: *This work was funded by the Project 2-PTE/2016 (LEGO-FERT), financially supported by UEFISCDI, Ministry of Research and Innovation.*

References:

[1]. Orozco-Cárdenas ML, Garcia D, Narváez-Vásquez J. Tomato (*Solanum lycopersicum*). Plant Transformation Research Center, University of California Riverside, CA 92507-0124.

[2]. Motohashi R, Enoki H, Fukazawa C, Kiriiwa Y. Hydroponic Culture of 'Micro-Tom' Tomato. Bio-protocol. 2015;5(19):1-7.

ENZYMATIC SYNTHESIS OF THE ETHYL ESTERS OF FATTY ACIDS FROMUSED COOKING OIL

A.M. Galan[1,2]*, S. Velea[2], E. Radu[1,2], A.C. Vintila[1,2], A.R. Trifoi[1,3], A. Crucean[1,3], O. Blajan[1,3]

[1]SC SOLVAGROMED SRL, 551022,Medias, Carpati Nr.8, Jud. Sibiu
[2]National Research & Development Institute for Chemistry and Petrochemistry ICECHIM, 202 Splaiul Independentei, 060021, Bucharest, Romania.
[3]Research Institute of Auxiliary and Organic Producs S.A., 8 Carpati St., 551022 Medias, Sibiu, Romania
**Corresponding author: e-mail:anamariagalan88@gmail.com*

Keywords: used oil; enzymatic catalysis; ethyl esters; biosolvent

Introduction: The used cooking oil is an important source of unconventional raw material for the production of industrial fluids. Worldwide, it represents more than 15 million liters [1]. The process of transesterification / esterification of oils / fats by biocatalysis is a recent concern for the development of an ecological technology because it has considerable advantages over alkaline catalysis (classical), such as: mild reaction conditions; easy recovery of glycerin, possibility of enzyme reuse (lower costs), high specificity of the enzymatic catalyst - no secondary products are formed (polymers and oxidation products), biodegradability of the enzyme. The aim of this work was to investigate the optimal parameters (working temperature, ratios of enzyme and used oil: ethanol) in order to obtain ethyl esters of the fatty acid by the transesterification of the used cooking oil in enzymatic catalysis. In addition, the cycles number of biocatalyst reutilizationwasestablished.

Materials and methods: Used oil recovered from the fast – food chain, characterized by an acidity index 16.6 mg KOH/g oil, lipase acrylic resin from *Candida antarctica,* ≥5,000U/g, recombinant, expressed in *Aspergillus niger,* having amaxim activity in the range of 50-60 °C, ethanol, 96 % and anhydrous hexane, 96 %, purchased from NOVACHIM TRADING SRL are used in this experiment. The ethyl esters of fatty acids obtained were analyzed by the GC-MS method using an AGILENT 7000 /TRIPLE QUAD gas chromatograph coupled with mass spectrometer, by using the NIST data library to identify the components.

Results: The obtained results reveal an increase in the yield of ethyl esters with the increase of the percentage of catalyst and the extraction time, respectively. The maximum yield was determined by using of 2 % enzyme and a reaction time of 24 h. Also, after 10 cycles of enzyme reutilization, the activity of the enzyme is approximately unchanged.

Conclusions: The yield of the ethyl esters is greatest in the case of 2 % catalyst, a reaction temperature of 55 °C for 24 h. The obtained ethyl esters are recommended to be used to obtain ecological solvents, degreasing agents, organic lubricating and cooling fluid.

Acknowledgements: *The research leading to these results has received funding from the Romanian MECS-ANCSI, Project ID P_38_452/104961, under the Contract No 96 / 09.09.2016.*

Reference:

[1**]**.Lam MK, Tan KT, Lee KT, Mohamed AR. Malaysian palm oil: Surviving the food versus fuel dispute for a sustainable future. Renewable and Sustainable Energy Reviews 2009;13:1456-1464.

LIPOSOLUBLE VITAMIN EMULSIONS FOR TRANSDERMAL APPLICATION

D.S.Vărăşteanu, I.E.Chican*

National Research and Development Institute for Chemistry and and Petrochemistry- ICECHIM Bucharest, 202 Splaiul Independentei, 060021, Bucharest, Romania

**Corresponding author: organica@icechim.ro*

Keywords: Bio-based surfactants; emulsions; liposoluble vitamin

Introduction: Hydrophobic bioactive agents such betacarotene, vitamin A, vitamin B2, vitamin D, vitamin E, with beneficial effects on human health have low bioavailability. The formulation of the therapeutic systems is an important biopharmaceutical parameter, because it can improve the pharmacological properties of vitamins. The transdermal therapeutic systems formulated as emulsions shows a higher absorption and bioavailability of drug substances [1-3]. Vitamin A increases the activity of skin enzymes, improves skin elasticity and helps prevent wrinkles.

Three steps were required to make a stable emulsion: determination of required HLB, selection of surfactants and establish the surfactant concentration.

Materials and methods: A series of emulsions containing retinol acetate (vitamin A) in sunflower oil were made. The tested surfactants were galactose palmitate (PG) and digluconamidooctane (DGAO), synthesized in the laboratory from renewable raw materials, in combination with the surfactants Span 80 (sorbitan monooleate) and C12-14 fatty alcohols 3OE ethoxylates (Rolflor LA 30).

Results: The ratio between the two surfactants was chosen in order to obtain a final HLB corresponding to the hydrophobic phase. The ratio between the aqueous phase and the oil phase was 1:1. Total emulsion volume: 20 mL. The aqueous phase was added under agitation over the oily phase. The stability of the emulsions was evaluated after 24 hours.

Conclusions: It is found that Span 80 + DGAO surfactant couple is not effective in making stable emulsions. Also, unfavorable results were obtained in the case of Span 80 + PG and Rolflor LA 30+ DGAO. To ensure the stability of the retinol acetate emulsion, the PG + Rolflor LA 30 couple is effective at a total surfactant concentration of 6.5%.

Acknowledgements: *This work was financially supported by National Authority for Scientific Research and Innovation, in the frame of Nucleu Programme-Project* ***PN 16.31.02.03****.*

References:

[1]. McClements, D. J., Saliva-Trujillo, L., Zhang, R., Zhang, Z., Zou, L., Yao, M., & Xiao, H., Boosting the bioavailability of hydrophobic nutrients, vitamins, and nutraceuticals in natural products using excipient emulsions, *Food Research International*, 2016,*88*, pp.140-152.

[2]. Saberi, A. H., Fang, Y., & McClements, D. J., Stabilization of vitamin E-enriched mini-emulsions: Influence of organic and aqueous phase compositions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 2014, *449*, pp. 65-73.

[3]. Yang, Y., & McClements, D. J., Encapsulation of vitamin E in edible emulsions fabricated using a natural surfactant. *Food Hydrocolloids*, 2013, *30(2)*, pp.712-720.

MODERN LEARNING TOOLS FOR ENTREPRENEURS WHO START BUSINESS IN THE FIELD OF LIFE SCIENCES

N. Radu[1*], A. A. Chirvase[1], N. Babeanu[2], O. Popa[2], F. Hastaran[3],B. Velykiene[4]

[1]*I.N.C.D.C.P. ICECHIM Bucharest, Biotechnology Department, Bucharest, Romania*

[2]*University of Sgronomic Sciences and Veterinary Medicine, USAMV Bucharest, Faculty of Biotechnology*

[3]*Association pour la Formation en Milieu Rural, AFMR Etcharry, France*

[4]*Kauno mokslo ir technologijų parkas, Kaunas, Lithuania*

**Corresponding author: nicolbiotec@yahoo.com*

Keywords: modern learning tools; entrepreneurs; life sciences bussines

Introduction: Enhancing creativity and innovation, including entrepreneurship, in education and training is a long-term objective for 'Education and Training 2020', the strategic framework for European cooperation. Entrepreneurship education is being increasingly promoted in EU countries, according to a new report published by the European Commission in 2012: Entrepreneurship Education at School in Europe. Private actors (business associations, companies, entrepreneurs, consultants) are becoming more involved in education and training, both by sponsoring initiatives and by participating directly in teaching, as mentors. [1-3].

Materials and methods: The purpose of this approach is to get the key entrepreneurship competences regarding the starting up of innovative SMEs in bio economic sector and to associate a short characterization of each defined key competences.

Results: In the case of bio entrepreneurship, it requires an even rarer individual, with the skills, knowledge, talent and personality traits that are essential to launch this type of endeavor. But opportunity recognition is rarely mentioned in the programs, although it is recognized as one of the weaknesses of those with a science-based degree, when it comes to commercialization.

Conclusions: The bio entrepreneur' management and business knowledge and skills are in connection with the business development stage, such as: at start-up stage-critical skills set includes the ability to direct and lead R & D activities, and communicate the planned company' economic indicators to the stakeholders; at commercialization stage-manufacturing and commercialization capabilities and collaborations; as it approaches the market-marketing and sales skills, as sale agreements have indeep descriptors of profit and loss.

Acknowledgements: *The paper was supported by the project entitled: Improved Curricula and Modern Learning System to Promote the New Directions of Business Enhancement in Life Sciences Applications, Lifelong Learning Programme Leonardo da Vinci - Transfer of Innovation, project no: 2013-1-RO1-LEO05-28758. This publication reflects the views only of the author, and the Commission cannot be held responsible for any use which may be made of the information contained therein.*

References:

[1]. Friedman, Y. Continuing education in biotechnology. Journal of Commercial Biotechnology, 2008, 14: 275–276.

[2]. Fiore, S. Interdisciplinarity as teamwork: How the science of teams can inform team science. Small Group Research, 2008, 39: 251–277.

[3]. Meyers, A., Hurley, P. From the classroom: Bioentrepreneurship education programs in the United States. Journal of Commercial Biotechnology, 2008, 4: 2–12.

COMPETENCIES NEEDED TO START AND TO DEVELOP INNOVATIVE SME'S IN THE LIFE SCIENCES FIELD

N. Radu[1*], A. A. Chirvase[1], N. Babeanu[2], O. Popa[2], F. Hastaran[3],B. Velykiene[4]

[1]I.N.C.D.C.P. ICECHIM Bucharest, Biotechnology Department, Bucharest, Romania
[2]University of Sgronomic Sciences and Veterinary Medicine, USAMV Bucharest, Faculty of Biotechnology
[3]Association pour la Formation en Milieu Rural, AFMR Etcharry, France
[4]Kauno mokslo ir technologijų parkas, Kaunas,Lithuania
**Corresponding author: nicolbiotec@yahoo.com*

Keywords: entrepreneurs competencies; innovative company; life sciences field

Introduction: The framework for sustainable entrepreneurship which so far has covered business approaches with a strong inclusion of sustainability issues is further developed by including social entrepreneurship, i.e. the application of the entrepreneurial approach towards the primary goal of meeting societal goals. [1, 2]. By realizing such sustainability innovations sustainable entrepreneurs often address the unmet demand of a larger group of stakeholders. Stakeholders demands go beyond narrow economic interests of shareholders and are the ultimate sources of entrepreneurial opportunities for sustainability innovation, discovery and exploitation of which is at the core of sustainable entrepreneurship [3].

Materials and methods: One important step was the elaboration of a "Basic template regarding the entrepreneurship key competences needed to start and to develop innovative SMEs in the bio economic sector targeted to sustainable development applications".

Results: Entrepreneurs should be sure they possess these characteristics if they are going to start a biotech company, because they will need them, when they face the many challenges during company development.

Conclusions: According to this study, the main issues of the matrix of competencies for the entrepreneur which activate in the field of life sciences are the following: 1)Personality characteristics, 2) Technical Skills, 3) Management and Business knowledge and skills.

Acknowledgements: *The paper was supported by the project entitled: Improved Curricula and Modern Learning System to Promote the New Directions of Business Enhancement in Life Sciences Applications, Lifelong Learning Programme Leonardo da Vinci - Transfer of Innovation, project no: 2013-1-RO1-LEO05-28758. This publication reflects the views only of the author, and the Commission cannot be held responsible for any use which may be made of the information contained therein.*

References:

[1]. Opoku, R. A., Abratt, R., Bendixen, M. Communicating brand personality: Are the web sites doing the talking for food SMEs? Qual. Market Res.: Int. J. 2007, 10, 362–374.
[2]. Xu, B. Market differential evaluations of strategic alliances in the pharmaceutical/biotech industry. J. High Technol. Manag. Res. 2006, 17, 43–52.
[3]. Man Y., Thomas W.Y., Theresa Lau. The competitiveness of small and medium enterprises, a conceptualization with focus on entrepreneurial competencies.Journal of Business Venturing. 2002, 17, 123–142.

NEW PHYTOCOSMETIC PRODUCTS FOR THE MANTAINING AND IMPROVEMENT OF ELASTICITY AND OF CUTANEOUS TISSUE

V. Carabela*, N. Bordei, S. Manea, G. Alexandru, V. Tamas

S.C.HOFIGAL EXPORT IMPORT S.A. Intrarea Serelor No.2, sector 4, Bucharest, Romania
ResearchandDevelopmentDepartment
**Correspondingauthor: vikicarabela@yahoo.com*

Keywords: elasticity; multi skin test; safflower oil; rosehip oil; linoleic acid (omega-6)

Introduction: The aggressive action of environmental factors and the excessive use of soaps, shower gels and other degreasing detergents cause the dehydration of the skin, altering the composition of lipids in the corneal layer of the epidermis, the skin becoming thicker and devoid of elasticity. The paper presents the studies for developing new phytocosmetic products, designed to improve skin elasticity as skin elasticity enhancers. These products contain vegetal active ingredients, obtained by processing of local vegetal species, which ensure good hydration and nutrition of the skin, with the main role of prevention of the processes of biological or premature aging of the skin, by moisturizing, soothing, regenerating and protecting the skin.

Materialsandmethods: Essential fatty acids are crucial to skin elasticity, they are vital to strengthening cell membranes, stimulating their regeneration, restoring skin permeability and skin barrier function, helping to control transdermal water loss.In this context, vegetable sources rich in essential fatty acids (omega 6) have been identified: safflower oil, olive oil, rosehip oil, wheat germ oil, as well as other autochthonous vegetal extracts: passiflora, mallow, burdock, licorice, elm, rich in: polyphenol compounds (polyphenolcarboxylic acids, isoflavones, flavonoids, anthocyanins, procyanidins), polysaccharides, phytosterols, carotenoids and enzymes.The evaluation of cosmetic products as skin elasticity was done in vivo by cutometry, with the "Multiskin Test Center MC 1000". The method is based on suction or elongation of deep skin layers. The results of the measurements show the favorable effect of cosmetic preparations on the slowing of the premature aging of the skin.

Results: Obtaining safflower oil by "cold pressing" technology, rich in: polyunsaturated fatty acids, antioxidants, carotenes, phytosterols, phospholipids and minerals;performing elasticity measurements for 2-3 cosmetic products, according to the protocol procedure to highlight the effect of improving the elasticity of the skin; These products are: nourishing and relaxing night cream, regenerating cream, mature and sensitive skin cream, regenerating lip oil).

Conclusions: Measuring valuesin the system used before and after dermal application of new products have demonstrated a marked improvement of skin elasticity, making the skin firmer, supple and velvety**.**

References:

[1]. Dumitru, B., Croitoru, C., Olariu, L.: *Functional status of the skin; testing methods in dermatocosmetics*. RSCC Magazine, 7(1), (2007),pp. 24-31.

PLANT EXTRACTS WITH THERAPEUTIC VALUE, EXISTING IN THE DANUBE - DANUBE DELTA BASIN

E. Berteanu*, M. Paraschiv, C. Manole, A.-L. Zuav, L.Tcacenco

National Institute of Research and Development for Biological Sciences Bucharest

**Corresponding author: lili_berteanu@yahoo.com*

Keywords: medicinal plants; hydroalcoholic extracts; phenols; flavonoid; antiradical activity

Introduction: The Danube-Danube Delta region has a particular importance with regard to the variety of natural habitats and the high diversity of flora and fauna species. In this context, identifying resources with valorisation potential for biotechnological and therapeutically use is a priority in research. Thus, the study of the biodiversity of medicinal and aromatic plants, as well as the superior valorisation of these bioresources are of great interest for the food, pharmaceutical and cosmetic industries.

Of the many plants with therapeutic value in the Danube Delta (over 1 839 flora species), our research focused on two species of Asteraceae family, *Silybum marianum* known as adjuvants in the treatment of liver dysfunctions and *Artemisia annua L.* (against cancer).

Materials and methods: In this sense, hydroalcoholic extracts at concentrations of 40%, 50% and 70%, were made and subjected to analysis. Thus, the extracts were analyzed by spectrophotometric method and by gas chromatography coupled with mass spectrometry methods.

Results: Spectrophotometrically, the total phenolic content and flavonoids was monitored, as well as the antiradical activity manifested against the free radical DPPH and gas-chromatographic identification of the main classes of compounds.

With regard to the extraction method, the hydroalcoholic solution of 70% proved to be the best extraction solvent, the variation of the content in the analyzed compounds being directly proportional to the alcoholic concentration [1-3].

Conclusions: With regard to the characterization of the plant species, *Artemisia annua L.* has a higher content of phenols and flavonoids and, implicitly, a higher antiradical activity than *Silybum marianum*.

Acknowledgements: *This work was supported by National Projec numberPN-16190106.04.*

References:

[1]. Fernandes de Oliveira A. M., Pinheiro L. S., Souto Pereira C. K., Matias W. N., Gomes R. A., Chaves O. S., Maria de Fátima Vanderlei de Souza, Nóbrega de Almeida R., Simões de Assis T., Total Phenolic Content and Antioxidant Activity of Some Malvaceae Family Species, Antioxidants, 2012;1(1):33-34.

[2]. Singleton V. L., Orthofer R., Lamuela-Raventos R. M., Methods in Enzymology, Oxidant and Antioxidants (Part A). In Packer L (eds.). Analysis of total phenols and other oxidation substrates and antioxidants by means of Folin-Ciocalteu reagent, Academic PressPublishing, San Diego, 1999.

[3]. Zhishen J., Mengcheng T., Jianming W., The determination of flavonoid contents in mulberry and their scavenging effects on superoxide radicals, Food Chem., 1999; 64(4):555-559.

COMMON PATHWAY TO UNPACK THE BUNDLE – INTEGRATIVE HYPOTHESIS IN KERATIN AND POLYSACCHARIDES BIODEGRADATION

D. Constantinescu-Aruxandei[1], M. Călin[1,2], I. Răut[1], G. Vasilescu[1], M. Badea-Doni[1], M.-L. Arsene[1], A.-M. Gurban[1],L. Jecu[1*], F. Oancea[1*], V. Lazăr[2]

[1]INCDCP-ICECHIM, Spl. Independentei 202, Bucharest, Romania

[2]University of Bucharest, Faculty of Biology, Spl. Independentei 91-95, Bucharest

**Corresponding author:jecu.luiza@icechim.ro,florin.oancea@icechim.ro*

Keywords: keratin; cellulose; LPMO; cerato-platanin; fungi

Introduction: Although much is known about the mechanism of polysaccharides and keratin deconstruction by microorganisms, new descoveries still emerge. One example is the relatively recent discovery of lytic polysaccharide mono-oxygenases (LPMOs), metal dependented enzymes that are able to disrupt the structure of recalcitrant carbohydrate biopolymers [1]. Recently, a new hypothesis proposed that these enzymes might also have a role in keratin biodegradation [2], but this has not been tested yet. Similarly, microbial expansins and expansin-like proteins such as the cerato-platanin proteins (CPPs),which have no enzymatic role andloosen plant cell walls and cellulosic materials without lytic activity [3, 4], could have a similar role in keratin biodegradation. In this study we report the influence of cellulose on keratin degradation and, for the first time to the best of our knowledge, the influence of keratin on cellulose deconstruction by a fungal strain isolated from soil.

Materials and methods: The isolated strain (*Fusarium* sp.) was grown in the presence of keratin (horse hair strands), cellulose, and keratin + cellulose, respectively. The keratinolytic and cellulolytic activities were measured *in vitro* by the keratin azur ($A_{595\ nm}$) and dinitrosalycilic acid (DNS) assay ($A_{540\ nm}$), respectively. The enzymatic activity was also monitored semiquantitavely on agar plates supplemented with feather keratin powder and/or cellulose.

Results: Keratin increased the cellulose degradation by *Fusarium* sp. The feather powder showed a positive effect on fungus growth. Cellulose, but not glucose, increased the keratinolytic activity.

Conclusions: These results show, for the first time to the best of our knowledge, that keratin can have a positive effect on the cellulolytic activity of a microorganism. The mechanism of keratin and polysaccharide biodegradation might share a common element, such as certain auxiliary enzymes from the recently discovered LPMO and/or the expansins/CPPs. Further investigations are needed in order to confirm this hypothesis.

Acknowledgements: *This research was financially supported by the Ministry of Research and Innovation in the frame of the project PN.16.31.01.03/2016, CORE Program and by MCI-UEFISCDI - project "Convert-Si", contract No. 62/2016.*

References:

[1]. Vaaje-Kolstad G., Westereng B., Horn S. J., Liu Z., Zhai H., Sorlie M., et al. An oxidative enzyme boosting the enzymatic conversion of recalcitrant polysaccharides. Science 2010;330:219–222.

[2]. Lange, L., Huang, Y. & Busk, P. K. Microbial decomposition of keratin in nature-a new hypothesis of industrial relevance. Appl Microbiol Biotechnol 2016;100:2083–2096.

[3]. Baccelli, I. Cerato-platanin family proteins: One function for multiple biological roles? Front. Plant Sci.2014;5:769.

[4]. Cosgrove, D. J. Microbial Expansins.Annu. Rev. Microbiol. 2017;71(1):479-497.

INHIBITORY ACTIVITY OF NEW SYNTHETIC STRIGOLACTONES ON IMPORTANT PHYTOPATHOGENIC FUNGI

I. Răut[1], F. Oancea[1*], E. Georgescu[2], M. Călin[1,3], D. Constantinescu-Aruxandei[1], G. Vasilescu[1], M. Badea Doni[1], M. L. Arsene[1], A. M. Gurban[1], L. Jecu[1*]

[1]National Research & Development Institute for Chemistry & Petrochemistry–ICECHIM, Spl. Independentei 202, RO-060021 Bucharest

[2]Research Center Oltchim, St. Uzinei 1, RO-240050 Ramnicu Valcea

[3]University of Bucharest, Faculty of Biology, 91-95 Independentei Spl., Bucharest

**Corresponding author: jecu.luiza@icechim.ro,florin.oancea@icechim.ro*

Keywords: strigolactones analogs; strigolactone mimics;plant hormones; hyphal branching

Introduction: Strigolactones (SLs) arethe newest described plant hormones, that function is to optimize plant growth and development [1]. Moreover, SLs are signalling molecules used by plants for communication in soil and interaction with both mycorrhizal fungi and parasitic plant seeds [2]. In the present study, we describe the responseof several important phytopathogenic fungi to the new synthesized SL mimics(SL2, SL3, SL13) [3] and the synthetic SL GR24 [4], considered as standard for SL analogues.

Materials and methods: The tests were performed according to the method of Dor et al. [2]. Strigolactones were tested on the following phytopathogenic strains: *Fusarium graminearum* Schwabe, *Sclerotinia sclerotiorum* (Libert) De Bary*, Macrophomina phaseolina* (Tassi) Goid *and Rhizoctonia solani* Kühn.

Results: Theinhibition effect of all synthetic strigolactones on the phytopathogenic fungi was visible from the lowest teste SL mimics and analogue concentration ($3{,}4\times 10^{-6}$ M).The tested SL induced the most significant increase in hyphal branching at the highest concentration (85×10^{-6} M).

Conclusions: The results demonstrate for the first time that synthesized SL mimeticsare able to inhibit the growth of soil-borne plant pathogens and inducehyphal branching. The SL mimetics show biological activities against plant pathogens comparable with GR24 analogue.

Acknowledgements: *This material is based upon work supported by the Ministry of National Education – Research Activity, CNDI– UEFISCDI, in the frame of the project number PN-II-PT-PCCA-159/2014 (CERES), Programme PN2 P4 Partnership PCCA 2013.*

References:

[1]. Pandey, A.; Sharma, M.; Pandey, G.K. Emerging roles of strigolactones in plant responses to stress and development. Front. Plant Sci. 2016; 7, 434.

[2]. Dor, E.; Joel, D.M.; Kapulnik, Y.; Koltai, H.; Hershenhorn, J. The synthetic strigolactone GR24 influences the growth pattern of phytopathogenic fungi. Planta.2011; 234:419–427.

[3]. Oancea, F., Georgescu, E., Matusova, R., Georgescu, F., Nicolescu, A., Raut, I., Jecu, M-L., Vladulescu, M-C., Vladulescu, L., and Deleanu, C. New strigolactone mimics as exogenous signals for rhizosphere organisms. Molecules.2017; 22:961.

[4]. Johnson, A.W.; Gowada, G.; Hassanali, A.; Knox, J.; Monaco, S.; Razavi, Z.; Rosebery, G. The preparation of synthetic analogues of strigol. J. Chem. Soc. Perkin Trans. 1981; 1734–1743.

EVALUATION OF HORSE HAIR DEGRADATION BY KERATINOLYTIC FUNGI

M. Călin[1,2], D. Constantinescu-Aruxandei[1], E. Alexandrescu[1], I. Răut[1], V. Purcar[1], M. Badea Doni[1], M. L. Arsene[1], G. Vasilescu[1], L. Jecu[1*], V. Lazăr[2]

[1]*National Institute for Research & Development in Chemistry and Petrochemistry-ICECHIM, Biotechnology Department, 202 Independentei Spl., 060021, Bucharest, Romania*

[2]*University of Bucharest, Faculty of Biology, 91-95 Independentei Spl., Bucharest, Romania*

**Corresponding author: jecu.luiza@icechim.ro*

Keywords: keratin; keratinolytic fungi; keratin degradation; SEM; TGA; FTIR

Introduction: The keratin rich wastes represent troublesome environmental contaminants and are available in increasing quantities as byproducts from agro industrial processes. The hydrolysis of keratin wastes by microorganisms is considered a biotechnological alternative for recycling and valorization through the potential of keratinolytic microorganisms.The current work asses the dynamics of the keratins biodegradation by several keratinophilic fungal strains isolated from soil.

Materials and methods: Ability of fungal strains to degrade horse hair keratin was evaluated based on microscopic observations (Scanning Electron Microscopy, SEM), Fourier Transform Infra-Red Spectroscopy technique (FTIR) and thermogravimetric analysis (TGA).

Results: SEM images have shown that all tested strains were able to develop adequate structures related to surface erosionand radial penetration, such as: fungal filaments attached to strand surface, erosion pocket, separation of macrofibrils bundles, cuticles degradation. Signs of biodegradation initiation are shown in FTIR spectra from all samples, as the appearance of the bands at 1035-1075 cm^{-1} assigned to sulfoxide bond from S-S bond breaking.Results of TGA profiles showed some differences in the characteristic behavior of keratin substrates after incubated with different fungal strains.

Conclusions: Among tested strains, *Fusarium* sp. was found to be the most active in degradation process with the strongest denaturation of polypeptide chains. Since keratinolytic microorganisms and their enzymes keratinases represents a subject of scientific and economic interest due to their capability to hydrolyzed keratin, the strain was selected for further studies.

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

References:

[1]. Lange L, Huang Y, Busk PK. Microbial decomposition of keratin in nature—a new hypothesis of industrial relevance. Appl Microbiol Biotechnol 2016; 100: 2083-2096.

[2]. JinH-S, Park SY, Kim K, Lee Y-J, Nam G-W, Kang NJ, Lee DW. Development of a keratinase activity assay using recombinant chicken feather keratin substrates. PLoS ONE 12(2):e0172712

[3]. Gupta R, Ramnani P. Microbial keratinases and their prospective applications: an overview. Appl Microbiol Biotechnol 2006;70:21–33.

QUALITATIVE AND QUANTITATIVE EVALUATION OF FUNGAL WOOL FIBERS DIGESTION

M. Călin[1,2], D. Constantinescu-Aruxandei[1], I. Răut[1],E. Alexandrescu[1], V. Purcăr[1], G. Vasilescu[1], L. Jecu[1*], M. Badea-Doni[1], M.-L. Arsene[1], A.-M. Gurban[1], F. Oancea[1], O.-N. Corneli[3], V. Lazăr[2]

[1]*INCDCP-ICECHIM, Spl. Independentei 202, Bucharest, Romania*

[2]*University of Bucharest, Faculty of Biology, Spl. Independentei 91-95, Bucharest*

[3]*The National Institute of Research & Development for Microbiology and Immunology "Cantacuzino", Spl. Independentei 103, Bucharest, Romania*

**Corresponding author: jecu.luiza@icechim.ro*

Keywords: wool fibers; wool digestion; keratinolytic fungi; keratin

Introduction: The keratin from the wool waste is hard (alpha) type and is not easily degraded in nature causing serious pollution problems. That is why environmentally friendly methods using keratinolytic enzymes from microorganisms for valorisation of keratinous wastes are increasingly used.The objective of this work was to evaluate the biodegradative ability of geophilic fungal isolates on wool fibers subtrate.

Materials and methods: The experiments were carried out with sterile wool fibers and two fungal strains isolated from soil,*Fusarium* sp and *Cladosporium* sp. The substrate (wool) was incubated with fungal strains in basal culture medium, for 30 days, at 27°C and 100 rpm. After the incubation period, the wool was collected, gently cleaned from fungal mycelium, gently washed, and oven dried at 75°C for 48 hours. The biodegradationof the substrate was evaluated by several qualitative (optic and electronic microscopy), as well as quantitative methodes (FTIR,TGA,weight loss of substrate, and enzymatic assay).

Results: The substrate showed a good rate of digestion by the isolated strains. *Fusarium* sp. presented a higher enzymatic activity than *Cladosporium* sp. The FTIR and TGA data indicated structural changes in the substrate due to microbial digestion.

Conclusions: Two geophilic isolated strains, *Fusarium* sp and *Cladosporium* sp., are reported to degrade wool keratin, *Fusarium* sp. being more efficient. The experimental resultsshow several changes in the substrate structure and provide useful information about the degradative potential of keratinolytic isolates.

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

References:

[1]. Broda J., Przybyło S., Kobiela-Mendrek K, Binia D., Rom M., Grzybowska-Pietras J., Laszczak R., Biodegradation of sheep wool geotextiles. Int Biodeterior*Biodegradation*. 2016,115: 31-38.

[2]. Fang Z., Zhang J., B. Liu., G. Du, Chen J.. Biodegradation of wool waste and keratinase production in scale-up fermenter with different strategies by Stenotrophomonas maltophilia BBE11-1, Bioresour Technol.2013, 140: 286–291.

[3]. Verma A., Singh H., Anwar S., Chattopadhyay A, Tiwari KK, Kaur S., Dhilon GS., Microbial keratinases: industrial enzymes with waste management potential. Crit Rev*Biotechnol*. 2016, 13:1-16.

STRUCTURAL AND THERMOPHYSICAL INVESTIGATIONSFOR N-(P-IODOPHENYL)-N'-(2-THENOYL)-THIOUREA IN (C_2H_5OH+H_2O) SOLVENT

F. Sirbu[1], A. Stefaniu[2],C. Badiceanu[3],D. Dragoescu[1], C. S. Stoicescu[1,3], C. A. Marinescu[1*],I. Gheorghe[1], L. Pintilie[2]

[1]*Institute of Physical Chemistry Ilie Murgulescu of the Romanian Academy, Bucharest, Romania*
[2]*National Institute for Chemical - Pharmaceutical Research and Development – ICCF Bucharest, Romania*
[3]*University of Medicine and Pharmacy Carol Davila, Bucharest, Romania*
**Corresponding author: alcorina@chimfiz.icf.ro*

Keywords:QSAR prediction; thermophysical properties; pharmaceutical compounds*; *ternary system

Introduction: In the present work, the halogenated thiourea derived compounds withpotential antimicrobial activity, and pharmaceutical important applications have been studied by structural and thermophysical analysis. Thermodynamic behavior ofN-(P-Iodophenyl)-N'-(2-Thenoyl)-Thioureacompound has been studied in ternary mixtures of alcoholic aqueous solution.

Materials and methods: The new synthesizedhalogenated thiourea compound[1]was provided by University of Medicine and Pharmacy Carol Davila from Bucharest. The ethylic alcoholusedin this work were supplied by Merck.A computational study using Spartan'14 software Wavefunction, Inc. Irvine CA USA was conducted on the 3D optimized structure for the pharmaceutical compound. The obtainedminimized geometryis presented in following figure:

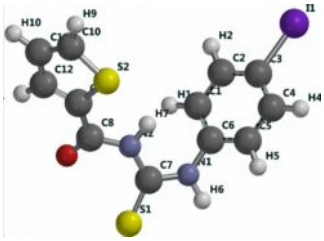


Figure 1. 3D optimized structure of N-(P-Iodophenyl)-N'-(2-Thenoyl)-Thiourea (Ball and spoke model)

Results: The calculated parameters: HOMO-LUMO energy gap, ionization potential (*I*), electron affinity (*A*),electronegativity (χ), global hardness (η), softness (σ) chemical potential (μ), global electrophilicity index (ω), molecular electrostatic potential and local ionization potential maps.Density, speed of sound, and refractive index were measured in 50% C_2H_5OH solutions from (288.15 up to 318.15) K, for molarities between (0.5 and 1.05) mol·dm^{-3}. The derived thermophysical properties [2,3] for N-(P-Iodophenyl)-N'-(2-Thenoyl)-Thiourea+C_2H_5OH+H_2O systemhave been calculated, and the refractive indices data were evaluated using Lorentz-Lorenz equation.

Conclusions: The structural and thermophysical investigations ofhalogenated thiourea compoundinethylic alcohol solutions have significant importance in bio-resources and biomaterials domains.

Acknowledgements: *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, and the research programme Chemical Thermodynamics of "Ilie Murgulescu" Institute of Physical Chemistry is gratefully acknowledged.*

References:

[1]. Badiceanu CD et all.Rom. Biotech.Lett.2010; 15:5545-5551.
[2]. Ion I, Sirbu F, Ion AC. J. Chem. Eng. Data, 2013; 58:1212–1222.
[3]. Dragoescu D, J. Mol. Liq. 2015; 209:713-722.

COMPARATIVECHARACTERIZATION OF THE PURETHIOUREA DERIVATIVES TO THEIR INCLUSION COMPOUNDS WITHHPβCD

A. D. Neacsu[1], A. Sofronia[1], C. Badiceanu[2], C. A. Marinescu[1*], C. S. Stoicescu[1,2]

[1]*Ilie Murgulescu Institute of Physical Chemistry of the Romanian Academy, 202 Splaiul Independentei, Bucharest, Romania*

[2]*Carol Davila University of Medicine and Pharmacy, Traian Vuia 6, Bucharest, Romania Bucharest, Romania*

**Corresponding author: alcorina@chimfiz.icf.ro*

Keywords: HPβCD;UV-Vis spectra; particle size distribution; zeta potential; conductivity

Introduction: The host-guest interaction is a topic of special interest in nanomedicine and drug design. 2-hydroxypropyl-β-cyclodextrin (HPβCD) is the most widely used modified cyclodextrin in formulation of drug products [1]. Thebiocompatibility and inclusion capability of HPβCD make it attractive to improve the physico chemical properties and also the pharmacological effects of hydrophobic 2-thiophene carboxylic acid thioureas (2THIO): N-(p-chlorophenyl)-N'-(2-thenoyl)-thiourea (I), N-(p-bromophenyl)-N'-(2-thenoyl)-thiourea (II), N-(p-iodophenyl)-N'-(2-thenoyl)-thiourea (III), N-(p-metoxyphenyl)-N'-(2-thenoyl)-thiourea (IV), N-(p-metylphenyl)-N'-(2-thienyl)-thiourea (V), N-(p-metylphenyl)-N'-(2-thenoyl)-thiourea (VI), N-(p-metylphenyl)-N'-(3-thenoyl)-thiourea (VII). Allcompounds come to offer significant advantages in future antibacterial treatment strategies [2] and theirs inclusion compounds are valuable in pharmaceutical formulations[3].

Materials and methods: In this work, the solid state inclusion compounds between HP-β-CD and thioureas with two different molar ratio (HP-β-CD:2THIO= 1:1 and 2:1) were obtained by co-precipitation method. The solid powders of pure substances and HP-β-CD/2THIO - complexes were investigated by thermogravimetry coupled with differential scanning calorimetry,infrared spectroscopy in attenuated total reflectance mode and scanning electron microscopy methods. For pure drugs,UV-Vis spectra were registered and refractive index, particle size distribution, zeta potential / conductivity of pure substances and mixtures solutions were evaluated.

Results: Decomposition kinetics in nonisothermal conditions of pure compounds (I), (II) and (III) in solid state obtained by DSC using different heating rates were reported.

Conclusions: The results showed that not only 1:1, but also stable 2:1 inclusion complexes can be formed between HP-β-CD and analyzed thioureas and the 2:1 host:guest molar ratio of complexes show a properly fitting of drug with two HP-β-CD molecule.

Acknowledgements: *This work benefits from the support of the Romanian Academy as well as E.U. (ERDF) and Romanian Government support for acquisition of the research infrastructure under POS – CEE 2.2.1 Project INFRANANOCHEM/2007 - 2010, is also acknowledged.*

References:

[1]. Brewster, M.E., Loftsson, T. Cyclodextrins as pharmaceutical solubilizers. Adv. Drug Deliv. 2007;59: 645–666.

[2]. C. D. Badiceanu, Al. V. Missir, Farmacia, 2009, 57(3), 339-349.

[3]. Wang E, Lian Z, Cai J. The crystal of the 1:1 inclusion complex of β-cyclodextrin with benzamine. Carb. Res. 2007; 342: 767-771.

PLANT BASED EXTRACTS AS BIORESOURCES FOR BIOLOGICAL ACTIVE COMPOUNDS

S. Rodino, A. Butu*, M. Butu

National Institute of Research and Development for Biological Sciences, Bucharest, Romania, Splaiul Independentei 296, P.O. Box 17-16, 060031, Bucharest, Romania, Tel. / Fax. +4 021 220 0880

**Corresponding author, e-mail: alina_butu@yahoo.com*

Keywords: plant extracts;secondary metabolites; bioresources

Introduction: The search of natural sources of phytochemicals usable in the development of antimicrobial products is currently ongoing in various science fields such as chemistry, microbiology and pharmacology.For example, it was reported that traditional medicinal plants are able to produce secondary metabolites that can be used for the development of precursors or lead compounds in the pharmaceutical industry [1]. Starting from these premises research was performed for the investigation of plant based extracts as a source of active compounds known for their antimicrobial activity, extending their practical application in agriculture.

Materials and methods: The vegetal material is collected from wild flora on non-polluted fields or cultivated crops. The harvested plants are pest and disease free. Medicinal plants such as *Urticadioica*, *Equisetum arvense,* and other vegetal sources (*Lycopersiconesculentum*shoots) are investigated. The qualitative evaluation of plant extract from the point of view of bioactive compounds involves the use of common phytochemical screening methods: Ferric chloride test, Dragendorf test, Frothing test, Cyanidine test, phenolics test. Spectrophotometric methods are widely used in phytochemical screening of plant extracts.

Results: The goal of this study was to overview plant extracts as a primary natural source of useful compounds, providing a better understanding of the role of use of plant natural compounds. Preliminary screening of phytochemical constituents allows the detection of main classes of compounds, such as phenolics, carotenoids, alkaloids, saponins, terpenes, tannins, and coumarins.

Conclusions: Useful plant secondary metabolites (such as pyrethrins and rotenone) are already commercially available, being used in agricultureal practices in recommended concentrations as pesticide substances. Biologically active compounds of plant origin are playing an increasing role in the development ofbioproducts for pest and disease control, plant growth stimulation as well as for weed control.

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-2016-1544, contract number 14PED/2017, within PNCDI III and Program NUCLEU PN 16/2016.*

References:

[1]. Shinwari, Z.K., S. Malik, A.M. Karim, R. Faisal, M. Qaiser. 2015. Biological activities of commonly used medicinal plants from Ghazi Brotha, Attock District. Pak. J. Bot., 47(1):113-120.

ANTIOXIDANT CAPACITY ASSAY OF SOME EXTRACTS FROM BYPRODUCT OBTAINED BY COLD-PRESSING OF MILK THISTLE SEEDS

C. V. Popa[1*], S.-C.Litescu[2], A.-F. Danet[3], G.Badea[2], L. Lungu[4]

[1]University of Bucharest, Department of Organic Chemistry, Biochemistry and Catalysis, Sos. Panduri 90-92, 050657, Bucharest, Romania
[2]Centre of Bioanalysis, National Institute for Biological Sciences, 296 Spl. Independentei, Bucharest, 060031, Romania
[3]University of Bucharest, Department of Analytical Chemistry, Sos. Panduri 90-92, 050657, Bucharest, Romania
[4]Institute of Organic Chemistry C.D. Nenitzescu, Bucharest, Romania
**Corresponding author: popa_vali2006@yahoo.com*

Keywords: Milk thistle; silymarin; antioxidant capacity; total phenols analysis

Introduction: Milk thistle (*Silybum marianum* (L.) Gaertneri) has been widely used in traditional European and Assian medicine mainly for treatment of liver disorders and in present many products based on this plant are used as liver protector, complement for the treatment of viral hepatitis, anti-cancer agent, antioxidant which scavenges for free radicals that injure cells exposed to toxins etc. [1-3]. Major active component of this plant is silymarin, which is a mixture of flavonoidsincluding taxifolin, silychristin, silydianin, silybininA, silybinin B, isosilybinin A, isosilybinin B [3]. By cold-pressing the seeds of Milk thistle a precious oil and a byproduct reach in silymarin (1.5 - 4.0 %) were obtained.

Materials and methods: From Milk thistle byproduct it were obtained extracts by different extraction methods and following solvents: water, alcohols, acetone, ethyl acetate.In the obtained extracts the total phenols by Folin-Ciocalteu method were determined. The antioxidant capacity by using a chemiluminometric method based on Co(II)/EDTA-H_2O_2-luminol system was assayed. The extracts have been analyzed by HPLC for different constituents of silymarin.

Results: The macerates obtained in ethanol and methanol have the highest values of the total antioxidant capacity and the content in total phenols. The highest content of polyphenols and other antioxidants was found for the extract obtained from silymarin by-product by Soxhlet extraction with methanol.

Conclusions: The results confirm that the byproduct by cold-pressing the seeds of Milk thistle has an important content of silymarin and others antioxidant phenolic compounds.

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

References:

[1]. Mendoza N.V., Santillan E.M., Gonzalez A.M., Soto J.E., Chirino C.E., Luna M.G., Rubio G., Gayosso-dw-Lucio J.A., Morales-Gonzales J.A. Hepatoprotective effect of silymarin. World J. Hepatol. 2014;6:144–149.

[2]. Loguercio C., Festi D., Silybin and the liver: From basic research to clinical practice. World J Gastroenterol. 2011;17:2288-2301.

[3]. AbouZid S., Agricultural and Biological Sciences. Phytochemicals - A Global Perspective of Their Role in Nutrition and Health, Venketeshwer Rao editors, ISBN 978-953-51-0296-0, 2012;255-272.

FTIR METHOD FOR CHARACTERIZATION OF HUMIC AND FULVIC ACIDS IN MATRIX OF BIOFERTILIZERS FOR PLANTS

S. M. Doncea*, I. Ciobanu, I.I. Minca,M. Manolache

[1]*National Research& Development Institute for Chemistry and Petrochemistry ICECHIM, Bucharest, Romania.*

**Corresponding author: sandamariadoncea@gmail.com*

Keywords:FTIR method; humic acids; fulvic acids;biofertilizers matrix

Introduction: As it is well known, humic acids contain a wide variety of compounds, especially organic ones, the most important of which: substituted phenols, quinones, 1,2-dihydroxybenzene, sugar moieties, aromatic nuclei with phenol or carboxyl substituents which bind clays to form complex compounds. The chemical structure of fulvic acids is similar to humic, but they have lower molecular weight and higher concentration of oxygen.

Materials and methods: The Fourier transformed infrared spectroscopy method, FTIR, was used both in the transmission technique, in KBr pellets, and in the attenuated total reflectance technique, ATR, for both classes of acids. As a standard for humic acids, a Sigma Aldrich product has been used. As a reference for fulvic acids, a separated humus fraction, prepared in Bioresources, from ICECHIM, was used.In order to identify by FTIR the fulvic acids in the presence of humic acids, the spectra of commercial preparations, P1 HA B20, P3 HA BJ fertilizer and organic humus ameliorator P2 HA NS,were recorded.

Results: The product P1 HA B20 has absorption bands characteristic of the C-O bond in the COO- group and characteristic of the C-C bond in the aromatic ring, specific for fulvic acids. For humic acids, the characteristic absorption bands correspond to the -CH2 group of alkylcelluloses from cellulose and/or hemicellulose and/or lignin.For the P3 HA BJ product having higher concentrations of humic acids, they are highlighted by the band corresponding to the - CH2 group of alkylcelluloses from cellulose and/or hemicellulose and/or lignin. For fulvic acids in addition to the C-O bonding band of the COO- group, the characteristic of the C-C bond in the aromatic ring was also identified. The P2 HA NS product which has the smallest amount of humic and fulvic acids together, the spectrum is poorer in absorption bands, only the bands corresponding to the C-C bond in the benzoic acid ring for humic acids andcorresponding to the CH_2 group of alkylcelluloses from cellulose and/or hemicellulose and/or lignin [1-3].

Conclusions: Although the acids are found in different matrices, the presence of the two classes of organic acids could be simultaneously highlighted.Future spectrometric investigations will focus on identifying characteristic vibration bands in any matrix of fertilizer, ameliorator or biostimulator.

References:

[1]. Bellamy L.J., *The infrared spectra of complex molecules, Chapman and Hall*, 3rd ed., Vol. 1, London, 1975.

[2]. Gerasimowisz W.V., Byler D.M., *Carbon-13 CPMAS NMR and FTIR spectro-scopic studies of humic acids,* Soil Sci. 139 (1985) 270–278.

[3]. Hernandez M.T., Moreno J.I., Costa F., Gonzalez-vila F.J., Frund R., *Structural features of humic acid-like substances from sewage sludge,* Soil Sci. 149 (1990) 63–68.

SPECTROSCOPIC AND THERMAL CHARACTERIZATION METHODS OF BIOSTIMULANTS BASED ON SODIUM HUMATE

R.Stoica[1*], I.Minca[1], S.-M. Doncea[1], L.Capra[1,2],R. Senin[1,2], M. Mateescu[1], G. Ivan[1,2], I. Ciobanu[1], F. Bacalum[1], M. Manolache[1], F. Oancea[1]

[1]*National Research & Development Institute for Chemistry and Petrochemistry ICECHIM, 202 Splaiul Independentei Street, 060021, Bucharest, Romania*

[2]*University POLITEHNICA of Bucharest, 313 Splaiul Independentei Street, 060042, Romania*

**Corresponding author: rusandica.stoica@gmail.com*

Keywords: sodium humate; humic acids; FTIR; TGA; ICP-OES; biostimulant

Introduction: Plant biostimulants represent a feasible option for an efficient and sustainable agriculture. A plant biostimulant product is composed of substances, micro-organisms and/or other materials, and is stimulating processes in the plant or surrounding growing environment that improve plant nutrition processes, general plant vigour and/or plant tolerance to abiotic stress, with the effect of improving plant quality traits and/or yield [1]. The development and characterization of these formulations have become of scientific interest.

Materials and methods: The objective of this work was to characterize commercial humate biostimulants through different analytical techniques (Fourier transform infrared spectroscopy - FTIR, thermogravimetric analysis-TGA) and to evaluate their chemical (pH, C, N, humic acids, inorganic components) parameters.

Results: The first derivative curve from TG analysis showed decomposition of different compounds, classified according to the results obtained by FTIR. The humic substances determined by TGA method was comparable with the results obtained by gravimetric reference method. The inductively coupled plasma-optical emission spectrometry (ICP-OES) technique was applied to determine the inorganic elements either from the production process of humate or from raw materials, as well as for the control of humate in terms of requirements for safety and quality.

Conclusions: Their complementary properties obtaining through different analytical techniques provide essential information on the chemical characteristics of the humate plant biostimulant formulations.

Acknowledgements: *This research was supported by the Ministry of Education and Research from Romania through the Financial Agreement Research of Contract no. 34 N / 15.03.2016, project PN. 16.31.01.02.*

References:

[1].COM (2016) 157: Proposal for a REGULATION OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL laying down rules on the making available on the market of CE marked fertilising products and amending Regulations (EC) No 1069/2009 and (EC) No 1107/2009.

SYNTHESIS AND CHARACTERIZATION OF A HYDROXYETHYL FATTY AMIDE MONOMER FROM SOYBEAN OIL

N. Chira[1*], A. Hanganu[2], C. Stavarache[2], A. Oancea[3],R. Komartin[1]

[1] *"C. Nenitescu" Organic Chemistry Department, University POLITEHNICA of Bucharest, 1-7 Polizu Str. Postal code 011061, Bucharest, Romania*

[2] *NMR Laboratory, University of Bucharest, Faculty of Chemistry, 90-92 Panduri Str., Bucharest, Romania*

[3] *Inorganic Chemistry, Physical Chemistry and Electrochemistry, University POLITEHNICA of Bucharest, 1-7 Polizu Str. Postal code 011061, Bucharest, Romania*

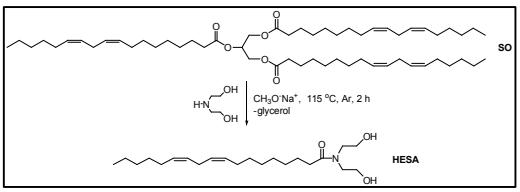
**Corresponding author:nicoleta.chira@chimie.upb.ro*

Keywords: soybean oil; vegetable oils; [1]H-NMR; FT-IR

Introduction: Organic coatings are largely used to prevent corrosion of metallic structures, being low-cost and easily applicable. Polymer coatings are usually additivated with corrosion inhibitors to confer additional active protection against corrosion. With respect to the polymer matrix,there is a large choice of vegetable oils with potential applications for the coatings industry; recently in Romania, there is an increased interest in technical oil crops (especially linseed, rapeseed and soybean). [1] The present work aims to present the synthesis and characterization ofN,N-*bis*-(2 hydroxyethyl) soybean amides(HESA) from renewable raw resources (soybean oil); HESA will be further used as a diol type monomer to obtain alkyd resin matrices for composite films with corrosion inhibitors.

Materials and methods: HESA was obtained through soybean oil (SO) aminolysis with diethanolamine in the presence of sodium methoxide as a catalyst (*Scheme 1*). The reaction course was monitored by TLC. SO fatty acids profile was determined through CG. The raw materials (SO, diethanolamine) and HESA were characterized through FT-IR and ^{1}H-NMR.

Results: The FT-IR (Figure 2) and ^{1}H-NMR spectra confirmed the diol and fatty amide structure of HESA.



Scheme 1. Synthesis of HESA from soybean oil

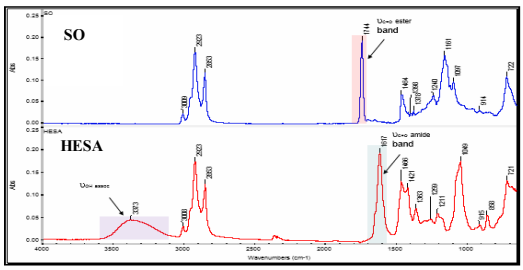


Figure 1. Stacked FT-IR spectra of SO and HESA

Conclusions: The obtained results for the diol tipe monomer from soybean oil are promissing; therefore, the idea of using vegetable oils as renewable resources for polymer matrices will be further exploited.

Acknowledgements: *This work has been funded by University Politehnica of Bucharest, through the "Excellence Research Grants" Program, UPB – GEX 2017. Identifier: UPB- GEX2017, Ctr. No.CH 38-17-04 /2017 (ECONANOCOAT)".*

References:

[1]. Romanian Statistical Yearbook 2012– 2016. INS data regarding the production of the main agricultural crops in 2012.National Institute for Statistics; 2016.

[2]. Chira N.; Raicopol M.; Pilan L.; Andronescu C.; Stavarache, C.; Stan, R., "Waterborne anticorrosive coatings from vegetable oil-based PEG-ylated polyesteramides", European Polymer Federation (EPF) Congress 2015; June 21-26; Dresden, Germany, 2015.

[3]. Hintze-Bruning H. Utilization of vegetable oils in coatings. Ind. Crops Prod. 1993;1:89-99.

DEVELOP OF A SPECTROPHOTOMETRIC METHOD FOR THE DETERMINATION OF PROLINE FROM BIOSTIMULATORS FOR PLANTS

M. Mateescu,I. Ciobanu, I. I. Minca*,F. Bacalum,M. Manolache

National Research& Development Institute for Chemistry and Petrochemistry ICECHIM, Bucharest, Romania
**Corresponding author: iulian_minca_m@yahoo.com*

Keywords: proline;biofertilizers samples; spectrophotometric method

Introduction: The proline concentration which characterized biological activity of plants represents the physiological response of various abiotic stresses to which the plants are subjected. Proline also participates in the plant tissue production program. L-proline also has osmo-protective properties being used in biotechnological applications. Proline has a protective effect against salinity and exhibits anti-stress activity, especially through the antioxidant effect. To achieve the characterization of proline, it is necessary to develop and validation of rapid and affordable methods [1-3].

Materials and methods: This study is focused on the development and optimization of a simple and accurate analysis by spectrophotometric UV VIS detection method[1], for the determination of proline in biofertilizers and organic fertilizers. The proline separation from the organic components was done by using the reaction with ninhydrin acid and extraction with toluene. Optimum working conditions were established for the new method. The maximum absorbance was measured at 520 nm.

Results: The developed method provided to be selective, and calibration curve was linear from 0.0 to 50 mg L^{-1} proline. The correlation coefficient was of 0.9983. The calculated detection limit and quantification limit, for independent fortified samples, were 2.5 mg L^{-1} and 8.3 mg L^{-1}. Repeatability and intermediate precision tests gave an RDS % between 0.32% and 0.57% for sample P1SA, respectively for sample P3S8, values which are significantly lower than the imposed limits.

Conclusions: The developed method for the determination of proline by UV - VIS spectrophotometry from plant biostimulators using ninhydrin in acid medium is selective, linear, accurate.

Calibration curves obtained by the spectrophotometric method with UV VIS detection for quantitative analysis of proline in fertilizer samples had high correlation coefficients > 0.998. The method developed and optimized in this study was applied for determination the proline content in the some types of biofertilizers for plants and organic fertilizers available on Romanian market. Obtained analytical results have demonstrated that the spectrophotometric method can be applied to determine the proline content from the studied organic fertilizers matrices, for plants.

Acknowledgements: *This research was supported by the Ministry of Education and Research from Romania through the Financial Agreement Research of Contract no. 34 N / 15.03.2016, project PN. 16.31.01.02.*

References:

[1]. Bates LS, Waldren RP, Teare ID. Rapid determination of free proline for water-stress studies. Plant Soil. 1973;39:205–207.

[2]. Marin JA, Andreu P, Carrasco A, Arbeola A. Determination of proline concentration, an abiotic stress marker, in root exudates of excised root cultures of fruit tree rootstocks under salt stress.Revue des Régions Arides. 2/2010;24.

[3]. KhanageSG, MohitePB, JadhavS. Development and validation of UV-visible spectrophotometric method for simultaneous determination of eperisone and paracetamol in solid dosage form. Adv Pharm Bull. 2013;3(2):447-451.

DETERMINATION OF THE BIOAVAILABLESILICONE FROM BIOSTIMULANTS FOR PLANTS. MATRIX STUDY

M. Mateescu*, L. Capra, G. Ivan, R. Stoica, M. Deaconu

National Institute for Research & Development in Chemistry and Petrochemistry - ICECHIM Bucharest, 202 Splaiul Independentei, 060021, Bucharest, Romania
**Corresponding author: marinamateescu@yahoo.com*

Keywords: silicon; biostimulators for plants; colorimetric method; ICP-OES method

Introduction: The literature does not present standardized or validated methods of bioavailable silicon analysis from innovative biostimulants for plants.In the present work, a method has been developed for the processing of samples to remove of organic compounds interfering with the colorimetric method, by coloring and influencing the formation of the molybdenum complex as well as with the ICP-OES method by disturbing the plasma function. By using this method, the domain of silicon determination methods extends to biostimulants for plants. This paper presents the matrix effect study on the two methods of determining Si.

Materials and methods: The ICP-OES measurements were performed using the Perkin Elmer Optima 2100 DV ICP-OES System (Perkin Elmer). The colorimetric test was purchased from Merck (in the range 0.01 – 0.25 mg /L SiO_2 or 0.021 – 0.53 mg /L SiO_2).

The methods of determination were preceded by a first stage of the extraction of water soluble silicon followed by the mineralization step with the mixture of HCl and H_2O_2. Four samples of biostimulants of different origin and matrices were analyzed. The influence of the matrix was evaluated by comparing the results provided by the two measurement methods.

Results: The bioavailable silicon concentrations in the analyzed samples were in the 0.0019-0.067% range. The absence of matrix influence was evaluated by the criterion: $|c_1 - c_2| \leq \sqrt{U_1^2 - U_2^2}$ where:

c_1 and c_2 represent the concentration of the sample by the colorimetric method and ICP-OES method;

U_1 and U_2 represent the extended uncertainty of the colorimetric method and ICP-OES method.

The differences between the results provided by the two methods of analysis do not exceed the acceptable values obtained by composing the uncertainties of the two measurement methods for none of the tested matrices. Thus, there was no significant influence of the nature of the matrix on the result of the measurements.

Conclusions: The applied mineralization method is fast and efficient and can be used both in combination with the colorimetric method and the ICP-OES method for determining the bioavailable silicon from a wide range of plant biostimulants.

Acknowledgements: *This research was supported by the Ministry of Education and Research* from *Romania through the Financial Agreement Research of Contract no. 34 N / 15.03.2016, project PN. 16.31.01.02.*

SCREENING OF SOME NEWLY-ISOLATED BACTERIAL STRAINS PRODUCING LIPOLYTIC ENZYMES

C. Tomulescu[1,2*], M. Moscovici[2], M. Vladu[1,2], M. Petrescu[2], R. Stoica[2], A. Vamanu[2]

[1]*University of Agronomic Sciences and VeterinaryMedicine, USAMV Bucharest, 59Mărăști, 011464*

[2]*National Institute for Chemical-Pharmaceutical R&D, ICCF Bucharest, 112 Vitan Ave., district 3, 031299*

**Corresponding author: caterina_tomulescu@yahoo.com*

Keywords: bacteria; screening; lipolytic enzymes

Introduction: Microorganisms are natural resources for lipase production, mainly strains of the genera *Candida, Rhizopus, Aspergillus, Mucor, Penicillium, Pseudomonas* and *Serratia* [1]. Demand for microbial enzymes and, in particular for lipase, worldwide is steadily increasing due to the wide range of industrial applications [2]. The aim of this research was to carry out experimental studies in order to evaluate the biotechnological potential for lipolytic enzymes production using bacterial strains isolated from natural biotopes.

Materials and methods: *Biological material* - newly-isolated bacterial strains: 8 (*B. cereus*), 13, 15, 25 (*B. cereus*), 30, 37, 45 (*Ps. chlororaphis*), 49 (*B. thuringiensis*), 54 and 64 (*Lysinibacillus fusiformis*). *Culture media*: various liquid media with different substrates: Tween 80, Tributin, Triolein, Olive Oil, Sunflower Oil and Castor Oil. Bioprocess conditions: 30º-31ºC, initial pH 7.0-8.0,24-48h, 220 rpm and inoculation volume 2, 3 or 10%.The main sources of carbon: glucose - M3, M5, sucrose - M4, glycerin - M6 and various substrates for stimulation of enzymatic activity (olive oil - M3, M4, M8; castor oil - M5, sunflower oil - M9 → 12, triolein - M7, tributirin - M2, M13). Inducers such as Tween 80 (0.5, 1 or 2%) and calcium chloride (0.05 or 0.1%) were introduced into the fermentation media. Determination of enzymatic activity: titrimetrically with 0.05N NaOH.

Results: In order to evaluate the enzymatic activity, 5 experiments were conducted, in which selected strains from a preliminary screening on various specific solid media, with lipolytic enzyme synthesis inducers were used. The results demonstrated: a maximum of **7.46 UL FIP/ml** and **6.63 UL FIP/ml** were obtained using the strain **30** and M2 medium (48h and 36h, respectively; pH = 7.0); **6.95 UL FIP/ml** using the same strain and an original medium - M5 (48h, pH 7.0); **4.92 UL FIP/ml** and **4.83 UL FIP/ml** using the strain **64**, ***Lysinibacillus fusiformis*** and M2 medium (36h and 24h, respectively, pH 7.0).

Conclusions: 2 of the tested bacterial strains - **30** and **64** (***Lysinibacillus fusiformis***) have proven to have potential for lipolytic enzymes production in submerged cultivation, when tributirin or castor oil were used as substrates and other 3 could be promising (**8, 13** and **45**). Laboratory experiments have yielded positive responses that encourage the initiation of detailed studies of the influence of various factors (temperature, time, pH, nutrients) on the production of bacterial lipases.

Acknowledgements:*This study was funded by the National Authority for Scientific R&I - grant **PN 09-11 04 03**.*

References:

[1]. Gurung N., Ray S., Bose S., Rai V. A Broader View: Microbial Enzymes and Their Relevance in Industries, Medicine, and Beyond. BioMed Research International; 2013, article ID 329121.

[2]. Singh R., Manoj Kumar M., Mittal A., Kumar M. P. Microbial enzymes: industrial progress in 21st century. Biotech; 2016, 6:174, 1-15.

ENHANCING THE ANTIOXIDANT ACTIVITY OF HONEY BY DIRECT MACERATION OF CERTAIN MEDICINAL PLANTS

A.D.Dima*, C.M.Luntraru, V. Tamas

S.C. HOFIGAL Export-Import S.A.

**Corresponding author: cercetare@hofigal.eu*

Keywords: antioxidant activity; honey; maceration; phytotherapy

Introduction: Honey is known to have the largest appreciation among the hive products. It is a complex natural food, enclosing numerous types of phytochemicals which contribute to its antioxidant and anti-inflammatory activities [1].The present studyaims to investigate the enhancement of the antioxidant activity of honey by direct extraction of certain phytotherapeuticprinciples from medicinal plants in honey,from which polyphenols are the most interesting, as showing an important pharmacological action and heath benefits.

Materials and methods: Theused vegetal material originate from the own ecological culture of HOFIGAL Company. For this study, Lavender, Wild Pansyand Marigold were chosen.This were washed and dried in specific conditions and introduced in polyfloralhoney (S0), from Prahova region, as 10 % weight and cold macerated for 14 days. After separation of the vegetal material, the obtained samples (denoted by S1, S2 and S3 for honey with Lavender, Wild pansy and Marigold, respectively) were analyzedfor the determination of the antioxidant activity by the CUPRAC assay and for total polyphenols using the Folin-Ciocalteu method.

Results: In the conditions of our study, comparing the initial honey with any of the three obtained samples, it is notable that the antioxidant activityhas remarkably increased, in correlation with the polyphenolic content, as presented in Figure1.The honey after maceration with Marigold presents the highest content of total polyphenols.

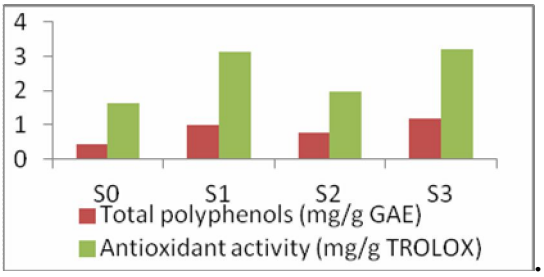


Figure1. Antioxidant activityand total polyphenols of samples

Honey also enriches in other phytotherapeutic compounds, especially components of the volatile oils.

Conclusions: By maceration of medicinal plants in honey, new honey based products could be obtained, with increasedantioxidant activity andelevatedphytotherapeutic principles concentrations.

References:

[1]. Badolato M,Carullo G, Cione E, Aiello F, Caroleo MC. From the hive: Honey, a novel weapon against cancer. European Journal of Medicinal Chemistry. 2017.https://doi.org/10.1016/j.ejmech.2017.07.064. Accessed 10 August 2017.

AMS-CARRIER-*CHLORELA* BIOFILM IS USEFUL IN AQUACULTURE WASTEWATER MANAGEMENT

B. Miu[1,2], I. I. Karpathakis[2], C. Moga[3], N. Craciun[1,2*],A. Ionascu[2], G. Stoian[1,2]

[1]*Aquaterra, Bucharest, Romania*

[2]*University of Bucharest, Bucharest, Romania*

[3]*S.C. DFR Systems S.R.L. Bucharest*

**Corresponding author: nicolae.craciun@yahoo.com*

Keywords: moving bed biofilm reactor; AMS-Carrier; Chlorella spp.;aquaculturewastewater

Introduction: Aquaculture wastewater is usually treated to get rid of undesirable substances by subjecting the organic matter to biodegradation by microorganisms. The aerobic biodegradation involves the degradation of organic matter to smaller molecules (CO_2, NH_3, PO_4 etc.), and requires constant supply of oxygen. The process of supplying oxygen is expensive, tedious, and requires a lot of expertise and manpower. These problems are overcome by growing microalgae in the ponds and tanks where wastewater treatment is carried out. The algae release the O_2 while carrying out the photosynthesis which ensures a continuous supply of oxygen for biodegradation process. Fish farm algae - based wastewater treatment systems are mainly used for nutrient removal (removal of nitrogen and phosphorous). The added benefit is the resulting biomass that can be used as biofuel feedstock.

The AMS-Carrier (S.C. DFR Systems S.R.L. Bucharest)is an efficient media for moving bed biofilm reactor (MBBR) in aerobic applications. The plastic surface (small cylindrical shaped polyethylene carrier elements with a specific density of 0,96 g/cm^3 and specific surface area of the packing has about 850 m^2/m^3 of bulk packing volume) is especially designed to provide a suitable home for biological colonies of bacteria and protozoa to grow and flourish. The aim of this study was to analyze the behavior and development of a *Chlorella* population biofilm on a series of AMS-Carrier.

Materials and methods: The effect of different composition/hydrophylicitiesAMS-Carrier on Chlorella cultures has been studied.The chlorophyll content, the algae biofilm viability (MTT test), protein and lipid content, as well as the efficiency of a biologically salt synthetic wastewater biodegradation with a concentration of 1 g N (NH^{4+}/L) in presence of a specific trace nutrients were analyzed.

Results: Our results show that the increasing of hydrophilic component of AMS-Carrier leads to an increase in biofilm formation capacity coupled with an increase of biodegradative yield of ammonia by *Chlorella*.

Conclusions:AMS-Carrier are suitable for the treatment of waste water from aquaculture farms and AMS-Carrier does not appear to degrade and release toxic substances for Chlorella biofilm.

Acknowledgements: *Research was supported by COFUND-WATER WORKS ERANET2015-ABAWARE (3).*

TECHNO-ECONOMIC ANALYSIS OF TRICHODERMA BIOPRODUCT MANUFACTURING AND USE

V. Zamfiropol-Cristea[1,2], T.-E. Şesan[2,3], I. Răut[2], A. Cociu[4], F. Oancea[2,1*]

[1]*University of Agronomic Sciences and Veterinary Medicine of Bucharest, 59 Mărăşti Blvd., sector 1, 011464 Bucharest, Romania*

[2]*National Institute for Research & Development in Chemistry & Petrochemistry - ICECHIM, 202 Spl. Independentei, 060022, Bucharest, Romania*

[3]*University of Bucharest, Faculty of Biology, 91-95 Spl. Independentei, 050095, Bucharest, Romania*

[4]*National Agricultural Research and Development Institute, 1, Nicolae Titulescu Str., 915200 Fundulea, Călăraşi county, Romania*

**Corresponding author: florino@ping.ro*

Keywords: Bioproduct; Trichoderma; techno-economic analysis; conservationagriculture

Introduction. Bioproducts based on *Trichoderma* plant biostimulant strains represent one of the solution to the conservation agriculture (CA) drawbacks [1]. We performed a techno-economic analysis regarding: (*i*) manufacturing a bioproduct based on plant biostimulant *Trichoderma* strain, *T. asperellum* T36, on optimal conditions and (*ii*) using the *Trichoderma* bioproduct.

Material and methods. For techno-economic calculation of bioproduct manufacturing we used a model for *Trichoderma* industrial cultivation [2], based on a cascade of batch bioreactors. Stoichiometry of the conversion of culture medium components into plant biostimulant *T. asperellum* T36 biomass was considered that of our surface response optimized production [3].We use the costs of the main agro-industrial raw materials, glucose, soymeal and yeast extract, used for the *Trichoderma* growing media, as being the average price for such agricultural commodities on European Union during the last year (EC, 2017). For inorganic ingredients of cultivation medium, ammonium sulphate and potassium mono- and di-hydrogen-phosphates, we considered the price for fertilizers (EC, 2017). Costs were expressed in EUR. For techno-economic analysis of production we used the data from T36 bioproduct field trials [1].

Results.Our results shown that, to produce 1 kg of *T. asperellum* T36 biostimulant strain the total costs for medium ingredients is 2.05 EUR. More than 75% of this cost with medium ingredients is for glucose, which represent almost 81.5% from the weight of the cultivation medium ingredients. The use of T36 bioproduct on CA system is profitable for the farmers, the added value of additional yield being 76 EUR, more than 10 time the value for the acquisition of the T36 bioproduct.

Conclusion. Production and use of bioproducts based on Trichoderma strains are profitable.

Acknowledgements: This work is supported by the Ministry of Research and Innovation UEFISCDI, Project PN-II-PT-PCCA-2013-4-0846 - CERES, contract 159/2014.

References:

[1]. Oancea, F., Raut, I., Şesan, T.E., Cornea, P.C., Badea-Doni, M., Popescu, M., Jecu, M.L., 2016. Hydro-gelified and film forming formulation of microbial plant biostimulants for crop residues treatment on conservation agriculture systems. *Studia Universitatis Vasile GoldisSeriaStiinteleVietii (Life Sciences Series)* 26, 251-260.

[2]. Klein-Marcuschamer, D., Oleskowicz-Popiel, P., Simmons, B.A., Blanch, H.W., 2012. The challenge of enzyme cost in the production of lignocellulosic biofuels. *Biotechnology and bioengineering* 109, 1083-1087.

[3]. Zamfiropol-Cristea, V., Raut, I., Şesan, T.E., Trică, B., Oancea, F., 2017, Surfaceresponseoptimization of submergedbiomassproduction for a plant biostimulant Trichoderma strain, *Scientific Bulletin. Series F. Biotechnologies*, 31, 56-65.

PHOTOCATALYTIC DEGRADATION OF ORGANIC COMPOUNDS FROM WATER ON Ti-MESOPOROUS SILICA MATERIALS MODIFIED WITH Ce

M. Ciobanu[1*], G. Petcu[1], D. Negoescu[1], S. Somacescu[1], M. Mureseanu[2], V. Parvulescu[1]

[1] *"Ilie Murgulescu" Institute of Physical Chemistry, 202 Spl. Independentei, 060021, Bucharest, Romania*

[2] *Department of Chemistry, Faculty of Sciences, University of Craiova, 107 I Calea Bucureşti, 200478, Craiova, Romania*

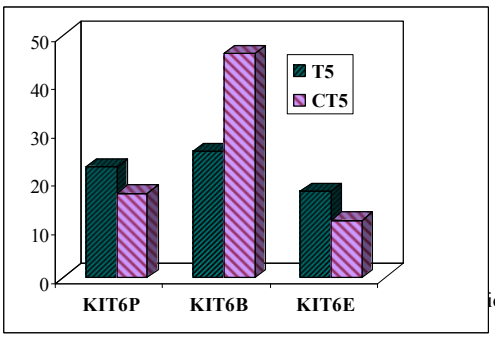
**Corresponding author: mciobanu@icf.ro*

Keywords: photocatalytic reactions; phenols and dyes degradation; TiCe-modified mesoporous silicas

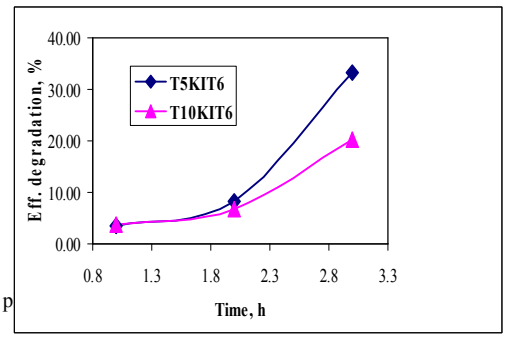
Introduction: Phenolic compounds and dyes are important families of wastewater polluting agents. Degradation of such compounds by catalytic and photocatalytic reactions are the main performing methods used. In this work we present results obtained in photocatalytic degradation of phenols (phenol, catechol) and dyes (methyl orange, Brilliant Blue) from water.

Materials and methods: Block copolymer P123 and hexadecyltrimethylamonium bromide were used as surfactants and tetraethylortosilicate, titanium butoxide and cerium nitrate as silica and metals precursors. Titanium dioxide (5%) supported on silica with hexagonal (MCM-41, SBA-15) and cubic arrangement of mesopores (MCM-48, KIT-6) were obtained by direct and post-synthesis methods and cerium was impregnated from aqueous solution of precursor. The obtained materials were characterized by XRD, SEM and TEM microscopy, XPS and UV-Vis spectroscopy. The photocatalytic reactions were carried out under UV and visible light.

Results: The obtained results showed mesoporous materials with structure, morphology and porosity typical for the ordered mesoporous silicas. A strong interaction between titania and ceria was evidenced by XPS results who have highlighted a high percent of Ce^{3+} on the surface. Very good results were obtained in degradation of phenol, MO and BB dyes degradation under UV irradiation and lower efficiency of degradation was obtained in degradation of phenols from water under visible light (Fig.1).



ion of p



Conclusions: Variation of TiO_2 dispersion on mesoporous silica, properties of the silica support and doping with cerium influence the photocatalytic activity of CeTi-mesoporous silica (MCM-41, SBA-15, MCM-48 and KIT-6) materials in degradation of phenols and dyes from water.

BACTERIAL CALCIUM CARBONATE PRECIPITATION AS AN ALTERNATIVE OF SELF HEALING METHOD OF CEMENTITIOUS MATERIALS

V. Fruth[1*], I. Atkinson[1], J. Pandele-Cusu[1], A. Rusu[1], S. Petrescu[1], I. Raut[2], M. Arsene[2], M. Doni[2], L. Jecu[2], I. Barcan[3], A. Badanoiu[3]

[1]Institute of Physical Chemistry, Romanian Academy, 202 Spl. Independentei, 060021, Bucharest Romania

[2]INCDCP-ICECHIM, 202 Spl. Independentei, 060021 Bucharest, Romania

[3]University Politehnica of Bucharest, 1-7 Polizu Str., 011061 Bucharest, Romania

**Corresponding author: vfruth@gmail.com*

Keywords: calcium carbonate; bacterial precipitation; cementitious materials

Introduction. The self-healing ability of cementitious materials has been improved by the incorporation of bacteria, which can induce calcium carbonate precipitation. These precipitates can build up and form an effective seal against crack related water ingress. Many bacterial microorganisms are developing metabolic activities with the production of urease enzyme which leads to the precipitation of calcium carbonate. This property has many applications in sand consolidation, remediation of damaged structured, as ornamental stones and filling of cracks and holes [1, 2]. The carbonate layer produced on material surface represents an innovative approach to increase the durability of the concrete and protection against water and other destructive agents protection by decreasing the material porosity. The present study investigates the potential of a bacterial common strains to be used for the biological production of calcium carbonate based minerals.

Materials and methods. The strains were grown in solid and liquid medium containing urea and Ca^{+2} ions. Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD) analyses, and scanning electron microscopy (SEM) and thermal analysis were performed in order to confirm the presence of calcium carbonate in the precipitate.

Results. The potential of two common bacteria strains was evaluated for the biological production of calcium carbonate based minerals. There were established the optimal condition. When bacterial concentration increases in the system, the quantity of calcium carbonate rises and the compression resistances go up to 50% compared to a standard sample. Presence of the bacteria in the system infers the aragonite form of $CaCO_3$.

Conclusions. The incorporation of bacterial cells in building materials has improved the self-healing ability of cementitious materials. Use of bacterial cells to improve strength and durability of cementitious materials provides greener and economic options.

References:

[9]. Vahabi A, Ramezanianpour AA, Sharafi H, Zahiri HS, Vali H, Noghabi KA. Calcium carbonate precipitation by strain *Bacillus licheniformis* AK01, newly isolated from loamy soil: a promising alternative for sealing cement-based materials, J. Basic Microbiol. 2015;55:105–111.

[10]. Rodriguez-Navarro C, Jroundi F, Schiro M, Ruiz-Agudo E, González-Muñoz MT. Influence of substrate mineralogy on bacterial mineralization of calcium carbonate: Implications for stone conservation. Appl. Environ. Microbiol. 2012;78: 4017-4029.

CONTRIBUTIONS TO THE INTERPRETATION OF MASS SPECTRA OF METHOXY-ETHOXY TRANSESTERS OF TEOS. LINKED SCANS AND ACCURATE MASS

Virgil Badescu

National Research & Development Institute for Chemistry & Petrochemistry – ICECHIM, 202 Spl. Independentei, 060021, Bucharest, Romania

**Corresponding author: virgil_badescu@yahoo.com*

Keywords: methoxy transesters; mass spectra; linked scans; accurate mass

Introduction: The aim of this article is the study of the fragmentation reactions of methoxy-ethoxy transesters of tetraethoxysilane (TEOS), obtained in sol-gel process, initiated by electronic impact in the ionization chamber of a double focusing mass spectrometer. The transesterification reactions in nonparental solvents (CH_3OH) advance to the total replacement of ethoxy group by methoxy groups [1].

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: B/E linked scan: This method of scanning allows obtaining daughter ions m_2^+ from a preset precursor ion m_1^+; $(B/E)(1-E)^{1/2}$ linked scan is used to obtain the ions which lose small molecules with a preset mass [2-4].

Results: The mass spectra of the methoxy transesters of TEOS are similar to that of TEOS but contain molecular and fragmentation ions with 14 units less which correspond to the difference between the mass of the CH_2 - and C_2H_5 - groups (Figure 1 a-d).

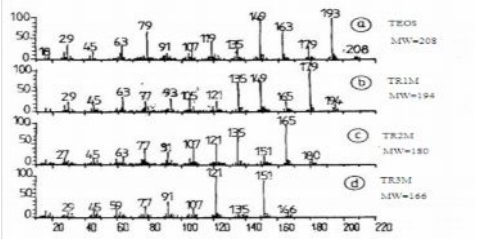
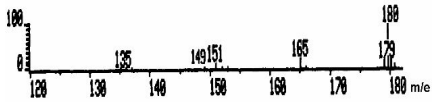
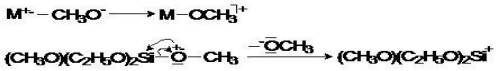


Figure 1 Mass spectra of TEOS and methoxy transesters TR1M-TR3M

Quantum calculations by MOPAC 7 for neutral and ionized TEOS methoxy transesters show that the initiation center of fragmentation reactions is located on oxygen atom of an methoxy or ethoxy group; e.g. for methoxy triethoxy silane (TR1M code) net negative charge on this atom decreases from -0.438 to -0.204 on methoxy group [4]. Daughter ions of dimethoxy diethoxy silane (TR2M) molecular ion obtained experimentally by linked scan B/E are the ions at m/x 179, m/z 165, m/z/151, m/z 149 and m/z 135. (Figure 2a)



a)



b)

$C_5H_{13}O_3Si$ M_{ELE} =149,0633 M_{OBS}=149,0583 ΔM =5,1 mmu c)

Figure 2a). Daughter ions of TR2M; 2b) Elimination of methoxy group from TR2

Accurate mass measurements at high resolution (5000) for the molecular ions and fragmentation ions of methoxy transesters were used to confirm their identification.

Conclusions: The ions of methoxy transesters of TEOS mass spectra were obtained experimentally by the B/E and B/E $(1-E)^{1/2}$ linked scans. Thus, there can be written the fragmentation pathways for the primary events (cleavage of methoxy and ethoxy groups) and eliminations of neutral molecules (acetaldehyde, ethylene, formaldehyde, hydrogen) by B/E $(1-E)^{1/2}$ linked scans.

References:

[1]. Badescu V, Zaharescu M, Radu M, Vasilescu A. Hydrolysis-condensation of tetraethoxysilane in nonparental solvents studied by GC-MS. J.Sol-Gel Sci.Tech. 1994;2:43-49

[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;60:1107-1115.

[3]. Badescu V. Contributions to the interpretation of mass spectrum of tetraethoxysilane (TEOS). Part I. The molecular ion. Primary events. Rev. Roum. Chim. 2014;59:875-882.

[4]. Badescu V. Ph. D. Thesis, Roumanian Academy, Bucharest, Inst. Phys. Chem., 1998.

INDUSTRIAL WASTEWATER TREATMENT WITH MAGNETIC NANO-STRUCTURED MATERIALS

M. Hetvary[1*], D. Vâju[1], E. Matei[2], D.M. Ignat[1], A. Predescu[2]

[1]*S.C. ICPE Bistrita S.A., 7 Parcului Str., 420035, Bistrița, Bistrita-Nasaud, Romania*

[2]*ECOMET UPB, 313 Spl. Independentei, 060042, Bucharest, Romania*

Corresponding author: mihaela.hetvary@icpebn.ro

Keywords: wastewater treatment; magnetite; metals; pre-oxidation; nanostructured material

Introduction: The innovative system for industrial wastewater treatment from electroplating industry uses magnetic nanostructured materials. This is made by SC ICPE Bistrita SA and his purpose is metal recovery and water reuse, so ensuring a substantial decreasing in water consumption. The technology is based on results obtained by UPB ECOMET in the water depollution with nanomagnetic materials. SC ICPE Bistrita will make the wastewater treatment system, which will be implemented at SC BETAK SA Bistrita, in order to reduce water consumption and to ensure adequate quality of water discharged into the sewer. This system has been tested experimentally in laboratory, in order to adapt the technology to real conditions and to optimize processes and increase efficiency retention metals. This system consists of: electrochemical step which use physical-chemical process of advance oxidation with oxidants obtained in situ, settling step were the suspensions are eliminated from water, and the step of metal adsorption on iron nano-oxides (magnetic nanostructured material) and retaining of this nano-oxides in a magnetic module.

Materials and methods: Tests were realised on which step and the purpose was to reduce the target parameters, in this case dissolved heavy metals (iron, zinc, copper, nickel). The probe was analysed conform standardised methodes**.**

Results: From the analysis of the quality indicators of treated water, on the treatment steps, it was obtained an increased efficiency for wastewater treatment, at all parameters studied.

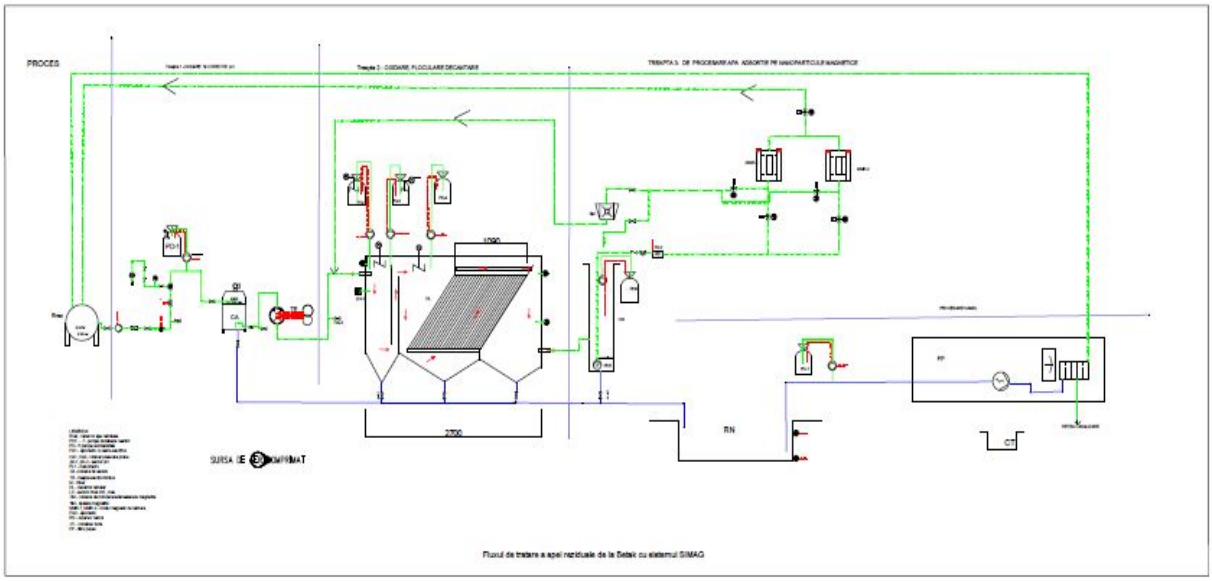


Figure 1 – Technological scheme of SIMAG module

Conclusions: After the water passes through the innovative wastewater treatment system, the water quality is adequate for its reuse in the process of production and also can be eliminated in the sewerage network of the city, its parameters fall into NTPA 002/2002.

Acknowledgements: *This work was supported by grants of the Romanian National Authority for Scientific Research and Innovation, CNCS/CCCDI – UEFISCDI, project number PN-III-P2-2.1-PTE-2016-0063, contract 7PTE/2016*

WATER TREATMENT USING CATALYTIC OZONATION IN RECIRCULATED CONTINUOUS FLOW-FUNCTIONAL MODEL

S.C. Ulinici[1*], G. Vlad[1], R. C. Fierascu[2], E. Grosu[1], S.M. Avramescu[3]

[1]*S.C ICPE Bistrita S.A., 7 Parcului Str., 420035, Bistrița, Bistrita-Nasaud, Romania*

[2]*National Research & Development Institute for Chemistry & Petrochemistry – ICECHIM, 202 Spl. Independentei, 060021, Bucharest, Romania*

[3]*University of Bucharest, PROTMED Research center, 36-46 Mihail Kogalniceanu Blvd., 050107, Bucharest, Romania*

**Corresponding author: sorin_ulinici@icpebn.ro*

Keywords: catalytic ozonation; numerical simulation; dissolved ozone

Introduction: The Advanced Oxidation Processes (AOPs) are intended for quasi-total removal of organic pollutants or for their conversion into non-toxic or biodegradable by-products. This paper presents the functional model of water treatment system using catalytic ozonation processes in a continuous flow, its description and the numerical model used to simulate the operation of the hydraulic system and ozonation.

Materials and methods: The functional model is designated to operate continuously, at a maxim flow of 1 m^3/h, with recirculation and includes two contact steps water/ozone, and a catalytic ozonation step (heterogenous catalysis) followed by a step of adsorption on granular activated carbon. The first contact step water/ozone is an innovative step which involves the use of a contactor without bubble generation, derived from an ultrafiltration system of "hollow fiber" made from PTFE.

Results: The numerical model for system simulation was generated using EPANET 2,0 [1], using the lagrangeian approximation from the fluid mechanics [2]. The numerical simulation was made on different water flows, in order to highlight the dissolved ozone concentration. The equations underlying modeling, are given by the equation of convective transport in the pipeline, (the equation of the mixture at the junctions), and the mixing equation of fluid storage elements [1].

Conclusions: The results obtained on the basis of the numerical simulation denote the fact that in the catalytic ozonation stage are obtained dissolved ozone concentrations between 1-4 mg/L, depending on the flow regime and the ozone dynamics in the contact steps. The ozone injected dose taken into consideration, in three points, was of 8 mg O_3/min in each point, which is an operational one.

Acknowledgements: *This work was supported by grants of the Romanian National Authority for Scientific Research and Innovation, CNCS/CCCDI – UEFISCDI, project number PN-III-P2-2.1-PTE-2016-0063, contract 8PTE/2016,*

[11].Rossman L.A. EPANET 2 Users Manual, National Risk Management Research Laboratory, United States Environmental Protection Agency, 2000

[12]. Egon K. “Fluid Mechanics”, Springer-Verlag, Berlin Heidelberg, 2005

CHARACTERISTICS AND INFLUENCES OF SF_6 GAS ON THE ENVIRONMENT AND CLIMATE-FRIENDLY ALTERNATIVE TO SF_6

G.M. Fierăscu[1,2*], R. Porumb[1], M. Deaconu[1,2]

[1]*Politehnica University of Bucharest, Faculty of Power Engineering, 313 Spl. Independentei, 060042, Bucharest, Romania*

[2]*ABB Group, 169A Calea Floreasca, 014459, Bucharest, Romania*

**Corresponding author: gratian.fierascu@gmail.com; gratian.fierascu@ro.abb.com*

Keywords: SF_6; environment; energy; greenhouse; air-plus molecule

Introduction: SF_6 is the dominating technology for gas insulated switchgear due to its excellent dielectric, thermal and arc quenching properties. Gas insulated switchgear (GIS) technology with sulfur hexafluoride (SF_6) gas provides the most compact dimensions, highest reliability and maximum safety. Unfortunately, SF_6 is a potent greenhouse gas and suffers from a very high global warming potential (GWP). The paper presents all the properties and used of SF_6, the climate policy aspects and information about friendly alternative to SF_6.

Materials and methods: Different safety elements, used technology and structural components of SF6 will be analyzed using non destructive techniques or laboratory tests. The paper is a theoretical study.

Results: The aim of this paper is to illustrate the latest methods used for gas insulated switchgears, the proprieties of the SF_6 and the influence on the environment establish practical new climate friendly alternative. ABB together with partner 3M has developed a promissing alternative to SF_6, ABB AirPlus insulation gas. While coming close to the technical performance of SF_6, the new gas – with a GWP of around 0,5 has virtually no impact on global warming. More than 80% by volume is made up of dry air and the remaining part is NOVEC 5110 dielectric fluid, a C5 fluoroketone C5 FK or $C_5F_{10}O$.

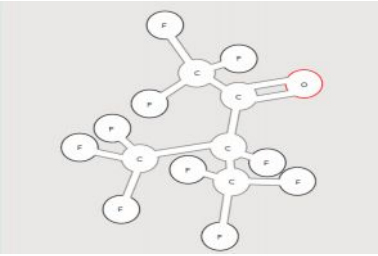


Fig. 1 The C5 fluoroketone molecule.

Conclusions: Despite all its advantages, SF_6 gas is a potent greenhouse gas if released into atmosphere but there are new friendly alternative.

References:

[1]. Husain B, Williams A, Sieder C. SF_6-free GIS now for medium-voltage applications. ABB Review. 2017;1:11. Available online at: http://new.abb.com/about/technology/abb-review

[2]. ***. Guide to the safe use of SF_6 in gas insulated electrical equipment. UNIPEDE/EURELECTRIC Documentation. 1998; Ref : 1998-560-0008. Available online at: http://www.eurelectric.org/Download/Download.aspx?DocumentID=2136

[3]. Saxegaard M, Kristoffersen M, Stoller P. Dielectric properties of gases suitable for secondary medium voltage switchgear, 23rd International Conference on Electricity Distribution Lyon, 15-18 June 2015, Paper 0926

[4]. Kieffel Y, Biquez F. SF_6 alternative development for high voltage switchgears. Electrical Insulation Conference (EIC), 2015 IEEE Xplore, DOI: 10.1109/ICACACT.2014.7223577.

[5]. Wartmann S, Harnisch J. Reductions of SF_6 emissions from high and medium voltage electrical equipment in Europe. Environ. Sci. 2005;2(2-3):273-281. DOI: 10.1080/15693430500402234

INNOVATIVE APATITIC MATERIALS WITH ENHANCED ANTIMICROBIAL ACTIVITY FOR BUILDING MATERIALS AND CULTURAL HERITAGE CONSERVATION

R. C. Fierascu[1*], I. Fierascu[1], R. Somoghi[1], B. Trica[1], G. Vasilievici[1], C. A. Nicolae[1], A. Moanta[2], A. Ortan[1,3], L.M. Ditu[4]

[1]National Research and Development Institute for Chemistry and Petrochemistry-ICECHIM, 202 Spl. Independentei, 060021, Bucharest, Romania

[2] CEPROCIM SA, 6 Preciziei Blvd., 062203, Bucharest, Romania

[3]University of Agronomic Science and Veterinary Medicine, 59 Marasti Blvd, 011464, Bucharest, Romania

[4]University of Bucharest, Microbiology Department, 1-3 Aleea Portocalelor, 060101, Bucharest, Romania

**Corresponding author: radu_claudiu_fierascu@yahoo.com*

Keywords: apatitic materials; building materials; cultural heritage conservation

Introduction: The present paper aims to present the project PN-III-P2-2.1-PED-2016-0198, financed by the Romanian National Authority for Scientific Research and Innovation, CNCS/CCCDI—UEFISCDI through the competition PED 2016; the project proposes the use of metal-substituted hydroxyapatite ($Ca_{10-x}M_x(PO_4)_6(OH)_2$, where M=Sr, Cu, Ag, etc.) as antimicrobial component for building materials and for cultural heritage conservation. The consortium responsible for the implementation of the project is formed between INCDCP-ICECHIM and CEPROCIM S.A.

Materials and methods: Hydroxyapatite was prepared after a recipe previous developed by the authors presented in several scientific papers [1, 2]. The apatitic derivatives are obtained during synthesis using metal salts or post-synthesis by incorporating metal salts or metal nanoparticles. The materials are characterised in terms of structure (XRD, XRF, ICP-AES, thermal analyses, FTIR, XPS, Surface area and pore size determinations), morphology (TEM) and potential applications (by using several *in vitro* anti-microbial assays, as well as multiple tests for the evaluation of their behaviour as construction materials).

Results: All the apatitic derivatives obtained in the project presents higher antifungal properties than the pure hydroxyapatite. For example, the results regarding silver-apatite materials, recently published [3] show very good antimicrobial properties, especially for the materials prepared using *post-synthesis* incorporation route.

Conclusions: The results obtained in the project will allow the development of new alternatives, for both construction materials and for cultural heritage conservation.

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-2016-0198, within PNCDI III.*

References:

[1]. Fierascu I, Fierascu RC, Ion RM, Radovici C. Synthesized apatitic materials for artefacts protection against biodeterioration. Rom J Mat. 2014;44(3):292-297.

[2]. Fierascu I, Avramescu SM, Petreanu I, Marinoiu A, Soare A, Nica A, Fierascu RC. Efficient removal of phenol from aqueous solutions using hydroxyapatite and substituted hydroxyapatites. React Kinet Mech Cat. 2017;122:155-175

[3]. 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. 2017; doi: 10.1016/j.apsusc.2017.08.08

INNOVATIVE FERRITE/BETA-CYCLODEXTRIN CORE-SHELL NANOCOMPOSITES FOR REMOVAL OF POLLUTANTS FROM AQUEOUS EFFLUENTS

I. Fierascu[1*], R. C. Fierascu[1], B. Trica[1], R. Somoghi[1], C. A. Nicolae[1], S.O. Dima[1], E. Radu[1], S.M. Avramescu[2], A.E. Olaru[2], A. Nica[2], N. Stanica[3]

[1]National Research and Development Institute for Chemistry and Petrochemistry-ICECHIM, 202 Spl. Independentei, 060021, Bucharest, Romania

[2]Research Center for Environmental Protection and Waste Management, University of Bucharest, 36-46 Mihail Kogalniceanu Blvd., 050107, Bucharest, Romania

[3]Institute of Physical Chemistry "Ilie Murgulescu", 202 Spl. Independentei, 060021, Bucharest, Romania

**Corresponding author: dumitriu.irina@yahoo.com*

Keywords: magnetic composites; pollutants removal; aqueous effluents

Introduction: The present paper aims to present the project PN-III-P2-2.1-PED-2016-0251, financed by the Romanian National Authority for Scientific Research and Innovation, CNCS/CCCDI—UEFISCDI through the competition PED 2016; the project proposes the use of core-shell magnetic nano-structures for the removal of organic and inorganic pollutants from aqueous effluents. The consortium responsible for the implementation of the project is formed between INCDCP-ICECHIM and University of Bucharest, PROTMED Research Center.

Materials and methods: Several materials were obtained, consisting of a magnetic core and an organic shell (mainly using β-cyclodextrin) [1, 2]. The materials are characterised in terms of structure (XRD, XRF, ICP-AES, thermal analyses, FTIR, Surface area and pore size determinations), morphology (TEM) and potential applications (by establishing their magnetic properties, as well as their capacity for removal toxic pollutants, both organic and inorganic, from aqueous effluents).

Results: The depollution studies were mainly focused on the removal of ubiquitous pollutants knowns generally as PPCP's (Pharmaceuticals and Personal Care Products). In order to investigate the suitable isotherm for pollutants adsorption on the prepared solids, different isotherm models, like Freundlich, Langmuir and Sips were applied on the equilibrium data.

Conclusions: All the materials obtained in the project shows good potential for their use in environmental protection applications.

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-2016-0251, within PNCDI III.*

References:

[1]. Avramescu SM, Bradu C, Olaru AE, Fierascu RC, Fierascu I. Application of catalytic ozonation process for triclosan removal from aqueous solutions. 13th European Congress on Catalysis, EuropaCat, Florence, Italy, 2017.

[2]. Fierascu I, Avramescu SM, Fierascu RC, Olaru A, Bradu C, Nica A, Nicolae CA, Trica B. Removal of phenolic derivatives from water by crosslinked β-cyclodextrin. 10th International Conference on Materials Science & Engineering, BRAMAT 2017, Brasov, Romania.

[3]. Fierascu I, Fierascu RC, Somoghi R, Avramescu SM, Olaru AE, Bradu C, Nica A. Removal of organic pollutants using cyclodextrin-based adsorbents. Proceedings of the 9th International Conference Environmental Engineering and Management: Circular Economy and Environmental Sustainability. 2017;377-378.

CORROSION PROTECTION OF ALUMINIUM IN SULPHURIC ACID USING NATURAL PLANT EXTRACT

S. Caprarescu[1*], V. Purcar[2], V. Raditoiu[2], M. (Neagu) Pascu[3]

[1]*Politehnica University of Bucharest, Faculty of Applied Chemistry and Materials Science, Inorganic Chemistry, Physical Chemistry and Electrochemistry Department, 1-7 Polizu Street, 011061, Bucharest, Romania*

[2]*National Research and Development Institute for Chemistry and Petrochemistry-ICECHIM, 202 Spl. Independentei, 060021, Bucharest, Romania*

[3]*SC HOFIGAL S.A., Analytical Research Department, 2 Intr. Serelor, 077085, Bucharest, Romania*

**Corresponding author: scaprarescu@yahoo.com*

Keywords: aluminium; corrosion; plant extract

Introduction: Aluminium is the most widely used non-ferrous metal that is 100% recyclable without any loss of its natural qualities [1]. In recent years have been conducted study of corrosion protection efficiency using extracts from plants and natural products [2].

Materials and methods: The inhibitive effect of Petroselinum crispum leaf extract on the corrosion of aluminium in aqueous solution of 1N sulphuric acid was investigated by gravimetric method. The experiments for the aluminium were performed in acid solution, in the absence and in the presence of plant extract. The extraction process of plant was performed using different chemical composition (50% ethylic alcohol; 70% ethylic alcohol; 50% methanol; 50 % acetone) with maceration for 30 minutes, followed by filtration on filtering cloth. For each experiments containing blank solutions (1N sulphuric acid) was added small amount of plant extract. The surface of each aluminium samples was 1.43 cm^2. The samples were weighed and then complete suspended in small glass recipients containing prepared solutions, for 240 h. The corrosion rate in the absence and presence of plant extract was determined by gravimetric method. The inhibitor efficiency (IE%) of the plant extract was also determinated.

Results: The obtained results showed that the corrosion rate decreases when the plant extract was used. The best results for IE% (>74%) was obtained for plant extract with 50% ethylic alcohol.

Conclusions: The results showed that Petroselinum crispum leaf extract plant extract appreciably decrease the corrosion rate of aluminium in the acidic medium. The Petroselinum crispum leaf extract extract could serve as an effective inhibitor for the corrosion of aluminium in acidic medium.

Acknowledgements: *This work has been funded by Politehnica University of Bucharest, through the "Excellence Research Grants" Program, UPB – GEX. Identifier: UPB–EXCELENTA–2016 Research project title "Membrane polimerice pe baza de tincturi din plante medicinale pentru epurarea apelor uzate sintetice ce contin ioni de metale grele/Polymer membranes based on tinctures from medicinal plants for treatment of synthetic wastewaters containing heavy metal ion and by a grant of the Romanian National Authority for Scientific Research and Innovation, CNCS/CCCDI -UEFISCDI, project number PN-III-P2-2.1-PED-2016-1332, within PNCDI III.*

References:

[1]. Sangeetha M, Rajendran S, Sathiyabamaa J, Krishnavenic A. Inhibition of corrosion of aluminium and its alloys by extracts of green inhibitors. Port Electrochim Acta 2013;31(1):41-52.

[2]. Njoku DI, Ukaga I, Ikenna OB, Oguzie EE, Oguzie KL, Ibisi N. Natural products for materials protection: Corrosion protection of aluminium in hydrochloric acid by *Kola nitida* extract. J Mol Liq. 2016;219:417–424.

EXPERIMENTAL RESEARCH FOR IRON RECOVERY FROM INDUSTRIAL WASTES AND MINE WATERS

G. Moise*, A. Chirea, V. Predica, L. Mara, D. Mihaiescu, M. Ghita, V. Dragut

National Research and Development Institute for Nonferrous and Rare Metals, 102 Biruintei Blvd, Pantelimon, Romania

**Corresponding author: moise_geo_alexa@yahoo.com*

Keywords: iron oxides; microwave field; electrolysis; mine waters

Introduction: The study presents the major advantages of the iron oxide magnetization under the influence of the microwave field. This alternative method starts to develop, to simplify or improve the most commonly used methods. The benefits of this method compared to the classical ones are the simplicity of the method, the efficient reduction of working time (from days to minutes) and the reduction of the amount of reactants and solvents used.

Materials and methods: Compared to classical methods of production, the method of obtaining under the influence of microwaves has other advantages at the level of the obtained material - through the rapid nucleation process under the influence of microwaves, by heating and controlled pressure, small particles with a distribution homogeneous granulometry [1]. Also, this study presents laboratory studies that aimed at establishing working parameters for obtaining bivalent iron sulphate solutions that can be processed to obtain iron by electrolysis. According to literature data [2, 3], the electrolyte used in the electrolytic deposition of iron must meet the following conditions: medium- H_2SO_4 solutions rich in iron; the bivalent iron concentration in the solution: 55-60 g / l; iron ionic species: Fe^{2+}; trivalent iron concentration: max. 2 g / l; pH of the solution: 1.5-2. To obtain ferrous sulphate solutions, two kind of wastes were used as raw materials: iron waste resulting from the wire drawing process and precipitate resulting from the treatment of acid mine waters.

Results: After the microwave field treatment of the gypsum and iron oxides mixture in the presence of a reducing material, Fe_2O_3 was reduced to maghemite, a material with magnetic properties. Following the solubilization experiments, it was taking into account: the effect of the duration of the process on the solubilization efficiency of the iron present in the waste and the effect of the process and temperature duration on the reduction of the solubilized iron from the trivalent to the bivalent form.

Conclusions: After the microwave, field treatment of the hydrolytic precipitate an iron material with magnetic properties was obtained. The solutions obtained from the solubilisation of both types of wastes, fall within the requirements of the electrolytic iron deposition process.

Acknowledgements: *The Core Program is the source of funding.*

References:

[1]. Holland H, Yamaura M. Synthesis of magnetite nanoparticles by microwave irradiation and characterization. Seventh International Latin-American Conference on Powder Technology (PTECH 2009).

[2]. Mostad E, Rolseth S, Thonstad J. Electrowinning of iron from sulphate solutions, Hydrometallurgy. 2008;90:213-220.

[3]. Yuan B, Haarberg GM. Electrowinning of iron in aqueous alkaline solution using rotating disk electrode. Rev. Met. Paris. 2009;106(10):455-459.

ECO-EFFICIENT AND SUSTAINABLE REVITALIZATION OF LAND CONTAMINATED WITH HEAVY METALS. CHARACTERIZATION OF NATURAL ZEOLITES BEFORE AND AFTER THE SORPTION PROCESS OF Cu AND Pb

D.C. Mihaiescu*, L. Mara, G.A. Moise, A. Chirea (Gradinaru), E. Neagu, V. Badilita, D. Valentin, G. Mihai, S. Florentin

National Research and Development Institute for Nonferrous and Rare Metals, 102 Biruintei Blvd, Pantelimon, Romania

**Corresponding author: danielcristian2000@yahoo.com*

Keywords: adsorbtion; zeolite; lead; copper; pollution

Introduction: This paper presents the characterisation of natural zeolite, from Barsana (Maramures area), in the initial state and after sorption process by FT-IR, SEM and EDAX techniques. Zeolite has been tested for Cu and Pb removal from synthetic aqueous solutions. Experimental parameters (contact time, pH variations) were analysed to get optimum conditions. The kinetic of the adsorbtion was studied by application of the most important kinetic models: pseudo-first order, pseudo-second order, factional power equations.

Materials and methods: Pb and Cu solutions were prepared by dissolving a quantity of copper sulphate and lead nitrate measured in 1000 ml of distilled water for initial concentrations of 1000 mg / l and, after dilution with distilled water, the initial concentrations of solutions were tested for about 100 mg / l of metal content prepared. The effect of the different parameters on the Pb and Cu adsorption process was studied under intense stirring, at ambient temperature. For each experiment, the concentrations and pH were measured.

Results:

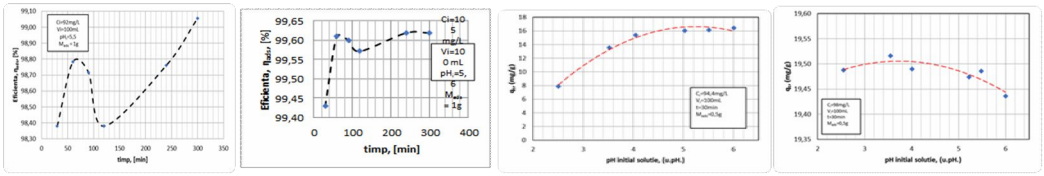


Fig.1 Adsorption of Cu and Pb on zeolite depending on the contact time and pH

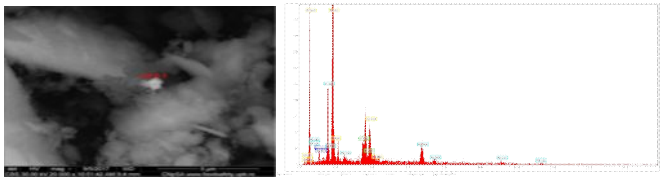


Fig.2 Zonal image of the zeolite after adsorption of Pb (at surface) and associated EDAX

Conclusions: The results shown optimal order model for adsorbtion of Cu and Pb (pseudo-second order model). The equilibrium data fitted best the Freundlich isotherm from Cu and also Pb. The results confirmed the ability of natural zeolites to adsorb the two elements, Cu and Pb, from various aqueous media, with reference to polluted soils.

References

[1]. Shaheen SM, Derbalah AS, Moghanm FS. Removal of heavy metals from aqueous solution by zeolite in competitive sorption system. Int. J. Environ. Sci. Develop. 2012;3:362-367.

[2]. Gunay A, Arslankaya E, Tosun I. Lead removal from aqueous solution by natural and pretreated clinoptilolite: Adsorption equilibrium and kinetics. J. Hazard. Mat. 2007;146:362–371.

[3]. Hana R, Zou W, Li H, Li Y, Shi J. Copper(II) and lead(II) removal from aqueous solution in fixed-bed columns by manganese oxide coated zeolite. J. Hazard. Mat. 2006;B137:934–942.

FAST CONFIRMATION OF QUATERNARY AMMONIUM CHLORIDE COMPOUNDS (QACs) IN DISINFECTANTS

E. Radu*, R. Stoica, M. Manolache, L. Capra, G. Ivan

National Institute for Research and Development in Chemistry and Petrochemistry - ICECHIM, 202 Spl. Independentei, 060021, Bucharest, Romania

**Corresponding author: nina.radu58@yahoo.ro*

Keywords: quaternary ammonium compounds; biocides; disinfectants; time-of-flight; electro-spray ionization

Introduction: Quaternary ammonium compounds (QACs) can destroy the membrane of bacteria and are widely used as biocides [1] and disinfectants [2], due to their convenient to use and low cost. European Union (EU) regulations are in place to evaluate the use of didecyldimethyl ammonium chloride (DDAC) and benzalkoniumonium chloride (BAC), both the Biocidal Products Directive (BPD) and Registration, Evaluation and Authorisation of Chemicals (REACH), use risk assessment procedures to determine whether compounds are acceptable for use in Europe [3]. Many instrumentals methods have been developed to determine QACs, but the analytical processes remain still problematic. We presented a fast method to identify benzyldimethyldodecyl ammonium chloride (C12-BAC), benzyldimethyltetradecyl ammonium chloride (C14-BAC), benzyldimethylhexadecyl ammonium chloride (C16-BAC), benzyldimethyloctadecyl ammonium chloride (C18-BAC) and DDAC in different matrices of disinfectants.

Materials and methods: Confirmation of the all target QACs was achieved by time-of-flight liquid chromatography Agilent Technologies 6224 TOF LC/MS system, using electro-spray ionization source (ESI) in positive mode, a capillary voltage of 3.5 kV, a desolvation temperature of 350 ºC, 5 mL/min flow rate of drying gas (N) and a 40 psig nebulizer pressure.

Results: Mass spectra of analysed samples were compared with mass spectra of QACs standard solutions by monitoring ion pair (m/z), corresponding to $[M\text{-}Cl]^+$ main signal.

Conclusions: We proposed a fast method with high selectivity, which could be included in multicomponents identification scheme in complex matrix of disinfectants.

References:

[1]. Walsh SE, Maillard JY, Russell AD, Catrenich CE, Charbonneau DL, Bartolo RG. Activity and mechanisms of action of selected biocidal agents on Gram-positive and -negative bacteria. J. App. Microbiol. 2003; 94(2): 240-247.

[2]. McGeechan PL, Woods W. Disinfectant and sanitizer formulations comprising biguanide and/or monoguanide in combination with quaternary ammonium salt. Arch Chemicals, Inc., USA, 2012-35153820120157540, Application: US.

[3]. Bassarab P, Williams D, Dean JR, Ludkin E, Perry JJ. Determination of quaternary ammonium compounds in seawater samples by solid-phase extraction and liquid chromatography–mass spectrometry. J. Chromatogr. A 2011; 1218, 673–677.

STUDY ON USING VARIOUS ORGANOCATALYSTS TO OBTAIN POLYOLS FOR POLYURETHANE FOAMS FROM WASTE AND RENEWABLE MATERIALS

M. Duldner[1*], E. Bartha[2], S. Capitanu[1], B. Cursaru[1], S. Nica[2], S. Garea[3], M. Pandele[3], A. Sarbu[1], S. Apostol[1], T. Sandu[1]

[1]National Research-Development Institute for Chemistry and Petrochemistry- ICECHIM, 202 Spl. Independentei, 060021, Bucharest, Romania

[2]Center of organic Chemistry "C.D. Nenitescu", Romanian Academy of Science, 202 B Spl. Independentei, 060023, Bucharest, Romania

[3]University "Politehnica" Bucharest, 1-7 Str. Polizu, 011061 Bucharest, Romania

**Corresponding author: em_duldner@yahoo.com*

Keywords: organocatalysts; PET wastes; renewable materials; glycolysis; polyurethane (PUR) foams

Introduction: The need for a green chemical industry requires a paradigm shift from concepts, as process efficiency, to new ones, focusing on replacing fossil resources with renewable raw materials, eliminating wastes and avoiding the use of hazardous substances [1]. A major challenge is to deliver efficient, sustainable and less energy demanding processes through developing green organocatalytic alternatives to metal-based catalysis [2]. As an approach to reducing environmental waste, the chemical depolymerization of PET into monomers for the ultimate formation of high-value polymeric materials has attracted significant interest [3]. In this context, our study aimed at obtaining polyols for PUR rigid foams, from PET wastes and renewable co-monomers, in milder conditions than by traditional processes, using commercial organocatalysts, mixtures thereof, or modified organocatalysts.

Materials and methods: PET wastes were cleaved/chemically modified via glycolysis followed by esterification reactions, in the presence of (potentially) renewable reagents such as: linear and branched diols/polyols, vegetable oils, aliphatic/aromatic dicarboxylic acids or anhydrides, using pyridine, amidine and guanidine derivatives, as such, in mixtures, or modified with thiourea derivatives, as well as phosphazenes and ionic liquids, as catalysts.

Results: The products were analyzed by physical-chemical methods, FTIR, ^{1}H-NMR and tested in spray PUR foams formation, which were further characterized by TGA and DMA, as well as in terms of physical-mechanical properties and thermal conductivity.

Conclusions: Polyols suited for PUR foams were obtained in milder conditions than by conventional processes, with the best results for commercial 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) and 1,5,7-Triazabicyclo [4.4.0] dec-5-ene (TBD) derivatized with phenylthiourea.

Acknowledgement: *The support of the Romanian Ministry of Education and Research, through PN-II-PT-PCCA-2013-4-1388 project PERCIT, contract 61/2014 and contract PN 16.31.02.01 is gratefully acknowledged.*

References:

[1]. Sheldon RA. Engineering a more sustainable world through catalysis and green chemistry. J. R. Soc.Interface 2016;13(116):20160087. http://dx.doi.org/10.1098/rsif.2016.0087

[2]. Al-Sabagh AM, Yehia FZ, Eshaq Gh, Rabie AM, ElMetwally AE. Greener routes for recycling of polyethylene terephthalate. Egypt. J. Petroleum. 2016;25(1):53–64.

[3]. Jones GO, Yuen A, Wojtecki RJ, Hedrick JL, Garcia JM. Computational and experimental investigations of one-step conversion of poly(carbonate)s into value-added poly(aryl ether sulfone)s. Proc. Natl. Acad. Sci. U.S.A. 2016;113(28):7722–7726.

POLYMER COMPOSITES BASED ON RECYCLED POLYPROPYLENE REINFORCED WITH GLASS BALLS

M. Rapa[2], B. Spurcaciu[1]*, P. Ghioca[1], L. Iancu[1], R. Grigorescu[1], C. Nicolae[1], R. Gabor[1], I. Bujanca[1], E. Grosu[2], E. Matei[3]

[1] The National Institute of Research and Development for Chemistry and Petrochemistry – ICECHIM, 202 Spl. Independentei, 060021, Bucharest, Romania.

[2] S.C. ICPAO S.A., 8 Carpati Str., 551022, Medias, Sibiu, Romania

[3] Politehnica University of Bucharest, Center of Research and Eco-Metallurgical Expertise, 313 Spl. Independentei, 060042, Bucharest, Romania

**Corresponding author: bogdansssss@hotmail.com*

Keywords: polymer composites; polypropylene; thermoplastic elastomers; glass balls

Introduction: The study aim was the improvement of mechanical and thermal properties of recycled polypropylene composites with styrene-butadiene and styrene-isoprene block-copolymers using as filler glass balls.

Materials and methods: Polymer composites based on recycled polypropylene were obtained by melt compounding in a Brabender palstograph with thermoplastic elastomers and glass balls.

The use as additives of styrene-butadiene (SBS) and styrene-isoprene (SIS) block-copolymers aimed the composites endurance and impact strength improvement.

The reinforcing with glass balls aimed the composites toughness and hardness increase.

Results: The polymer composites based on recycled polypropylene with thermoplastic elastomers and glass balls were characterized by Differential Scanning Calorimetry (DSC), Thermo-gravimetric Analysis (TGA), Dynamic mechanical analysis (DMA), and physical-mechanical analysis.

Conclusions: The results indicated an improvement of mechanical and thermal properties of recycled polypropylene reinforced with glass balls.

Acknowledgements: *This* work *was supported by the Romanian National Authority for Scientific Research Core Program, under Grant PN.16.31.03.01*

References:

[1]. Ghioca P, Iancu L, Grigorescu R, Spurcaciu B, Rapa M, Cincu C, Pica A, Matei E**.** Recovered Polypropylene Composites with High Impact Strength. Mater. Plast. 2017;1:18-22.

[2]. Holden G, New Developments in Block Copolymer Applicaions, in Recent Advances in Polymer Blends, Grafts and Block from Polymer Science and Technology, vol 4, Edited Sperling L.H., Plenum Press, Ed. 4, 2014, p. 274.

[3].Visakh PM, Aro Y. Thermal Degradation of Polymers, Blends, Composites and Nanocomposites: Springer Switzerland, 2015.

COAGULATION-FLOCCULATION PROCESS OF DIRECT RED 81 DYE AND DIETHYLENE GLYCOL FIXING AGENT

L.Mocanu, M.Gonta

State University of Moldova, 60 A. Mateevici str., Chisinau, MD-2009, Republic of Moldova

** Corresponding author: mvgonta@yahoo.com*

Keywords: Direct red 81; diethylene glycol; fixing agent; chemical coagulation – floculation process

Introduction: Textile industrial wastewater contains various pollutants such as organic matters, dyes and auxiliaries. The most important problem in relation to textile industrial wastewater treatment is residual non-biodegradable organic compounds. These compounds associated with some problems for the environment. Coagulation-flocculation process is the most effective method for treatment DR_{81}-DEG system.

Objectives: The aim of this study was to investigate the efficiency of the coagulation process and to determine the optimal process conditions.

Materials and methods: This is a cross-sectional study conducted on a laboratory scale**.** The effective parameters in the coagulation-flocculation process include pH, aluminum sulphate concentration, dye concentration, fixing agent concentration, and room temperature.

Results: According to the obtained results of the DR_{81}-DEG system, maximum removal efficiency was 93.0-95.0% at pH=5.0-5.1, concentration of Al (III) was 8.1mg/L, initial concentration of dye was 100.0-200.0 mg/L, and initial concentration of the fixing agent was 20.0-60.0 mg/L. The time of reaction was 60 minutes, and the room temperature was 25^{o} C. Results showed that increasing the pH value and aluminum sulphate concentration, removal efficiency decreased, but increasing the initial concetrations of organic compounds to a certain extent resulted in increasing removal efficiency. Results also indicated that increasing a temperature resulted in increasing removal efficiency.

Conclusions: The coagulation-flocculation process with optimized parameters can be used to conduct high efficiency dye and fixing agent removal. This process is not expensive and is done without much sophisticated equipment.

Acknowledgements: The present study was financed through the institutional project 15.817.02.35A.

References

[1]. Ahmad, A., Puasa, S. *Reactive dyes decolourization from an aqueous solution by combined coagulation/micellar – enhanced ultrafiltration process*. Chemical Engineering Journal. 2007 – V.132. p. 257-265.

[2]. Patel, H., vashi, R. T. Treatment of textile wastewater by adsorption and coagulation. E-J. Chem. 2010, 7, pp. 1468−1476.

[3]. Matveevici, V., Duca, Gh., Gonța, M., Iambarțev, V., Mocanu, L. Studierea procesului de diminuare a concentratiei colorantilor directi din solutiile model prin aplicarea metodelor fizico – chimice. STUDIA UNIVERSITATIS, seria „Științe reale ale naturii", 2011. nr.1(41), pp. 147-160..

HYDROCONVERSION OF FURAN ACETALS ON Pt-Pd CATALYST

S. Velea[1], M. Bombos[1], R. Doukeh[2], G. Vasilievici[1], A. Radu[1], M. Mihalache[3], D. Bombos[2]

[1]The National R&D Institute for Chemistry and Petrochemistry- ICECHIM, Spl. Independentei nr. 202, Bucharest,

[2]Petroleum-Gas University of Ploiesti, 39 Bucharest Blv., 100680 Ploiesti, Romania

[3]Faculty of Applied Chemistry and Materials Science, Politehnica University of Bucharest, Spl. Independentei nr. 313, Bucharest

**Corresponding author: serenity12ar@gmail.com*

Keywords: biofuels, hydroconversion, furfural, acetal

Introduction: Polymeric hexosans and pentosans represent a major fraction of biomass, an abundant, inexpensive and readily available source of renewable materials. The valorization of this carbohidrates assumes as intermediates furan derivatives, whose conversion can lead to the production of fuels [1-3]. Catalytic transformation of biomass into liquid hydrocarbon fuels appears an interesting approach for the production of advanced biofuels [4]. Thus, furfural derivatives have high octane numbers and they are suitable compounds for blending gasoline.

Materials and methods: The substances used in this study were reagent grade and purchased from Sigma-Aldrich. The final products were characterized by GC-MS/MS TRIPLE QUAD (Agilent 7890 A) method.

Results: The aim of this study was to synthesis gasoline additive by hydroconversion of propylene glycol acetal of furfural over Pt-Pd/γAl_2O_3 catalyst. Optimum reaction parameters were studied. The experimental results indicates that the main reactions are hydrogenolysis of the acetal structures and hydrogenation of the furan ring.

Conclusions Pt-Pd/γAl_2O_3 catalyst has a very good catalytic activity and a high selectivity in tetrahydrofurfuril alcohol and furfuril alcohol.

Acknowledgements: *The authors gratefully acknowledge the financial support of the UEFISCDI, Romania, in the framework of National Partnership Program PN II/2013, financing contract no. 95/2014 (CARFURAL)*

References:

[13]. Qian, M.-d., Xue, J.-l., Xia, S.-j., Ni, Z.-m., Jiang, J.-h., & Cao, Y.-y. (2017). Decarbonylation and hydrogenation reaction of furfural on Pd/Cu(111) surface. *Journal of Fuel Chemistry and Technology, 45*(1), 34-42.

[14]. Wang, Y., Miao, Y., Li, S., Gao, L., & Xiao, G. (2017). Metal-organic frameworks derived bimetallic Cu-Co catalyst for efficient and selective hydrogenation of biomass-derived furfural to furfuryl alcohol. *Molecular Catalysis, 436*(Supplement C), 128-137.

[15]. Yan, K., Wu, G., Lafleur, T., & Jarvis, C. (2014). Production, properties and catalytic hydrogenation of furfural to fuel additives and value-added chemicals. *Renewable and Sustainable Energy Reviews, 38*(Supplement C), 663-676.

[16]. Yuan, Q., Zhang, D., Haandel, L. v., Ye, F., Xue, T., Hensen, E. J. M., & Guan, Y. (2015). Selective liquid phase hydrogenation of furfural to furfuryl alcohol by Ru/Zr-MOFs. *Journal of Molecular Catalysis A: Chemical, 406*(Supplement C),58-64.

BITUMEN FLUXANTS OBTAINED BY GLYCEROL VALORIZATION

A. Vintilă[1*], A-M. Gălan[1], S. Velea[1], E. Radu[1], I. Banu[2], G. Bozga[2]

[1] *National Institute for Research and Development in Chemistry and Petrochemistry - ICECHIM, 202, Spl. Independentei Street, 060021, Bucharest, Romania*

[2]*Department of Chemical and Biochemical Engineering, University "Politehnica" of Bucharest, 1-7 Polizu Street, 011061, Bucharest, Romania*
**Corresponding author: vintila_alin_94@yahoo.com*

Keywords: bitum fluxants, glycerol, acetines.

Introduction: In the past years, the demand for biodiesel increases sharply and also the glycerol amount resulting as a byproduct of transesterification reaction of natural oils with alcohols (C1–C4). The preparation of the glycerol esters by the its acetylation with short carboxylic acids is one of the possibilities of glycerol valorization [1, 2]. This process may be carried out in the presence of a suitable acidic catalyst. Homogeneous catalysts such as sulfuric, hydrofluoric and p-toluensulfonic acids are toxic, corrosive and hard to remove from the reaction products. These problems can be overcome by the use of heterogeneous catalysts. Among them, cation-exchange resins showed excellent activity as well as selectivity toward higher esters in the esterification of glycerol with acetic acid [1, 3].

The aim of this work was to determine the operating conditions that maximize the glycerol conversion to di and tri acetines with applications as bitumen fluxants.

Materials and methods: In order to evaluate the process behavior in typical operating conditions, there were varied molar ratio of glycerol to acetic acid, reaction time, catalyst amount and structure. The catalytic activity of two ion exchange ions (Amberlyst 35 and Purolite CT-275) was studied.

Results: The experimental results show maximum glycerol conversion of 85-95 %.

Conclusions: According to the results, Amberlyst 35 shows a better conversion than Purolite CT-275.

Acknowledgements: *The work has been funded by the Project 80BG/2016.*

References:

[1]. Goncalves VLC, Pinto BP, Silva JC, Mota CJA. Acetylation of glycerol catalyzed by different solid acids. Catalysis Today 2008;133: 673–7.

[2]. Melero JA, Grieken R, Morales G, Paniagua M. Acidic mesoporous silica for the acetylation of glycerol: synthesis of bioadditives to petrol fuel. Energy & Fuels 2007; 21:1782–1791.

[3]. Liao X, Zhu Y, Wang S, Li Y. Producing triacetylglycerol with glycerol by two steps: esterification and acetylation. Fuel Processing Technology 2009; 90:988–993.

DESIGN, SYNTHESIS AND MOLECULAR DOCKING STUDIES OF A SARTAN COMPOUND

L.Pintilie[1], C. Negut[1], A. Stefaniu[1], C. Tanase[1], M.T. Caproiu [2]

[1]National Institute for Chemical - Pharmaceutical Research and Development (ICCF) - Bucharest, 112 Vitan Av., 031299, Bucharest, Romania

[2]Organic Chemistry Center "C.D.Nenitescu", 202 B Splaiul Independentei, Bucharest 6, Romania

**Corresponding author: lucia.pintilie@gmail.com*

Keywords: angiotensin receptor blockers (ARBs); sartan; molecular design; molecular docking.

Introduction: Sartans belong to a new series of non-peptidic drugs that can block Angiotensin II receptors and regulate blood pressure. Angiotensin II (AII) is a vasoconstrictor peptide hormone formed inside the renin-angiotensin system (RAS), which plays an important role in the regulation of cardiovascular homeostasis[1].

Materials and methods: In this study we present design studies, synthesis and molecular docking studies of the Candesartan cilexetil. The computational study of predicted molecular parameters, vibrational wavenumbers, frontier molecular orbitals energy diagram, molecular electrostatic potential map and other electronic distributions maps have been realised using Density Functional B3LYP algorithm- 6-31G*, for energy equilibrium at ground state[2]. Candesartan has been docked into the AT1R crystal structure (PDB ID: 4ZUD) [3] using the docking protocol implemented by the CLC Drug Discovery Workbench.

Results: It was realized synthesis studies for a sartan compound, who was characterized structurally. It was realized design studies. It was realized molecular docking studies.

Conclusions: In the present study, we have reported the synthesis of a sartan compound. The silico molecular docking simulation was performed to position the sartan compound into the preferred binding site of the protein receptor AT1R, to predict the binding modes, the binding affinities and the orientation.

Acknowledgements: *This paper has been financed through the NUCLEU Program, which is implemented with the support of ANCSI, project no. PN 16-27 02 03.*

References:

[1]. Elliott ME, Catt KJ, Goodfriend TLN, Angiotensin receptors and their antagonists. Engl. J. Med. 1996, 334(25), 1649-54.

[2]. Spartan'14 Wavefunction, Inc. Irvine, CA.

[3]. Zhang H , Unal H, Desnoyer R, Won Han G, Patel N, Katritch V, Karnik SS, Cherezov V, and Stevens RC. Structural Basis for Ligand Recognition and Functional Selectivity at Angiotensin Receptor. The Journal Of Biological Chemistry, 2015, 290 (49), pp. 2 9127–39.

OXAZOLIDINONE COMPOUNDS: DESIGN, SYNTHESIS, MOLECULAR DOCKING AND ANTIBACTERIAL SCREENING

L.Pintilie[1], A. Stefaniu[1], A.I. Nicu[1], C. Negut[1], C. Tanase[1], M.T. Caproiu [2]

[1]*National Institute for Chemical - Pharmaceutical Research and Development (ICCF) - Bucharest, 112 Vitan Av., 031299, Bucharest, Romania*

[2]*Organic Chemistry Center "C.D.Nenitescu", 202 B Splaiul Independentei, Bucharest 6, Romania*

**Corresponding author: lucia.pintilie@gmail.com*

Keywords: molecular design; molecular docking; antimicrobial activity; linezolid; oxazolidinone.

Introduction: The oxazolidinone compounds are a significant class of antibacterial drugs with broad spectrum of action[1,2].

Materials and methods: A series of oxazolidinone compounds have been obtained and characterized by physico-chemical methods and antimicrobial activity For these compounds there have been performed calculations of characteristics and molecular properties [3] and molecular docking studies. The docking studies have been carried out using CLC Drug Discovery Workbench Software.

Results: It was obtained some oxazolidinone compounds, who was characterized structurally and pharmacologically. It was realized design studies. It was realized molecular docking studies in order to to identify and visualize the most likely interaction, the binding affinities and the orientation of the docked ligands at the active site of *Staphylococcus aureus* ribosomal subunit (PDB ID: 4WFA) [4].

Conclusions: We have synthesized some oxazolidinone compounds and we have investigated their antibacterial activity. For the synthesized oxazolidinone derivatives, a study of the characteristics and molecular properties has been realized. The docking studies revealed that the all compounds showed good docking score. The docking score is a measure of the antimicrobial activity of the studied compounds.

***Acknowledgements**: This paper has been financed through the NUCLEU Program, which is implemented with the support of ANCSI, project no. PN 16-27 01 01*

References:

[1]. Barbachyn MR, Hutchinson DK, Brickner SJ, Cynamon MH, Kilburn JO, Klemens SP, Glikman S.Z., Grega KC, Hendges SK, Toops DS, Ford CW, and Zurenko GE. Identification of a Novel Oxazolidinone (U-100480) with Potent Antimycobacterial Activity. J.Med. Chem.1996; 38:680-5.

[2]. Brickner SJ, Barbachyn MR, Hutchinson DH and Manninen PR Linezolid (ZYVOX), the First Member of a Completely New Class of Antibacterial Agents for Treatment of Serious Gram-Positive Infections. J.Med. Chem. 2008;51: 1981-90.

[3]. Spartan'14 Wavefunction, Inc. Irvine, CA

[4]. Eyal Z, Matzov D, Krupkin M, Wekselman I, Paukner S, Zimmerman E, Rozenberg H, Bashan A, Yonath A, Structural insights into species-specific features of the ribosome from the pathogen Staphylococcus aureus, Proc.Natl.Acad.Sci.USA 2015; 112: E5805-E5814, DOI: 10.1073/pnas.1517952112.

SYNTHESIS OF GLYCEROL FORMAL CATALIZED BY TUNGSTOPHOSPHORIC ACID SUPPORTED ON MESOPOROUS SILICA

A.Trifoi[1*], D.Delia[1], R. Doukeh[1], T. Gherman[1], M. Râpă[1], F.Petru[2], M. Verziu[2],

[1]SC Research Institute For Auxiliary Organics Products SA, 8 Carpaţi,551022, Mediaş, Romania

[2]Romanian Academy, "C. D. Nenitescu" Organic Chemistry Centre, 202B Spl. Independentei, 060023, Bucharest, Romania

**Corresponding author: ancuta_trifoi@yahoo.com*

Keywords: glycerol formal, tungstophosphoric acid, mesoporous silica

Introduction: Glycerol formal has low toxicity when given orally or intravenously to animals and it has a large application as a solvent in oral, dermal and injectable products [1]. The objective of this work is to study the catalytic properties of tugstophosforic acid H3PW (20, 30 and 40 wt.%) supported on mesoporous silicas (HMS and MCM41) in the condensation reaction of glycerol with p-formaldehyde, without the use of a secondary distilling agent for the removal of the water. Supporting the heteropolyacids on solids with high surface areas is a useful method for improving catalytic performance in liquid-solid and gas-solid surface heterogeneous reactions [2].

Materials and methods: The catalysts were characterized by determining their textural properties and total acidity and by SEM, IR and TG techniques. They were tested in the reaction of glycerol with p-formaldehyde in a batch reactor.

Results: 30 H3PW/HMS had the highest activity under the conditions: temperature of 120 ºC, glycerol: formaldehyde molar ratio of 1:1, catalyst: glycerol mass ratio of 2,7 wt.%.

Conclusions The synthesis of glycerol formal by the mesoporous silica supported tungstophosphoric acid has good prospects.

Acknowledgements: *PN-III-P2-2.1-PTE-2016-0062, C 33PTE/2016*

References:

[1] Committee for veterinary medicinal products. Summary report EMEA/MRL/108/96-FINAL

[2] Yang S., Du Xx, He L., Sun Jt, Synthesis of acetals and ketals catalyzed by tungstosilicic acid supported on active carbon, J Zhejiang Univ Sci B. 2005; 6(5): 373–7.

EFECTS OF ISOPROPANOL ADDITION ON BIODIESEL PROPERTIES

S. G. Raluca[1], I. Niță, E. Stepan, S. Osman[2], I. Olga[1]

[1]Depart of Applied Physical Chemistry and Electrochemistry, "Politehnica" University of Bucharest
[2]Departof Technology and Chemical Engineering, "Ovidius" University of Constanta"
[3] INCDCP ICECHIM, 202 Splaiul Independenței, 060021 Bucharest, Romania
**Corresponding author: stoica_raluca@yahoo.com*
Keywords: biodiesel mixtures;viscosity;density;biofuel;

Introduction: Biofuels can be promising sources of alternative fuels, particularly in the transport sector. In the last years, there is an increasing interest of alcohols for gasoline and diesel replacement. The use of oxygenated fuels involves oxygen enrichment, improve pre-mixed combustion phase and improve diffusion combustion. The bio-alcohols (acetone, butanol, ethanol, methanol, and propanol) can be used with minimal changes to existing diesel engines, they have the potential to reduce greenhouse gas emissions and replace the fossil fuels [1].The aim of thisstudywas to examine the impact of isopropanol addition to biodiesel on the density and viscosity of the fuel mixtures.

Materials and methods: Biodiesel wasobtained by transesterificationfromsunflower and methanol. The meanmolar mass of biodiesel wasdeterminedbased on itsfattyacidmethyl ester concentration profiledetermined by gaschromatography. Isopropanol of 99.7 % puritywaspurchasedfromMerck. The experimental measurements of density and viscosity were carried out using an Anton Parr DMA4500 density meter and Anton Paar SVM 3000 viscosity meter.

Results: Experimental results of the density and viscosity for the pseudo-binary mixture over the entire composition range and for temperature ranging from 293.15 K to 323.15 K were reported. The capacity of different models used to predict the density and viscosity of biodiesel mixtures was evaluated[2,3].

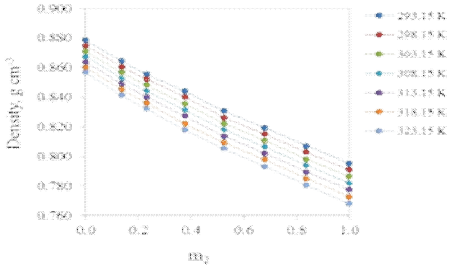


Fig. 1. Density vs alcool mass fraction for biodiesell(1)+isopropanol(2) binary system at different temperatures

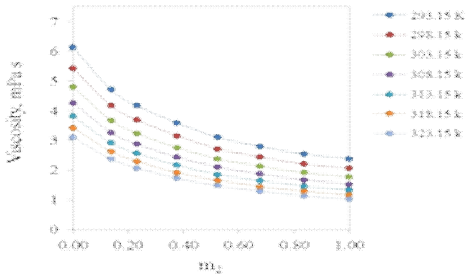


Fig.2. Viscosity vs mass alcohol fraction for biodiesel (1)+isopropanol(2) binary system at different temperatures

Conclusions: A monotonously decreasing of density and viscosity with composition was observed for the investigated systems, the values remaining within the range set in biodiesel standard (EN 14214).The density and viscosity of pseudo-binary mixtures canaccuratelypredictedfrom pure components properties by simple mixingruleswithsatisfactorily absolute average deviations.

References:

[1] Kumar S, Cho JH, Park J, Il Moon. Advances in diesel–alcohol blends and their effects on the performance and emissions of diesel engines. Renewable and Sustainable Energy Reviews.2013;22: 46–72.

[2] Verduzco LFR. Density and viscosity of biodiesel as a function of temperature: Empirical models. Renewable and suitable energy reviews, 2013;19:652-65.

[3] Grunberg L, Nissan AH. Mixture law for viscosity. Nature.1949; 164: 4175: 799–800

POSIBILIES ON DEVELOPMENT OF BIO-PACKAGING FROM MEDICINAL PLANTS WITH SUSTAINABILITY IN THE AGRO-FOOD SECTOR

M. Rapa[1*], M. Stefan[2], L. Barbu-Tudoran[2], E. Grosu[1], A. Turcanu[1], A. Andras[1], A. Trifoi[1], T. Gherman[1], G. Gavril[3]

[1]*Research Institute of Auxiliary and Organic Producs S.A., 8 Carpati St., 551022 Medias, Sibiu, Romania*

[2] *National Institute for Research and Development of Isotopic and Molecular Technologies INCDTIM, 67–103 Donath St., 400293 Cluj-Napoca, Romania*

[3]*NIRDBS/"Stejarul" Biological Research Centre, 6 Alexandru cel Bun, 610004 Piatra Neamt, Romania*

**Corresponding author: rapa_m2002@yahoo.com*

Keywords: medicinal plant; renewable polymeric matrix; total phenols; surface analysis; bio-packaging

Introduction: The market demand is rapidly rising for packaging that are derived from sustainable resources that are recyclable, or biodegradable and inexpensive reinforcement materials (cellulose plant, wood fiber, etc.) [1] that are low cost and less weight.

The aim of this paper is to investigate the posibility of medicinal plants to be introduced into polymeric matrix by melt technique in order to evidence the distribution capacity of vegetal plants and the antioxidant activity for further detailed analyses.

Materials and methods: Plasticized poly(lactic acid) (PLA)/medicinal plants [*Satureja hortensis* (thyme), *Mentha piperita* (mint), *Melissa officinalis* (melissa) and *Salvia officinalis* (sage)]) samples were prepared by melt blending processing technique. The effect of medicinal plants on the properties of plasticized PLA was investigated in terms of morphological (using Scanning Electron Microscopy – SEM) modifications and quantification of total phenol content (TPP) by UV-VIS spectrophotometry.

Results: The total phenolic amount ranged from 16 mg to 22 mg Gallic Acid Equivalent (GAE)/g on a dry weight basis. The SEM images show the relatively uniform distribution of medicinal plants on the surface of polymer film (Figure 1).

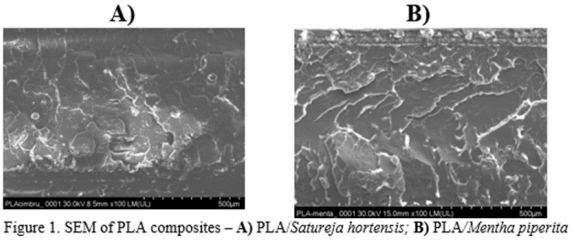


Figure 1. SEM of PLA composites – **A)** PLA/*Satureja hortensis;* **B)** PLA/*Mentha piperita*

Conclusions: The quantitative analysis performed on the prepared composites reveals that the content in bioactive compounds is not dependent of the distribution capacity of medicinal plants into PLA and their formulations are promising for development of bio-packaging in agro-food sector.

Acknowledgements: *The work was sustained from BIODIVERS project PN16-190401, financed by the UEFISCDI, Romania.*

References:

[1] Montanty AK., Misra M., Drzal LT. Sustainable Bio-Composites from renewable resources: Opportunities and challenges in the green materials world, J. Polym. Environ. 2002; 10, 19-26.

[2] Loureiro NC, Esteves JL, Viana JC, Ghosh S. Development of polyhydroxyalkanoates /poly(lactic acid) composites reinforced with cellulosic fibers, Composites Part B: Engineering 2014; 60:603–611.

COMPLETE OXIDATION OF HARMFUL ORGANIC COMPOUNDS OVER ALUMINA SUPPORTED Cu-Cr MIXED OXIDE CATALYST

V. Georgescu[1*], G. Vasilievici[2], D. Bombos[3]

[1] *Institute of Physical Chemistry " Ilie Murgulescu", Romanian Academy, 202 Spl. Independentei, 060021 Bucharest, Romania*

[2]*The National R&D Institute for Chemistry and Petrochemistry - ICECHIM, Spl. Independentei nr. 202, Bucharest*

[3] *Petroleum-Gas University of Ploiesti, Bucuresti 39, Ploiesti 100680, Romania*

**Corresponding author: vgeorgescu@icf.ro*

Keywords:Cu-Cr oxide, complete oxidation

Introduction: Mixed Cu-Cr oxide catalyst are among the mostly used in the heterogeneous oxidation and reduction processes and depollution. The neutralization of harmful components in waste gases and elimination of air pollution is one of the important domain of the use this type of the catalyst .

Materials and methods: The investigations on the Cu-Cr mixed oxide catalyst require the determination of the active element / or phase, as well as the influence of various factor on the active phase generation. Among these, an important role is played by the preparation method (the precursors, the conditions of calcinations, etc.), the nature of support as well as its interaction with various compounds, etc. The catalysts were investigated by IR, XRD, TPR, TPD and TGA.

Results: The catalytic activity of the samples was measured with respect to the complete oxidation of CO, benzene, toluene, ethyl-benzene, isopropyl-benzene and ethyl-acetate. One of the important modern tasks associated with the use of catalytic processes for neutralization of harmful components in waste gases and elimination of air pollution is the decrease in temperature of the catalytic reactions with a view to economizing energy and expenses needed for heating the waste gases which are large in amount and have low temperatures. The investigations associated with the solution of this problem are aimed at developing more effective low temperature catalysts or finding new catalytic processes.

Conclusions: In this respect the catalytic oxidation in the presence of ozone, seems very promising since it allows the catalytic process to be carried out at low temperature the high catalyst efficiency being preserved.

COMPOSITIONS BASED ON MICROENCAPSULATED ESSENTIAL OILS AND BIOSTIMULANTS

E. Stepan[1*], S. Velea[1], C.-E. Enascuta[1], E. Radu[1], E.-E. Oprescu[1], A. Radu[1], G. Vasilievici[1], D.-G. Epure[2]

[1]National Research and Development Institute for Chemistry and Petrochemistry ICECHIM Bucharest

[2]SC Probstdorfer Saatzucht Romania SRL., Bucharest

**Corresponding author: bioresurse@icechim.ro*

Keywords: *essential oil; microencapsulation; complex coacervation; biopesticide*

Introduction: The use of synthetic pesticides creates problems with their toxicity, low-biodegradability and too high amounts for optimal necessary, which can damage crops and contaminate the environment. Controlled release formulation by microencapsulation of pesticides seems to be the best choice for increasing the effciency and minimization of environmental damage. Use of essential oils as biopesticides is the subject matter of many investigations in recent years, due to its eco-friendly and biodegradable nature. They are completely non-toxic to mammals, have increased specificity, and pests do not acquire resistance over time due to the intensive use of pesticides. Nevertheless, essential oils are volatile and susceptible to oxidation. This paper presents an innovative process for obtaining microencapsulated essential oils and their formulation to obtain biopesticide compositions containing microcapsules and biostimulants.

Materials and methods: Microencapsulation of essential oils was performed by the complex coacervation method. Complex coacervation is the separation of a macromolecular solution and composed of two oppositely charged macro ions into two immiscible liquid phases [1].

Results: The compositions of the following essential oils were determined: thyme, basil, eucalyptus, rosemary, sage, mint, cloves, and cinnamon, by gas chromatography coupled with mass spectrometry (GC/MS), using a GC-MS/MS TRIPLE QUAD (Agilent 7890 A). Hydrolyzed proteins from waste have been used as microencapsulation agents. The microcapsules had a central core formed by an essential oil, covered with a shell made of polymeric material, *i. e.* hydrolyzed proteins and a phase-type which induce coacervation, containing a polyelectrolyte. Post-treatment of complex coacervated microcapsules was performed by crosslinked with dialdehydes. The effect of various process parameters which contribute to increasing the efficiency of microencapsulation was studied.

Conclusions: The microencapsulation resolved problems related to volatility and susceptibility to oxidation of biopesticides based on essential oils and also was performed controlled release of them. The microcapsules were used in plant treatments, to protect against pests, in compositions formulated as concentrated suspensions, containing plant biostimulants based on hydrolyzed proteins.

Acknowledgements: The authors gratefully acknowledge the financial support of the UEFISCDI, Romania, under the research project PN III, contract 55PTE/2016 - BIOFOL_CER

References:

[1] Devi N. Encapsulation of active ingredients in polysaccharide–protein complex coacervates. Adv Colloid Interface Sci. 2017;239:136-145

SYNTHESIS OF ALKYL LACTATES BY ACID CATALYSIS AND ENZYMATIC CATALYSIS

S. Velea[1], G. Vasilievici[1*], A.-M. Galan[1], E. Radu[1], M. Bombos[1], C. Enascuta[1]

[1]The National R&D Institute for Chemistry and Petrochemistry - ICECHIM, Spl. Independentei nr. 202, Bucharest

**Corresponding author: gabi.vasilievici@gmail.com*

Keywords: ethyl lactate, methyl lactate

Introduction: In the recent years alkyl lactates gained importance due to the use as a green solvent and economically viable alternative to traditional solvents, minimizing the use and generation of hazardous substances. Alkyl lactates are considered nontoxic and highly and readily biodegradable. Biosolvents have applications in the field of printing inks, coatings, adhesives, food processing, fragrances and cleaning products [1-3]. The green and biosolvents market worth 8.17 billion USD by 2020 [4].

Materials and methods: The esterification of lactic acid with ethanol in acid heterogeneous catalysis was carried out into a batch three neck glass flask with a reflux condenser and Dean-Stark. Esterification catalysts were prepared on various supports and characterized. Batch enzymatic esterification experiments were conducted in different organic solvents in the presence of lipases immobilized on hydrophobic supports. The resulting products were characterized by GC-MS and FTIR.

Results: This paper presents a comparative study on alkyl lactate synthesis by lactic acid esterification with ethanol / methanol in acid catalysis and enzymatic catalysis. The acid strength distribution of the synthesized catalysts were characterized by thermodesorbtion of diethylamine and textural characteristics by nitrogen adsorption measurements.

Conclusions: Alkyl lactates producing technologies by acid catalysis and enzymatic catalysis has a great potential for industrial application.

Acknowledgements: *The authors gratefully acknowledge the financial support of the UEFISCDI, Romania, financing contract no. 96/2016 BioFluInd*

References:

[1].Farrán A., Cai C., Sandoval M., Xu Y., Liu J, Hernáiz MJ., Linhardt RJ., Green Solvents in Carbohydrate Chemistry: From Raw Materials to Fine Chemicals, Chem. Rev., 2015;115:6811

[2].Li K.-T., Wang C.-K., Esterification of lactic acid over TiO_2–Al_2O_3 catalysts, Appl. Cat. A: Gen., 2012;433: 275

[3].Aqar D.Y., Rahmanian N., Mujtaba I.M.,Methyl lactate synthesis using batch reactive distillation: Operational challenges and strategy for enhanced performance, Sep. Purif. Technol., 2016; 158: 193

[4].Solvent Market by Type; Global Forecast to 2020, MarketsandMarkets, http://www.marketsandmarkets.com/ PressReleases/ green- bio- solvents .asp. Accessed 1 Sep 2017

AMINO ACIDS BASED PRODUCTS FROM HYDROLYSATES FOR RAPESEED TREATMENT – YIELD AND SELECTIVITY INCREASE PATHWAY

C.-E. Enascuta[1*], E.-E. Oprescu[1,2], E. Radu[1], E. Stepan[1], S. Velea[1], D.-G. Epure[3], V. Lavric[4]

[1]*National Research & Development Institute for Chemistry and Petrochemistry ICECHIM, 202 Splaiul Independentei St., P.O. Box 194, 060021, Bucharest, Romania*

[2]*Petroleum-Gas University of Ploiesti, 39 Bucharest Blv., 100680, Ploiesti, Romania*

[3]*SC Probstdorfer Saatzucht Romania SRL, 20 Siriului Street, 014354, Bucharest, Romania*

[4]*University "POLITEHNICA" Bucharest, Faculty of Applied Chemistry and Materials Science, 1-7 Polizu St., 011061, Bucharest, Romania*

**Corresponding author* : cristina.enascuta@gmail.com

Keywords: rapeseed crops, amino acid, protein hydrolysates, experimental design

Introduction: Global rapeseed production has a sustained growth over the last years. Rapeseed is primarily grown for meal and its oil, which can be further processed. From 2013, the use of the neonicotinoids in European agriculture, especially on rapeseed crops, has been banned by the European Commission [1].

To increase rapeseed resistance to drought and pests attack, during germination, there is an urgent need for new products to replace neonicotinoids. The key could be the products based on amino acids for seeds treatment.

This work presents a pathway to obtain protein hydrolysates, rich in amino acids, from different type of organic sources, by chemical hydrolysis. Both Box-Behnken experimental design technique and the Response Surface Method were used, on one hand, to investigate the influence of the reaction parameters upon the yield of the process and, on another, to optimize the operating conditions such as to maximize the yield.

Materials and methods: The analysis of protein hydrolysates was performed using LC-MS/TOF (Agilent 6224).The raw material, subjected to chemical hydrolysis, came from waste by-products of livestock, meat, leather and other industries.

Results: The operating parameters of choice, subject to investigation, were the catalyst amount, the temperature and the time of reaction.

Conclusions: Using the aforementioned approach, the yield was increased, there is still work to be done to obtain a product which could replace the neonicotinoids without having an insecticide effect.

Acknowledgements:*The authors gratefully acknowledge the financial support of the UEFISCDI, Romania, in the framework of National Partnership Program, financing contract no. 93EUK /2017 and PN. 16.31.01.05*

References:

[1]. McGrath P.F., 2014. Politics meets science: the case of neonicotinoid insecticides in Europe. Sapiens (7), no.1.

ECOLOGICAL COMPONENT FOR GASOLINE BASED ON FURFURAL DERIVATES

S. Velea[1], M. Bombos[1], E.-E. Oprescu[1,2*], R. Doukeh[2], G. Vasilievici[1], D. Bombos[2]

[1]The National R&D Institute for Chemistry and Petrochemistry- ICECHIM, Spl. Independentei nr. 202, Bucharest,

[2]Petroleum-Gas University of Ploiesti, 39 Bucharest Blv., 100680 Ploiesti, Romania

**Corresponding author: sanda.velea@icechim.ro*

Keywords: biofuels, biomass, furfural, hydrogenation

Introduction: The valorization of furfurals, major products obtained by conversion of natural carbohydrates into component for fuel, could be the best choice a main way to reduce dependence from hydrocarbons derived from crude oil and to improve the characteristics of the gasoline [1-4]. Derivatives obtained by hydrogenation of furfural can be valuable components for gasoline, with optimal oxygen content and with a reduced tendency to the formation of gums [5]. The objective of this research is to obtain different derivatives with potential uses in the biofuel industry by furfural hydrogenation.

Materials and methods: The precursors used for the impregnation of the catalyst support and all the substances used were reagent grade and purchased from Sigma-Aldrich. The products were characterized by GC-MS/MS TRIPLE QUAD method.

Results: The aim of this study was to synthesis an gasoline additive by hydrogenation of furfural over Cu-Pd/γAl_2O_3 catalyst. The prepared catalyst was characterized by the determination of the textural characteristics and the distribution of the acidic strength. The experimental results indicates that the yield in tetrahydrofurfuril alcohol, a valuable compound for gasoline, depends on the temperature, pressure and catalyst loading.

Conclusions: Hydrogenation of furfural by catalyst based on Cu-Pd led to the formation of oxygenated compounds readily biodegradable with low toxicity. Thus the main compounds obtained on the catalyst were furfuryl alcohol and respectively tetrahydrofurfuryl alcohol.

Acknowledgements: *The authors gratefully acknowledge the financial support of the UEFISCDI, Romania, in the framework of National Partnership Program PN II/2013, financing contract no. 95/2014 (CARFURAL)*

References:

[1]. Fulajtárova, K., Soták, T., Hronec, M., Vávra, I., Dobročka, E., & Omastová, M. (2015). Aqueous phase hydrogenation of furfural to furfuryl alcohol over Pd–Cu catalysts. *Applied Catalysis A: General, 502*(Supplement C), 78-85.

[2]. Jiménez-Gómez, C. P., Cecilia, J. A., Márquez-Rodríguez, I., Moreno-Tost, R., Santamaría-González, J., Mérida-Robles, J., & Maireles-Torres, P. (2017). Gas-phase hydrogenation of furfural over Cu/CeO2 catalysts. *Catalysis Today, 279*(Part 2), 327-338.

[3]. Musci, J. J., Merlo, A. B., & Casella, M. L. (2017). Aqueous phase hydrogenation of furfural using carbon-supported Ru and RuSn catalysts. *Catalysis Today, 296*(Supplement C), 43-50.

[4]. Panagiotopoulou, P., & Vlachos, D. G. (2014). Liquid phase catalytic transfer hydrogenation of furfural over a Ru/C catalyst. *Applied Catalysis A: General, 480*(Supplement C), 17-24.

[5]. Tarabanko VE, Chernyak MY, Simakova IL, Kaigorodov KL, Bezborodov YN, Orlovskay NF. Antiknock Properties of Furfural Derivatives.Russian Journal of Applied Chemistry, 2015, 88 (11). pp. 1778−1782.

CATALYTIC CONVERSION OF BIOMASS-DERIVED OXYGENATED COMPOUND (FURFURAL) INTO FUEL ADDITIVE

E.-E. Oprescu[1,2*], S. Velea[1], C. Enascuta[1], A. Radu[1], M. Bombos[1], G. Vasilievici[1], D. Bombos[2]

[1]The National R&D Institute for Chemistry and Petrochemistry- ICECHIM, Spl. Independentei nr. 202, Bucharest,

[2]Petroleum-Gas University of Ploiesti, 39 Bucharest Blv., 100680 Ploiesti, Romania

**Corresponding author: oprescuemilia@gmail.com*

Keywords: biofuels, biomass waste, furfural, acetalization

Introduction: A main way to reduce dependence from hydrocarbons derived from crude oil and to improve the characteristics of the fuel for gasoline (diesel) engines is to apply biomass-derived oxygenated compounds [1]. Catalytic transformation of platform molecules into liquid hydrocarbon fuels appears an interesting approach for the production of advanced biofuels [2].

Furfural is one of important oxygen-containing heterocyclic compound produced from plant residues which are rich in pentoses. Furfural derivatives have high octane numbers (ON) and they are suitable compounds for blending gasoline [3].

Materials and methods: All the substances used in this study were reagent grade and purchased from Sigma-Aldrich. The final products were characterized by GC-MS/MS TRIPLE QUAD (Agilent 7890 A) method.

Results: The aim of this study was to synthesis one gasoline additive by acetalization of propylene glycol with furfural over Purolite® CT 175 macroporous strong acid resin catalyst. Optimum reactive parameters were studied. The experimental results indicates that yield in propylene glycol furfural acetal during the acetalization depends strongly on the reaction time, catalyst loading and propylene glycol to furfural molar ratio.

Conclusions: Purolite® CT 175 resin has a very good catalytic activity and selectivity in propylene glycol acetalization reaction with furfural.

Acknowledgements: *The authors gratefully acknowledge the financial support of the UEFISCDI, Romania, in the framework of National Partnership Program PN II/2013, financing contract no. 95/2014 (CARFURAL)*

References:

[1]. Chernyak MY, Tarabanko VE, Morosov AA, Kondrasenko AA. Preparative Synthesis of Furfural Diethyl Acetal Through the Direct Interaction of the Alcohol and Aldehyde. Journal of Siberian Federal University. Chemistry 2, 2016 (9) 146-151.

[2]. Climent MJ, Corma A, Iborra S. Conversion of biomass platform molecules into fuel additives and liquid hydrocarbon fuels. Green Chemistry. 2014, 16, pp. 516-547.

[3]. Tarabanko VE, Chernyak MY, Simakova IL, Kaigorodov KL, Bezborodov YN, Orlovskay NF. Antiknock Properties of Furfural Derivatives.Russian Journal of Applied Chemistry, 2015, 88 (11). pp. 1778−1782.

NON-CATALYTIC HYDROTHERMAL CONVERSION OF RESIDUAL LIGNOCELLULOSIC BIOMASS

S.O. Dima, S.M. Doncea, M. Ghiurea, R.C. Fierascu, G. Vasilievici, F. Oancea*

INCDCP ICECHIM, 202 Splaiul Independenței, 060021 Bucharest, Romania

**Corresponding author: florino@ping.ro*

Keywords: hydrothermal conversion; lignocellulosic biomass; platform molecules; hydrothermal carbon.

Introduction: Hydrothermal conversion is a thermo-chemical process by which biomass is transformed under the action of water and pressure into bio-oil, biochar, water-soluble compounds, and gases. All phases, liquid, solid and gas, contain valuable compounds like hydrothermal carbon (HTC), platform molecules, and H_2 [1].

Materials and methods: Residual lignocellulosic biomass (LCB) consisting in wheat straws and corn stalks was mechanically grinded to 1.5 mm particles and subjected to hydrothermal conversion in water, under thermally generated pressure in a hermetic reactor, at different temperatures, and for different reaction times. The temperatures applied were 140°C, 180°C, 200°C, and 220°C, for 2h, respectively 4h. The solid:liquid ratio between LCB and water was chosen after a number of swelling experiments, and an excess of water equal to the quantity necessary for saturation was used. The optimal solid:liquid ratio was considered 1:20 w/v for corn stalks and 1:14 w/v for wheat straws. At the end of the reaction, both resulting phases, solid one and liquid one, were analytically characterized using XRD, TGA, and FTIR, respectively HPLC-TOF/MS, and UV-Vis spectroscopy.

Results: FTIR analyses applied on the solid phase of hydrothermally treated corn biomass evidenced an increase in aromaticity for samples submitted to a higher temperature, which is a sign for hydrothermal carbon formation (characteristic bands at 1605, 1515, 898, 835, 663, 617 cm^{-1}). Hydrothermal treatment of wheat biomass led to a decrease in adsorption intensities of –OH groups, which suggests the LCB decomposition in phenolic compounds. Also, at higher temperatures, starting with 180°C, it was observed the intensity decreasing of $–CH_2$ and CH_3 adsorption bands, evidencing the degradation of aliphatic chains. TGA results showed a weight loss between 200°C-350°C that corresponds to hemicellulose thermal decomposition, followed by cellulose and lignin dehydration, unzipping and levoglucosan formation. Between 350°C-420°C, levoglucosan decomposes and biochar is being formed, while after 420°C, polynuclear aromatic structures and graphyte carbon are formed.

Conclusions: Hydrothermal conversion of LCB in different processing conditions revealed a variation in solid and liquid phases' composition. Mild treatment conditions led to a liquid phase rich in polyphenolic compounds, while high temperature conditions led to a high content in hydrothermal carbon, respectively furans, furfurals, and levulinic acid in the liquid phase.

Acknowledgements: *The research was funded by ANCS-UEFISCDI through the project BIOMASS-BIOPROD number PN 16.31.01.01 / 2016.*

References:

[1]. Titirici MM, White RJ, Falco C, Sevilla M. Energy Environ. Sci., 2012;5(5):6796-822.

STUDY OF OBIDOXIME ACIDO-BASE AND REDOX REACTIONS

I.G. David[1], M. Corbu[*1], V. David[1], M.C. Cheregi[1]

[1]*University of Bucharest, Faculty of Chemistry, Department of Analytical Chemistry, 4-12 Regina Elisabeta Av., 030018, Bucharest 3, Romania*

**Corresponding author: corbumarius81@gmail.com*

Keywords: obidoxime, equilibria, spectrommetric investigation, voltammetry

Introduction: Obidoxime (OBD) is an acetylcholinesterase (AChE) reactivator used for the treatment of intoxications with organophosphates and/or nerve agents [1]. Through its two oximes groups, OBD can be involved in different equilibria, e.g. acid-base and redox. Oximes acting on the human brain have the pK_a in the range 7.5-10.5 and at physiological pH their nucleophilic attack on the deactivated AChE is realized only by the oximate ion [2]. Thus, the study of OBD acid-base equilibria and the determination of its pK_a is important. On the other hand, OBD pharmaceutical action relies on redox processes which are also related to the oxime groups. This type of reactions can be investigated by electrochemical techniques which are important tools in studying biologically redox processes.

Materials and methods: OBD working solutions were freshly prepared, just before analysis, by sccessive dilutions of the 10^{-2} M OBD stock solution. Absorption spectra were recorded in 1.00 cm quarz cuvettes using an UV-VIS spectrometer (V-530 Jasco-Japan) connected to a PC running the *„Spectra Manager"* software. An electrochemical system Autolab PGSTAT 12 equipped with a 3 electrodes voltammetric cell (working electrode: a glassy carbon electrode) and a PC running the GPES4.9 software was used for voltammetric studies.

Results: For pH > 6.5 the overlaid OBD absorption spectra emphasized two isosbestic points indicating that three species are involved in two acid-base equilibria. Cyclic voltammetry showed that OBD presents an irreversible, well-defined peak atttributed to a 2 electron diffusion controlled oxidation of one of the oxime groups, whereas the other oxime group generates a broad wave at more positive potentials [3]. OBD reduction generates four irreversible and diffusion controlled waves.

Conclusions: For 6.00 <pH< 8.80 in the solution there are two absorbing species OBD^{2+} (λ = 285 nm) and OBD^{+} (λ = 353 nm) with OBD pK_{a1} = 8.05 and two irreversible oxidation peaks (at ~750 and 1600 mV) are observed in the cyclic voltammograms. In the cathodic range 4 reduction waves appear throughout the pH range 3.0 – 9.8. Since the voltammetric signals vary with OBD concentration, they can be used to develop a method for OBD quantitative determination.

Acknowledgements: *This work was supported by the Romanian National Authority for Scientific Research and Innovation, (UEFISCDI), project number* ***PN-II-PCCA 197/2014*** *and University of Bucharest, project* ***UB 1490****/2017.*

References:

[1] Narasimha Rao C, Balaji K, Narasimha Rao C, Venkateswarlu P. Polarographic reduction of pralidoxime and obidoxime at hanging mercury drop electrode. Curr World Environ. 2009;4:133-6.

[2] Musil K, Florianova V, Bucek P, Dohnal V, Kuca K, Musilek K, Development and validation of a FIA/UV–vis method for pKa determination of oxime based acetylcholinesterase reactivators. J Pharm Biomed Anal. 2016;117:240–6.

[3] Novak I, Komorsky-Lovrić Š, Žunec S, Vrdoljak AL. Anodic Behaviour of Some Bispyridinium Oximes on a Glassy-Carbon Electrode. Int J Electrochem Sci. 2013;8: 9818 – 34.

OPTIMIZATION OF PIGMENT EXTRACTION FROM A BROWN ALGAE IN THE BLACK SEA (*CYSTOSEIRA BARBATA)*

B. Trica [1,2], C. Delattre [3], A.V. Ursu [3], P. Michaud [3], G. Djelveh*[3], T. Dobre [1]

[1]*Politehnica" University of Bucharest, Splaiul Independenţei 313, 060042, Bucharest, Romania*

trica.bogdan@gmail.com
[2]*The National Institute For Research & Development In Chemistry And Petrochemistry (ICECHIM), 202 Splaiul Independentei, 060021, Bucharest, Romania*
[3]*Université Clermont Auvergne, CNRS, Sigma Clermont, Institut Pascal, BP 10448, F-63000, Clermont-Ferrand, France*
Corresponding author: gholamreza.djelveh@sigma-clermont.fr

Keywords: fucoxanthin, antioxidant

Introduction: *Cystoseira barbata* is a common brown seaweed species found in the Black Sea which is known to contain a number of valuable biomolecules. One such biomolecule is fucoxanthin which is a pigment from the carotenoid family with known biological activities such as anticancer, antiobesity, antioxidant, anti-inflammatory and neuroprotective [1]. Phlorotannins, polyphenolic compounds from brown seaweed, were also identified and quantified.The purpose of this work is to identify the optimal conditions for extracting chlorophyll and fucoxanthin and to evaluate their purity with respect to phenolic compounds and extracted dry matter.

Materials and methods: Firstly, several solvents were screened. Acetone was then used to determine the total quantity of pigment which can be extracted. Extraction in ethanol was then optimized following a full factorial two level experimental plan. Three parameters were considered: temperature, solid-liquid ratio and granulometric fraction. For each extraction, the yield was expressed with respect to the total quantity of pigment which can be extracted. Purity was also determined as a percentage from the total dried matter.

After separating the extract by vacuum filtration, chlorophyll a and b, fucoxanthin and carotenoid content was evaluated by applying some colorimetric methods proposed in literature [2]. These methods require measuring the absorbance of the extracts at various wavelengths in the UV-Vis domain. Total phenolic content was also determined using Folin-Ciocalteu reagent.

Conclusions: Fucoxanthin and chlorophyll were quantified in *Cystoseira barbata* extracts by several colorimetric methods. Ethanol extraction was then optimized following a ful factorial experimental plan by considering temperature, solid-liquid ratio and granulometric fraction as significant parameters.

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-2016-1332 and by a grant of the Romanian National Authority for Scientific Research and Innovation, CNCS/CCCDI-UEFISCDI, project number PN-III-P2-2.1-BG-2016-0142, within PNCDI III.

References:

[1]. Kim, S.-K. and R. Pangestuti, *9 Biological Activities and Potential Health Benefits of Fucoxanthin Derived from Marine Brown Algae.* Advances in food and nutrition research, 2011. **64**: p. 111.
[2]. Seely, G.R., M.J. Duncan, and W.E. Vidaver, *Preparative and analytical extraction of pigments from brown algae with dimethyl sulfoxide.* Marine Biology, 1972. **12**(2): p. 184-188.

NOVEL EMULSION BASED- COSMETIC FORMULATIONS USING NATURAL INGREDIENTS

C. Scomoroscenco[1*], L.O. Cinteza[1], C. Chifiriuc[1], M. Bucur[1], C.L. Nistor[2], C. Petcu[2]

[1] *University of Bucharest, Physical Chemistry Department, 4-12 Elisabeta Blvd, Bucharest, Romania;* [2] *National R&D Institute for Petrochemistry and Chemistry ICECHIM, 202 Spl. Independentei, Bucharest, Romania*

** Corresponding author: scomoroscencocristina@gmail.com*

Keywords: natural surfactant; cosmetic emulsion; macadamia oil; essential oils.

Introduction: Nature offers a lot of material that can be used in cosmetic formulation. The objective of this work is to obtain a stable cosmetic emulsion using exclusively natural products [1]. Vegetable oils are used as oily phase, since they can act as good moisturizing agents with antioxidant proprieties and affinity for skin. Nonionic natural surfactants were used as stabilizers, and to avoid the synthetic preservatives, such as benzoate, essential oils are added as natural and efficient preservative agents. Macadamia oil (as oily phase) used in this study, was obtained by cold pressing method from the *Macadamia integrifolia* nuts [2]. Development of the emulsions is based on HLB and required HLB approach, in order to minimize the concentration of surfactant mixture, but in the same time to obtain a stable cosmetic emulsion. The prepared cosmetic emulsions were characterized by determination of the droplet size, appearance and viscosity. Some essential oils were studied as both as possible active ingredients with anti-aging effect and as preservative, replacing the synthetic reagents used in the commercial cosmetic creams [3].

Materials and methods: *Macadamia integrifolia* oil, Cetearyl glucoside, Cetearyl olivate, Sorbitan olivate, Glyceryl Stearate, Sucrose tristearate as emulsifiers and distilled water. ULTRA – TURRAX was used for homogenization. Optical microscop MOTIC and Malvern Zetasizer Nano ZS ZEN3600 was used for see particle size of emulsion formulation.

Results:

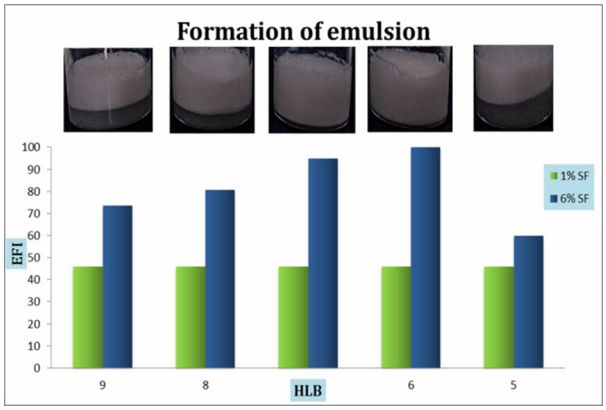


Figure 1. Variation of emulsion formation index EFI with HLB for the systems containing macadamia oil and surfactant blend

Conclusions: Novel emulsions with Macadamia oil with high stability based on exclusively natural ingredients was obtained as cosmetic cream.

References:

[1]. Mohammad A., Syed MN. Taxonomic perspective of plant species yielding vegetable oils used in cosmetics and skin care products. Afr. J. Biotechnol. 2005; 4 (1):36 – 44

[2]. Naveed A, Mahmood A, Asadullah M, Malik SB. EVALUATION OF BASIC PROPERTIES OF MACADAMIA NUT OIL. 2006; Gomal Univ J Res. 22 (1):21 -27

[3]. Bruna FMTA, Lidiane NB, Isabella SP, Ary FJ. Antimicrobial activity of essential oils. J ESSENT OIL RES. 2014; 26 (1):34-40

ASSESSING THE ELECTROPERMEABILIZATION OF MICRO-ALGAE CELLS MEMBRANE BY EXPOSURE IN ELECTRIC FIELDS

N. O. Butoi[1], C. Mateescu[*1], A.M. Luchian, A. Voina

[1]*National Institute for Research and Development in Electrical Engineering ICPE-CA Bucharest*

** Corresponding author: carmen.mateescu@icpe-ca.ro*

Keywords: microalgae suspension, electroporation, electrical conductivity

Introduction: Experimental research has been carried out having as main objective to identify the behavior of the *Chlorella sorokiniana* micro-algae after exposure in continuous, respectively alternative electric fields. The research interest was addressed to the electroporation phenomenon which can cause irreversible alterations of the cell membrane, therefore increasing its permeability. For assessing the electropermeabilization of the cell membrane, electrolyte leakage in the aqueous slurry was monitored by studying changes in the electrical conductivity of the aqueous environment.

Materials and methods: An algal suspension of *Chlorella sorokiniana*, prepared in the laboratory of the pure UTEX 1230 culture and culture medium BG 11 was used for experiments. Samples were exposed for a total duration of 96 hours in an experimental device developed for generating DC electric fields of different intensities, as well as AC fields with frequencies of 15 and 50 Hz. In parallel to these experiments, the same treatment was applied for a blank sample (p_2).

Results: An increase in the electrical conductivity of the samples exposed in electrical field was observed from the initial measurements, reaching a maximum of 1.94 mS / cm for the sample exposed over a period of 96 hours at an alternating 15 Hz electric field with a field intensity of 20,752 V / m.

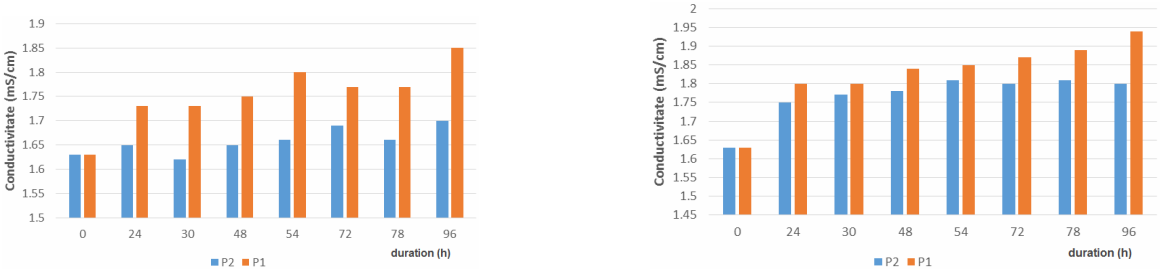


Figure 1. Conductivity-time variation for samples exposed in DC electric field (left), respectively AC (right)

Conclusions: Experimental results indicate an increase in the total concentration of ions in the algal suspension samples exposed in DC and AC electric fields. This behavior could be explained by a permeabilization of the micro-algae cell membrane with the formation of pores, followed by cell salts release. This experimental research can be applied for developing improved micro-algae species to provide better yields in biorefinary processes.

Acknowledgements: *The results presented in this paper were achieved under the research project Nucleu 5301/2016*

References:

[1]. Kanhaiya Kumar, Chitralekha Nag Dasgupta, Debabrata Das Cell growth kinetics of Chlorella sorokiniana and nutritional values of its biomass, Bioresource Technology 167 (2014) 358–366.

[2]. Hassan Nezammahalleh, Faezeh Ghanati, Thomas A. Adams II, Mohsen Nosrati, Seyed Abbas Shojaosadati, Effect of moderate static electric field on the growth and metabolism of Chlorella vulgaris, Bioresource Technology 218 (2016) 700–711

BIOCHEMICAL HYDROLYSIS OF α-PINENE OXIDE USING LIMONENE-1,2-EPOXIDE HYDROLASE ENZYME

S. Ion[1], M. Sandulescu[1*], V. Parvulescu[1]

[1]*Department of Organic Chemistry, Biochemistry and Catalysis, Faculty of Chemistry, University of Bucharest, Regina Elisabeta Blvd., no. 4-12, Bucharest 030016, Romania*

**Corresponding author: madalina.sandulescu@g.unibuc.ro*

Keywords: α-pinene oxide, LEH, enzyme, hidrolysis, diols.

Introduction: Limonene-1,2-Epoxide hydrolase enzyme (LEHs) is a new family of enzymes able to catalyse the hydrolysis process of the epoxide ring, producing diols with many applications in the industry of chemicals and drugs [1]. We propose the transformation of α-pinene oxide into different diols using limonene-1,2-epoxide hydrolase enzyme.

Materials and methods: Six types of enzymes were tested in the hydrolysis reaction of α-pinene oxide: Re-LEH, Tomsk-LEH, CH55-LEH, Tomsk-LEH-W62V, CH55-LEH-W60V and Sibe-EH. Methanol, ethanol, tetrahydrofurane, 2-methyl-tetrahydrofurane, acetonitrile and dimethylsulfoxide were used as reaction solvent. The reaction products were monitored calculating the conversion and selectivity after 4.5 h and 24 h reaction time (GC-MS analysis).

Results: Tomsk-LEH enzyme lead to the highest conversion in methanol (30.04 %) in comparison to the other tested enzymes (4.5 h reaction time). Also, using W62V variant, the highest selectivity into decahydro-2,7-naphtalenediol, 1-isopropenyl-4-methyl-1,2-cyclohexenediol and 1,7,7-trimethylbicyclo[2.2.1]heptane-2,5-diol were achieved (34.23 %). Dimethylsulfoxide allowed to achieve smaller conversions of α-pinene oxide (between 12.61 % for Tomsk-LEH enzyme and 18.33 % for Re-LEH enzyme) than acetonitrile, where the conversion of α-pinene oxide varied between 21.19 % for Sibe-EH enzyme and 35.83 % for Tomsk-LEH enzyme. The enzymes were also tested for 24 h reaction time and Tomsk-LEH-W62V enzyme in tetrahydrofurane converted 55.95 % α-pinene oxide into diols with 80.45 % selectivity.

Conclusions: The highest selectivities into diols were obtained for Tomsk-LEH enzyme (81.13 %) and for W62V variant (79.47 %) in the presence of dimethylsulfoxide for 4.5 h reaction time and for Tomsk-LEH-W62V enzyme in tetrahydrofurane (80.45 %) for 24 h reaction time.

Acknowledgements: *This work was financially supported by the PN II RU program, UEFISCDI, Romania (BioModAL project, contract no. 103/2015). We thank to Ms Daniela Monti for providing the enzymes.*

References:

[1]Ferrandi EE, Sayer C, Isupov MN, Annovazzi C, Marchesi C, Iacobone G, Peng X, Bonch-Osmolovskaya E, Wohlgemuth R, Littlechild JA, Monti D, FEBS J. 2015; 282(15):2879-94 (Discovery and characterization of thermophilic limonene-1,2-epoxide hydrolases from hot spring metagenomic libraries).

MODIFIED CARBON PASTE ELECTRODES WITH DIFFERENT NANOPARTICLES FOR VOLTAMMETRIC DETECTION OF FISETIN

L.I. Jinga[1], D. Bala[*1], L.O. Cinteză[1], C. Mihailciuc[1]

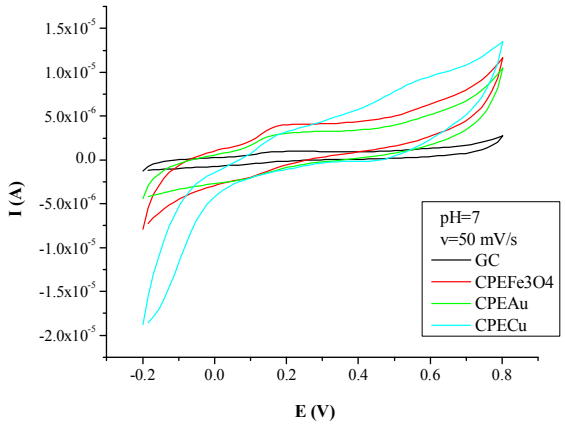
[1]*Physical Chemistry Department, Faculty of Chemistry, University of Bucharest 4-12 Regina Elisabeta, 030018, Bucharest*

**Corresponding author: daniela_bala@yahoo.com*

Introduction: Fisetin (3,3′,4′,7-tetrahydroxyflavone) is a bioactive molecule belonging to flavonoids. It was found in fruits and vegetables, such as strawberry (160 μg/g), apple (26.9 μg/g), persimmon (10.5 μg/g), and in lower concentrations in grape, onion and cucumber. Flavonoids have the ability to scavenge free radicals thus they have antioxidant activity. Fisetin presents activity as a reducing agent which can neutralize reactive oxygen species. This activity is due to its electron donating capacity, resulted from the presence of two hydroxyl groups on one ring and a hydroxyl group on another ring. Therefore it is important to know the redox behavior of fisetin [1-4].

Materials and methods: The electrochemical study was carried out in Britton-Robinson buffer solutions of different pH values (4, 5, and 7), using two voltammetric techniques (cyclic voltammetry, and differential pulse voltammetry) at various speed scan values. In order to increase the response of electrochemical active species, we fabricated several modified carbon paste electrodes (CPE), based on a mixture of paraffin oil-graphite and metal nanoparticles such as: magnetite, copper and gold [5].

Results: The dimensions of nanoparticles were determined. The best results were obtained with CPE modified with copper nanoparticles as working electrode. Therefore it was used for monitoring the fisetin from one type of strawberry wine.



Conclusions: Fisetin has a complex redox behaviour due to pH values of the buffer solution and the scan speed.

References:

[1]. A.Waldiceu Verri Jr, T.M.C.F Vicentini, M. Baracat, S.R.G. Cardoso, T.M. Cunha, S.H. Ferreira, F.Q. Cunha, M.J.V.F. and R. Casagrande, Bioactive Natural Products, 2012, Vol. 36. 297-330
[2]. E.S. Gil, R.O. Couto, Revista Brasileira de Farmacognosia Brazilian Journal of Pharmacognosy, 2013 23(3) 542-558,
[3]. J.M. Weber, A. Ruzindana-Umunyana, L. Imbeault, S. Sircar, Antivir Res., 2003 58 167–73
[4]. J. Alvesalo, H. Vuorela, P. Tammela, M. Leinonen, P. Saikku, P. Vuorela Biochem Pharmacol., 2006 71, 735–41
[5]. E.M. Maza, M.B. Moressi, H. Fernández, M.A. Zon, Journal of Electroanalytical Chemistry, 2012, 675, 11–17

THE DIFFERENTIAL STABILIZATION EFFECTS OF SOME NATURAL ANTIOXIDANTS ON γ IRRADIATED/UV-EXPOSED EPDM

A. M. Luchian[*1], **T. Zaharescu** [1], **M. E. Lungulescu** [1], **N. Butoi** [1]

[1] *INCDIE ICPE-CA, 313 Splaiul Unirii, Bucharest, Romania, 030138*

**Corresponding author: anamaria.luchian@icpe-ca.ro*

Keywords: weathering, γ irradiation, EPDM, degradation, antioxidant

Introduction: The present work presents an overview of the differences in the stabilization effects of natural antioxidants on EPDM that is subjected to UV and γ exposure. Gallic acid and rosemary are instances for improving oxidation resistance of this polymer as a representative example for polyolefins. The assessment of EPDM stability under accelerated oxidation aims to qualify it for long term applications.

Materials and methods: For the evaluation of the effect of natural antioxidants on the stability on γ-irradiation and artificial weathering, gallic acid and rosemary extracts were added to EPDM by dissolution in chloroform solution of the basic polymer. The dose rate of 1.29 kGy h^{-1} was applied for the different total radiation doses: 0, 25, 50, 100 and 200 kGy respectively. In parallel, the indoor weathering aging was performed for three different times: 0, 47 and 71 hours. Three analytical methods, chemiluminescence, FT-IR spectroscopy and UV-Vis spectroscopy were selected for this study in order to emphasize the oxidation development.

Results: The promotion of oxidative degradation by high energy and weathering exposures is restricted due the activities of used additives in respect with radical scavenging. Because of the stabilization, efficiency depends on the proton liability of hindered hydroxyls. Even though the progress of degradation rates increases with absorbed dose, the promotion intensities of oxidation on low temperature range is related to the protector ability for the inhibition of oxidation.

Conclusions: The stability behavior of EPDM modified by the addition of two efficient antioxidants namely gallic acid and rosemary powders was analyzed after the exposure to γ rays and weathering aging. The experimental results indicate that there is a main difference between the two degradation processes, because of the different variation of radical concentrations. In both cases, gallic acid proves a more revealed barrier for the progress of aging, inhibiting EPDM degradation with a higher efficiency.

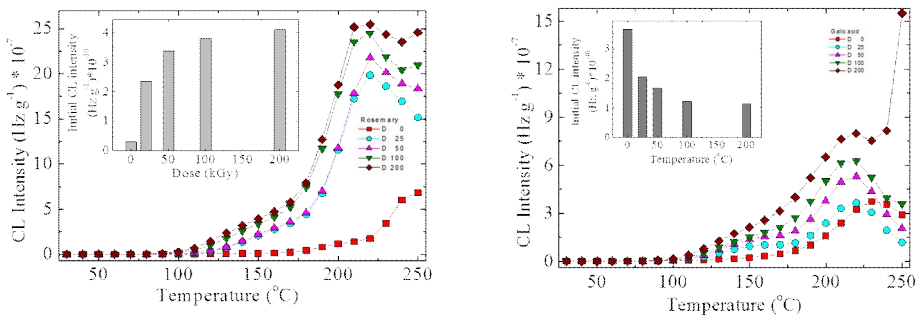


Figure 1. Nonisothermal chemiluminescence spectra of irradiated EPDM with rosemary (a) and EPDM with gallic acid (b) at high dose

Acknowledgements: *The results presented in this paper were achieved under the research project Nucleu 5211/2016*

References:

[1]. Rivaton A, Cambon S, Gardette JL. Radiochemical ageing of ethylene-Propylene-Diene elastomers. 4. Evaluation of some anti-oxidants. Polym Degrad Stabil. 2006; 91(1):136-143

BIOCHEMICAL AND MICROBIOLOGICAL STUDY CONCERNING IDENTIFICATION ROLE OF HYDROLASE ACTIVITIES ENZYMES (CHITINASE, LIPASE AND PROTEASE) FROM *TRICHODERMA HARZIANUM* AND *TRICHODERMA KONINGII* IN PATHOGENIC FUNGUS *F. OXYSPORUM* INHIBITION

M.N. Radhi[*1], F. Constantinescu [2], I. Roşca[1], H.B. Farhood[3], H. Abd- Al adheem[4], G. Stoian[3]

[1] Agricultural and Veterinary Sciences University of Bucharest; [2] Research Development Institute for plant protection, Băneasa, Bucharest, [3]University of Bucharest, Department of Biochemistry and Molecular Biology,[4]Faculty of medicine University of Thi-Qar/Iraq

Corresponding author: mradhi84@yahoo.com

Keywords: Trichoderma harzianum, Trichoderma koningii, F.oxysporium Chitinase, Lipase, Protease.

Introduction: The genus *Trichoderma* are a very large group of microorganisms that play a significant role in plant protection. Several *Trichoderma spp*. like *Trichoderma harzianum* and *Trichoderma koningii* strongly affected plants by stimulating plant growth, and protecting plants from fungal and bacterial pathogens such as *Fusarium oxysporium*. They are used as a biological plant protection as bio fungicides Members of the *Trichoderma spp*. are also utilized in different branches of industry -principally in the enzymes, antibiotics, and other metabolites. In this study we focus in the effect of *T. harzianum* strain ICCF 417 and *T.koningii* strain ICCF 418 on *F.oxysporum* (ZUM 2407) by microbiologic and enzymatic tests.

Materials and methods: Determination of the optimal density of *T.harzianum*, *T.koningii* and *F.oxysporium* on liquid medium malt extract., determination the optimum pH for enzymes activity, the ability of fungi *T.koningii* and *T.harzianum* to produce enzymes in liquid synthetic medium, determination of protein levels in liquid synthetic medium of enzyme from out cell and in cell of *T.koningii* and *T.harzianum* and characterization of enzymes that produced from *T.koningii* and *T.harzianum* that effect on *F.oxysporium* in PDA medium. **Results:** the results of fungal growth speed of the malt medium showed that the fungus *T. Koningii* was the fastest in growing, followed by *T. harzianum* and *F. oxysporium* after 72 hours of culture. While the degree of antagonism was 1 according to Bell scale in petri dish on the PDA medium the ability of fungi *T.harzianum* and *T. koningii* to overcome on fungus *F.oxysporium*. The results of the study showed the susceptibility of bio-fungi on production of an enzyme chitinase was 113.93 % in *T. harzianum* comparative to *T. koningii*, the lipase was 38.53% in *T.harzianum* comparative to *T. koningii* after 14 days of fermentation while the protease was 91.43 % in *T.harzianum* comparative to *T.koningii* after 30 days of fermentation. Also the optimum pH is measured and its results showed that the highest activity of chitinase was at pH=6, for lipase the highest activity was in pH= 9 and protease was pH= 6.**Conclusions:** Our results have been shown the inhibitory effect of *Trichoderma spp* which is represented by *T.harzianum* and *T.Koningii* against pathogen *F.oxysporum* by production of intracellular protein factors and extracellular enzymes which may effect on the action *F.oxysporum*.

Acknowledgements: *This work was carried out at the University of Bucharest Faculty of Biology and supported by the Iraqi government*

References:

[1]. Booth, C. The Genus Fusarium. Commonwealth Mycological Institute,1971. Kew, Surrey, United Kingdom
[2]. Abu hella, Abdullah bin Nasser.Basics mycology. Printer King Saud University. 1987.King Saud University Saud, page54
[3]. Walker, J. Fusarium wilt of tomato.1971. Monograph No-6-Puplished by the American Psychopathological Society. University Avenue. Stpaukl, Minnesota. PP: 56.
[4]. Bower, J.H., Cook,J.C. Effect of botanical extracts on the population density of Fusarium oxysporum in soil and control of Fusarium wilt in the greenhouse. Plant Dis.2000.84:300-305.
[5]. Rowe, R.C. and Farley, J.D. Strategies for controlling Fusarium crown and root rot in greenhouse tomatoes. Plant Dis.1981. 65: 107-112.

HYBRID SILICA PARTICLES WITH ENHANCED ANTIMICROBIAL ACTIVITY

C.L. Nistor[1], S.G. Nitu[*1], R. Ianchis[1], C. Petcu[1], E. Alexandrescu[1], I.C. Gifu[1], C.M. Ninciuleanu[1], R. Somoghi[1], B. Trica[1]

[1]National Research&Development Institute for Chemistry and Petrochemistry – ICECHIM
Splaiul Independentei no.202, 6th district, P.O. 35-174, 060021, Bucharest, Romania;
**Corresponding author: sabina.nitu@yahoo.com*

Keywords: hybrid silica particles, essential oils, antimicrobialactivity.

Introduction: Essential oils are aromatic medicinal compounds which are obtained from different aromatic plants and are used for various purposes: skin cleansing and skin tonicity, hair wetting and nourishment, wellness massage and therapeutic effects [1]. Therefore, use of such oils, in addition to inhibiting the growth of food infecting bacteria and molds, as well as increasing the shelf life of processed foods in the food system, due to the existence of aromatic compounds in their compositions, improves the flavor of food and results in increased consumer satisfaction [2]. Present work studies the possibility to encapsulate different types of essential oils such as: cloves, eucalyptus, tea tree, basil, thyme, cinnamon oil in silica particles.

Materials and methods: Silica network was realized by the sol-gel process between tetraethyl orthosilicate (TEOS) and dodecyl triethoxysilane (DOTES) in oil-in-water emulsion systems at 1:10 DOTES/TEOS molar ratio. Polyoxyethylene 10 oleyl ether (Brij O10) was used as tensioactive agent.

Particles dimensions, size distributions and particle charging of the final dispersions were evaluated by dynamic light scattering (DLS) technique and Zeta potential measurements. Surface morphology was observed by SEM. FTIR analyses were used to prove the entrapment of essential oils into silica matrix. The final dispersions were also evaluated for the effectiveness of the antimicrobial/antifungal effect.

The samples were dialyzed into dialysis tubes (Spectra/Por1 Dialysis Membrane) using aqueous Tween 20 solution. The washed, dried and calcined samples were thereafter investigated by N_2 adsorption-desorption analyses.

Results: Homogeneous and stable silica –essential oil dispersion were obtained. The type of essential oil influenced the particles dimensions, size distributions and particle charging of the final dispersions as well as the surface morphology and biological activity.

Conclusions: The all corellated analyses results proved the efficient encapsulation of the different types of essential oils.

Acknowledgements: *This work was supported by the grant funded by the Romanian National Authority for Scientific Research, project number PN 16.31.03.04.04 and by a grant of the Romanian National Authority for Scientific Research and Innovation, CNCS/CCCDI-UEFISCDI, project number 94BG/2016 (PN-III-P2-2.1-BG-2016-0142), within PNCDI III.*

References:

[1]. Filiptsova O.V., Gazzavi-Rogozina L.V., Timoshyna I.A., Naboka O.I., Dyomina Ye.V., Ochkur A.V., The essential oil of rosemary and its effect on the human image and numerical short-term memory, Egyptian Journal of Basic and Applied Sciences, 2017, 4:107-111.

[2]. Gharenaghadeh S., Karimi N., Forghani S., Nourazarian M., Gharehnaghadeh S., Vahidjabbari, Sowtikhiabani M., Samadi Kafil H., Application of Salvia multicaulis essential oil-containing nanoemulsion against food-borne pathogens, 2017,19:128-133.

RAPID EXTRACTION AND DETECTION OF FORBIDDEN CARCINOGENIC AMINES FROM TEXTILE MATERIALS

E. Perdum[1,2*], I. Dumitrescu[1], E. Visileanu[1], C.E. Mitran[1], O.G Iordache[1], R. Radulescu[1]

[1] *National R&D Institute for Textiles and Leather Bucharest (INCDTP) 16 Lucretiu Patrascanu, 030508 Bucharest, Romania;*

[2] *University of Bucharest, Faculty of Chemistry, Department of Analytical Chemistry, 90-92 Panduri Street, 050663 Bucharest, Romania*

Corresponding author: elena.varzaru@certex.ro

Keywords: carcinogenic amines, textile ecology, HPLC-MWD, GC-MS, ASE

Introduction

Textile manufacture utilises a wide range of chemicals that can be harmful to the environment, to people working in textile processing and to consumers. Regulation as Oeko-Tex Standard 100 clasifies several dyestuffs and pigments as carcinogenic; among them are Disperse Blue 1 and Disperse Yellow 3, dyes used to dye synthetic fibres, such as nylon, polyester and polyvinyl and acrylic fiber. Disperse Blue 1 is a blue to black colored aminoanthraquinone dye; exposure to disperse blue 1 irritates the eye and skin. It is also known to be mutagen and is reasonably anticipated to be a human carcinogen. Disperse Yellow 3 is an azo compound, in form of a brownish-yellow powder. It appears to be resposible for allergic, contact type dermatitis induced by nylon stockings tinted by this color. It has been reported that dyes toxicity may happen due to either the direct action of the original compound or its intermediate metabolites such as naphthalene, benzidine, and other aromatic amines, and also hydrazine compounds. Those compounds are by-products of cleavage of azo bond by microorganisms, and reported to be carcinogenic and mutagenic. In this paper, we investigated a rapid method of extraction and identification of other toxic compounds that are not prohibited by regulation, but are derived from common textile dyes.

Materials and methods:

2 dyed polyester fabrics have been used to extract and reduce Disperse Blue 1 and Disperse Yellow 3 to by products. A mass of 1 g textile material of each sample was soaked in 3 mL citrate buffer solution and 3 mL sodium dithionite for 5 min. Textile materials and solutions were transfered to ASE cell containing a glass fiber filter. After the extraction, using ASE conditions listed above, 1 µL of the extract were injected in GC-MS system for detection of components.

Results:

Compounds resulted after ASE extraction and detection by GC-MS for sample dyed with Disperse Blue 1 are: carbonic dihydrazide, hydrazine, methyl-4-(hydrazinocarbonyl)-benzoate, and hydrazinecarboxamide and for sample dyed with Yellow 3 are: antraquinone, carbonic dihydrazide, methyl 4-(hydrazinocarbonyl)benzoate, hydrazine.

Conclusions: In this paper, a new method of extraction and detection of toxic compounds from dyed textile materials was described. GC-MS analysis revealed toxic substances that are not prohibited by regulation, but represent a danger for human health.

Acknowledgements: The authors acknowledge the financial support of the Romanian Authority for Scientific Research and Innovation (ANCSI) in the frame of the Nucleu Programme, contract PN 16 34 04 05.

DETERMINATION OF CHITIN IN THE CELL WALL OF *SACCHAROMYCES CEREVISIAE* BY FLUORESCENCE SPECTROSCOPY

A. Dahham[1], C.V. Popa[*1], L.L. Ruta[1], I.C. Farcasanu[1]

[1]*Department of Organic Chemistry, Biochemisty and Catalysis, Faculty of Chemistry, Bucharest University, Sos. Panduri 90-92, Bucharest, Romania*

**Corresponding author: popa_vali2006@yahoo.com*

Keywords: chitin, cell wall, Saccharomyces cerevisiae, fluorescence spectroscopy

Introduction: Chitin is the second most abundant biomaterial in the living world, being surpassed only by cellulose. Chitin is industrially extracted from crab and shrimp shells obtained as a byproduct in the seafood industry, but the production of chitin and chitosan from fungal sources has gained increased attention in recent years due to potential advantages over the current source. It is a characteristic component of the *cell walls of fungi*, including the model yeast *Saccharomyces cerevisiae* [1-3].

Materials and methods: The main purpose of our work was to engineer *S. cerevisiae* cells for the overproduction of chitin at the cell wall level by obtaining yeast strains which overexpress chitin synthase. In this study we developed a fluorescence spectroscopy assay based on the chitin trait to form a fluorescent complex with calcofluor white (CFW). We present the determination of chitin both in live cells and in isolated cell walls.

Results: When bound to chitin, CFW exhibits fluorescence with emission spectra ($\lambda_{exitation}$ = 425 nm) are significantly different from the spectra of pure dye. The fluorescence intensity of the chitin-CFW increased with increasing of number of cells until cell density of 4 x 10^6 cells/mL.

Conclusions: Cells overexpressing chitin synthase 3 showed increased fluorescence, indicating that the proposed method can be used to monitor the amount of chitin in the yeast cell wall.

Acknowledgements: *This work was supported by the Executive Unit for Higher Education, Development, Research and Innovation Funding – UEFISCDI, Romania, under Grant PN-II-PT-PCCA-2013-4-0291*

References:

[1]. Darken M.A. Absorption and transport of fluorescent brightener by microorganisms. Appl. Microbiol. 1962; 10:387–393.
[2]. Piasek. J., Hoskova B. Solvatochromic effect in the optical spectra of calcofluor and its is relation to fluorescent staining of yeast cell wall. J. Fluoresc. 2010; 20:343-652.
[3]. Zinser E., Daum G. Isolation and biochemical characterization of organelles from the yeast *S. cerevisiae*. Yeast. 1995; 11:493-536.

PRELIMINARY STUDIES FOR OBTAINING BIOSURFACTANTS FROM MICROORGANISMS ISOLATED FROM NATURE

M.G. Soare[1,2*] , M. Moscovici[2], I. Lupescu[2], O. Popa[1], N. Babeanu[1]

[1]*University of Agronomic Sciences and Veterinary Medicine, Bucharest, Mărăşti Blv., 59, 011464, Romania,*

[2]*National Institute for Chemical Pharmaceutical Research and Development-ICCF, Bucharest, Vitan Avenue, 112, Bucharest, Romania*

**Corresponding author: marianagratielavladu@gmail.com*

Keywords: biosurfactants, Bacillus sp., Pseudomonas sp., emusifying index, surface tension.

Introduction: Biosurfactants are bioactive compounds used for reducing the surface tension. In the biosurfactants group are included various chemical structure compounds: lipopeptides, polysaccharides.These compounds play a very important role in the survival and the development of microorganisms that produce them. The biosurfactants as the glycolipides, lypopeptides and lypoproteines have, beyond the obvious role in bioavailabilty of the substrate, antimicrobial and antiviral action. Due to their unique properties the biosurfactants can be used in agriculture, bioremediation, chemical, pharmaceutical and food industry [1]. Either way being constituents of the cellular membrane or part of microbial metabolism they are produced both by bacteria, yeasts and fungi. Among bacteria, the species of *Bacillus* and *Pseudomonas* genus registered the best results regarding the biosurfactants production [2].

During experiments our goals was to obtain biosurfactants with strains from *Bacillus* and *Pseudomonas* genus, isolated from nature.

Materials and methods: Two of the previously selected microorganisms, *Bacillus mycoides* respectively *Pseudomonas putida,* because of their proved antimicrobial activity against a few phytopathogens, were tested for the capacity to produce biosurfactants on Luria Bertani and King B culture media. The biosurfactants production was evaluated in supernatant [3]. The supernatants of the *Bacillus mycoides* and *Pseudomonas putida* strains were tested for their capacity of emulsifying the sun flower oil, heptane and octane. In this case, the emulsifying index was calculated using the formula: E_{24}= (Height of emulsion layer/Height of total liquid column)*100. The experiments were performed in triplicate.

Results: The results obtained indicate that the biosurfactants emulsifying index for the sun flower oil of the two strains registered values comparable with those from literature. The biggest emulsifying index were obtained for *P. putida* strain on LB medium. These emulsions presented a good stability.

Conclusions: *P. putida* strain obtained the best results regarding the emulsifying capacity of sun flower oil, heptane and octane and the emulsions were stable for more than two months. The future researches with optimized media could enhance the production of the biosurfactants .

References:

[1]. Vijayakumar S, Saravanan V. Biosurfactants-Types, Sources and Applications. Research Journal of Microbiology, 2015; 10: 181-192.

[2]. Olteanu V, Sicuia OA , Ciuca M , Cirstea DM , Voaides C, Campeanu G, Cornea CP. Production of biosurfactants and antifungal compounds by new strains of *Bacillus* spp. isolated from different sources. Rom. Biotech. Lett., 2011, 16 (1): 84-91.

[3]. Cornea CP, Israel-Roming F, Sicuia OA, Voaides C, Zamfir M, Grosu-Tudor SS. Biosurfactant production by Lactobacillus spp. strains isolated from Romanian traditional fermented food products, 2016; 21. 11312-11320.

NEW HYDRAZIDE DERIVATIVES WITH ANTI-TUMOUR ACTIVITY

L. Matei[1], V.N. Stoica[2], A. Tatibouët[3], P. Ioniţă[2], C. Limban[4], C. Bleotu[1,5], I. Zarafu[2*]

[1]Ştefan S Nicolau Institute of Virology, Romanian Academy, Romania
[2]Faculty of Chemistry, University of Bucharest, Romania
[3]University of Orleans, ICOA-UMR7311, CNRS, France
[4]Carol Davila University of Medicine and Pharmacy, Romania
[5]Faculty of Biology, University of Bucharest, Romania
**Corresponding author: zarafuirina@yahoo.fr*

Keywords: Hydrazides, Hydrazones, 1,3,4-Oxadiazoles, Synthesis, Anti-tumour potential.

Introduction: The aim of our study was to synthesize some new hydrazides, hydrazones, and their 1,3,4-oxadiazole derivatives starting from 2-(phenoxymethyl)-benzoic acids, and to evaluate their anti-tumour potential.

Materials and methods: The new compounds were synthesized starting from isoniazid and 2-(4-substituted-phenoxymethyl)-benzoic acids. NMR spectra were recorded on a Varian Inova-400 spectrometer at selected temperatures, in deuterated solvent DMSO-d_6, isotopic purity 99.9%. IR spectra were recorded on a Bruker Vertex 70 spectrometer (solid sample, ATR). Melting points were determined with a Böetius apparatus and device Krous. MS spectra were recorded on MS type Agilent G1948B. *In vitro* evaluations of biological effect were performed on HCT-8 and HT-29 cell lines. In order to establish the anti-tumour potential of new compounds, the cells were treated for 24, 48, and 72 hours and cytotoxicity was evaluated using CellTiter kit. For quantification of apoptosis induction 2 methods were used: flow cytometry (Annexin FITC-propidium iodide kit) and Real Time PCR (expression of some genes involved in apoptosis). Also, effects of new compounds on cell cycle progression were evaluated by flow cytometry after staining of treated cells with propidium iodide and by relative quantitation of some cell cycle checkpoint genes by RT-PCR.

Results: Starting from isoniazid and 2-(4-substituted-phenoxymethyl)-benzoic acids thirteen new compounds were synthesized and purified. Their structures were established on the basis of NMR, IR, and mass spectral data. Regarding their biologic activity, the most toxic compounds proved to be hydrazones. As such, one of them induced apoptosis in 54% of cells after 72 hours, an effect that was preceded by the increased expression of caspase 3 and 7 at 24 hours. Also, all newly obtained hydrazones determined blocking of G1 phase.

Conclusions: Newly synthesized hydrazones seemed to present anti-tumour potential and the investigation of their action mechanism on cell cycle could bring some new significant data concerning their activity potential.

Acknowledgements: *This work was supported by CNCSIS–UEFISCSU, projects PCCDI III-116 BG/2016 and PCCDI III-52 PTE/2016.*

FLOW INJECTION SYSTEM INTEGRATING A GLUCOSE BIOSENSOR FOR MONITORING THE ALCOHOLIC FERMENTATION OF WINES

Ana Maria Titoiu [1, 2], Raluca Munteanu [1,2], Petru Epure[3], Roxana Porumb[4], Elena Brinduse[4], Szilveszter Gáspár [1], Alina Vasilescu[1*]

[1] International Centre of Biodynamics, 1B Intrarea Portocalelor, 060101, Bucharest, Romania
[2] University of Bucharest, Faculty of Chemistry, 90-92 Sos Panduri, Bucharest, Romania
[3] Epi-Sistem SRL, Brasov, Romania
[4] Institute for Research and Development in Vinegrowing and Winemaking (ICDVV) Valea Calugareasca,1 Valea Mantei, Valea Calugareasca, Prahova, Romania.
**Corresponding author: avasilescu@biodyn.ro*

Keywords: alcoholic fermentation; glucose; enzyme biosensor; flow injection system; screen-printed electrodes.

Introduction: The aim of the study was to develop a flow injection analysis (FIA) system, which allows monitoring the evolution of glucose concentration in the alcoholic fermentation of wines.

Materials and methods: A commercial glucose biosensor was used at the heart of the FIA system. This biosensor gives a glucose-proportional current signal through a cascade of reactions involving glucose oxidase (GOx) and $[Fe(CN)_6]^{4-}$ immobilized into the electrode. However, we had to make several adjustments in order to make this single-use glucose biosensor suitable for monitoring glucose in fermentations. The biosensor was completed in the FIA system with a flow-through cell, a peristaltic pump, an injection valve and a computer-controlled potentiostat.

Results: The commercial glucose biosensor was found to retain very well GOx but to leak out the $[Fe(CN)_6]^{4-}$ necessary for working at low, interference free, applied potential. Therefore, we used the FIA system with a running buffer which continuously supplies the biosensor with $[Fe(CN)_6]^{4-}$. In these conditions, the glucose sensor showed good stability (allowing glucose determinations for at least 5 days), and a linear range of 0.06 - 1 mM glucose. The experimental protocol was optimized for maximum sensitivity and minimized interferences and was successfully applied for monitoring an in-house fermentation. The concept of the FIA system was also transferred into an automated system for monitoring industrial fermentations.

Conclusions: The developed FIA system for glucose determination is adequate for monitoring wine fermentation and could be easily automated. Further optimization will concentrate on eliminating the need of added mediator and extending the linear range of the biosensor by using membranes.

Acknowledgements: *Financial support from the UEFISCDI, Romanian Ministry of National Education and Research for Manunet II project SENS4WINE, contract 32/14.06 2017 is gratefully acknowledged.*

SYNTHESIS AND ANION BINDING ABILITY OF BISHYDRAZIDE DERIVATIVES OF AZULENE

M. Tudor[1,2], A. Hanganu[1,2], A. E. Ion[1], D. Bala, S. Nica[1*]

[1]*Institute of Organic Chemistry "C. D. Nenitzescu" of the Romanian Academy, Splaiul Independentei 202B, 060023, Bucharest, Romania*

[2]*Faculty of Chemistry, University of Bucharest, Blv. Regina Elisabeta, no. 4-12, 030018, Bucharest, Romania*

**Corresponding author: simona.nica@ccocdn.ro*

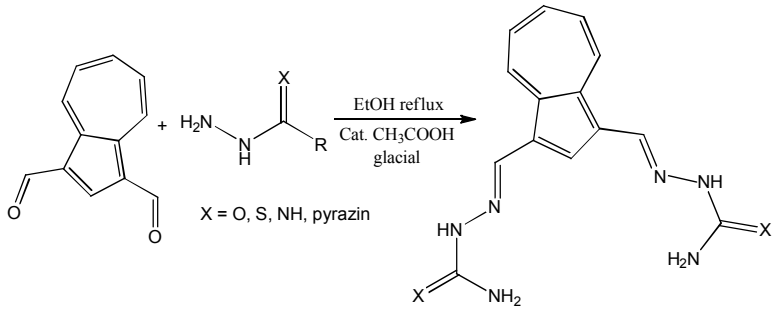
Keywords: bishydrazine; azulene; cleft cavity; anion receptor.

Introduction: Anionic species are of significant relevance in medicine, environment and industry [1]. While much progress has been achieved lately, the precise prediction of the properties of a new receptor still remains beyond our abilities and optimization of the properties of existing anion receptors for the better design of new receptors is still a hot research topic [2]. Among the various receptor class — amides, sulfonoamides, ureas and thiocarbonyl derivatives are often used because of their good binding ability.[3] Structurally similar to amides, hydrazones are good hydrogen bond acceptors and donors, and thereby provide the non-covalent interactions necessary for anion binding [3].

Materials and methods: Structural analysis of the designed compounds was performed by NMR-spectroscopy both through 1D (^{1}H, ^{13}C) and 2D–experiments (homonuclear and heteronuclear correlations).

Results: We have developed a novel generation of multifunctional conjugated hydrazones that can bind anions in a cleft-like fashion. The conjugated hydrazone frameworks were prepared *via* Schiff base condensation of azulen-1,3-dicarboxaldehyde with various hydrazides. Due to structural feature, namely ureido/thioureido moieties, the anion binding ability for different anions were tested by NMR spectroscopy, monitoring the acidic NH proton resonances in the presence of anions by NMR spectroscopy.

Conclusions: Preliminary investigations of the anion binding ability of *bis*-thiocarbohydrazide azulene derivative showed that small anions fit well within the receptor cavity.



References:

[1]. Leininger S, Olenyuk B, Stang PJ, Chem. Rev. 2000, 100: 853-871.
[2]. Gale PA, Busschaert N, Haynes C.J E, Karagiannidis LE, Kirby IL, Chem. Soc. Rev., 2014, 43: 205-219.
[3]. Zhao X, Li, ZT, Chem. Commun., 2010, 46: 1601-1604

NEW SALECAN/POLY(METHACRYLIC ACID)/CL 93A HYDROGEL NANOCOMPOSITES. INFLUENCE OF CLAY CONCENTRATION ON THE PHYSICO-CHEMICAL PROPERTIES OF THE NANOCOMPOSITE HYDROGELS

R. Ianchis[1], T. Munteanu[2], C.M. Ninciuleanu[*1], I.C. Gifu[2], E. Alexandrescu[1], S. Preda[2], R. Somoghi[1], B. Trica[1], C.L. Nistor[1], S.G. Nitu[1], C. Petcu[1]

[1]National R-D Institute for Chemistry and Petrochemistry ICECHIM – Bucharest, Spl. Independentei 202, 6th district, 0600021, P.O. Box 35/174, Bucharest, Romania;

[2] Institute of Physical Chemistry ''Ilie Murgulescu'', Romanian Academy, Spl. Independentei 202, 6th district, P.O. Box 194, 0600021 Bucharest, Romania

**Corresponding author: claudia.ninciuleanu@yahoo.com*

Keywords: hydrogels; clay; nanocomposites; Salecan

Introduction: Our present study examines the influence of Cl93A presence but also concentration variation on semi-interpenetrated Salecan/poly(methacrylic acid) hydrogel nanocomposites. The incorporation of clays into a polymer matrix can significantly enhance many performance characteristics of polymer composites as mechanical properties, swelling capacity, rheological properties, bioadhesion or cellular uptake. On the other hand, Salecan, which is a water soluble extracellular polysaccharide produced by fermentation from a new strain Agrobacterium sp. ZX09 was proved to assure antioxidative, non-toxic, anti-inflammatory, antimicrobial, antitumoural, antidiabetic excellent properties and futhermore provides greater flexibility to hydrogels. These properties recommend Salecan for SIPN hydrogels preparation with specific application in biomedicine [1].

Materials and methods: Cloisite 93A (Southern Clay Products Inc.) (methyl, tallow, bis-2-hidroxyethyl (methyl, dihydrogenatedtallow), PMAA (Janssen Chimica), Salecan (Souzhou Chemicals) and N, N'-methylenebisacrylamide (Sigma Aldrich) were used to form semi-IPN networks via free radical copolymerization in the presence of ammonium persulfate (Sigma Aldrich) as initiator. Deionized water was used throughout this study. The final materials were analyzed by FT-IR, TGA, X-ray diffraction and microscopy analyses (SEM, TEM).

Results: The presence of Si-O-Si groups at ~1045cm^{-1}, Si-O groups between 400-500 cm^{-1} and Salecan specific –Si-OH moieties in FTIR spectra, confirmed the incorporation of layered silicates but also the entrapment of Salecan into the PMAA hydrogel matrix. TGA analyses proved that the 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/TEM pictures.

Conclusions: The hydrogels physical-chemical properties, determined by several techniques, demonstrated that clay influenced the hydrogels physico-chemical properties.

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. This work was supported by the grant funded by the Romanian National Authority for Scientific Research, project number PN 16.31.03.04.04.*

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.

NEW SALECAN/POLY(METHACRYLIC ACID)/CLAY HYDROGEL NANOCOMPOSITES. EFFECT OF CLAY TYPE ON THE PHYSICO-CHEMICAL PROPERTIES OF THE NANOCOMPOSITE HYDROGELS

R. Ianchis[1], T. Munteanu[2], C.M. Ninciuleanu[*1], I.C. Gifu[2], E. Alexandrescu[1], S. Preda[2], R. Somoghi[1], B. Trica[1], C.L. Nistor[1], S.G. Nitu[1], C. Petcu[1]

[1]National R-D Institute for Chemistry and Petrochemistry ICECHIM – Bucharest, Spl. Independentei 202, 6th district, 0600021, P.O. Box 35/174, Bucharest, Romania;

[2] Institute of Physical Chemistry ''Ilie Murgulescu'', Romanian Academy, Spl. Independentei 202, 6th district, P.O. Box 194, 0600021 Bucharest, Romania

**Corresponding author: claudia.ninciuleanu@yahoo.com*

Keywords: nanocomposites; organomodified clay; Salecan; hydrogels

Introduction: This paper focused on the investigation of the effect of the clay type on semi-interpenetrated Salecan/poly(methacrylic acid)Clay hydrogel nanocomposites. Clay composites have attracted worldwide attention due to properties such as thermal stability or reduced permeability to small molecules and solvent uptake [1], thus being effectively used for drug delivery systems. As a drug delivery system component, clays have proven to act as a trap, preventing rapid gel swelling and uncontrolled diffusion of drug from the gel network [2]. Differnt studies indicated that the presence of clay in polymer composites leads to better or worse mechanical properties, swelling capacity and rheological properties as function of clay type [2]. For our investigation we have chosen commercially available clay and organomodified clay with different ammonium salts. The purpose of this study was to determine the most suitable clay for developing the desired semi-IPN nanocomposites.

Materials and methods: Clays were provided by Southern Clay Products Inc. and were used in the sodium form (ClNa) and organomodified with different ammonium salts (Cloisite 30B, Cloisite 20A and Cloisite 15A). PMAA (Janssen Chimica), Salecan (Souzhou Chemicals) and N, N'-methylenebisacrylamide (Sigma Aldrich) were used to form semi-IPN networks via free radical copolymerization in the presence of ammonium persulfate (Sigma Aldrich) as initiator. Deionized water was used throughout this study.

Results: In order to investigate the physico-chemical properties of the resulted Salecan/Poly(methacrylic acid)/Clay Hydrogel Nanocomposites as function of the presence/absence of Salecan but also clay type, FTIR, TGA, XRD, microscopy and swelling studies were performed.

Conclusions: The hydrogels physical-chemical properties, determined by several techniques, demonstrated that clay type influenced the hydrogels physico-chemical properties.

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. This work was supported by the grant funded by the Romanian National Authority for Scientific Research, project number PN.16.31.03.04.*

References:

[1] R. Ianchis, I.D. Rosca, M. Ghiurea, C.I. Spataru, C.A. Nicolae, R. Gabor, V. Raditoiu, S. Preda, R.C. Fierascu, D. Donescu, Synthesis and properties of new epoxy-organolayered silicate nanocomposites, Applied Clay Science 103 (2015) 28–33

[2] Koji Nagahama, Daichi Kawano, Naho Oyama, Ayaka Takemoto, Takayuki Kumano, and Junji Kawakami, Self-Assembling Polymer Micelle/Clay Nanodisk/Doxorubicin Hybrid Injectable Gels for Safe and Efficient Focal Treatment of Cancer, Biomacromolecules, 2015.

Wednedsay 25 October 2017

Workshop

15:00 -16:00

THERMOPLASTIC NANOCOMPOSITES WITH ENHANCED SCRATCH RESISTANCE

Z. Vuluga

National Research and Development Institute for Chemistry and Petrochemistry-ICECHIM Bucharest
zvuluga@icechim.ro

Keywords: PMMA, scratch resistance, masterbatch, thermoplastic nanocomposites

Introduction: Within the Project H2020-NMP-PILOTS-2015- IZADI-NANO2INDUSTRY-686165, ICECHIM, TECNALIA and MAIER have to develop formulations based on PMMA and multifunctional (nano)additives for optimizing scratch resistance of PMMA compounds used for B pillar manufacturing, while maintaining as much as possible the other principal aesthetic and thermo-mechanical properties (gloss, black colour, thermal stability, strength, stiffness and toughness). The solution proposed for this project in order to disperse uniformly the nanoadditives into the polymer matrix is by using masterbatches.

Materials and methods: For masterbatch obtaining, three different types of scratch additives have been used:

1. Organomodified siloxane
2. Migratory slip additives
3. Special mineral fillers

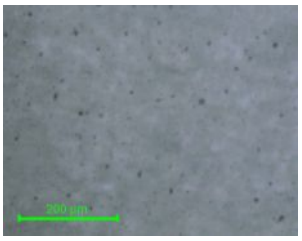
As polymer matrix PMMA black was used.

The masterbatch preparation was a two-stage process:

- Dry mixing of components
- Melt mixing of component mixture under heat and shear conditions

Results: The masterbatches are in granular form, have good thermal stability at processing temperature of PMMA and disperse uniformly into PMMA matrix due to their improved flowability and uniform dispersion of nanofillers within masterbatch.

Masterbatch granules



Optical microscope photo of Masterbatch

Conclusions: Masterbatches with high percentage of (nano)additives (≥ 20%) for improving scratch resistance of PMMA were developed by extrusion process. The masterbatches may be added to the polymer up to the accurate concentration, in function of the part requirement, through an intermediary extrusion step or directly during the injection manufacturing process of the B-pillar.

Acknowledgements: *Financial support by the EU Commission through Project H2020-686165-IZADI-NANO2INDUSTRY is gratefully acknowledged***.**

Wednedsay 25 October 2017

Round Table

15:00 -16:00

BITUMEN FLUXANTS OBTAINED BY THE UPGRADE OF THE ECOLOGICAL SOLVENTS TECHNOLOGY EXISTING AT SC ICPAO MEDIAS

Workshop

15:00 -16:00

Closing the loops in the agri-food sector - innovative (bio)products from side-flows of agri-food processing industries (SECVENT project)
Dr. Bioch. Florin Oancea;

Workshop

16:00-17:00

Regional circular economy models and best available technologies for biological streams - BIOREGIO project
Ing. Mihaela Frincu

INNOVATIVE APPROACHES FOR ENHANCING THE SUSTAINABILITY AND THE RESILIENCE OF BIOECONOMY IN ROMANIA

The European Union has identified bioeconomy as a transectoral domain, with a high potential to create growth and jobs. Bioeconomy can contribute to a resilient energy union, with a focus on reneweable resources and climate mitigation, and generate industrial development by creating a circular, resource-efficient economy. A key element of the EU Bioeconomy Strategy is to develop new technologies and processes for the bioeconomy. ICECHIM is involved in several national and international projects particularly aiming at the valorisation of side-flows from agri-food industries through innovative (bio)products and sharing best practices in this field.

Friday 27 October 2017

Round Table
9.30-11.00

BIOREGIO - POLICY AND GOOD PRACTICES IN BIO-BASED CIRCULAR ECONOMY

BIOREGIO (2017-2021) is an international project financed by the European Regional Development Fund (ERDF) within the Interreg Europe Programme, with the aim of boosting bio-based circular economy through transfer of expertise about best available technologies and cooperation models. The project involves 8 partners from 6 EU countries. The round table represents the 2nd BIOREGIO Stakeholder group meeting in Romania and brings together the regional actors in the field of bioeconomy. The topics to be discussed include best practies identified in the project, funding opportunities and the current situation of policy instruments that support circular bioeconomy

Round Table
10.15-11.00

INNOVATION, PATENTING AND TECHNOLOGY TRANSFER