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Chemistry&Petrochemistry **ICECHIM**

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International symposium

## Priorities of Chemistry for a Sustainable Development



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„Hofigal” este unul dintre cele mai faimoase nume de marca pentru produsele homeopate, gemoderivate si fitoterapice galenice din România, conditionate sub forma de, suplimente alimentare, produse cosmetice.

„Hofigal” este o societate pe actiuni cu capital social privat exclusiv romanesc. Suprafata utila a companiei este de 35 hectare.

In intreaga companie lucreaza aproximativ 400 angajati, fiind permanent motivati spre o perfectionare profesionala si personala continua; acestia isi desfasoara activitatea acoperind domenii diverse.

„Hofigal” este o companie specializata in fabricatia produselor exclusiv naturale, având caracteristic faptul ca își produce majoritatea materiilor prime folosite in serele si pe terenurile agricole proprii.

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Un punct forte privind portofoliul „Hofigal” il reprezinta faptul ca toate produsele sunt obtinute pe baza unor retete si tehnologii proprii, brevetate in tara si reprezinta premiere mondiale absolute.

Obiectivele majore ale companiei sunt de a aplica conditiile si masurile privind asigurarea calitatii, eficacitatii si sigurantei tuturor produselor, precum si obținerea de ingredientii farmaceutici activi de natura vegetala garantata ce corespund in totalitate normelor ecologice internationale in vigoare.

Produsele portofoliului Hofigal reprezinta premiere pe plan mondial: *cea mai mare concentrație de β-caroten in ulei de cătina, de proteina in Spirulina, Coenzima Q10 in ulei de cătina.*

Nomenclatorul de produse realizate de „Hofigal” a crescut de la 3 produse in anul 1990, la peste 450 in 2016. Produsele noastre pot fi găsite in toate farmaciile din Romania.

Totodata *Hofigal* are si o rețea proprie de farmacii. In cadrul acestora produsele *Hofigal* se vând fără adaos comercial, adică cu costul de producție. In incinta fiecarei farmacii *Hofigal* exista amenajat un cabinet de consultanta, in cadrul căruia medici autorizați, angajati ai *Hofigal*, cu pregătire atât in domeniul alopatiei, fitoterapiei cat si al homeopatiei, acorda gratuit consiliere oricărei persoane interesate de portofoliul companiei.

Prin întreaga sa activitate „Hofigal” este promotorul celor mai înaintate si moderne concepte legate de fabricatia nepoluanta. De la materiile prime pana la produsele finite, totul este natural, curat si nepoluat.

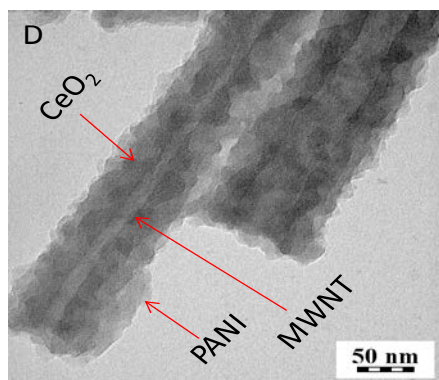
„Natura nu minte niciodata...” Mihai Eminescu

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**PREPARATION OF NEW ANTICORROSIVE NANO-PIGMENTS VIA SELF-SACRIFICIAL AND VIA HARD TEMPLATE METHODS****PERRIN FX, OUEINY C, BERLIOZ S***Laboratoire MAPIEM EA 4323 ,SeaTech-Ecole d'ingénieurs, Université de Toulon BP 20132, 83957 La Garde Cedex Email: [perrin@univ-tln.fr](mailto:perrin@univ-tln.fr)*

The widely used Cr compounds have been banned in Europe since 2007 and soon worldwide due to their highly carcinogenic effect. In the last three decades, polyaniline (PANI) has received much attention as an alternative to chromate pigments because of its easy preparation, low cost, good environmental stability and unique electronic properties. Common mechanisms of corrosion protection are interpreted as physical barrier, adsorption, anodic protection and shift of electrochemical interface. We will first report the formation of high quality PANI nanotubes and PANI nanofibers by interfacial polymerization using organophosphonic acid in the aqueous phase. The crucial template role of in situ formed and precipitated oligoanilines in the formation of PANI nanotubes by falling-pH self-assembly method will be highlighted. We will show that the higher efficiency of PANI-DPA nanotubes is not related to the different morphology (nanotube vs nanofiber) but to the inhibitive properties of the organophosphonic acid dopant of PANI nanotubes. In another approach, the facile preparation of MWCNT/Ce/polyaniline nanocomposites<sup>1</sup>, as new controlled release corrosion inhibitive pigments will be reported. TEM images showed that ceria nanoparticles of diameter around 10 nm decorated the walls of MWCNTs in the MWCNT-Ce-PANI composites (Fig. 1). We will show that the ternary composite is a pH-responsive assembly for controlled release of inhibitive cerium species. The excellent corrosion protection performance of MWCNT/Ce(IV)/PANI are due to the synergetic effect of ceria and PANI.



**Figure 1:** TEM analysis of MWCNT/Ce(IV)/PANI

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**ELECTROCHEMICAL MOLECULARLY IMPRINTED POLYMER AS SENSOR INTERFACES****Prof. PhD. BRISSET Hugues***Laboratoire MAPIEM, EA 4323, Université de Toulon, 83957 La Garde, France*

Combined with various transduction mechanisms, molecularly imprinted polymers (MIPs) are the key stones of a large panel of optical, electrochemical, acoustic, piezoelectric and calorimetric sensors thanks to their high recognition properties, easy synthesis and high stability.<sup>1</sup> Since a few years, we develop a new generation of MIPs including a redox tracer (in the form of a functional monomer) inside the binding cavities in order to enable the electrochemical quantification of the template.<sup>2,3</sup> This concept of electrochemical MIPs has been first used to quantify benzo[a]pyrene (BAP) and was recently extended to the detection of Bisphenol A (BPA) pollutant. During this talk the development of these new type of electrochemical MIP will be presented.

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  - 3 Branger C, Brisset H, Udomsap D (2015) Imprinted polymer and method for preparing the same US Patent US20150344607

# PHOTOPHYSICAL PROPERTIES OF NANOCOMPOSITES OF ALUMINUM TETRASULFONATED PHTHALOCYANINE WITH GRAPHENE QUANTUM DOTS LINKED TO FOLIC ACID

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**Keywords:** Triplet quantum yield, Singlet quantum yield, Graphene quantum dots, Aluminium tetrasulfonated phthalocyanine, Photodynamic therapy.

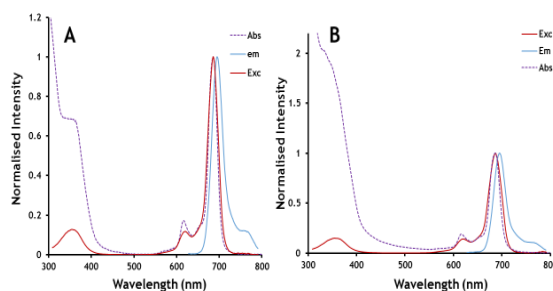
## Introduction:

Phthalocyanines (Pcs) are well known photosensitizers for PDT [1,2]. Thus, combining Pcs with GQDs may enhance PDT activity by synergistic effect. The combination of GQDs and Pcs has been employed in sensing [3], but there have been no reports on the studies of the photophysical behavior of Pcs in the presence of QDs for possible applications in PDT. Hence, this is the aim of the current work. We combine GQDs with ClAl tetrasulfophthalocyanine (ClAlTSPc) since AlPc derivatives have been employed for PDT [2]. Glutathione (GSH) capped GQDs are employed in this work (represented as GQDs@GSH). In this work, glutathione capped graphene quantum dots (GQDs@GSH) were covalently linked to folic acid (FA). Aluminium tetrasulfonated phthalocyanine (ClAlTSPc) was then adsorbed on the GQDs@GSH-FA conjugate to form GQDs@GSH-FA/ClAlTSPc or on GQDs@GSH alone to form GQDs@GSH/ClAlTSPc. We report on the photophysicochemical behavior of the resulting nanoconjugates. The fluorescence quantum yield of GQDs or GQDs@GSH-FA conjugate was quenched upon non-covalent interaction (2-2) with ClAlTSPc. There was an increase triplet quantum yields from 0.37 for ClAlTSPc alone to 0.75 and 0.73 when ClAlTSPc was linked to GQDs@GSH and GQDs@GSH-FA, respectively. The singlet oxygen quantum yields also increased from 0.38 for ClAlTSPc alone to 0.52 (for ClAlTSPc with GQDs@GSH) and 0.54 (for ClAlTSPc with GQDs@GSH-FA). Thus, the present work may lead to a new generation of carbon-based nanomaterial PDT agents with overall performance superior to conventional agents in terms of singlet oxygen quantum yield, water dispersibility, and biocompatibility.

## Materials and methods:

1, 3-Diphenylisobenzofuran (DPBF), quinine sulphate, folic acid (FA), 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide (EDC) and N-hydroxysuccinimide (NHS) were obtained from Sigma-Aldrich. Dimethyl sulfoxide (DMSO) was obtained from SAARCHM. All aqueous solutions were prepared using ultra-pure water obtained from a Mili-Q Water system (Millipore Corp. Bedford, MA, USA). All other reagents and solvents were obtained from commercial suppliers and were of analytical grade and were used as received. Aluminium tetrasulfonated phthalocyanines (ClAlTSPc) was synthesized and characterized in accordance with literature [4]. GQDs@GSH was prepared using pyrolysis of L-glutathione and citric acid [5].

**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.



**Fig. 5:** Absorption, emission and excitation spectra for GQDs@GSH/CIAITSPc (A), GQDs-FA/CIAITSPc (B).

### Conclusions:

We successfully employed a facile pyrolysis approach for the preparation of glutathione-functionalized GQDs (GQDs@GSH) with a fluorescence quantum yield as high as 27%. We also successfully linked these glutathione-functionalized GQDs to folic acid (GQDs@GSH-FA) via the carbonamide bond. Non-covalent interactions ( $\pi$ - $\pi$ ) were formed between GQDs@GSH or GQDs@GSH-FA and CIAITSPc. The fluorescence quantum yields of the CIAITSPc was found to be efficiently quenched by the respective GQDs nanohybrids, whereas the triplet and singlet oxygen quantum yields were enhanced.

**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 (UID 62620). We would also like to thank Rhodes University, as well as Dr Desmond E. Goddard bursary for their financial support.

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## MICROCALORIMETRIC ESTIMATION OF BACTERIAL GROWTH AND DECAY. KINETIC MODELING AND THERMAL SIGNAL PROCESSING.

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**Keywords:** *Monod growth model, complex reactions, steady state, microcalorimetry, thermogram processing.*

The Monod growth model [1] was analyzed from the chemical kinetics side [2] in “Langmuir adsorption” terms, or from the microbiology side [3] in “Michaelis-Menten” enzyme kinetics terms. An attempt towards a general kinetic derivation [4] of the Monod growth equation is presented here, providing a fairly general explanation of its capability to describe experimental data, within surprisingly broad limits concerning bacterial strains, nutrient and environment conditions. It is proven that the Monod equation may be derived in a strictly kinetic framework, within assumptions / approximations / methods borrowed from heterogeneous catalysis: (quasi)steady state approximation, most abundant reaction intermediate, kinetically significant step, reaction route or path. The main approximation involves considering bacterial individuals (in various stages of their growth) as some quasi-chemical species, the reactivity of which is subject to mass action law. The growth is amenable to a two-step sequence, where the term “step” stands for some complex, possibly single-route, and kinetically significant process. Consequently, the growth may be approached in quasi-chemical terms and the derivation of the Monod equation is straightforward for two limiting cases: 1) “starving conditions”, with substrate binding as a limiting step; 2) “normal” laboratory conditions with abundant nutrients (excepting possibly the growth controlling or limiting one) and bacterial fission as limiting step. Using the hypothesis of a most abundant growth intermediate, *magi*, as a kinetic key, several other mechanistic alternatives are presented, involving multiple-substrate binding before and/or after the formation of this key intermediate. Several experimental observations are discussed in connection with the mechanistic expressions obtained for the Monod growth parameters.

Application to microcalorimetric growth data in batch conditions involves the decomposition of the complex thermal signal via Peakfit decomposition of the raw thermogram and making use of the fundamental assumption that on the time scale of its thermal expression the bacterial population scales with the evolved heat. Various growth parameters are shown to have their calorimetric expression, accessible via a suitable processing of the recorded signal. The “thermal version” of the Monod equation describes component, non-steady growth processes surprisingly well. A possible explanation would be the conservation of the *magi* (and thus of the rate equation) over the whole extension of the “thermal growth” process. Bacterial decay thermograms, obtained in various mixing-batch experiments devised to monitor the antibiotic action, are also amenable to the presented approach. The typical sigmoid-shaped heat vs. time plots obtained from raw thermograms are conveniently expressed by means of various logistic-type empirical equations. The suitability of these equations is analyzed and discussed.

**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, is gratefully acknowledged.*

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## FROM WHERE TO WHERE IN CHEMICAL ENGINEERING

Dobre Tanase

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**Abstract.** The paper presents aspects concerning the past, the present and the future of Chemical Engineering Science. In the paper opening it shows the bible roots of this science and give some date respect the this science importance for development of the ancient world. Looking back on the chemical engineering road will find their strong roots in medieval alchemy. The basic three alchemists dreams (Diderot Encyclopedia) which sought to obtain i) the creation of the fabled philosopher's stone, ii) the ability to transmute base metals into noble metals (gold or silver), iii) the development of an elixir of life for youth and longevity, can be today three major directions in which chemical engineering can go on. The processes Leblanc and Solvay for industrial sodium carbonate production and the processes (distillation and others) characterizing the beginnings of petroleum industry are considered as roots of modern chemical engineering science. Now at the finish of 19<sup>th</sup> and starting of 20<sup>th</sup> century did time for chemical engineering to gather the results, to establish their theoretically explanation and to generalize them. Such have been created the conditions for her enrolling by specialists training in the triangle education-research-production. It is known that the name of chemical engineer began to be used since 1880 as it is known that the chemical engineer of this time was in fact a mechanical engineer by training with a very a good practical knowledge of applied chemistry (chemical engineering). George Davis, an inspector in the production of alkaline England hold in 1887 a total of 12 lectures with chemical engineering specifics and titles at the Technical School in Manchester. Recognizing the paradigm as a philosophical and theoretical framework of a scientific school or discipline within which theories, laws, and generalizations and the experiments performed in support of them are formulated, and looking with eyes to the passed time, we find for chemical engineering discipline three paradigms: the first paradigm called Unit Operations paradigm (1923-1960); a second paradigm called paradigm of Transfer Phenomena (1960 -2005), and that the third paradigm accepted as paradigm of Process Engineering as innovation, design and manufacture of high technology products (after 2005). In a different time period the chemical engineer training was done after one or other of these paradigms. Therefore a succinct characterization of these paradigms is of interest. An important attention is given to the Amundson report (1984) because it recommend an alliance of industry, academia and government to invest in the future of chemical engineering, which promises to serve society by: 1) Starting of New Technologies that would improve the quality of life with new products through: a) biotechnology and biomedicine; b) electronic, photonic, and recording materials and devices; c) microstructured materials; 2) Maintaining Leadership in Established Technologies and particularly in: a) in-situ processing of energy and mineral resources; b) liquid fuels for the future; 3) Protecting and Improving the Environment and Health by: a) responsible management of hazardous substances; b) protection from sudden plant disasters; 4) Developing Systematic Knowledge and Generic Tools that would be used in all three previous areas, and particularly in: a) advanced computation methods and process control; b) surface and interfacial engineering. The Amundson report keeps today their actuality. This paper shows this by presenting and commenting on some basic directions in which will be the future development of chemical engineering.

### Reference

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## CONDITIONING AND UTILIZATION OF CARBON DIOXIDE RESULTED FROM BIOMASS DIGESTION

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Atmospheric emissions of carbon dioxide contribute to the climate changes. Considering the growing amounts of emitted CO<sub>2</sub>, specifically from the alcohol digestion processes, this gas can be used for the different applications. Currently, no more than 2-3% of carbon dioxide formed in these processes is used for the production of liquid and solid carbonic acid. In addition, carbon dioxide make part of the biogas resulted from the biomass digestion.

Thus, during the alcohol digestion, the yield of carbonic acid makes 95,5% from the alcohol weight, 51,3% from saccharose weight and 54,2% from the starch weight. Considering that the average alcohol yield from 1 tone of starch makes 90,3% from the theoretical yield, which reaches 65,0 dal, the calculated carbonic acid yield makes 7,53 kg per 1 dal of alcohol produced, or 48,95 kg of carbonic acid per tone of the starch processed. As the admixtures, along with the carbonic acid formed during the digestion, the following products are formed: alcohol (0,4-0,8% with regard to CO<sub>2</sub> weight), esters (0,03-0,4%), acids (0,08-0,09%) and trace amounts of aldehydes.

Therefore, for the practical using of carbon dioxide, specifically, for micro-algae cultivation, the primary task is to purify it from the admixture components. Considering the composition of admixtures which may cause the ruin of micro-algae, it was proposed to use the combined adsorption-destruction photocatalytical technology to produce the purified gas. To enhance the microalgae growth rate, it was proposed to apply the LED lamps. For the separation of micro-algae biomass from water environment and ensure their thickening, it is envisaged to apply the micro-filtration process on the special self-regenerating filters, as well as a special electr-flotation technology. The separated micro-algae are subjected to the subsequent dewatering on centrifuge.

For CO<sub>2</sub> utilization formed as a biogas component during the biomass anaerobic digestion, a certain problem is its separation from biomethane and other components, including hydrogen sulphide, mercaptanes, some other organic compounds. We have considered the separation technologies of these gases, including the water-adsorption method based on the different water solubility of CO<sub>2</sub> and CH<sub>4</sub>. Hydrogen sulphide, as well as CO<sub>2</sub>, is water-soluble. To purify water saturated with CO<sub>2</sub> from hydrogen sulphide, it is proposed to apply the galvano-coagulation process with iron hydroxides generation as highly efficient reagents and coagulants. Galvano-chemical process is based on the “internal electrolysis” occurring during the contacts of galvanic pair elements Fe/C. Iron hydroxides thus formed are active coagulants promoting the adsorption and coagulation of organic admixtures and iron sulphide. The particles resulted from such treatment, containing iron sulphide and other admixtures, can be readily separated, whereas the water saturated with CO<sub>2</sub> is passed into the micro-algae cultivating basin.

The reactor design has been proposed for these processes realization.

*This work is implemented under the Bilateral Moldo-Romanian Research Project ASM-ANCSI, «Microalgal system used for CO<sub>2</sub> emissions mitigation resulted from biomass fermentation (ALGAE-CO<sub>2</sub>)» 16.80013.5807.11/Ro.*

## ANAEROBIC CO-DIGESTION OF FOOD WASTE AND SPENT MICROALGAE BIOMASS OBTAINED BY DIFFERENT EXTRACTION METHODS

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**Keywords:** *biogas, spent biomass, ultrasound assisted extraction*

**Introduction:** Besides the output of biogas as a valuable source of energy, the usage of anaerobic technology contributes to stabilization of organic wastes, greenhouse gas reductions, and reduction in pollution potential [1].

Anaerobic digestion can be performed using a single type of biomass or a mixture of biomass in a single equipment. Mono-digestion of microalgae spent biomass is difficult to perform, because of the high protein content, that leads to low C:N ratios. Another disadvantage of anaerobic digestion of spent microalgae biomass is the release of the ammonia, during degradation of protein, which induces inhibition of acidogenic bacteria and methanogens [1]. Co-digestion of microalgae with carbon-rich food waste has been proposed as a cost-effective and efficient approach to avoid ammonia inhibition and to increase the C:N ratio.

The microalgae cell wall deterioration is an important parameter in anaerobic co-digestion of microalgae and generally depending on the extraction method of lipid fraction from microalgae biomass. The aim of this study was to evaluate the effect of microalgae spent biomass obtained from two extraction methods (Soxhlet extraction and Ultrasound assisted extraction), on the yield of biogas and CH<sub>4</sub> concentration in the biogas obtained.

**Materials and methods:** Lab fermenter type Ralf (5L) for anaerobic co-digestion; Soxhlet Extractor for Soxhlet extraction of lipid fraction; Vibra-Cell Us 750 V for ultrasound assisted extraction of lipid fraction; Geotech Biogaz 5000 for gas analysis;

**Results:** Our results revealed that the best yields of biogas and maximum concentration of CH<sub>4</sub> were obtained, when was performed anaerobic co-digestion of food waste with spent microalgae biomass obtained after ultrasound assisted extraction of the lipid fraction.

**Conclusions:** The biogas yield and CH<sub>4</sub> concentration in biogas was significantly influenced by the microalgae cell disruption degree.

**Acknowledgements:** *The work has been funded by the PN 16.31.01.04.02. and Bilateral project Ro-Mo 33/2016*

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## BIO-SILICA RECOVERY DURING BIOREFINERY INITIAL STEP

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**Keywords:** *bio-silica, lignocellulose, enzymes, deep eutectic solvents*

Lignocellulose is naturally recalcitrant to dissolution [1]. Lignin matrix covers cellulose and hemicelluloses, acting as an adhesive [2]. Silicon, firmly bound to the cell wall lignocellulose, stabilizes further its network [3]. This silicon, which could reach more than 10% in cereal husks, complicates biomass further processing [4]. Recently, processes for a comprehensive utilization of bio-silica (BSi) lignocellulose were developed [5], utilizing rather expensive ionic liquid solvents. Despite the common perception of ionic liquids as environmental friendly solvents, there are still serious drawbacks, including ecotoxicological ones, which need to be addressed for a large utilization of such types of solvent for lignocellulose processing [6]. Less expensive and more environmental friendly alternatives for BSi lignocellulose dissolution are still needed.

In this work we review the use of enzymes and small catalytic protein acting on (ligno)cellulose (e.g. cerato-platanin), combined with deep eutectic solvents, as an initial step on lignocellulose biorefinery. During this step, weakening the strong H-bonds of cellulose and the removal of network stabilizing silicon should enhance the dissolution of lignocellulose. Such mild treatments allow the recovery of value added components from BSi biomass – e.g. anti-oxidants, essential oil terpenes and steroids, trapped and/or bound by/to the lignocellulose network.

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## PROTEIN STABILITY IN IONIC LIQUIDS AND THE TEMPERATURE DEPENDENCE OF THE HOFMEISTER SERIES

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**Keywords:** ionic liquids, cosolutes, Hofmeister series, proteins, thermodynamics.

**Introduction:** The use of ionic liquids (ILs) in biotechnology as alternatives to organic solvents has gained much attention lately [1]. Several enzymes such as lipases were previously found to be more active in the presence of ILs than in buffer solutions, the new aim being the synthesis and use of biocompatible ILs [2, 3]. Understanding the physicochemical properties that govern the effects of ILs on enzymes will help design novel and improved ILs-based solvents. A systematic investigation of ILs and other cosolutes effects on the structure and stability of RNase A is presented here.

**Materials and methods:** DSC, CD, SDS-PAGE electrophoresis. The Hofmeister series were first established from the effect on the melting temperature ( $T_m$ ) and next compared to those from the shifts of the entire protein stability curves (the temperature dependence of the unfolding Gibbs energy).

**Results:** Most ILs were found to shift  $T_m$  to lower temperatures. Only one IL - choline dihydrogen phosphate highly stabilized the protein, the phosphate anion being responsible for this. Moreover, all ILs inhibited protein aggregation and precipitation. In general, the more hydrophobic the cation/anion in the Hofmeister series, the stronger the protein destabilization. This effect is due to the larger destabilizing entropic compared to the stabilizing enthalpic contribution. If the effect on the protein stability curve is considered, the multiple intersections of the respective curves lead to temperature dependent ion rankings for both organic and anorganic cosolutes.

**Conclusions:** The cations and anions of ILs were ranked in Hofmeister series. Moreover, a novel classification scheme of cosolute effects is presented based on a widely ignored fact: the Hofmeister rankings are temperature dependent. This in depth thermodynamic analysis represents a fundamental framework for future simulations and molecular studies of cosolute effects.

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## DETERMINATION OF ANTIOXIDANT CAPACITY OF SOME EXTRACTS BY USING A CERIA NANOMATERIAL BASED METHOD

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**Keywords:** antioxidant capacity, nanomaterials, chemiluminescence, luminol, ABTS<sup>+</sup>.

**Introduction:** It was studied a new innovative ceria nanoparticle-based assay for rapid detection of antioxidants from food, vegetable extracts or other biological samples.

**Materials and methods:** The method is based on the use of immobilized ceria nanoparticle on paper, which changes colour after interaction with antioxidants by means of redox and surface chemistry reactions [1, 2]. The sensors are scanned by using a conventional office scanner and the red, green, blue (RGB) colour breakdown is analyzed. By plotting the inverse of blue colour intensity (1/BCI) versus the log of a standard antioxidant concentration it is obtained a calibration graph.

**Results:** The obtained calibration curves for gallic acid and for caffeic acid are linear in the domains  $4 \times 10^{-4} - 10^{-2}$  M and  $10^{-4} - 5 \times 10^{-3}$  M, respectively. A comparison of the results obtained by the method based on the use of ceria nanoparticle, a chemiluminometric method, and a conventional ABTS<sup>+</sup> method for the determination of antioxidant capacity of some fruit extracts has been done.

**Conclusions:** The ceria nanoparticle-based assay is very fast, requires very low cost, is portable, and it could be easily automated.

**Acknowledgements:** Financial support from the UEFISCDI, Romanian Ministry of National Education and Research for project PN-II-Partnerships no 145/2014 is gratefully acknowledged..

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## ONE STEP TOF LC/MS MEASUREMENTS OF MULTIPLE MYCOTOXINS FROM SINGLE MATRIX STORED GRAINS

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**Keywords:** *mycotoxins, ochratoxins, aflatoxins, fumonisins, time of flight liquid chromatography.*

**Introduction:** Mycotoxins are chemically stable, very toxic at low concentration and difficult to remove, even at high temperature such is breakfast cereals production [1]. Therefore it is very important to develop sensitive methods for detection and quantification. Due to the differences between the structures, there is no single technique to detect all mycotoxins from a sample matrix, and new methods with higher sensitivity should be used in the analysis of these toxins [2].

**Materials and methods:** A time of flight liquid chromatography with mass spectrometry (TOF LC/MS) method was used for simultaneous separation, identification and quantification of ochratoxins (OTA), of four major aflatoxins (AFT) B1, B2, G1 and G2, and fumonisins (FUM) B1 and B2. The method was developed using mycotoxin standards (Trylogy Analytical Laboratory, US). A certified sample of corn, naturally contaminated with mycotoxins (Trylogy Analytical Laboratory, US), was used in a comparative study with possible contaminated stored grains samples.

**Results:** An immunoaffinity column (IAC) (R.Biopharm Rhône Ltd., Scotland) for sample clean-up, a nano-column (C18) compatible with an UHPLC (Agilent Technologies, US) system for chromatographic separation and a high mass accuracy (less 5 ppm) detection were proved to be the best choice for simultaneous determination of mycotoxins from cereals.

**Conclusions:** High accuracy mass identification of mycotoxins contamination in stored grains matrix was the main achievement of this work.

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## PHYTOCHEMICAL CHARACTERISATION OF TWO FREEZE DRIED EXTRACTS OF *ROBINIA PSEUDOACACIA* AND *SOPHORA JAPONICA* FLOWERS

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**Keywords:** *Robinia Pseudoacacia*, *Sophora Japonica*, freeze dried extracts, flavones, antioxidant activity.

**Introduction:** *Robinia Pseudoacacia* and *Sophora Japonica* are two popular ornamental trees grown in North America and Europe. In Romania *Robinia Pseudoacacia* is very common, being a major honey plant, also its flowers are used in alimentation. As for the phytochemical composition the flowers contain mainly flavones and polyphenolic derivatives and they are used in traditional medicine for cough relieve and gastritis [1]. *Sophora Japonica* is not so common in Romania, but its flowers are well known and studied for their high content of rutin (15-20%) [2], which makes them used in traditional medicine for cardiac edema, liver failure and eye diseases [1].

Because there are not too many phytoterapeutic products with *Robinia Pseudoacacia* and *Sophora Japonica* flowers and the few known are commercialized as teas and tinctures, we intended to undertake a thorough study of these plants. For this purpose we chose to obtain and characterize freeze dried extracts do to their higher content of phytochemical compounds and they are easy to keep, the dried flowers being more easily attacked by pests like moths.

**Materials and methods:** *Robinia Pseudoacacia* and *Sophora Japonica* flowers were harvested in may - june from Teleorman area and dried in controlled conditions. The two extracts were prepared following the same procedure, the flowers were first extracted for 7 days with 50% ethylic alcohol then after filtration, they were concentrated under vacuum to eliminate the alcohol and freeze dried until a powder was obtained. These freeze dried extracts were analyzed with specific methods to determine their chemical composition (proteins, sugars, polyphenols, flavones and antioxidant activity) and some of the flavonoid derivatives were identified by HPLC.

**Results:** *Sophora Japonica* extract has a higher polyphenols content than *Robinia Pseudoacacia* extract (171.92 mg/g compared to 36.5 mg/g), hence a higher antioxidant activity. The total content of proteins and sugars is higher in *Robinia Pseudoacacia* extract (241.5 mg/g protein and 362.4 mg/g reducing sugars). The HPLC analyses revealed some of the flavonoid derivatives found in both extracts (especially quercetin and kaempferol).

**Conclusions:** We obtained and characterized two freeze dried extracts of *Robinia Pseudoacacia* and *Sophora Japonica* flowers. *Robinia Pseudoacacia* extract has a lower polyphenols content than *Sophora Japonica* extract but the higher content of proteins and sugars makes it of great interest for the development of dietary supplements.

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## NATURAL FOOD SUPPLEMENTS WITH SANOGENOUS EFFECT IN DIGESTIVE DISORDERS

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High frequency and diversity of digestive diseases, raise serious problems in allopathic medicine, mainly because their secondary effects. Thus the company Hofigal, involving a large team of researchers, drawing inspiration from folk medicine, conducted of obtaining of some natural alternative form as supplements to reduce suffering in many digestive disorders.

**Materials and methods** Raw materials used for the products realized are: by opotherapic provenance: - gizzard of chicken cuticle and vegetable products, some known for their beneficial effects in digestive diseases, other that we studied in terms of digestive enzyme content, presented by us in that paper. The methods used are biochemical conventional methods for digestive enzymes, and also have been used some known physical-chemical methods, for the bioactive compounds studied from the plant material. It refers to the experimental studies that conducted to a detailed selection and standardization of raw materials used to getting a group of 5 products as dietary supplements, which covers the most important segments of the digestive system. We have developed new formulas for supplements products produced in known pharmaceutical forms like solid and soft capsules and tablets.

**Results and discussion** paper are presented in total a number of 5 products, made and notified as dietary supplements, highly appreciated for their sanogenous effects on the market. They are: REGLACID- for regulation of gastric acidity and avoiding severe consequences; REDIGEST and REDIGEST F- are enzyme complexes of great interest and importance to normalize digestion processes; MAG-ANGHINAR - product with cholagogue-choleretic properties that ensure normal functioning of bile and liver and finally SANCOL product intended for colon health care.

**Conclusions** Products made and presented in that paper are proved highly successful phytotherapeutic effects. All products are registered and nationwide patents obtained. It's were also presented to Invention Expo's in the country and abroad where they received diplomas and gold medals.

## AN WORLD OF USEFUL COMPOUNDS OBTAINED BY TRANSFORMATION OF $\delta$ -LACTONE TYPE PROSTAGLANDIN INTERMEDIATES

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**Keywords:**  $\delta$ -lactone(s), cyclopentane compounds, prostaglandin intermediate, haloester compds,  $\gamma$ -lactone(s).

**Introduction:** The synthesis of prostaglandins and their structural analogues by the Corey methodology imply at an earlier or later stage, a step to open a  $\delta$ -lactone type compound followed by another step to build a  $\gamma$ -lactone structure. The so obtained key intermediates are used to build the side chains of prostaglandins in a sequence request for specified structure of the world of prostaglandin compounds. In previous papers we presented efficient procedures for closing the  $\delta$ -lactone skeleton to haloester compounds and then to Corey type compounds<sup>1</sup> or to obtain  $9\beta$ -halogen prostaglandin analogues<sup>2</sup>. Now we present a new procedure to obtain new protected aldehyde  $\gamma$ -lactone type compounds.

**Materials and methods:** The starting materials were obtained in our laboratory in racemic and pure enantiomeric (+)- and (-)- forms. The sequence of reactions is similar to that published by us for other prostaglandin intermediate compounds<sup>3</sup>. The pure compounds were obtained by pressure chromatography and the structure confirmed by IR, MS, <sup>1</sup>H-, <sup>13</sup>C- and 2D-NMR, X-ray crystallography.

**Results:** Transformation of  $\delta$ -lactone prostaglandin intermediates **1** were efficiently realized by the (two or three steps) methods, presented earlier, to stable Corey type aldehyde compounds, **2**, according with fig. 1. The compounds **2** could be used for building first the  $\alpha$ -side chain (then an entry to serie 1 prostaglandins) and then the  $\omega$ -side chain. The compounds are versatile also for changins the side chains building.

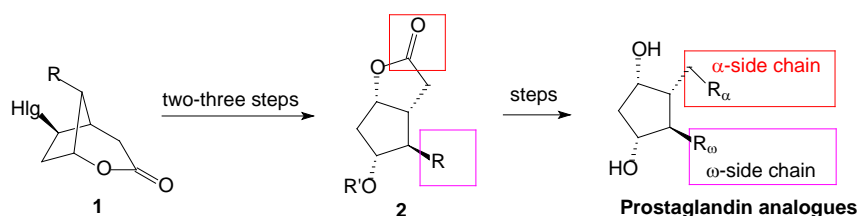


Figure 1. Corey prostaglandin synthesis from  $\delta$ -lactone **1**

**Conclusions:** The method is an efficient alternative to those presented in the literature.

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## STUDY REGARDING THE OPTIMIZATION OF POLYFURANS SYNTHESIS THROUGH TRANSESTERIFICATION

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**Keywords:** biopolymers, PEF, transesterification

**Introduction:** At the moment, one of the most widely used polyesters is polyethylene terephthalate (PET), a polyester derived from fossil fuels. As environmental concerns and our awareness that petroleum resources are finite grows, so does the need to replace traditional fossil fuels with polymers derived from renewable resources. [1] Among the best alternatives are polyfurans (PEF), derived from biomass, non-toxic, biodegradable and, hence, with a minimal impact on waste management. [2]

**Materials and methods:** The main goal of this endeavor was optimizing the technology for polyfurans synthesis starting from 2,5-furandicarboxylic acid (FDCA) derived from biomass. For this purpose we have studied the influence of several parameters (temperature, pressure, catalyst quantity, solvent, reaction time etc.) on the reaction yield.

The reaction was carried out into a stainless steel microreactor, under vigorous stirring, in two stages: i) obtaining the monomer through FDCA esterification with excess methanol; ii) obtaining the polyfurans through monomer polytransesterification with ethylene glycol, under nitrogen. The products were fully characterized by HPLC, IR and high resolution NMR.

### Results:

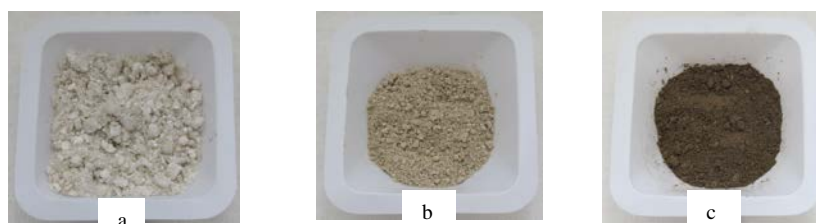


Figure 1. FDE (a) and PEF (b, c).

**Conclusions:** The reaction parameters influence both the degree of PEF polymerization (molecular weight, physical and chemical properties) and the yield of the polymerization reaction.

**Acknowledgements:** This work was supported by a grant from the Romanian National Authority for Scientific Research, CNDI – UEFISCDI, project number PN-II-PT-PCCA-2011-3.2-1683.

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## ACTION OF GEMMODERIVATES IN COMPLEMENTARY THERAPIES

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**Keywords:** diseases; gemmoderivates; gemmotherapy; complementary medicine

**Introduction:** The use of medicinal plants in the curative, the doctor assumes knowledge of each plant active principles, the parties used pharmacodynamic actions, the conditions in which plants can be effective as adjuvant. [1] Gemmotherapy act to organic dysfunctions, each glicerinohydroalcoholic extract, organotropism is well determined. Meristems have an important role through its high content of polyphenols, stimulating the activity of catalase enzyme system, anti-stress but also have many other compounds with antioxidant activity [2]. By composition and special qualities of gemmotherapies they action mainly by stimulating cellular function rebalance homeostasis and tissue.[3,4]. Complementary medicine is used not singular, but came with allopathic medicine, and conventional treatments to increase efficiency.

**Materials and methods:** Gemotherapy schemes were carried out under phytotherapy cabinet on human batch of human subjects aged 4-80 years on various types of diseases. Those schemes included various phytotherapy form.

**Results:** The results obtained after periods of 3 months; 6 months to 12 months have demonstrated the effectiveness of these products.

**Conclusions:** The general objectives were treating various disease etiologies by increasing non-specific resistance of the organism; ensure intake of bioactive substances necessary physiological functions of the immune system and relieve symptoms of acute infections, recurrent, general tonic effect.

**Acknowledgements:** The work was supported by the project PN-II-PCCA2013-4-1761 (Contract no. 204/2014), granted by the Ministry of National Education and Scientific Research (Romania), through the executive organism UEFISCDI Romania (Executive Unit for Financing Superior Education, Research, Development, and Innovation).

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## NEW COSMETICS BASED ON PASSIONFLORA (PASSIFLORA INCARNATA) EXTRACT FOR SKIN CARE AND BEAUTY

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**Keywords:** *Passiflora incarnata*, flavones, cosmetics, hidration.

**Introduction:** This paper presents new bio-products (cosmetics) based on innovative active ingredients, obtained through advanced processing of native plant species, for care, skin and hair beautification and their health maintenance. The authors have proposed to harness the medicinal plant "Passion Flower" (*Passiflora incarnata*) [1], a native vegetal species, cultivated in ecological conditions and processed through nonpolluting technologies, in order to obtain a liquid extract enriched in phytochemical compounds with stress relief, regenerative, toning and softening role, used especially for mature and sensitive skins, devitalized or abused by stress and pollution or time affected.

**Materials and methods:** The passionflower crop of own provenience was carefully monitored; harvesting was performed at the optimum time of plant development and allowed obtaining a vegetable mass (young branches and flowers) with a considerable content of active phytochemicals. This plant mass was processed through a clean technology and led to the obtaining of a liquid extract enriched in active phytochemicals. The extract was analyzed and physicochemically characterized in terms of total flavones expressed in equivalent vitexin, total polyphenols expressed in gallic and chlorogenic acids and antioxidant activity, etc., well determined by UV-VIS spectrophotometry [2]. The liquid extract was incorporated in new performing cosmetic formulations, face, body and hair care products respectively, designed specifically for deep nutrition and hydration, for the biological or premature skin aging process delay, for protection and revitalization of natural hair color and wide protection from aggressive polluting factors of the environment.

**Results:** From the range of cosmetics based on liquid extract of passion flower in association with other active herbal ingredients as: milk thistle, hemp, rosehip and sea buckthorn fatty oils, with concentrated hydroalcoholic extracts of marshmallow, blackcurrant and aloe and essential oil of lavender, three formulations of cosmetics were chosen for this presentation: revitalizing face cream, body toning lotion and stress relief shampoo, created with consideration on skin and hair physiology [3] and in compliance with the optimal results. Evaluation and efficacy studies were performed by sensory analysis with MultiSkin MC1000 device.

**Conclusions:** The developed products are in agreement with the actual ecological concepts by the use of renewable, biodegradable, non toxic plant material and via their effects of protection and regeneration of skin and hair tissues.

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**ACTION OF *AMARANTHUS CAUDATUS* IN REVIVAL OF THE BODY**

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**Keywords:** *Amaranthus caudatus*; disease; revival

**Introduction:** *Amaranth* is a gluten-free pseudocereal that tastes like coconut flavor and texture slightly spicy jelly. It is one of the most nutritious foods known with a high protein value. *Amaranth* is a rich source of calcium, magnesium and folic acid. Squalene contains chemicals that help reduce cholesterol and fight cancer. Squalene, a powerful antioxidant, has significant anticancer properties through cell regeneration, inhibition of vascularization and development of malignant tumors in some cases even helping to eradicate them.[1]

**Materials and methods:** Scientific research has demonstrated a link between consumption of amaranth and improving cardiovascular health. These changes in cholesterol levels help lower the risk of cardiovascular disease. For premature aging, regular use of amaranth prevents calcium and iron metabolism imbalances that occur in old age.[2,3] Herbal schemes were carried out under phytotherapy cabinet batch of human subjects aged 4-80 years on various types of diseases. Those schemes included various phytotherapeutic formulations.

**Results:** The results obtained after periods of 3 months; 6 months to 12 months have demonstrated the effectiveness of these products.

**Conclusions:** The general objectives were treating various disease of different etiologies by increasing non-specific resistance of the organism; ensure intake of bioactive substances necessary physiological functions of the immune system and relieve symptoms of acute infections, recurrent, general tonic effect.

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## PURIFICATION OF BIOCELLULOSE FROM KOMBUCHA BIOMEMBRANES

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**Keywords:** *bacterial nanocellulose; Kombucha; biopolymers; biomedical applications.*

**Introduction:** Biocellulose (BC) is one of the most intensively studied biopolymer at the moment due to the fact that it is an interesting renewable bioresource for preparation of nanocellulose (NC). NC has different appealing applications in multiple domains, from the biomedical field [1] where NC can be used for wound dressing due to its biocompatibility and transparency, to food industry where it can be used as functional food ingredient, food stabilizer, or for reinforcement of food packaging materials [2], and even to high tech applications in nanotechnology and photonics [1,3,4]. In the present work it is intended to purify the bacterial cellulose from biomembranes that result as secondary product of the fermentation of tea broth by symbiotic culture of bacteria and yeast (SCOBY / Kombucha).

**Materials and methods:** The raw material was represented by Kombucha biomembranes and NaOH solutions were used for purification by removal of melanoidins. Biocellulose characterization before and after various alkaline treatments was performed using XRD, TEM, TGA, and FT-IR analyses.

**Results:** In Fig. 1 it is presented the biocellulose membrane as it results after the fermentation of tea broth (brown), and after repeatedly alkaline washing procedures using also ultrasonication. XRD analyses evidenced an increase in cristallinity after washing procedure from 60% to 90%.

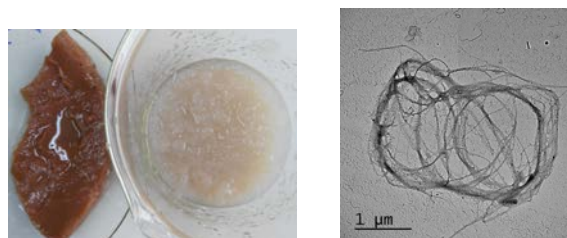


Fig. 1. a) Kombucha cellulose membrane before (brown) and after (white) NaOH washing; b) TEM image of cellulose fibrils.

**Conclusions:** The biocellulose resulted from Kombucha is free from contaminants like lignin and hemicellulose, which means better mechanical strength, hydrophilicity, transparency, and crystallinity than plant cellulose, which makes it suitable for various biomedical applications, and not only.

**Acknowledgements:** *The research was funded by UEFISCDI through the project Conversion of phytogenic silica reach food industry by-products into value-added products - CONVERT-SI, contract nr. 62/2016.*

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**REVERSE MICELLES - A MULTIFUNCTIONAL NANOSTRUCTURED MEDIUM****M.L. Arsene<sup>1\*</sup>, L. Jecu<sup>1</sup>, M. Badea-Doni<sup>1</sup>, I Răut<sup>1,2</sup>, M. Călin<sup>1,2</sup> G. Vasilescu<sup>1</sup>,****D. Aruxandei Constantinescu<sup>1</sup>**<sup>1</sup> INCDCP-ICECHIM, Spl. Independentei 202, 060021, Bucharest, Romania<sup>2</sup> University Bucharest, Faculty of Biology, Spl. Independentei 91-95, Bucharest, Romania

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**Keywords:** *reverse micelles; nanostructures; biocatalysis; inorganic synthesis.*

**Introduction:** Structural flexibility of reverse micelles (RMs), a surfactant-based nanostructured system, is the basic characteristic for their multifunctionality in various scientific fields, from biotechnology to chemical synthesis. The possibility to modulate in a controlled-manner their physical parameters, as size and inside volume, is supported by the simple change of the ratio between the surfactant concentration and the water content from inside pools of the reverse micelles (known as the hydration degree,  $w_0$ ).

**Materials and methods:** Herein, we aim to evaluate different biomimetic potentials of a RM system, consisting of AOT (sodium bis(2-ethylhexyl) sulfosuccinate) in isooctane, in terms of both biocatalytic and nano-synthesis performance versus modulated parameters of the nanostructured medium.

**Results:** As a typical membrane mimetic system, RMs have been widely used as nanostructured reaction media or nanoreactors for performing biocatalysis in a simple cell-like structure, as well as for biomimetic synthesis of various inorganic nanoparticles with targeted morphology and size. Enzymatic oxidation of alcohols with different structures was selected as the experimental model for biocatalysis, while the precipitation of  $\text{CaCO}_3$  was the model for synthesis of nanomaterials.

In a first experiment, RMs perform a biomimetic medium by simulating, in a great extend, the microsurrounding medium of the protein structure inside the cells, with special reference to the properties of inside water (e.g., electrical conductivity, viscosity, water activity, pH, ionic strength and other physical parameters).

In the domain of synthesis of inorganic nanostructures, the ability of RMs to self-assemble the surfactants in a organized structure is supporting the acute need for the controlled fabrication of well-defined inorganic nanostructures.

**Conclusions:** The ability of the RMs to perform as a multifunctional medium is discuss according to the specific results performed in each experimental model, namely the extension of the range of available substrates with substrates characterized by more or less water insolubility, respectively, to control the polymorphism and crystal size of calcium carbonate produced by crystallization in RMs, with the final target to obtain morphological controllable  $\text{CaCO}_3$  particles.

**Acknowledgments:** This research was financially supported by the project PN-II-PT-PCCA-2013-4-0995, Contract 160/2014.

## INFLUENCE OF VOLATILE AND NONVOLATILE METABOLITES OF *TRICHODERMA* SPP AGAINST *V. DAHLIAE* AND *S. SCLEROTIORUM*

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**Keywords:** *biocontrol; Trichoderma spp.; phytopathogen;secondary metabolites.*

**Introduction:** Non-target effects and hazardous nature of usual pesticides are worrying topic for both human health and environment, becoming serious constrains and criteria for implementation of new strategies to control the plant diseases.

**Materials and methods:** Present researches were focused on the possibility of enlarging the biocontrol portofolio of our new strains of *Trichoderma aspellerum*, isolated from autochthonous sample of soil, against infections with virulent phytopathogens, such as *Sclerotinia sclerotiorum* and *Verticillium dahlia*, which affect a wide range of crops. The experimental evaluation *in vitro* of the antagonistic properties of new isolated strains of *Trichoderma* spp. is describes in terms of production of volatile and non-volatile compounds capable of induce mostly or totally reduction of the infections severity.

**Results:** *Trichoderma* strains used in our experiments have demonstrated the ability to limit and even stop the development of both tested pathogens, but they have different pattern of mycelial growth inhibition for non-volatile and volatile metabolites. Both types of metabolites act synergic only against *Verticillium dahliae*, while against *Sclerotinia sclerotiorum* they have a limited antagonistic action, expressed only by the non-volatile compounds. On the other hand, non-volatile compounds have similar fungistatic effects, unlike volatile compounds which have pathogen specificity.

**Conclusions:** As the volatile and non-volatile metabolites have different mechanisms of interaction, through direct or indirect actions, with long or short distance effect, the experimental findings will be extremely useful in the future targeted application of *Trichoderma spp.* in greenhouse and/or field, as well in the choice of the formulation to be use.

**Acknowledgments:** This research was financially supported by the project PN-II-PT-PCCA-2013-4-0995, Contract 160/2014.

## NEW IMPROVED FORMULATIONS OF TEAS BASED ON SEA BUCKTHORN BERRIES

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**Keywords:** *buckthorn berries, degreased powder, tea.*

**Introduction:** Sea buckthorn berry (*Hippophaë rhamnoides*) tea is available on the market as sachets (single dose), having in their composition only small quantities of sea buckthorn berry powder (max 5%), the explanation being given by the increased content in oil which diffuses through the primary packaging of tea, compromising its quality. This paper presents studies in order to find a method to increase the amount of sea buckthorn berries powder, as much so as to be able to achieve a qualitative tea, with improved content of active substance from the fruit of sea buckthorn [1], known as the richest source of essential nutrients (vitamins A, E and D<sub>2</sub>, carotenoids, large amounts of vitamin C, group B and PP vitamins, amino acids, microelements, essential fatty acids, polyphenols etc.). [2]

**Materials and methods:** In this study, the authors have harnessed the sea buckthorn dried fruit powder as such and a by-product (BPBB) resulting from the extraction of oil by cold pressing of sea buckthorn dried fruit, as well as other herbs that can adsorb and retain the excessive fat and improve the palatability and therapeutic effect of the tea. Qualitative and quantitative analysis of the plant material was performed by common physicochemical methods, specifically aiming to discriminate the dissemination of oil through the primary packaging of tea, at fixed times, depending on the amount of sea buckthorn fruit in the realized powder mixtures.

**Results:** With the referred materials and using the sea buckthorn berries, a large number of tea formulas were developed, finally obtaining a formula based only on buckthorn fruit and leaves (formula 1), the content of BPBB (with an oil content of 7.0-8.0 wt%) being increased to 30-40% proved adequate in terms of quantity and quality. Non degreased material, in the same conditions, does not give satisfactory results. Simultaneously, other forms of sea buckthorn tea were developed in association with medicinal herbs and/or berries, in which BPBB content can be increased up to 50%.

**Conclusions:** In order to avoid the diffusion of sea buckthorn oil through the primary packaging of tea, formulations were based on partially degreased sea buckthorn fruit, with a subsequent increase of water-soluble essential nutrients content. Thus, a very good quality tea formula based on sea buckthorn fruit and leaves (40-60%) was successfully realized. Moreover, the use of BPBB allows the admixing with other plants and/or fruits in pursuit of realizing teas with specific phototherapeutic indications.

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## NIGELLA SATIVA SEED OIL EXTRACTION FOR BIOACTIVE COMPOUNDS EXPLORATION

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**Keywords:** *nigella sativa*, solvent extraction, seed oil

**Introduction:** *Nigella sativa* L. also known as „nigella” or „black cumin”, is an annual herbaceous flowering plant in the family *Ranunculaceae*. The seed oils extracted from this plant are used for food and clinical applications [1, 2]. Oils extracted from the nigella seeds does not have yet a significant market at global level, however these should represent a market niche especially due to its pharmacological, antimicrobial, and anticancer properties [3, 4]. The objectives of this research are to determine the optimum conditions for the solvent extraction of *Nigella sativa* oil, identification and isolation of valuable bioactive compounds.

**Materials and methods:** n-hexane, cyclohexane, and n-heptane have been used as extraction solvents. The nigella seeds were grinded and sieved to get particles powder with diameters of about 630 µm. By the means of laboratory Soxhlet extraction with n-hexane as solvent, the initial oil content in *Nigella sativa* seeds was determined. Gas chromatographic analysis was performed in order to establish the extracted oil composition.

**Results:** A thermal regime near to solvent boiling point was proposed. About 30 g of grinded seeds was weighted and subjected to extraction with 100 mL n-hexane for 6 h. The average of the initial oil content was 38 %, volatile and fixed oils being identified.

**Conclusions:** This research paper could be a starting point in developing processes to a higher valorization of *Nigella sativa* seeds rich in essential oils and unsaturated fatty acids with high potential for innovative agrouseful and nutraceutical [5] bioproducts.

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## SCREEN PRINTED CARBONELECTRODES MODIFIED WITH COBALT PHTHALOCYANINE VSPOLY(2,6 – DIHYDROXYNAPHTHALENE) FOR PEROXYNITRITE DETERMINATION

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**Keywords:** cobalt phthalocyanine; 2,6-dihydroxynaphthalene; electrochemical sensors; peroxynitrite

**Introduction:** Peroxynitrite (PON) is a strong non-radical oxidant resulted from the reaction of free radical of nitric oxide and the free radical of superoxide. PON has an important role in the oxidation of oxymyoglobin, with the formation of metmyoglobin, in the raw meat giving its brown colour. Several electrochemical sensors were reported in the last years for peroxynitrite determination based on hemin [1], hemin-functionalized reduced graphene oxide [2], poly(cyanocobalamin) [3]. Unfortunately, these sensors are able to measure peroxynitrite at high oxidation potentials (+0.75 V - +1.1 V). The modification of screen printed carbon electrodes (SPCE) with the electropolymerised poly(2,6-dihydroxynaphthalene) film vs the modification with cobalt phthalocyanine for PON determination is discussed in this work.

**Materials and methods:** Screen printed carbon electrodes were modified by drop-casting with the mediator cobalt (II) phthalocyanine (CoPC) and by electropolymerisation of the poly(2,6-dihydroxynaphthalene) film (poly 2,6-DHN). Electrochemical methods like cyclic voltammetry (CV), linear sweep voltammetry (LSV), chronoamperometry (CA) and differential pulse voltammetry (DPV) were used for characterisation of the developed PON sensors.

**Results:** Both type of sensors showed an electrocatalytic effect on the peroxynitrite oxidation allowing the detection of peroxynitrite at a much lower potential (around +0.1 V) comparing with the unmodified one (+0.9V). The analytical features of the optimized sensors were evaluated regarding the linear concentration range of peroxynitrite, LOD, sensitivity, intra-day and inter-days reproducibility, stability of the response in operational and in storage conditions, interferences of nitrite, ascorbic acid and hydrogen peroxide, etc.

**Conclusions:** The PON sensor based on CoPC allows the determination of PON in the range 25 – 500  $\mu\text{M}$  (LOD = 12.5  $\mu\text{M}$ ), with no interference of ascorbic acid or nitrite. On the other hand, the analytical performances of the PON sensor based on poly(2,6-DHN) are defined by the linear range 10 – 350  $\mu\text{M}$  PON (LOD = 5  $\mu\text{M}$ ) with a reduced interference of nitrite, ascorbic acid and  $\text{H}_2\text{O}_2$ .

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## OMEGA-3 FATTY ACIDS ESTERS FROM FISH WASTES

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**Keywords:** fish wastes, transesterification, molecular distillation, mathematical models

**Introduction:** The waste from fish processing, becomes a major problem for industries causing environmental pollution and loss of valuable nutrients [1]. In this context, due to their rich content in omega-3 fatty acids, fish wastes can become an important source of oils and various proteins, with applications in functional foods, dietary supplements, or pharmaceuticals. Polyunsaturated fatty acids (PUFA), can be transformed in their alkyl esters by transesterification, through one or two stages.

**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. The *Aspen HYSYS 7.2*. software was used for the process simulation of omega-3 fatty acids separation by molecular distillation.

**Results:** The purpose of this study was to optimize the omega-3 fatty acids esters separation process extracted from fish wastes. The acidity was reduced by esterification of free fatty acids with alcohol over solid acid catalyst, then the pre-treated oil was transesterification over a heterogeneous base catalyst and finally the unsaturation content was reduced by molecular distillation.

**Conclusions:** The mathematical models parameters determined showed a good recovery of omega-3 fatty acids esters with a high degree of purity.

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## SCREENING OF INULINASE PRODUCING MICROORGANISMS

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**Keywords:** *inulinase, inulin, microbial screening.*

**Introduction:** Inulinase, an enzyme catalyzing hydrolysis of polyfructosans, is interesting because fructose can be prepared from various plant sources. According to the literature, various microorganisms, such as fungi, yeast, bacteria, and actinomycetes, can synthesize inulinase. Such producers are the micromycetes *Aspergillus*, *Penicillium*, *Rhizopus*, and *Fusarium* [1, 2] the yeast *Kluyveromyces* [3] and the bacteria *Clostridium thermosuccinogenes* and *Bacillus subtilis* [4]. Inulinase producers can use inulin, sucrose, fructose, lactose, raffinose, xylose, and maltose as carbon sources [1–7]. In our study we present the results obtained after screening performed for inulinase production by microbial strains.

**Materials and methods:** Microbial strains from Microorganisms Collection of the National Institute for Chemical-Pharmaceutical Research and Development-ICCF, belong to the three major classes of microorganisms (bacteria, yeasts and fungi). Criteria used for microbiological screening and selection of strains producing inulinase, consisted of applying a method of testing the ability of microorganisms to metabolize inulin.

**Results:** The only bacterial strain able to metabolise inulin was *E. coli* ICCF 144. After 10 days microbial growth stopped. Yeast strains of *C. arborea* and *S. Chevalier* have been highlighted, featuring the largest volume of gas produced after metabolization of inulin. Similarly (as the strain *E. coli*) gas production was evident after only 7 days, reaching a maximum in 10th day. Fungal strains developed an abundant biomass after 10 days of bioprocess and also produced more gas.

### Conclusions:

- ✓ 17 of the strains tested in liquid media of screening in view of their potential to produce inulinase enzymes had positive results (gas production due to metabolization of inulin, the only source of carbon in the screening medium).
- ✓ 9 strains of microorganisms (yeasts and fungi) had favorable results, above average.

**Acknowledgements:** *This research was supported by Grand “Studies on obtaining and immobilization of microbial inulinase” supported by National Center for Programs Management.*

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## USE OF BACTERIA TO REPAIR CRACKS IN CEMENTOUS MATERIALS

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**Keywords:** aragonite, *Bacillus*, biological precipitation of  $\text{CaCO}_3$ , concrete, self-healing

**Introduction:** In concrete, cracking is a common phenomenon due to the relatively low tensile strength. Without immediate and proper treatment, cracks tend to expand further and eventually require costly repair. Micro-cracks are therefore precursors to structural failure. The aim of our work was to develop a self-healing concrete able to produce biologically limestone to heal cracks that appear on the surface of concrete structures. Specially selected *Bacillus* strains are supplementary added to concrete ingredients. In the appropriate conditions, the bacteria added in concrete may develop metabolic activities with the production of calcium carbonate. This feature has many applications in sand consolidation, remediation of damaged structured, as ornamental stones and filling of cracks and holes [1, 2]. The precipitation depends on type of microorganism, concentration of carbon and nitrogen sources, pH values, concentration of calcium ions and presence of nucleation sites. Also, environmental conditions are involved [3].

**Materials and methods:** The present study investigates the potential of two *Bacillus* strains from the ICECHIM microbial collection to be used for the biological production of calcium carbonate based minerals. These strains were grown in solid and liquid medium containing urea and  $\text{Ca}^{+2}$  ions. The bacteria ability of inducing  $\text{CaCO}_3$  precipitation was evidenced with alizarin coloration test. Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD) analyses, and scanning electron microscopy (SEM) were performed to confirm the presence of calcium carbonate in the precipitate.

**Results:** It was observed that the calcium carbonate precipitation increases with the bacteria concentration. Compression residences increase 50% also with the bacterial cells concentration. Presence of bacterial cells in the system infers the aragonite form of  $\text{CaCO}_3$ .

**Conclusions:** The experimental data showed promising results and further studies will be performed to implement on a larger scale this eco-friendly biological treatment.

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## THERMAL AND DYNAMIC MECHANICAL ANALYSIS OF POLYHYDROXYALKANOATES AND THEIR COMPOSITES

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**Keywords:** poly (3-hydroxybutyrate); cellulose fibers; dynamic mechanical analysis, TGA; nanocomposites

**Introduction:** Polyhydroxyalkanoates (PHAs), a family of biodegradable polyesters synthesized by bacteria, are characterized by biodegradability and biocompatibility, lack of immunogenic effects and lack of toxicity, being intensively studied for the biomedical field [1-3]. Poly (3-hydroxybutyrate) (PHB) and its copolymers are the most studied of the PHAs. The high brittleness and low crystallization rate as well as the poor thermal stability prevent their large application. In this work, cellulose micro and nanofibers and PHA copolymers with medium chain length were used to tailor the thermal and mechanical properties of PHB.

**Materials and methods:** Blends and composites from PHB/PHA and bacterial cellulose nanofibers (BCNF) or cellulose microfibrils were obtained by solution casting and melt compounding techniques. The composite materials were characterized by DMA and DSC/TGA.

### Results:

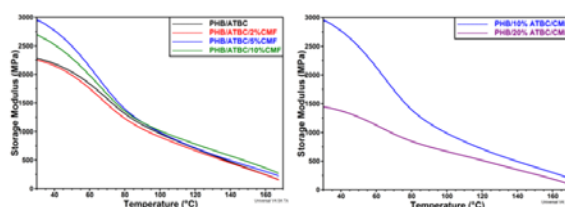


Figure 1. DMA results for PHB composites with cellulose microfibrils; influence of microfibrils (left); influence of the plasticizer (right)

**Conclusions:** BCNF and cellulose microfibrils improved both the thermal and mechanical properties of PHB/PHA blends.

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## NEW STRIGOLACTONE MIMICS

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**Keywords:** Strigolactones; signaling molecules; synthetic mimics

Natural strigolactones are molecules biosynthesized in the lower parts of the stem and roots of various plant species, which act as endo- and exo-signals. In the last few years strigolactones are identified as a novel class of plant hormones. They can only be obtained from plants roots exudates or by long multistep syntheses in minute amounts. Due to their structural complexity and their importance in plant biology, simplified strigolactone synthetic mimics are developed. The importance of strigolactones prompted us to obtain new strigolactone mimics easily accessible in significant amounts as biomimetic cues for rhizosphere beneficial microorganisms and as plant biostimulants, enhancing plant tolerance to biotic and abiotic stress and improving nutrient uptake and nutrient use efficiency.

The new strigolactone mimics derived from simple and available starting materials contain an aromatic ring connected by an ether link to a furan-2-one moiety. They were synthesized either by coupling reactions of several commercially accessible aromatic hydroxy ketones with 5-bromo-3-methyl-5H-furan-2-one or by treating 4-(4-hydroxyphenyl)pyrimidine, obtained from 4-hydroxyacetophenone and trisformylaminomethane, with the same intermediate, 5-bromo-3-methyl-5H-furan-2-one. The structures of all synthesized compounds were assigned based on chemical and IR, <sup>1</sup>H and <sup>13</sup>C NMR spectral data. Based on a bioassay for fast screening of biological activity of strigolactone mimics some of new synthesized compounds were selected for field trials. Several new strigolactone mimics synthesized in laboratory are tested as plant and beneficial microorganisms biostimulants.

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

## RESEARCH REGARDING OBTAINING HERBAL EXTRACTS WITH ANTITUMOR ACTIVITY. Note I. QUALITY EVALUATION OF RAW MATERIALS

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**Keywords:** *Chelidoni herba*, *Medicaginis herba*, *Berberidis cortex*, phytochemical analysis

**Introduction:** The discovery of active substances from herbal products as antitumor agents has become an area of great interest in recent years, due to cancer high incidence among population, chemotherapy limits and a small number of active substances isolated from herbs, that are currently used in oncology. Taking into consideration the scientific data, we have choosen aerial parts of *Chelidonium majus* L. (greater celandine), and of *Medicago sativa* L. (alfalfa) and the bark of *Berberis vulgaris* L. (common barberry) for obtaining dry extracts with potential antitumor activity [1-5].

**Materials and methods:** We have first determined the raw materials quality and established the optimum extraction parameters that lead to a high content of active substances. We have evaluated total polyphenols, flavones and phenolcarboxylic acids contents by means of spectrophotometric methods. The alkaloids were identified by chemical reactions. All assays were conducted using ethanol (96%, 70%, 50%) as solvent, heating under a reflux condenser for 30 min.

**Results:** The contents of active compounds varies with solvent and raw material (fig. 1).

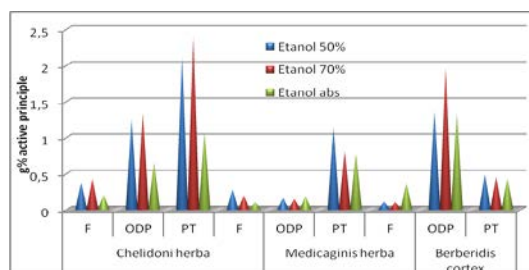


Fig. 1. Quantitative analysis

**Conclusions:** The highest content of phenolic compounds was found in 70% ethanol.

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**VARIATION IN COMPOSITION OF ESSENTIAL OIL FROM *TANACETUM VULGARE* L. FLOWERS FROM DIFFERENT LOCATIONS**

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**Keywords:** *essential oil; GC-MS; tansy; Asteraceae.*

**Introduction:** The common tansy, *Tanacetum vulgare* L. (Asteraceae) is widespread in many countries of Europe, including Romania [1]. The species areal varies from plains to the mountains, with few morphological differences [1,2]. However, regarding the essential oil quantity and quality, the composition varies in very large thresholds. The literature mention as predominant compound of the essential oil either camphor, bornyl acetate, or even thujone [3,4]. In order to obtain new antimicrobial resources, we obtained an essential oil from tansy flower harvested from two different locations and analyzed the chemical composition by GC-MS.

**Materials and methods:** The plant material was harvested from Buzau (plain region) and Brasov (mountainous region) counties. The plant material was used fresh and the volatile oil was obtained by hydrodistillation using a Clevenger apparatus. GC-MS analysis was performed on a Thermo Finnigan Focus GC-MS equipped with a split/splitless injector and MS detector (DSQ). The temperature started with 45°C for 5 min and then increased with a rate of 7°C /min to 100°C and maintained for 15 min, then rise up to 150°C, with a rate of 5°C/min and kept at this temperature for 2 min. Carried gas was helium with a flow rate of 1.2 mL/min. Injections of 0.5 ul were made in the split mode, mass range 30-650 m/z.

**Results:** The yield of the volatile oil varied from 1.6 to 1.75 %. Both essential oils contain artemisia ketone (3,3,6-trimethyl-1,5-heptadien-4-one) as major compound and the second abundant compound was *p*-cymene (1-isopropyl-4-methylbenzene). The differentiation of the two volatile oils can be made due to the presence of several compounds, among the most abundant is eucalyptol (1,3,3-trimethyl-2-oxabicyclo[2.2.2]octane).

**Conclusions:** Our research provides valuable data regarding the composition and the preparation of essential oil from *Tanacetum vulgare* L. as potential antimicrobial agents targeting the bacterial sortases.

**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.

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## STUDY OF SOME STEROIDAL GLYCOSIDES EXTRACTED FROM ROOTS OF PEPPER *CAPSICUM ANNUM L.* AND THEIR CHEMICAL CHARACTERIZATION

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**Keywords:** *pepper Capsicum annum L./ spirostanolic glycosides/ furostanolic glycosides*

**Introduction:** Steroidal glycosides possess a broad spectrum of biological activities: membranolytic, hemolytic, hipocolesterinemic, fungicide, etc. This important class of natural compounds present interest to agriculture from plant selection, in pharmacognosy, ecological biochemistry and others. The objectives of the work consist in indentification of steroidal glycosides in different organs of pepper *Capsicum annum l* and elucidation its structure.

**Materials and methods:** Steroidal glycosides was extracted from plants with ethanol. As feedstock for extraction of spirostanolic and furostanolic glycosides were used roots, leaves and seeds of this crop. The separation of glycosides was made by thin layer chromatography and gas-liquid chromatography. Their structure was elucidated by IR,  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR spectroscopy, mass spectrometry and chemical methods.

**Results:** A source rich in steroidal glycosides is pepper *Capsicum annum l*, widely cultivated crop in Moldova, Romania and many other countries. Research has shown that spirostanolic and furostanolic glycosides are present in the seeds and roots. By chemical analysis, such as full and partial acid hydrolysis, methanolysis and methylation it was elucidated their structure. In pepper's roots were identified spirostanolic glycosides the aglycons of which are ghitogenin, tigogenin and diosgenin and furostanolic glycosides containing the next aglycones: (25R)-5 $\alpha$ -furostan-2 $\alpha$ , 3 $\beta$ , 22 $\alpha$ ,26-tetraol, (25R)-5 $\alpha$ -furostan-3 $\beta$ ,22 $\alpha$ ,26-triol and (25R)-furost-5-en-3 $\beta$ , 22 $\alpha$ ,26-triol. The carbohydrate part of the obtained compounds consists of galactose, glucose and xylose.

**Conclusions:** An interesting composition of steroidal glycosides is established from roots of pepper *Capsicum annum l*, cultivated in Moldova. Complex composition of the glycosides of pepper roots presumes their interesting biological activity and creates important prospects for the future research.

## ABILITY OF BASIDIOMYCETES TO GROW ON AGRO-INDUSTRIAL WASTES

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**Keywords:** *basidiomycetes; fungi; hyphae; mycelium, SEM*

**Introduction:** The *Basidiomycetes* belonging to the *Polyporaceae* have been widely used in traditional medicine for its immunomodulating properties and its antitumor effects. The mycelia and fruiting bodies contain important bioactive compounds, such as triterpenoides, polysaccharides, nucleotides, steroids, fatty acids and proteins. Also, mycelium is an important part of our ecosystem, and plays a vital role in the recycling of minerals and carbon and in the nitrogen-fixing cycle. In recent years, the mycelium began to be considered an attractive option for the replacing of synthetic packaging and structural materials. Therefore, in the present study, different lignocellulosic materials, agro-industrial wastes, have been investigated as basal substrates for fungal cultivation in solid-state fermentation process (SSF).

**Materials and methods:** A piece of actively growing mycelia was inoculated into Erlenmayer flasks containing 2 g of various lignocellulosic substrates as well as fixed amount of inorganic salts. The cultivation was carried out in SSF system for 14 days, at 24°C. The observations were performed by Scanning Microscopy Electronic (SEM) with Fei Quanta 2000.

**Results:** A successful artificial cultivation has been obtained by supplementing the main media components with polymeric wastes, or construction materials wastes. The SEM micrographs showed significant mycelium aspects, such as: a structure similar to a fibrous material; hyphae networks attached to substrate surface; growing hyphae under and over substrate pieces; mycelium suspended in air once the material has been desiccated.

**Conclusions.** The tested lignocellulosic substrates seem to be suitable media for the cultivation of the *Basidiomycetes* strain, as the microscopically data have revealed.

**Acknowledgments.** The researches were financially supported by project PN-II-PT-PCCA-2013-4-1709/085/2014 (BIO-THERM).

## MICROSCOPIC EXAMINATION OF POLYMERS SURFACE UPON EXPOSURE TO DEGRADING MICROORGANISMS

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**Keywords:** burial soil; composites; fungi; polypropylene; SEM

**Introduction:** Different microscopic methods can be successfully applied for the characterization of polymer surface modified by microbial degradation. The investigation is very important for understanding of basic processes taking place, and also for subsequent usage of the polymeric materials. In last years, many studies have been developed on composites reinforced with lignocellulosic fibers from agro-industrial wastes, the advantages of its using are the low cost, high availability and environmental considerations [1, 2, 3]. Within our concerns regarding the polymers biodegradation, several polymeric composites based on polypropylene and wood were exposed to natural environmental conditions by burial soil. The present paper presents the modification of polymer surface after long contact with soil microorganisms.

**Materials and methods:** Composites films containing virgin (vPP) or recycled (rPP) polypropylene and wood flour in different proportions were obtained by baking a mixture of components, and mixing on a Brabender Plastograph, followed by calendering and extrusion as films. The samples were buried in garden soil at the depth of 15 cm and were exposed to natural weathering for a period of 24 months. The material surface was investigated with FEI Quanta 2000 Scanning Electron Microscope. The weight loss was evaluated as difference between initial and final sample weight.

**Results:** All the composites presented morphological modifications throughout the soil burial test: fungal colonization as hyphae networks; cracks, holes and exfoliation of polymer surface. As it was expected, the weight loss was greater in composites with higher wood content, but the values did not exceed 7-8%.

**Conclusions.** The composites were relative recalcitrant to naturally occurring biodegradation process and these features can be useful for outdoor applications.

**Acknowledgments.** The researches were financially supported by project PN-II-PT-PCCA-2013-4-1709/085/2014 (BIO-THERM).

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## THE ANALYTICAL CHARACTERIZATION OF HUMIC ACIDS FROM BIOSTIMULATORS OF PLANTS

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Biostimulators plant contain several active ingredients as humic and fulvic acids [1], nitrogen compounds and a number of beneficial elements [2-4]. Among these ingredients, the presence of humic acids in biostimulators of plants have an important role because they improve nutrient availability and impact on other important chemical, biological, and physical properties of soils. Due to the positive effect of humic substances on the visible growth of plants, the biostimulators plant contain humic acids have been widely used by the growers instead of other substances such as pesticides etc [5].

In order to regulate the biostimulators of plant containing humic acids and obtaining a reproducibility of the biological activity of these byproducts, is necessary their standardization and characterization. To achieve such a characterization and standardization it was developed a rapid and accessible analysis method for determination of humic acids from biostimulators of plants, to be used in the process of obtaining these byproducts.

**Acknowledgements:** This work was supported by the Nucleus Program: “Priorities for development of domains of specialization chemistry intelligence-SMART-PRIOCHEM”, Code:PN. 16.31.01.02.01

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## OLEIC ACID AMIDES DERIVATIVES WITH PERSPECTIVE IN THE TREATMENT OF OBESITY

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**Keywords:** *oleic acid amides, obesity.*

**Introduction:** Obesity became for the past few years a public health problem in all over the world. Usually many other illnesses are associated with obesity. The success of effective prevention or treatment of obesity might rely on therapies that control the energy metabolism and help the subject to regain a proper feeding behavior. Oleamides or oleic acid amides are a group of lipid mediators enzymatically biosynthesized in the body in response to many physiological and pathological stimuli [1].

**Materials and methods:** The oleic acid amides analogues were synthesized within the Department of Synthesis from the National Institute for Chemical and Pharmaceutical Research and Development ICCF, Bucharest. Albino Swiss mice were purchased from the Animal Biobase of U.M.F. „Carol Davila”, Bucharest. The animals were i.p. treated daily with oleic acid amides analogues for 10 days. The animal body weights and food-intakes were daily monitored. The oleic acid amides analogues concentration used for the study are molar equivalent with the therapeutic dose recommended for i.p. administration of OEA (5mg/Kg bw) [2].

**Results:** The treatment with the new structural analogues of oleoylethanolamide demonstrated a similar effect comparing to OEA treated group. The body weight and food-intake were slightly decreased comparing to the control group.

**Conclusions:** The new oleic acid amides analogues demonstrate the potential use of these molecules in obesity treatment.

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## PHYTOCHEMICAL STUDY OF A BAMBOO SHOOTS, A COMMON INGREDIENT IN CHINESE CUISINE

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**Keywords:** *bamboo shoots, antioxidant activity, polyphenolic content*

**Introduction:** The bamboo shoots are used as food, being a source of proteins, carbohydrates, natural fibers, minerals, phytosterols and polyphenols. The shoots are reported to have anticancer, antibacterial and antiviral activity [1]. The therapeutic uses of bamboo are linked to flavonoidic compounds and phenol carboxylic acids [2,3]. We evaluated the main active principles and the antioxidant activity of bamboo shoots, in order to obtain pharmacologically active extracts

**Materials and methods:** The bamboo shoots were purchased from a local market with Chinese products. The identity of the main active principles was established by specific reactions in etheric, methanolic and aqueous solutions. The quantitative determination aimed to assess the polyphenolic and mucilage content using spectrophotometric method (Folin-Ciocalteu method) and gravimetric procedure, respectively. The antiradical action was established using two methods: reducing power assay and radical scavenging capacity (reducing 1,1-diphenyl-2-picrylhydrazyl = DPPH).

**Results:** Phenolic compounds are prevailing in bamboo shoots, but the total phenolic content ( $0.5305 \pm 0.0454/100$  g raw material) is modest. The mucilages are found in higher quantity than phenols ( $2.4775 \pm 0.1601/100$  g raw material). Antiradical activity of bamboo shoots is lower than trolox in both antiradical methods.

**Conclusions:** Bamboo shoots are a source of phenolic compounds and mucilages.

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## WHEY PRE AND PRO-BIOTIC NUTRITIONAL SUPPLEMENTS DERIVATIVES AND THEIR TESTING ON POULTRY IN LAB AND PRODUCTION CONDITIONS

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**Keywords:** whey, prebiotic, probiotic, lactose, *Kluyveromyces marxianus*

**Introduction:** The research aims to valorize one of the most important industrial wastes – the whey – and to transform it from an important polluting factor into a raw material having active principles applicable in animal nutrition and health.

**Materials and methods:** After the whey separation and purification the lactose was quantified, and this growth medium, prepared within ROMVAC Company, was used for the cultivation of a wide range of microorganisms -14 species.

**Results:** The best cultivability has been observed in lactose-positive microorganisms – *Kluyveromyces*, *Enterococcus*. The first two were cultivated both for the obtaining of biomass and pre and pro-biotic fodder premixes. Until now, two products were achieved: *OLIGOLAC - ANIMAL PREMIX* made up of yeasts, selenite & proteins chelate compounds, selenite yeasts, kaolin and lactose, and *OLIGOLAC BIOENTEROM*, a probiotic containing *Enterococcus faecium* NCIMB 11181. Results achieved for the experiments conducted on SPF (species pathogen free) poultry referred to the influence over some raising parameters (growth rate, fecundity) or over health state, including over immune response after vaccination against *Newcastle* and *Gumboro* diseases. Flocks fed with fodder containing *OLIGOLAC - Animal premix*, as compared to the ones fed with conventional fodder, have shown growth rates at 50 days with 15-20% higher and at 80 days with 4.1-4.7% higher, too depending on mixture ratios. SPF fecundity rate fed with premix was with 5.3-10.7% higher than of poultry fed with conventional fodder. Immune response (NDV, IBD) was also positively influenced.

**Conclusions:** The two products are already marketed, the research work continuing both within the project and after its completion, with the aim to obtain other valuable products based on whey.

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## COMBINATORIAL LIBRARY DESIGN TARGETED ON BREAST CANCER CELLS

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**Keywords:** aminopyrazole, antiproliferative, optimal biopharmaceutical profile

**Introduction:** Combinatorial libraries represent an important source of chemically related compounds for high-throughput screening enabling the rapid exploration of novel regions of the chemical space. In order to find new potential anticancer substances with a better selectivity and efficiency and using the structural pattern of our previous synthesized pyrazole derivatives and the fragment based drug discovery concept we designed a library of novel molecular structures targeting major protein kinases.

**Materials and methods:** The small library was constructed based on the 5-amino-3-phenylpyrazole scaffold. This drug design strategy was reinforced by the use of modern computerized prediction methods and by the high priority exhibited towards the biopharmaceutical profile. The computer aided predictions of the compounds ADME profile were performed on ADMET Predictor™ version 5.5, PreADMET version 2.0 and OSIRIS Property Explorer. In addition to the biopharmaceutical profile estimation, we predicted the druglikeness of the molecules to discriminate between druglike compounds and non-drug substances in order to avoid future liabilities.

**Results:** The integration of virtual screening of the combinatorial library function as a priority filter restricting the synthesis efforts. The molecules with an optimal biopharmaceutical profile are designed for future synthesis in order to obtain new anticancer substances targeted on breast cancer cells.

**Conclusions:** A small library of new compounds was obtained and optimized in order to synthesize future new antiproliferative agents for breast cancer patients.

**Acknowledgements:** This work was supported by a grant of the Romanian National Authority for Scientific Research and Innovation, CCCDI – UEFISCDI, project number 46 BM/2016 Code PN3-P3-246.

## FT-IR SPECTROSCOPIC ASSAY METHOD FOR ACETYL CYSTEINE IN SOLID FORMULATIONS

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**Keywords:** pellets, ATR, acetylcysteine

**Introduction:** In order to obtain pharmaceutical formulations with a high concentration of acetylcysteine we prepared pellets using the extrusion-spheronization technique. The content of the active drug was measured by developing a simple and rapid FT-IR ATR method.

**Materials and methods:** The pellets were prepared using microcrystalline cellulose (Avicel PH 101, Cork, Irland), monohydrate lactose 200 mesh (Meggler GmbH, Germany), and various amounts of acetylcysteine. The mixture was sprayed with a polyvinylpyrrolidone (PVP K30, BASF, Germany) aqueous solution and the wet mass was extruded, the resulting extrudates were spheronized into pellets, which were subsequently oven-dried at 40°C. The IR assay was developed on a JASCO FT/IR-4200 spectrometer (JASCO, Japan) with an ATR PRO450-S accessory. Full length spectral range (4000 to 400 cm<sup>-1</sup>) was scanned during the experiment with a resolution of 4 cm<sup>-1</sup>. The pellets were grounded to a fine powder and measured without separation from excipients.

**Results:** A simple, precise and rapid method has been developed for the quantification of acetylcysteine in solid formulations. The method involves the measurement of thiol group (-S-H) peak and evaluation of drug content from the measured absorbance values using calibration plots.

**Conclusions:** The method was validated and found to be precise with high recovery levels.

**Acknowledgements:** This work was supported by a fellowship of the Romanian National Authority for Scientific Research and Innovation, CNCS - UEFISCDI, project number PN-III-P1-I.1-BT-2016-0003, within PNCDI III and by the Sectoral Operational Programme Human Resources Development (SOP HRD), financed by the European Social Fund and by the Romanian Government under the contract number POSDRU/159/1.5/S/137390.

## SYNTHESIS OF NEW PHENAZONE DERIVATIVES AS POTENTIAL BACTERIAL SORTASE A INHIBITORS

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**Keywords:** pyrazole, thiourea, anti-virulence agents

**Introduction:** The emergence of antibiotic-resistant bacteria is a major health concern due to therapeutic failure of many drugs currently in use against pathogenic microbes. Sortases are transpeptidases that occur in almost all Gram-positive bacteria and attach surface proteins to the cell wall playing an important role in virulence and infection [1]. A number of promising inhibitors of sortases have been identified, most of them targeting the enzyme active thiol moiety.

**Materials and methods:** The analysis of the structural patterns of the described sortases inhibitors revealed important scaffold like rhodanines, pyridazinones, pyrazolethiones and diarylacrylonitriles [2]. Based on these scaffolds, we designed and synthesized new derivatives of 4-aminophenazone incorporating a thiourea moiety. The compounds purity was certified by thin layer chromatography and elemental analysis.

**Results:** The structures of the newly obtained compounds were confirmed on the basis of their IR and NMR spectroscopic analysis. The compounds are under evaluation for the preliminary assessment of their anti-virulence properties on various pathogenic bacteria.

**Conclusions:** We designed and synthesized a number of 8 new 4-amino-1,5-dimethyl-2-phenylpyrazole-3-one derivatives as potential anti-virulence agents targeting the microbial sortase family. The structures of the synthesized compounds were confirmed by IR and NMR spectroscopic analysis and elemental analyses.

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## THE OBTAINING AND ANALYSIS OF *SALVIA GLUTINOSA* L. (LAMIACEAE) VOLATILE OIL

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**Keywords:** volatile oil; GC-MS; sticky sage; Lamiaceae

**Introduction:** The genus *Salvia* L. comprises about 900 species from which, 13 species and 9 hybrids are growing in the wild flora of Romania [1,2]. *Salvia glutinosa* L. is a small shrub that grows in moist places in deciduous forests in Carpathian Mountains. The aerial parts of the plant are covered with sticky trichomes and rare glandular hairs [3]. Previous research indicate that the volatile oil is in small quantities, the flowers having the highest content [3]. In the present study we obtained the volatile oil from flowers, and leaves with stems. The volatile oil was analyzed and characterized by GC-MS.

**Materials and methods:** The plant material was obtained from our local botanical garden, where it was acclimatized five years ago, the original plant cuttings originating from Doftana valley. The plant material was used fresh and the volatile oil was obtained by hydrodistillation using a Clevenger apparatus. GC-MS analysis was performed on a Thermo Finnigan Focus GC-MS equipped with a split/splitless injector and MS detector (DSQ). The temperature started with 45°C for 5 min and then increased with a rate of 7°C /min to 150°C and maintained for 25 min. Carried gas was helium with a flow rate of 1.2 mL/min. Injections of 0.5 ul were made in the split mode using a mass range 30-650 m/z.

**Results:** The yield of the volatile oil from flowers was 0.05%. No volatile oil could be obtained from stems and leaves. The dominant compound of the volatile oil was germacrene D.

**Conclusions:** The results are a prerequisite for further research on the volatile oil from *Salvia glutinosa* L. as potential antimicrobial agents targeting the bacterial sortases.

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## HPTLC DETERMINATION OF $\beta$ -AESCIN IN EXTRACTS FROM FIVE SPECIES OF *AESCULUS* L. (SAPINDACEAE)

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**Keywords:** *Sapindaceae*, *Hippocastanaceae*; *HPTLC*; *saponins*.

**Introduction:** *Aesculus* L. genus (Sapindaceae) has about 12 species of trees and shrubs spread mainly in the northern hemisphere. *Aesculus* belonged previously to Hippocastanaceae family and, since APG classification it was moved in Sapindaceae family. The species are grouped in five sections: *Aesculus* L., *Pavia* (Mill.) Persoon, *Calothyrsus* (Spach) K. Koch, *Macrothyrsus* (Spach) K. Koch and *Parryanae* Wiggins<sup>1</sup>. The plant species contain various polyphenols and aescin, compounds well-known for their therapeutic value<sup>1</sup>. In the present work we evaluated the presence of aescin by high performance thin layer chromatography (HPTLC) in aqueous, hydroethanolic and ethanolic extracts from five species of *Aesculus*: *A. hippocastanum* L., *A. pavia* L., *A. octandra* Marshall, *A. parviflora* Walter and a hybrid species, *Aesculus x carnea* Hayne (*A. hippocastanum* x *A. pavia*).

**Materials and methods:** The plant material was harvested from Botanical Garden "Dimitrie Brandza", Bucharest. Crude extracts were obtained from the leaves of each plant material using three solvents. Chromatographic separation of aescin and polyphenols was performed on silicagel 60 F254 HPTLC plates using a LinomatV applicator and a TLC Scanner 3 (254, 366 nm). The determination was carried out using the densitometric absorbance mode at 254 nm and 366 nm<sup>2,3</sup>.

**Results:**  $\beta$ -aescin was identified in *Aesculus* extracts. The higher intensity of the signal was registered in ethanolic preparations, followed by hydroethanolic and aqueous extracts.

**Conclusions:** The results of the study indicate a higher content of aescin and that the method allow the analyses of multiple samples as very rapid and cost efficient.

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## SIMULTANEOUS DETERMINATION OF PHENOLIC ACIDS AND FLAVONOIDS IN EXTRACTS FROM THREE *FALLOPIA* ADANS. SPECIES BY HPLC

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**Keywords:** *Polygonaceae*; *HPLC*; *polyphenols*.

**Introduction:** Polyphenols are promising bioactive compounds with positive implications for human health and, at the same time, are considered bio-markers at species level<sup>1</sup>. Plants belonging to *Fallopia* genus are invasive species used in traditional medicine for their anthelmintic, purgative, hepatoprotective, febrifuge and anti-inflammatory properties. Their chemical composition includes phenolic acids, flavonoids, stilbenes and anthraquinones<sup>2,3</sup>. The objective of the present study was to develop a HPLC method in order to identify the major phenolic compounds in hydroethanolic extracts from three species of *Fallopia* (Polygonaceae): *F. aubertii*, *F. convolvulus* and *F. dumetorum*.

**Materials and methods:** The plant materials were harvested from wild flora (*F. convolvulus* - herba and *F. dumetorum* - herba) and from a local garden (*F. aubertii* - herba and flowers). The HPLC method was performed according to the Tan *et al.* protocol with some modifications<sup>4</sup>. Chromatographic separation was performed on a Varian Prostar liquid chromatography system with a PDA Prostar 330 detector and Rheodine 7125 injector, using an Inertsil 5 ODS C<sub>18</sub> (250 mm x 4.6 mm, 5 μm) reversed-phase column. The mobile phase consisted of 0.05% aqueous phosphoric acid and acetonitrile in gradient. The flow rate was 1.0 ml/min, at 35°C and the UV detection wavelength was set at 280, 325, 345 and 355 nm. The standard polyphenols used were *p*-coumaric, gallic, ferulic, caffeic and chlorogenic acids and rutin, isoquercitrin and hyperoside.

**Results:** Gallic acid, chlorogenic acid and caffeic acid were identified in our plant extracts. Among flavonoids, isoquercitrin and hyperoside were found in *Fallopia* extracts.

**Conclusions:** The results of the study indicate a higher phenolic content and that the method allow the analyses of multiple samples as very rapid and cost efficient.

**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.

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## HIGHLIGHTING THE ACTION MECHANISM OF SOME NEW PLANT BIOSTIMULANTS

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**Keywords:** plant biostimulant, nitric oxide modulators, *Arabidopsis*, cabbage, fluorescence

**Introduction:** Nitric oxide (NO) is the signaling molecule that orchestrates metabolic pathways involved in plant development and metabolism, as well as in plant response to stress [1]. Its generation into plant tissues is related to an increase of reactive oxygen species-ROS [2]. NO and ROS modulation was demonstrated to be the main mechanism of action of some bio-based plant biostimulants like chitosan [3]. We developed new synthetic plant biostimulant compositions and we studied their effects in generation of NO and ROS on *Arabidopsis thaliana* and *Brassica oleracea* var. *capitata* tissues, using specific diaminofluoresceine dyes as fluorescence indicators.

**Materials and methods:** The tested concentrations of new biostimulants ranged between 0.1 and 1 mM. Experiments were performed on *Arabidopsis thaliana* (cruciferous model plant) and on cabbage (on controlled and experimental field conditions), by foliar application. Effects of new synthesized compounds on NO and ROS generation in vegetal tissues were studied using specific diaminofluoresceine dyes as fluorescence indicators: H2DCFA (2',7'-dichlorodihydrofluorescein diacetate) and DAF-FM DA (4-amino-5-methylamino-2',7'-dichlorodihydrofluorescein diacetate). Fluorescence measurements were recorded on an AXIO - OBSERVER D1, Zeiss, equipped with a video digital camera AxioCam MRc using an AxioVision Rel.4.6 software.

**Results:** Fluorescence microscopy and image analysis showed the presence of NO and ROS in all plant tissues analyzed treated with the new biostimulant compositions, compared to the negative control. We also observed differences in the synthesis of NO and ROS between the different compositions used. The obtained results demonstrated the involvement of NO and ROS into the mechanism of action of the new plant biostimulants compositions.

**Conclusions:** The obtained data suggested that some of the new biostimulant compositions promote the NO and ROS accumulation in plant tissues, thus being able to modulate plant development and metabolism and to contribute to defense mechanisms of plants against biotic or abiotic stress.

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## INFLUENCE OF TWO BIOPLASTICIZERS OVER SOME PROPERTIES OF PLA BIOCOMPOSITES FOR FOOD APPLICATIONS

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**Keywords:** biocomposite; bioplasticizer; food packaging; property

**Introduction:** PLA materials show good transparency and mechanical properties, but they are considered inappropriate for food packaging applications due to the low flexibility, low melt viscosity, bad gas barrier properties, relative low heat distortion temperature and slow crystallization rate [1]. As consequence its properties must to be tailoring.

**Materials and methods:** Poly(lactic acid) (PLA) was type 2003D from NatureWorks LLC (Minnetonka, MN, USA). Tributyl *o*-acetyl citrate (ATBC) was supplied by Proviron Belgium. Lapol 108 as masterbatch (MB) (up to 30 % in PLA) was purchased from Lapol, LLC (USA). Medium molecular weight chitosan (CS) was purchased from Sigma-Aldrich. PLA based biocomposites were investigated by means of processing behavior, FT-IR spectroscopy, DSC analysis, mechanical properties, water ecotoxicity and fungal activity.

**Results:** A comparative study on the influence of two different bioplasticizers on the mechanical, thermal and antifungal properties of PLA based biocomposites containing 1% chitosan revealed that the ATBC led to a good procesability, elongation at break, barrier to oxygen and increase of crystallinity compared with MB. All PLA based biocomposites did not influence the germination capacity and the first stage of plants growth. Also, the prepared samples showed antifungal properties against *Aspergillus brasiliensis* ATCC 16404, *Fusarium graminearum* G87 and *Penicillium corylophilum* CBMF1 fungi.

**Conclusions:** Based on the obtained results it can appreciated that the PLA based biocomposites could be designed for flexible or rigid food packaging, for fatty/acidic food and also for aqueous, alcoholic and milky food depending of the bioplasticizer used.

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## **IN VITRO CHARACTERIZATION OF SCAFFOLDS BASED ON PHB AND BACTERIAL CELLULOSE BIOCOMPOSITES**

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**Keywords:** *biopolymer; thermal properties; spectral characteristics; in vitro degradation*

**Introduction:** PHB alone does not fulfill all technical specifications for using as a biomaterial in medical and tissue-engineering applications. In consequence, the mixing of PHB with other polymers and additives is a good strategy to obtain the desired properties. It is found that the reinforcement of PHB with bacterial cellulosic gives to the polymer composite a good biocompatibility [1].

**Materials and methods:** Bacterial poly(3-hydroxybutyrate) (PHB), powder, coded T19, was supplied by BIOMER, Germany. Bacterial cellulose (BC) powder was provided by ICCF Bucharest. Tributyl citrate (TBC) was supplied by SIGMA-ALDRICH. Phosphate buffered saline (PBS) medium (pH 7.4) was prepared in laboratory. The effect of BC content on the thermal properties (DSC), spectral characteristics (ATR-FTIR), water absorption and *in vitro* degradation (weight loss and thermal properties (by DSC analysis) after the immersion of specimens in PBS over 20 days) was investigated.

**Results:** The results of DSC analysis evidence a significant decrease in degree of crystallinity of blends with increasing of BC content into biocomposites which favors the water absorption. The decrease of crystallinity index (CI) with BC content was found for all biocomposites. All biocomposites showed the increased degree of crystallinity after 20 days immersion in PBS, in good agreement with weight loss, which denote their degradation under PBS medium.

**Conclusions:** The obtained results showed that BC can reduce the PHB crystallinity and promote its degradation under PBS medium. Also it was found that the water absorption increased with the percentage of BC. The composites could be recommended for the recovery of damaged tissues.

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## CHARACTERIZATION OF *TRICHODERMA* ISOLATE FOR ANTAGONISTIC ACTIVITY AGAINST PHYTOPATHOGENS

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**Keywords:** antagonism; biocontrol; phytopathogens; *Trichoderma*

*Trichoderma* spp. are used as biological control agents against plant diseases caused by pathogenic fungi [1], but there is still interest to find more efficient fungi within *Trichoderma* genus. A *Trichoderma asperellum* T50 isolated from soil was evaluated for *in vitro* antagonism against ten aggressive phytopathogenic fungi. Also, several characteristics of fungal isolate as capacity to produce hydrolytic enzymes and factors stimulating the plant growth have been determined.

The antagonism between *Trichoderma* isolate and pathogens was evaluated with dual culture method [2, 3]. The radial growth of the pathogens was measured and the inhibition percent of average radial growth was calculated relative to the control using formula:

$$I = [(C - T)/C] \times 100$$

where I is the percentage inhibition of radial mycelial growth; C is the radial growth of the pathogen in the control; T is the radial growth of the pathogen in the presence of antagonistic *Trichoderma*.

The isolate revealed differential reaction patterns against the test pathogens. *T. asperellum* T50 strongly inhibited the mycelial growth of *P. ultimum* (92,6%), followed by *R. solani* (91,3%) and *V. dahliae* (90%). *B. allii* was more resistant to antagonistic strain with only 31.2% inhibition of mycelial growth. The antagonistic strain was found to produce cell wall degrading enzymes (chitinases and cellulases), to solubilize phosphorus into plant accessible forms, and to secrete siderophores that play an essential role in competition for iron with other microorganisms in the rhizosphere. These features revealed that *T. asperellum* T50 could be a good candidate for future use in biological control of plant pathogens.

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## MORPHO-PHENOTYPIC AND MOLECULAR CHARACTERIZATION OF *KLUYVEROMYCES* YEAST STRAINS ADAPTED TO MODIFIED PARAMETERS

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**Keywords:** *Kluyveromyces marxianus*; molecular characterization; phenotypic characterization;

*Kluyveromyces marxianus* ZIM 1867 and *Kluyveromyces marxianus* NRRLY 1195 yeast strains are unicellular microorganisms, eukaryotic, non-motile, widely used on an industrial scale because of its ability to metabolize whey lactose with accumulation of biomass. By changing the process parameters were obtained lactic adapted yeast strains, which were characterized compared with the parental ones.

**Materials and methods.** Morphological characterization was carried out microscopically. Yeast strains phenotypic characterization was performed by inoculation on specific solid and liquid culture media (ATCC 200, Sabouraud), in order to set some features of the colony (surface, edges, color, profile). For evidence of DNA molecular markers and the effect of environmental factors on the stability of DNA were used PCR-based methods. Thermal denaturation profile analysis was done by two methods: melting type analysis and HRM analysis (high resolution melting).

**Results.** Microscopically, yeast cells are spherical or oval, solitary or with 1-2 apical or side buds and have sizes between 2 - 6.5 × 3.8 - 8 µm.

On solid media, after 24 hours, yeast strains formed smooth colonies, whose consistency is like a thick paste (young colonies), diameter between 2-4 mm, circular shape with creamy, smooth, matte, domed profile, white-cream color.

Yeast strains develop sediment on liquid media, made up of individual cells or micro-colonies resulting from intimate association of cells belonging to different generations. Ring is formed at the surface of medium, foaming and disturb uniform the growth medium.

In terms of molecular characterization, data obtained show that both for *Kluyveromyces marxianus* ZIM 1867 and *Kluyveromyces marxianus* NRRLY 1195 the number of obtained polymorphic bands does not change depending on the conditions in which the experiments were performed. The *Kluyveromyces* strains growth media does not cause genomic instability or the expansion of some repetitive sequences. Melting type analysis and HRM analysis revealed clear differences between DNA extracted from the two *Kluyveromyces* strains and showed that genetic material of each species does not change in the conditions in which they were grown.

**Conclusions.** Both adapted *Kluyveromyces marxianus* yeast strains shows the cultural characteristics identical to those of the parental strains. Modification of growth process parameters does not change the genetic material of each species.

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## EXTRACTION OF THE MAIN POLYSACCHARIDES FROM *KLUYVEROMYCES MARXIANUS* STRAINS CELL WALL

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**Keywords:** *Kluyveromyces marxianus*; induced autolysis;  $\beta$ -glucans; monnoproteins;

*Kluyveromyces marxianus* is dairy yeast with ability to metabolize lactose due to the presence of  $\beta$ -galactosidase. The *Kluyveromyces* yeast cell wall has valuable structural polysaccharides such as  $\beta$ -glucans ( $\beta$ -1.3 D-glucose and  $\beta$ -1.6-linked branches) and mannan oligosaccharides (which are linked to most of the protein, referred as mannoprotein complex), with many applications in food, feed and pharmaceutical industry. The aim of the work was to extract the main polysaccharides of the yeast cell walls and to study methods of mannan oligosaccharides deproteinization.

**Materials and methods.** Process for the isolation of the main polysaccharides was performed in several steps: yeast cell wall preparation by induced yeast autolysis using an autolysis promoter; separation of cell walls (solid residue) from supernatant by centrifugation; extraction of yeast cell wall  $\beta$ -glucans and mannoproteins by alkaline method; separation of alkali soluble mannoproteins from alkali insoluble  $\beta$ -glucans connected to chitin by centrifugation; recovery of mannoproteins by alcohol precipitation; deproteinization of mannoproteins by two methods. Optimization of extraction process was carried out under certain alkali concentrations, sample/alkaline solution ratio (w/v), temperatures and extraction time.

**Results.** The optimum conditions for the extraction of  $\beta$ -glucans and mannoproteins are: 0,75N NaOH solution, sample to alkaline solution ratio 1:5 (w / v), temperature 75<sup>0</sup>C, 2 hour. Mannoproteins and soluble  $\beta$ -glucans are found in supernatant. Alkali insoluble  $\beta$ -glucans connected to chitin remain as a solid residue.

Regarding the techniques for deproteinization, trichloroacetic acid method was better than Sevage method. Trichloroacetic acid 10%, 20 hours, two times was the optimum condition for the separation of proteins. The mannan oligosaccharides were precipitated from aqueous phase with three volumes of ethanol.

**Conclusions.** Increasing sample: alkaline solution ratio and temperature and prolongation of time exposure are not economic.

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## IN VITRO EVALUATION OF ANTIDIABETIC ACTIVITY OF *MOMORDICA CHARANTIA* PLANTS TREATED WITH MULTIFUNCTIONAL PRODUCTS

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**Keywords:** bitter melon, *in vitro* analysis, insulin secretion, antidiabetic effect

**Introduction:** Diabetes mellitus is a chronic metabolic disorder manifested with elevated levels of glucose in the body, which is an effect of impaired insulin secretion, insulin effect, or both. According to the latest reports, the prevalence of global diabetes in 2013 was 8.3% and expected to reach 10.1% in the year 2035 [1]. Long term management with oral hypoglycemic agents, can lead to adverse effects and drug resistance [2]. Nowadays, many studies are carried out to explore plant natural products that contain certain phytochemicals with antidiabetic potential as alternative therapy. One of such herbal plants is bitter melon (*Momordica charantia*) [3], which have been used in the treatment of several diseases including inflammation, infection and diabetes. The aim of this study was to evaluate *in vitro* antidiabetic activity of *M. charantia* plants cultivated in Romania and treated with multifunctional products.

**Materials and methods:** *In vitro* evaluation of antidiabetic activity was conducted on a mice insulinoma cell line (βTC-3). Pancreatic beta cells were cultivated in normal (5.6 mM) and hyperglycemic (16.7 mM) conditions in the absence and presence of ethanolic extracts of treated *M. charantia* plants. Insulin secretion was determined by ELISA assay.

**Results:** The obtained results demonstrated that *M. charantia* extracts presented *in vitro* antidiabetic effects and indicated that the treatments with multifunctional products influence the antidiabetic activity of *M. charantia* plants.

**Conclusions:** *Momordica charantia* plants treated with multifunctional products have an increased potential to be used in diabetes therapy.

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## PHARMACOLOGICAL RESEARCH REGARDING THE ANTI-INFLAMMATORY EFFECT OF SOME EXTRACTS OBTAINED FROM PLANTAGINACEAE FAMILY

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**Keywords:** anti-inflammatory effect; hind paw edema; Plantaginaceae.

**Introduction:** In this paper we investigated the anti-inflammatory effect of the aqueous and hydroalcoholic dry extracts obtained from the aerial parts of *Cymbalaria muralis* (ivy-leaved toadflax), Plantaginaceae. We chose this species due to its composition in iridoides and mucilages, active ingredients with anti-inflammatory properties<sup>1</sup>.

**Materials and methods:** The anti-inflammatory activity, after the oral administration of a single dose of the dry extracts (100 mg/kg b.w.), was evaluated using two standard experimental models of inflammation - dextran and kaolin induced hind paw edema. The paw volume was measured before and at 1, 2, 3, and 4 h, after inflammatory agents administration<sup>2,3</sup>. The anti-inflammatory effect was compared with a control group, treated by gavage with distilled water (1 mL/100 g b.w) and a reference group, treated by gavage diclofenac (100 mg/kg b.w).

**Results:** For the dextran - induced inflammation model, it was observed that the aqueous extract exhibits anti-inflammatory activity when compare both with the control and the reference group. For the kaolin - induced inflammation model, both extracts exhibit anti-inflammatory activity when compare the control. For the aqueous extract the effect is higher than the one recorded for the reference group.

**Conclusions:** The two extracts, aqueous and hydroethanolic, obtained from the aerial parts of *Cymbalaria muralis* showed anti-inflammatory properties. For the aqueous extract the anti-inflammatory effect is higher than the one observed for the reference substance, diclofenac.

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## INFLUENCE OF TREATMENTS WITH *TRICHODERMA* ON PHYSIOLOGICAL AND PHYTOCHEMICAL PARAMETERS OF *PASSIFLORA CAERULEA* L.

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**Key words:** *Trichoderma*, *Passiflora caerulea*, physiological and phytochemical parameters

**Introduction.** There is a growing trend in the consumption of functional foods/ food supplements from plants (nutraceuticals) recently introduced in culture in Romania. In the present study, it has been performed a complex approach (botanical and phytochemical) of *Passiflora caerulea*. In order to obtain an evaluation scale of *Trichoderma* consortia multifunctional bioproducts, different variants of treatments in vegetation were tested in experimental field under the good practice conditions recommended in this area.

**Material and methods.** Physiological investigations: coefficient k, leaf area index (LAI), chlorophyll fluorescence (fluorometer Walz Sam-2500), stomatal conductance (porometer Delta F Devices AP4) and yield of green plant biomass (gravimetry). Phytochemical investigations: active principles (polyphenols, flavonoids) content, in correlation with their antioxidant activity and determination of cytotoxicity of *P. caerulea* extracts in NCTC cell line.

**Results.** The best results, statistically confirmed, were obtained with vegetation treatment in Variant V2 (*Trichoderma* 10<sup>7</sup> ufc/ml), V4 (*Saturaja hortensis* oil and nutrients), V3 (*Trichoderma* 10<sup>8</sup> ufc/ml), and The Neutral Red method showed a good biocompatibility of *P. caerulea* extracts in NCTC cell line, up to 10-150 µg/ml concentration, sustained by normal cell morphology. At concentrations higher than 250 µg/ml, the plant extracts become cytotoxic, altering the cell membrane structure, the cells viability and proliferation.

**Conclusions.** The products based on *Trichoderma* and essential oils are directly active against phytopatogenic agents. The results allowed selecting the optimal range of noncytotoxic concentrations of the *P. caerulea* extracts (less than 250 µg/ml) that will be use in further experiments.

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## COMPUTED MOLECULAR DESCRIPTORS FOR SULFUR-CONTAINING AMINO ACIDS

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**Keywords:** *Sulfur amino acids; molecular descriptors.*

**Introduction:** This work provides a computational study on 3D molecular structure of two essential sulfur-containing amino acids (Methionine and Cysteine) and reports values of various molecular descriptors and properties, predicted using Spartan'14 software.

**Computational method:** 3D structure compounds build; geometry optimization by energy minimization; properties and molecular descriptors calculations using Spartan'14 Software from Wavefunction, Inc. Irvine, CA. Algorithm: Density Functional B3LYP Method, basic set 6-31G\*[1,2], in vacuum, for equilibrium geometry at ground state.

**Results:** Properties applied in quantitative structure–activity relationships (QSAR), orbitals and energies, atom charges and bond orders (Mulliken charges, electrostatic charges, natural charges), vibrational modes, orbitals and energies and thermodynamic properties were predicted. Energy diagram for frontier molecular orbitals HOMO and LUMO, their gap and UV vis allowed transitions are listed. Also, important properties and topological indices, that interfere with compounds reactivities are predicted and analysed: electrostatic potential map, local ionization potential map, LUMO map, atoms and bonds density, total polar surface area (TPSA), octanol-water partition coefficient (logP), HBD and HBA counts (no. of hydrogen-bondings: donor and acceptor), dipole moment, polarizability, ovality, area and volume for the studied conformers of Methionine and Cysteine. Results have been interpreted in terms of electronic effects, molecular deformability, steric factors and reactivity, aiming to achieve a complex structural analysis.

**Conclusions:** Due to their ability to form disulfide bonds, by an oxidation reaction of thiol groups, sulfur amino acids plays an important role in proteins folding. Our predictive, computational structural study has brought additional information to the existing properties data, in order to enhance the researchers ability to control mechanisms involved in sulfur–containing amino acids biosynthesis, important aspects for nutrition and metabolism.

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## STUDIES CONCERNING THE BIOLOGICALLY ACTIVE COMPOUNDS IN *M. CHARANTIA* L. EXTRACTS AND THEIR *IN VITRO* BIOCOMPATIBILITY

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**Keywords:** *Momordica* extracts, phytochemical screening, biocompatibility, anti-tumoral capacity

**Introduction:** *Momordica charantia* L. is a medicinal plant belonging to the family *cucurbitaceae*, widely grown in India, Asia, South America and used as food and in traditional medicine. The fruits and leaves contain alkaloids, glycosides, saponins, phytosterols, proteins, flavonoids, tannins, aromatic volatile oil, gums and mucilages. *M. charantia* L. is used for its anti-inflammatory, anticancer, anxiolytic, antibacterial and especially antidiabetic properties [1]. The aim of this study was to perform a phytochemical screening of alcoholic extracts of *M. Charantia* L. (cultivated in Romania) treated with different bioactive compounds and also to test the biocompatibility and anti – tumoral effect of these extracts.

**Materials and methods:** *M. charantia* L. plants were treated with some bioactive compounds (a suspension of *Trichoderma* in concentrations of  $10^7$  - V2 and  $10^8$  - V3 CFU/mL, thyme oil - V4A, *Trichoderma* compost - V5 and ceramics - V6). Total polyphenols and flavonoids content were determined in the alcoholic plants extracts [2]. The extracts' antioxidant capacity was evaluated by measuring the inhibition of ABTS cationic radical [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 Neutral Red (NR) assay [3].

**Results:** All extracts contain significant amounts of antioxidants, polyphenols and flavonoids. *M. charantia* L. plants treated with V2, V3, V4A contain a higher amount of flavonoids and polyphenols than the other analyzed plants. The results of NR assay demonstrated that the extracts of plants treated with V2, V3, V4A and V6 did not affect the cell viability at 50-150  $\mu\text{g/mL}$  after 72 h of cultivation. V4A treatment sample had a strong anti-tumoral effect at concentration of 100-150  $\mu\text{g/mL}$  on HEP2 cell line being also biocompatible in this concentration range. The morphological test confirmed the results of NR assay.

**Conclusions:** V2, V3, V4A extracts contain the biggest antioxidants amount. V4A is the treatment that induced in *M. charantia* L. plants both a non-cytotoxic effect on normal cells and an anti-proliferative effect on tumoral cells.

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**KERATINOPHILIC *MICROSPORUM GYPSEUM* ISOLATED FROM SOIL**

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**Keywords:** *keratinophilic; keratin; Microsporium gypseum; Vambreuseghem hair baiting method.*

**Introduction:** Keratinophilic fungi play an important role in the biodegradation of keratinized materials (skin, hair shaft and nails in humans and claws, hair, horns, hooves or wool in animals) [1] and have the ability to use keratin as the sole source of carbon and nitrogen [2]. The aim of the present work was to isolate a geophilic *Microsporium gypseum* (*Nannizzia gypsea*) [3] strain from soil. This strain is able to produce superficial mycoses in humans, especially the ones who come in contact with soil often [4].

**Materials and methods:** The fungus was isolated by the Vambreuseghem hair baiting method. The identification of the isolated strain was done by macroscopic and microscopic observations (at Olympus BX51 microscope) and by additional tests, such as urea hydrolysis and *in vitro* hair strand perforation test.

**Results:** The isolate strain shows features specific for *Microsporium gypseum*, such as, colonies flat, suede-like to granular, with a white, deep cream to pale cinnamon colored avers and beige to yellow-brown reverse. The strain produce many fusiform, rough, thin walled, 4-6 celled macroconidia with symmetrically rounded tip and pyriform microconidia. Moreover, the results were positive for urea hydrolysis and *in vitro* hair strand perforation tests which also indicate that the isolated strain belongs to *Microsporium gypseum* species.

**Conclusions:** The isolation and characterization of this strain is important for its ability to degrade keratin and produce superficial mycosis both in humans and animals.

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## THE EFFECT OF LIGHT INTENSITY ON CARBON DIOXIDE SEQUESTRATION BY *NANNOCHLORIS SP.* CULTURE

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**Keywords:** microalgae, light intensity, sequestration

**Introduction:** The biological processes like forestation, ocean fertilization and microalgae cultures can be applied to CO<sub>2</sub> sequestration. Many researchers have investigated the use of microalgae culture as a biological process for industrial gas purification [1,2]. Microalgae are microorganism, more photosynthetically efficient than terrestrial plants and are the candidates as efficient CO<sub>2</sub> fixation [1]. The aim of this work was to evaluate the capacity of the strain *Nannochloris sp.* to fix CO<sub>2</sub> from flue gas and to produce lipid using different light intensities (37 μmol/m<sup>2</sup>/s<sup>-1</sup>, 85 μmol/m<sup>2</sup>/s<sup>-1</sup> and 175 μmol/m<sup>2</sup>/s<sup>-1</sup>).

**Materials and methods:** Nannochloris sp. microalgae strain (CCAP 251/10); Zarouk culture medium; Biostat PBR 2S Sartorius BBI System for microalgae cultivation; Geotech Biogaz 5000 for gas analysis; Ultrasound assisted extraction from microalgae lipid fraction extraction; GC-MS analysis for FAME distribution.

**Results:** Our results revealed that the maximum growth rate of the microalgae culture and lipid accumulation was observed when was used a light intensity of 85 μmol/m<sup>2</sup>/s<sup>-1</sup>. When was used a strong light intensity the photoinhibition was observed.

**Conclusions:** The microalgae growth rate, lipid accumulation and CO<sub>2</sub> fixation were significantly influenced by the light intensity used. Also, distribution of fatty acids varies with light intensity used.

**Acknowledgements:** The work has been funded by the PN 16.31.01.04.02.

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## OPTIMIZATION OF CULTIVATION MEDIUM FOR BIOMASS BIOSYNTHESIS OF A BIOSTIMULANT *TRICHODERMA* STRAIN

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**Keywords:** *Trichoderma*, biostimulant strain, cultivation media, optimization, surface response methodology

**Introduction:** *Trichoderma* strains are versatile, being antagonists against major plant pathogens [1], stimulating vegetable growth [2], enhancing bioactive accumulation into nutraceutical crops and promoting development on early stages of the plants cultivated into high residues systems [3]. Innovative formulations were developed for above mentioned applications of plant biostimulant *Trichoderma* strains [4,5]. In this work, we describe the optimization of cultivation medium composition for biosynthesis of *Trichoderma asperellum* T36 biomass. In order to improve the eco-efficiency of T36 based bio-products production, a maximum conversion of cultivation media components into fungal biostimulant biomass is required.

**Materials and methods:** The cultivation media was optimized by a designed experiment, based on surface response methodology, wherein several parameters of cultivation media were modified in the same time. These parameters were: carbon source, inorganic nitrogen and sulfur source, organic nitrogen and growth factors source, phosphorus source and buffering ingredients.

**Results and conclusions:** The optimal composition of cultivation medium, resulted after experimental data analysis with Design-Expert<sup>®</sup> v10.0 (Stat-Ease, Minneapolis, MN, USA), was: 49 g/l glucose, 0,37 g/l ammonium sulfate, 3,2 g/l yeast extract, 2,7 g/l soymeal, 12,3 g/l K<sub>2</sub>HPO<sub>4</sub>, 4,7 g/l KH<sub>2</sub>PO<sub>4</sub>. We concluded that the optimized conditions for *Trichoderma asperellum* T36 cultivation assure the eco-efficiency of the fungal biomass production.

**Acknowledgements:** The scientific works for this study were financial supported through project PN-II-PTPCCA-2013-4-0846-159/2014 (CERES), founded by UEFISCDI, Ministry of National Education – ANCSI.

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## AMYLASE PRODUCTION IN SUBMERGED CULTIVATION USING A NEWLY ISOLATED *BACILLUS MYCOIDES* STRAIN

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**Keywords:** *B. mycoides*, amylase, Taguchi, chip electrophoresis.

**Introduction:** Microbial amylases (E.C.3.2.1.1), mainly derived from the genus *Bacillus*, *Aspergillus* and *Penicillium* have vast applications in starch processing, detergent, alcohol, textile, food, paper, analytical chemistry and pharmaceutical industries. Following a screening performed on agar medium (substrate-specific), 29 bacterial and fungal strains were selected for experimental trials on liquid media. The role of various factors has been analyzed for optimization of fermentation conditions, using a newly isolated strain of *Bacillus mycoides*. [1]

**Materials and methods:** microbial strains included in CMII-ICCF-WFCC 232 Culture Collection; the DNS method and chip electrophoresis were applied for the enzyme dosage activity and the amylase electrophoretic profile investigation, respectively; L9 Taguchi matrix and ANOVA were used for the optimization of bioprocess parameters.

**Results:** *B. mycoides* was selected in order to optimize the fermentation conditions: carbon sources (corn, wheat bran, rice flour, oatmeal, soluble starch, potato starch, malt extract and dextrin), nitrogen sources (soybean peptone, yeast extract, soybean meal, tryptone and ammonium sulphate), citric acid, calcium chloride and inoculum volume were tested in different concentrations. Preliminary results: enzymatic activities of 3.864 U/ml and 4.969 U/ml on malt extract substrate. The use of UniProtKnowledgeBase allowed the identification of an amylase - 60 kDa, characteristic for *Bacillus* sp.

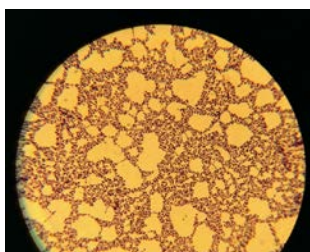


Fig. 1 *B. mycoides* – microscopic aspect

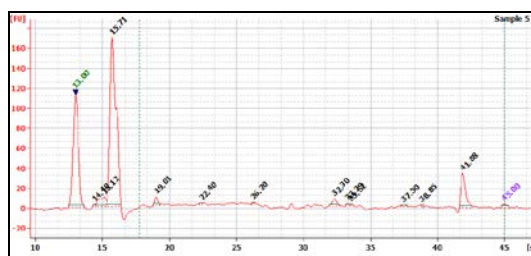


Fig. 2 *B. mycoides* amylase - electrophoretic profile

**Conclusions:** Bacterial amylase still finds it's way to the enzymes global market and new sources need to be exploited in order to achieve the industrial necessities.

**Acknowledgements:** grant PN 09-11 04 03 (UEFISCDI, Romania).

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## USE OF UV MUTAGENESIS FOR OBTAINING MUTANT STRAINS OF *ASPERGILLUS BRASILIENSIS* ATCC 16404 REGARDING THEIR ABILITY TO PRODUCE XYLANASES

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**Keywords:** xylanase, *Aspergillus*, UV, mutagenesis

Xylanases hydrolyze the major component of hemicellulose, xylan, breaking the  $\beta$ -1,4-glycosidic linkages, in order to produce xylose and other monoresidues. There are many microorganisms that produce xylanases, fungi being considered the most important producers for these enzymes, due to high yields and extracellular release of the enzymes. In this study, our aim was to obtain mutants from *Aspergillus brasiliensis* ATCC 16404, previously selected as xylanase producer and compare their enzymatic activities with that of the original strain. The physical mutagenesis by UV was carried out at the distance of 30 cm and the Petri plates with the fungal spores were exposed to UV light for 5-20 minutes. After the radiation procedure, the cells viability decreased with almost 23%. Several mutants were randomly selected and tested for their ability to produce xylanase, by being cultivated on selective xylan agar medium with 0.8% oat spelt xylan as the only carbon source. In addition, the selected strains were subjected to a quantitative analysis, the xylanase activity being determined according to the DNS assay for reducing sugars. The comparative analysis of the selected colonies showed that there are differences concerning the xylanase activity between the mutant strains obtained by UV mutagenesis and the original strain.

**Acknowledgements:** This work was supported by a grant of the Romanian National Authority for Scientific Research and Innovation, CCCDI – UEFISCDI, project number ERA-IB-15-129 Convert-Si, contract 62/2016, within PNCDI III.

## CONTRIBUTIONS TO THE INTERPRETATION OF MASS SPECTRUM OF HEXAETHOXYDISILOXANE. LINKED SCANS AND ISOTOPIC EFFECTS

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**Keywords:** hexaethoxydisiloxane, mass spectrum, linked scans, M+1, M+2 isotopic effects

**Introduction:** The aim of this article is the study of the fragmentation reactions of hexaethoxydisiloxane initiated by electronic impact in the ionization chamber of a double focusing mass spectrometer. Hexaethoxydisiloxane as TEOS dimer (D), with structural formula  $(C_2H_5O)_6Si_2O$  and molecular weight  $M=342$ , is obtained in sol-gel process by hydrolysis–condensation reactions. Mass spectrum of an organic substance, as well as a silicon alkoxide such as hexaethoxydisiloxane is the result of a series of unimolecular consecutive and competitive chemical reactions, which constitutes a pattern of fragmentation (Figure 1).

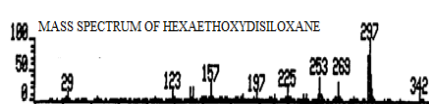


Figure 1

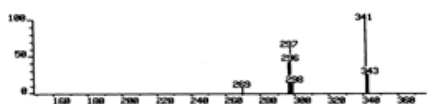


Figure 2

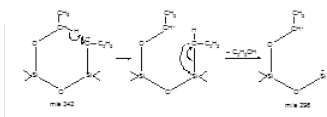


Figure 3

**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)<sup>1/2</sup> linked scan: It is used to obtain the ions which lose small molecules with a preset mass (e.g. ethanol, ethylene, acetaldehyde, etc.).

**Results:** Daughter ions of hexaethoxydisiloxane (D) molecular ion obtained experimentally by linked scan B/E are shown in Figure 2. The ion in hexaethoxydisiloxane mass spectrum with ion mass  $m/e$  296 shown in Figure 2 is obtained by removing ethanol with H atom transposition according to the reaction in figure 3. The paper presents further the fragmentation ions of hexaethoxydisiloxane that eliminate acetaldehyde and ethylene by linked scans B/E(1-E)<sup>1/2</sup>. Thus there can be written the reaction paths to obtaining the ion with mass  $m/e$  139 from the ion with  $m/e$  297 by elimination of ethylene and water and to obtaining the ion with  $m/e$  123 from the ion  $m/e$  185 by elimination of acetaldehyde and water. The obtained fragmentation ions were confirmed by the M+1 and M+2 isotopic effects of silicon atom.

**Conclusions:** The ions of hexaethoxydisiloxane mass spectrum were obtained experimentally by the B/E and B/E (1-E)<sup>1/2</sup> linked scans. Thus there can be written the 28 fragmentation pathways for the primary events and eliminations of neutral molecules.

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## TRENDS IN NUTRIENTS CONCENTRATIONS IN THE LOWER DANUBE (1996-2012)

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**Keywords:** *Danube River Protection Convention; nutrients pollution; ammonium*

**Introduction:** The Danube is considered the most international river in the world, it's basin including 19 European countries, and about one third of the Danube basin and one third of its length are located on Romanian territory. Nutrients concentrations are important for aquatic ecosystems, therefore their long-term evolution should be carefully monitored, however few studies have been published on this topic [1]. Romania is part of the Danube River Protection Convention, the overall legal instrument for co-operation on transboundary water management. The TransNational Monitoring Network (TNMN) was launched in 1996 in order to provide an overview of pollution and long-term trends in water quality and pollution loads in the major rivers in the Danube River Basin [2].

**Materials and methods:** The data used in this study were taken from the public TNMN database, and were analysed using statistical methods. For 21 monitoring sections along the Romanian section of the Danube and its tributaries, ammonium, nitrates, nitrites, total nitrogen and total phosphorus concentrations were analysed for the period 1996-2012.

**Results:** Monitoring data indicate that some of the Romanian tributaries have a nutrient load significantly higher than upstream concentrations in the Danube. In particular the average  $\text{NH}_4\text{-N}$  concentrations in the Argeș river are almost ten times higher than upstream values. This can be explained by the fact that during this period two of the largest cities in Romania did not have functional wastewater treatment plants (WWTP) and were discharging sewerage water via the Dâmbovița and Argeș rivers into the Danube [3]. Moreover, the  $\text{NH}_4\text{-N}$  concentration in the Argeș river had an ascending trend and, despite the fact that WWTPs were commissioned in 2011 both in Pitești and Bucharest, this trend continued also in 2012. However, nutrient concentrations also depend on flow, so further analysis would be needed in order to explain the continuing high values [4].

**Conclusions:** Romanian tributaries have a significant impact on nutrients concentrations in the Danube, so efforts should be continued to ensure advanced municipal wastewater treatment, particularly in large urban agglomerations.

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## RECYCLING OF WASTE POLYPROPYLENE AS HIGH IMPACT RESISTANCE COMPOSITES

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**Keywords:** *waste polypropylene, styrene-isoprene block-copolymers, composites.*

**Introduction:** The recycling study of waste polypropylene was achieved by its melt modification with styrene-isoprene block-copolymers in order to obtain polypropylene composites with performance properties, especially with high impact strength.

**Materials and methods:** The styrene-isoprene block-copolymers were synthesized through sequential anionic polymerization of monomers in cyclohexane solution, initiated with n-buthyl lithium, by adding the next monomer only after the total consumption of the previous one. The polypropylene composites were obtained by melt alloying on a laboratory roller at 180-190 °C. Plates of 1 and 4 mm were made from the rolled sheets by pressing them at a temperature of 185-190 °C for 15 minutes, under a pressure of 200 kgf/cm<sup>2</sup>, that were used for physical-mechanical properties determination.

**Results:** The styrene-isoprene block-copolymer domains dispersed mainly into the RPP amorphous phase acts as an extender and have an elasticizing role, the effect being demonstrated specifically by the increase of the elongation at break to the detriment of the tensile strength that decrease and also by the maximum values of the impact strength of the corresponding polypropylene composites both at positive and negative temperatures.

**Conclusions:** The study established that the maximum values of composite's physical-mechanical properties, and especially of the impact strength, were obtained when the components have close melt viscosities. In order to respect this condition, the adjusting of elastomers component viscosity was achieved by blending in various proportions of two synthesized styrene-isoprene block-copolymers with different molecular mass and thus with different melt viscosity. Thus waste polypropylene composites with high impact strength and maximum physical-mechanical properties were obtained, highlighting especially the impact strength values higher on average with 25 % compared to the composites with individual styrene-isoprene block-copolymers.

**Acknowledgements:** *This work was financed by The Romanian National Authority for Scientific Research, UEFISCDI, project no. 67/2012.*

## SYSTEM AND METHOD OF IRRIGATION WITH DILUTED WASTE WATER

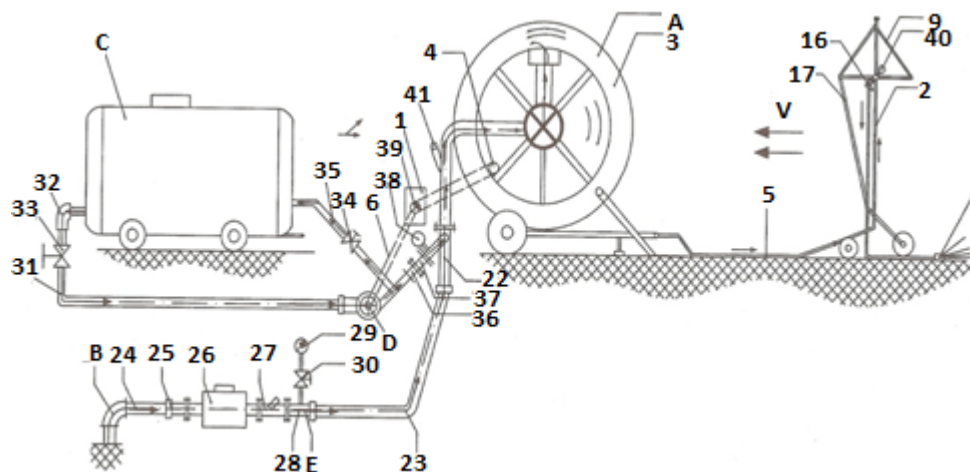
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**Keywords:** *irrigation; wastewater; micro-sprinkler; fertigation.*

The technical problem to be solved solution consists of applying a controlled manner, wastewater diluted depending on the specific crop and avoiding environmental pollution. The technical solution consists of an installation of irrigation and hose drum A, which distributes the wastewater with a ramp and some hoses equipped with a water source B, which can be a mobile pumping aggregate absorbing water area front / ground water or be a hydrant posed on a network of pipes under pressure, a trailer tank C, carrying manure from a treatment plant / mechanical separator plant of irrigation, a pump D, which absorbs manure in tanks and they injected into the irrigation system, and a monitoring device is that the flow of water and slurry counting, the pressure in the drum, the pump and the ramp, the concentration of salts, fertilizers and pH of the solution tachometer for measuring velocity / the watering.



By applying the technical solution we obtain the following benefits: better homogenisation of manure-water mixture; there is no risk of environmental pollution by monitoring the equipment process measurement and control; enables solution administration when the culture is growing; you can easily modify rules dilutions and watering according to plant requirements, conditions of soil / water and weather; localized watering, the soil surface, ramp hose located in movement, reduce waste and wastewater into the soil through evaporation; reduce the work pressure on the system because of low pressure nozzles required distribution, use of thermal actuation hose rolling of the plant and manure injections; distribute small livestock manure liquid dilution as in high dilutions there is a risk of pollution of soil and water.

**BIOFILM ON INVAZIVE ACTIVITIES EXTRA-CELLS OF MICROBIOTA****F. Dumitrescu\****Technical College "General David Praporgescu", 2 Taberei Str., Turnu Magurele, Teleorman, Romania**\*Corresponding author: floridein10@gmail.com****Keywords: biofilms; observation.***

Biofilms - using for associative of the biostructure of architectural cells by the microbiota environment surrounded by matrix poly-glucosinated glucoses, were is done by the most reticular and molecular glucanases and another's bacteria or mycospecies by the extra or invasive activity.

Microbiologically, is done by Gram ++ / --, fungal denomination by *Microsporum*., *Trichophyton*, *Candida albicans*, *C. parapsilosis*, *C. glabrata*, *C. tropicalis* biorezistente la antifungice, *Epidermophyton floccosum*, *Malassezia furfur*; *Pityrosporon orbiculare*, *P. ovale*; *Cryptococcus neoformans*, *Aspergillus fumigatus*; *Zygomycete Rhizopus*, *Mucor*; *Paracoccidioides brasiliensis*, *Blastomyces dermatitides*, *Histoplasma capsulatum*, *Coccidioides immitis* and *Sporothrix schenckii*.

By using forwarding of these species is under microscopic objectives 5 - 10 x binocular or under stereomicroscopic of LCD were the images are observed bistrate; in this case, to applied the bacterial or mycological colorants for diagnosis of these microbiota species of the bioadhesions.

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## HPLC-UV DETERMINATION OF NITROFURAN ANTIBIOTICS USING MOLECULARLY IMPRINTED POLYMERS FOR SAMPLE ENRICHMENT

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**Keywords:** nitrofurans; liquid chromatography; imprinted polymers; solid-phase extraction

**Introduction:** Furaltadone and nitrofurantoin are two important compounds that belong to a class of synthetic broad spectrum antibiotics containing a characteristic 5-nitrofuran ring. These nitrofurans have been largely used as feed additives for growth promotion, and mainly used for livestock, aquaculture and bee colonies in the prophylactic and therapeutic treatment of bacterial and protozoan infections, such as gastrointestinal enteritis caused by *Escherichia coli* and *Salmonella* spp. However, they have been banned from use EU since 1995, due to many concerns on the potential carcinogenicity of their residues in natural matrices [1]. Therefore, the analytical methods for their determination have to take into consideration low concentrations and complex matrices where they are found.

**Materials and methods:** A complete analytical study based on molecularly imprinted polymers (MIPs) for sample enrichment, and HPLC with Uv detection for sample analysis was undertaken for being applied to the determination of sub-ppm levels of furaltadone and nitrofurantoin in aqueous samples. MIPs were synthesized by new methods using these analytes as template molecules [2] and used as selective adsorbents for the solid-phase extraction (SPE) of chosen nitrofuran antibiotics [3]. The HPLC separations were based on reversed-phase mechanism using a C18 stationary phase, or hydrophilic interaction mechanism using silica derivatized with sulfobetaine functionality [4].

**Results:** Backthrough parameters for SPE procedure using synthesized polymers as adsorbents; elution conditions for HPLC separations (mobile phase composition; pH and temperature); analytical parameters for method development, optimization and validation: injection volume, detector linearity, recovery, precision and accuracy, detection and quantitation limits.

**Conclusions:** The new developed analytical method can be applied for the determination of sub-ppm levels of furaltadone and nitrofurantoin in aqueous samples.

**Acknowledgements:** The financial support provided by Romanian National Authority for Scientific Research, UEFISCDI, project PN-II-PT-PCCA, no. 197/2014 is acknowledged.

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## STUDIES ABOUT THE MICROBIAL COMPOSITION OF AN WASTEWATER RESULTED FROM THE GLUCOSE INDUSTRIAL MANUFACTURE

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**Keywords:** *microbial composition, industrial wastewater*

**Introduction:** Important quantities of wastewaters result daily from the chemical industry, representing a highly potential source of environmental pollution. One of these cases may be represented by the glucose's production. Thus, all bioremediation technologies based on microbial degradation of xenobiotics contained within the industrial effluents seems to be always of a special interest. This paper presents our experimental results concerning the microbial composition of the residual water stored in two tanks to a glucose factory. The importance of such an activity is justified by the reason that these already adapted strains of microorganisms can later be used to remedy the waters in question.

**Materials and methods:** The samples were taken during autumn and spring, as these tanks are located outside. The microbiological analyses carried out have watched 20 groups of microorganisms such as: bacteria, yeasts, microscopic filamentous fungi or microscopic algae. In additional for each group of microorganisms taken into study, there were used selective, appropriate culture media.

**Results:** The obtained results indicate that the analyzed wastewater samples contain a very diverse microbial load, concerning the physiological groups of bacteria. From these prevailed those which can develop at a neutral or slightly acidic pH, involved in the cycles of Carbon, Nitrogen, Sulfur and Iron. The yeasts have been reported in a very low number. The microscopic filamentous fungi were reported, belonging to the next genera: *Penicillium*, *Verticillium*, *Cladosporium*, *Fusarium*, *Aspergillus*. The density of the reported microorganisms has not varied significantly from one sample to another, neither from one season to another, so that we cannot notice an obvious seasonal dynamic of the microbial composition in these analyzed samples.

**Conclusions:** Togheter with the support of our colleagues from the Institute of Biology of the Romanian Academy, we selected some microbial strains wich can be used to obtain the biofilters for wastewaters bioremediation.

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## SYNTHESIS AND PROPERTIES OF TWO-HEADED SURFACTANT DIGLUCONAMIDODODECANE

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**Keywords:** *surfactants, carbohydrates, bolaamphiphiles, self-assembly*

Bolaform-type and gemini-type surfactants have gained much interest over the last years, because of their unusual aggregation properties, as a result of molecular geometry or external conditions. They are able to form more open structures than micelles, such as vesicles, rods, cylinders, sheets, etc. conferring them a great potential in drug delivery systems [1-4].

The basic concepts that govern self-assembling of surfactant molecules into micelles in aqueous solutions are also involved in the formation of larger aggregates systems. Surfactants which are forming larger aggregates have generally poor solubility in water, small volume hydrophilic groups or large volume hydrophobic groups, too bulky to pack as normal micelle. Self-assembling process is thermodynamically controlled, due to the tendency of the system to adopt a state of maximum thermodynamic stability.

In this paper we report the synthesis of a bolaform surfactant 1,12 digluconamidododecane in mild reaction conditions (room temperature), according to the principles of green chemistry. The best reaction yield (90%) is obtained with a reaction time of 24 hours. The surfactant was analyzed by Fourier transform infrared spectroscopy. The evaluation of aggregates dimension and visualization of aggregates were performed by dynamic light scattering technique and transmission electron microscopy. The surface activity of surfactant was evaluated with a KSV Sigma 700 automated tensiometer, using DuNouy Ring technique. 1% aqueous solution of 1,12-digluconamidododecane presents a moderate efficiency in reducing the surface tension of water, from 71 mN/m to 57 mN/m.

The surfactant is synthesized in mild reaction conditions, the use of carbohydrate derivatives leads to a product with low toxicity, which can be used as encapsulating agent.

**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**.

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## ENVIRONMENT FRIENDLY METHOD OF OBTAINING POLYOLS FOR POLYURETHANE FOAMS FROM WASTE AND RENEWABLE MATERIALS

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**Keywords:** PET wastes; glycolysis; aminolysis; organocatalysts; PUR foams

**Introduction:** The challenge for the future chemical industry is to ensure environmental protection: conserve the natural resources, preserve the natural environment and, if possible, reverse its degradation. On this line, green chemistry, based on concepts as: waste prevention, atom economy, energy efficiency, use of renewable feedstock, generation of safer products, use of effective catalysts, has been recognized as both a culture and a methodology for achieving sustainability [1]. Following above mentioned guidelines, our study aimed at obtaining polyols for polyurethane (PUR) rigid foams, from PET wastes and renewable co-monomers, in milder conditions than by traditional processes. Nowadays, PET recovery is more critical than ever, given its positive effect on energy balance and cutting CO<sub>2</sub> emissions [2], while chemical recycling opens new ways for generating bio-based products [3]. Over the last decades, major efforts are being conducted to prepare polymer materials from renewable resources [4]. Organocatalysis is, as well, one of the hot research topics in chemical synthesis, targeting the improvement of process conditions and avoiding metal contamination [5].

**Materials and methods:** PET wastes were cleaved/chemically modified via glycolysis and aminolysis followed by esterification reactions, using (potentially) renewable reagents such as: linear and branched diols / polyols, alkanolamines, (poly)amines, vegetable oils, aliphatic / aromatic dicarboxylic acids or anhydrides, in the presence of amidine and/or guanidine derived catalysts.

**Results:** The products were analyzed by physical-chemical methods, viscosity measurements, FTIR, <sup>1</sup>H-NMR, HPLC and tested in spray PUR foams formation. The foams 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 from waste and renewable materials in organic catalysis, in milder conditions than by conventional processes, with an E-factor of 0.03-0.05.

**Acknowledgement:** The support of the Romanian Ministry of Education and Research, through PN-II-PT-PCCA-2013-4-1388 project PERCIT, contract 61/2014, is gratefully acknowledged.

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## NEW ECO AGENT FOR WASHING / TREATMENT OF WOOL FIBERS

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**Keywords:** wool, enzymes, treatment, antifelting, antishrinkage

The key issue to tackle competitiveness increasing in textiles is the quality embodied not only by technical properties but also through compliance with environmental requirements under the directives and regulations on environmental protection, knowing use of toxic compounds for human and environment within the flow technological classic textile chemical processing [1,2,3].

The paper shows encouraging results in technically and environmentally the development of a new green technologies antifelting/antishrinkage treatment fibers of wool on the basis of a new surfactant special ecological which can be used both in domestic areas (washing machine) and in industry.

The target was the product designed to be easy to use, protecting the integrity of the fibers of wool, health technologist finisher and the beneficiary / consumer without harmful emissions in wastewater as when using toxic products (based on Cl \*) used so far industrial environment, in line with the objectives of Directive 2000/60/ EC. To this end it was chosen enzymatic treatment, mild, organic, but quite difficult to manage given: the risk of fiber damage and risk of loss of wool enzyme activity.

To get the effect of unfelting in one phase (given the use in the household), was made the first experiments with a gentle detergent in the presence of two raw enzymes. FTIR analysis degradations occur tracked us, denoting wool fiber smooth scales.

When treating enzymatic degradation observed growing in order of increasing concentrations of treatment and observed that this degradation when treating enzyme is milder than in the annealed samples classic oxidizing agent, pollutant.

The experiments will continue through the use of new enzymes and the selection will be based on the results obtained from the characterization.

**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 MECS-UEFISCDI.

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## SYNTHESIS AND CHARACTERIZATION OF SILICA ORDERED MESOPOROUS MATERIALS

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**Keywords:** mesoporous material, surfactant, templating synthesis route, X-ray diffraction, nitrogen sorption

**Introduction:** Ordered mesoporous materials offer unique opportunities in a large area of applications in catalysis, adsorption, separation and drug delivery, which is based mainly on their high surface area, high pore volumes and narrow pore size distribution [1-3]. The objective of this work is to study comparatively the synthesis of mesoporous silica by different surfactant-templated procedures and structural and textural features of synthesized materials.

**Materials and methods:** The cationic surfactant assisted synthesis of MCM-41 was performed using tetraethylorthosilicate and fumed silica as silica sources and cetyltrimethylammonium bromide (CTAB) as surfactant. The synthesis was carried out at 100°C for 48h under continuous stirring. The neutral surfactant assisted synthesis of SBA-15 was performed in the presence of triblock- copolymer (Pluronic P123) using tetraethylorthosilicate as silica source. The synthesis was carried out at room temperature for 24 h under stirring followed by heating at 90°C for 48 h under static conditions. The neutral surfactant assisted synthesis of HMS was performed using dodecylamine (DDA) as surfactant and tetraethylorthosilicate as silica source. The synthesis was carried out at room temperature for 24h under static conditions. The structural and textural properties were checked by X-ray diffraction and nitrogen adsorption-desorption measurements.

**Results:** XRD patterns evidenced the formation of well-defined mesoporous structure of MCM-41, SBA-15 and HMS, respectively. All the samples exhibited type IV adsorption-desorption isotherms, typical of mesoporous structure [1]. Physical sorption data revealed high surface areas of 900-1200 m<sup>2</sup>/g and pore volumes of 1.0-1.3 cc/g. Narrow pore size distribution curves and average diameters of 3 nm for MCM-41 and HMS, respectively and 5.8 nm for SBA-15 have been obtained.

**Conclusions:** MCM-41, SBA-15 and HMS type mesoporous materials have been synthesized using cetyltrimethylammonium bromide, Pluronic P<sub>123</sub> triblock-copolymer and dodecylamine as structure directing agents. Both XRD and N<sub>2</sub> sorption data confirmed the formation of typical MCM-41, SBA-15 and HMS mesoporous structure by using cationic and neutral surfactants assisted synthesis protocols.

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## MECHANICAL PROPERTIES OF DOCUMENT PAPER TREATED WITH HYDROXYAPATITE NANOPARTICLES

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**Keywords:** *document paper; hydroxyapatite; nanoparticles; mechanical properties*

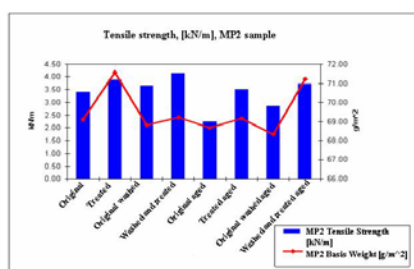
**Introduction:** This study is focused on the research of mechanical properties of the book paper, such as tensile strength, tensile index, breaking length and modulus of elasticity, parameters which reflect the changes causing by sustainability loss, in time, for documents [1].

**Materials and methods:** Results were obtained for some samples of paper, taken from a book from the second half of the nineteenth century, marked as MP1, and from a book of the first half of the twentieth century, marked as MP2, (from private collections), without heritage value, namely:

- MP1 printed in 1931, in Berlin, Germany
- MP2 printed in 1867, in Paris, France

All samples were analyzed before and after treatment with the nanoparticles of hydroxyapatite, as a new and revolutionary conservation and stabilization process of the paper.

**Results:** Tensile strength of the Original washed paper is with 22% higher than the Original one and with 15% higher for Treated paper relative also to the Original one. The increase percentages of this mechanical property show the efficiency of the treatment, with hydroxyapatite nanoparticles, upon the historical paper.



**Conclusions:** For further improvement the properties of paper documents is essential a detailed study of the outcome of the nanoparticles action on the mechanical properties of cellulose fibers treated with hydroxyapatite.

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## THE ACTIVITY OF MDR1 TRANSPORTER ON A NEUROBLASTOMA CELL LINE, AFTER EXPOSURE TO SEVERAL CNS ACTIVE DRUGS

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**Keywords:** MDR1 transporter, neuroblastoma cell line, CNS active drugs

**Introduction:** MDR 1 is a transmembrane efflux pump involved physiologically in the elimination of degradation products of cell metabolism. Recent studies suggest that MDR1 transporter can limit the ability of antidepressants to cross the blood-brain barrier, thus resulting in low levels of the drug in the brain and contributes to the low rate of success of current antidepressant therapies. In this study we aimed to investigate the efflux pump transport activity after exposure to central nervous system active (CNS) drugs and also to investigate the modulatory effect of glutathione (GSH, at physiological concentration) on MDR 1 transport activity, which are intended to inhibit the efflux pump which is directly involved in multidrug resistance.

**Materials and methods:** 10<sup>5</sup> cells/mL murine N2a neuroblastoma cell suspension, solutions of quinidine (Q), fluoxetine (F), lithium (Li), risperidone (R), thioridazine (T) and valproic acid (V): 12.5 μM, 25 μM, 50 μM, 100 μM and 200 μM prepared in culture medium. The cells were incubated with the drugs in temporal dynamics (t=0,15,30,60 minutes). Quinidine was used as classical inhibitory agent of the MDR1 pump, not for its pharmacological effect. There were performed the cytotoxicity and the calcein inhibition tests. In the next step it was added GSH, at physiological concentration (10 mM). After all the procedures were performed, the fluorescence intensities for all samples were recorded.

**Results:** The studied drugs have shown no cytotoxic effect and for the calcein test the strongest inhibition effect was obtained for risperidone and thioridazine. After adding glutathione in the system, the greatest inhibition was observed for lithium.

**Conclusions:** None of the studied drugs have shown cytotoxic effects and the physiological concentration of GSH antagonized the inhibition effect of MDR1 pump, exerted by risperidone and thioridazine.

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## RESEARCH ON THE DEVELOPMENT OF TEXTILE FABRICS, WITH THE ROLE OF PREVENTING THE SPREAD OF TICK INFECTIOUS DISEASES

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**Keywords:** *multifunctional textiles; essential oils; repellent; tick.*

**Introduction:** The necessity of creation of textile fabrics with repellent properties is determined by the presence of an increasing number of ticks that lead to diseases difficult to treat. Textile fabrics with repellent properties can be used as barriers to eliminate or reduce the risk of infection caused by ticks especially in forest, agriculture and tourism areas [1].

The main objective is to develop new multifunctional textile structures, including biologically active compounds extracted from plants in nanostructures, with the role of preventing the spread of infectious diseases such as borreliosis and other bacterial diseases caused by ticks[2] [3].

**Materials and methods:** Thus, studies were performed on the main categories of plants with repellent potential that contained compounds that reduce the risk of illness. Chemical compounds derived from plants that kills or remove ticks are isolated from different parts of the plant and plant organs (flowers, fruits, leaves and wood) [4].

**Results:** Thus, it was considered as plant extracts containing compounds with repellent activity the following oils: (*Juniperi aetheroleum* - juniper oil): (*Eucalypti aetheroleum* - eucalyptus oil) (*Lavandulae officinalis aetheroleum* - lavender oil) (*Rosmarini aetheroleum* - rosemary oil). All oils selected were physico-chemicaly and microbiologically characterized for their: appearance, color, smell, taste, chromatographic profile (content  $\alpha$ - pinene, sabinene,  $\beta$  - pinene,  $\beta$  - myrcene,  $\alpha$  - felandren, limonene, terpinen 4-ol, ethyl Borne - $\beta$ - caryophyllene), relative density, optical rotation, refractive index, peroxide value, fatty oils and resinified oils content, microbial contamination, etc.

**Conclusions:** Eucalyptus oil was selected to be included in a formula based on his hight content of cyneol (eucalyptol) more than 90% from essential oils total, and repelecncy tests showed us good results against ticks.

**Acknowledgements:** EUREKA project No. 332! Tickotex.

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## STUDY OF PROLONGATION EFFECT OF SOME ANTIMICROBIAL SUBSTANCES FUNCTIONALIZED ON THE SUPPORT OF COPOLYMERS OF N-VINYLPYRROLIDONE AND OTHERS

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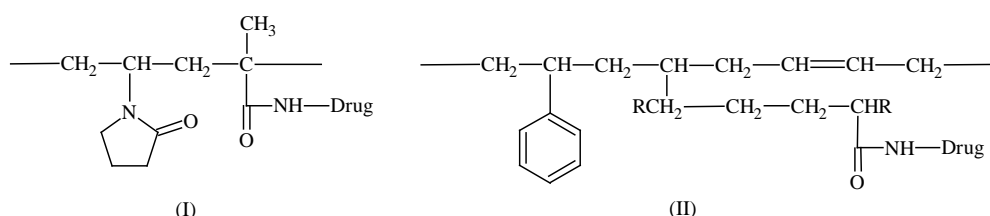
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**Keywords:** antimicrobial, prolongation effect, copolymers.

**Introduction:** Nowadays, it is known that the development of new antibiotic materials encounters difficulties, so since the early of the '90s of XX century the chemists proposed the use of polymeric materials with known antimicrobial or antibacterial compounds. These biologically active polymers, obtained by drugs grafting to polymeric supports, usually show a prolonged action effect and effective results in tuberculosis and other diseases treating [1, 2].

**Materials and methods:** In the paper are described the research results of prolongation effect of isofural and ampicillin grafted to two kinds of medicinal copolymers: I – based on copolymer of N-vinylpyrrolidone (N-VP) with methacrylic acid (ACM) for both external and internal use; II – based on technical copolymer of styrene (ST) with 1,2 - butadiene (1,2-BD) and 1,4 - butadiene (1,4-BD).

**Results:**



**Figure 1.** Structure fragments of the medicinal copolymers: I – N-VP: ACM (50:50 mol %); II – ST: 1,2-BD : 1,4-BD (70:30 mol %)

For testing the prolongation effect - the release of the active substance from the copolymer material, the dialysis method was applied using a semipermeable membrane with 35-40  $\mu\text{m}$  thickness [3]. The active substances crossing the membrane were accumulated in a glass beaker with water or dimethylformamide. To determine the drug concentration from the beaker solution, periodically there were taken samples and analyzed using a spectrophotometer SP-8001 at the wavelength specific for isofural - 373 nm and for ampicillin - 246 nm.

**Conclusions:** Researches have shown that drugs from control samples (without copolymers) passes semipermeable membrane in 30-60 minutes compared to 6-8 hours for the drugs fixed to copolymers.

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## PILOT E-BEAM PVD FACILITY OF NOVEL MATERIALS WITH APPLICATION AS FUNCTIONALLY GRADED MATERIALS

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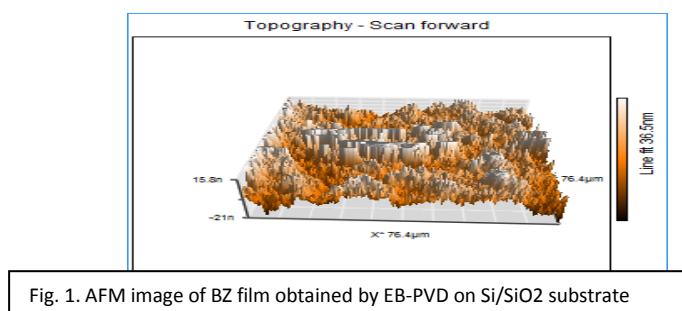
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**Keywords:** Electron beam, nanostructured films, FGM, barium zirconate, nano-indentation

**Introduction:** Nanostructured coatings are expected to bring innovation and major achievements in reducing or even fully replacing critical raw materials (CRMs) in extreme environments applications, some notable examples being replacement of Ytria and rare earths oxides in functionally graded materials [1]. Nanostructured films based on stable zirconates (e.g. BaZrO<sub>3</sub>, LaZrO<sub>3</sub>) synthesised by hydrothermal procedure) with stable perovskite or pyrochlore structures on a large temperature range (no structure or phase transition up to 2500<sup>0</sup>C) have been obtained.

**Materials and methods** An unique electron beam installation ( Torr Int Inc, USA), endowed with 5 e-guns having a 4 crucibles carousel and 5 separate high voltage power supplies with 10KW each, was used to obtain combinatorial coatings on 350 mm diameter substrates. On-line control of thickness was done with a quartz balance. The high vacuum pumps up to 10<sup>-8</sup> torr allow thin film and coating deposition simultaneously or layer by layer starting from BZ and LZ sintered pellets [2].

**Results:** The influence of the coating parameters (vacuum level, deposition rates and contact angle of the substrate) on the coating thickness and structure was studied. First results of the studied regarding the crystallographic structure and lattice parameters vs. thermal treatment temperature to assess the thermal stability and mechanical properties will be presented. Computer simulations have significantly contributed to the understanding of damage processes in materials in different environments.



**Conclusions:** Nanostructured BaZrO<sub>3</sub> and LaZrO<sub>3</sub> films have been obtained by EB+PVD of hydrothermally synthesised perovskites enabling to be used at high temperatures.

**Acknowledgements'** National Authority for Research and Innovation in the frame of grant PN 16 20 02 01 and European Commission for Grant H2020-Twinn-692216 SUPERMAT,

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## IMPORTANCE OF CHEMICAL PROCESSES FOR THE DEVELOPMENT OF COMPLEX NANOSTRUCTURED SYSTEMS. APPLICATIONS IN MEDICINE

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**Keywords:** hydrothermal, high pressure, hybrid nanostructures, hydrothermal-electrochemical method

**Introduction:** Hybrid organic–inorganic materials retained the attention of the scientific community due to their unique properties and innovative applications. Various synthesis routes for the preparation of hybrid nanomaterials are known: co-precipitation, sol-gel [1], microemulsion [2], hydrothermal/solvothermal [3], thermal decomposition [4], etc. The aim of the present work is to emphasize the advantages of high pressure hydrothermal method. Thus, an example of hybrid nanomaterials based on branched polyethyleneimine (PEI) and iron oxide with different mass ratios, synthesized in a single step by hydrothermal procedure at high pressure and low temperature, is given. Also, the advantages of hydrothermal–electrochemical method for thin films deposition are highlighted, showing the development of new hybrid nanostructured thin films based on polyaniline (PANI) and gold (Au) nanoparticles for potential application as VOCs biosensor.

**Materials and methods:** Hybrid nanostructures based on iron oxide and branched PEI were prepared in aqueous solution starting from iron chloride and commercial branched PEI (Sigma Aldrich). HAuCl<sub>4</sub> and commercial PANI (emeraldine) were used for the deposition of nanostructured thin films.

**Results:** Hybrid organic-inorganic nanostructures prepared in high pressure conditions consists of very small iron oxide nanoparticles with 2-4 nm diameter, as well as large aggregates or agglomerates. The thickness of the Au-PANI films deposited by hydrothermal-electrochemical method is 80-90 nm.

**Conclusions:** Hydrothermal process represents a possible solution to avoid particle aggregation, control the size and morphology and to obtain perfect organic-iron oxide nanostructured hybrids. Biological interaction of these hybrid nanomaterials with MSC cells in vitro showed no cytotoxic effect and preservation of the cells morphology. Au-PANI thin films deposited on commercial glass /Au sensor (Dropsens) were tested as possible biosensors for NH<sub>3</sub>, CO<sub>2</sub> and formaldehyde detection.

**Acknowledgements:** The authors gratefully acknowledge the financial support of projects PN 16200301/2016; Romania-Swiss Research Programme, Ctr. No. 14214/2012; MSCA-RISE-2014, Grant no. 645758/2014 and Structural Funds Project-HighPTMet ctr. 253/2010. The authors thank Dr. Eugeniu Vasile, University Politehnica of Bucharest, for HRTEM analysis.

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## MORPHOLOGY STUDY AND PHOTOVOLTAIC PERFORMANCE OF THE PHTHALOCYANINES/PERYLENE THIN FILMS

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**Keywords:** *metallophthalocyanines, perylene, thin film, absorption, photovoltaic device*

**Introduction:** The new world-record for an OPV multi-junction cell which combines three different absorbers, each dedicated to efficiently converting green, red or near-infrared light to electricity reached a record conversion efficiency of 13.2% [1]. In this context, metallophthalocyanines (MPc) appear as excellent candidates for incorporation in photovoltaic systems, as they present intense absorption in the UV/blue and the red/near IR region of the solar spectrum.

**Materials and methods:** In this work, we will present (Cu, Zn)Pc/perylene two-layer films obtained by close space sublimation method and solar cells based on them. The evolution of the surface morphology of the (Cu, Zn)Pc and (Cu, Zn)Pc/perylene films after deposition and annealing at different temperatures in hydrogen atmosphere are shown in Figure 1.

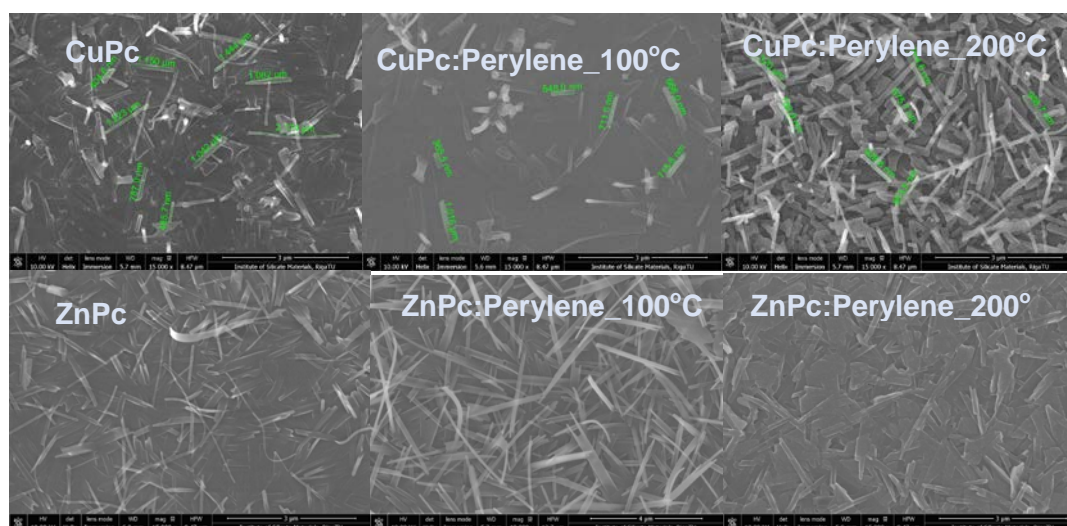


Figure 1. SEM images of the CuPc, ZnPc and (Cu,Zn)Pc/perylene thin films

The SEM images suggest that the mixed layer of two pigments after annealing in hydrogen atmosphere at 200°C for 30 min improve the structure in both cases and this mixed layer may act as an efficient carrier photogeneration layer. Two-layered organic solar cells with of n-type perylene and p-type metallophthalocyanine (Cu, Zn)Pc were fabricated on glass substrate covered with ITO. In this cell, the CuPc or ZnPc was used to absorb visible light and transport holes to the ITO electrode, while the perylene accept electrons from the (Cu, Zn)Pc and transport them to the Al top electrode.

**Conclusions:** All of the solar cells gave limited performance and the efficiency of these devices are primarily limited by the current density ( $J_{sc}$ ) and fill factor (FF). The open circuit voltage for ITO/PEDOT:PSS/ZnPc/Perylene/Al device reached a value of about 0.8 V.

**Acknowledgements:** This research was supported by the Institutional Grant of the Moldova State University of the Ministry of Education of the Republic of Moldova 15.817.02.39A

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## IMPROVED DELIVERY OF A POORLY SOLUBLE QUINOLONE FROM MESOPOROUS SILICA

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**Keywords:** mesoporous silica; quinolones; poor solubility.

**Introduction:** Mesoporous silica materials can be applied in various fields including matrices in drug delivery systems. In this study, norfloxacin, a very slightly soluble drug, which belongs to the quinolone antibacterial class, was used to prepare drug delivery systems based on mesoporous silica in order to assess the influence of textural properties and surface modification of the carriers on the drug release profiles. For this purpose, pristine and functionalized mesostructured silica materials with different pore size and geometry and surface modification with hydrophobic and hydrophilic groups were used.

**Materials and methods:** The drug adsorption into the mesopores of the mesostructured-silica carrier was performed through incipient wetness impregnation method. The mesostructured silica materials and norfloxacin-based composites were characterized by small-angle and wide-angle X-ray diffraction, N<sub>2</sub> adsorption/desorption isotherms, FT-IR spectroscopy and thermogravimetric analysis.

**Results:** The norfloxacin release profiles were performed *in vitro*, in simulated body fluid, pH=7.4, and showed an increased solubility of the drug.

**Conclusions:** In the present study, the ability of pristine and functionalized mesoporous silica to improve solubility of norfloxacin was confirmed *in vitro*.

## BIOHYBRID MATERIALS OBTAINED FROM PLANT EXTRACTS SUPPORTED ON MSN OR COMPOSITE MSN-ORGANIC POLYMER SUPPORTS

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**Keywords:** *biohybrid materials, polysaccharides, mesoporous silica, delivery vehicle*

**Introduction:** Mesoporous silica nanoparticles (MSN) have gained much attention in the last decades due to their biofunctionality and biocompatibility and applicability as biohybrid delivery vehicles bioactive compounds from plants or drugs. The present work reports the synthesis of biohybrid materials from mesoporous silicas and composite MSM-organic polymer supports by immobilization of bioactive compounds extracted from plants.

**Materials and methods:** MSN materials (SBA-15, KIT-6) were obtained by hydrothermal synthesis from tetraethyl orthosilicate, TEOS, as silica source, and triblock copolymer Pluronic P123 as the structure directing agent. The obtained mesoporous silicas were characterized by SEM and TEM, XRD and N<sub>2</sub> adsorption-desorption. The composite supports were obtained from MSN and a natural polymer (chitosan). Biohybrid materials for biomedical applications were obtained by immobilization of bioactive compounds extracted from plants (*Althaea officinalis* L, *Betonica officinalis*) and were characterized by different techniques (TGA, UV-Vis, XRF, SEM, EDAX).

**Results:** The obtained results confirmed the ordered porous structure, biocompatibility and stability, as well as large surface area, high porosity, adjustable pore diameter, and modifiable surface properties of MSN materials. The immobilization efficiency of the main active compounds from *Althaea officinalis* L and *Betonica officinalis* and effect of supports characteristics were evidenced. The higher concentration was obtained for both supports in case of the bioactive compounds extracted in acidic conditions from *Althaea officinalis* and the best yield of immobilization was obtained for all extracts immobilized on KIT-6 support.

**Conclusions:** In conclusion, the active hybrid materials were obtained by immobilization of phytocomplexes extracted from plants on mesoporous silica nanoparticles and hybrid MSN-chitosan composite obtained by incorporation of silica nanoparticles into a natural polymer solution.

**Acknowledgements:** This work was supported by a grant of the Romanian National Authority for Scientific Research, CNDI-UEFISCDI, project number 202/2014.

## NEW CATALYST FOR SET-LRP REACTION AND BLOCK COPOLYMERS SYNTHESIS

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**Keywords:** catalyst; copper nanoparticles; silica nanoparticles; SET-LRP; block-copolymers

**Introduction:** The aim of this study was to develop a catalyst for ATRP reaction based on copper nanoparticles ( $\text{Cu}^0$ ) supported on different substrates in order to facilitate its recovery and reutilization. Thus, we have shown that following the polymerization reaction the catalyst can be separated by centrifugation and reutilized for another process. Further, the realization of block copolymers was evidenced.

**Materials and methods:** ( $\text{Cu}^0$ ) has been obtained by ultrasound assisted *in situ* reduction of  $\text{CuSO}_4$  on the surface of the  $\text{SiO}_2$  support. ATRP polymerization experiments were devised starting from Enayati et al. examples [1,2].

**Results:** In this study we present the ultrasound assisted synthesis of copper nanoparticles on different supports and the utilization of the catalyst for ATRP processes. The reusability of the catalysts was proven using butyl acrylate as monomer. Further, the catalyst was successfully employed for the realization of block copolymers poly(butyl acrylate-co-styrene) by ATRP reaction.

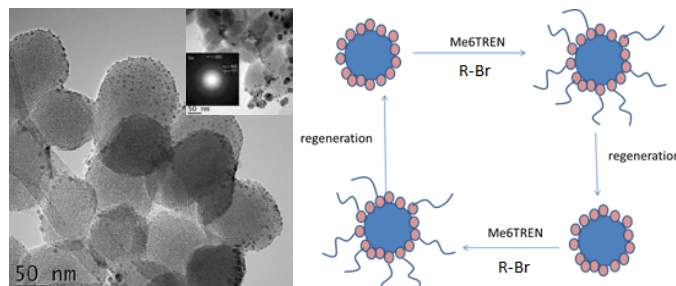


Figure 1. TEM images of Cu nanoparticles supported on silica and representation of the polymerization process

**Conclusions:** Regarding the mechanism, we consider that the process follows SET-LRP steps better due to the following observations: (1) the high reaction rate observed; (2) the capacity of  $\text{NaBH}_4$  to completely reduce all the species in the system to  $\text{Cu}^0$ ; (3) the reaction takes place in the absence of Me6TREN (which usually has the role to facilitate the disproportionation of  $\text{Cu}^{\text{I}}$  to  $\text{Cu}^0$  and  $\text{Cu}^{\text{II}}$ ) (4) the polymerization rate is not dependent on the  $\text{Cu}^{\text{I}}$  concentration, respectively the size of catalyst (specific area).

**Acknowledgements:** A.D. acknowledges financial support from the POC-A1-A1.1.4-E-2015-ULTRA-MINT project financed by contract: 47/05.09.2016. The authors would like to thank for the financial support provided by the National Authority for Scientific Research through the PN-II-PT-PCCA-2011-3.2-0042-RPETUM project.

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## DEGRADATION OF SOMAN THROUGH COPPER-ION CATALYZED ALCOHOLYSIS

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**Keywords:** *catalytic detoxification, GD, copper-catalyzed methanolysis*

**Introduction:** The chemical detoxification of organophosphorous chemical warfare agents (CWAs) such as soman (GD) through metal-ion catalyzed alcoholysis is a far better alternative to other reported GD destruction methods, due to its inexpensive and environmentally benign character, the process occurring at ambient conditions and, most importantly, advancing rapidly. Herein we report an unpollutant system for GD decomposition, based on a copper complex methanolysis.

**Materials and methods:** For this purpose we have used freshly prepared Cu complex catalysts [1]. These catalysts were generated in situ by adding measured amounts of copper triflate, 1,5,9-triazacyclododecane stock solutions to anhydrous methanol to form a solution which is later adjusted to the pH value of 8.75 by dropping in N-ethylmorpholine. The CWA used in this study was also freshly prepared by trained CBRN personnel following several synthetic procedures typically employed in these cases [2]. The reaction was evaluated for different time intervals (5, 20, 30, 60, and 120 min.), and then the reaction mixture was analyzed by GC-MS.

### Results:

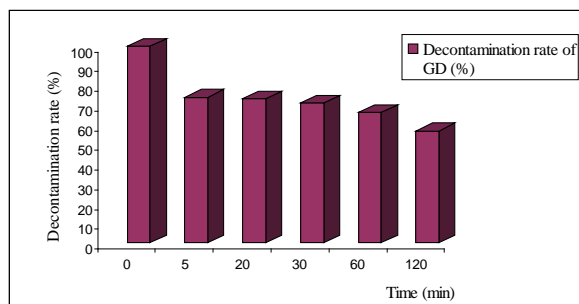


Figure 1. Decontamination rate of GD.

**Conclusions:** The present study provides valuable information regarding GD decomposition. This is the first use of copper-catalyzed alcoholysis on real chemical weapons, the data obtained in this study proving that GD methanolysis could be an effective strategy for the solvolytic decomposition of this organophosphorus CWA, under highly basic conditions.

**Acknowledgements:** This work was supported by a grant from the Romanian National Authority for Scientific Research, CNDI – UEFISCDI, project number PN-II-PT-PCCA-2011-4-1468.

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## DEGRADATION OF SOMAN THROUGH COPPER-ION CATALYZED ALCOHOLYSIS

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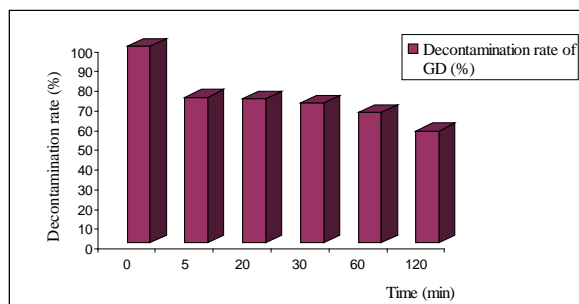


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## CHARACTERIZATION AND APPLICATION OF POROUS CARBON FROM DIFFERENT PRECURSORS

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**Keywords:** *porous carbon; activated carbon; carbon foam; biomass; polymer waste.*

**Introduction:** Different porous carbons – activated carbon (AC) and carbon foam - were synthesized, characterized and used for various applications – adsorption, electrodes, catalysis, etc..

**Materials and methods:** Carbon foam is synthesized by heating coal tar pitch up to 120 °C and H<sub>2</sub>SO<sub>4</sub> is added slowly with continuous stirring. The product was heated at 600 °C in N<sub>2</sub>.

Synthetic porous carbon was obtained from mixtures of coal tar pitch and furfural in different proportions which were treated with H<sub>2</sub>SO<sub>4</sub> at 120 °C until solidification. The obtained solid product was heated at 600 °C under N<sub>2</sub> atmosphere. The obtained solid product after carbonization was further submitted to steam activation at 800 °C for 1 h for synthesizing the porous carbon.

**Results:** The obtained carbon foam is distinguished with high degree of graphitization and extremely high compressive strength of 17 MPa. Synthetic carbon have promising hydrogen storage properties – a composite with Mg desorbs hydrogen about twice faster than magnesium composite with AC from biomass. This is due to the high surface area of the synthetic activated carbon.

It was established that the activated carbon, prepared from biomass, coal products and polymers could be successfully used for the preparation of highly active catalysts for methanol decomposition to hydrogen and CO. Obtained nanoporous carbons have been investigated as electrodes in electrochemical applications.

**Conclusions:** Carbon foams with an anisotropic texture and high mechanical strength were produced using precursors obtained after thermo-oxidation treatment of commercial coal–tar pitch 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 (surface area, pore structure, electro resistance and amount of oxygen-containing groups on the surface) of the obtained activated carbon. Increasing furfural content of the precursors leads to nanoporous carbons with large surface area and oxygen functionalities of basic nature. The obtained results show the possibilities for different applications of carbon foam and synthetic carbon..

**Acknowledgements:** *The authors appreciate the funding by two projects: the Project in the frame of collaboration between Romanian Academy and Bulgarian Academy of Sciences „Water purification by polymer membranes and carbon adsorbents from polymer products-WAPUMECA” and Project DFNP-226/ 17.05.2016 z with Bulg. Academy of Sciences*

## ELIMINATION OF RISK FACTORS IN USE OF PROSTHETIC MEDICAL DEVICES USING ECOLOGICAL PLASTICIZERS IN MEDICAL PVC RECIPES

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**Keywords:** ecological plasticizers, polyvinyl chloride, recipes, medical devices, risk factors

**Introduction:** In present study it were prepared several recipes based on polyvinyl chloride containing di-2-ethyl-hexyl phthalate and two ecological bio-based plasticizers from citrates and adipates category to achieve sensitive and safe applications, which provide an excellent compatibility and flexibility. It were tested the physical and mechanical properties of the polymeric recipes. The crystallinity of recipes calculated from DSC curves exhibit that no important changes occurred within material during storing and manipulation.

**Materials and methods:** The materials used in the experiments were: polyvinyl chloride with K-vert 70, plasticizers: di-2-ethylhexil phthalate (DEHP), tributyl 2-acetylcitrate and bis(2-(2-butoxyethoxy)ethyl) adipate; stabilizers, antioxidants, silver nanoparticles. Recipes were prepared via usual PVC melt compounding and granulating technology.

### Results:

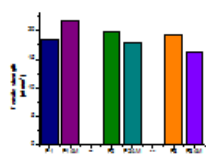


Figure 1. Tensile strength of plasticized PVC recipes

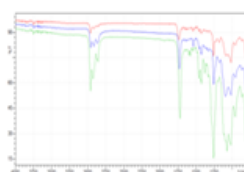


Figure 2. FTIR of plasticized PVC recipes

**Conclusions:** Experiments carried out in order to perform medical grades recipes of PVC for use in medical devices with antimicrobial properties in order to increase biocompatibility have shown that the use of adipates and citrates plasticizers instead of DEHP, does not significantly influence physical and mechanical properties.

**Acknowledgements:** This work was supported by a grant of the Romanian National Authority for Scientific Research, CNDI-UEFISCDI, Project no. 94/2012.

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## MULTIFUNCTIONAL MATERIALS BASED ON CARBON NANOTUBES- REINFORCED EPOXY COMPOUNDS

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**Keywords:** epoxy resin, carbon nanotubes, mechanical properties, thermo-mechanical properties

**Introduction:** Epoxy–amine systems represent an important type of materials in terms of designing carbon fiber-reinforced composite matrices. Currently, the existing high performance epoxy resin matrices are primarily composed of multi-functional epoxy resins cured with aromatic amines. However, work with epoxy matrices deals two main drawbacks, as they are relatively brittle and show low tensile strength [1, 2].

**Materials and methods:** To improve mechanical properties, i.e. flexibility, epoxy resins derived from glycol-type aliphatic structures may be involved. In this respect, various diglycidyl ethers were herein obtained by synthesizing starting from different of low molecular glycols.

According to literature, carboxylic groups- functionalized carbon nanotubes may be involved as reinforcing element of these three-dimensional structures, rendering them compatible with the epoxy matrix [3-5]. This approach has been adapted herein. The obtained materials were characterized using various physical - mechanical methods (tensile, elongation at break and impact strength) and thermal analysis under dynamic regime (DMA and TGA). Physical and mechanical properties of epoxy matrices obtained were improved compared to those of standard epoxy materials having a similar concentration (0.5 %) in carbon nanotubes

**Results:** Study on composites obtained from standard resin / glycols-modified (reinforced with 0.5 % of carbon nanotubes) resin compounds revealed that the modification process yields a significant improvement in flexibility as evidenced by the elongation at break and the glass transition temperature ( $T_g$ ).

**Conclusion:** The composite materials developed herein are suitable to be used in the field of surface coatings, which requires high flexibility and proper adhesion to various substrates. The main aimed objective of obtaining epoxy systems with enhanced features was accomplished.

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## TRI-DOPED Ti-KIT-6 MULTIFUNCTIONAL PHOTOCATALYSTS USED FOR DEGRADATIONS OF DYES AS WATER CONTAMINANTS

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**Keywords:** KIT-6 multifunctional photocatalyst dye degradation

**Introduction:** Titanium dioxide has attracted much attention as a promising environmentally friendly photocatalyst in the field of organic pollutant removal from waste water [1]. Dispersion of TiO<sub>2</sub> on a support with high surface area and doping with lanthanide ions (Ce, Sm, Pr, Eu) [2,3] and nonmetal atoms (N,P,S) [4] can slow the recombination rate of electron-hole pairs, increase the adsorption. This paper presents the synthesis and properties of multifunctional materials obtained by doping of Ti-KIT-6 photocatalyst with Pr, N and P.

**Materials and methods:** Pr(N,P)-Ti-KIT-6 photocatalysts were obtained by direct synthesis with hydrothermal treatment and post synthesis methods. Titanium(IV) butoxide, praseodymium nitrate, tetraethylorthosilicate, nitric and phosphoric acid and urea were used as precursors. In the second method Ti-KIT-6 was obtained by direct synthesis and the obtained support was doped by impregnation. The obtained materials were characterized by XRD, UV-Vis spectroscopy and SEM and TEM microscopy. The photocatalytic properties were tested in degradation of Brilliant Blue dye from aqueous solution in condition of visible light irradiation.

**Results:** A low effect of metals and nonmetals incorporation by direct synthesis on ordered KIT-6 mesoporous structure. A significantly effect was evidenced for samples obtained by post synthesis method. The typical morphology and cubic porous structure were evidenced for all the samples. A red shift and increased of adsorption was evidenced by UV-Vis spectra for doped titania samples. Pr reduced the red shift, compared with N and influenced the ratio anatase/rutile in the samples obtained by direct synthesis. The energy gap decreased for all the doped samples. The photocatalytic tests evidenced the improved of Brilliant Blue photocatalytic degradation by titania doping. A higher activity was obtained for PrNP-Ti-KIT-6 samples. The increasing of photocatalytic activity was evidenced for samples obtained with urea.

**Conclusions:** Mesoporous materials with high photocatalytic activity in degradation of BB from water were obtained by dispersion of Ti on mesoporous silicas and doping of supported titania with Pr, N and P.

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## SWELLING STUDIES OF BACTERIAL CELLULOSE COMPOSITES

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**Keywords:** bacterial cellulose; swelling; drug delivery.

**Introduction:** Bacterial cellulose (BC) is a biomaterial with excellent biocompatibility, biodegradability, elasticity, high crystallinity, high mechanical strength, high water content, high absorption capacity of liquids; features that make BC an ideal material for drug delivery applications. The aim of this paper was to investigate the swelling behavior of BC composites in order to further use them as matrices for drug loading and drug release. For this purpose, various BC composites were prepared and characterized, evaluating the degree of swelling (SR, g/g), the equilibrium degree of swelling (SRE, g/g) and stability.

**Materials and methods:** BC membranes were prepared in static culture using *Acetobacter sp.* strain from vinegar in a modified Hestrin–Schramm medium containing fructose (2 %). The BC- composites were prepared by immersion method using different materials like chitosan (BC-C), gelatin (BC-G), alginate (BC-Alg), carboxymethyl cellulose (BC-CMC) at various concentrations. SR and SRE were determined by gravimetric measurements in water at room temperature. The water uptake mechanisms were investigated using the power law model.

**Results:** From the prepared BC composites the higher values of the degree of swelling (SR<sub>max</sub> > 80) were obtained for BC-CMC (all sample tested), and one of BC-chitosan composites (BC-C 0.5%). The highest SR value was observed at low concentrations of carboxymethyl cellulose (SR<sub>rmax</sub> = 139.72 g/g for BC- CMC 0.1 %). Also, the BC-CMC samples with lower CMC concentrations (< 0.25%) presented the best stability in water. Swelling mechanisms were governed by pseudo-Fickian diffusion.

**Conclusions:** These preliminary findings suggest that BC composites are promising materials for drug delivery applications.

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## TWO-COMPONENT COMPOSITES BASED ON MODIFIED CLAYS AND BIOACTIVE COMPOUNDS

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**Keywords:** *modified clays; montmorillonite; methotrexate; 5- fluorouracil.*

**Introduction:** Montmorillonite, a smectite-type clay, consists of aluminosilicate layers stacked one above the other. A bioactive compound, 5-fluorouracil (5-FU), is a drug widely used within the last few decades[1]. Other well-known bioactive compound is methotrexate (4-amino-10-methyl folic acid; amethopterin; noted hereafter MTX)[2].

**Materials and methods:** MMT was modified (submitted to organophilization), yielding porous heterostructured clay (noted hereafter PHC). Two-component composites were obtained from PHC involving two bioactive compounds: 5-FU and MTX, respectively. Aiming at characterizing the obtained hybrid materials and at confirming the presence of the bioactive compound within PHC, samples were characterized by various modern technique as follows: Dynamic Light Scattering (DLS); Inductively Coupled Plasma Atom Emission Spectroscopy (ICP-AES), Nitrogen Adsorption-Desorption Technique (Brunauer- Emmett- Teller; BET) and X- Ray Fluorescence (XRF), respectively.

**Results:** ICP-AES and XRF were involved to investigate encapsulation efficiency and to determine the time required for controlled release. BET was employed to investigate the embedding of bioactive compounds.

**Conclusions:** DLS revealed that size and stability depend on synthesis conditions. ICP-AES and XRF proved the entrapment of drugs in PHC. BET confirmed the embedding of both 5-FU and MTX.

**Acknowledgements:** This work was supported by PN2 Research Project 154/2012 (DELPOCLAY) and RUTE Project 44/2015 (BIOGELFARM).

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## CHROMOGENIC LUMINESCENT ACETYLACETONE DERIVATIVES OBTAINED UNDER MICROWAVE IRRADIATION

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**Keywords:**  *$\beta$ -diketon; Aldehydes; Microwave irradiation; Acetylacetone.*

**Introduction:** To develop and diversify series curcumin derivatives with improved properties in terms of photostability and increase efficiency fluorescence emission, structural changes were made fluorophore by alkylation, acylation or by complexing metal. The fluorophore compounds  $\beta$ -diketone have applications in nonlinear optics [1], as labels for the detection of heavy metals [2], sensors [3] and biomedical [4].

**Materials and methods:** The known method for obtaining derivatives of curcumin involves two main steps: the first step consists in blocking by esterification the methylene groups of acetylacetone compound with boron trioxide and in the second phase formed boric acid ester is condensed with the benzaldehyde derivatives. The condensation reaction occurs in solvent at room temperature, weakly basic catalysis for 20 hours. Given the cumbersome conditions and long reaction time of the classical method of obtaining curcumin derivatives, in order to simplify the method we searched a series of tests of synthesis through irradiation with microwave using a domestic microwave oven (1000 W, selectable power, 2.4 GHz Samsung). In the study were investigated a series of condensation reaction parameters namely: the molar ratio of reactants, catalyst, microwave power, reaction time.

**Results:** Through condensation reaction of a boronic ester with aromatic aldehydes (vanillin, benzaldehyde, 4-nitrobenzaldehyde, o-phthalaldehyde acid and 4-hydroxybenzaldehyde) were synthesized five  $\beta$ -diketone derivatives. The products obtained were characterized by elemental analysis, electronic spectra, IR and <sup>1</sup>H-NMR.

**Conclusions:** Compared to the classical obtaining method [5] of acetylacetone derivatives, the ecological synthesis of them in a microwave field has following advantages: work without solvent, reducing reaction times, higher yield and higher purity of the final product.

**Acknowledgements:** *Financial support from the National Authority for Scientific Research and Innovation (Project PN 16.31.03.03) is gratefully acknowledged.*

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## STUDY OF LDPE PHOTODEGRADATION FOR SHORT DURATION MATERIALS

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**Keywords:** *TiO<sub>2</sub>; polyethylene; nanocomposites; photocatalytic degradation.*

**Introduction:** For LDPE–TiO<sub>2</sub> nanocomposites, the photodegradation of LDPE mainly happens on the film surface where electrons or holes combine with adsorbed oxygen molecules or hydroxyl ion to produce O<sub>2</sub><sup>·-</sup> or ·OH, two very important reactive oxygen species for a new and useful way to decompose solid polymer. In this paper, solid-phase photocatalytic oxidation of LDPE with TiO<sub>2</sub> nanoparticles as photocatalyst under artificial light irradiation was investigated.

**Materials and methods:** LDPE A-22, a low-density polyethylene with 0.3 g/10 min melt flow index (190°C, 2.16 kg) and a tensile strength of 13.4MPa was used as polymer matrix and Degussa P25 as TiO<sub>2</sub> photocatalytic nanoparticles. Morphological, thermal, mechanical and optical changes in polyethylene nanocomposites as a result of TiO<sub>2</sub> nanofiller and exposure to artificial light were investigated by thermogravimetric, dynamic mechanical analysis, FT-IR analysis and POM analysis. Thin films of low density polyethylene nanocomposites with 1 and 2 wt% nano-TiO<sub>2</sub> filler were prepared by direct mixing. The compounding was performed in the Brabender Plasti-Corder mixer chamber. The film samples used for the measurements—square plates 150×150×0,50mm for thermal, mechanical and optical characterizations—were prepared by hot pressing in an electrically heated press at 170 °C for 5 min, with a force of 50 kN. After pressing, the samples were cooled to room temperature under pressure.

### Results:

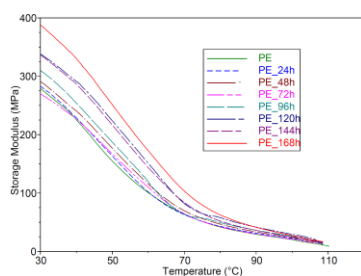


Figure 1. DMA analysis of LDPE

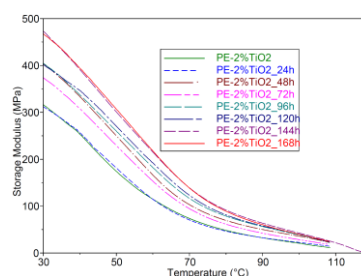


Figure 2. DMA analysis of LDPE + 2% TiO<sub>2</sub>

**Conclusions:** Low density polyethylene nanocomposites with nano-TiO<sub>2</sub> filler shows better photocatalytic degradation than LDPE, which goes on as more reactive oxygen species are generated.

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



## THERMAL, OPTICAL AND DYNAMIC MECHANICAL PROPERTIES OF POLYPROPYLENE/TiO<sub>2</sub> NANOCOMPOSITES

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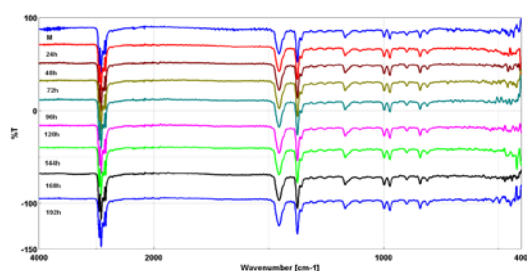
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**Keywords:** titanium dioxide, polypropylene, nanocomposites, photocatalytic degradation.

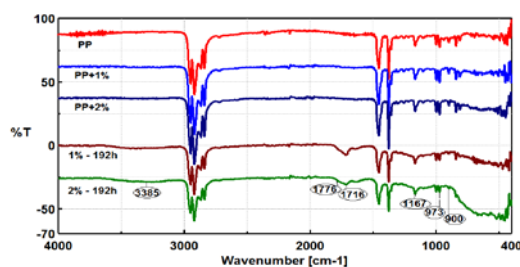
**Introduction:** A photocatalytic technique using Titanium Dioxide (TiO<sub>2</sub>) activated by light, due to its high oxidation efficiency, producing total decomposition of polymers (has been considered as an economical method to solve the problem of plastic waste disposal, called “white pollution”).

**Materials and methods:** Polypropylene (PP-HP-500N) based nanocomposites were prepared using a commercially available TiO<sub>2</sub> (Degussa, P25) nanopowder. To study photocatalytic degradation, PP/TiO<sub>2</sub> nanocomposites were exposed to artificial light and their mechanical and morphological properties were investigated before and after the irradiation and were compared with pure polypropylene (DMA, DSC, TGA, FT-IR, POM analysis).

**Results:** The FTIR spectra of the pure PP and PP nanocomposite films after 192 hours of irradiation using artificial light showed the absence of carbonyl peak in the case of PP film, while in the case of nanocomposite films the intensity rises as the TiO<sub>2</sub> content increases.



ATR-FTIR spectra of pure PP



Influence of TiO<sub>2</sub> on photocatalytic degradation of PP by FT-IR

**Conclusions:** POM micrographs show that both the surface of PP nanocomposite and pure PP are smooth before irradiation and after 192h some cavities are formed on the surface of PP nanocomposites showing photodegradation of PP nanocomposites films comparatively with pure PP films.

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

## REMOVAL OF DYE FROM SYNTHETIC WASTEWATERS USING POLYMER MEMBRANES ENHANCED WITH PLANT EXTRACT

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**Keywords:** dye; wastewater; membrane; plant extract.

**Introduction:** This study is aimed at developing an innovative approach for Methylene blue dye removal from synthetic solutions by a mini-laboratory electrochemical cell using polymer membranes containing plant extract. The percentage removal of dye was determined by spectrographic analysis. Several technological methods used for dyes removal have been developed, including: adsorption, ultrafiltration, nanofiltration, reverse osmosis, electrocoagulation, electrochemical oxidation etc.

**Materials and methods:** Methylene blue solution with an initial concentration of  $5 \cdot 10^{-5}$  M was used in a mini-laboratory electrochemical cell consisting of three compartments in configuration with two pure lead electrodes and two membranes. The experiments were carried out under constant applied voltage to the electrodes. The operation time was 1 h for each experiment. A spectrophotometer was used for the determination of absorbance at maximum absorbance wavelength (668 nm) of the Methylene blue dye. The percentage removal of dye was calculated. The final membranes were characterized by Fourier Transforms Infrared (FTIR-ATR) and Environmental Scanning Electron Microscopy (ESEM).

**Results:** The percentage removal of dye for membrane with plant extract was over 80% in comparison with membrane without plant extract (45%) after 1h of treatment. The peak observed at  $2331 \text{ cm}^{-1}$  indicated that the plant extract was successfully introduced into the membrane structure. ESEM images of the obtained membranes showed that the introduction of plant extract into the mesoporous channels reduces the cracks and pore size of the membrane.

**Conclusions:** The percentage removal of dye over 80% obtained after 1 h, at applied constant voltage is very high. The surface morphologies showed that the plant extract are compatible with the polymer blend and were distributed relatively uniform in the bulk of membrane matrix.

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## FABRICATION OF BILAYER COATINGS ON GLASS SURFACE USING HYDROPHOBIC SILICA NANOPARTICLES OBTAINED BY SOL-GEL PROCESS

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**Keywords:** sol-gel process; silica nanoparticles; bilayer coating; wettability.

**Introduction:** The aim of this work is to study the possibility to prepare bilayer coatings on glass surface, using silica nanoparticles (SiO<sub>2</sub> NP) functionalized with different alkoxyxilanes substituted with dimethyl and methyl, vinyl, phenyl, or octyl alkyl group. The comparative analysis bring new information on the interactions between the alkyl group from the functionalized SiO<sub>2</sub> NP layer and hexadecyltrimethoxysilane (C<sub>16</sub>TMS)/tetramethoxysilane (TMOS) hybrid film. Our coating method with functionalization of SiO<sub>2</sub> NP is useful for the modification of surface polarity and wettability.

**Materials and methods:** Different alkoxyxilanes: methoxytrimethylsilane (TMeMS), ethoxydimethylvinylsilane (DMeVES), ethoxydimethylphenylsilane (DMePhES), methoxydimethyloctylsilane (DMeC<sub>8</sub>MS) were used to functionalized the SiO<sub>2</sub> NP by sol-gel process. The glass substrates were firstly covered with acidic solution (prepared in a similar way to that previously reported [1]) containing C<sub>16</sub>TMS and TMOS, resulting the *first layer* (left to dry at room temperature for 24 h). Then, a second solution (dried functionalized SiO<sub>2</sub> NP and dispersed in ethanol) was deposited over the first layer in order to obtain *bilayer coatings*. Resulted coatings were characterized through various techniques including DLS, FTIR, TGA, ESEM, TEM, AFM and Water Contact Angles.

**Results:** Bilayer coating with C<sub>16</sub>TMS/TMOS and SiO<sub>2</sub> NP modified with alkoxyxilane substituted with C<sub>8</sub> alkyl chain (SiO<sub>2</sub> NP-C<sub>8</sub>) has micro and nano structure. Hydrophobicity of functionalized SiO<sub>2</sub> NP-C<sub>8</sub> and its higher degree of nanometer-scale roughness gave rise to ultrahydrophobicity performance for bilayer coating C<sub>16</sub>TMS/TMOS + SiO<sub>2</sub> NP-C<sub>8</sub> (145°), comparing with other similar hybrid structures.

**Conclusions:** The new functionalized SiO<sub>2</sub> NPs were able to modify the surface of C<sub>16</sub>TMS/TMOS hybrid film. The obtained bilayer coatings can be useful and helpful to construct artificial anti-wetting surfaces for numerous practical applications.

**Acknowledgements:** The work has been funded by the Program ERANET "Towards an ERA in Industrial Biotechnology" (ERA-IB), project number 62/2016 and by University Politehnica of Bucharest, through the "Excellence Research Grants" Program, UPB – GEX. Identifier: UPB-EXCELENȚĂ-2016 Research project title "Membrane polimerice pe bază de tincturi din plante medicinale pentru epurarea apelor uzate sintetice ce conțin ioni de metale grele/Polymer membranes based on tinctures from medicinal plants for treatment of synthetic wastewaters containing heavy metal ions, Contract number 62/26.09.2016.

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## FAST SCREENING OF WHOLE BLOOD SAMPLES FOR COLON CANCER BIOMARKERS

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**Keywords:** P53; KRA; blood sample; stochastic sensors; colon cancer.

**Introduction:** Colon cancer is the fourth leading cause of cancer-related deaths in the world [1]. The risk for 30% of cancers can be reduced by changes in diet and lifestyle [2]. That's why early detection is the key. The tumor protein 53 (P53) and Kirsten rat sarcoma viral oncogene homolog (KRAS) are considered to be essential in the early-stage development of colon cancer

**Materials and methods:** Twelve stochastic sensors based on graphite, diamond and metal nanocomposites-graphene pastes modified with different types of porphyrins and oleamides were employed for the pattern recognition of colon cancer biomarkers: P53 and KRAS.

**Results:** Blood samples from patients diagnosed with colon cancer were analyzed using stochastic sensors to detect the levels of P53 and KRAS knowing that the levels in sick patients are high. Stochastic sensors could reach low determination limits for the detection of P53 ( $5.63 \times 10^{-9} \mu\text{g mL}^{-1}$ ) and of KRAS ( $1.97 \times 10^{-9} \mu\text{g mL}^{-1}$ ).

**Conclusions:** Stochastic sensors are a good alternative for the assay of P53 and KRAS from biological samples because they provide both qualitative and quantitative analysis.

**Acknowledgements:** This work was supported by UEFISCDI PNII Program Partnership 2014-2016, MULTIMODESENS, Contract nr. 22/07.2014.

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## SYNTHESIS AND CHARACTERIZATION OF STYRENE-DIENE BLOCK COPOLYMERS REINFORCED WITH BENTONITE

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**Keywords:** *block-copolymers, bentonite, elastomers*

**Introduction:** Styrene-butadiene block-copolymers (SBS) and 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.

**Materials and methods:** The mixtures of styrene-diene block copolymers with bentonite (Valea Chioarului montmorillonite) were made in toluene, followed by desolvation using centrifugal casting at 60 °C. The polymer solutions with bentonite were added in small amounts at intervals of 20 minutes to avoid the formation of a gradient of reinforcement in the film thickness.

**Results:** The elastomers reinforced with bentonite were characterized by Fourier Transform Infrared Spectroscopy (FT-IR), Differential Scanning Calorimetry (DSC) Thermo-gravimetric Analysis (TGA), Dynamic mechanical analysis (DMA), and X-ray Diffraction (XRD).

**Conclusions:** The results indicate an improvement of thermal and mechanical properties.

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## THERMO-OXIDATIVE AND DYNAMIC MECHANICAL PROPERTIES OF STYRENE-ETHYLENE BLOCK COPOLYMERS WITH CLAY REINFORCEMENT

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**Keywords:** *thermoplastic elastomers, bentonite, clay nanocomposite*

**Introduction:** Polymer/clay nanocomposites are promising materials due to their combination of ease in processing and change in properties at low amounts of clay loadings. The aim of the study was the improvement of thermal and mechanical properties of thermoplastic elastomers by preparing mixtures with layered silicates.

**Materials and methods:** Styrene-ethylene-butylene-styrene block copolymers (SEBS) and styrene-ethylene-butylene-styrene grafted maleic anhydride block copolymers (SEBS-MA) nanocomposites were prepared by centrifugal casting obtaining thin films of 1 mm thickness. Two types of layered silicates were used: bentonite (more than 70 % montmorillonite) and modified montmorillonite (Nanomer I.28E). The copolymers were dissolved in toluene at 20 % concentration, followed by adding 20% clay (reported to polymer). The solvent was removed by heating the mixtures at 60 °C, in a centrifuge over a period of 4 hours.

**Results:** The block-copolymers mixtures with nanoclays were characterized by Differential Scanning Calorimetry (DSC), Thermo-gravimetric Analysis (TGA), Dynamic mechanical analysis (DMA), and X-ray Diffraction (XRD).

**Conclusions:** The materials presented a good homogeneity and an improvement of thermal and mechanical properties.

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## PREPARATION OF POLYMER MEMBRANES ENHANCED WITH MEDICINAL PLANT EXTRACT FOR REMOVAL OF HEAVY METALS

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**Keywords:** medicinal; membrane; plant extract.

**Introduction:** The most existing plants extract have a great medicinal potential, that can be used as an nutritional supplements that stimulating the immune system, increase energy levels, being a remedy for digestive issues etc. The extract obtained from medicinal plants can be used as a medicinal agent in the form of tinctures and fluid extracts. **The main objective** of this study was to prepare polymer membranes doped with medicinal plant extract by phase inversion method. Furthermore the obtained membranes can be used in recovery of heavy metals from synthetic wastewaters.

**Materials and methods:** The plant extract was obtained by maceration of the powdered dried plant for 7 to 10 days with 50% - 70% ethylic alcohol followed by filtration on filtering cloth.

The membrane was obtained using a mixture composed of acrylic copolymer and polyvinyl alcohol dissolved in dimethyl sulfoxide with constant stirring at 100 C for 2 h. At this homogenous solution was added a small amount of plant extract. After the air bubbles have been removed, the polymer solution was cast at room temperature on a glass plate. The obtained films were quickly immersed in the coagulation bath containing water-isopropyl alcohol mixture. Membranes were characterized by Fourier Transforms Infrared (FTIR-ATR) and Scanning Electron Microscopy (SEM) techniques.

**Results:** The peak observed at 2358 cm<sup>-1</sup> attributed to the aliphatic CH group indicated that the plant extract was successfully introduced into the membrane structure. SEM images of the obtained membranes indicated positive interactions between extract and polymer matrix.

**Conclusions:** The plant extract was successfully introduced into the membrane structure, being compatible with the polymer blend and reducing the pore size of the membrane.

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## THE PERFORMANCE OF REINFORCING FIBRES IN POLYMER COMPOSITE MATERIALS

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**Keywords:** polymer composite materials; carbon nanotubes.

**Introduction:** Fibre-reinforced polymer composite materials (FRPCMs) have gained recognition in the recent years and are commonly used wherever high strength-to-weight ratio is required. FRCMs tend to be used in the manufacture of high-performance products that need to be lightweight and also very strong, such as: aerospace industry components, boat hulls, competition motorbikes and racing car frames, etc. FRPCMs are made from three or more constituent materials with radically different chemical and physical properties, that when combined, create a material with noticeably advanced characteristics, different from the individual components.

In this respect we studied the possibility of using FRCMs in military applications as reducing blunt trauma for ballistic protection equipments and hazardous chemicals protection.

**Materials and methods:** The FRPCMs considered are composed of a polymer matrix reinforced with fibres. The polymer matrix is polyurea and the achieved fibres are functionalized multi-wall carbon nanotubes which were specifically selected and dispersed by ultrasonication in a masterbatch.

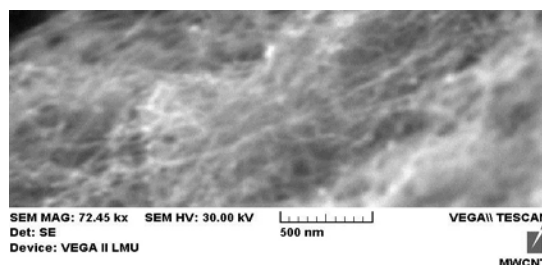


Figure 1. SEM image of functionalized multi-wall carbon nanotubes

**Results:** The progress beyond the state of the art consisted in producing of FRPCMs with excellent chemical and mechanical resistance. The use of functionalized multi-wall carbon nanotube at a very low concentration (below 0.4 %) as reinforcing fibres led to an increase of more then 15% of FRPCM tensile strength.

**Conclusions:** FRPCM presented in this paper have exceptional mechanical characteristics, appropriate for dynamic stress mitigation and, in addition, present durability and resistance to the external factors.

**Acknowledgements:** This work was supported by a grant of the Romanian National Authority for Scientific Research, CNDI-UEFISCDI, project number PN-II-PT-PCCA-2013-4-0707.

## ASSESSMENT OF THE BULLET IMPACT ON A NEW BALLISTIC GELATIN

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**Keywords:** *polydimethylsiloxane; gelatin composite; shooting.*

**Introduction:** Tissues destruction by projectile depends on various factors: projectile stability after perforation, tissue density and compressibility, number of secondary fragments, projectile fragmentation in the tissue, bullet deformation rate. The bullet impact with the human body may be assessed using simulants, such as ballistic gelatin.

**Materials and methods:** The evaluation of the bullets effects has been addressed through ballistic shootings with real munitions, 10x22T cal. bullets shot with a Walther P99, in blocks of hybrid gel composites of 85% gelatin (Gelita), 7.5% nanosized gelatin (Fluka), 5% polydimethylsiloxane, 2% silicone oil and 0.5% glutaraldehyde aq. sol.

**Results:** 3 series of 10 shots have been performed on representative batches of blocks of ballistic hybrid composites (Figure 1). The average penetration depth obtained, of 29.7 mm, is very close to the one obtained using standard ballistic gelatin (30.8 mm), with less than 5% deviation.



Figure 1. Penetration depth of a 10x22 T cal. bullet in the ballistic gelatine

**Conclusions:** Gelatin composite synthesized in this study gives better performances than simple ballistic gelatin in terms of stability and mechanical properties, while framing the international standards.

The results obtained show that it is possible to use the new ballistic gelatin composition in forensic science, in order to evaluate the bullet impact with the human body.

**Acknowledgements:** *This paper has been financially supported by a grant of MEN – UEFISCDI under PARTENERIATE program, “Hybrid composite structures simulating the human body for dynamic impact evaluation in high risk potential environments”- HYBRIDSIM, contract number 307/2014.*

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## SYNTHESIS AND CHARACTERIZATION OF NANOSIZED COPPER(II) - PHTHALOCYANINE PIGMENT (P BL 15:3) WITH THE MODIFIED SURFACE

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**Keywords:** copper (II)-phthalocyanines (PBl 15:3); functionalization; modified pigment; phisico-chemical and morphostructural characterization.

**Introduction:** The aim of the research presented in this paper is to find the processing methods of valuable coloring materials (organics pigments) by synthesis and conditioning - enabling the expanding use of pigments to the natural leather dyeing in an aqueous medium in which pigments are insoluble. To achieve the objectives, we have designed the transformation of pigments by functionalization and conditioning thereof (dispersion and encapsulation in form of liposomes).

**Materials and methods:** The study was focused on the organic blue pigment (PBl 15:3). The main methods researched for the self-dispersible pigments with surface-modified was:

**A) Synthesis:** the functionalization [1] of pigment particles by attaching of functional groups to its surface, by means of: a) diazotation reaction and coupling reaction of the pigment with aromatic diazonium salts; b) sulfonation or c) sulfonation+oxidation; **B) Conditioning:** micro/ nano- dispersion and encapsulation, in forms of liposomes; **C) Stabilization** [2] of colloidal dispersion/ solution with functionalized pigment; **D) Experiments** dyeing on natural leather with coloidal solutions/ nanodispersions containing the blue pigment self-dispersible.

**E) 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 and the average particle diameter distribution and elemental analysis

**Conclusion and results:** we realized:- 3 methods to functionalization of PBl 15:3;

-nanodispersion of functionalized pigment particles and nanoencapsulation in forms of liposomes; - average particles diameter of the functionalized dispersed and/or encapsulated pigment was 150 - 300 nm, representing good results; -stabilization of dispersions / colloidal solutions with 3 thickeners types; -the selected experiments for natural leather dyeing showed promising/good results

**Acknowledgement :** 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 III/2016.

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## OXYTETRACYCLINE DELIVERY SYSTEMS CONTAINING MESOPOROUS SILICA-TITANIA COMPOSITES

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**Keywords:** mesoporous silica-titania composites, antibiotic, drug delivery systems

**Introduction:** Mesoporous silica nanoparticles with 1D hexagonal pore framework and large porosity are widely investigated as carriers for various biologically active molecules because of their ability to incorporate organic molecules. Mesoporous titania is also a biocompatible inorganic material already accepted as ingredient in various drug formulations, but usually has lower porosity than silica.

**Materials and methods:** The mesoporous silica-titania composites were prepared using tetraethyl orthosilicate and titanium oxychloride as silica and titania precursor, respectively, in the presence of triblock copolymer, Pluronic P123 as structure directing agent. To obtain drug delivery systems containing mesoporous silica-titania carriers, oxytetracycline was used as model molecule, which was loaded into the carrier mesopores by incipient wetness impregnation method using a drug concentrated aqueous solution. The silica-titania composites and oxytetracycline-loaded materials were characterized by various techniques: small- and wide-angle XRD, SEM and TEM, FTIR spectroscopy and N<sub>2</sub> adsorption-desorption isotherms.

**Results:** The antibiotic molecules were adsorbed into the carrier mesopores in amorphous state as wide-angle XRD proved. The N<sub>2</sub> sorption analyses of oxytetracycline-loaded materials demonstrated a decrease of drug-loaded materials porosity in comparison with the corresponding carrier. The oxytetracycline release profiles from mesoporous silica-titania carriers, determined by UV-vis spectroscopy in saline phosphate buffer solution, at 37°C, were compared with those from mesoporous titania and SBA-15 supports. The increase of titania content in mesoporous carrier slowed down the drug delivery kinetics. The oxytetracycline-loaded materials showed very good antimicrobial activity against *Staphylococcus aureus* ATCC 25923 strain.

**Conclusions:** This study proved that titania-silica composites can be employed as carriers for oxytetracycline delivery systems. Moreover, the oxytetracycline release profile could be tuned by modifying the support titania content.

**Acknowledgements:** We gratefully acknowledged the financial support from project PCCA no. 131/2012.

## STUDY ON MATERIALS AVAILABLE FOR BALLISTIC PROTECTION VEST FABRICATION

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**Keywords:** ballistic package; polyaramid fiber; ultra-high resistant polyethylene.

**Introduction:** Individual protection equipment is essential for the combat staff survival. Next to the ballistic protection level, comfort represents the main issue of this equipment, especially when taking into consideration female staff, when shape and weight of the standard outwear are conceived for men. Thus, new materials are needed in order to comply with these demands.

**Materials and methods:** Shooting and wearability tests have been performed for twilled consecutive layers of KEVLAR<sup>®</sup> Comfort and TWARON<sup>®</sup> (KCT), at first, and KEVLAR<sup>®</sup> Comfort, TWARON<sup>®</sup> and Dyneema<sup>®</sup> (KCTD), secondly, for 30 layers. The evaluation of 7.62 mm cal. bullet impact on these materials has been performed.

**Results:** The tests performed on the twilled polyaramid fibers returned lower results than when including ultra-high resistance polyethylene. At  $v=450\text{m/s}$ , the absorbed energy has been  $120\text{ J/kg}\cdot\text{m}^2$  for KCT versus  $232\text{ J/kg}\cdot\text{m}^2$  for KCTD, while ballistic polyaramid gives a value of only  $39\text{ J/kg}\cdot\text{m}^2$ .



Figure 1. Ballistic package for individual protection vest

**Conclusions:** The best state-of-the-art materials for ballistic protection are considered polyaramid fibers KEVLAR<sup>®</sup> Comfort, which has a 15% higher energy absorption capacity than the previous KEVLAR<sup>®</sup> 129 and 15% lower weight than KEVLAR<sup>®</sup> HT, and TWARON<sup>®</sup>, whose unique characteristics derive from aramid molecules capability to self-orient during spinning resulting straight fibers. Twilling those two types of fibers should conduct to increased performances both in terms of ballistic protection and comfort. Moreover, including in the ballistic package the ultra-high resistance polyethylene (Dyneema<sup>®</sup>) increases dramatically the ballistic protection.

**Acknowledgements:** This paper has been financially supported by a grant of MEN – UEFISCDI under PARTENERIATE program, contract number 303/2014.

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## STUDIES OF OXYGEN PERMEABILITY THROUGH PROTON EXCHANGE MEMBRANES

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**Keywords:** *Proton exchange membrane, Polyphenylene oxide, gas permeability, gas chromatography*

**Introduction:** One of the main properties requested for proton exchange membrane in PEM Fuel Cell is the low permeability toward reactant gases. The membrane acts as barrier for gaseous reactants, preventing the direct mixing of hydrogen and oxygen. Hydrogen passing to cathode decreases the fuel cell efficiency and the oxygen permeating through membrane is possible to form O-radical species responsible for membrane degradation. Experimental studies of the membranes permeability used several techniques, some of them based on in situ electrochemical (chronoamperometric) measurements and other based on chromatography techniques. Gas permeability is function of temperature and membrane relative humidity (swelling). We use the chromatography as experimental method to determine the oxygen permeability of the sulfonated polyphenylene oxide membrane and composite membrane from sulfonated polyphenylene oxide and silica particles. The oxygen permeability through Nafion type membrane was also measured for comparison.

**Materials and methods:** The samples tested for oxygen permeability are: 1) sulfonated poly(2,6-dimethyl-1,4-phenylene oxide) (sPPO) with ion exchange capacity 2 miliequivalents/g, 2) composite sPPO with silica nanoparticles formed "in situ" from TEOS as a precursor (5% wt silica from sPPO) (sPPO+TEOS), and 3) Nafion N112 tested for comparison.

**Results and conclusion:** The results show a reduced oxygen permeability for sPPO and sPPO+ TEOS samples in the compared to Nafion.

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## IN VITRO INVESTIGATIONS OF HIGHLY ADHERENT BIOLOGICAL HYDROXYAPATITE THIN FILMS FOR A NEW GENERATION OF IMPLANTS

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**Keywords:** *biological hydroxyapatite films, high adherence, human mesenchymal stem cells, implantology.*

**Introduction:** We report on the synthesis by Pulsed Laser Deposition technique of hydroxyapatite (HA) thin films from renewable biological sources. The role of reinforcement agents (e.g., MgF<sub>2</sub>, Li<sub>3</sub>PO<sub>4</sub>, Li<sub>2</sub>O, or Li<sub>2</sub>CO<sub>3</sub>) on the morphology, structure, bonding strength and cytocompatibility of the films was investigated.

**Materials and methods:** The morphological, structural, compositional, and mechanical properties of the films were evidenced by Scanning Electron Microscopy (SEM) coupled with Energy Dispersive X-Ray Spectroscopy (EDS), Atomic Force Microscopy (AFM), X-Ray Diffraction (XRD), Fourier Transformed Infrared (FTIR) Spectroscopy, and pull-out tests, respectively. *In vitro* tests were performed on the deposited films to evaluate the viability of human mesenchymal stem cells (hMSC) in the presence of reinforcement elements, using calcein AM/ethidium homodimer method.

**Results:** SEM investigations of the films evidenced a surface morphology consisting of particulates with mean diameters of (2–3) μm. The roughness of the surface, inferred from AFM measurements, was in the range of (3–10) nm. XRD analyses demonstrated that the synthesized structures consisted of a pure HA phase, with different degrees of crystallinity mainly influenced by the reinforcement agents. FTIR spectra showed a remarkable growth of a biomimetic HA layer after only three days of immersion in Simulated Body Fluids, which proves an excellent bioactivity of the films. Besides the main constituents of the mineral bone part, EDS spectra indicated the presence of typical natural bone doping elements. We emphasize that the measured bonding strength values of HA structures were superior to the ones imposed by International Standards. *In vitro* viability tests revealed that high concentrations of Li<sub>2</sub>O within HA thin films were very toxic for hMSC, whilst deposition of Li<sub>2</sub>CO<sub>3</sub>, Li<sub>3</sub>PO<sub>4</sub> or MgF<sub>2</sub> promoted the cell growth on all thin film surfaces.

**Conclusions:** Taking into consideration the proven characteristics, low fabrication cost from renewable resources and the good biocompatibility of these reinforced materials, one should consider them a prospective candidate for a new generation of metallic implants.

**Acknowledgements:** GPP, ACP, INM and LD acknowledge with thanks the support of the Romanian National Authority for Scientific Research and Innovation, CNCS-UEFISCDI, under project number PN-II-RU-TE-2014-1570 (TE 108/2015) and Nucleus programme - contract 4N/2016. GES, ME, CB and IZ are thankful for the financial support of Core Programme PN 16 48-3/2016. PEF, LES and AR acknowledge support of the Romanian Academy, Project 1/2016.



## STUDIES ON MESOPOROUS SILICA AS CARRIERS FOR KETOPROFEN

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**Keywords:** *mesoporous silica, ketoprofen, drug delivery systems*

**Introduction:** Drug delivery systems have focused many research efforts due to their therapeutic efficiency. Our study deals with the possibility to employ mesoporous silica with different pore size and surface properties as carrier for ketoprofen, which is a non-steroidal inflammatory drug with analgesic and antipyretic properties.

**Materials and methods:** Mesoporous silica with different pore size and geometry as MCM-41 and MCF were synthesized using cetyl or tetradecyl trimethylammonium bromide and Pluronic P123 as surfactants, besides the swelling agent, 1,3,5-trimethylbenzene. The functionalized mesoporous silica with 3-aminopropyl groups were obtained by post-grafting method. In order to obtain drug delivery systems containing pristine and functionalized mesoporous silica carriers, ketoprofen was loaded into the carrier mesopores by incipient wetness impregnation method using an alcoholic solution of drug. The carriers and ketoprofen-loaded samples were investigated through: small- and wide-angle XRD, FTIR spectroscopy and N<sub>2</sub> adsorption-desorption isotherms.

**Results:** Wide-angle XRD demonstrated that the drug molecules were in amorphous state in ketoprofen-loaded samples. The N<sub>2</sub> adsorption-desorption isotherms of prepared materials containing ketoprofen proved the adsorption of drug molecules into the mesopores. The ketoprofen delivery experiments carried out in ionic phosphate buffer solution, pH=7.4, at 37°C, showed a fast kinetics for pristine silica supports depending on their pore size, while the presence of aminopropyl groups linked on silica surface led to the decrease of the drug release rate.

**Conclusions:** By tailoring the surface properties and pore size of mesoporous supports, the ketoprofen delivery can be controlled.

**Acknowledgements:** *We gratefully acknowledged the financial support from project PCCA no. 131/2012.*



## ELECTROCHEMICAL RESPONSE OF SONOGEL CARBON ELECTRODE TOWARD MELATONIN

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**Keywords:** *melatonin, carbon sonogel, gold nanoparticles, sensor*

**Introduction:** Melatonin, the molecule of darkness, is a lipophilic hormone secreted by the pineal gland and this is produced during the night. It is well known the effect of melatonin in restoring the natural cycle of organism functions, can eliminate disruption in our circadian rhythm, for situations as shifting work, changing of time zones or insomnia. Also, researchers have noticed the involving of melatonin in the regulation of seasonal reproduction, body weight and energy balance [1]. It can be detected in biological samples using classical methods as HPLC [2], spectrofluorimetry, calorimetry [3] or electrochemical techniques. The present work is focused on the electroanalysis of melatonin at sensors based on carbon sonogel electrodes modified or unmodified.

**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). These sensors are prepared by means of an original method. The obtained sensors have been characterized by using cyclic voltammetry and electrochemical impedance spectroscopy.

**Results:** The LODs obtained were competitive with the previous reported. Additionally, the portability of the system makes it very valuable for wide spread use without the need of skilled personnel. All these features make these electrochemical approaches very valuable screening tools before the use of more sophisticated analytical techniques. The analytical performance of the proposed sensor, in terms of LOD, linear response range, response time, sensitivity, repeatability and reproducibility, was also assessed.

**Conclusions:** This work demonstrates that carbon sonogel electrodes, provide an easy, fast and reliable analytical tool for the detection and determination of melatonin.

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## DIMINISHING THE MORPHOLOGICAL DEFECTS OF NEW RENEWABLE MATERIALS BY CONTROLLING THE SHEAR STRESS AT MELT EMBEDDING OF TARGET FILLER

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**Keywords:** *Renewable, processability, structuration, cracks, voids, fractures, thermoformability.*

**Introduction:** The research aimed to find the best method for embedding a target filler into a renewable polymer matrix in order to improve the components miscibility in view of achieving new thermoformable materials with functional properties for short life goods.

**Materials and methods:** A target filler was controlled embedded into a polymeric matrix based on renewable polymers and additives considering well designed shear rate cycles. The resulted material was characterized both into melted (rheology) and solid (SEM, DMA, mechanical properties, etc.) state and also by testing its thermoformability.

**Results:** The functional properties and SEM morphologies highlighted that the most convenient embedding procedure that allows a good dispersion of the minor components into the matrix is the extrusion in two phases, the first one achieved with a transport screw at low and/or medium speed and the second one with a compression screw working at medium speed.

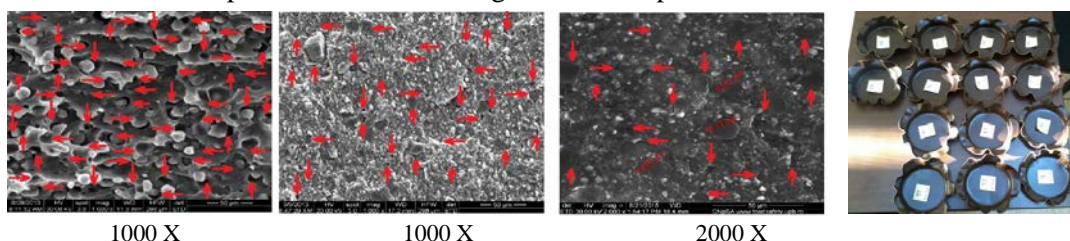


Figure 1 SEM morphologies of the new renewable materials and thermoformed items

**Conclusions:** The obtained results showed that the proposed procedure allows the achievement at shear rates of maximum  $100 \text{ s}^{-1}$  and low temperatures ( $120\text{--}140^\circ\text{C}$ ) of new renewable materials that do not degrade, show less morphological defects (voids, cracks, fractures) and present extensibility, plastic deformability and dissipation properties which allow the thermoforming in selected conditions. The items obtained from the new obtained materials, thermoformed in chosen conditions had smooth surface even in the area of the contact with the negative mold. The process presented a very good reproducibility.

**Acknowledgements:** *The research was supported by UEFISCDI – grant no. 59/2012.*

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## PRUSSIAN BLUE NANOPARTICLES FOR LASER ABLATION OF TUMORS

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**Keywords:** Prussian blue, nanoparticles, photothermal

**Introduction:** During the last years, the photothermal ablation has attracted a growing interest as a less invasive technique for the cancers therapy. The laser ablation of solid tumors employs the special features of different nanoparticles to convert the adsorbed light into local heat to kill the cancer cells. In this work we report on the synthesis of Prussian blue nanoparticles (PBNPs) with good photothermal properties and their potential applications in the laser ablation of solid tumors.

**Materials and methods:** PBNPs have been synthesized according to a wet chemical method at 55°C, by mixing equimolar quantities of ferric citrate (as Fe<sup>3+</sup> source and to prevent the nanoparticles agglomeration by mean of citrate ions) and potassium ferrocyanide. The as synthesized PBNPs have been characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and dynamic light scattering measurements (DLS). UV-Vis spectrometry was also employed in order to assess the optical properties of PBNPs.

**Results:** SEM and TEM data have evidenced PBNPs with uniform morphology and well defined cubes whereas the DLS measurements revealed a hydrodynamic diameter of about 144 nm. The UV-Vis spectra showed a broad absorption band with maximum at 710 nm suggesting good photothermal properties of PBNPs under laser irradiation and their potential application for the thermal therapy of cancers consequently. The temperature of an aqueous dispersion containing 0.1 mg/ml PBNPs under laser irradiation (980 nm) reached 50°C in less than 3 minutes and the UV-Vis spectra recorded before and after laser irradiation showed no significant changes in absorbance indicating good photothermal stability of PBNPs.

**Conclusions:** PBNPs with uniform distribution and good photothermal properties have been synthesized by a simple, rapid and cost effective method. The results suggest that PBNPs can be used for the thermal therapy of solid tumors.

**Acknowledgements:** Mr. Cornel Munteanu for SEM and TEM measurements.

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## THE EFFICIENCY OF SILANE TREATMENT OF HEMP FIBERS IN POLYPROPYLENE COMPOSITES

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**Keywords:** Hemp fibers; Silane treatment; EDX; SEM; Polypropylene

**Introduction:** Polypropylene (PP) composites containing natural fibers may contribute to high specific stiffness and to weight and cost savings when used in car industry, also ensuring a reduction of oil-based material consumption [1,2]. However, the high water absorption of natural fibers and their sensitivity to moisture, besides the poor interfacial adhesion between the hydrophilic fibers and the hydrophobic polymer matrix, are barriers in the fabrication of highly efficient materials. In this work, the influence of several silane treatments on the surface properties of hemp fibers (HF) was studied.

**Materials and methods:** PP copolymer with high melt flow index was used as matrix. Short cut HF were surface treated with  $\gamma$ -aminopropyltriethoxysilane (APS),  $\gamma$ -glycidoxy-propyltrimethoxysilane and  $\gamma$ -methacryloxypropyltrimethoxysilane (MPS). SEM-EDX was used to characterize HF surface properties, whereas thermal and mechanical analyses were used to emphasize their reinforcing capacity.

**Results:** Silane treatments led to the splitting of HF bundles into smaller ones and to improved thermal and mechanical properties in PP composites, MPS treatment being the most efficient. SEM-EDX images showed the covering of HF with different silanes and allowed highlighting the differences between treatments.

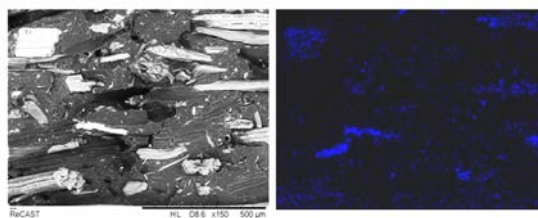


Figure 1. SEM image of hemp fibers treated with APS (left); EDX-SEM image (right) – blue spots represent the signal obtained for Si

**Conclusions:** Different reinforcing capacity was noted for the silane treated HF. SEM-EDX results highlighted the efficiency of the silane treatments.

**Acknowledgements:** This work was supported by the European Community's Seventh Framework Programme under grant agreement 314744 (EVOLUTION project) and by INOVA-OPTIMA SMIS Project Code 49164 (contract 658/2014).

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## SYNTHESIS OF PANI/Fe<sub>3</sub>O<sub>4</sub> NANOCOMPOSITES; TRANSMISSION ELECTRON MICROSCOPY CHARACTERISATION

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**Keywords:** *transmission electron microscopy, nanocomposites, polymer shell, Fe<sub>3</sub>O<sub>4</sub> particles.*

**Introduction:** Hybrid nanocomposites of Fe<sub>3</sub>O<sub>4</sub> – OLA nanoparticles with a shell of polyaniline (PANI) have been studied through transmission electron microscopy. Initial particles of Fe<sub>3</sub>O<sub>4</sub> polymerized with PANI don't have a polymer shell due to the inversion phase polymerisation.

**Materials and methods:** Radical polymerization of ANIHCl and Fe<sub>3</sub>O<sub>4</sub> - OLA in the presence of ammonium persulfate was achieved. Aniline molecules were bonded onto the Fe<sub>3</sub>O<sub>4</sub> nanoparticles and polymerized, to obtain uniform polyaniline/Fe<sub>3</sub>O<sub>4</sub> (PANI/Fe<sub>3</sub>O<sub>4</sub>) nanoparticles (approximately 15 nm). **Results:** Different types of analyses were achieved on the resulted samples HRTEM, STEM, EDX in order to demonstrate the chemical structure and the morphology of Fe<sub>3</sub>O<sub>4</sub> nanoparticles in the final composites.

**Conclusions:** Due to the presence of PANI as a shell on the Fe<sub>3</sub>O<sub>4</sub>-OLA nanoparticles, the main application of the final products can be immobilization of enzymes and bioactive compounds.

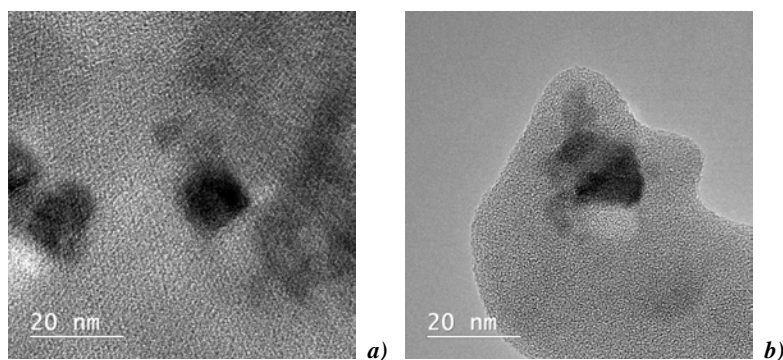


Fig.1 TEM images of Fe<sub>3</sub>O<sub>4</sub> nanoparticles with (b) and without (a) PANI shell

**TEM STUDIES ON NEW SYNTHESISED NANOCOMPOSITE MEMBRANES  
BASED ON POLYETHERSULFONE AND ADVANCED MODIFIED MINERAL  
CLAY USED IN WASTEWATER TREATMENT**

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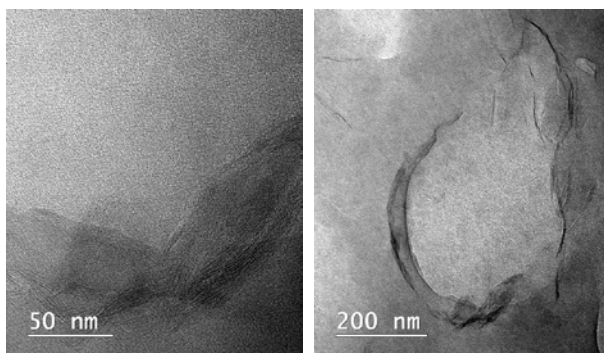
**Keywords:** *electron microscopy, nanocomposites, montmorillonite*

**Introduction:** Present study followed the morphologies of new synthesized polymer membranes based on **polyethersulfone** (PES) and organically modified montmorillonite.

**Materials and methods:** PES and commercial montmorillonite functionalized with **vinyl - Vy and C18 alkyl chains** were used to prepare membranes through a combination of solution dispersion and wet-phase inversion methods in the presence of advanced modified clay.

**Results:** TEM images obtained for the organomontmorillonite polymer (nano)composite membranes showed that clay had a good dispersion in the polyethersulfone matrix and mostly intercalated nanocomposites were obtained.

**Conclusions:** An inspection of TEM micrographs of commercial montmorillonite functionalized with vinyl membrane revealed agglomerated organomontmorillonite layers in the polymer matrix very probably due the grafted alkyl chains.



**Fig. 1 TEM images of Vy (I) and C18 (II) polysulphone composite membranes**

## TETRAMETHYLTHIURAM DISULFIDE IN THE SYNTHESIS OF HETEROCYCLIC COMPOUNDS

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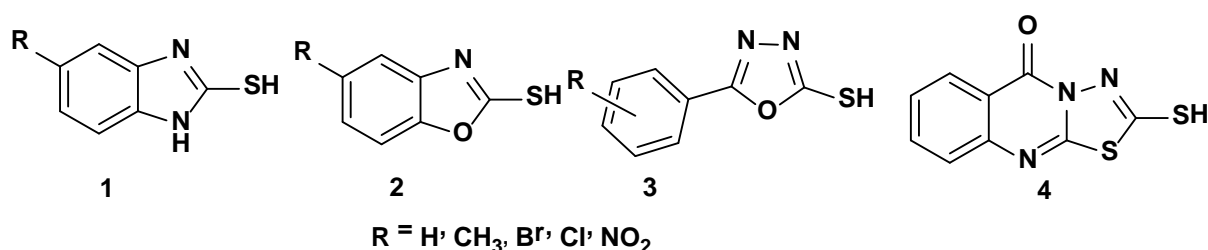
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**Keywords:** *thiuram / 2-mercaptobenzimidazole / 2-mercaptobenzoxazole / 1,3,4-oxadiazole*

**Introduction:** Tetramethylthiuram disulfide (TMTD) is used as accelerator and vulcanization agent in the rubber industry and as a fungicide on seeds. TMTD is rarely used in organic synthesis. The objectives of the work consist in elaboration of preparation methods of heterocyclic compounds using TMTD.

**Materials and methods:** TMTD and reagents used were of analytical grade. The synthesized compounds were analyzed by NMR and IR spectroscopy.

**Results:** TMTD give rise a variety of heterocyclic compounds when the reacting aromatic substrate contains two amino or one amino and one acetamido or one hydroxyl group situated in ortho-position. Thus, 2-mercaptobenzimidazoles **1** can be obtained by treatment of o-phenylenediamines with TMTD in molar ratio 2:1 in propan-1-ol or butan-1-ol



The ortho-aminoacetanilides with TMTD form also 2-mercaptobenzimidazole in propan-1-ol, butan-1-ol or dimethylformamide (DMF).

Ortho-Aminofenols undergo smooth cyclization on treatment with TMTD in different polar solvents such as alcohols, DMF and yield 2-mercaptobenzoxazoles **2**. On heating the reaction mixture for a long period of time the yields of 2-mercaptobenzoxazoles decreased in result of formations of 2-dimethylaminobenzoxazoles as a by-product.

Arylhydrazides form with moderate yields 1,3,4-oxadiazole derivatives **3** in DMF when treated with TMTD. The 2-aminobenzoic acid hidrazide with TMDT in DMF forms the tricyclic heterocycle **4** with high yield.

**Conclusions:** The present study describes a simple, inexpensive, and easy method for synthesis of benzimidazole, benzoxazoles and 1,3,4-oxadiazole derivatives with mercapto groups.

## MACROPHAGE RESPONSE TO BIOMIMETIC-COATED MATERIAL

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**Keywords:** *biomaterial; lactoferrin; hydroxyapatite; MAPLE; inflammation.*

**Introduction:** In order to increase biocompatibility and capacity of integration of bone metallic implants, the developing of new biointerfaces that influence cell behavior is of great interest[1]. Macrophages, cells involved in foreign body reaction to biomaterials can change their response in relation to environmental factors [2]. Thus, this study follows the *in vitro* influence of a new coating with embedded biomimetic anti-inflammatory components (lactoferrin-Lf, hydroxyapatite-HA) into a biodegradable polymer composite (Co-PEG-PCL) on human macrophage cells.

**Materials and methods:** MAPLE (Matrix Assisted Pulsed Laser Evaporation) functionalized surfaces were analyzed using scanning electron microscopy (SEM), atomic force microscopy (AFM) and infrared spectroscopy (FTIR) techniques. Biological assays comparatively evaluated the *in vitro* behavior of THP-1 cells on coated and uncoated surfaces in the presence or absence of bacterial endotoxin (LPS). Cellular viability and proliferation of THP-1 cells grown onto modified surfaces was evaluated using a MTS colorimetric method. Cell morphology was investigated by immunofluorescent imaging of actin and vinculin proteins. Enzyme-linked immunosorbent assay (ELISA) was performed to quantify the secreted pro-inflammatory TNF- $\alpha$  cytokine.

**Results:** Chemical and morphological analysis confirmed uniform distribution and chemical integrity of the coatings. Hybrid components supported attachment and viability of THP-1 cells differentiated to macrophages with a higher metabolic activity onto Co-HA-Lf surfaces. Coated surfaces determined increased cell attachment and decreased relative TNF- $\alpha$  pro-inflammatory cytokine release. Fluorescent imaging showed modified morphology of the macrophages adhered on hybrid coatings.

**Conclusions:** The results of this study provide insights into Co-HA-Lf coatings capacity of controlling macrophages behavior and directing early cytokine secretion leading to a promising biointerface that promotes a limited inflammatory reaction upon implantation.

**Acknowledgements:** *The research was supported by the Romanian Ministry of National Education, CNCS-UEFISCDI, under the project PN-II-PT-PCCA 239/2014, Romanian Academy Project 1/2015-2016 of the Institute of Biochemistry and University of Bucharest-Biology Doctoral School.*

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## Antimicrobial properties of coatings based on *Nigella sativa* functionalized Fe<sub>3</sub>O<sub>4</sub> nanoparticles deposited by MAPLE

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**Keywords:** antimicrobial thin films, nanoparticles, biocompatibility

**Introduction:** *Nigella sativa* extracts are commonly used in various alternative medicine systems like Ayurveda, Siddha, Unani and Tibb. Scientific studies on *Nigella sativa* demonstrated its pharmacological actions like antimicrobial, analgesic, spasmolytic, anti-inflammatory, hepatoprotective, etc [1]. This study aims for Matrix-Assisted Pulsed Laser Evaporation (MAPLE) fabrication of novel biocompatible surfaces containing iron oxide nanoparticles functionalized with *Nigella sativa* oil (Fe<sub>3</sub>O<sub>4</sub>@*Nigella sativa*) and Fe<sub>3</sub>O<sub>4</sub>@*Nigella sativa* embedded into poly(lactic-co-glycolic acid) (PLGA) with anti-biofilm properties.

**Materials and methods:** Fe<sub>3</sub>O<sub>4</sub> functionalized nanoparticles were prepared by co-precipitation method. Optimal MAPLE deposition parameters were used for nanostructures assembling on silicon and glass substrates followed by physical-chemical and biological characterization.

**Results:** Surface morphology was investigated by Scanning Electron Microscopy (SEM). Fourier Transform Infrared Spectroscopy (FTIR) and Infrared Mapping Spectroscopy (IMS) were employed to infer compositional features of Fe<sub>3</sub>O<sub>4</sub>@*Nigella sativa* and Fe<sub>3</sub>O<sub>4</sub>@*Nigella sativa*-PLGA. The viability assay and live/dead cells staining evidenced no-cytotoxic effect due to MAPLE deposited thin films for all cell lines investigated.

**Conclusions:** We obtained biocompatible Fe<sub>3</sub>O<sub>4</sub>@*Nigella sativa* and Fe<sub>3</sub>O<sub>4</sub>@*Nigella sativa*-PLGA coatings with anti-biofilm effect against *E. Coli*, *S. Aureus* and *C. albicans*. All tests recommend our coatings as new nonantibiotic defense strategies against biofilm formation and removal, resulting in a challenging alternative for production of reliable and cheap human medical devices.

**Acknowledgements:** The work has been funded by the Romanian National Authority for Scientific Research, CNCS-UEFISCDI, project number PNII-RU-TE-2014-4-1590 TE 188/2015 and National Program PN 4N/2016(1647-LAPLAS IV)

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## Antimicrobial properties of coatings based on *Nigella sativa* functionalized Fe<sub>3</sub>O<sub>4</sub> nanoparticles deposited by MAPLE

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**Keywords:** antimicrobial thin films, nanoparticles, biocompatibility

**Introduction:** *Nigella sativa* extracts are commonly used in various alternative medicine systems like Ayurveda, Siddha, Unani and Tibb. Scientific studies on *Nigella sativa* demonstrated its pharmacological actions like antimicrobial, analgesic, spasmolytic, anti-inflammatory, hepatoprotective, etc [1]. This study aims for Matrix-Assisted Pulsed Laser Evaporation (MAPLE) fabrication of novel biocompatible surfaces containing iron oxide nanoparticles functionalized with *Nigella sativa* oil (Fe<sub>3</sub>O<sub>4</sub>@*Nigella sativa*) and Fe<sub>3</sub>O<sub>4</sub>@*Nigella sativa* embedded into poly(lactic-co-glycolic acid) (PLGA) with anti-biofilm properties.

**Materials and methods:** Fe<sub>3</sub>O<sub>4</sub> functionalized nanoparticles were prepared by co-precipitation method. Optimal MAPLE deposition parameters were used for nanostructures assembling on silicon and glass substrates followed by physical-chemical and biological characterization.

**Results:** Surface morphology was investigated by Scanning Electron Microscopy (SEM). Fourier Transform Infrared Spectroscopy (FTIR) and Infrared Mapping Spectroscopy (IMS) were employed to infer compositional features of Fe<sub>3</sub>O<sub>4</sub>@*Nigella sativa* and Fe<sub>3</sub>O<sub>4</sub>@*Nigella sativa*-PLGA. The viability assay and live/dead cells staining evidenced no-cytotoxic effect due to MAPLE deposited thin films for all cell lines investigated.

**Conclusions:** We obtained biocompatible Fe<sub>3</sub>O<sub>4</sub>@*Nigella sativa* and Fe<sub>3</sub>O<sub>4</sub>@*Nigella sativa*-PLGA coatings with anti-biofilm effect against *E. Coli*, *S. Aureus* and *C. albicans*. All tests recommend our coatings as new nonantibiotic defense strategies against biofilm formation and removal, resulting in a challenging alternative for production of reliable and cheap human medical devices.

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# LASER PYROLYSIS VERSUS LASER ABLATION IN IRON BASED NANOPARTICLE FABRICATION

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**Keywords:** *pyrolysis, ablation, nanoparticle, fabrication*

**Introduction:** In the recent development of nanobiotechnology, iron based magnetic nanoparticles (NPs) have gained increasing attention for use in various areas, particularly in biomedical application. In vivo drug transport could take advantage of their small size and large surface area, while their magnetic properties are relevant for targeted drug delivery.

**Materials and methods:** Maghemite ( $\text{Fe}_2\text{O}_3$ ) is a suitable material for the core of magnetic NPs because it is least likely to cause major health hazards: (it is known that iron(III) ions are widely found in the human body, so leaching of metal should not cause significant side-effects. The use of  $\text{Fe}_3\text{O}_4$  magnetite NPs in spite of the possible release of Fe(II) ions which generate toxic hydroxyl radicals via Fenton reaction could still have interesting application as contrast agents in biological and non-biological applications. In spite of their lower productivity (compared with chemical methods) laser methods are still desirable for magnetic NPs production as “clean” fabrication techniques or sometimes due to their structural properties.

**Results:** Here we present some comparative results for two laser methods, respectively laser ablation and laser pyrolysis. Produced nanoparticles are compared from morphological and structural point of view.

**Conclusions:** Comparative results on the obtained properties based on the principles of the fabrication techniques are presented here pointing out advantages and drawbacks of both methods.

# SURFACE DIFFUSION CONTROL IN PLD/VLS GROWING

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**Keywords:** VLS, self-assembling, PLD, oxide nanowires, nanostructure morphology

**Introduction:** Vapor-Liquid-Solid (VLS) grow is among the most popular techniques for Bottom-Up nanostructures fabrication, and particularly for oxide nanowires. The technique consists of several elementary processes as: absorption and desorption into catalyst, surface diffusion and nucleation (fig. 1). In spite of the very good efficiency of the chemical-vapor-deposition approach, laser ablation is giving in many cases better performances in terms of nanostructure morpho-structural properties. Furthermore, investigations using pulsed laser ablation was giving interesting insides about absorption and desorption processes control of the nanowire growing through the critical saturation level within the catalyst droplet [1] and and on the catalyst size limitations [2]. Among the VLS elementary processes, surface diffusion is still known as a fundamental process but very few experimental investigation were performed to clarify it's influence on the nanostructure growing process and the corresponding key parameters.

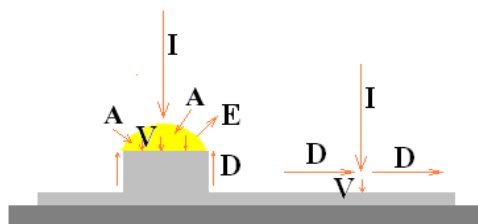


Figure 1: Vapor-Liquid-Solid grow elementary processes: I - impinging particles, D - diffused particles, A - catalyst absorbed particles, E - catalyst desorbed particles, V - deposited particles

**Materials and methods:** In the present work, oxide nanowires were grown using VLS technique in a PLD system using gold as liquid catalyst. Special system geometries (as plume reflection) were used as the experimental setups for plume filtering purpose but also for elementary processes investigations through plume propagation control. Also laser patterned masks were fabricated for catalyst surface positioning, in order to investigate VLS elementary processes through the nanowire morphology control but with a particular interest for surface diffusion process.

**Results:** Observed influences of this process over the nanostructure growing and obtained properties are summarized and discussed.

**Conclusions:** Catalyst properties and surface disposal together with the particle flux seems to control the grown nanostructure morphology.

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## DEVELOPMENT PHOTOCONDUCTOR POLYMERS BASED ON LIGNIN AND 9-EPOXYPROPYL CARBAZOLE

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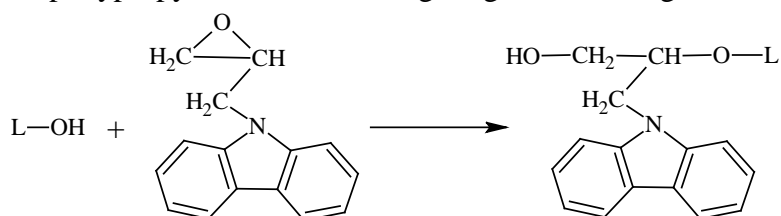
**Keywords:** *photoconductor polymers, lignin, 9- epoxypropyl carbazole.*

**Introduction:** At the present, organic photoconductive polymers are very precious and useful materials in optoelectronics for the development of the systems for registration of information using electrophotographic and also photochemical method. In recent years in the literature is emphasized the possibility of using these materials for photovoltaic cells with relatively good characteristics.

**Materials and methods:** Synthesis of polymer analogues lignin-9-EPC was carried out in glass ampoules at  $T = 120^{\circ}\text{C}$  for 2 and 3 hours. The new obtained polymers were dissolved in toluene or chloroform and precipitated in hexane.

**Results:** In the paper is analysed the synthesis of polymer analogues based on lignin and 9-epoxypropyl carbazole (9-EPC). Using lignin as a support polymer lead to increased stickiness compared to metallised polyethylene terephthalate used as support and compared to optic glass, covered with a conductive layer.

Condensation of 9-epoxypropyl carbazole with lignin goes according to scheme:



**Conclusions:** From purified copolymer solution were obtained thin layers,  $d = 2,0 \text{ mm}$ , sensitized with 2,4,7-trinitrofluorenone. On installation of decay of the potential has been shown that layers have a relatively low electro photosensitivity  $10^{-1} - 10^{-2} \text{ lx}^{-1}\cdot\text{s}^{-1}$ , which allows us to recommend them for optoelectronics. Photosensitive layers may be recommended for the creation of a dual-layer photo-thermoplastic media for registration of information using electro-photographic method [1].

Sensitizing photoconductive layers with triiodomethane leads also to photosensitive layers in the blue-green region of the spectrum and can be used as a negative photoresist [2].

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## PERFORMANCE OF RECYCLED POLYPROPYLENE COMPOUNDED WITH THERMOPLASTIC ELASTOMERS

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**Keywords:** waste, polypropylene; elastomer; property; performance

**Introduction:** The use of recycled polypropylene (RPP) as raw material for various industries has been known. However, the mechanical and thermal properties of recycled products are lower than those of virgin material [1, 2]. The objective of this study is to obtain and investigate the modified recycled polypropylene (RPP) with commercial elastomers for possible applications.

**Materials and methods:** Recycled polypropylene (RPP) was coming from post-consumer boxes; commercial thermoplastic elastomers namely, styrene–ethylene/butylene–styrene (SEBS) (Dynasol, Spain) and styrene–isoprene–styrene (SIS) (KRATON, USA). The compounded RPP-based thermoplastic elastomers were investigated by thermal properties (MFI, DSC, VICAT, HDT), structural characteristics (XRD, optical microscopy) and mechanical properties (tensile properties, density, IZOD impact, Shore hardness).

**Results:** The samples compounded with 10 % elastomers recorded high tensile properties than unmodified RPP. Also, Izod impact strength increased from  $4.3 \pm 0.2$  kJ/m<sup>2</sup> for PPR till  $21.7 \pm 2.5$  kJ/m<sup>2</sup> for PPR/SIS20 blend, while the degree of crystallinity was decreased with addition of elastomers. The performance of RPP compounds was proved by pressing, extrusion and injection moulding technologies.

**Conclusions:** The obtained results recommend the RPP/elastomers compounds both to the remediating of environmental from postconsumer PP wastes as well as to realize new goods with high performance for various applications.

**Acknowledgements:** This work was supported by a grant of the Romanian National Authority for Scientific Research, CNDI-UEFISCDI, project number 67/2012.

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## SBIODIESEL FROM WASTE OIL

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**Keywords:** biodiesel; alternative feedstock; emissions reduction.

**Introduction:** Given the current European policy regarding the reduction in fossil fuel usage, alternative energy sources must be identified and used at a larger scale. With up to 20% of the total energy consumption being supplied by renewable sources in the following years, biodiesel can still be a viable candidate as an alternative fuel, being compatible with diesel fuels and engines, which are largely used in Europe, and having a positive effect on combustion quality in engines by reducing green house gases emissions [1-3].

**Materials and methods:** An alternative feedstock for the production of biodiesel was proposed, the resulting biodiesel being analyzed to establish if the sample was in concordance with current European standards.

**Results:** Biodiesel was obtained from a cheap feedstock, which in the present is considered a waste without any practical uses.

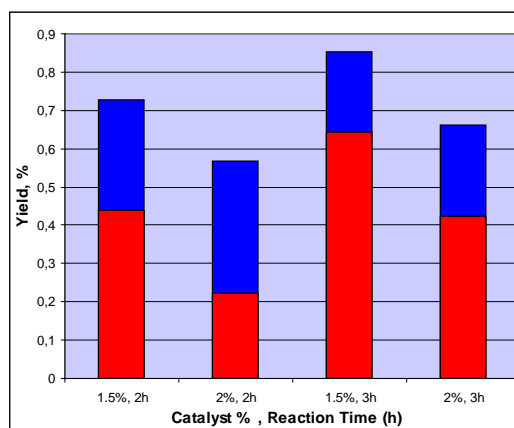


Figure 1. Biodiesel yields for 6:1 (red) respectively 18:1 (blue) alcohol:oil ratio

**Conclusions:** By implementing a production method with optimized parameters, a type of waste oil without any notable uses could be used as an alternative feedstock for producing biodiesel.

**Acknowledgements:** This research was financially supported by Sectoral Operational Programme Human Resources Development, financed from the European Social Fund and by the Romanian Government under the contract number POSDRU/156/1.2/G/135764 „Improvement and implementation of university master programs in the field of Applied Chemistry and Materials Science - ChimMaster”.

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## MODIFICATION OF LAVENDER OIL BY HYDROGENATION

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**Keywords:** *selectivity, hydrogenation, lavender oil, catalysts acidity.*

**Introduction:** Hydrogenation reactions are commonly used in the pharmaceutical, fine chemicals and agrochemicals industries for the preparation of a wide range of organic compounds. Essential oils, mixtures of volatile, organic compounds originating from a single botanical source, find applications in various fields. Oils have been hydrogenated nearly a hundred years to prolong their shelf stability. Thus, essential oils become more stable and more resistant to oxidation by hydrogenation. Lavender oil contains terpene alcohols with conjugated double bonds that have a low stability to oxidation, so their stability can be improved by hydrogenation without diminishing the fragrance characteristics.

**Materials and methods:** Catalytic precursors were purchased from Sigma Aldrich and the catalysts were synthesized using wetness impregnation technique. The acid strength and distribution of strength acid centers have been highlighted by thermal desorption of diethylamine and the textural characteristics, respectively the specific surface area as well as the pore size distribution by adsorption / desorption of nitrogen. The hydrogenation was performed on a fixed bed reactor. Characterization of lavender oil and the reaction products was performed by GC-MS.

**Results:** Efficiency of the selective hydrogenation process was evaluated by determination of the parameter influence on the yield in 2,3,6-trimethylhept-3-en-1-ol. Saturated products which have lower fragrance characteristics were obtained either by hydrogenation of both olefinic bonds (ex. 2,6 dimethyloctan-2-ol), either by cyclization and hydrogenation of only one olefinic bond (ex. [4-(propan-2-yl) cycloheptyl]methanol and 2-(4-methylcyclohexyl)propan-1-ol).

**Conclusions:** Selective hydrogenation of a only one olefinic bond from compounds with fragrance characteristics that contain conjugates olefinic bonds is favored by using a high excess of hydrogen.

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## ALKYLATION OF CRESOLS ON TUNGSTOPHOSPHORIC ACID

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**Keywords:** alkylation, cresols, heteropoly acids, anti-stripping additive

**Introduction:** The compounds with surfactant characteristics based on alkylphenol shows a high efficiency. Such alkylphenols obtained by depolymerisation of lignin can be modified for the synthesis of bitumen anti-stripping additive. The surfactants obtained by alkylation of phenols with higher olefins shows improved hydrophobic characteristics and may enhance the flow characteristics of the bitumen emulsions.

**Materials and methods:** The alkylation of cresols with 1-decene was studied on catalysts doped with heteropoly acids. The experiments were performed in batch on catalysts type tungstophosphoric acid deposited on mesoporous supports by impregnation. Catalysts characterization where performed by determining the acid strength and textural characteristics. Acidity and distribution of strength acid centers have been highlighted by thermal desorption method -diethylamine and the specific surface area as well as the pore size distribution by adsorption of nitrogen.

**Results:** Alkylation process was accompanied by isomerization - oligomerization reactions of 1-decene. Alkylation process performance are influenced by textural characteristics of the catalyst as well as by tungstophosphoric acid concentration deposited on the catalytic support.

**Conclusions:** The increase of the catalyst concentration favors the increase of cresol conversion. Optimizing of textural characteristics is one of the main way to improve the performance of cresols alkylation.

**Acknowledgements:** The authors gratefully acknowledge the financial support of the UEFISCDI, Romania, in the framework of National Partnership Program PN II, financing contract no. 151/2012 (LIGSALCHEM).

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**FURFURAL HYDROGENATION ON Ni-Co-Mo CATALYSTS DOPPED WITH Ba****M. Bombos<sup>1</sup>, R. Doukeh<sup>2</sup>, S. Velea<sup>1\*</sup>, G. Vasilievici<sup>1</sup>, D. Bombos<sup>3</sup>**

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**Keywords:** *hydrogenation, furfural, catalysts acidity, fuel*

**Introduction:** The manufacture of components for fossil fuels by capitalizing of biomass, represents a first stage in replacing of fossil fuels. In this context, the valorization of carbohydrates into component for fuel, could be the best choice. The objective of this research is to obtain furan derivatives, component for gasoline, with high stability in the formation of gums and with optimal oxygen content, by hydrogenation of furfural on Ni-Co-Mo catalysts dopped with Ba.

**Materials and methods:** The hydrogenation reaction was performed in a continuous system and fixed bed reactor. Catalysts characterization where performed by determining the acid strength and textural characteristics. Thus, acidity and distribution of strength acid centers have been highlighted by thermal desorption method of diethylamine and the specific surface area as well as the pore size distribution by adsorption / desorption of nitrogen.

**Results:** The significant reaction products identified where ,tetrahydro-furfuryl alcohol, methyl-tetrahydrofurfuryl ether, methyl-furfuryl ether and furfuryl alcohol. Furfural conversion varies by a parabolic curve, decreasing it at the temperatures higher than 200°C being determined by catalysts deactivating due to the formation of gums that clog catalysts pores. The main compounds obtained on the two catalysts were eters of furfuryl alcohol and respectively of tetrahydrofurfuryl alcohol with methanol.

**Conclusions:** Optimizing of acid strength distribution of catalysts is the main way to improve the performance of the hydrogenation process of 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).

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## NEW OXYGENATED FUEL ADDITIVES OBTAINED BY REACTIVE DISTILLATION

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**Keywords:** *fuel additives; reactive distillation; characterisation.*

**Introduction.** Glycerol based acetals and ketals have been identified to have particular qualities as fuel additives (improve the octane number and cold flow properties, reduce particulate emission and gum formation) [1, 2]. Glycerol acetals/ketals coming from low molecular weight aldehydes/ketones has a low solubility in diesel fuel. Esterification of free OH from glycerol acetals/ketals structures is an effective solution to improve their solubility in hydrocarbons. The purpose of this work is to present a process for obtaining new glycerol ketal esters, difficult to synthesize using classical techniques, based on reactive distillation, in order to be used as diesel fuel additives.

**Materials and methods.** Syntheses were performed by reacting 1,2-O-isopropylidene-glycerol esters and ethyl levulinate, in acid catalysis. Heterogeneous catalysts were prepared. Experiments were conducted in Asia 330, an integrated flow chemistry system.

**Results.** The prepared tungstophosphoric acid catalyst supported on  $\gamma$ -alumina extrudates and characterized by means of FT-IR, TG-DTA, XRD, EDX-TEM and BET had good activity, stability and reusability during experiments. The effect of temperature in the range of 120-150°C, and of reaction time was studied, using the stoichiometric feed ratio. To achieve high conversions, the reaction equilibrium was displaced by continuous removal of acetone, by reactive distillation. An excess of ethyl levulinate was avoided, due to difficulty to remove them by distillation, ethyl levulinate having high boiling temperatures. At 120°C, ethyl levulinate glycerol ketal propanoate yield continuously increases, first rapidly in 60 minutes reaching 58.8%, and then slowly towards 72.3%, during the next 290 minutes.

**Conclusions.** A new method for obtaining glycerol ketal esters has been developed, and its viability has been proven by synthesizing two new compounds, having structures of ethyl levulinate glycerol ketal. Recycling the heterogeneous catalyst, acetone and avoiding the use of solvents as reaction medium should increase the eco-friendliness of this method..

**Acknowledgements:** *The authors gratefully acknowledge the financial support of the UEFISCDI, Romania, in the framework of National Partnership Program, financing contract no. 65/2014..*

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## SPECTROSCOPIC PROPERTIES OF COPPER (II) COMPLEXES OF SCHIFF BASES DERIVED FROM SUBSTITUTED BENZALDEHYDES

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**Keywords:** *Schiff bases; copper complexes; spectroscopic properties.*

Copper is an important element component of a lot of copper enzymes, that plays an crucial role in human metabolism. Human body contains cca. 150 mg of copper, and needs cca. 2-5 mg copper per day from a good function [1,5,6]. Some important copper enzymes in human body are superoxide dismutase, tyrosinase, amine oxidase, galactose oxidase, dopamine beta-hydroxylase, nitrite reductase, nitrous oxide reductase. Copper as active site in these enzymes have diverse environments and symmetries. Their symmetries are versatile, low, predominant square pyramidal and interchangeable during reactions. Copper (II/I) is a redox potential element, that sustains enzyme functions. The symmetries of copper in enzymes and metal complexes are very good determined by NMR, UV-VIS and EPR spectroscopy [2-4]. In this report we compare copper symmetry in copper enzymes of human body and copper symmetry in copper complexes of Schiff bases derived from substituted benzaldehydes from a future mimetism experiment [2,4,7].

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## MOLECULAR MODELING AND SAR STUDIES OF SOME QUINOLONE DERIVATIVES

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**Keywords:** antimicrobial activity; quinolones;

**Introduction:** The quinolones are a significant class of antibacterial drugs with broad spectrum of action [1-3]. The molecular modeling study has been performed on quinolone derivatives to investigate the structure-antimicrobial activity relationships.

**Materials and methods:** The molecular modeling study has been performed using SPARTAN'14 software package (Wavefunction Inc., Irvine, CA, 2013). In this study, the DFT/B3LYP/6-31 G<sup>\*</sup> level of basis set has been used for the computation of molecular structure.

**Results:** In order to perform structure-activity relationship (SAR) studies, some electronic properties, such as HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital) energy values, HOMO and LUMO orbital coefficients distribution, molecular dipole moment, LUMO map (Fig. 1), atoms and bonds density have been calculated. electrostatic potential map (MEP) (Fig. 2), local ionization potential map.

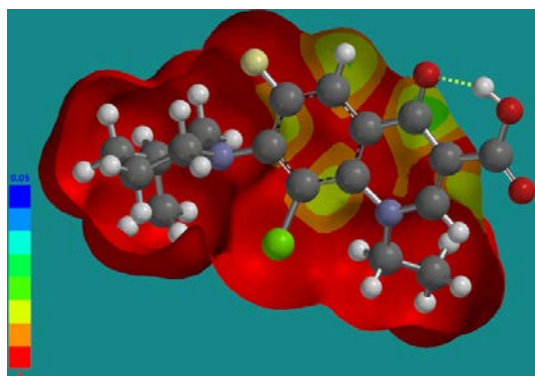


Fig. 1 LUMO map of FPQ 30

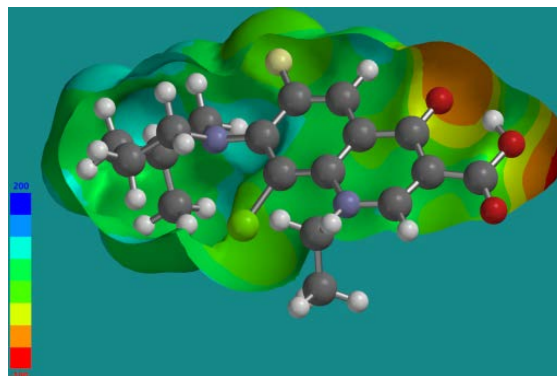


Fig. 2 Electrostatic potential map of FPQ 30

**Conclusions:** The antimicrobial activity of the quinolones could be related to the electronic properties (LUMO, LUMO map and MEP). The analyses of the molecular properties could be useful for designing new antimicrobial agents

**Acknowledgements:** This paper has been financed through the NUCLEU Program, which is implemented with the support of ANCSI, project no. PN 09 11 01 01 and project PN 09 11 09 09

**References:** Reference citations in the text should be identified by numbers in square brackets. Please provide a list of up to five references. The entries in the list should be numbered consecutively, using the following style:

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## STUDY OF DENSITY AND VISCOSITY OF DIESEL FUEL + i-PROPANOL MIXTURES

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**Keywords:** diesel fuel; i-propanol; bioalcohol; density; viscosity.

**Introduction:** The interest in biofuels is due to the increase of environment pollution and oil price fluctuation [1,2]. Basic properties of liquid fuels, like density and viscosity directly influence spray properties, atomization and combustion processes developed in diesel engine. The main purpose of this research was to report experimental data of density and viscosity for diesel fuel+i-propanol mixtures over the entire composition range and for temperature ranging from 298.15 to 323.15 K. Another objective was to evaluate the accuracy of different models used to estimate these properties.

**Materials and methods:** Density and viscosity measurements were carried out at atmospheric pressure by using an Anton Paar SVM 3000 viscometer. Commercially available diesel fuel was obtained from a local company.

**Results:** Fig1a,b presents experimental data of density (a) and viscosity (b) of diesel fuel+i-propanol mixtures.

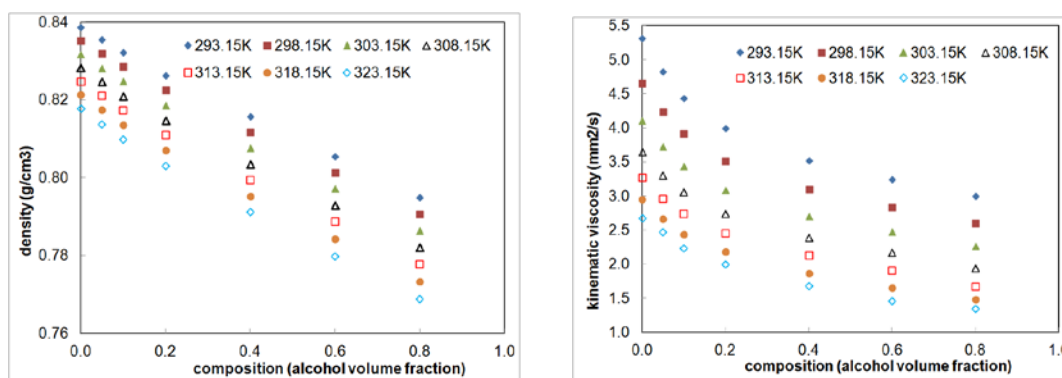


Fig.1. Density and viscosity of diesel fuel+i-propanol mixtures variation with composition at different temperatures

**Conclusions:** It was concluded that density and viscosity data of pure diesel fuel and i-propanol can be used to predict with a good accuracy the density (Kay's rule) and viscosity (Grunberg-Nissan equation) of the mixtures. Empirical regression equations of second degree polynomial type can also be recommended to calculate these properties.

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## DEHYDRATION OF FRUCTOSE TO HYDROXYMETHYL FURFURAL, CATALYSED BY DIFFERENT HETEROGENEOUS CATALYSTS

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**Keywords:** *hydroxymethyl furfural, fructose, heterogeneous catalysis*

The valorization of monosaccharides like fructose into 5-hydroxymethyl-2-furfural (HMF) is of current interest because is one of the promising intermediate chemicals derived from biomass that finds diverse applications such as fuel additive (2,5-dimethylfuran), polymer precursors e.g., alternative for terephthalic acid (2,5-furandicarboxylic acid (FDCA) and 2,5-diformylfuran (DFF) and as platform molecule for value-added chemicals [1,2]. This paper present a comparative study between different types of heterogeneous catalyst for the dehydration process. The most promising catalyst was p-toluene sulphonic acid polymer bound, with a yield in HMF of 90,62%, Zn-ZSM 5 with 82,2 % and mesoporous silica supported 10% tungsten phosphoric acid, with a yield in HMF of 77,27%. The dehydration reactions were performed in a discontinuous system, in the presence of DMSO, at different temperatures and different fructose/catalyst ratios. The content of 5-hydroxymethyl-2-furfural was determined by GC and HPLC methods.

**Acknowledgements:** *PN-II-PT-PCCA-2013-4-1006, C 65/2014*

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## GLYCEROL DERIVATES USED FOR DIESEL FUELS FORMULATION

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**Keywords:** Glycerol; Glycerol-derived products; Diesel.

**Introduction:** Biodiesel (FAME) production by vegetable oil transesterification leads to large amounts of glycerol as by product. Thus:

$$100 \text{ kg of oil} + 10.5 \text{ kg MeOH} = 100 \text{ kg FAME} + 10.5 \text{ kg glycerol}$$

Nowdays, on the market there is a surplus of glycerin which led to lower prices of this product [1]. For this reason, the transformation of glycerol into valuable compounds is an actual trend [2,3].

By reacting glycerol with ketones, different ketals can be obtained. These ketals be used as additives for diesel fuels in order to improve the properties [4,5].

In this paper, the influence of glycerol ketals on diesel-FAME blends properties was studied.

**Materials and methods:** Ketals of glycerol with acetone and methyl-ethyl ketone were used in mixture with diesel-FAME fuels. These mixture were characterized according to SR EN 590/2009.

**Results:** Ketals of glycerol were obtained by reaction glycerol with acetone (k<sub>1</sub>) and methyl-ethyl ketone (k<sub>2</sub>) using H<sub>2</sub>SO<sub>4</sub> 5% as catalyst, temperature 80°C, time reaction 2h and ethyl acetate as solvent. The syntetized ketals were used as components in a 1-10 g/100 g fuel concentration.

The influences of these compounds on the fuels viscosity, density, flash point, Diesel and cetane index were studied. The results for viscosity and cetane index are presented in figure 1 and 2.

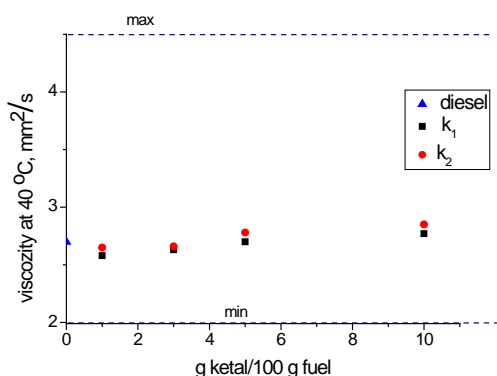


Figure 1. Influence of ketal concentrations on blend viscosity

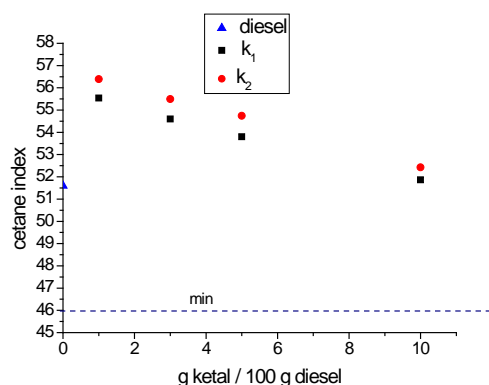


Figure 2. Influence of ketal concentrations on blend cetane index

**Conclusions:** Addition of these ketals on fuels do not affect the utilization properties of diesel fuels.

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## MODIFIED ROAD BITUMEN WITH RUBBER CRUMB SPENT

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**Keywords:** bitumen, crumb rubber

**Introduction:** Improving the elastic characteristics of the bitumen road is achieved by modifying with elastomers. The use of crumb rubber used for this purpose is hampered due to the high degree of cross-linking induced by vulcanization. The decrease in the sulfur content of crumb rubber used in a process of devulcanization favoring its dispersal efficiency in bitumen. The objective of this work is to reduce the sulfur content of crumb rubber particles by adsorption on nanostructured reactive.

**Materials and methods:** Partial devulcanization of rubber crumb spent was performed in the presence of oxide nanoparticles prepared by precipitation in the presence of anti-caking. Devulcanization of the rubber crumb was carried out in a batch system at a temperature of 200°C. Devulcanised rubber was used in road bitumen modification.

**Results:** Homogeneity of bitumen, determined by fluorescence microscopy, was superior in case of modification with devulcanised rubber compared to the case of modification of bitumen with vulcanised rubber. Adhesiveness of bitumen road increases significantly after modification with desulfurized rubber compared to the case of bitumen modified with vulcanised rubber.

**Conclusions:** Partial vulcanization of rubber crumb represents the cheapest way to modify the road bitumen with elastomers.

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## EXCESS MOLAR ENTHALPIES AT HIGH DILUTION FOR HALOGENATED IMIDAZOLIUM IONIC LIQUIDS (ILs) WITH 1-BUTANOL OR WATER SYSTEMS

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**Keywords:** *1-butyl-3-methylimidazolium chloride and bromide; molar enthalpy of solution; infinite dilution.*

**Introduction:** Successful representation of the activity coefficient of a component  $i$  in a multicomponent mixture,  $\gamma_i$ , is essential to the design of fluid phase separation equipment. The modeling of solution behavior is usually focused on the molar excess Gibbs energy,  $G_m^E$ . Its models accurately correlate vapor-liquid equilibria data but often fail when predicting excess molar enthalpies  $H_m^E$ . The  $H_m^E$  has to be evaluated directly. Besides, its derivative at infinite dilution,  $\Delta_{sol}H_{m,i}^\infty$ , reflects almost completely solute-solvent interactions [1]. The present work deals with  $H_m^E$  and  $\Delta_{sol}H_{m,IL}^\infty$  direct determination for selected titled ILs + classical solvents systems and data interpretation.

**Materials and methods:** Pure ILs were dried till constant mass under high vacuum and stored afterwards under the same conditions. Pure 1-Butanol was dried and stored on molecular sieves. Water was double distilled and deionized. The calorimetric measurements were carried out in a SETARAM C80 3D computer-controlled calorimeter using reversal mixing cells. Details on the calibration and heat measuring procedure have been reported recently [2]. The heats uncertainties are: 0.6% for  $\Delta_{sol}H_{m,i}^\infty$  and 0.1% for  $H_m^E$ . Mole fraction uncertainty is of  $\pm 0.0001$ .

**Results:** Enthalpies of solution at 303.15 K and 318.15 K for 1-butyl-3-methylimidazolium chloride ([bmim]Cl) and bromide ([bmim]Br) + water systems up to 0.0171 mole fraction of the IL and for [bmim]Cl + 1-butanol system up to 0.0793 mole fraction of [bmim]Cl have been measured. The results are reported in terms of  $H_m^E$  and  $\Delta_{sol}H_{m,IL}$ . The latest data have been used to calculate  $\Delta_{sol}H_{m,IL}^\infty$ . The experimental temperature and concentration dependence of  $H_m^E$  is correlated well with Redlich-Kister equation. In the water systems the  $H_m^E$  for chloride are smaller than for bromide; up to 0.0130 mole fraction of IL, they increase with increasing temperature in both cases; for chloride system, they are negative at both temperatures, while for bromide only in the range 0.0040-0.0125 mole fraction at 303.15 K; the  $\Delta_{sol}H_{m,IL}^\infty$  for chloride is negative while for bromide is mainly positive. For 1-butanol system,  $\Delta_{sol}H_{m,IL}^\infty$  are more negative than those for the same IL + water system.

**Conclusions:** In the investigated systems, the H-bond interactions strength varies in the order: 1-butanol/chloride > water/chloride > water/bromide.

**Acknowledgements:** *to Romanian Academy and EU(ERDF)/Romanian Government by INFRANANOCHEM project supports.*

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## KINETIC ANALYSIS OF TOTAL OXIDATION OF BENZENE USING MIXED OXIDES TYPE CATALYST Cu-Cr SUPPORTED ON $\text{Al}_2\text{O}_3 + \text{SiO}_2$

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**Keywords:** *mixed oxide catalysts, complete oxidation of hydrocarbons, kinetic analysis*

**Introduction:** Purifying the industrial residual gases is a major and actual problem. To solve this problem the obtaining of efficient catalysts in the neutralization of organic volatile toxic residues process, at low temperature and concentrations is the most important target. A great number of papers were published in literature concerning the optimization of the total oxidation process of volatile organic compounds from wasted gases. Some of these [1-4] are related to mixed supported oxides Cu-Cr, Co-Cr or Cu-Mn as catalysts. The kinetic study of total oxidation reaction of organic volatile compounds is a very difficult job because the reactions are highly exotherm.

**Materials and methods:** The aim of the present paper is to achieve a simplified kinetic analysis of the total oxidation of benzene using a Cu-Cr catalyst supported on  $\text{Al}_2\text{O}_3 + \text{SiO}_2$ . The selected catalysts has a moderate activity in order to extend the temperature domain for the kinetic regime.

**Results:** The differential analysis of experimental data for low conversions ( $X \leq 0.1$ ), was used to compute the apparent kinetic constants. The activation energy suggests the dominant process taking place, together with the temperature range: the total oxidation and breaking of the aromatic ring ( $E = 40 \text{ Kcal/mol}$ ). The apparent kinetic constants that correspond to the integral reactor.

**Conclusions:** The kinetic analysis of experimental data evidenced, in spite of the assumptions and simplifying hypothesis, the principal components of oxidation process and temperature domains. The Arrhenius plots are very useful: in the absence of a complete analysis of the reaction products, they permit a semi quantitative analysis of the reaction kinetics and the estimation of the dominant processes in different temperature domains.

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## PHYTOCHEMICAL DETERMINATION OF *ROSMARINUS OFFICINALIS* EXTRACT OBTAINED BY USING DIFFERENT SOLVENTS AND METHODS

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**Keywords:** extract, total phytochemical content, antioxidant activity.

**Introduction:** Rosemary (*Rosmarinus officinalis*) is an aromatic plant, member of the *Lamiaceae* family along with mint, oregano, thyme, basil, or lavender. It is used for culinary condiment, perfume industry and potential medical benefits. This study was made to investigate and compare two extraction method using different types of solvents, and to determinate antioxidant activity, total polyphenolics, flavonoids, tannins and terpenoids content.

**Materials and methods:** The curves calibration were made using standard solutions of vanilin, catechin, linalool, gallic acid have been elaborated. For determination of antioxidant activity it was used 2,2-diphenyl-1-picryl-hydrazyl-hydrate. An UV-VIS Specord M40 equipment, using specific wavelength for each method, has been utilized.

**Results:** All determinations were made in triplicate and were calculated using calibration curves, with very good regression indices. The final values of phytochemical content and antioxidant activities of the samples presented higher values at samples extracted using Soxhlet method and hidroalcoholic solvent, than aqueous samples extracted at room temperature.

| Plant                         | Solvent extraction  |             |                               | Extraction method |                  | Extract cod |
|-------------------------------|---------------------|-------------|-------------------------------|-------------------|------------------|-------------|
|                               | Distilled water (A) | Ethanol (E) | Ethanol: distilled water (EA) | Hot (Soxhlet)     | Cold (room temp) |             |
| <i>Rosmarinus officinalis</i> |                     | X           |                               | X                 |                  | ROH-E       |
|                               |                     | X           |                               |                   | X                | ROC-E       |
|                               | X                   |             |                               |                   | X                | ROC-A       |
|                               | X                   |             |                               | X                 |                  | ROH-A       |
|                               |                     |             | X                             | X                 |                  | ROH-EA      |
|                               |                     |             | X                             |                   | X                | ROH-EA      |

Figure 1. The types of solvents and extraction method used for rosemary plant

**Conclusions:** The results of phytochemical content and antioxidant activity of the rosemary extract, indicate that this plant contains significant quantities of polyphenols, flavonoids, tannins and terpenoids, proving them to be perfect sources of antioxidants.

**Acknowledgements:** This work was supported by a grant of the Romanian National Authority for Scientific Research, CNDI-UEFSCDI, project number PN II 185/2014 and BM11/2016.

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## FERMENTATION BUTANOL USABLE AS ALCOHOLIC FUELS

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**Keywords:** *fermentation butanol, alcohol-based fuels, catalyst for isomerization*

**Introduction:** Alcohol-based fuels have been important energy sources. Butanol is a chemical that has excellent fuel characteristics. It contains approximately 22% oxygen, which when used as a fuel extender will results in more complete fuel combustion. Use of butanol as a fuel will contribute to clean air by reducing smog-creating compounds, harmful emissions (CO) and unburned hydrocarbons in the tail pipe exhaust. The value of octane boosting is dependent of isomers content of butanol. [1-3]

**Materials and methods:** Butanol can be made from either petroleum or fermentation of agricultural products. Orginally, butanol was manufactured from agricultural products in a fermentation process refered to as ABE, because it produced: Acetone, Butanol and Ethanol.

**Results:** In this work  $\text{Li}_3\text{Cr}_2(\text{PO}_4)_3$  catalyst was prepared and studied. The catalyst possessed high catalytic activity and stability in the isomerization of butanol. The highest activity in the transformations of butanol was obtained after treating the catalyst with plasma.

**Conclusions:** After plasma treatment, number of dehydration centres increase and number of dehydrgenation centres to diminich. By isomerization of fermentation butanol, the value of octane boosting increase with 8-10%.

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## POLYPHENOLS CONTENT AND TOXICITY ASSESSMENT OF SOME PLANT EXTRACTS WITH ANTI-DERMATITIS POTENTIAL

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**Keywords:** polyphenols; UV-VIS spectroscopy; IR spectroscopy.

**Introduction:** Polyphenols are bioactive compounds that have been shown to inhibit histamine release from both rat RBL-2H3 cells stimulated with antigens and from rat mast cells stimulated with the polymer compound 48/80 [1]. In this work we obtained three extracts from the leaves of *Plantago lanceolata* L. (Plantaginaceae) and characterized their phenolic content. The toxicity of the extracts was also evaluated by the *Daphnia magna* bioassay.

**Materials and methods:** The extracts from *Plantago lanceolata* were prepared by extraction under reflux with ethanol, ethanol 50% and water, followed by concentration and lyophilization. The total polyphenol content was determined according to the Folin-Ciocalteu method and the total flavonoids were assayed using the method with AlCl<sub>3</sub>. Fourier Transform Infrared (FT-IR) spectra were performed on the lyophilized extracts according to the method described in the literature [2]. Toxicity screening was carried on young organisms of *Daphnia magna* Straus. The young daphnids were collected from a parthenogenetically culture maintained at “Carol Davila” University (Department of Pharmaceutical Botany and Cell Biology), since 2012. The bioassay was performed in duplicate on ten organisms at seven levels of concentrations ranging from 50 to 1500 µg/mL according to the protocol described in the literature [3].

**Results:** The hydroethanolic extract contains the highest concentration of polyphenols, whereas the extraction in ethanol yielded the highest quantity of flavonoids. The large band close to 3100 cm<sup>-1</sup> registered for the extract is considered an indicator of polyphenols content. All three extracts were not toxic to *Daphnia magna*, the highest lethality observed being of 10 %.

**Conclusions:** Following the results obtained in this study, we conclude that our extracts are rich polyphenolic sources and are non toxic.

**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.

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## MORPHOLOGICAL ASPECTS OF KERATIN SUBSTRATES BIODEGRADED BY KERATINOLYTIC FUNGI

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**Keywords:** keratin; keratinases; biodegradation; fungi.

**Introduction:** Keratin is a complex and stable protein that is found in keratinized materials [1]. Since the keratin wastes substrates are accumulating in the environment, there is a great concern for developing biotechnological alternatives to valuate such wastes and keratinolytic microorganisms have become biotechnologically important. The aim of the present study was to investigate the microscopic aspects of keratin biodegradation process by keratinolytic fungi which are important for understanding mechanism of action in biodegradative process.

**Materials and methods:** The tested keratinolytic fungal strains were isolated from soil. In order to characterize the biodegradative process, the fungal stains were incubated with different keratinized substrates for 21 days in minimal liquid medium, in an orbital incubator [2]. The morphological aspects of the substrate biodegraded were observed by light microscopy and Scanning Electron Microscopy (SEM). Also, the weight loss of keratin substrates after microorganisms contact was determined.

**Results:** Several mechanisms and/or sequences of keratin degradation were observed: networks of fungal hyphae closely attached to the hair strand or feathers, erosion of the hair strand and perforating organs. The keratin substrates are degraded through different mechanisms, depending both on the substrate and the fungal strain.

**Conclusions:** All fungal strains were able to colonize the keratinized substrates, and among them, *Microsporum gypseum* (*Nannizzia gypsea*) [3] strain produced the highest rate of keratin degradation expressed as weight loss.

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

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## EFFECT OF PROCESS FACTORS ON PERVAPORATION DEHYDRATION OF ALCOHOLS

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Pervaporation is a widely used membrane technique for separation of liquid mixtures, especially for close boiling or azeotropic mixtures. Due to its high separation efficiency, low operational costs, ability to break the azeotrope, process control simplicity, process design and integration flexibility, pervaporation is a promising alternative to distillation.

The influence of process factors on pervaporation dehydration of alcohols has been studied in this paper. The process performance has been evaluated in terms of effective membrane surface area ( $A$ ), estimated according to the following algorithm: (i) select the appropriate membrane type needed for separating the mixture alcohol-water; (ii) determine the correlations between the membrane total flux ( $J_t$ ) and selectivity ( $\alpha$ ) and the process factors, *i.e.*, feed flow rate ( $F$ ), feed water concentration ( $x_F$ ), operation temperature ( $t$ ) and permeate pressure ( $p_P$ ), using a second order response surface (SORS) model [1] based on experimental data; (iii) select a value for each process factor in the fields considered in the factorial experiment as well as a value for water separation degree ( $s_W$ ) and calculate the corresponding values for flow rates and mass fractions of permeate and retentate ( $P$ ,  $R$ ,  $y$  and  $x$ ); (iv) verify the correctitude of  $P$ ,  $R$ ,  $y$  and  $x$  values and, if they are inappropriate, repeat the calculations for another  $s_W$  value; (v) calculate  $A$  as the ratio between  $P$  and  $J_t$ . Pervaporation dehydration of isopropanol-water mixture using a Pervatech ceramic membrane was studied under the following conditions:  $F=1000$  kg/h,  $x_F=0.1-0.2$ ,  $t=60-90$  °C,  $p_P=1000-9000$  Pa and  $s_W=0.90-0.95$ . Correlations between  $J_t$  and  $\alpha$  and process factors were determined by applying a SORS model with 3 factors, *i.e.*,  $x_F$ ,  $t$ ,  $p_P$ , on the basis of data reported in the related literature [2].

The results obtained highlighted that  $A$  increased with  $s_W$  and  $x_F$  and its lowest values ( $13\text{ m}^2$  for  $x_F=0.1$  and  $24\text{ m}^2$  for  $x_F=0.2$ ) were attained for  $t=60$  °C and  $p_P=9000$  Pa.

These findings could be applied for optimizing the process of isopropanol dehydration by pervaporation.

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## FRUIT – MEDIATED BIOSYNTHESIS OF SILVER NANOPARTICLES

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Silver nanoparticles (AgNPs) are intensively studied especially in the last decade due to the very good antimicrobial properties of silver known for more than 2.000 years. There are many routes used for the synthesis of AgNPs, either chemical or, more recent, green methods involving different plant extracts, yeast or bacteria<sup>1</sup>. The major advantages of the biosynthesis of AgNPs are, besides the fact they are eco-friendly, no toxic chemicals are used and no saponinshazardous by-products are obtained<sup>2, 3</sup>.

This work presents the fruit – mediated biosynthesis of AgNPs using aqueous extracts of *Sea buckthorn* (*Hippophae rhamnoides* L.) and *Gooseberry* (*Ribes Grossularia*), fruits with multiple pharmacological properties: antimicrobial, antiulcerogenic, antioxidant, anticancer, etc. Also, the AgNPs obtained from the two aqueous extracts are compared to those chemically obtained by the sodium – citrate method and the results are also presented. Different spectral techniques are used to characterize the obtained AgNPs, including UV-Vis, FTIR and the nanometer size is determined dy means of DLS measurements, confirming that the two plants are able to bioreduce Ag<sup>+</sup> to Ag<sup>0</sup>.

Also, this work presents the qualitative and quantitative analysis of the two aqueous extracts in order to determine if *Sea buckthorn* and *Gooseberry* contain active compounds such as polyphenols, terpenoids, saponins, anthocyanins, tannins, etc.

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<sup>2</sup> Marta Espina Palanco et.al. – Beilstein Journal of Nanotechnology, 2015, 6, 293-299  
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## SYNTHESIS AND MOLECULAR MODELING STUDIES OF SOME BENZIMIDAZOLES AND MANNICH BASES

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**Keywords:** benzimidazoles, Mannich bases, molecular modeling, electronic and geometric parameters.

**Introduction:** Benzimidazole and its derivatives are an important class of bioactive molecules of pharmaceutical interest [1]. They are important not only as structural units in natural compounds and synthetic pharmaceuticals but have also elicited considerable theoretical interest. We propose to synthesize some benzimidazoles, new Mannich bases and a DFT study for these structures.

**Materials and methods:** All chemicals and reagents were purchased from Sigma-Aldrich without further purification. FTIR spectra were performed using a Vertex 70-Bruker spectrophotometer, in KBr pellet. The NMR spectra were performed on a Varian Inova-400 (500 MHz), in deuterated chloroform or dimethyl sulfoxide (DMSO-d<sub>6</sub>). A quantum mechanical modeling was performed on each benzimidazole compound, using the GAMESS 2012 software.

**Results:** All benzimidazole compounds, including new Mannich bases (Fig. 1) were synthesized using a eco-friendly method. A DFT analysis of molecular structure and HOMO-LUMO orbitals [2] was performed using the GAMESS 2012 software.

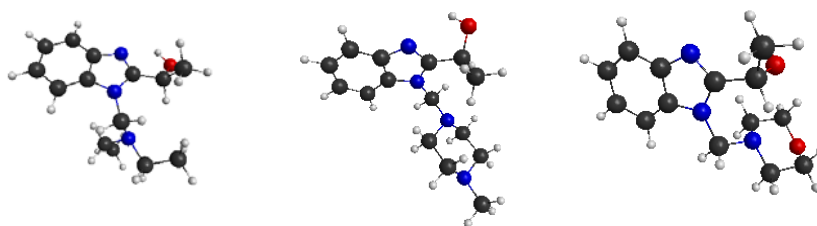


Figure 1. The optimized structures of new Mannich benzimidazoles

**Conclusions:** Very similar HOMO-LUMO energy gap were found for all three new Mannich bases, so we expect to very similar biological properties. The presence of the nucleophilic group on the molecule, like -OH or even -CH<sub>3</sub> may be correlated with a good biological activity.

**References:** Reference citations in the text should be identified by numbers in square brackets. Please provide a list of up to five references. The entries in the list should be numbered consecutively, using the following style:

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## ELECTROCHEMICAL STUDIES OF EXTRACTS OBTAINED FROM BLACK FETEASCA AND LARGE BURGUNDY

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**Keywords:** *alcoholic extract, cyclic voltammetry, antioxidant activity*

**Introduction:** In the last years many scientists have tried to find solutions from natural products to treat the most common ailments. Anthocyanins are a class of polyphenols with excellent antioxidant properties, thus becoming a subject of many articles. In the present work there were performed electrochemical studies of some anthocyanins present in alcoholic extracts obtained from black Feteasca and large Burgundy.

**Materials and methods:** The two samples analyzed were obtained from the marc resulting in the wine making process using two grape varieties: black Feteasca and large Burgundy. The extraction method was based on the use of a mixture of solvents consisting of water: alcohol: acid in a certain ratio. Besides the two alcoholic extracts, it was also analyzed gallic acid, considered the standard for polyphenolic compounds, copper chloride and the complex between gallic acid and copper chloride. The study of antioxidant activity of these samples was performed by means of two electrochemical techniques: cyclic voltammetry and differential pulse voltammetry.

**Results:** The obtained results indicated that the extracts have different chemical compositions and different concentrations of electrochemically active substances. The voltammograms obtained shows that extracts contains quinone compounds which first undergoes a reduction process and then oxidation. The results of this study revealed that the extracts obtained from black Feteasca and large Burgundy are able to reduce and then to oxidize and can thus be regarded as having antioxidant activity and also, their activity could be improved by complexation with copper chloride.

**Conclusions:** In conclusion, in this study it was demonstrated that alcoholic extracts obtained from large Burgundy and black Feteasca have antioxidant activity. Moreover, the complexation of these samples containing polyphenolic compounds with a copper salt such as copper chloride results in the improvement of the antioxidant activity.

## pNIPAM-BASED BIOINTERFACES EFFECT ON CELLULAR BEHAVIOR

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**Keywords:** *thermoreponsive pNIPAM; hMSC; MAPLE; tissue engineering scaffold.*

**Introduction:** Thermo responsive poly N-isopropylacrylamide (pNIPAM) surfaces are studied for their capacity to suport cell growth and cell sheet detachment for transplantation [1,2]. By altering chemical and physical properties of surfaces can be created micro-environments that affect the dynamic of stem cell attachment, proliferation and morphology [3]. Here we study the behavior change of human mesenchymal stem cells (hMSCs) cultured on pNIPAM based surfaces with a specific chemistry.

**Materials and methods:** Modified-based pNIPAM surfaces for controlling cell adhesion were fabricated by MAPLE method. Chemical and morphological characteristics of the pNIPAM based thin films were determined by Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM) and atomic force microscopy (AFM). hMSC cells derived from the normal bone marrow of a healthy donor were used for this study. In vitro cytotoxicity, proliferation and adhesion analysis of hMSC cells seeded onto the control and modified surfaces were investigated by quantitative and qualitative methods.

**Results:** Live/Dead cell viability assay based on ethidium homodimer-1 quantification showed no cytotoxic effect of pNIPAM modified surface on hMSC cells. Moreover, an increase proliferation rate of osteoprogenitor cells on these modified biointerfaces has been observed. SEM, fluorescence and phase-contrast microscopy investigations performed at 3h and 72 h of hMSC cell culture showed direct connection between surface chemical groups and early and late-cell biomaterial attachment and cell morphology changes.

**Conclusions:** These results revealed a good biocompatibility of modified pNIPAM surfaces on hMSC cells making it a potential cell culture substrate for regenerative porpoises.

**Acknowledgements:** *The research was supported by the Romanian Academy project 1/2015-2016 of the Institute of Biochemistry and University of Bucharest - Biology Doctoral School.*

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**CONSIDERATIONS ON BIODIESEL SYNTHESIS WITH FED BATCH REACTOR**

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**Keywords:** *biodiesel, fed batch reactor, used oil, oil conversion, green process.*

**Abstract.** Homogeneously or heterogeneously catalyzed alcoholysis of vegetable oils to produce biodiesel is conducted in general using an isotherm batch system as one of the most used technique. Many studies in literature regarding this type of process reported reactors with batch system. Discontinued reactor with while feeding one or multiple reagents (fed batch system), continuously stirred tank reactor (CSTR) or plug flow reactor (PFR) were also studied conducting alcoholysis of vegetable oils reaching different biodiesel yields. In this work a novel technique was proposed to convert three different types of vegetable oils to biodiesel, using fed batch system, but varying some of the reaction parameters characterizing transesterification reaction. A novel laboratory installation to conduct this process was developed. Methoxid (methanol and alkaline compounds were used) was formed in situ followed by feedstock drip feeding (pretreated and heated oil), which allowed to initiate the transesterification reaction, as part of fed batch technique. Then a post-processing batch stage started by keeping the reactants for a pre-established time to complete the transesterification reaction. The biodiesel yield reached was more than 90 % and the purity of the main products was higher than the purity reached in classical fed batch system. The effect of feedstock characteristics on post-processing batch reaction time influencing biodiesel and glycerol yield was studied along with the effects of catalyst type, methanol/oil molar ratio and the post-processing reaction time on biodiesel and glycerol yield. This novel installation allowed us to apply this new technique (fed batch/post-processing batch) to conduct alcoholysis of vegetable oils for biodiesel production and showed superior processing capacity comparing with the classical fed batch system in terms of reaction time, purity and products yield.

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## ESSESMENT OF P53 USING GRAPHITE BASED AMPEROMETRIC SENSORS

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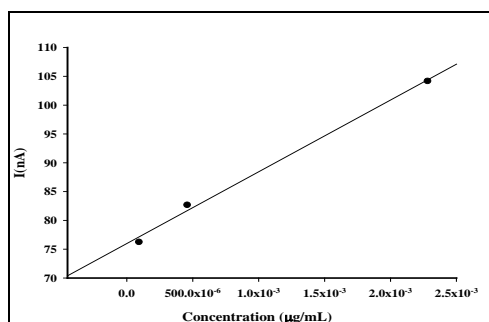
[\\*ahmed.mukleef@yahoo.com](mailto:ahmed.mukleef@yahoo.com)

**Keywords:** P53, colon cancer, amperometric sensors, blood samples

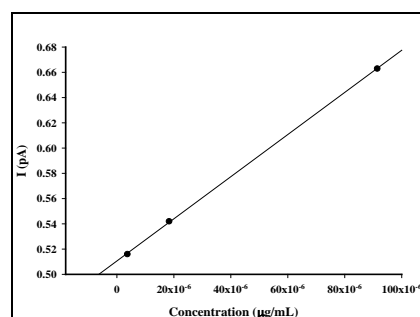
**Introduction:** P53 tumor suppressor gene is considered one of the most important genetic biomarkers for colon cancer. Detection of P53 at early stages of this disease can help for improving the outcomes for patients. Consequently it is very significant to create a sensitive sensor for assessment of P53.

**Materials and methods:** Proposed amperometric sensors were design in the laboratory for the determination of P53. The sensors were based on graphite and graphene powder with electro active modifiers such as porphyrins and oleamides.

**Results:** Very low concentrations of tumor suppressor gene were made by utilizing the proposed amperometric sensors. These limits are in the range of early detection, but can also allow the assay of P53 in stages 3 or 4 of the colon cancer. The sensors showed excellent sensitivity when compared with others colon cancer biomarkers. But also over other components from whole blood such as neurotransmitters. The recovery tests performed proved the convenient of these sensors for the early detection of P53 in whole blood samples.



**a**



**b**

The calibration curves for p53 obtained using the amperometric sensors based on:  
(a) MEG107/Graphite; (b) 5-Graphite;

**Conclusions:** The determination of P53 by using the proposed amperometric sensors based on physical immobilization of porphyrins and oleamides in graphite and graphene based pastes, revealed excellent results that can be used as a reliable method for the assessment of P53 in whole blood samples.

**Acknowledgements:** The authors want to thank to UEFISCDI, Partnership 22/2014 for the financial support.

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## ENCAPSULATION OF THYMOL IN ALKYLATED MESOPOROUS SILICA CARRIERS

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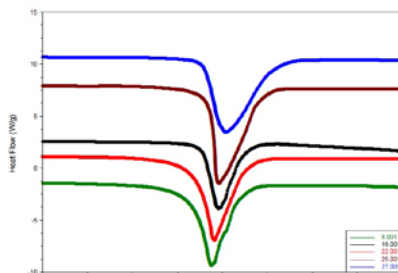
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**Keywords:** thymol, encapsulation, silica carriers, mesoporous silica.

**Introduction:** Silica micro- and nanoparticles, based on tetraethyl orthosilicate (TEOS) and three different alkyl-functionalized co-precursors (octyl triethoxysilane (OTSO), dodecyl triethoxysilane (DOTEOS) and octadecyl triethoxysilane (ODTES), have been explored as mesoporous hosts for encapsulation of thymol (extra pure). Thymol is an antibacterial agent found in many medicinal and / or aromatic plants, among which thyme (*Thymus* sp.) has a very high content.

**Materials and methods:** In comparison with our previous work [1], where sodium silicate was the main source of silica and the oleic acid - sodium oleate complex was the stabilizing system, in this work tetraethyl orthosilicate was used as silica building blocks and Brij O10 was the tensioactive agent. Each of the three co-precursors - ODTMS, DOTEOS and respectively OTSO - was mixed in oil-water emulsion systems at different co-precursor/TEOS molar ratios (1:1, 1:2 and 1:10).

**Results:** Were investigated and identified the reaction conditions required for preparation of homogeneous and stable emulsions, after Thymol addition. Thus, the use of a lower concentration of alkyl-silica derivatives (TEOS/alkyl-trialcoxy silane molar ratio = 1/10) and of the adequate amount of surfactant are the key factors to achieve an efficient encapsulation of thymol. Also, the thermal behavior of water present in the obtained microemulsion systems was analyzed and compared (Fig.1).



**Figure 1.** The melting endotherms for the investigated systems

**Conclusions:** Variation of silica co-precursor type and ratio in sol-gel system lead to the modification of mesoporous particles morphology and of pores size, shape and distribution, due to the different self-assembling pattern of alkyl chains.

**Acknowledgements:** This work was supported by the grant funded by the Romanian National Authority for Scientific Research, project number PN16.31.03.04.02.

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## ADSORPTION AND DESORPTION OF VOLATILE ORGANIC COMPOUNDS IN/FROM ADSORBANT FIXED BED

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**Keywords:** *n*-hexane, activated carbon, adsorption/desorption, copper impregnation

**Introduction:** This paper has aimed at measuring and predicting fixed bed saturation curves of *n*-hexane adsorption from air stream onto copper impregnated GAC (Cu/GAC) under various operation conditions. *N*-hexane and methyl ethyl ketone are commonly used solvents, which can have negative effects at concentrations higher than the permissible limits and may occur during storage, transport or use thereof. Adsorption of different porous materials, treated or impregnated with various agents, is a very effective technique commonly used to remove volatile organic compound (VOCs) from waste gas streams, especially at very low concentrations (ppm or below-ppm).

**Materials and methods:** Two species of VOC (*n*-hexane (HEX) and methyl ethyl ketone (MEC)) and two type of adsorbents (*granular activated carbon (GAC)* and *granular silicagel*) were used as materials in the adsorption/desorption process. Adsorption of VOC species from air stream onto granular activated carbon (GAC) in a laboratory scale fixed bed column as well as their thermal desorption were studied. The effect of process factors (air superficial velocity, operation temperature, and mass percentage of copper in GAC) on the adsorption performances was established. Moreover, electrothermal desorption of *n*-hexane from Cu/GAC was analyzed.

**Results:** Experimental saturation curves shows that the performance of process in case of adsorbent 13.8 % Cu/GAC don't varies with operation temperature (*t*). For adsorbent 4.6 % Cu/GAC, saturation (equilibrium) adsorption capacity ( $q_{i,sat}$ ) and mean adsorption rate ( $v_i$ ) increase with temperature (*t*) (down to 6% and 18 %, respectively). In case of *n*-hexane, it was observed that  $v_i$  increase significantly (with 67-93%), and  $q_{i,sat}$  decreases (4-9%) with increasing of air superficial velocity (*w*). For MEC, it was also revealed that  $v_i$  increase (by 32-86%) and  $q_{i,sat}$  decreases (by 5-78 %) with increasing of air superficial velocity (*w*).

**Conclusions:** The obtained results may be useful to optimizing the operation of adsorption columns used for the remediation of gas streams contaminated with VOC.

**Acknowledgements:** This work was supported by the grant funded by the Romanian National Authority for Scientific Research, project number PN16.31.03.04.02.

**THE INFLUENCE OF TECHNOLOGICAL PARAMETERS-VOLTAGE AND ELECTRICAL CAPACITY ON GENERATING OF CARBON SPATIAL FORMATIONS FULLERENE TYPE, AT THE TREATMENT OF METAL SURFACES BY ELECTRICAL DISCHARGES IN PULSE WITH GRAPHITE CATHODE METHOD;(POSTER)**

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The metal plates on whose surface a graphite pellicle was deposited with an electrical discharges in pulse procedure, were submitted to an electronic microscopic analyse SEM, and revealed a number of regular globular formations which are not part of graphite film. Following the thermo-gravimetric analyse, an addition of mass in significant values, 1,365-2.769 %. was found, although the thermogravimetric analyse was conducted under nitrogen atmosphere The SEM analyse corroborated with thermo-gravimetric analyse results, leads to the conclusion that the electrical discharges in pulse with graphite cathode surface treatment procedure for obtaining the graphite film, also conduct to the obtaining of spatial formation composed of carbon atoms type fullerenes, able to incorporate in a reversible process small molecules (N<sub>2</sub>, HOH). Technological parameters of the electrical discharges in pulse with graphite cathode procedure were voltage (electromotive force), V, and electrical capacity of the capacitor of discharge,  $\mu\text{F}$ . Following the undertaken investigations on an significant number of samples, it was came to the conclusion that the technological parameter responsible for the appearance of these formations it is capacitor capacity. Thus, the number of globular formations obtained is directly proportional with the amount of electricity transferred after an electrical discharges in pulse

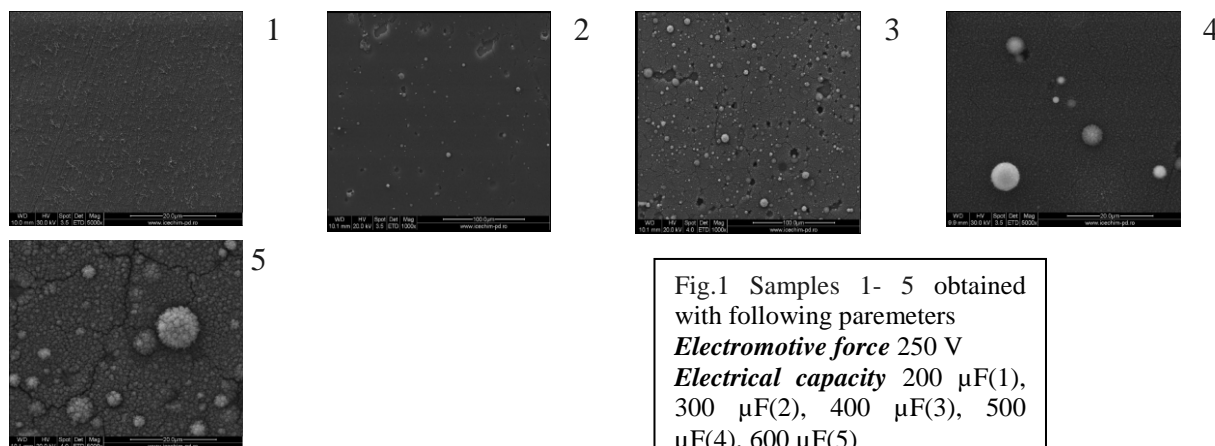


Fig.1 Samples 1- 5 obtained with following paremeters  
**Electromotive force** 250 V  
**Electrical capacity** 200  $\mu\text{F}$ (1), 300  $\mu\text{F}$ (2), 400  $\mu\text{F}$ (3), 500  $\mu\text{F}$ (4), 600  $\mu\text{F}$ (5)

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## QUALITATIVE ANALYSIS OF PHYTOCHEMICALS IN DIFFERENT AQUEOUS PLANT EXTRACTS

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Plants mainly consist of various and different phytochemicals such as vitamins, terpenoids, phenolic acids, tannins, flavonoids and many other metabolites rich in antioxidant activity. Researches proved that the majority of these antioxidant compounds exhibit anti-inflammatory, antibacterial, antitumor and antiviral activities<sup>1</sup>. Studies also showed that when these natural antioxidants are ingested, the risk of cancer, cardiovascular diseases, diabetes and other age-related diseases is considerably reduced<sup>2,3</sup>.

This paper presents the qualitative analysis of phytochemicals found in different plants by investigating their aqueous extracts. Therefore, different plants (*Artiplex hortensis*, *Sambucus nigra*, *Allium ursinum*, etc.) were used in order to obtain their aqueous extracts, at room temperature and standard procedures were applied to qualitatively characterize the contained plant metabolites. The main phytochemicals analyzed are: alkaloids, tannins, saponins, anthraquinones, flavonoids, steroids, triterpenoids, sugars and catechins.

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## IDENTIFICATION OF FORGED BIOMETRIC TRAVEL DOCUMENTS

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**Keywords:** *document fraud, biometric, forged, safety elements, security.*

**Introduction:** Document fraud is a phenomenon based on the relationship between demand and supply. On the black market are available forged biometric travel documents whose quality varies depending on the purpose of they're using, the amount of money that the buyer is willing to pay and technique and equipment used by people involved in their falsification. By analyzing examples of forged biometric documents we can highlight the main ways to identify them using the necessary equipment, showing if certain safety features used in biometric documents are insufficient in relation to continuous evolution of this phenomenon.

**Materials and methods:** Different safety elements and structural components of forged and genuine biometric travel documents will be analyzed using non destructive techniques and methods like optical microscopy, Infrared (IR) light and Ultraviolet (UV) light in different wavelengths.

**Results:** The aim of this paper is to illustrate the latest methods used in document fraud, establish practical ways for their detection and to offer information for improving the safety elements.

**Conclusions:** Document fraud is considered to be a threat especially for irregular migration but lately, concerning the terrorist attacks committed on the territory of some European countries it is associated with a possible threat to the internal security of the countries from European Union because there is the risk that persons in connection with terrorist organizations will try to reach the territory of EU countries using forged document.

## EXAMINATION OF THE CELLULOSIC SUPPORT FROM THE COUNTERFEITED PASSPORT

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**Keywords:** documents, forged, counterfeit

Forensic science is used to determine different forms of forgery or counterfeiting of the authentic documents. The role and preservation of these documents have a close connection with the evolution of society [1]. Forensic documents examination differs from other types of forensic examinations by its purpose: identification of the author document; technical expertise of the documents (technical state, structural and functional characteristics, placement conditions – techniques and manufacturing processes) and physicochemical expertise of the documents (chemical nature of materials, their conservation status, archaeometry, artofactometry and chemometrics characteristics etc.). Therefore this study presents the evaluation of the physico-chemical properties of the support of different documents suspected to be forged or counterfeit, using microscopic techniques (Zeiss electron microscope, IOR optical microscope and MX-4, LOMO Stereo-microscope) and spectrophotometric measurements such as micro FTIR (HYPERION FT-IR microscope, Bruker Optics Courtney) in order to determine the nature of the material between the substrate of the genuine document and the forged one [2,3]. In order to determine the composition of the fibrous material from which the substrate which supports documents are made, it was used small portions of the documents and it was prepared as a suspension of fibre which was treated with colour reagents [4]. These suspensions of fibre have been analysed using the microscope and stereomicroscope, both in natural and different length of artificial light. IR spectrometry absorption using micro FTIR device was used to analysed filler material.

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## EVALUATION OF KRAS BIOMARKERS USING GRAPHITE BASED AMPEROMETRIC SENSORS

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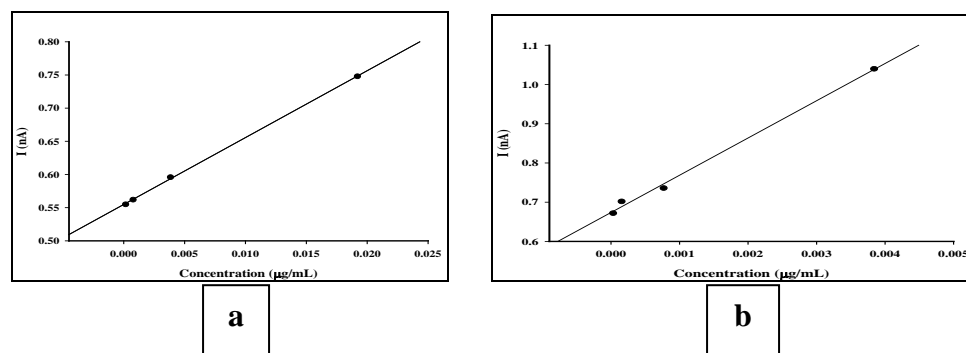
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**Keywords:** KRAS, colon cancer, amperometric sensors, blood samples

**Introduction :** KRAS it is considered one of the most important biomarkers for colon cancer. The determination of this biomarkers have a considerable value for early detection of colon cancer especially at early stages of this disease and it has strong impact for improving the health state for patients suffering from this disease. Therefore it is very important to design a sensor for the detection of KRAS.

**Materials and methods:** Proposed amperometric sensors were designed for the determination of KRAS. The sensors were based on graphite and graphene powders with electroactive modifiers such as porphyrins and azulenes.

**Results:** Very low concentrations of Kras biomarkers were reached by utilizing the proposed amperometric sensors. These limits are in the range of early detection, but can also allow the assay of Kras in stages 3 or 4 of the colon cancer. The recovery tests performed proved the convenient of these sensors for the early detection of KRAS in whole blood samples.



**Figure 1.** The calibration curves for KRAS obtained using the amperometric sensors based on: (a) MEG107/Graphite, (b) M613F3/PtTiO<sub>2</sub>/Graphene

**Conclusions:** The determination of KRAS by using the proposed amperometric sensors based on physical immobilization of porphyrins and azulenes in graphite and graphene based pastes revealed excellent results that can be used as a reliable method for the assessment of KRAS in whole blood samples.

**Acknowledgements:** The authors want to thank to UEFISCDI, Partnership 22/2014 for the financial support.

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# ANTAGONISM OF SOME MICROBIAL STRAINS, ISOLATED FROM VARIOUS PLANT MATERIALS, AGAINST *Erwinia carotovora* AND *Xanthomonas campestris*

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**Keywords:** biological control; phytopathogen; antagonist; *Bacillus* sp.; *Pseudomonas* sp.

**Introduction:** Microbial antagonists, through their mechanisms (induced resistance, direct competition, parasitism, predatorism, production of antibiotics, fungicides, siderophores, biosurfactants) may substantially contribute to prevention of illness caused by phytopathogenic microorganisms. Under the name of microbial antagonists can be found bacteria from different genera (*Bacillus*, *Streptomyces*, *Pseudomonas*), yeasts (*Pichia* sp., *Candida* sp., *Saccharomyces* sp.) and fungi (*Trichoderma* sp.).

This paper presents the results obtained from *in vitro* experiments on the control of phytopathogens using microorganisms isolated from various plant materials.

**Materials and methods:** A number of 25 microorganisms isolated from various plant materials were studied in order to be selected as microbial antagonists. Newly isolated microorganisms were grown on agarized medium along with the phytopathogenic strains *Erwinia carotovora* ICCF 138 and *Xanthomonas campestris* ICCF 274 by dual cultures method.

**Results:** *Bacillus mycoides* presented the best action against phytopathogens mentioned above. It was followed, in descending order, *Pseudomonas putida* and *Bacillus subtilis*.

**Conclusions:** Three of the 25 microorganisms isolated from various plant materials showed antagonism against phytopathogens *Erwinia carotovora* ICCF 138 and *Xanthomonas campestris* ICCF 274. These strains will be used in further studies for obtaining microbial origin products for plant protection.

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## COMPARISON OF EXTRACTION METHODS FOR THE RECOVERY OF PEANUT PROTEINS FROM OILS AND FATS

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**Keywords:** *peanut allergens, oil, extraction methods*

**Introduction:** Peanut and nut allergens represent nowadays a challenge for health and food manufacturers both. The threat of an adverse reaction can be present for sensitive people everywhere in food. Peanut seeds are rich in oil (40-50 %) and used like an excellent source of oil. In the last years oils and margarine consumption were associated with allergic sensitization too [1]. Major peanut allergens are Ara h1 (vicilin), Ara h 2 (conglutin) and Ara h 3 (glycinin) with Ara h 4 an isoallergen of Ara h 3. Minor allergens are Ara h 5 (profilin) and two conglutinin-homologous proteins Ara h 6 and Ara h 7. Belong to these proteins there are lipid transfer proteins (LTPs) responsible for high resistance to heat treatment and proteolytic digestion and an ideal candidate for cross-reactivity too.[2,3] Each manufacturer uses own protein extract method, content determination method and standards. The manufacturing processes are very different and the residual protein content too. This study will report a comparison and assessment of peanut allergens extraction methods from oils and fats.

**Materials and methods:** The test samples were obtained spiking pasteurized fresh margarine (Unirea Original margarine, 60% fat) with peanut reference material 481 (IRMM). Butter was spiked with peanut grinded and peanut extract in Tepnel buffer without gelatine for 10.000 ppm, 1000ppm, 100ppm, 10 ppm and 1ppm concentrations.

**Results:** Taking in account the mainly methods used by different laboratories to extract and concentrate the oil/fat proteins we followed the core ideas of some of its. So we extracted by 3 methods and extracted and concentrated the oil/fat proteins by 2 methods. To evaluate the capacity of extraction and concentration of the methods used we processed and analyzed the same spiked peanut and we reported the results to the same starting quantity 1g margarine spiked with peanut.

**Conclusions:** As a general conclusion to evaluate samples regarding peanut protein included into a mass with a large quantity of an outsider protein it is a difficult task because that protein can hidden the protein what we looking for. There had been some speculations that total extractable proteins were not correlated to their allergenicity or allergen contents. However our results like other presented in different articles show that between total proteins an allergen proteins exist a significant correlation.

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## **THE BIOGAS – A PROMISING BIOFUEL – ABLE TO IMPROVE THE ENERGY DEMAND AND REDUCTION OF GREEN HOUSE EFFECTS**

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**Keywords:** *Biogas, Digestor, Co-generation, Bio-methane, ALgae*

The paper underlines the importance of biogas producing in the current political-economical context, when fossil methane became uncertain to be reasonably purchased from free market. At the same time, taking in account that the raw materials, conducting to biogas, proceed basically from residual biomass or other organic matters, which mostly suffer a non-controlled field natural degradation, the valorization of such resources means diminishing of greenhouse exhausting, i.e. positive impact on environmental protection.

This fuel is one of the main biofuel, produced in countries dealing with huge quantities of various forms of bio based wastes. Romania has an appreciable waste biomass potential (at least 9.0 tep/y), coming from agriculture, forestry or marine resources (algae) doublet by other sources like breeding, catering, livestock, domestic, etc., not sufficiently valorized. The biogas can contribute to growing up the renewable contribution in the energetic balance of 20% from total energy demand till 2020, as per figures assumed by E. U. countries, through the Directives in the field.

The work underlines the achievements based on Romanian technologies, developed in the past, based on perfect mixing (continuous flux) or plug principle as regard the main process occurring in the digester. Their advantages, compared with other outside technologies, comprise reduced investment costs, simplicity of operation, easy maintenance and versatility of the materials to be processed.

The palette of raw materials, used for biogas production is very large, including algae, which represent a big potential in Romania. Part of work is focused on this aspect

Depending on the local energy demands and resources, the biogas can be directed to a cogeneration plant producing thermal and electrical energy or purified to obtain bio-methane, which is injected to the grid or liquefied for car stations. Based on the own or outside available technologies the work proposes solutions both for developing of biogas plants in Romania – saving fossil fuels – and environmental protection.

Tables, graphics, schemes, diagrams and figures give information for involved people in the domain, rousing interest for such researching and investments.