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Priorities of Chemistry for a Sustainable Development

PRIOCHEM



ABSTRACTS VOLUME



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INCDCP -ICECHIM-ACHIEVEMENTS AND PROSPECTS

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Who we are?

ICECHIM, National Institut for R&D in Chemistry and Petrochemistry, is among the top 10 National Institutes and the first National Institute in chemistry, biology / biomedical sciences and environmental protection, in terms of main performance indicators: number of papers published in ISI international journals, relative influence score, number of citations, number of national patents, EPO and WIPO patent applications.

What are our plans for the near future?

Increasing research capacity by capitalizing the infrastructure created in the last years and infrastructure in progress by POSCCE-AGRIFLUX project, increasing participation in Horizon 2020 projects, reactivating the sustainable chemistry platform RO-SusChem and establishing a BIO-ECONOMY cluster, developing technology transfer activity, improving quality of scientific research and raising competitiveness.

Cine suntem?

Locul ICECHIM, ca Institut national de cercetare-dezvoltare in domeniul chimiei si petrochimiei, din punct de vedere al principalilor indicatori de performanta: numar de lucrari publicate in reviste cotate ISI, scor relativ de influenta, numar de citari, numar de brevet nationale acordate, numar de cereri de brevete EPO si WIPO, este intre primele 10 Institute Nationale si primul dintre Institutele Nationale din domeniul chimiei, biologiei/stiintelor biomedicale si a protectiei mediului.

Ce ne propunem pentru viitorul apropiat?

Cresterea capacitatii de cercetare prin valorificarea infrastructurii create in ultimii ani si in special a celei in curs de realizare din proiectul POSCCE, AGRIFLUX, cresterea participarii la proiectele Horizon 2020, reactivarea platformei de chimie durabila RO-SUSCHEM si infiintarea unui cluster de BIO-ECONOMIE, dezvoltarea activitatii de transfer tehnologic, imbunatatirea calitatii productiei stiintifice si ridicarea nivelului de competitivitate.

**COSTIN D. NENITESCU FONDATORUL SCOLII ROMANESTI DE
CHIMIE ORGANICA**

Sorin I. ROSCA

Universitatea "Politehnica" Bucuresti

Este prezentata personalitatea profesorului Costin D. Nenitescu, uriasa sa munca de organizare si de conducere stiintifica si academica prin care s-a fondat ceea ce numim "Scoala romaneasca de chimie organica".

Sunt ilustrate prin documente ale vremii (fotografii, scrisori, marturii ale unor ilustri contemporani din intreaga lume) principalele etape din viata si evolutia personalitatii savantului. Este pusa in evidenta clarviziunea si forta de cercetare a scolii fondate de el, care au facut posibile descoperiri fundamentale in mai multe domenii ardente ale chimiei organice din vremea sa : chimia compusilor heterociclici, reactii catalizate de clorura de aluminiu, chimia ciclobutadienei, a carbocationilor, aplicatii industriale pentru mase plastice, cauciuc sintetic, medicamente si pesticide.

Generatia de astazi ii datoreaza, pe langa descoperirile stiintifice fundamentale si cartile sale de valoare universala, si organizarea si inzeestrarea unor institutii stiintifice si de educatie superioara in chimia organica precum Departamentul de chimie organica al Universitatii " Politehnica" din Bucuresti care astazi ii poarta numele, Institutul de Chimie Organica "C.D. Nenitescu" al Academiei Romane sau Institutul de Cercetari Chimice - ICECHIM Bucuresti.

CHEMICAL ENGINEERING ASPECTS IN SYNTHESIS AND USE OF BACTERIAL CELLULOSE

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Bacterial cellulose should be a very interesting biodegradable biopolymer. It is a versatile polymer that could be changed or by biosynthesis or after it has been obtained. It could also be used to obtain composite materials. Bacterial Cellulose and its composites are currently being studied for use in various biomedical applications, but bacterial cellulose shows considerable potential for other technical applications as well, electronic paper, transparent composites, conductive and resistive membranes, bio molecularly imprinted polymers, special membranes, etc. Most of these applications are still looking. In this work it is given results which show the use of the specific methods of chemical engineering in many directions characterizing the synthesis and use of bacterial cellulose. For the synthesis of the bacterial cellulose he attracted attention with several statistical models developed to identify the culture medium composition and the operating conditions to have static reactors in work with good productivity [1]. The simplex regular method is illustrated in the case of optimization of drum reactor. The problem of swelling of membranes and composites based on bacterial cellulose, contained in some proper work [2, 3], is analyzed using a new model, capable of finding the most common models. The use of composites in bacterial cellulose packaging with antimicrobial behavior [4] is analyzed by using of chemical engineering specific methods. Sorption of water in the sandwich with bacterial cellulose membrane follows the law of diffusion where the effective diffusion coefficient is specific to the membrane (BC) and binder to [5]. The statistics models with three or four factors and also diffusion based models are successfully used to characterize the global and dynamics of drugs (ibuprofen, tetracycline) release from pure and composite bacterial cellulose membranes. Sorption of volatile organic compounds in a fixed layer of bacterial cellulose is analyzed by a dynamic model where at the elementary level the process is controlled by the sorption kinetics. The use of membranes of bacterial cellulose as ultrafiltration membranes and pervaporation is supported by experimental data which are capitalized by specific models. Interesting results were obtained in terms of improving in bioreactors of oxygen transfer when bacterial cellulose impregnated with magnetite is used as special oxygen vector [6].

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ROMANIAN EXPERIENCE ON NANOMATERIALS FOR CULTURAL HERITAGE

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Due to mankind activity, the historical artifacts from world patrimony have been affected by several weathering factors¹. Some deterioration and weathering factors such as soling, pollution, oxidation, air temperature and relative humidity especially in industrial environment, affect irreversible their quality and stability². The weathering processes induces different alteration processes for all the materials, as chemical weathering, which contain the support solubility or its reactivity with other deterioration factors (air pollutants), and physical weathering, which involves the salt crystallization within the pore or channels structure³.

Modern chemicals, as inorganic nanocompounds, are essential to preserve the world's artistic and cultural heritage. Tasks belonging to nanoparticles chemistry (type of nanoparticles, structure, and analysis) are discussed in this paper for the conservation and restoration of different mobile and immobile patrimony pieces (old books and manuscripts, wax seals, stone buildings, stucco pieces, pictures, so on). Some nanomaterial suspensions based on hydroxyapatite, strontium hydroxyapatite, $\text{Ca}(\text{OH})_2$, $\text{Mg}(\text{OH})_2$, $\text{Ba}(\text{OH})_2$ nanoparticles, have been presented and discussed in this paper, testing them on different supports: paper books^{4, 5, 6}, stone^{7, 8}, ceramics⁹, polymers¹⁰, so on. In order to obtain good results in restoration, some physico-chemical investigations (obeying the artefact integrity), could be used: infrared spectroscopy Fourier-transformed, infrared spectroscopy Fourier-transformed microscopy, Raman spectroscopy, Scanning Electron Microscopy, atomic force microscopy, thermal analysis, in order to complete the sample composition. Some exemplifications on: Basarabi Churches Ensemble, Romanian Gospel 1740, stucco from Vacaresti Church, will be offered, and with the relevant results obtained up to now.

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¹ RM Ion, SM Doncea and ML Ion, Nanomaterials for Chemical and Biological Restoration of Old Books, in "New Approaches to Book and Paper Conservation and Restoration", Wien/Horn: Verlag Berger 2011, XXIV, 748 S.

² Ion, R.-M., Doncea, S.M., Ion, M.-L., Rădițoiu, V., Amărieuței, V. **Surface investigations of old book paper treated with hydroxyapatite nanoparticles**, *Applied Surface Science*, 285, 2013, pp. 27-32.

³ RM Ion, RC Fierăscu. I, Fierăscu, RM Senin, Biserițele de creta de la Basarabi-Murfatlar-Aspecte științifice asupra stadiului actual, *ArheoVest*, JATE Press Kiadó, Szeged, 2013, pp.713-725.

⁴ Ion RM, Ion ML, et al., Spectral analysis of original and restaured ancient paper from Romanian Gospel. *Romanian Journal of Physics*, 52(5-6)(2008) 781-791

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⁷ R.M. Ion, IR Bunghez, SF Pop, RC Fierăscu, ML Ion and M. Leahu, Chemical Weathering of chalk stone materials from Basarbi Churches, *Metalurgia International*. 2, 2013, pp.89-93.

⁸ D. Turcanu-Carutiu, R.M. Ion, Pre-Restoration Investigations of the Basarabi Chalk Monument Diagnosis, Treatment and Implications, *European Scientific Journal*, 3, (2014) 124-134.

⁹ RC Fierăscu, RM Ion, I. Fierăscu, Analytical Study of Some Romanian Ceramic Artefacts, *URLA 2014, Istanbul 2014*

¹⁰ RM Ion, M Geba, RC Fierăscu, I. Fierăscu, V. Raditoiu, Analysis, Compositional and Corrosion Understanding of Wax Seal 1858 - United Principates, *URLA 2014, Istanbul 2014*

SCANNING ELECTROCHEMICAL MICROSCOPY (SECM); A STEP IN DEVELOPMENT STUDYING THE MICROWORLD

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The scanning electrochemical microscopy is a relatively new technique. The invention of it dates back to the second part of the eighties of the last century. In that time the scanning tunneling microscopy (STM), and the atomic force microscopy (AFM) with their enhanced resolution and simplicity have already revolutionized the tools of surface examinations. Miniaturization of electroanalytical sensors was also advancing. It was realized by several groups that the small electrode size provides several advances in basic electro chemistry as well as in chemical analysis. Parallel research groups working in experimental life sciences developed miniature electrochemical transducers and applying them achieved remarkable results measuring local concentration of different species in biological systems like animal tissue slices or in different areas of anesthetized experimental animals, or living plant tissues.

When reports, those we consider today as ground breaking steps in SECM appeared many of us could not immediately see the power of the new technique.

Question can arise about the special features of the SECM that made it a new, well known separate technique of electrochemistry. Trying to answer this, we need to consider the followings:

-In earlier studies the positioned microelectrodes were just passive sensors. No interaction between the sample and the electrode was planned and used in evaluation. The smallest possible invasion on the investigated system was favored. In practice of SECM, however often the sample system is tested through its interaction with the electrode process taking place at the positioned microelectrode. This opened new ways in characterizing local properties of microstructures. Selecting properly the electrode process new feature like local catalytic activity, rate of surface reactions, transport characters of different species as well as viability or metabolic activity of living cells can be studied with SECM.

- Appearance of commercial instrument developed in cooperation with the pioneering research groups of the field made the technique easily accessible for other research groups not specifically interested in complex instrument developing research.

- Intensive work with the theory of SECM showed the potential and limits of its applications.

- Workshops and good reviews made good jobs in dissemination of the technique.

In our days the scanning electrochemical microscopy is recognized as an intensively developing variety of the quite popular probe microscopic techniques. Similarly to the other methods it employs positioned, or scanned micro sized probe, three dimensional positioning devices, computerized data collection and evaluation. Its special features are however, that in their practice electrochemical micro probes are used, and therefore conditions, allowing reliable electrochemical data collection – like application of electrochemical measuring cells - are needed.

In the lecture the SECM as a member of the “family” of the probe microscopic methods will be introduced with its history, advantages and limitations. Some of the recent results of our laboratory achieved in the field will be also presented.

AGRO-BIO-ECONOMY – A ROMANIAN APPROACH FOR CLUSTERING GREEN CHEMISTRY, BIOTECHNOLOGY AND AGRICULTURAL RESEARCHES

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Bio-economy is a trans-sectorial domain encompassing sustainable production of renewable resources from land, fisheries and aquaculture environments and their conversion into food, feed, bio-based chemicals and bio-energy. It includes agriculture, forestry, fishing and aquaculture, food industry, pulp and paper, as well as a part of the chemical, biotechnological and energy industries [1].

Romania has a significant potential to produce renewable resources in terrestrial and aquatic (agro)systems. ARUP study noted that in Romania the skills and technologies in the field of chemicals is above the average, being medium advanced [2]. Agro-bio-economy represents an opportunity to synergize the existing Romanian natural potential on the production of renewables bio-resources with the existing human resources on chemical technologies.

We proposed an integrated approach, to process renewable agro(bio)resources into bio-based chemicals, which produce also new innovative inputs (plant biostimulants) for agricultural technologies. The core of this integrated systems are micro-fluidics (bio)chemistry systems. Such systems allow the recovery of value added components from lignocellulose biomass, like antioxidants, osmoprotectants, nano-cellulose, prebiotic fibers, and very effective conversion of recalcitrant lignocellulose into bio-based monomers for bio-based plastics, bio-solvents, technological fluids and ointments, active ingredients for plant biostimulants, suitable components for conversion into microbial biomass (including plant inoculant biomass). The research and development infrastructure corresponding to this approach is under development, being supported by a project, Agri-flux, ID1938 / 645, code SMIS-CNSR 46695, founded by European Regional Development Fund.

Microfluidics (bio) chemical flow systems are easy to be scale-up into mobile processing units, which could represent a solution to the logistic issues of biomass processing. Such high-tech mobile processing units could represent a solution for efficient conversion of surface spread, highly variables, bio-resources produced by Romanian agro(eco)systems. Obtainment of agricultural inputs into an integrated plant based bio-economy value chains represents a practical solution for the required sustainable intensification of plant production and closes in a biomimetic manner the industrial circuits.

1. COM (2012) 60 final, „Innovating for Sustainable Growth: A Bioeconomy for Europe”

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NEW COSMETICS FOR A HEALTH AND A BEAUTY SKIN, BASED ON HEMP OIL AND OTHERS PLANT EXTRACTS. MEASUREMENTS OF SAFETY, QUALITY AND EFFICACY THROUGH MODERN METHODS

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Health and beauty of skin depends largely on the presence and retention of water. Aggressive action of environmental factors such as air, sun and excessive use of soaps, shower gels and other detergents degreasers cause skin dehydration. Avoiding degradation and its irritation can be achieved by applying the new skin care products based on hemp oil, an excellent natural emollient that hydrates the skin. Hemp oil particularly is rich in polyunsaturated essential fatty acids, linoleic acid-(omega 6) and alpha-linolenic (omega3) in a ratio of 3: 1, optimal for the human body and health maintenance, flexibility of cell membranes and epithelial tissue, while having antiviral, antifungal, hypoallergenic and antibacterial properties. Based on the bioactive properties of essential unsaturated fatty acids from hemp oil associated with certain vegetable oils, plus other natural bioactive compounds, Hofigal company, aims to create new advanced cosmetic formulas and perform studies in which evaluated its safety, quality and effectiveness that would provide special care and maintenance of skin and hair, which is the primary role of preventing biological processes and premature skin aging. For this purpose we follow the studies and evaluation of the potential irritation for three products: cosmetic oil, cream for mature and sensitive skin, moisturizing and protective day cream. Also, were used the physico-chemical analyzes with specific techniques (spectrophotometry, HPLC, capillary electrophoresis, MALDI-TOF). Based on studies were drafted technical specifications for plant raw materials used and also for finished products obtained.

Studies have yielded three new cosmetic products, as well as tested, with good results.

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**NATURAL PRODUCT AS BALM AND/OR GEL FOR IMPROVING MUSCLE
AND JOINT PAIN**

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Muscle and joint pain are among the most common causes of discomfort in the human body. In many cases, muscle pain is due not only to strenuous activities or prolonged muscular stress, but it have a more profound cause due to contusions, or of rheumatic diseases accompanied by the damage of the cartilage.

In these cases the local blood circulation is affected and it is important to ensure it reactivation by intake of essential nutrients for cell recovery and evacuation of local degradation products that maintain a topical painful inflammation.

For this purpose the authors have studied the possibility of obtaining a topical use balm or gel form in which to incorporate some natural extracts with a vaso-dilator revulsive effect, for improving local blood circulation, containing also the components with anti-inflammatory and regenerative cell function.

Therefore we have selected a group of plants that we have processed into extract forms, concentrated into interest substances. We studied following plants: red pepper, horseradish, arnica, chestnut etc. and some essential oils that can make an improvement in local blood circulation with useful effects.

The extracts selected were dosed in certain substances such as: polyphenols, flavones, polysaccharides, coumarins, capsaicin, escin, vitamins (C, B), and minerals etc., which are included in the two types of bases: a gel (based on carbomer), another an balm form (based on natural bees wax).

The final products were primary tested in muscle and joint pain, proving the beneficial effects: local pain relief and inflammation reducing by stimulation of blood circulation area, improving overall comfort.

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NEW CONTRIBUTIONS TO THE DEVELOPMENT OF CHEMISTRY AND BIOCHEMISTRY OF GLYCOLIPIDS AND HYDROSOLUBLE GLYCOSIDES
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Glycolipids comprises a vast group of natural and synthetic compounds: glycoglycerolipids, glycosphingolipids, glycoesters, glycosides of liposoluble vitamins, hydrosoluble glycosides, etc.

We analyzed the action of seminolipid on phospholipase A2 from viper (*Vipera ammodytes*) and from bull seminal gland, based on a structural analogy between the natural substrates of phospholipase A2 - phosphatidyl choline or phosphatidyl ethanolamine - and seminolipid, a sulfated glycerolipid.

Concerning glycosphingolipids and sphingolipids, glycolipids/lipids based on ceramide or sphingosine as hydrophobic tail, we have elaborated technologies for the isolation and characterization of the main representatives - cerebroside, sulfatide, ganglioside, sphingomyelin - by NMR and MS inclusively; we have prepared also the corresponding lyso-derivatives and investigated some of their chemistry. On the other hand, we have found and applied a mathematical formula destined to the evaluation of molecular diversity of gangliosides. We have imagined and synthesized two new drug delivery systems for ceramides, by using cerebroside and sulfatide as precursors. PPaPaP

We have synthesized new glycoesters, based on the interesting biological and biochemical properties of these compounds: P- and α-D-galactofuranosyl cholesterol as well as the P-D-galactofuranosides of estrone, 5-α-androstanolone, 11-α-hydroxyprogesterone and prednisolone.

Glycosides of α-tocopherol with some aldohexoses having pyranosic ring proved to be excellent antiallergic and anti-inflammatory agents. In a tentative to improve these properties, we have synthesized the furanose glycosides of α-tocopherol with P-D-galactose and α-D-mannose.

We have synthesized and characterized, enzymatically inclusively, a series of enzymatic substrates for exoglycosidases, based on chromogenic properties of 4-nitrocatechol. They could prove useful in organic chemistry, genetics, ecology, medicine, microbiology.

THE INFLUENCE OF THE EXTRACTION METHOD UPON TANNINS CONTENT AND ANTIOXIDANT ACTIVITY OF *VACCINIUM VITIS IDAEA* LEAFS

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In this paper we present different methods of extraction active compounds with phytotherapeutic action, especially polyphenolic compounds, from *Vaccinium vitis idaea* (cranberry) leafs and their effect upon the content of tannins and antioxidant activity.

Tannins are polyphenolic compounds with high molecular weight. They are responsible for the astringency of many fruits and plants, due to the fact that they can bind and precipitate proteins, which is the ground for some of their properties including antibacterial activity against pathogens and some toxins inactivation¹. Also the polyphenolic compounds insure the antioxidant activity which has an important role in health protection. Antioxidant compounds scavenge free radicals and thus inhibit the oxidative mechanisms that lead to degenerative diseases².

We started our research with the analysis of the cranberry leafs, for which we determined the tannins content with the spectrophotometric method using phosphowolframic acid and the antioxidant activity with Cuprac assay.

There is not a standard procedure for extracting tannins, variable methods, with different solvents and extraction times, being used. Thereby, we used 3 different solvents: water, mixture ethanol-water 50% (v/v) and mixture acetone-water 50% (v/v), as for the methods, we used an extraction in 3 steps with water (maceration, hot water extraction and extraction under reflux), maceration with mixture ethanol-water and sonication with mixture acetone-water. The joint water extracts, the alcoholic extract and the acetone extract were then lyophilized. All extracts, liquid and lyophilized, were analyzed using the same methods used for cranberry leafs analysis.

The results showed that the mixture acetone-water is the most effective for tannins extraction from cranberry leafs and therefore for a high value of the antioxidant activity.

¹ Michel Cardoso Vieira, Roberto Carlos Costa Lelis, Bruno Couto da Silva, Gisely de Lima Oliveira, Tannin Extraction from the Bark of *Pinus oocarpa* var. *oocarpa* with Sodium Carbonate and Sodium Bisulfite, *Floresta e Ambiente* 2011 jan./mar.; 18(1):1-8

² Aruna Prakash, PhD, Fred Rigelhof and Eugene Miller, PhD, Antioxidant Activity, A publication of Medallion Labs, Editor Dr. Jonathan DeVries

**EVALUATION OF THE OPTIMUM SOLVENT FOR URSOLIC ACID DOSAGE
FROM SALVIA OFFICINALIS, BY HPLC ANALYSIS
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In the last decades there has been an intense research activity regarding natural compounds with the purpose of replacing synthetic drugs (which have many adverse reactions). One of this natural compounds is ursolic acid (UA), a pentacyclic triterpenic compound, which appears to be one of the most promising natural compounds by exhibiting many pharmacological activities (sustained by in vitro and in vivo experiments and clinical trials): anti-inflammatory, anti-tumor, anti-HIV/AIDS, antimicrobial, anti-hyperlipidemic and antiviral.

¹. Ursolic acid can be found in many plants like: sage, thyme, oregano, basil, rosemary, etc., the content varying from 0.1 to 2 g in 100 g dried plant.

Our study's purpose is to determine the optimum extraction solvent for UA, which is absolutely necessary for the correct quantification of ursolic acid content in plants. To achieve that, we used Sage (*Salvia officinalis*) powder, which has a significant amount of UA 0.4-2g%, according to the literature. The extraction procedure employed the use of 5 solvents (acetone, methanol, ethanol 96%, ethanol 70% and ethanol 50%), an plant:solvent ratio of 1:20, a wetting time of the powdered sage of 10 min. and ultrasonication of the samples for 50 min. at room temperature. The content of UA was determined by HPLC, on a C₁₈ column, an isocratic mixture of methanol and acetonitrile, and DAD detection at 210nm. The obtained results are presented in the following table:

Solvent	Acetone	Methanol	Ethanol 96%	Ethanol 70%	Ethanol 50%
Ursolic acid (mg/100 g dried plant)	849.6	759.0	689.0	412.1	80.4

As it can be observed the optimum solvent for UA extraction is acetone, followed by methanol (used in almost every HPLC method of UA quantification). A very interesting thing is that when ethanol is used, the extracted amount decreases dramatically with the decrease of ethanol concentration. For generalization purposes this study will be repeated on other ursolic acid containing plants (*Rosmarinus officinalis*, *Epilobium parviflorum*, etc.).

¹ Ibrahim T Babalola, Francis O. Shode – „Ubiquitous Ursolic Acid: A Potential Pentacyclic Triterpene Natural Product.”, Journal of Pharmacognosy and Phytochemistry, Vol. 2, No. 2, 2013, pp. 214.

OLEAMIDE ANALOGUES: SYNTHESIS AND ELECTROCHEMICAL CHARACTERIZATION

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N-acylethanolamides fatty acids are a group of lipid mediators enzymatically synthesized in the body in response to many physiological and pathological stimuli, particularly obesity, inflammation, intake food, etc. For example, oleic acid ethanolamide (OEA) is a lipid mediator with multiple roles depending on the type of tissue or organ. Furthermore, administration of OEA in experimental animals resulted in weight loss and appetite suppressant, already opening new research directions for new drugs. Due to their importance, we have found useful to synthesize new amides of unsaturated fatty acids by replacing ethanolamine with other amines.

Previously^{1,2}, we synthesized oleic acid amides with the following amines: phenylalaninol, phenethylamine, 2-(4-methoxy-phenyl)ethylamine, 1-naphthylamine, cyclohexylamine.

The synthesis of 7 oleamides was performed using different amines. The compounds were fully characterized by IR and high resolution NMR. The electrochemical behavior of some oleamides was also investigated. Some of the synthesized compounds were tested on Wistar rats and the effect on decreasing the body weight and food intake was examined.

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**ANTIOXIDANT EFFECT OF THE EUROPEAN BEECH LEAVES EXTRACT,
BASIS FOR ITS ANTI-AGING AND ANTIBACTERIAL PROPERTIES**

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Folk medicine has been widely spread for centuries and, in recent years, was proven to be very effective against a great variety of diseases. In this context, we focused our interest on the European beech (*Fagus sylvatica* L.) leaves as a new alternative source of polyphenolic compounds, which were proven to have different biological activities, including antioxidant and anti-aging properties.

The European beech leaves used in this study were harvested in September from the Sinaia region, from a single tree grown at an altitude of approximate 1000 meters. First, the leaves were dried, then grinded and polyphenols were extracted using ethyl alcohol 70%. Afterwards, polyphenols and flavonoids content were assayed and identified accurately by HPTLC.

In order to test the antimicrobial activity of the extract, we used *Escherichia coli* because this Gram-negative bacterium is one of the most common microorganism that was identified in the urinary tract infections. Also, there are numerous strains that are resistant to antibiotics so this is why we chose these bacteria for our study. The tests for antimicrobial activity consisted of the agar diffusion method, minimal inhibition concentration determination, growth curves and assay of some important enzymes for the bacteria cells such as superoxide dismutase and catalase, involved in bacterial defense against oxidative stress.

Our studies showed that the *Fagus sylvatica* L. leaves are rich in polyphenols, containing a concentration of 33.55 mg/g galic acid equivalent and have a moderate antimicrobial activity against *Escherichia coli* ATCC 8739 because the oxidation of these compounds increased the oxidative stress in the culture media that lead to the break of cell walls or to irreversible damage to macromolecules like DNA or proteins.

In conclusion, European beech leaves could be considered a new viable source of antimicrobial compounds that can be further studied in order to find non-antibiotic cures for bacterial infections.

A NEW GREENER SYNTHETIC ROUTE FOR THE SYNTHESIS OF BIO-FURAN TO BE USED IN THE PRODUCTION OF BALLISTIC PROTECTION EQUIPMENTS

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This paper proposes a new green route to synthesize 2,5-Furandicarboxylic acid (FDCA) starting from biomass (5-Hydroxymethylfurfural 5-HMF), using non-noble heterogeneous catalysts, in order to obtain from this platform molecule bio-based furan polyesters (PEF), which will be implemented in the production of ballistic protection equipments. **From the vast number of polyesters prepared, those containing furan residues have attracted particular interest¹** because they are non-toxic and biodegradable and, hence, have minimal impact on waste management. They can be safely incinerated and, by composting, can be returned to the ecosystem harmlessly in a carbon dioxide-neutral process.

FDCA is a greener monomer derived from biomass with a huge market potential, and may replace terephthalic acid in the production of polyethylene terephthalate (PET).

Our challenges were: i) to prepare non-noble and stable catalytic systems which could be recovered and later reused; ii) to find the proper oxidative agent to synthesis FDCA in water; to establish the proper working parameters for obtaining the best FDCA selectivity.

For this aims we prepared and characterised a lot of catalytic systems ($Mg_xNi_yAl_z$, $Mg_xCu_yAl_z$, $Mn_xCu_yAl_z$, Mn_xFe_y , Ni_xAl_y , Cu_xFe_y), using different techniques. The catalysts were used in prepared, calcinated, as well as rehydrated form, for a better comparison.

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INFLUENCE OF ELECTROMAGNETIC RADIATION

ON *Nannochloris sp* MICROALGAE GROWTH

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Recent studies on electromagnetic stimulation of microalgae provides a new extended domain of disciplines and methodologies for cultivation of microalgae for production of biofuels, bioenergy and added value bioproducts.¹

Microwaves are electromagnetic waves. Their frequencies (wavelengths) are in the range from 300 MHz ($\lambda=1\text{m}$) up to 300GHz ($\lambda=1\text{ mm}$). There is few information on bioeffects of microwaves on microalgae. A recent study demonstrates that samples exposed to microwave various intensities showed significantly higher growth rates and biomass than that of non-irradiated controls.²

The aim of this study is to investigate the influence of microwave radiation on growth rates and biomass concentration of *Nannochloris sp.* microalgae. To perform the experiments, a microwave oven was connected in series to a photobioreactor with a capacity of 3L. The results obtained after microwave irradiation of algal suspension will be compared with the results obtained for cultivation of microalgae in the same conditions, without microwave treatment.

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² A.Asadi, R.-A. Khavari-Nejad, N. Soltani, F. Najafi and A. Molaie-Rad, 2011, *Physiological variability in cyanobacterium Phormidium sp. Kützing ISC31 (Oscillatoriales) as response to varied microwave intensities*, African Journal of Agricultural Research Vol. 6(7), pp. 1673-1681.

**NEW OF SYNTHETIC ORIGIN DRUGS ANTIBACTERIAL
(PREPARAT ANTIBACTERIAN NOU DE ORIGINE SINTETICA)
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În rezultatul cercetarilor efectuate pe parcursul anilor în cadrul laboratorului stiintific „Infectii intraspitalicesti” a USMF Nicolae Testemitanu au fost depistate mai multe substante indigene, de natura sintetica si vegetala, cu proprietati antibacteriene si antifungice pronuntate. Una din ele, Isonicotinoilhidrazona aldehidei 5–nitro-2-furanice, derivat al nitrofuranului, a stat la baza elaborarii unui nou preparat antibacterian Izofural.

Rezultatele investigatiilor experimentale preclinice (bacteriologice, farmacologice, farmaceutice) a substantei initiale si formeii farmaceutice (Izofural –sol 0,05%), au demonstrat activitate bactericida pronuntata fata de microorganisme grampozitive si gramnegative mai înalta (de 2-4 ori) în comparatie cu furacilina. Totodata, toxicitatea izofuralului (LD 50>1500 mg/kg) este de 8 ori mai joasa decât a furacilinei (LD 50=166,7 mg/kg).

Preparatul sa dovedit a fi stabil la pastrare (în medie 2,5 ani).

Studiul activitatii antibacteriene la diferite termene dupa contactul cu culturile de microorganisme, în comparatie cu analogul structural – furacilina a demonstrat ca preparatul inhiba completamente cresterea streptococilor începând deja din a 5-10-lea minut dupa contact, iar a stafilococilor – dupa prima ora de contact, în timp ce furacilina inhiba cresterea stafilococilor si streptococilor dupa 2-4 ore de contact. Inhibarea cresterii P.vulgaris începe dupa 2 ore de contact în comparatie cu 5 ore de contact cu furacilina, iar P.aeruginosa la 4 ore si 24 ore, respectiv.

Rezultatele cercetarilor „în vivo” pe modele de laborator (sobolani albi) au demonstrat ca solutia de izofural înlatura mai rapid procesul purulent (3,3 zile) în comparatie cu 4,4 zile dupa prelucrarea plagei cu furacilina si faciliteaza caderea mai rapida a creslei, dupa 6,2 zile în comparativ cu 7,3 zile dupa prelucrarea cu furacilina.

Efectuarea studiilor clinice prin utilizarea solutiei de izofural în tratamentul infectiilor septicopurulente (plagi purulente, ulcere terofoce, abcese, boala arsilor), cât si în prevenirea complicatiilor septico-purulente postoperatorii a demonstrat rezultate pozitive.

IMOBILIZATION OF MINT ESSENTIAL OIL IN POLYMER MATRIXES**RACOTI Anca^a, CALINESCU Ioan^a, DIACON Aurel^a, PINTILIE Cosmin^b**

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Essential oils are very valuable natural plant products and among other qualities they possess various biological properties. In order to widen the applications of volatiles, it is necessary to lower their volatility. By lowering the volatility, one can also imagine a possibility to better test the biological effects of these compounds. The encapsulation processes are means by which a liquid essential oil is enclosed in a carrier matrix to provide a dry, free-flowing powder¹. The choice of the microencapsulation technique for a particular process will depend on the size of the microparticles needed, the physico-chemical properties of core and coating, the microparticles application, the proposed mechanism for active core release, and on the process costs. Materials commonly used as carriers in the makeup of encapsulated ingredients, are synthetic polymers and co-polymers, and bio based materials such as carbohydrates, fats, waxes, and animal and plant derived proteins².

The mint essential oil was obtained by microwave assisted hydrodistillation (MAHD), from dry leaves of *Mentha Spicata*. The encapsulation was conducted using two different polymers, poly glycidyl methacrylate (PGMA) and poly methyl methacrylate (PMMA). As a suspension agent we have used poly vnylic alcohol (PVA) and as polimerization initiators we have used benzoyl peroxide (BP), lauroyl peroxide (LP) and azobisisobutyronitrile (AIBN). The obtained microcapsules were observed by SEM analysis. Both the essential oil and the PGMA and PMMA capsules containing the oil were analized by TGA, in order to determine the behavior of the essential oil and the release characteristics of this oil from the microcapsules. A GC/MS/HS analysis was also performed on the essential oil and the oil loaded microcapsules, at different temperatures, in order to establish the components of the mint essential oil and which components are released from the microcapsules and in which conditions.

Acknowledgments: The work was supported by the Sectoral Operational Programme Human Resources Development - PERFORM /159/1.5/S/138963.

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A NEW TOPICAL PRODUCT CONTAINING GEMODERIVATES WITH ANTISOLAR PROTECTIVE PROPERTIES

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OBJECTIVE A preparation was realised with topical anti-inflammatory activity and can also be used to treat skin affected by sunburn.

MATERIALS AND METHODS We prepared a gel that contains gemoderivates 5% solution fresh shoots of *Vaccinium myrtillus*, *Ribes nigrum* fresh buds, *Salix Alba* fresh buds, *Rosmarinus officinalis* fresh shoots, fresh shoots of *Betula pubescens*.

New product obtained was analyzed from the point of view of the chemical composition, physico-chemical, HPLC method, microbiological composition and from the point of view of cicatrizing and anti-inflammatory action determined on the white masculs Wistar rats, having 220-250g. The clinical studies were realized on 30 patients having sunburn monitorized over a period of 4 days.

RESULTS It was tested the action of semisolid preparation for topical use with gemoderivates in the study of experimental wounds in rats produced by burning, in comparison with the base gel with untreated control animals. Track and evaluation of anti-inflammatory topical semi-solid preparation containing gemoderivates studied. The clinical studies were realized on 12 patients having sunburn monitorized over a period of 4 days.

CLINICAL STUDIES You can prevent sunburn and related conditions by protecting your skin. This is especially important when you're outdoors, even on cool or cloudy days. If you are sunburned, you can try several home remedies and treatments to relieve pain and speed healing.

Photo damaged skin

Parameters: 4 days, double-blind dermatologist, expert grader evaluation, 12 subjects

- **Gel containing gemoderivates** (*once daily application*)
- **Antiwrinkle cream (containing seabuckthorn oil, spirulina platensis and coenzyme Q10)** (*once daily application*)
- **Eyecontour gel (containig seabuckthorn oil, echinacea extract)** (*once daily application*)
- **Cleansing milk (containing seabucktorn oil, chamomilla extract)** (*once daily application*)

CONCLUSIONS: Topical product obtained realize the healing action of burning in 4-5 days on experimental rats compared to controls that healing took 8-9 days. New topical product obtained show anti-inflammatory action in both experimental models. Also this topical product healing the photo damaged skin on human feminine subjects in 4 days.

ADVANCED ANALYTICAL METHODS FOR COMPLETE SCREENING OF STEROIDALS COMPOUNDS

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The class of biomolecules low molecular weight includes the steroidal compounds are well known for their high economic potential in pharmaceuticals, biotechnology.

In this study was reported a first nano-ESI-Chip mass spectroscopy and GC-MS complete identification of major compounds from two different types of Romanian truffles: *Tuber magnatum* and *Tuber brumale*. The advantage of the advanced analytical methods such as: chip-based electrospray (ESI) ionization mass spectrometry and GC-MS analysis consist in ability to obtain high quality results from small amounts of complex natural matrix.

The efficiency of these analytical strategy and general experimental condition for screening of bioactive compounds from natural products are described. The computational chemistry was used to investigate the steroidal compounds bioactivity.

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Carex arenaria – A STUDY OF COMPARATIVE EXTRACTION TECHNIQUES
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The inflorescence of *Carex arenia* are used in traditional medicine as diuretic, laxative, tonic, coleretic, detoxification, etc¹.

The present paper investigate the influence of ultrasound-assisted solvent extraction and microwave-assisted solvent extraction on recovery yield of organic and anorganic compounds from entire plant²⁻³. Extraction of plant bioactive compounds was studied in methanol vs. hexane at different extraction time: 5 and 15 minutes. The extracts composition was investigated on FT-IR and MS methods.

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MICROENCAPSULATED BIOPESTICIDES

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The use of synthetic pesticides creates problems with their toxicity, low-biodegradability and too high amounts for optimal necessary, which can damage crops and contaminate the environment. Controlled release systems are an alternative to the conventional pesticide applications. An important way of controlled release is achieved by microencapsulation of pesticides.

Essential oils and their derivatives are considered to be an alternative to control agricultural pests. Using essential oils as biopesticides, is stimulated by the fact that they are completely non-toxic to mammals, many essential oils being used as culinary herbs or spices. In addition, they have a ready biodegradability in the environment and increased specificity, and pests do not acquire resistance over time due to the intensive use of pesticides, contributing to the sustainable development of agricultural production. Despite these promising properties, essential oils are volatile and susceptible to oxidation.

This paper presents a new process of complex coacervation and microencapsulation of essential oils. Protein hydrolysates have been used as microencapsulation agents. The microcapsules have a central core formed by an essential oil, covered with a shell made of polymeric material, *i. e.* protein hydrolyzates and a phase-type which induce coacervation, containing a polyelectrolyte. Post-treatment of complex coacervated microcapsules was performed by crosslinked with dialdehydes.

The microencapsulation resolved problems related to volatility and susceptibility to oxidation of biopesticides based on essential oils and also was performed controlled release of them. The microcapsules was used for seed treatment, to protect against pests.

INDIGENOUS *URTICA DIOICA* ROOT: A STUDY ON THE CONTENT OF ACTIVE SUBSTANCES AS A PROMISING PHYTOTHERAPIC ALTERNATIVE TO *SERENOA REPENS* AND OTHER EXOTIC PLANTS FOR TREATING BENIGN PROSTATIC HYPERPLAZIA SYMPTOMS

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Benign prostatic hyperplasia (BPH) is a constant problem in many men over age 60 and often it has its onset about age 40. 50% of men present histopathologic BPH by age 60.¹

BPH is considered by medical and scientific community to be part of the normal ageing process and it is characterized by an enlargement of the prostate gland that affects the normal flow of urine from bladder by urethral and bladder outlet obstruction.¹

There are a number of natural treatments that are used to treat or to prevent the symptoms of BPH. Besides *Urtica dioica* root (UDR), some exotic plants like *Serenoa repens* and *Pygeum africanum* are extensively used in various formulations alone or combined.

Studies on the use of these plants to treat BPH show insufficient evidence to report a final conclusion. Moreover, recent and more reliable research is showing that the widely used *Serenoa repens* has no effect other than placebo in treating BPH symptoms² and the Natural Medicines Comprehensive Database rating for this plant is “Possibly Ineffective”.

Our study began analyzing several indigenous plants for the purpose of creating a combination of active substances that can synergically have a positive effect in treating BPH. From these, UDR has been used for more than 30 years in various formulations for BPH. Some *in vitro* and *in vivo* studies, and also clinical trials had showed beneficial results.

We analyzed dried UDR from spontaneous flora (marchland area of Bucharest) for active substances relevant in BPH condition: beta-sitosterol, ursolic acid and stigmasterol - HPLC analysis; total polyphenol content (expressed as caffeic acid) and total free amino acid (AMAC) content (expressed as glutamic acid) – UV-VIS analysis; total protein content.

Total protein content was 7.55% and total free AMAC content was 0.772%. We also found beta-sitosterol (21 mg/100g), polyphenols (143 mg/100g) and stigmasterol.

In the in-extenso paper we will present additional results on different UDR extracts, including a lyophilized aqueous extract.

All the above chemical compounds and also some lignans, polysaccharides, isolectins and coumarins are thought to play a role in the positive effect of UDR on BPH symptoms.

¹Assessment report on *Urtica dioica* L., *Urtica urens* L., their hybrids or their mixtures, radix EMA/HMPC/461156/2008, pp. 18

² WebMD News Archive - *Does Saw Palmetto Treat Enlarged Prostate?* (<http://www.webmd.com>)

REGIOSELECTIVE REACTIONS ON A BICYCLOOCTANE SKELETON
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Bicyclooctanic skeleton is encountered in many natural products with different substitutions.

Working with this skeleton, substituted with two hydroxymethyl groups (**1**) we already realized synthesis of many derivatives mono or bis-substituted with an acyl or an ether protecting group¹ or hydroxylated intermediates useful for synthesis of isoprostan analogues², substances similar to prostaglandins. Also, starting from these intermediates we obtained new carbacyclin-like compounds ("pseudocarbacyclins")³.

The steric conformation of hydroxymethyl group in relation with the double bond in unprotected starting compound made possible some high yield regiospecific reactions; the result is synthesis of new pentalenofuranic compounds, useful in obtaining new important natural analogues.

Extending the study to a compound with carboxyl groups instead of hydroxymethyl ones, the results were similar.

The structure of the compounds was confirmed by high resolution NMR and also by X-ray crystallography data.

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HALOPHILIC MICROORGANISMS UBIQUITOUS PRODUCING BIOMATERIALS WITH BIONANOTECHNOLOGICAL POTENTIAL

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The biosphere supports astronomical numbers of free-living microorganisms that belong to an indeterminate number of species. One view is that the abundance of microorganisms drives their dispersal, making them ubiquitous and resulting in a moderate global richness of species. The microbial world encompasses most of the phylogenetic diversity on Earth, as all *Bacteria*, all *Archaea*, and most lineages of the *Eukarya* are microorganisms. These live in every kind of habitat (terrestrial, aquatic, atmospheric, or living host). Their diversity enables them to thrive in extremely cold or hot environments and also makes them tolerant of many other conditions, such as limited water availability, high salt content, low oxygen levels, radiation, pollutants, etc. The beneficial effects of microorganisms derive from their metabolic activities in the environment, their associations with plants and animals, and from their use in food production and many other biotechnological processes¹.

Halophilic microorganisms are able to grow in hypersaline environments distributed throughout the world, such as salt lakes, salterns, solar salts, and subsurface salt formation. Halophiles belonging to all three domains of life: *Archaea*, *Bacteria* and *Eucarya* and are classified in different categories: halotolerant, slight halophile, moderate halophile and extreme halophile². Extremely halophilic archaea (haloarchaea) are being the object of basic studies in relation to the origin of life in our planet and the molecular mechanisms of adaptation to hypersaline conditions. Apart from their evolutionary and ecological significance, haloarchaea have promising biotechnological applications³. Halophilic bacteria represent an excellent model of adaptation to frequent changes in the extracellular osmolarity, being regarded as an interesting group of microorganisms from a biotechnological point of view. They have the advantage that most of the species are able to survive in a wide range of salinities, comparing to the very precise salt content required by the haloarchaea. Thus, their eurihaline response allows them to be used in different processes in which the salt or metal ions concentration are variable, recommending them for a multitude of actual or potential applications in several fields of biotechnology.

This study reports the isolation and characterization of some haloarchaeal and halophilic bacterial strains harvested from different saline habitats or polluted with crude oil or heavy metals. The results revealed that three bacterial strains from the *Pseudomonas* genus, noted C₁₆, Ps3d and CMM₃ have an eurihaline character being capable to grow between 0 – 20% NaCl and produced metabolites like polihidroxyalkanoates and rhamnolipids, which were tested for their biodegradation potential. The percent of crude oil consumption was significant, with values nearly 62.45% for Ps3d bacterial strains isolated from polluted areas.

The investigated haloarchaeal strains were characterized by optimal growth at 2.0 – 5.0 M NaCl. The haloarchaeal isolates showed different enzymatic activity and had the ability to grow in the presence of 2 and 4 % crude oil. The 16S rDNA sequence data together with some biochemical and molecular features supported the affiliation of the investigated strains to genera *Haloarcula* and *Halorubrum*.

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SODIUM CHLORIDE FOR HEMODIALYSIS SOLUTION

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Hemodialysis is a medical procedure designed to remove wastes, toxins and fluids from the blood when the kidneys have failed ^{1,2}. The principle of hemodialysis consists of coming into contact (outside the body) of uremic blood with a plasma-like electrolyte solution (dialysis solution) through a semi-permeable membrane (dialysis). Hemodialysis solution (dialysate) is an aqueous solution without organic components (except acetate and glucose which are added to correct acidity in blood) with a similar electrochemical composition to the normal human extracellular fluid.

Cacica salt contains sodium, calcium and magnesium sulfates (which causes nausea, vomiting, acidosis³) in the range of 0,1-0,4%, which is over the maximum limit of European Pharmacopoeia (0,02%) and can not be used for pharmaceutical purposes.

This paper describes the method for purifying Cacica salt. Sulfate removal was performed by precipitating sulfate with barium chloride and retention of barium sulfate particles on a packed column. Stoichiometric ratio of Ba^{2+} and SO_4^{2-} precipitation and retention on a packed column with treated Aghires sand, reduced sulfate concentration in salt below 0.02%.

The purified salt solution is used for preparation of concentrated hemodialysis solution by SC Medisan 2010 SRL.

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DEPOLYMERIZATION OF LIGNIN BY SUCCESSIVE PROCESSES OF HYDROLYSIS AND HYDROGENOLYSIS

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After cellulose, lignin gains a considerable attention in the last years, representing a major fraction of biomass (10-30%), an abundant, inexpensive and readily available source of renewable materials [1,2]. The development of lignocellulose process technology towards ethanol using cellulose and hemicellulose with lignin obtaining as residue, makes lignin as abundant available biopolymer. Energetic crisis and global warming, capture the attention of many researchers in order to find the technological alternatives for obtaining of the liquid fuels and valuable chemical products by thermal treatment of lignin through its depolymerization and conversion in the presence of hydrogen. Depolymerization of lignin represents a highly challenge for catalytic chemistry due to the complexity structure of lignin through its carbon/hydrogen and carbon/carbon bond types in the monomer units and re-polymerization of the deconstructed polymer. The limitations regarding the depolymerization yield is reported in the literature and yield not exceed 20-23 wt. % of product oil [3]. Specialized literature mentions different variants for depolymerization of lignin that tackles single variant for depolymerization [2,4].

The experiments were directed toward modifying kraft lignin by consecutive catalytic processes of hydrolysis – hydrogenolysis. First stage, hydrolysis was carried out in acid catalysis. The process was carried out in batch reactor and the catalyst used was phosphotungstic acid deposited on MCM41. Hydrogenolysis of hydrolized Kraft lignin was carried out in a continuous tubular reactor and the catalyst used was W–Mo/Al₂O₃. By combining the two processes the yield in alkyl phenols increases.

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VALORISATION OF POLYSACCHARIDES AND PROTEINS FROM DEFATTED MICROALGAE BIOMASS

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The economic feasibility of using microalgae as biofuel feedstock can be increased by adding value to the co-products derived after lipid extraction such as polysaccharides and proteins. The algal biomass contains in general ~40% proteins and ~20 % polysaccharides, reported to dry weight.

The aim of this study is to optimize the extraction process of polysaccharides and proteins from defatted microalgae biomass by enzymatic hydrolysis. Enzymatic hydrolysis is selected instead of chemical hydrolysis to produce a high quality product, free of toxic degradation products because the process is carried out under eco-friendly conditions.

First time, we extracted polysaccharides with commercial cellulase enzyme. The sugar content of the extract obtained was determined using the method described by Dubois et al.²

The protein hydrolysates were obtained from biomass resulting after polysaccharides extraction, using commercial proteases. The protein content was estimated by Kjeldahl method,³ the hydrolysis degree was determined spectrophotometrically and amino acids composition by LC-MS method.⁴

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METALLOKINETIC OF VANADIUM, ADMINISTERED AS A VANADYL CHRY SIN COMPLEX

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Vanadium based compounds exerted hypoglycemic activity in different experimental models of diabetes; nevertheless their use as therapeutic agents is limited by their toxicity¹. The design of vanadium complexes with flavonoid ligands, such as bis(chrysinato)oxovanadium(IV), di- μ -hydroxo-bis(quercetinato)oxovanadium(IV), bis(hesperetinato)oxovanadium(IV)², improved the pharmacotoxicology of vanadium, with variable results on the hypoglycemic activity. The complexes containing quercetin and hesperetin as ligands reduced the blood sugar levels of alloxan diabetes rats ($p < 0.05$)³. The complex containing chrysin as ligand proved a low hypoglycemic effect ($p > 0.05$) that appears to be correlated with the pharmacokinetic parameters (volume of distribution, half time and micro-constants). The calculated micro- and macro- constants for Vanadium administer as the bis(chrysinato)oxovanadium(IV) complex showed a tendency to a fast elimination. In order to manifest its biologic activity, vanadium species have to interfere with different cytosolic enzymes⁴. As a consequence, the inappropriate pharmacokinetic profile can lead to a low pharmacodynamic effect intracellular target. All procedures were carried out in accordance with the Directive 86/609/EEC of 24th November 1986, on the protection of animals used for experimental and other scientific purposes. *This paper was co-financed from the European Social Fund, through the Sectorial Operational Programme Human Resources Development 2007-2013, project number POSDRU/159/1.5/S/138907 "Excellence in scientific interdisciplinary research, doctoral and postdoctoral, in the economic, social and medical fields -EXCELIS", coordinator The Bucharest University of Economic Studies".*

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COMPARISON OF DIFFERENT COMMERCIAL *CLOPIDOGREL* DRUG PRODUCTS BASED ON BIORELEVANT *IN VITRO* RELEASE KINETICS STUDIES

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Present study evaluates the release kinetics of the thienopyridine-class antiplatelet agent clopidogrel (CLO) from four multisource immediate release (IR) drug products containing 75 mg active substance. Dissolution studies of the investigated immediate release products were performed by using the USP rotating paddle apparatus at 50 rpm.

Two different dissolution media were used in the experiment: the USP¹ pH 2.0 buffer and a biorelevant media simulating the intestinal fasted state conditions (FaSSIF)² with pH=6.5 and containing physiological surface active agents (sodium taurocholate and lecithin).

Quantitative analysis of CLO in the dissolution samples was performed using a validated HPLC method³, with UV detection at 220 nm. The resulting profiles were compared by model-independent, model-dependent and ANOVA-based statistical methods. The difference factor (f_2) was used for the comparison of dissolution rate, whereas the Area Under Curve (AUC) and Dissolution Efficiency (DE %) were used as measure of dissolution extent.

The results indicated a very rapid and complete dissolution (>85% in 30 min.) in the pH 2.0 buffer with similar profiles for all tested products. On the contrary, dissolution in FaSSIF was slow and incomplete, with the amount of drug dissolved in 120 minutes between 25 and 60% of the nominal concentration. Significant differences between the products occurred: the comparison between the two extreme profiles led to a f_2 value of 26,1 and AUC ratio of 2.56. Since CLO is almost exclusively absorbed in the intestinal environment, the differences in intestinal release will most likely impact on drug in vivo absorption.

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ENZYMATIC OXIDATION OF ALCOHOLS IN A BIO-MIMETIC MEDIUM

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A challenge for the modern research in biocatalysis field is represented by the performing of enzymatic reactions in a bio-mimetic medium, using one of the supramolecular systems which are model either for simple cell-like structure/biological membranes/microsurrounding medium inside the cells.

The experimental model assumed in this paper is focused on the microheterogeneous biphasic system, namely reverse micelles (RMs). These systems are interesting because the intramolecular water inside the water-pool of the RMs, having different properties from the bulk water, is more similar with the intracellular water. The different characteristics are referring to the electrical conductivity, viscosity, water activity, pH, ionic strength and other physical parameters.

The evaluation of the bio-mimetic potential of the system consisting in Aerosol-OT (AOT) in isooctane, applied to enzymatic oxidation of different alcohols in the presence of alcohol oxidase, is the main goal of the study. Two research cases have been approached: firstly, the substrate partition between the phases of RM versus hydration degree of the system (w_0), and secondly, the chemical structure of the substrates versus w_0 .

The experiments have been performed with enzymatic substrates with different water solubility, which correspond to an appropriate partition between the major phases of RM, namely aqueous and non-polar organic phase, beside the amphiphilic surfactant interface between the two major phases. On the other hand, these enzymatic substrates have different chemical structure, respectively linear or branched aliphatic chain with 1-4 atoms of carbon, unsaturated or aromatic bonds.

From catalytic point of view, we have demonstrated that AOT-isooctane RM with different intramolecular environments is a convenient medium for enzymatic oxidation of alcohols with various water solubility and it may be considered, from many reasons, a bio-mimetic approach for the experimental model.

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DETERMINATION OF OIL CONCENTRATION IN SOLVENT USING THE ABBÉ REFRACTOMETER

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In this research, oil/solvent mixtures were made at different mass ratios, and the refractive index¹ was determined.

Rapeseed oil was mixed with n-Hexane and with n-Heptane at the mass ratios of 10/0, 9/1, 8/2, 7/3, 6/4, 5/5, 4/6, 3/7, 2/8, 1/9, and respectively 0/10 oil/solvent.

The refractive index was measured using the Abbé refractometer, for rapeseed oil at different mass ratios with n-Hexane and n-Heptane.

Rapeseed oil has a refractive index, n_D^{20} , of approximately 1,46 at 20°C; n-Hexane 96%, n_D^{20} has 1,375; and n-Heptane, n_D^{20} , has 1,387.

Using the experimental data achieved, charts were made in order to show the refractive indexes depending on the concentration of solvents. Tendency lines were drawn which have R² approximately 0,99.

Thus, we can observe that the closest the refractive index value is to the solvent concentration, the less is the oil concentration, and respectively that the closest the refractive index value is to the oil concentration, the less is the solvent concentration.

This analysis method is more faster than conventional methods, and can be utilised in determining the oil concentration in solvent, because the refractive index helps us see after how long the solvent extraction ends.

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FLOW INJECTION SYSTEM FOR SIMULTANEOUS DETERMINATION OF GLUCOSE AND ETHANOL DURING FERMENTATION BIOPROCESSES

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A simple and robust flow injection analysis (FIA) system for the alcoholic fermentation monitoring was developed. This system allows to follow the consumption of the substrate, which is glucose, simultaneously with the ethanol production. The proposed FIA method is based on the electrochemical determination of the hydrogen peroxide generated by the enzymatic oxidation of glucose and ethanol by passing the fermentation broth sample through micro-columns with immobilized glucose oxidase (GOD) and, respectively, alcohol oxidase (AOD). The hydrogen peroxide was amperometrically determined with a sensitive sensor based on the deposition of Prussian Blue (PB) onto screen-printed carbon electrodes (SPCEs). In order to have a robust sensor for H₂O₂ determination in flow analysis conditions and in complex samples such as the fermentation broth, we covered the PB layer with an electropolymerized nonconducting film with a high permselectivity for H₂O₂. This film is a copolymer based on 2,6-dihydroxynaphthalene (2,6-DHN) and 2-(4-aminophenyl)-ethylamine (APEA)¹. The SPCE/PB/copolymer sensor demonstrated improved stability in FIA conditions and excellent interference rejection properties. The SPCE/PB/copolymer sensor maintained for a long period its response for H₂O₂ (89 % response after 85 days of storage and 87% response after 84 hours working in FIA system).

The FIA system was optimized regarding the enzymatic columns preparation, flow design, flow rate, sample volume, carrier composition and pH, temperature, etc.

The optimized FIA method showed a linear response in the ranges 0.05 – 4 mM glucose and 0.1 – 15 mM ethanol, with LODs of 0.02 mM glucose and, respectively, 0.025 mM ethanol.

The developed flow system can be used for direct monitoring of the alcoholic fermentation processes, since the needed sample preparation steps as filtration or dilution may be done also on-line.

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**ISOLATION BY AFFINITY CHROMATOGRAPHY OF THE BIOACTIVE PRODUCTS FROM
HELLEBORUS PURPURASCENS AND INVESTIGATION OF THEIR ANTI-TUMOR ACTIVITY
TOWARDS A PANEL OF 12 CELL LINES**

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Further investigation will focus on the biological, especially antitumoral activity *of the helleborus extracts and isolated derivatives as hellebrine, glycosides and peptide*. In vitro anti-tumor activity of 9 extracts and hellebrine towards a panel of 12 cell lines was assessed using a monolayer cell survival and proliferation assay. By exhibiting a mean IC₅₀ value of 0,007 µg/ml fraction 6 was the most potent fraction (peptide fraction) followed by hellebrine (mean IC₅₀ = 0.011 µg/ml. Individual IC₅₀ values of sample 6 were in the range from 0.003 µg/ml (lung cancer cell line LXFL 529) and 0,012 µg/ml (ovarian cancer cell line OVXF 899), corresponding to a 7.2-fold difference between the most sensitive and most resistant cell line. Individual IC₅₀ values of hellebrine were in the range from 0.003 µg/ml (lung cancer cell line LXFL 529) and 0.029 µg/ml (ovarian cancer cell line OVXF 899). Individual IC₅₀ values of sample 9 were in the range from 0.005 µg/ml (lung cancer cell line LXFL 529) and 0,038 µg/ml (ovarian cancer cell line OVXF 899)

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BENEFICIAL BACTERIAL STRAINS ORIGINATED FROM DIFFERENT TYPE OF SILAGES

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Silage is a preservation method of moist crops whereby lactic acid bacteria convert water-soluble carbohydrates into organic acids, mainly lactic acid under anaerobic conditions; as a result the pH decreases and the silage is preserved as long as it is not exposed to air. During fermentation phase lactic acid bacteria become the predominant microbiological population, lactic and other acids are produced and the pH decreases¹.

Corn and alfalfa silages were sampled in feed-out phase for microbiological analysis. Structural polysaccharide decomposing and lactic acid bacteria were isolated using selective culture media. For structural polysaccharide decomposing bacteria Bushnell Haas medium (BHM) medium agar plates with different carbon sources (carboxy-methyl-cellulose, cellulose, xylane, phytate and pectin), and for lactic acid bacteria MRS and Rogosa medium agar plates were used. A total number of 150 novel bacterial isolates were obtained and used for further analysis. The most promising isolates were selected, identified using molecular methods and characterised biochemically. Several bacterial strains were further analysed for polysaccharide fermentation capacity.

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THE INFLUENCE OF THE HYDROCHLORIC ACID TO THE PROCESS OF OBTAINING 5-CLOROMETHYL-FURFURAL FROM D-FRUCTOSE

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This paper presents a study of the producing process of 5-chloromethyl-furfural from D-fructose by varying the reaction parameters. According to the literature^{1, 2}, dehydration and conversion of D-fructose was performed by using hydrochloric acid both as a catalyst and reagent, achieving yields of 70-90%. The study reports the influence of the hydrochloric acid excess, using different molar ratios of D-fructose: hydrochloric acid, the reaction yield of the following: a molar ratio of 1:1.2 result a yield of 32.5% 5-chloromethyl-furfural, while the best conversion was obtained with molar ratio of 1: 3 when the yield reached 96.65%. Using hydrochloric acid in excess also enhance the side reactions, at 1: 4 molar ratio the yield dropped to 93.23%. Furthermore the study reports the influence of the solvent nature, used to extract the product out of the reaction, to the reaction yield. Conversion was studied in toluene, 1,2-dichloroethane, cyclohexane and n-heptane. The highest yield (96.65%) was obtained using toluene.

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**EVALUATION BIODEGRADATION, BIOCOMPATIBILITY OF MEMBRANES
CONTAINING COLLAGEN/CHITOSAN/ALKALINE PHOSPHATASE**

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The aim of this study was to develop a new variants of membranes based on collagen, chitosan and alkaline phosphatase immobilised by cross-linking with glutar aldehyde (GA) at different concentration.

It was investigate the biodegradation in the presence of collagenase and the biocompatibility evaluated by MTT assay, with mouse fibroblast cell culture type NCTC (clone 929).

The results indicates that membranes biodegradation in the presence of collagenase has 6.59% degradation more that the cross-linking samples.(1-5). Samples non cross-linking are biocompatible. Membranes cross-linking with GA low concentration, respectively 0.04% and 0.08% is also biocompatible. High concentrations of GA lead to decreased biocompatibility.

The results demonstrated that the biomaterials has a good potential for future application in bone tissue engineering .

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BIOACTIVITY AND CHEMICAL COMPOSITION OF VARIOUS *ORIGANUM VULGARE* EXTRACTS

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Development of medicinal and aromatic plant resources for both commercial exploitation and to meet the needs of the population in terms of health problems must be a measure of utmost importance for any country. This involves the existence of long-term strategies for the conservation of medicinal and aromatic plants, personnel training, cultivation or passage in culture of valuable species, adopting sustainable methods of harvesting and processing plants to promote scientific research and validation of traditional remedies. Today, researches on natural compounds are mainly focusing on their role in improving health (1). Valorification of native plant species of flora is necessary in both scientific and economic terms.

Therefore to obtain these products with added value extraction processes are needed consuming as little resources having in the same time pharmacologic activity.

This paper shows obtaining methods for various extract of *Origanum vulgare* species, analyzing the qualitative and quantitative chemical composition, and their antioxidant and antimicrobial potential. Given the use of extracts obtained from *Origanum vulgare* species in many preparations with therapeutic value, the results presented in this paper, respectively the obtaining method, can be used at industrial level with significant reductions in production costs, while obtaining products with superior therapeutics value.

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CHARACTERISATION OF POTASSIUM ULTRA MICROPIPETTE ION SELECTIVE ELECTRODE FOR POTENTIOMETRIC SECM IN BIOLOGICAL APPLICATION

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The microelectrodes are special tools used in experimental methods of different research areas. Electrodes with active measuring diameter in the mm range could be called microelectrodes in the middle of the last century. In our days however, the size of a microelectrode is in the micrometer range. The diameter of the “ultramicro” voltammetric electrodes is usually smaller than a micrometer while ion selective micropipettes with a few nanometer tip size are used regularly. The development of selective potentiometric microelectrodes and voltammetric ones proceeded mostly separately in our laboratories. Driven by our practical needs, we worked out the version of ion selective microsensors. The microelectrodes can give information about values of local, instantaneous concentration or ion activity of different species with high spatial resolution. It can be introduced without major invasion into certain area of a structured sample, e.g. living tissue of a plant.

In this poster the construction, properties and applications of potassium ion selective microelectrode is discussed. Special emphasis is given to the forms of potentiometric glass microelectrodes developed in our laboratory. Advances in preparation solid contact, that means electrodes without internal liquid filling microelectrodes are introduced. The instructions for preparation, handling and storage of them are given briefly. Special mechanical, electrical and analytical properties of this fragile electrode form is discussed. The potassium ion selective microelectrode works well in the 10^{-5} - 1 M concentration range, displaying Nernstian slope 57 ± 1 mV per decade of K^+ ion activity. The selectivity coefficients measured by the mixed solutions method ranged from 3.2×10^{-3} to 7.2×10^{-4} . The membrane resistance was measured by the voltage divider method.

Finally an example selected from major application fields of potassium microelectrode for *vivo* measurements in SECM study will be described briefly.

PRELIMINARY STUDIES ON THE USE OF MICROBIOLOGICAL RESOURCES TO ENHANCE THE SUPPRESSIVE SOIL EFFECT

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Suppressive soils represent an alternative to replace rootstock and fumigation and reduce farmer expenditures. Considering that organic fertilizers and biological control agents increase soil repressive effect on some pests and pathogens of agricultural and silvicultural interest, we performed laboratory experiments, in order to assess the effect of farm manure and compost on biological parameters of some *Beauveria bassiana* strains selected for obtaining biological insecticides. Likewise, we tested the survival of different PGPR, with antifungal activity, in manure. There were tested three *B. bassiana* strains belonging to the entomopathogenic microorganisms collection of the Romanian Research-Development Institute for Plant Protection and two bacterial strains of *Bacillus subtilis* and *Bacillus amyloliquefaciens*. Barkley kernels colonized by fungal strains was incorporated in soil fertilizers; after a six months incubation period at 24°C the fungal strains were re-isolated from test fertilizers and the following biological parameters of single-conidium isolates: vegetative growth, conidiogenesis, viability and virulence were quantified. To test the virulence, aqueous spray of conidia were applied on *Plodia interpunctella*, used as test insect. *B. bassiana* strains colonized organic substrates, the saprophytic development was abundant, the vegetative multiplication and the sporulation were not inhibited in any of the experimental variants. The average size of fungal colonies and their daily average growth rates of were close to the control variants. Conidia viability estimation showed a mean percent germination up to 91%. The biological activity assessed on *P. interpunctella* used as insect-test revealed 85-89% larval mortality. The bacterial strains were applied as aqueous suspensions in manure. During one month incubation period at room temperature the bacterial load was weekly quantified. We also analyzed by comparison the antifungal properties of the aqueous suspension harvested from the *Bacillus* inoculated manure, un-inoculated manure and *Bacillus* spp. pure inoculum. These studies showed the biological compatibility between the plant protection bioproducts based on *B. bassiana* and *Bacillus* spp. respectively, with some fertilizers products used in organic agriculture.

NOVEL STRIGOLACTONE ANALOGS SYNTHESIS

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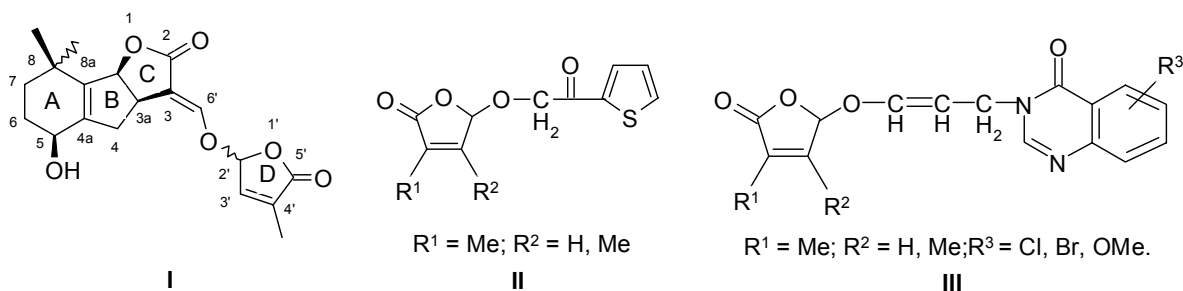
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Strigolactones are a class of signaling molecules emitted by host plants that control the germination of parasitic plant seeds in the rhizosphere,¹ hyphal branching in arbuscular mycorrhizal fungi,² and others processes in higher plants including germination, branching, and root development.³⁻⁸

At least 19 naturally occurring strigolactones have been identified in root exudates of different monocyledonous and dicotyledonous plant species, and most of them have been structurally characterized. Natural strigolactones (**I**) present a common four cycle skeleton (A, B, C, and D), cycles A and B bearing various substituents and cycles C and D being lactone heterocycles connected by an ether enol bond. All currently known natural and active synthetic strigolactone analogs possess the same CD rings with a methyl substituent at the C4' position suggesting the importance of this structure for bioactivity.

Our research focuses on the efficient synthesis of new strigolactones analogs, in order to select the most biological active compound and to use it on conservation agricultural systems.

Based on QSAR data⁹⁻¹² we are obtained two different major structures (**II** and **III**) containing the D ring attached to a suitable unsaturated C3'-C4' and / or C3-C6', essential for bioactivity, and a Michael acceptor in the same molecule, essential for hormonal activity of strigolactone analogs.



The bioactive properties of novel compounds will be investigated in order to identify the potential candidate for practical applications.

**VALUATION OF EDIBLE WILD PLANTS OF THE GUINEAN SAVANNAH:
THE CASE OF *DETARIUM SENEGALENSE* (J.F.Gmel)**

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Detarium senegalense (Caesalpinioideae) seeds are wasted when processing, however the kernel or the oil pressed might be used as a food ingredient for humans, like bread.

The objective of this study was to characterize physical and chemical proprieties of the oil obtained from the kernel of the non toxic variety to evaluate it potential as food.

Detarium senegalense seeds from Guinea were used. The seeds were separated and cracked manually, kernel was dried by air and then pulverized: the fine powder was used for bread preparation. The oil was obtained by Soxhlet and solid-phase extraction using an Oekotec press machine. The overall yield was 16.51% by solvent extraction where the extraction by pressing give 15,90%. We analysed the oil of *Detarium senegalense* using combined GC and GC/MS.

The principal constituents identified in the volatile part of *Detarium* oil were: 2E, 4E- deca-2,4-dienal, 14E,16E-octadeca-14,16-dienoic acid methyl ester, docosanoic acid methyl ester, phthalic acid cyclohexyl isobutyl ester, hexanedioic acid bis (2-ethylhexyl) ester. The major fatty acids were unsaturated (linoleic 61.3% and oleic acids 24.1%), the saturated fatty acid were palmitic (7.0%) and stearic (2.4%). The physicochemical data for *Detarium senegalense* oil are: light yellow liquid with characteristic odour, density - 0,917, refractive index - 1,4498, acid value - 1,95 mg/KOH/g oil, saponification index - 197,75 mg/KOH/g, iodine value - 121,3 and unsaponifiables - 2,29%. The extraction of oil from the kernel of *Detarium* solve also a nutritional and economical problems since in Guinea the most production of *Detarium* lost while no conservation or transformation technology is available for the waste. Quality of edible oil depends on the presence of fatty acids. The higher the level of unsaturated fats, the better the nutritional quality. Oil from *Detarium senegalense* contains 90% unsaturated fat, however the oil was stable after three years and heating at 180°C. This study provides data useful to future research on the use of *Detarium* kernel powder as flour and kernel oil as edible oil or resource for polymerisation.

**EVALUATION OF SOME MICROBIAL STRAINS ABLE TO PRODUCE AN ENZYME
CELLULOSOLYTIC COMPLEX, SUBSEQUENTLY USED AS PART OF A NEW TECHNOLOGY IN
ORDER TO OBTAIN BIOGAS FROM VEGETABLE WASTES**

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Biogas typically refers to a gas produced by the biological breakdown of organic matter in the absence of oxygen. Using agricultural waste grain as single carbon and energy source for biogas production is not yet described in the literature. There is presented the lignocellulosic grain waste recovery especially for bioethanol⁽¹⁾, while for biogas production are mentioned recently only wastes resulted from vegetables and fruits.⁽²⁾

This paper presents the results obtained for improving biogas production, starting from a better enzymes system and optimal fermentation conditions. Most producers of hydrolytic enzymes are using strains of *Aspergillus niger* and *Trichoderma viride* grown on different natural substrates, in submerged systems or surface cultures. These microorganisms have the ability to produce generally an enzyme's complex having a hydrolytic action and offers several advantages over the sources of enzymes with animal or vegetable origin. After the selection of some fungal strains with high producing performances (demonstrated experimentally), we aimed to choose the most appropriate media for the biosynthesis of requested enzymes. Thus, in order to obtain a system of enzymes with synergistic activities, including both endo-and exo-glucanases, tests were made with different compositions of fermentation media and, moreover, a study on the effect of pH variation in the biosynthesis pathway was figured out.

Our researches were carried out by using some selected strains of *Aspergillus niger* and *Trichoderma viride* grown on medium with soybeans wastes and ground corn cobs, during 120 hours at a temperature of 28-30 C, in shaken flasks. The enzyme preparation was later used as part of a technology for obtaining biogas from agricultural waste grain and this new method has obtained a patent in 2013.

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**EVALUATION OF STABILITY OF SEVERAL ANTITUMOR PYRAZOLE
DERIVATIVES UNDER STRESS CONDITIONS**

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Drug decomposition may result in loss of activity or even adverse effects during the formulation and condition. Thus, among the biopharmaceutical properties, stability studies are essential for the development of a new drug¹. International Conference on Harmonisation (ICH) guidelines require for the new pharmaceutical compounds the determination of stability conditions². Several protein kinases emerged as promising therapeutic targets for new antitumor agents, rendering the development of selective kinases inhibitors a top priority³. The aminopyrazole scaffold is an important pharmacophore of selective, targeted anticancer agents functioning as protein kinases inhibitors^{4,5}. In our previous research we designed and synthesized a series of new pyrazole derivatives with good cytotoxic profile⁶. In this study, forced degradation studies under acidic, alkaline, oxidative, photodegradation and temperature conditions were performed according to ICH guidelines in order to improve the drug design process of new aminopyrazole antitumor derivatives^{2,7}. All pyrazole compounds tested showed good stability profiles, making them candidates for further biopharmaceutical investigations. This work received financial support through the project entitled "CERO – Career profile: Romanian Researcher", grant number POSDRU/159/1.5/S/135760, cofinanced by the European Social Fund for Sectoral Operational Programme Human Resources Development 2007-2013.

SYNTHESIS OF NEW AMINOPYRAZOLE DERIVATIVES AS POTENTIAL ANTICANCER AGENTS

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Cancer is a major international health problem and the therapeutical solutions are limited by the drugs toxicity, low efficiency and disease diversity. Several protein kinases emerged as promising therapeutic targets for new antitumor agents, rendering the development of selective kinases inhibitors a top priority. Urea is an important scaffold in the structure of various protein kinases inhibitors, like doramapimod, tivozanib and sorafenib¹. The pyrazole scaffold is an important pharmacophore of selective, targeted anticancer agents². Based on the isosteric relation between the thiourea and urea groups and on the antitumor properties of the pyrazole scaffold, we designed and synthesized a series of new thiourea derivatives as potential anticancer agents targeting the cyclin dependent kinases family. The structures of the newly synthesized compounds were confirmed by IR and NMR spectroscopic and elemental analyses. This work received financial support through the project entitled "CERO – Career profile: Romanian Researcher", grant number POSDRU/159/1.5/S/135760, cofinanced by the European Social Fund for Sectoral Operational Programme Human Resources Development 2007-2013.

CYTOTOXICITY SCREENING OF SEVERAL EXTRACTS FROM *CONSOLIDA REGALIS* GRAY. USING *DAPHNIA MAGNA* AND *PHYSA ACUTA* BIOASSAYS

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Cancer is the most important cause of death and morbidity, being responsible for over 3.5 millions deaths people annually all over the world¹. Natural products represents a promising alternative of the available synthesis compounds for the treatment of cancer, usually, having low toxicity and satisfactory efficacy². *Delphinium consolida* L. syn. *Consolida regalis* Gray (Ranunculaceae) is a species widespread in Northern Hemisphere, which contains C₁₉ diterpenoid alkaloids with antitumor potential³⁻⁶. Considering this, different types of extracts obtained from aerial part of *D. consolida* were evaluate for cytotoxic effect by *Daphnia magna* and *Physa acuta* bioassays⁵. All extracts showed satisfactory cytotoxic activity. Thus, *D. consolida* aerial parts could represent a reliable bioresource for anticancer compounds extraction and isolation. This work received financial support from UEFISCDI through the project PN-II-PT-PCCA-2013-4-1953 No. 199/07.01.2014.

PROTECTIVE BIOFORTIFICATION WITH SELENIUM OF CRUCIFEROUS CROPS FOR PRODUCTION OF FUNCTIONAL FOOD

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Selenium (Se) is an important element for human and animal nutrition because of its function in a number of physiological processes. Cultivation of the selenium biofortified plants can be an effective way of producing functional foods, which determine benefits to human health.

For these reasons we are developing a project in order to establish a new biotechnology of obtaining safe functional food, with an optimal content of chemopreventive compounds, by selenium protective biofortification of cruciferous crops. Biofortification of the food chain through treatments applied to plants (agronomic biofortification) have the advantage of a supplementation with controlled levels of seleno-compounds with a high bioavailability, widely available to different categories of people exposed to risks of chronic diseases.

The originality of the project is resulting from the integrated approach, which focus on both safe and effective supplementation with selenium of the food chain, and cruciferous plants protection against abiotic stress (lack of water, high temperature, excessive solar radiation) and biotic stress (pests and diseases).

The project objectives are: development of new means of technological intervention (spraying adjuvants, products with controlled release of betaine, nitric oxide inductors in plant tissues), testing and identifying the best solutions for the integration of new technological means of intervention in cruciferous crop technology, proving the character of safe functional food.

The end products of the project are: (i) a technology for biofortification of cruciferous crops, which includes new innovative products / agricultural inputs, intended to maximize the protective effects of selenium and accumulation of chemopreventive selenocompounds constant levels, and methods of their application; (ii) selenium biofortified functional foods, affordable, with reproducible biological effects and maximum safety for human health.

The expected result following the practical implementation of this project is a safe and effective way of food chain selenium supplementation.

ANALYSIS METHODS OF BIOLOGICALLY ACTIVE COMPOUNDS IN *MOMORDICA CHARANTIA* AND *PASSIFLORA INCARNATA* PLANTS

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The therapeutic value of medicinal plants is due to the potential of their bioactive constituents (polysaccharides, glycosides, tannins, flavonoids, saponins, alkaloids, triterpenoids, etc.) that have physiological action on the human body. The two model plants studied have multiple and well known beneficial effects on human health. *Momordica charantia* is known for its antidiabetic activity¹ due to the polypeptide-P (also called the “green” insulin), but also for its antibacterial, antiviral, antifungal, antiparasitic and immunomodulatory action. *Passiflora incarnata* is known for its anxiolytic action², the plant being used as sedative, antispasmodic and nervous tonic.

In this paper, we aimed to qualitatively identify several biologically active compounds in extracts from studied dried plants, namely: alkaloids, polysaccharides, glycosides, triterpenoids and saponins, by colorimetric methods³.

We also performed quantitative analysis in order to determine the total content of polyphenols and flavonoids (by spectrophotometric methods) and to assess their antioxidant capacity (ABTS and DPPH methods). The analytical methods we have selected allowed the identification and determination of the main ingredients and a comparison between the two plants. Analysing the obtained results, we observed a correlation between the amount of polyphenols and the antioxidant activity of the studied extracts.

The influence of the extraction environment on the content of some active principles was also observed during the study. Analysis of the obtained values showed a correlation with the literature data reported for other varieties of these species.

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**PHYSICO-CHEMICAL CHARACTERIZATION OF SOME SEMISOLID TOPICAL
SYSTEMS CONTAINING VEGETAL BIOPRODUCTS**

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Topical administration of bio products for the treatment of certain local diseases of skin is one of the oldest methods of drug administration, but with certain limitations. Therefore, in recent years a number of encapsulated systems have been developed for the transport and release of bioactive substances.

In this paper we aimed in investigating the physico-chemical properties of Carbopol 940 hydrogels with liposomes loading dill bio products.

Liposomes composed of phosphatidylcholine and cholesterol and incorporating dill bio products were prepared by thin film hydration method and dispersed into two types of hydrogels (0.5%, respectively 1% carbopol). Macroscopic examination aimed at a series of visual (aspect, consistency, homogeneity, color), olfactory (smell), tactile (touch and thermal sensation) features, according to F.R.X guidelines. The *in vitro* release studies were performed using a modified Franz cell. In order to evaluate the kinetic parameters of the bioproduct release, the experiments were carried out in a range from 0 to 24 hours. The amount of gel displayed on synthetic membrane area was 1 g in all analyzed cases.

In vitro release studies showed that the designed hydrogels follow a 0 order kinetic model after an interval of three hours from the start of the kinetic experiment.

This study suggests that gels containing bio products from *Anethum fructus* entrapped in liposomes can give the desired therapeutic effect, due to local controlled release, which leads to an increase in efficiency and compliance, in addition to increased stability of the tested topical formulations.

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***ANTHRISCUS SYLVESTRIS* AND *ANHRISCUS CEREFOLIUM* FRUITS AS A SOURCE OF PHENOLIC COMPOUNDS**

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Polyphenols are bioactive compounds that naturally occur in small quantities in plant and food products. Because of their therapeutic properties, in the last years, numerous studies focused on finding new sources especially in the food industry¹. *Anthriscus sylvestris* Hoffm. - wild chervil and *Anhriscus cerefolium* (L.) Hoffm. - chervil are two herbaceous species from Apiaceae family. The leaves are used in human nutrition, whereas the root is studied intensively/extensively in anticancer therapy due to the presence of deoxypodophyllotoxin^{2,3}. Recently, leaves and stems from both species were studied for the content of phenolic compounds with antioxidant properties, such as luteolin, quercetin and kaempferol glycosides^{4,5}. In the present work we evaluate the phenolic content of the fruits belonging from the two species of chervil in order to establish if this organ is a reliable source of polyphenols. The assessment of phenolic compounds was performed on several extracts from both species by Folin Ciocalteu method. Following the results obtained in this study, we conclude that fruits from both species of *Anthriscus* are rich phenolic sources.

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STUDIES REGARDING THE TRANSFORMATION OF A WASTE (*OSTRICH FAT*) IN PRODUCTS WITH HIGH ADDED VALUE

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This paper presents studies concerning the refining of crude ostrich oil, obtained through wet melting of ostrich fat provided by Suraki Srl. (Rasuceni, Giurgiu district), in a good quality purified ostrich oil that can be used in cosmetic and pharmaceutical industry^{1,2}. According to the literature standards³, an ostrich oil adequated for pharmaceutics must have the following properties: peroxide index < 2 mE/kg, acidity index < 0.1 mg KOH/g and water content < 0.05%.

The process of refining used consisted of various treatments, such as: neutralization, drying, bleaching and deodorization. For each stage were performed numerous experiments to find the optimal working conditions, thereby at bleaching were tried different types and quantities of clays, temperature values, contact times and at deodorization different temperatures and times.

The best results for bleaching were obtained using a combination of acid activated bentonite (2.5%) and basic clay (2.5%), sodium bentonite or veguum, process mentained for 30 minutes, at 90-100°C, under vacuum of 2mm Hg. The optimal conditions for deodorization were found at 50°C, under vacuum of 2mm Hg, 5-7 hours. At the end of the refining process, is obtained a colorless and odourless oil, with stable properties during at least six months, after the addition of 0.05% tocoferol, as antioxidant.

Refined oil was used for the synthesis of fatty acid esters (fatty acid methyl esters, fatty acid ethyl esters), in cosmetics (creams, soaps) and food supplements.

Key words: *ostrich oil, bleaching, deodorization, clay, bentonite.*

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**ISOLATION AND SCREENING FOR AMYLASE PRODUCING MICROORGANISMS
FROM WATER AND SOIL FROM DIFFERENT AREAS OF ROMANIA**

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Among different types of enzymes obtained from microbial sources, amylases are the most widely used in industries as well as on commercial basis. With the emergence of biotechnology, the use of amylase has widened in clinical research, medical chemistry and starch analytical chemistry. These increased uses have placed greater stress on increasing indigenous amylase production and search for more efficient processes. The major advantages of using microorganisms for production of amylases are the ability to produce in bulk and ease at which it can be manipulated for desired products.

The aim of the current study was to isolate amylase producing microorganisms from the soil and water samples collected from different areas of Romania. The isolation was done by serial dilution and plating method. A total of 110 microorganisms, 70 bacterial colonies, 16 yeast colonies and 24 fungus colonies were isolated from the collected soil and water samples. All isolates were screened for amylolytic activity by starch agar plate method. Among 70 bacterial isolates, only 33 isolates showed the amylolytic activity. Out of these, 18 isolates were selected on the basis of maximum hydrolysis for further study. Amylase production from bacteria is economical as the enzyme production rate is higher in bacteria as compared to other microorganism. None of the yeast isolate showed amylolytic activities but among the 24 fungus isolates, 8 isolates showed amylolytic activity. Out of these, two isolates were selected on the basis of maximum hydrolysis for further study.

BEECH FOREST, AN IMPORTANT, RENEWABLE SOURCE OF ACTIVE INGREDIENTS AND NOVEL BIOPRODUCTS

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Beech forest, precisely *Fagus sylvatica* L. *folium* (beech leaves) raw material, represents a valuable, renewable source of active ingredients to use in all, chemical, pharmaceutical and cosmetic industries. The high value of this vegetal raw material derives from beech leaves interesting chemical content, respectively the combination of polyphenols with triterpenic acids (ginsenosid Ro-type). Concerning beech leaves polyphenols' profile, studies revealed that it depends of the harvesting time. Exactly, our previous studies indicated that if May to June leaves are dominated of one major kaempferol derivate aside only traces of caffeic acid derivates, July to August leaves abound in apigenin and caffeic acid derivates next to small quantities of kaempferol, quercetin and catechin derivates; in contrast, September to October leaves indicated caffeic acid and kaempferol derivates decreasing *versus* apigenin, catechin and quercetin derivates augmentation. Starting from these data proving beech leaves dynamic chemical composition, subsequent studies on a series of whole and selective beech leaves extracts prepared in different vegetation time had to reveal gastroprotective, and antioxidant and also antimicrobial properties of *Fagus sylvatica* leaves derived products. Moreover, material protecting (anticorrosive) properties of the beech leaves alcoholic extracts has been revealed. Finally, there were evidenced some pro-oxidant, potential toxic compounds at the level of non-polar (dichloromethane) extracts. Given these and also other literature data proving beech leaves anti-cancer potency, it was clearly revealed high usefulness in all, chemical, pharmaceutical and cosmetic industries of this very abundant vegetal raw material with the mention that beech leaves active compounds need to be better studied for the development of novel and safe highly effective vegetal bioproducts.

Keywords: *beech leaves, gastroprotective and antioxidant bioproducts*

DIMINUTION OF CONTAMINATION RISKS FOR STORED GRAINS PROTECTION

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Diminution of residues and contaminants from the post harvested yield in storage is a great challenge for the farmers. Some of the most dangerous risk factors are the agricultural insect pests and fungal diseases which destroy the crops in storage, generating huge economical losses. Mycotoxins produced by pathogenic fungi in cereal crops are transferred from field to storage, then in feed, animal bodies and humans thus affecting food quality and health. Finding effective means for limitation the populations of pathogenic microorganisms and insects developing in storage grains is a major goal of new project "Ecological products based on diatomaceous earth and essential oils for the residues and contaminants reduction from the food chain (PEDIOL). ICECHIM as Partner in this project proposes to research and develop an innovative organomineral product based on local mineral diatomaceous earth with insecticidal properties and indigenous renewable raw materials extracted from wild or cultivated aromatic plants as ecological alternatives to chemical fumigants such Fostoxin or methyl bromide banned by environmental protection organisations. Modern formulation as concentrated suspension, microcapsules, dried granules or beads, experimental models for their preparation based on interfacial polymerization, complexation or cross-linking reactions and technological development for entrepreneurial transfer to SME were proposed.

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COMPARATIVE METHODS FOR DETERMINATION OF PHOSPHORUS IN VARIOUS MATRICES: INDUCTIVELY COUPLED PLASMA SPECTROMETRY VERSUS GRAVIMETRIC METHOD

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Conventional methods for the determination of total phosphorus are difficult and lengthy processes. While these methods offer great sensitivity and certain degree of flexibility in linear ranges, it is necessary to explore new methods for a faster, easier analysis. Present and future research in phosphorus methodology will undoubtedly be in the further application of emission spectroscopy. Although the argon-inductively coupled plasma-optical emission spectrometry (ICP-OES) method has not widely used for determination of nonmetals, partly due to the location of prominent emission lines outside the range of conventional spectrometers, finding the optimal conditions provides possibility of applying them to the analysis of phosphorus.

The aim of the paper is to evaluate the magnitude and characteristics of the difference between ICP-OES method and gravimetric method (as reference method) for phosphorus analysis.

Laboratory experiments consisted in the determination of phosphorus present in various matrices, including a Certified Reference Material with declared phosphorus content.

In order to evaluate the correctness of the results obtained and to compare the two methods at different analyte concentrations, a statistical procedure consisting in drawing of a regression graph was adopted: one axis of this regression graph is used for the results obtained by the new ICP-OES method, and the other axis for the results obtained by applying the reference method to the same samples. Finally, the slope (*b*), the intercept (*a*) and the correlation coefficient (*r*) of the regression line are then calculate. By comaprison with the "ideal" situation ($a = 0$, $b = r = 1$), we can appreciate if the two analytical procedures gives results in good agreement for all the samples.

The benefit of this study is to propose an alternative ICP-OES method to the standard gravimetric method; by comparing their, we can conclude that ICP-OES is a fresh approach that is attracting more attention, particularly for low-level analysis and speed analysis too.

IMPROVING FOOD SAFETY THROUGH THE DEVELOPMENT AND IMPLEMENTATION OF ACTIVE AND BIODEGRADABLE FOOD PACKAGING SYSTEMS

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A big effort to extend the shelf life and enhance food quality while reducing packaging waste has encouraged the development of new active food packaging systems. Active packaging is an innovative concept that can be defined as a food/package/environment system that works in a coordinated way to change the condition of the packed food product and are designed to extend shelf life, improve safety and/or enhance sensory properties in foods and beverages, while maintaining the quality of the packed food^{1,2}.

The paper aims on the development of new innovative food packaging biomaterials with antimicrobial and antioxidant properties, by obtaining of bioactive complex systems based on PHAs (PLA) and chitosan biopolymers as well as on the design and embedding of encapsulated forms with active substances in order to: a) prolong the shelf-life of the food packaged products; b) inhibit pathogenic microorganisms growth and also c) impart to packaging other functionality (antioxidative, bioactive).

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THE EFFECT OF BIODEGRADATION ON SURFACE AND BULK PROPERTY CHANGES OF POLYPROPYLENE AND RECYCLED POLYPROPYLENE COMPOSITES

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The polymers have a commercial importance because of intense applications in the form of composites. With a production over 150 million tons produced worldwide every year, the environmental pollution of polymeric wastes has been recognized as a major problem. The biodegradation of polymeric materials based on certain microorganisms seems to be an efficient way to eliminate some plastic wastes ^{1, 2, 3}. The largest fraction of polymers wastes consist of polyolefins, such as polyethylene and polypropylene. The biodegradation of polyolefins is a slow process, but the relatively inert polymer could become more degradable by introducing a biodegradable component or group in a non biodegradable polymer matrix ^{4, 5, 6}.

In the present study, virgin polypropylene and processed polypropylene from plastic wastes mixed with natural polymer from renewable resources were exposed to microorganisms. The changes in the material properties after microorganism contact were analyzed by infrared spectroscopy, thermal gravimetric analysis, and scanning electron microscope. The FTIR spectra of biodegraded samples showed the increasing peak of carbonyl group at 1740 cm⁻¹ due to the scission reactions of the chain in polymer matrix and at 1046-1450 cm⁻¹ assigned to polysaccharides. There are detectable changes between control and biodegraded samples evidenced by thermal gravimetric measurements. SEM micrographs showed the presence of biofilm on composite surface.

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USEFULNESS OF *TRICHODERMA SPECIES* AGAINST PLANT PATHOGENS

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Trichoderma is known as one of the most important biological control agents used in fight against plant diseases. Their ability to control pathogens is associated with different kinds of mechanism, such as competition for space and nutrients, mycoparasitism and antibiosis.^{2, 5} *Trichoderma* species produce hydrolytic enzymes (endochitinases, beta-glucanases, glucanases, proteases, DNases, RNases, cellulases) which facilitate the degradation of certain natural substrates. *Trichoderma* also produces metabolites with an antifungal, antiviral, and antibacterial activity that can be used to obtain bioformulations with multiple applications. The initial step in the selection of most efficient antagonistic strains is based on the assessment of their antifungal activity against pathogenic fungi. Therefore, the *in vitro* study was carried out to find the antagonistic potential of several *Trichoderma* strains against three aggressive plant pathogens, as *Verticillium dahliae*, *Botrytis allii* and *Sclerotinia sclerotiorum*.^{1, 3, 4} . The evaluation of volatile compounds from *Trichoderma* strains have demonstrated the higher ability of *Trichoderma asperellum* T36 and *T. asperellum* T50 in inhibiting the mycelial growth of plant phytopathogens.

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COMPARATIVE STUDY OF *Kluyveromyces sp.* GROWN ON LIQUID SWEET AND SOUR CHEESE WHEY

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Whey is a by-product from cheese-making process and because of its high organic content, when is discharged to the environment, causes serious polluting problems. The use of whey for the production of yeast biomass is an advantageous process as the pollutant load is significantly reduced and whey lactose is converted into yeast biomass.

The aim of this study is the investigation of liquid sweet and sour cheese whey suitability as substrates for the development of *Kluyveromyces sp.* which is capable of metabolizing lactose, the major constituent of the whey. Sweet and sour whey have been supplemented with salts of ammonium and phosphor for the complete conversion into biomass.

It was performed chemical analysis of raw materials. Cultivation was carried out in aerobic condition on a rotary shaker at pH 6.09 for sweet whey and pH 4.63 for sour cheese whey, respectively, cultivation temperature 28⁰C, 5% (v/v) inoculum of 24 h – old culture, on a rotary shaker under agitation (150 rpm), propagation time being 24 hours. Whey was inoculated with *Kluyveromyces sp.* to obtain an initial count of 10⁶cells/mL. The amount of biomass, dry matter and moisture were determined. In addition, cell concentration was estimated by measuring the optical density at 620 nm in a spectrophotometer. The typical growth curves are represented function of time (h) and biomass (g/mL). The analysis of variances pointed out that there is a significant difference between the strains regarding dry matter.

The results achieved in experiments showed that *Kluyveromyces sp.* strains grown better on sweet whey (2.81%) than sour cheese whey (2.14%) based on determination of cell dry weight.

The study showed the feasibility of utilization of sweet whey as a cheap substrate for yeast biomass production.

INFLUENCE OF NATURAL WASTE SUBSTRATES COMPOSITION ON YEAST STRAINS BIOMASS PRODUCTION

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The aim of the research is to study the influence of several types of waste substrates on quantity and quality biomass production by yeast strains.

The widely available food-processing wastes considered as carbon sources were whey and beet molasses which were enriched with different mineral salts in various concentrations, taken into account the nutritional growth needs of yeast cell. Different synthetic media, with addition of complex substances (e.g. yeast extract), were prepared in laboratory and used as nutrient sources, too. Waste substrates were characterized from chemical point of view.

There were tested six yeasts strains, denoted by SL-I, SL-II, SL-III, KM-I, KM-II, KM-III, which metabolize lactose and sucrose. The strains originate from ICECHIM culture collection, where they are conserved on malt-agar slopes, in darkness, at 4⁰ C. Experimental assay was carried out in flasks, aerobically, at a temperature of 28⁰C, at permanent shaking, for 24 hours. The multiplication degree of yeast strains was analyzed in comparison with natural and synthetic media. All strains were able to growth on all natural and synthetic substrates. Biomass production was more different according to substrate type. The biomass separation was made by centrifugation and the amount of biomass, the dry matter and moisture were determined. Morphological and culture aspects of yeast strains grown on selected media have been evaluated, too. Experimental results showed a biomass increase and an increase of overall biomass yield on natural substrate, in contrast to the synthetic media. Biomass obtained could be used as feed additives products with high nutritional value.

The raw materials used are agro-food by-products which constitute a valuable, energetic substrate for different yeast strains, which, by multiplication, generate biomass with high nutritional and biological value, representing a source of protein, mineral salts and bioactive compound with immune modulation activity, for veterinary and human use.

**STUDY ON THE CATALYTIC ACTIVITY OF POLYMER
MEMBRANES-BASED ENZYMATIC COMPOSITES****T. SANDU, A. SÂRBU, T. V. IORDACHE, A. ZAHARIA, L. MARIN, C. MARIN,
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The present work aimed at investigating the ability of using acrylonitrile-based polymer membranes as supports for enzymes immobilization and at proving that both free and immobilized enzyme, show catalytic activity. To meet these purposes, a polymer membrane was prepared using an acrylonitrile-vinyl acetate copolymer (C, with a monomer ratio of 2.35) in mixture with polyvinyl alcohol (PVA). According to literature¹, polyacrylonitrile is suitable for membrane forming but it does not exhibit functional groups able to bind enzymatic protein. For this reason, PVA was introduced to allow the membrane functionalization with glutardialdehyde. Functionalization occurs at PVA, resulting in carbonyl groups formation on membranes surface which are further available in enzyme immobilization. The enzyme used in this study, mushrooms Tyrosinase (Tyr), exhibits both monophenolase and diphenolase activity². Enzymatic composites based on Tyr and membranes combine the advantages of individual components. Membranes are widely used in separations and enzymes represent well known catalysts, so the obtained composites may be used in catalytic filtration, for phenolic compounds removal from wastewaters.

For enzymatic activity studies, UV spectra were recorded using pyrocatechol (PC) as substrate. Two membranes (M1 and M2) were prepared dissolving two C-PVA mixtures (80/20 and 90/10, respectively) in DMSO. Afterwards, the solutions were cast on glass and immersed in a coagulation bath (50 % water-50 % isopropyl alcohol, volume ratio). UV spectra revealed that both, free and immobilized enzyme, show catalytic features. Immobilization results in an activity decrease, a part of the active sites being consumed for immobilization. Furthermore, it was observed that enzymatic activity depends also on the content in PVA. The obtained composites will be further characterized in terms of their separation ability.

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MULTIFUNCTIONAL AND INNOVATIVE PRODUCTS FOR SAFE AND BIOENHANCED FUNCTIONAL FOOD FROM NEWLY CULTIVATED PLANTS IN ROMANIA

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In last years, there is a growing trend in the consumption of functional foods/food supplements from plants (nutraceuticals), mainly due to: the increased interest in disease prevention; the increasing cost of medical care; significant success in validating the safety and efficacy of functional foods / nutritional supplements; improving the legislative framework for functional foods / nutritional supplements from plants¹. The general objective of the project is to develop multifunctional and innovative products for protection of nutraceutical plants newly introduced in Romania (*Momordica charantia*^{2, 3} and *Passiflora incarnata*⁴) and to stimulate concomitantly formation of biologically-active compounds in these plants, at stable levels and with reproducible biological effects. The specific innovative project objectives are: i) Development of multifunctional for treatments of soil and in vegetation, based on: (a) consortia of *Trichoderma* strains; (b) porous ceramics with high bioavailability of silica; (c) essential oils included in mesoporous silica; ii) Testing products, developing methods of application and integrating them with the sustainable cultural technology of nutraceutical plants; iii) Characterization of functional foods through *in vitro* alternative tests on human cell cultures and highlighting the biological role of silica forms accumulated in treated plants in animal cells; iv) results exploitation by protection of intellectual innovative solutions after techno-economical analysis and opportunities of results exploitation.

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PHYTOPATHOGEN CONTROL OF HORTICULTURAL SHRUBS WITH PLANT EXTRACTS. II. *ALTERNARIA ALTERNATA*

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Alcoholic extracts from different aromatic plant, manufactured by Hofigal S.A. were tested *in vitro* and *in vivo* for their biological activity against *Alternaria alternata* (Aa20 strain), isolated from blackcurrant (*Ribes nigrum* L.).

Satureja hortensis and *Valeriana officinalis* extracts (tested at 20% concentration) presented the highest fungitoxic activity *in vitro* (with an efficacy of 100% inhibition of fungal development compared to untreated control). Other extracts demonstrate a lower antifungal activity *in vitro*: extracts from *Rosmarinus officinalis* (E = 88.6%), *Tagetes patula* (E = 78.5%), *Mentha piperita* (E = 77.1%) and *Allium sativum* (E = 72.8%), all tested at 20% concentration. Among these, the extracts of *Rosmarinus officinalis*, *Tagetes patula* and *Mentha piperita* showed efficacies between 72.8 to 64.3%, tested at 10 and 5% concs. A moderate activity against *Alternaria alternata* (E = 31.4% - 57.1%) has been noticed for the extracts from *Allium sativum* (tested at 10% conc.), *Achillea millefolium* (tested at all concs.) and *Hyssopus officinalis* (tested at 20% conc.). The lowest activity against *Alternaria alternata*, respectively no effect compared to untreated control, was noted when extracts from *Artemisia dracuncululus* 'sativa', at all concs., and *Hyssopus officinalis* at 10-5% concs, are used. The extracts of *Valeriana officinalis* and *Saturaja hortensis* proved to be efficient also in protecting blackcurrant plant against *Alternaria* disease. Compared with the untreated control, where a 9.05% average disease prevalence index was record, the disease prevalence index on blackcurrant treated with *V. officinalis* and *S. hortensis* was 0.85% and, respectively, 1.4%. These extracts, highly efficient *in vivo* against *Alternaria alternata*, can be recommended as an environmental-friendly alternative, especially on organic horticulture, for the protection of blackcurrant crop against blight disease.

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**PHYTOPATHOGEN CONTROL OF HORTICULTURAL SHRUBS WITH PLANT
EXTRACTS. II. *BOTRYTIS CINEREA***

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There were tested and screened, for the first time in Romania, *in vitro* and *in vivo*, nine respectively six aromatic plant alcoholic extracts manufactured by Hofigal S.A. Company against *Botrytis cinerea* (strain Bc 27) isolated from blackcurrant (*Ribes nigrum* L.) crop. The highest antibotrytis *in vitro* activity (efficacy between 80% and 100%) was obtained using the following extracts: *Hyssopus officinalis* (tested at 20%, 10% and 5%), *Satureja hortensis*, *Allium sativum*, *Tagetes* sp. (at 20% and 10%) and *Mentha* sp. (at 20%). A moderate antibotrytis activity (efficacy 35.7%-65.7%) has been noticed for the extracts from *Mentha* sp. (at 10% and 5%), *Satureja hortensis*, *Allium sativum* and *Tagetes* sp. (at 5%). The lowest antibotrytis activity with no efficacy was noticed using extracts obtained from *Achillea millefolium*, *Artemisia dracunculus* 'sativa', *Rosmarinus officinalis* and *Valeriana officinalis* even applied at 20%. Five from six plant extracts were tested and screened *in vivo*, under field conditions at Hofigal S.A. Company, Bucharest. The extracts from *Satureja hortensis*, *Allium sativum*, *Hyssopus officinalis*, *Mentha* sp. and *Tagetes* sp. have been efficient in limiting gray mold disease in blackcurrant compared to untreated control (12% severity), applied at 20% and 10%, with exception of *Valeriana officinalis* extract. The highly efficient extracts for their antibotrytis activity can be recommended as a non-polluting and environmental-friendly alternative (organic horticulture) in the protection of blackcurrant crop as medicinal plant against grey mold, the most economically important diseases in Europe at present.

Poster

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**NEW CARBOCYCLIC NUCLEOSIDE ANALOGUES AS POTENTIAL ANTICANCER
AND/OR ANTIVIRAL COMPOUNDS**

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Carbocyclic nucleoside analogues have been recognized as efficient antiviral drugs, but researches are also developed for their antitumor activity. The introduction of a CH₂ group instead of *endo*-cyclic oxygen atom of the usual sugar moiety increased the metabolic stability of nucleoside analogues which are unaffected by phosphorylases and hydrolases that cleave the glycosidic bond.

We replaced the usual sugar moiety with an optically active bicyclic fragment containing a norbornane skeleton obtaining a number of carbocyclic nucleoside analogues of L-serie. As base we used 6-substituted adenine, thymine or uracil.

The analogues were synthesized by building the heterocyclic base on an amine key intermediate¹.

The compounds were analyzed by IR, ¹H, ¹³C and 2D NMR spectra and together with X-ray crystallography confirmed the structure of new nucleoside analogues.

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BIOTECHNOLOGICAL PROSPECTING STUDIES ON NATURE ISOLATED MICROBIAL STRAINS FOR LIPASE PRODUCTION

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This paper presents the results of preliminary experiments in order to obtain biologically active substances through biosynthesis, by using microorganisms isolated from various biotopes in Romania.

The main research objective is defined by a bioprospecting study on some bacterial and yeast strains, aiming at the selection of those with biotechnological potential in producing lipolytic enzymes. Lipases have attracted particular attention in recent years, being estimated at 21% of the global industrial enzymes production. Lipases [triacylglycerol acylhydrolases, EC (3.1.1.3)] catalyze the hydrolysis of triglycerides to glycerol and fatty acids. Microorganisms are valuable sources for obtaining these enzymes, the most commonly used strains belonging to the genera *Candida* sp., *Rhizopus* sp., *Aspergillus* sp., *Penicillium* sp., *Pseudomonas* sp., *Bacillus* sp. ' .

After collecting and processing the various nature originated samples (soil, sand, mud, water, vegetal material) for the isolation of lipase producing microorganisms, a total of 110 microbial strains, including 70 bacteria, 16 yeasts and 24 fungi, were obtained. For the isolation and identification of the microorganism categories, the decimal serial dilutions technique on specific agar media was used. In order to naturally select lipases producing microorganisms, a screening was performed, using five different solid media formulas containing inductors, such as Tween80 and Tributyrin. Positive results were recorded for 54 strains: clear or opaque areas were observed around the colonies, formed due to enzymatic hydrolysis. Further experiments are to be conducted only with those microorganisms that demonstrated enzymatic activity (considering the diameter of the clear or opaque areas of hydrolysis) for all of the culture media variants: 22 microbial strains - 18 bacteria and four yeasts.

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OXIDATION OF GLYCEROL BY NANOSTRUCTURED CATALYSTS**Mihaela BOMBOS, Gabriel VASILIEVICI***National Research and Development Institute for Chemistry – Petrochemistry ICECHIM-Bucharest,**Splaiul Independetei, No. 202, 060021, Bucharest, Romania*

A variation of applicative interest recovery of glycerol resulting from biodiesel production is the synthesis of functional derivatives market with high demand as anti-icing and de-icing fluids. Glycerol is used as such in the preparation of antifreezing fluids, but its effectiveness is limited to a narrow area of concentration so that melted ice diluting it's effect is greatly diminished. A class of organic compounds with high efficiency represents some glycerol carboxylic derivatives which may be obtained by its oxidation.

Oxidation of glycerol was performed in the presence of nanostructured catalysts based on iron. The catalysts were prepared by precipitation of iron salts in the presence of anti-caking agents and some reducing agents. The particle sizes were determined with a Malvern Zetasizer instrument NanoZS (Red Badge), performing measurements using a process called DLS - Dynamic Light Scattering (also known as PCS - Photon Correlation Spectroscopy). The images of a catalysts sample have been achieved by SEM image analysis. Oxidation experiments were carried out in batch system in presence of air at atmospheric pressure and temperatures up to 80 ° C.

DLS analysis of the nanostructured catalysts in the presence of reducing agents and anti-caking agents at higher concentrations shows a lower mean particle size and a narrow size distribution. Characteristics of glycerol oxidation were assessed by determining the freezing point. It was revealed that the highest catalytic activity shows catalysts with smaller dimensions.

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METABOLIC EFFECTS OF A *RUBI IDAEI FOLIUM* POLYPHENOLIC EXTRACT IN AN ALLOXAN INDUCED DIABETES MODEL

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Diabetes is a disease with increase morbidity. The pharmacological treatment of diabetes has a negative impact on the patients' quality of life and healthcare system. Identifying bioresources and new biomaterials in order to gain benefits in diabetes treatment is a well-sustained research direction in this field.

The aim of the paper is to evaluate the hypoglycemic and hypolipidemic effects of a polyphenolic extract from *Rubi idaei folium* and the association of the extract and metformin in an alloxan induced diabetes to Wistar rats.

The obtained results were compared to a control group of diabetic rats treated with saline and a reference group treated with metformin. The oral administration of the extract exerted a low hypoglycemic effect and an improvement in the triglycerides profile ($24,97 \% \pm 20,34$) compared to the control group.

The oral administration of the association improved the glucose profile of the diabetic rats compared to the control and reference groups and improved the survival rated of the treated animals. All procedures were carried out in accordance with the Directive 86/609/EEC of 24th November 1986, on the protection of animals used for experimental and other scientific purposes.

This work received financial support from UEFISCDI through the project PN-II-PT-PCCA-2013-4-0953 No. 176/2014.

**NON-CLINICAL ANTIINFLAMMATORY EFFECT EVALUATION OF TWO
PHARMACEUTICAL DOSAGE FORMS CONTAINING AN NSAID AGENT BY
PLETHYSMOMETRY**

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The generic drugs authorization usually requires procedures that implies clinical trials with high costs in money, time and volunteers sufferance.

Finding alternatives, with reliable results to those procedures will lead to an increase of generic drugs market that will generate a higher access for the patients to affordable pharmacological treatments.

The present study is design to compare the antiinflammatory effect of two parenteral dosage forms containing an NSAID agent, meloxicam by plethysmometry in two induced acute inflammation rat models.

The results revealed no significant differences for the inflammation evolution ($p>0.05$) and anti-inflammatory effect ($p>0.05$) between the reference pharmaceutical dosage form (MOVALIS) and tested pharmaceutical dosage form, for a 90% confidence interval.

The anti-inflammatory effect of tested pharmaceutical dosage form is equivalent with 90% Confidence Interval, with MOVALIS.

This work received financial support from UEFISCDI through the project PN-II-PT-PCCA-2013-4-2071.

ANTIINFLAMMATORY EFFECT EVALUATION OF NOVEL RUTHENIUM(III)-NORFLOXACIN COMPLEX WITH ANTICANCER PROPERTIES

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Cancer is a wide spread and nonselective disease affecting people with different social status. Cancer disease appears to be correlated with inflammatory response^{1,2}. Metal based anticancer agents development is motivated by the benefits brought by platinum derivatives used in therapy³. Ruthenium(III) complexes with cytotoxic properties are promising agents in cancer therapy⁴. The investigation of the antiinflammatory effect of a novel ruthenium(III)-norfloxacin complex with cytotoxic properties⁵ might prove a new approach for understanding its anticancer activity.

The anti-inflammatory effect of the ruthenium(III)-norfloxacin complex was evaluated in acute inflammation model induced with kaolin to Wistar rats. The results shown a maximum antiinflammatory effect 2 hours after the oral administration of the complex, compared to control group ($p < 0.05$).

This work received financial support from UEFISCDI through the project PN-II-PT-PCCA-2012 No. 136/2012.

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**DETERMINATION OF TOXIC VOLATILES FROM SOLID SAMPLES
(POLIMERS, ADHESIVES) BY DISCONTINUOUS GAS EXTRACTION COUPLED
WITH GC-FID AND GC-MS TANDEM**

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The discontinuous gas extraction (DGE) method has been developed for the qualitative and quantitative analysis of volatile compounds in solid samples_{1,4}. In the DGE method a glass tube of special construction, containing the solid sample (0.2-1 g) was introduced in a thermostated extractor (50-200 °C). After an equilibration time (10-30 minutes), depending on the state of the sample, the trace volatiles from the solid sample (polymer, adhesive, etc.) were eluted by the carrier gas (H₂, N₂) in the separation column of a gas chromatograph by switching a bypass in open position during a few seconds. After a new solid-gas equilibration, the extraction tube was again eluted. In this way some peaks on the chromatogram for each volatile component were obtained, having exponentially decreasing areas. The logarithm of the peak area as a function of the equilibria numbers was represented; a straight line was obtained which is extrapolated at the zero ordinate value. By a graphical or Kolb-Pospisil method (Eq. 1) the total area S, corresponding to the total amount of each volatile component was calculated. The volatile component of interest is quantitatively determined by calibration with an external standard in the same chromatographic conditions. When it was necessary a GC-MS tandem was used for the identification of the unknown volatiles by means of the NIST or NBS mass spectra libraries. With this gas extractor device of proper construction coupled with Carlo Erba 2450 GC-FID or Perkin Elmer Clarus 500 GC-MS tandem, the toxic volatiles components in some adhesives were determined at the trace level: acetic acid, cyano-, ethyl ester, isocyanic acid, methyl ester and vinyl acetate in polyvinylacetate.

$$S = \frac{e^{1/2 \ln(A*B) + 1/4 (A*B)/(C*D)}}{1 - e^{-1/4 \ln(A*B)/(C*D)}} \quad (\text{Eq. 1})$$

where A, B, C, D were the first four exponentially decreasing areas of a volatile compound in chromatogram.

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Determination of volatiles in low density polyethylene and in APPC polymers

THE CONTRIBUTION OF THE VOLATILE ORGANIC COMPOUNDS EMISSIONS TO THE ENVIRONMENTAL IMPACT

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The nature protection, its natural resources, biological diversity and the defining ecological structures, is a national, economic, social and human interest concern, with crucial role in the sustainable development strategy of the company.

This paper deals with issues related to the role and the influence of volatile organic compounds on the environment and human health. It is also approached the issue of installations and activities that use organic solvents and the compliance with the Directive 2010/75 / EU regarding Industrial Emissions (IED), transposed into national law by Law 278/2013.

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APPLICATION OF SODIUM ALUMINATE RECOVERED FROM INDUSTRIAL PROCESSES AS COAGULANT FOR THE TREATMENT OF BIOLOGICAL SLUDGE

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Bauxite is the raw material for alumina fabrication. Liquid and solid wastes are generated in the industrial processes and some of them can be converted into useful products such as inorganic coagulants based on sodium aluminate¹²³.

Food industry is a pollution source despite the high level of raw materials processing which is achieved in present modern factories, including dairy factories.

Commonly, each dairy factory has a wastewater treatment plant which produces treated water, according to quality discharging limits, but also biological sludge which has to be processed (dewatered, stabilized) before controlled disposal or agriculture purposes.

Coagulation treatment step of the biological sludge is one of efficient and less expensive method to separate (after settling, filtration or centrifugation) and to stabilize the solid phase of the sludge^{4, 5}.

The effect of recovered sodium aluminate to the treatment efficiency of biological sludge from the wastewater treatment plant of dairy factory was investigated.

Sludge conditioning tests were performed with, without lime adding, and for three different flocculants. Compliance with quality standard for harmless waste of the treated sludge was the aim of experimental tests. Leaching tests were performed in order to establish this.

Recovered coagulant and lime doses were the crucial parameters in order to have DOC (dissolved organic carbon) leachate concentration below 800 mg/kg d.w. (Romanian limit for disposal into harmless waste landfill).

Sodium aluminate, which was recovered inside of Romanian alumina factory, proved to be a good conditioning sludge reagent. After the treatment flow the dried substance content increase 20 times, the volume is reduce with 80% after one hour and the smell is disappearing.

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VALUE NORMALISATION FOR POLLUTANTS CONCENTRATION IN GASEOUS EFFLUENTS

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From the perspective of environmental protection, the most important area of human activities is the industry. Industrial development had in mind that the actual progress of human society depends, not only on the goods they offer, but also the environmental damage

Electricity is a clean form but often, its production is based on fossil fuel combustion processes.

As a result of these processes are large quantities are released into the surrounding atmosphere of carbon monoxide, carbon dioxide, oxides of sulfur, oxides of nitrogen (NO/NO₂), unburned hydrocarbons, volatile salts (chlorides, fluorides, sulphates) and water vapor.

Currently, the share of solid fuels used for electricity production is still large thermal power plants has become a major source of environmental pollution

Through chimneys, power plants emit into the atmosphere continuously and consistently huge volume of flue gas containing gaseous pollutants and particulate concentrations. As a result, justifiably classic conventional boiler power plants are considered significant anthropogenic emission stationary sources. At Member State level, the National Emissions Ceilings Directive (NEC Directive) imposes emission ceilings (or limits) for emissions of four main pollutants of air (nitrogen oxides, sulfur dioxide, non-methane volatile organic compounds and ammonia) which harm human health and the environment. Control of emissions from large combustion plants¹ (with rated thermal input equal to or greater than 50 MW) plays an important role in the EU's efforts to combat air pollution.

Large combustion plant operators are required, under GD no. 541/2003, Art. 17, to monitoring the emissions of particulates, sulfur dioxide and nitrogen oxides.

Measurement method of gaseous components from industrial emissions used by NIRD INSEMEX is the direct method with Multigaz unit.

The concentration of pollutants discharged from large combustion plants are calculus of the mass of pollutant measured in volumes of flue gas. Measured values are reported at standard humidity condition to normalize the obtained values.

¹ www.minind.ro / strategia energetică a româniei pentru perioada 2007 - 2020]

QUALITY ASSURANCE FOR EMISSION MONITORING PERFORMED WITH AUTOMATED MEASUREMENT SYSTEMS

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Abstract

Current trends in environmental requirements impose continuous monitoring of air emissions for most industrial units that carry processes with considerable pollutant emission.¹ The monitoring is realized with automatic monitoring systems (SAM), which generate and store continuous emissions data for specific pollutants and must ensure the quality of the results.

According with SR EN 1481/20013, three different levels of quality assurance (QAL1, QAL2, QAL3) are used for measurements performed with SAM. The most important and complex quality assurance level is QAL2.

QAL2 represents a procedure for determining the calibration function and its validity and a variability test for the values measured with SAM compared to the uncertainty allowed by environmental legislation. A calibration function is determined from the results of a number of parallel measurements made with a standardized reference method (MRS).² QAL2 must be realized after the installation of any SAM and after major changes in the operation of the plant³.

This paper presents a case study conducted at a large combustion plant that monitors the total particulate emissions with a SAM. In order to realize the SAM validation we used the QAL2 report methodology which cover the equipment installation, its calibration using parallel measurements with MRS, SAM variability determination and verification of the required uncertainty.

Key words: QAL2, SAM, MRS, particulate matter, large combustion plants;

¹ISO 6879 SR ISO 6879:2004 – Air quality. Performance characteristics and concepts regarding different methods of air quality monitoring;

²SR EN 14181 - November 2003 – Quality assurance of automated measuring systems;

³ISO 9169 SR ISO 9169:2004 - Determination of performance characteristics for monitoring methods.

**EXPERIMENTAL RESEARCHES REGARDING THE COMPLEX
VALORIFICATION OF PHOSPHATIC RAW MATERIALS IN THE
NITROPHOSPHATES INDUSTRY**

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The goal of these experiments was the obtaining of a technology for phosphoric acid synthesis, using the reaction of nitric acid with phosphatic rocks, simultaneously with the complex valorification of the phosphatic raw materials.

The obtaining of phosphoric acid – an intermediary in the synthesis of phosphoric salts – by using the nitric acid attack over phosphatic rocks competes with the obtaining of phosphoric acid by the wet route – the dihydrate process, based on the attack of sulphuric acid over phosphatic rocks – if the nitric acid resulted from the proposed process is recirculated resulting a nitric acid „closed cycle” and the byproducts – fluorosilicic acid, calcium nitrate, rare earths – can be capitalized as fluorine compounds, calcium phosphates and rare earths. Simultaneously, the phosphoric acid obtained by this process can replace the phosphoric acid used in the synthesis of technical phosphoric salts that are necessary to various sectors belonging to the economy and to the fertilizers industry.^{1,2}

The collapse of the activity on various industrial platforms belonging to the fertilizers industry in Romania led to cessation of sodium phosphates, calcium and ammonium phosphates, metallic surface treatment salts production, all these salts being presently imported. It's obvious that by using this technology at an industrial scale, various phosphoric technical salts can be produced that can be used in agriculture, zootechnics, the textile industry, detergents industry, food industry or pharmaceuticals.

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YOU KNOW THE CONTENT OF BATHING WATERS

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This paper aims to determine the chemical elements and characterization of five waters , collected in the summer of 2014 , used mainly in annual leaves bathing, namely:

1. Drinking water Bucharest (Ferentari, District 5) , which is also in swimming pools
2. Water in pools Felix - Cordău (source F2), county Bihor
3. Black Sea area Năvodari, county Constan□a
4. Egeos Sea , south-east Thasos , Greece
5. Lake Techirghiol , Eforie South, county Constanta

Were determined 24 chemical elements at the same time, without special processing or separation, by Optical Emission Spectrometry with Inductively Coupled Plasma (ICP - OES) after dilutions were made (10, 100, 1000 and 10000 times), and acidified with 1% HNO₃. Dilutions were required to spectral interference reduction and framing in the optimum measuring range of the method, from 0.2 to 5.5 mg/l. Has also been determined: pH, density and by evaporation bath, the total dissolved salts (TDS).

	Na g/l	Mg g/l	K g/l	Ca g/l	S g/l	TDS g/l	d g/ml	pH
1 Bucure□ti	0.010	0.0046	0.0025	0.038	0.011	0.157	0.9990	6.0
2 Băile Felix	0.018	0.018	0.0041	0.122	0.025	0.432	1.0010	6.1
3 M. Neagră	4.70	0.57	0.172	0.23	0.51	16.0	1.0100	6.3
4 M. Egee	9.75	1.25	0.36	0.40	0.96	34.5	1.0245	6.4
5 Techirghiol	25.3	3.25	0.71	0.26	3.50	86.0	1.0570	7.6

Values less than 0.0002 g/l was obtained for the elements: Al, Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Sb, Ti, Zn and Zr . Small values of B and Sr were determined ascending in the last three waters. Very small values of Si, P and Pb found in some water must be reconfirmed.

ICP-OES spectrometer is from the company Agilent Technologies, model 725 simultaneously, with radial view, between 167–785nm, he can analyze 73 chemical elements.

APPLICATION OF THE MACROPOROUS ION EXCHANGE RESIN OF VARIOUS TYPES IN DYES REMOVAL FROM INDUSTRIAL WASTEWATER

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Synthetic azo dyes are extensively used in textile dyeing, paper, colour photography, printing, pharmaceuticals, cosmetics and other industries. Approximately 10-15% of the dyes are released into the environment during manufacture and usage and are major sources for polluting the water resources. Dyeing process is a significant consumer of water and producer of huge contaminated aqueous waste streams. The majority of synthetic dyes are considered as recalcitrant xenobiotic compounds due to the presence of an N=N bond and groups such as aromatic rings that are not easily degraded.

The discharge of these colored compounds into the effluents causes considerable environmental pollution by eutrophication of aquatic ecosystem and serious health -risks factors by bioaccumulation.

Therefore, decolorization of dyes is another important aspect of wastewater treatment before discharge into environment. There are several methods for dye removal: coagulation-flocculation, oxidation-ozonation, biological treatment, membrane technologies and **adsorption techniques**.

Materials and methods. In the research from this project we proposed a method for decolorization of the industrial wastewater using macroporous adsorbents type ion exchange resin -IER. The removal of anions and cations from industry effluents containing dyes can be carried out **by ion exchange method**, by passing the wastewater through the column with beds of IER.

In the research were taken to study the following IER- PUROLITE type: **strongly basic anion and free base form of weak basic anion** exchanger and strongly acid cation exchanger.

- ◆ The studied wastewater contained **acid, direct and reactive anionic azo dyes**: an **acid blau dye, direct dyes** [Solophenyl Violet BL and Brilliant Grun 2GL, Solar Blau 2GL] and **pyrimidine reactive dyes** [Drimarene Rot HF-6BL, Orange HF-2GL, Blau X-3LR].
- ◆ The experimental study followed the identification and characterization the **analytical methods for the determinations of various quality parameters** of colored wastewater and decolored wastewater: pH, solid-total, conductivity, chlorides, sulphates, total nitrogen, chemical oxygen demand –COD, turbidity and colour.

Results

- This study shows that the strongly base anion exchanger with macroporous structure containing tertiary amine functionalized on the polystyrene crosslinked with DVB matrix can find practical application in **total removal of colour from the wastewater** containing anionic azo dyes.
- The discoloration performance of IER is illustrated by the percentage of quality para-meters of treated wastewater: **remove of 50% solid-total, 87-96% sulphates and 91% COD.**

**CLEAN METHOD OF OBTAINING OLIGOESTER-POLYOLS FOR
THERMOINSULATING RIGID POLYURETHANE FOAMS FROM PET WASTES**
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"Clean technologies" are, according to Clean Edge¹, "processes that dramatically reduce the use of natural resources, and cut or eliminate emissions and wastes". In this spirit, polyethylene terephthalate (PET) recycling induces a great interest, for conservation of oil resources, reduction of greenhouse effect and energy preservation². Chemical recycling is the most acceptable technique according to sustainable development principles, because it can lead to formation of monomers from which the polymer was originally made, but has, as well, the potential to generate value-added products, with targeted properties³.

Oligoester-polyols were prepared by a “clean” method, consisting in PET glycolysis with various diols, followed by mono-esterification of the products with phthalic anhydride and propoxylation. Both mono-esterification and propoxylation processes occur under relatively mild conditions, leading to energy savings and no by-product or waste result from the processes, in contrast with conventional similar technologies of PET recycling⁴. Physico-chemical, gas chromatographic, HPLC and NMR investigations, as well as testing the products in rigid polyurethane foams formulations, revealed that their chemical composition was fully suitable for reaction with di-isocyanates, in order to form polyurethane rigid foams with excellent physico-mechanical and flame retardant properties.

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THE IMPACT OF SOME INSECTICIDES UPON PHYSIOLOGICAL PARAMETERS IN TWO FISH SPECIES (*PERCA FLUVIATILIS* L AND *ALBURNUS ALBURNUS* L)

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Pesticides derived from chemical syntheses are the best examples of risky compounds because they spread all over the environment. This paper aims to investigate the changes of some important physiological indices (energy metabolism, respiratory rate, number of erythrocytes, blood glucose level, survival) in two common species found in the Arges River (*Perca fluviatilis* Linnaeus 1758 and *Alburnus alburnus* Linnaeus 1758), exposed to the action of two insecticides (Reldan 40 EC and Actara 25 WG) under different conditions (0.064 and 0.128 mg Reldan 40 EC/ l water; 0.01 and 0.02 ml Actara 25 WG/ l water). The choice of these species is based on the fact that they are widely spread and can be well preserved in laboratory conditions. The results were interpreted statistically using the SPSS 13.0 programme for Windows, in accordance with the specialised studies.

Each experimental sample (one for each product, plus a control sample) had two subsamples, corresponding to the two fish species under study. The products were investigated using two different concentrations at two temperature levels (18-20°C and 6-8 °C). Fish adaptation to laboratory conditions was monitored for two weeks. We used glass aquariums with a capacity of 100 l under natural photoperiodic conditions. The amount of dissolved oxygen in the water samples was not lower than 80% of the maximum possible at the respective temperature and pressure. Feeding during this period was “*ad libitum*” once a day, at around 10 o’clock; during the experiments fish were not fed, to avoid the additional influence of the food factor, thus allowing a better interpretation and comparison of results.

The experimental samples were used to test for the presence of respiratory and hematological changes in perch and bleak adapted to different temperatures (18-20°C and 6-8 °C) and revealed differences in the reactivity of the two species to changing environmental conditions.

The two insecticides tested had a similar effect on the oxygen consumption of the species, translated into a stimulating phase, particularly for samples adapted to room temperature with variable length, usually in inverse proportion to the concentration, followed by a slower reduction period or stabilization of the physiological index.

REMOVAL OF AZO DYES FROM AQUEOUS SOLUTIONS USING CYCLODEXTRIN BASED POLYMERS

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Synthetic dyes are common water pollutants and due to their good solubility they may frequently be found in trace quantities in industrial wastewater. Many of these dyes are also toxic and even carcinogenic and these pose a serious hazard to aquatic living organisms. Decomposition byproducts of these dyes which caused by different factors are responsible for harmful effect on humans and environment in general.

Various chemical and physical processes are currently in use for the removal of dyes by conventional treatment technologies including biological and chemical oxidation, chemical coagulation, foam flotation, electrolysis, biodegradation, advanced oxidation, photocatalysis and adsorption processes as discussed in the present reports. However, among all the techniques solid-phase extraction (SPE) using sorbents is one of the most efficient and popular methods for the removal of organic compounds from wastewater. The sorbents may be of mineral or organic origin such as: silica, activated carbon, zeolites, different resins, gels, chitosan and β -cyclodextrin are significant examples.

β -cyclodextrin (β -CD)-based polymers were synthesized as sorbents for the removal of azo dyes Acid Red 88 and Acid Yellow 14 from aqueous solutions. The sorption experiments were carried out by using batch-wise procedure involving the determination of pH effect, sorbate concentration and contact time. The equation isotherms such as Langmuir and Freundlich were successfully applied to model the experimental data.

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RESEARCHES ON THE INFLUENCE OF METYL THIOPHANATE ON THE PLANTLETS OF *CAPSICUM ANNUUM* L.

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The influence of a fungicide which contains 70% metyl thiophanate (T) on the *Capsicum annuum* L. plantlets growth, has been studied by applying them in the seed stage. The following concentrations of fungicide were applied: 0.1% (V1T), 0.25% (V2T), 0.5% (V3T) and 1% (V4T). The seeds were hydrated for one hour, 10 seeds for each variant, and they were subsequently immersed into the fungicide for one hour. The seeds, thus treated, were laid to germinate in Petri boxes. The culture vessels were closed with cover, sealed with Parafilm, and placed in the growth room at 25°C during the day and 15°C during night, under a 16-hour photoperiod (8 hours of darkness). In order to determine the longwise growth of the plantlets (roots and stems), they were periodically measured, and the arithmetic mean value was calculated for each variant. The measurements conducted to determine the length of the roots and stems (8, 15 and 29 days from the inception of the experiment) indicate the fact that the fungicide stimulates growth, in nearly all the experimental variants (excepting roots growth at 8 day) (Fig. 1, Fig. 2). The results obtained agreed with the physiological effect of the cytokinetic type exerted by the metyl thiophanate and its main metabolite, carbendazyme (Huțanu-Bashtawi et al., 2008; Soare et al., 2010), to stimulate seedlings growth.

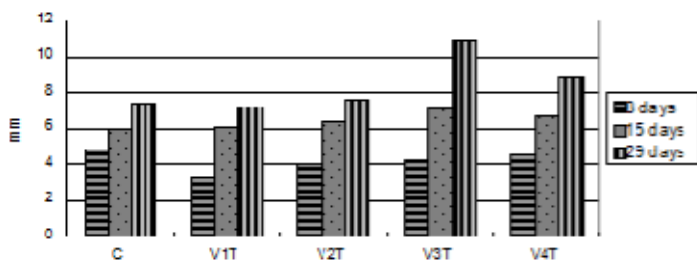


Fig.1 The influence of metyl thiophanate on the *Capsicum annuum* roots growths.

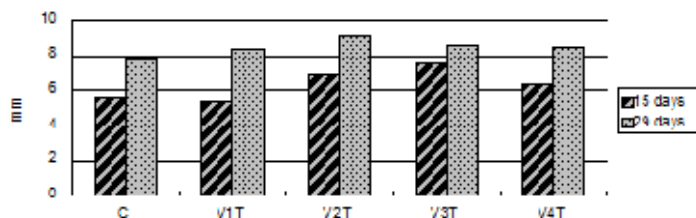


Fig.2 The influence of metyl thiophanate on the *Capsicum annuum* stems growths.

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THE USE OF NATURAL EXTRACTS FOR THE SYNTHESIS OF NOBLE METAL NANOPARTICLES

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Over time, noble metals have been tested for the biosynthetic process assisted by plants (using different spontaneous flora), in order to obtain metallic nanoparticles with control over shape and size. Metallic nanoparticles obtained by biosynthesis using plants can be noble metals nanoparticles (gold, silver, palladium, etc) or common metallic nanoparticles, like copper; also, plants can be used in alcoholic extracts, aqueous extracts or hydroalcoholic extracts, obtaining different compositions, sizes, shapes and controlled polydispersity.

In the present work, we will focus on our experience regarding the field of green chemistry, presenting some of our results in the field of nanomaterials phytosynthesis, using extracts obtained from different native plants (*Caledula Officinalis*, *Rosmarinus Officinalis*, *Zantedeschia aethiopiea*). The potential ability of these plants for the bioreduction of Ag^+ to Ag^0 was investigated by spectral methods (UV-VIS, FTIR, SEM, XRF). The antioxidant property was determined using DPPH method.

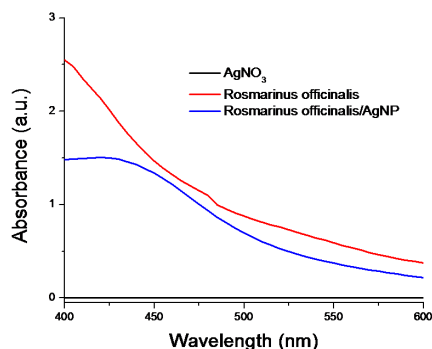


Fig.1 The UV–VIS spectra of AgNO_3 , rosemary extract and AgNPs in rosemary extract

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EFFECT OF ADDITIVES ON THE MELT PROCESSING AND PROPERTIES OF POLYHYDROXYALKANOATES

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Polymers from renewable resources have become interesting topics due to environmental concerns and the depletion of oil resources. Polyhydroxyalkanoates (PHA) are linear polyesters produced in large quantities from renewable resources by several bacteria. They have a regular structure and show thermoplastic properties, are resistant to water and are fully biodegradable.¹ Strong barriers for their large application are the poor mechanical properties and low thermal stability compared to synthetic polymers. Different additives were tested to improve their mechanical and thermal behavior.²⁻⁴

Considering that further progress in application of PHA is mainly conditioned by the smart choice of additives and innovations in the manufacturing process different additives and manufacturing routes were applied in our laboratory. Epoxidised soybean oil, polyethylene glycol with different molecular weights and citrate esters were tested to improve the melt processing of polyhydroxybutyrate and poly(hydroxybutyrate-co-valerate). Cellulose nano and micro reinforcements were also tested for diminishing brittleness. FTIR, DSC – TGA, AFM and mechanical testes were performed to establish the optimal conditions. The results have shown that small amount of bacterial cellulose is efficient for improving both processing and mechanical behavior of PHA without significant changes in thermal stability.

Acknowledgement

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REMOVAL OF COPPER (II) FROM AQUEOUS SOLUTIONS WITH DIFFERENT TYPES OF BIOCHAR PRODUCED FROM BIOMASS

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Since in the last decade wastewater are being generated in increasing amounts due to the rapid urbanization and industrialization, a growing interest has been devoted in developing cost effective and renewable disposal alternatives for their treatment. Among them, the manufacture of adsorbents to remove metal ions from water and wastewater appears to be promising, also considering the high cost of commercial adsorbents. In this paper sorption of copper from wastewater using biochar, pyrolytically derived, produced from various raw materials, namely from nuts shell, corn cob, strings grape, and waste from the beer manufacturing was studied. Biochar obtained from nuts shell, strings grape and corn cob are predominantly microporous and this characteristic enhance the adsorption process of heavy metal ions from wastewater ¹. The influence of pH, adsorbent type and concentration, initial Cu^{2+} concentration and contact time of the removal process were investigated ². Equilibrium isotherms were obtained for the sorption of this metal in single system solution. The equilibrium isotherms, for the sorption of copper, were analysed using 2 widely used isotherm models (Langmuir and Freundlich models) and their constants were evaluated at initial copper concentrations between 40 and 100 mg / L ³. Langmuir and Freundlich isotherms established for various initial copper concentrations, for different doses of adsorbent material and for a range of values, were used to fit the equilibrium data ^{4,5}. The equilibrium data were analysed using different error analysis equations using the linear correlation coefficients (r^2). Adsorption process was found to be highly pH and initial concentration of pollutant dependent. The optimum pH range for adsorption of Cu^{2+} was found to be between 4.5 and 5, with sorption yield over 70%. The goal for this work is to develop inexpensive, highly available, effective adsorbents from other types of biomass that are most common.

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LOW MIGRATION PLASTICIZERS FOR PVC, FROM POLYETHYLENE TEREPHTHALATE (PET) WASTES

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Chemical recycling involves the cleavage of PET polymer chain, usually by means of solvolysis, leading either to monomers or to oligomers¹. The degradative transesterification of PET may be realized, inter alia, with long-chain aliphatic alcohols. The products were found to be promising for use as plasticizers for PVC², in order to replace the common di-octyl phthalate (DOF), banned from use by EU in the last decade, especially in toys or childcare articles and food packaging³.

This study presents the results concerning a flexible synthesis procedure of some oligoester plasticizers for PVC with tuned chemical structures and molecular weights, as well as performance properties, from scrap PET as raw material. PET wastes were depolymerized with long chain alcohols, and the products further modified with some aliphatic or aromatic di- or tri- carboxylic acids or derivatives. Physico-chemical, FTIR, TLC, NMR, GPC and DSC-TGA investigations revealed that the chemical structures, compositions and properties of the products were appropriate for use as plasticizers for PVC. The oligoesters were tested as plasticizers in PVC processing; the physico-mechanical characteristics of the PVC samples were similar or superior to those of control sample containing DOF, and the loss of plasticizer was lower.

The financial support of UEFISCDI (PNII-PCCA-2013-4-1388 - contract No. 61/ 2014 - PERCIT) is gratefully acknowledged.

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FLUID DYNAMICS PHENOMENA SIMULATION IN FILTER-VENTILATION AND ACCESS AREAS

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Abstract

The quality of the air introduced in protected buildings mainly depends on the characteristics and the parameters of the fluid movement through the filter-venting systems. Safe, efficient and long-term functioning of the filter-ventilation systems may be assured through optimization of the air stream flow in the filtration chambers. The best way to achieve a reproducible analysis and an optimization of the air stream is to use numerical simulation¹.

In this regard, the target of the present study was to analyze the fluid dynamics phenomena that occur in the filtration chambers, in various constructive configurations, and to build an improved functional model for the air filter from the filter-ventilation systems², through numerical simulation and design.

Several models were achieved, in Fig. 1 being presented a discretization model for the optimized constructive variant.

The optimization of the materials employed for the filters was studied, such as the porosity and density, in order to achieve the best filter-ventilation system for secured areas.

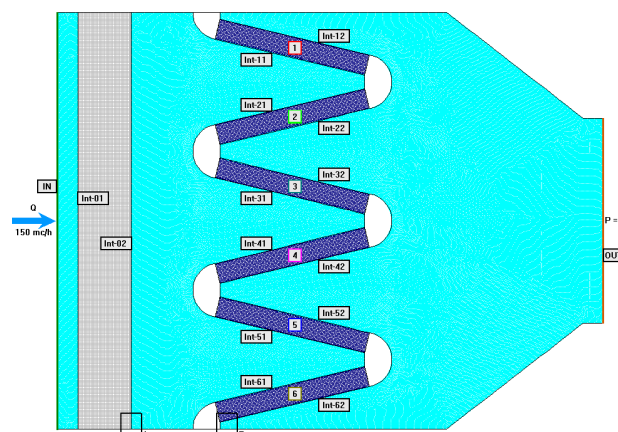


Fig. 1 – Discretized model with cells for the air filter

Further, the study simulated real conditions for checking the protection against CBRN agents, vapors or aerosols.

Acknowledgements

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STUDIES OF ALKALI REMOVAL APPLIED TO LOW-ALKALINE BAYER RED MUD PRODUCTION, USING CO₂-SORPTION NEUTRALIZATION AGENT. GREEN COMBINATION FOR PREPARING FOAMS

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Approximately 0.8-1.5 tons of red mud residue, strongly alkaline (pH>11.0) is generated for production of 1 ton of alumina from aluminium refinery plant of the world ^{1, 2}. This strong alkaline character of red mud restricts the disposal conditions and their applicability in order to minimize environmental problems such as soil contamination and ground water pollution ^{2,3,4}.

In this work, a simple and scalable process was developed to prepare red mud precursors foams with low-alkaline content. Kinetic studies have been carried out on the removal of Na(I) by CO₂-sorption neutralization agent. This study considers alkali removal by CO₂-sorption kinetics on a promising acid treated alkaline and DSP (desilication products) sorbents process. The experiments were performed in batch mode, and the alkali removal process has been investigated as a function of Na(I) concentration, contact time, temperature and pressure. The morphology and the physico-chemical properties of red mud precursors were tuned as a function of the chemical nature of the cations varying with the age of the red mud (between 6 to 12 years). It was found that a Langmuir model is the best to describe the alkali removal from red mud. The temperature, contact time between CO₂ bubbles and reaction environment are parameters relevant to the decrease by half the Na₂O content and pH (~6.5-7.3) from the initial red mud. On this basis, it is speculated that the alkali removal rate over the acid treated porous DSP in red mud is dominated by a surface reaction and the reaction mechanism was governed by a combination of chemical reaction and CO₂ diffusion on solid surface. The samples were characterized using different analytical techniques including X-ray diffraction, N₂ adsorption isotherm analysis (BET) and Scanning Electron Microscopy-X-ray Energy Dispersive Spectroscopy (SEM-EDX) in order to detect composition, crystalline phases and morphology.

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NEW POSSIBILITIES FOR USE OF THE CROSS-LINKED POLYMERS

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Heavy metal pollution is one of the most important environmental issues, particularly with regard to water contamination.¹ The present work was aimed at highlighting the ability of using crosslinked-polymers in the adsorption process (carried out as a potential alternative for heavy metal ions removal) and at investigating the optimal conditions for copper adsorption.^{2,3}

The polymer used in the present study, maltodextrin, was crosslinked with a tricarboxylic acid, namely citric acid, using sodium hypophosphite as catalyst. The obtained crosslinked polymer was characterised using different techniques including Fourier Transform Infrared spectroscopy (FTIR), Differential Scanning Calorimetry (DSC), Scanning Electron Microscopy (SEM).

The paper presents optimal conditions for the adsorption of copper from sulphate medium. It has been studied the efficiency of that metal ion adsorption at different values of adsorption parameters (pH, contact time, concentration of the solution, thus achieving the kinetics and adsorption isotherms). The optimum pH range for Cu²⁺ adsorption was found to be around 5. The optimum contact time was about 2 hours and the solution concentration was 0.1 g/L. For copper sorption, the equilibrium isotherms were analyzed using Langmuir and Freundlich models.⁴

Copper ion retention efficiency on the cross-linked polymer about 90%.

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**PRODUCTION, CHARACTERIZATION AND APPLICATION OF NANOSIZED IRON
OXIDE IN METALURGICAL AND MINING INDUSTRY**

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Iron oxides whose characteristic dimensions are between 1 nm and 100 nm have size-dependent properties. This presents a great scientific interest because with size decreasing of an adsorbent material adsorption processes intensifies due to high specific surface. The purpose of this paper is to remove metal ions from wastewater with iron nanoxides with magnetic proprieties obtained by coprecipitation of both pure substances and secondary metal materials. The synthesis method used to obtain nanomaterials, was customized by modifying working conditions on pressure and temperature, this method is reproducible and does not involve complicated purification processes can be widely used^{1,2}. Following microstructural characterization of nanopowders after iron oxides showed no major differences in terms of their characteristics depending on the raw materials used³. General aspects are arising from the interpretation of microstructure analysed samples by Transmission Electron Microscopy Images Brightfield (TEMBF). Phase-composition was analysed by Analysis of Selected Area Electron Diffraction (SAED), crystallinity evaluation was performed using High-Resolution Microscopy (HRTEM) and crystallite size was performed by X-ray diffraction. The study was conducted on the nanomagnetite surface adsorption capacity of Cu²⁺ ion from sulphate solutions at different pH values, different concentrations of Cu²⁺ ion and different adsorbent material / waste water report. The data resulting from the optimization of the process parameters were used in determining the mechanism of adsorption resulted in achieving equilibrium isotherms using Langmuir and Freundlich⁴.

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EFFECT OF SURFACE TREATMENT IN POLYPROPYLENE – HEMP FIBERS COMPOSITES

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Polymer composites with hemp fibers are increasingly considered as a viable alternative to glass fiber reinforced polymer composites in auto industry. This arises mainly from the advantages of hemp fibers such as biodegradability, low density, specific mechanical properties comparable to those of glass fibers, reduced tool wear, and cheapness¹⁻³. Moreover, they are obtained from renewable resources in practical unlimited quantity as compared with glass or carbon fibers. Further progress in application of hemp fibers polymer composites in industry is mainly conditioned by the pre-treatment of fibers and the manufacturing process.

Several treatments were applied to hemp fibers and their efficiency in surface modification of fibers and in the improvement of mechanical and thermal properties of polypropylene/hemp fibers composites was studied. Part of our results were shown in this presentation. FTIR spectra of treated and untreated hemp fibers showed the reduction in free hydroxyl groups and absorbed water after treatment. TGA-DTG results showed that silanes have favorable effect on the thermal stability of hemp fibers. Some silane and potassium permanganate treatments led to double tensile modulus in polypropylene composites with 40 wt% hemp fibers and to the increase of storage modulus with more than 50%. Treatments which led to the best mechanical properties were selected for up-scaling polypropylene-hemp fibers composites.

Acknowledgement

This work is supported by the FP7 EVOLUTION project.

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**RESEARCHES REGARDING THE INFLUENCE OF MINING WASTE DEPOSITS
ON THE DEGREE OF POLLUTION OF MURES RIVER AQUIFERS AND
RELATED BIOLOGICAL ENVIRONMENTS FROM HUNEDOARA COUNTY DUE
TO DRAINAGE OF THE MINING WATERS**

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Mining specific activities are one of the main economic sectors of Hunedoara county, since hundreds of years ago. Tailings dams and waste dumps resulting from ore processing tailings deposition obtained in preparation plants are relatively large, sometimes altering fundamentally the zonal morphology and by the content of pollutants represent important factors and sources of air, water and soil pollution by various toxins: suspensions, flotation reagents by metal ions, etc.

The purpose of this paper is to evaluate the effects of mining waste deposits in Hunedoara County in terms of pollution on water quality and biological environments of the Mureş river. For the study of the degree and effects of pollution were collected and analyzed water samples from the Mures river, solid samples (sediment) and biological samples from the creek Certej and Deva Valley which collects water from the tailings related. Determinations were carried out regarding the pH and the conductivity and heavy metals concentrations by optical emission spectrometry with inductively coupled plasma.

Following the undertaken research were obtained information regarding the degree of pollution of rivers in Hunedoara County, and of border watercourses, located in the adjacent mining areas, studying the effects of mining waste on the environment. Pollution effects on water, soil and air last long time even after the operation in question ends. Greening the mining and adjacent areas help improve the quality of life being an essential condition for sustainable development.

Keywords: mining water, heavy metal, bioaccumulation, acid water drainage, tailing dams

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**DATA CONCERNING ESTABLISHING THE ECOLOGICAL STATUS OF THE
ABRUD RIVER CATCHMENT AREA USING BIOINDICATORS (ROSIA
MONTANA, ROMANIA)**

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This preliminary study presents data on the ecological status of the watershed of Abrud River, a small watercourse in Apuseni Mountains (Romania) heavily affected by mining related pollution. Sixteen sites have been sampled seasonal on Abrud River and its main tributaries.

It was observed a large quantity of organic matter, originating from untreated urban water, that together with the high concentrations of NO_3^- , draw attention on the mediocre quality of water. Moreover, the values of the measured physical and chemical parameters (i.e. pH, salinity, conductivity, O_2) and the concentrations of SO_4^{2-} , Fe, Pb, Ni, Cu, Cd and Zn also indicates quality alterations caused by the mining waters flowing into some tributaries and the river.

Also, it was observed the structure of the communities of benthic diatoms from the same sampling sites. The best represented diatom genera were *Navicula*, *Nitzschia*, *Cymbella*, *Gomphonema* and *Fragilaria*. Qualitatively, the number of diatom species exhibited significant variation among sampling sites, also suggesting seasonal dynamics. For instance, in some sampling sites, algal assemblages were absent, as diatom communities were strongly affected by acid mine waters, released from old mining works and waste rocks depots. In conclusion, the diatom data are according chemical ones, some dominant taxa suggesting also a large quantity of organic matter in the water.

The preliminary studies concerning the determination of microorganisms communities existing in samples harvested from the control sites on the Abrud River and its main tributaries, revealed the presence of the main groups of microorganisms involved in the biogeochemical cycles of C, N, Fe and S elements and the absence of pathogenic bacteria such as, total and faecal coliforms and faecal streptococci. The heterotrophic bacteria strains obtained which are high adapted to the heavy metals present in the investigated habitats could be used as new microorganisms in the bioremediation processes of this water resource in future studies.

Acknowledgements: This work was supported by a grant of the Romanian National Authority for Scientific Research, CCCDI – UEFISCDI, project number 3-005 SUSMIN.

INNOVATIVE SOLUTIONS INTENDED TO INCREASE ENERGY EFFICIENCY IN BUILDINGS AND INDUSTRIAL EQUIPMENT BY USING BIODEGRADABLE THERMAL INSULATING COMPOSITE MATERIALS

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There is a focus today on energy efficiency and global warming. The European Union has decided to decrease the energy with 20% in 2020 and with 50% in 2050 compared to the energy use in 1990.¹ A large part of the energy use is related to heating of buildings and production of domestic hot water.² Conventional thermal insulation materials used in the building industry today, such as glass wool, rock wool, expanded polystyrene (EPS) and extruded polystyrene (XPS), require a thick building envelope to reach a sufficiently low thermal transmittance. EPS is the most cost effective insulation material for building and construction.³ However, its slow rate of decomposition causes numerous negative effects on people health and the environment.⁴ Many researches have been focused on materials from renewable resources and decreasing consumption of non-renewable resources having as result increasing revenue stream for producer of renewable resource, and decreasing the amount and cost of non-renewable material disposed of in landfills.⁵

The main objective of the project PN-II-PT-PCCA-2013-4-1709 (BIO-THERM), partners involved and their contributions, the end products and the expected results presentation are the aim of this paper. The overall goal of the project is to obtain new biodegradable thermal insulating composite materials and to innovatively use them in order to increase the industrial building and equipment energy efficiency. The project develops existing solutions for obtaining insulating materials made of foamed structures formed by fungi grown on lignocellulosic wastes through contributions that reduce the disadvantages of known solutions.

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ORIENTATION TOWARDS THE REAL NEEDS OF THE INDUSTRY - A MAJOR OBJECTIVE OF THE ACADEMIC SECTOR STRATEGY IN A RAPIDLY CHANGING WORLD

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The phenomenon of globalization and the financial crisis have led emergency rethinking relations in the triple helix academic – industry – government , with a focus on innovation, competitiveness and growth [1]. As a result, mainly in developed countries, the academic sector (universities, research institutes, foundations) has been mobilized to meet the needs of industry and society as a vector of change based on knowledge, contributing to the renewal of products and services, development of entrepreneurial skills and strengthen partnerships. Unfortunately, Romania has recorded modest position in the world rankings on innovation and competitiveness due to strategic errors by neglecting the consistency of the sector and, therefore, distanced from the integration of innovation with the economic and social policies as best practices [2-4]. Based on relevant data provided by the national study "*The technological resources management in the innovative firms*" (UPB-IMST 2014), this paper identifies the respondents opinions from the manufacturing industry in some key issues: (i) *the domestic R&D offer* (interest and barriers to collaboration), (ii) *the portfolio of products and services* (motivation and jams modernization), (iii) *anti-crisis solutions*, (iv) *the national innovation system benefits*, (v) *the entrepreneurial skills development*, (vi) *proposals to improve relations within the triple helix academic-industry-government*. A simultaneous restructuring of the industry and the academic sector, accompanied by a general change in mentality, means premises to relaunch Romanian society beyond the narrow horizon focused on corruption, untruth and non-values. Hopefully prediction come true.

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**ESTABLISH BY ICP – OES, CHEMICAL COMPOSITION
AND THICKNESS OF METAL LAYERS**

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The proposed method is based on the fact that the dissolution (mineralization) of a sample of metal, they start to the acid attack from the outside towards the sample to gradually over time and at a speed depending on the acid used , their concentration , the temperature of dissolution and do not finally by type of material. Thus if the acid attack is made in successive stages (stages 5-10) from short attacks, with dilute acids and finally longer and concentrated acids, and each step is collected in separate flasks , we have an accurate picture in the chemical elements present of the layers deposited (successively passed into solution), the thickness of the layers and material basis on which to make the deposit . Between attacks rinsed with distilled water sample was collected in volumetric flask. The sample can be weighed between stages of dissolution (after drying them), but if all the elements present is determined by adding their weight we can know the mass dissolved . The sample is weighed at the beginning and (if you do not want the full dissolution of the base) the final weigh after acid attack. Acid attack can be successfully used aqua regia. From stages spectrometric measurements can know the order of layers, the base composition and total content of each element. For determining the thickness of the layers is necessary to know the area of the sample subjected to dissolution (a sample or portion of sample is preferred, with known geometry). Knowing the existing quantity of each chemical found, knowing densities, calculate the volume occupied, then knowing the sample area dissolve, calculate the average thickness of the deposited layer, occupied by that chemical.

Optical emission spectrometer with inductively coupled plasma (ICP-OES) used is from the company Agilent Technologies, model 725, simultaneously, with radial view, between 167 – 785 nm, he can analyze 73 chemical elements, so all elements present in the deposited layers or in the core. It can be used FAAS technique. ICP -OES method proposed due to lowered detection limits can calculate the average thickness even below one micron (for precious metals). The method of determining the thickness of the layers was accompanied by optical microscopy measurements, which can be measured only by differentiation the layers by color, can not know the elements present and can not descend below a micron measurements. Determinations were made on coins, badges, jewelry, buckles etc. determining Zn , Ni , Au, Cu, Cr, Ag, Pt, Rh

**REVERSIBLE PHYSICAL INTERACTION BETWEEN CDSE QUANTUM DOTS AND
PERYLENEDIIMIDE (PDI) AGGREGATES IN AQUEOUS MEDIA**
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 DIACON Aurel ^a**

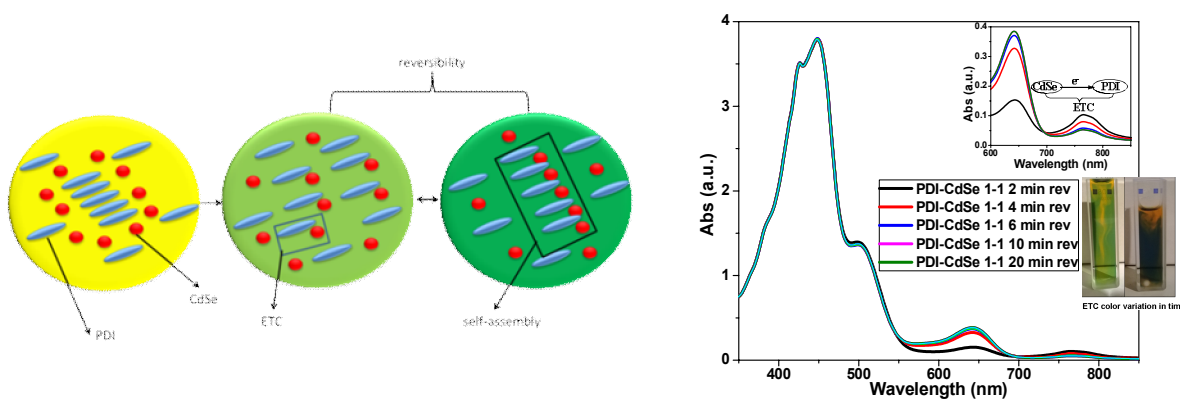
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The current research related to colloidal semiconductor quantum dots (QDs) has been focused mainly on their utilization either as optical markers in biological systems¹ or for the properties enhancement of optical materials in applications such as photovoltaic devices.² Special attention should be paid to each component energy levels and to the formation of QDs–dye assemblies in order to optimize the controlled processes such as photoinduced charge transfer³ or energy transfer.⁴

The aim of this study was the investigation of reversible physical interactions between CdSe quantum dots and a water soluble perylenediimide (PDI) derivative. Original processes, dependent on the concentration of the two species, contact time, temperature and pH, were observed. The combining of the two solutions resulted in the formation of an electron transfer complex (ETC) due to the transfer of an electron from the CdSe nanoparticles to the PDI, followed by the formation of the final particularly stable dianion PDI²⁻ species through another electron transfer process.



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THE INFLUENCE OF PLASMA CHEMICAL TREATMENTS ON THE ACTIVITY OF THE CATALYSTS

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The plasma chemical technology for obtaining catalysts with predictable properties is based on the character of plasma action on solids. Of special interest are low-temperature glow-discharge plasmas in gases (Ar, O₂, H₂, etc) and H₂O vapors. These plasmas can be successfully used to modify catalysts, adsorbents, carriers, and cements [1-3] without changing their initial structure. As distinct from the other types of gas discharges, glow-discharge treatment has several advantages.

Fairly large concentration of active particles can be obtained under milder conditions determined by the condition of plasma existence such as low pressures of plasma-forming gases (0.1 – 2 torr), low temperatures (373 – 673 K), and treatment duration from several seconds to dozens of minutes. The modification of the surface of catalysts and their regeneration under the action of a plasma causes the appearance of new surface structures, which increase activity, selectivity, and operation stability [4].

The purpose of this work was to study the influence of treatments of lithium chromium phosphate (Li₃Cr₂(PO₄)₃) in oxygen, hydrogen and argon plasmas on its catalytic activity in the isomerization of fermentation butanol.

As distinct from the samples treated in oxygen and hydrogen plasmas, the activity of the sample treated in argon changed substantially in repeated catalytic experiments shows that the yield of ketone decreased and that of butenes increased above 330°C, alcohol conversion also increased.

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THE COMPOSITES OF WASTE POLYPROPYLENE MODIFIED WITH STYRENE-ISOPRENE BLOCK-COPOLYMERS. THE MELT VISCOSITY EFFECT OF STYRENE-ISOPRENE BLOCK-COPOLYMERS

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The linear styrene-isoprene block-copolymers (SIS) were synthesized via anionic three stages sequential polymerization of monomers in cyclohexane solution initiated with n-butyllithium, by adding the next monomer only after the total consumption of the previous one. At the end of each reaction step, samples were removed from the polymerization reactor in order to determine the monomer conversion and the molecular mass of the constituent blocks.

The block copolymers molecular weight were determined by gel permeation chromatography (GPC) and were characterized by Fourier Transform Infrared Spectroscopy (FT-IR), mechanical properties, differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), thermogravimetric analysis (TGA), X-ray diffraction (XRD) and optical microscopy.

The waste polypropylene was modified in melt state with 5 – 30 % amount of linear styrene-isoprene block-copolymers with different molecular mass and the composites were physical-mechanical characterized.

The present research focuses especially on establishing the best properties, in particular the melt viscosity of linear styrene-isoprene block-copolymers which ensure the highest modified in melt state of waste polypropylene.

The main effect of modified waste polypropylene with linear styrene-isoprene block-copolymers consists in the obtaining the cheap composite materials which show high performance impact strength especially below 0°C, usual higher impact strengths (2-4 times higher) even than the virgin polypropylene from current production.

MULTIFUNCTIONALIZATION OF THE CROSS-LINKED IONIC POLYMERS CONTAINING STRONGLY BASIC GROUPS

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Many technologies of concentration, separation and purification of different types of water and gases are unthinkable without using of the ionic cross-linked polymers containing strongly basic groups. The largest quantity of these polymers, a high tonnage product of the chemical industry, is used to water treatment at thermoelectric and nuclear stations. The main function of these polymers is the ion exchange process. The biggest drawback of ionic crosslinked polymers containing strongly basic groups is the lack of selectivity of sorption of anions, especially the inorganic ones. The smart technologies require new materials with selective sorption and catalytic properties.

In our previous study^{1,2} it was shown that in the phase of strongly basic crosslinked ionic polymers can be synthesised inorganic compounds of some metals. The metal compounds in the polymer phase are in the form of ultrafine particles which are located both inside and on the surface of polymer beads. The inorganic compounds in the polymer phase are in the form of jarosite mineral type: $R_4N[M_3(OH)_6(SO_4)_2]$, where R_4N^+ are functional groups of the polymer.

In this paper are presented research results of functionality modification of strongly basic cross-linked ionic polymers, through the composites synthesis in their phase by ion-molecular constructions. Were obtained and investigated the composites AV-17(Fe), Varion-AD(Fe), AV-17 (Cr), Varion-AD(Cr), AV-17(Fe-NCS), Varion-AD(Fe-NCS), AV-17(Fe-NCO), Varion-AD(Fe-NCO), AV-17(Fe-SCC-Ag), Varion-AD(Fe-SCC-Ag), AV 17(Fe-NCS- Cu). The composites consisting of polymer and metallic compounds radically changes the physical and chemical properties of strongly basic cross-linked ionic polymers^{3,4}.

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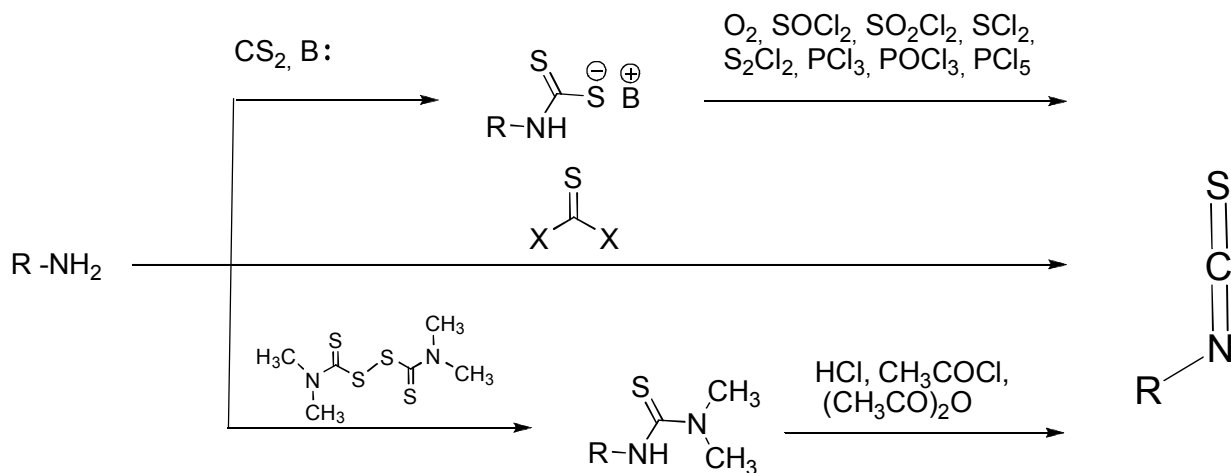
NEW SYNTHESIS METHODS OF ISOTHIOCYANATES

GUȚU Iacob

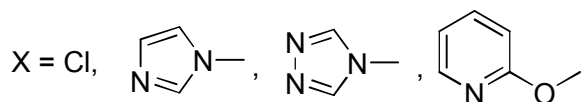
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Isothiocyanates are a class of natural compounds which are abundant in many cruciferous vegetables. Its play a significant role in the cancer chemopreventive activity. Moreover, isothiocyanates are important intermediates in the synthesis of sulfur-containing heterocycles.

The paper discusses new methods for the synthesis of isothiocyanates by various ways. Numerous methods have been developed to synthesise isothiocyanates. The most well known method is based on decomposition of N-substituted dithiocarbamate salts or esters. Another method includes interaction of amines with thiocarbonyl transfer' reagents such as thiofosgene, thiocarbonylditriazole, thiocarbonyldiimidazole or dipyridyl-thionocarbamate. A particular interest represents the decomposition of substituted thioureas in the presence of a reagent of acid nature. The trisubstituted thioureas for these goals are easily obtained from amines and tetramethylthiuram disulfide.



R = alkyl, aryl, heteryl; B = Et₃N



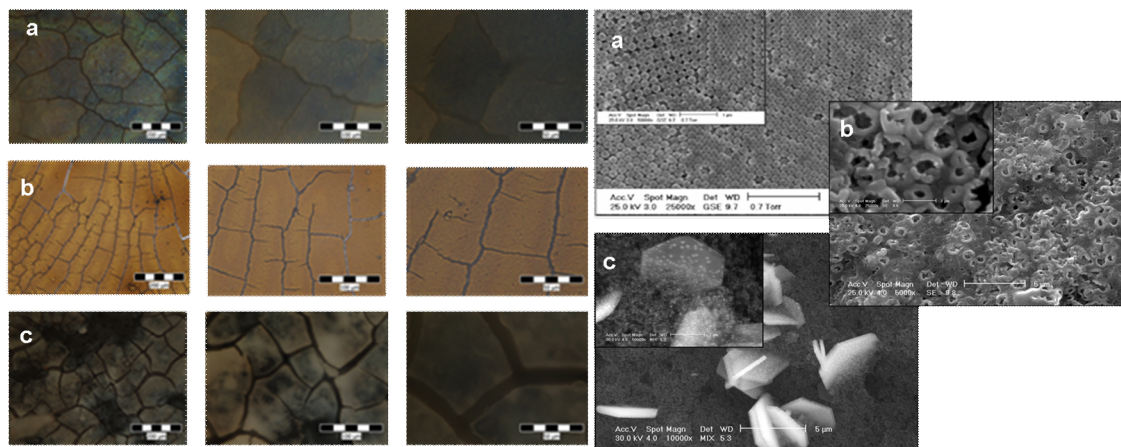
HYBRID MATERIAL SYNTHESIS BASED ON POLYMER PHOTONIC CRYSTALS CORE AND MAGNETITE PARTICLES SHELL

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Polymer photonic crystals (PPCs) are generally characterized by highly ordered structures which inhibit the propagation of light in all directions for a certain frequency range. The main consequence consists in the formation of photonic band-gaps (PBG) due to Bragg diffraction¹. Based on their optical behavior, the PPCs films were intensively used in chemosensing devices in order to amplify the photoluminescent properties of various organic compounds^{2,3}.

A hybrid material with core-shell structure based on polymer photonic crystals (PPCs) core and magnetite particles shell (Fe_3O_4) was obtained. The optical properties of this material were investigated in the presence of an aqueous solution of sulfuric acid (H_2SO_4) confirming an unusual blue-shift of the photonic band-gap (PBG). The formation of ferric sulfate in the presence of organic phase under acid conditions led to the synthesis of an optical sensor with possible applications for acid rain investigations.



Scheme 1. Optical microscopy and SEM images for : **a)** ST-HEMA-AA; **b)** ST-HEMA-AA- $\text{Fe}_3\text{O}_4\text{-H}_2\text{SO}_4$ (H_2SO_4 destroys in the first step the organic particles); **c)** ST-HEMA-AA- $\text{Fe}_2(\text{SO}_4)_3$

A.D. and A.M. acknowledge financial support from the Sectoral Operational Programme Human Resources Development 2007-2013 of the Ministry of European Funds through the Financial Agreement POSDRU/159/1.5/S/132395. and POSDRU/159/1.5/S/132397.

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STUDY ON FIXING INCREASED REACTIVE DYES USED IN FUNCTIONALIZED CELLULOSIC TEXTILE DYEING WITH THE REDUCTION OF WASTEWATER LOAD
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This paper presents first results, encouraging in terms of technical / economic and environmental protection, concerning the dyeing of 100% cotton fabrics functionalized with reactive dyes (reactive compounds with a characteristic group) able to paint in alkaline primarily cellulose fibers (the only fiber that binds covalently).

They provide the most vivid and beautiful colors for dyeing cotton, but they always had trouble their process of retaining on cellulose fibers. Therefore, dyeing with reactive dyes workflow involving several successive rinsing and soaping, leading to a high consumption of water, detergent, electricity, and sewage loading with dyes, detergents, etc., which made that time to be tried several solutions to mitigate unintended application's consequences.

The eco-innovative method that aim to develop it consists in dyeing with reactive dye (to start using a dye type chloropyrimidine) of a 100% cotton fabrics (the next steps can be tested combinations of synthetic celulozicelor, etc.) previously functionalized by chemical finishing workflow classic textile. There are used products, methods / techniques for obtaining functionalized fabric, application of that fabric dye reagent and test / mechanical characterization, physico-chemical and colors.

Contact: Oproiu Loti - lotio144@yahoo.com

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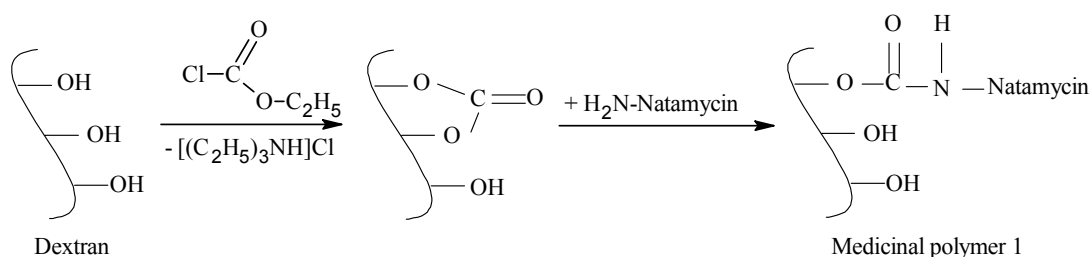
ANTIMYCOTIC POLYMER COMPOUNDS OF NATAMYCIN, DEXTRAN, COPOLYMERS OF N-VINYLPYRROLIDONE WITH ACRYLOIL CHLORIDE AND SPIRULINA PLATENSIS

Stefan Robu¹, Albert Ivancic¹, Natalia Lupol¹, Viorel Prisacari², Gheorghe Duca¹, Ana Dizdari²

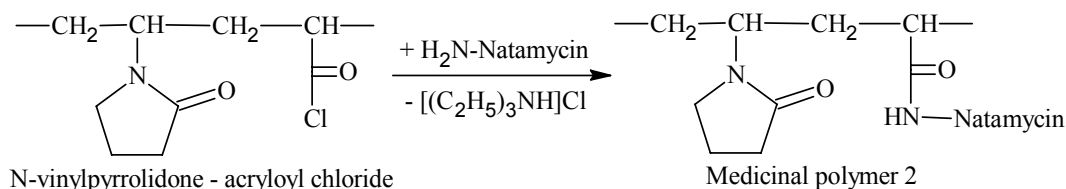
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The research work has been done to obtain antimycotic polymers based on natamycin conjugated with dextran macromolecules, as well as with copolymers of N-vinylpyrrolidone with acryloyl chloride. Antifungal effect of synthesized polymer was studied, as well as prolongation effect. Composite based on synthesized polymers and *Spirulina platensis* was obtained, to enhance the antifungal effect.



Synthesis scheme of dextran-natamycin medicinal polymer



Synthesis scheme of medicinal copolymer of N-vinylpyrrolidone - acryloyl-natamycin

Medicinal polymers 1 and 2 were purified by sedimentation from diethyl ether. Medicinal polymers structure was confirmed by IR spectroscopy (the occurrence of vibrations characteristic to peptide -CO-NH- group) and elemental analysis (nitrogen content found for medicinal polymer 1 - 1.67% and medicinal polymer 2 - 7.4% was practically identical to the theoretically calculated one).

Medical tests of grafted polymers dextran-natamycin and copolymers N-vinylpyrrolidone - acryloyl-natamycin demonstrate antifungal activity comparable with natamycin activity. Composites of medicinal polymers 1 and 2 with *Spirulina platensis* have practically the same antifungal activity as natamycin and therapeutic effect 5-6 fold more prolonged than the last (prolongation effect was studied by dialysis method).

NEW HYBRID MATERIAL WITH APPLICATION IN WATER TREATMENT
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Abstract:

Presently, there are considerable efforts worldwide toward the design and development of novel and highly efficient material for a suitable wastewater treatment, immediately linked to the amelioration of living conditions of the affected populations, particularly through improvement of the drinking and agricultural water quality, reduction of pollution and elimination of health risks.

Technical progress in the field of municipal wastewater treatment, which includes removal of eutrophication pollution loads, has improved significantly in the past few years.

The paper aims to design a new hybrid material based on zeolite, alumina and ferrite for wastewater treatment. The morphostructural properties of the hybrid material was investigated by XRD, SEM, EDAX techniques.

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DESIGNED TITANIUM COATED POLYMERIC SUBSTRATE MICRO-TOPOGRAPHY FOR BONE TISSUE ENGINEERING

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Nowadays, there is an extensive interest in understanding cellular responses to wide range of configurations of surface features. Beyond surface chemistry, surface topography represents one major issue in cell-surface interfaces dictating the biological reactions. Designing and obtaining highly reproducible and large area polymeric surfaces represent still a challenge in biology. This work presents large area polymeric surfaces microstructured using excimer laser processing technique, and used as model surfaces to answer the question in how far anisotropy in defined surface microstructuring affects and steer stem cell behaviour. The structures (pits similar to those of a bone transversal section) with various depths (200 nm-7 µm) were produced by an ablation process of polycarbonate on a large surface exposure set-up and a consecutive titanium coating process (magnetron sputtering). The potential inflammatory effect of microstructured surfaces covered with titanium on premonocytic THP-1 cells was evaluated and the response of human mesenchymal stem cells (hMSCs) was analysed and quantified. Cell growth and adhesion were depending on the topography of the substrates. The cell proliferation was apparently not affected for depths below 2 µm after 72 h, but slightly decreased for those in the range of 3-7 µm. The cell shape modifications induced by interaction with microtopography were analysed by SEM and immunofluorescence microscopy following actin filaments labelling. Data were correlated with osteogenic differentiation potential quantitated by mineralization assay. The results indicate that substrate depth features play a key role in hMSCs short-term spreading response and contact guidance, and long-term differentiation modulation. Our data demonstrate the potential use of laser micropatterned substrates to modulate cell fate during bone implantation.

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3 - Multifunctional materials and nanocomposites - O

ASSESSMENT OF THE PERCOLATION THRESHOLD VALUE OF NOVEL THERMOPLASTIC COMPOSITES BASED ON MIXED MATRICES AND CONDUCTIVE NANOFILLERS

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Conductive composite materials consisting of a polymer matrix and dispersed conductive fillers (such as metal particles, carbon black, graphite, carbon nanotubes or conducting fibers) are a relatively new class of materials fit for industrial applications. Their thermal, electrical and dielectric properties have been the subject of numerous studies due to their versatility, especially the possibility to tailor some characteristics (*e. g.*, tuning the conductivity by adjusting the amount of the conductive filler). It has been proven that the percolation threshold strongly depends on the polymer nature and processing, given that nanofillers are rather difficult to disperse and tend to agglomerate along with the formation of secondary aggregates.

The major advantage of such polymer composites is that electrical characteristics are close to the fillers, whereas their mechanical properties are typical for plastics. They can be used as antistatic/antiradiative materials and in applications such as switching devices, medical equipment, cables, transducers and gas sensors, as well as devices for electromagnetic radiation shielding and electrostatic discharge¹. Composites based on polymer blends successfully combine properties of all components. Thus, co-continuous structure of polymer blends can simultaneously give the maximum contribution of the mechanical modulus from each component.

Main factors that influence the distribution of the conducting filler inside the matrix are: the components viscosity, processing (temperature, blending time and rotor speed, components order of introduction), the filler wettability. Thus, by adjusting one or more factors it is possible to control the formation of the conductive phase within the polymer matrix and design composites with tailored properties.

This paper presents some conductive composites with mixed matrices (PP and PA), and different dispersed fillers (iron and carbon nanotubes). Their electric properties were critically assessed in correlation with the polymers compatibility, nature and amount of filler, and affinity towards one of the polymers within the matrix blend.

¹ V.E. Gul, "Structure and Properties of Conducting Polymer Composites", Utrecht: VSP, 1996.

**UPCYCLING INDUSTRIAL WASTE: THERMOPLASTIC GREEN COMPOSITES MADE OF
RECYCLED WOOD CHIPS AND POLYMER WASTE**

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Development of wood-plastic composites (WPCs), starting from the already existing industrial wood and plastics waste, is indispensable and offers the prospect of reducing the environmental impact of waste disposal problems and designing new materials with low production costs.¹ Nowadays, WPCs emerge as some of the most dynamic growth materials and become more and more commonplace with the development of new production techniques and processing equipment. A major advantage of these materials over wood is their ability to be molded, bent and fixed, as to meet almost any desired form and environmental conditions.

The optimization of interfacial adhesion between cellulose-based fillers (hydrophilic) and thermoplastics (hydrophobic), as well as the filler dispersion within the polymer matrix, are problems that can be solved by two methods: (1) a chemical pre-treatment of the natural filler which yields in an increased reactivity towards the polymer matrix or (2) the addition of a compatibilizer to the composite formulation that can improve the interfacial adhesion between components.

This study is focused on the evaluation of the mechanical and morphological properties of some new green composites made of wood chips, as natural filler, and recycled polyethylene (rPE) or recovered aliphatic copolyamide (coPA) as matrix, with and without a compatibilizing agent. Experimental data showed a better dispersion of particles inside the compatibilized matrix, as well as the slight improvement in the interfacial adhesion and bending strength of rPE-W composites containing 5-20% coPA.

¹ Krstic S., An Integrated Model for Education, Information and Decision Support on Polymer Waste Management, J. Environ. Prot. Ecol. 2002, 3(1), 170-174.

SYNTHESIS AND CHARACTERIZATION OF COMPLEXES OF ONS DONOR LIGAND TYPE.

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A series of Ni(II), Cu(II), Zn(II) and Cd(II) complexes on ligand (L) 2-hydroxy-1-naphtalidene-2-mercaptoaniline, by template synthesis are reported. Complexes are colored powders, stable to high temperatures (250-325⁰C), insoluble in common organic solvents but soluble in DMF and DMSO. Weak values of electric conductivities suggest nonelectrolyte character of complexes, while IR spectra suggest that they are free from coordinate and crystal water molecules. The 1:2 complex of nickel [M(L)₂] (M=Ni), has four coordinate square-planar geometry, the 1:2 zinc and cadmium complexes [M(L)₂] (M=Zn and Cd), have tetrahedral stereochemistries, while for 1:1 copper complex [M(L)]₂ (M=Cu), distorted square-planar geometry is suggested. Ligand appears to coordinate as an NS donor in nickel, zinc and cadmium cases and as an ONS donor in copper case. Analytical, magnetic and spectroscopic (IR, UV-Vis-NIR, ¹H-¹³C-NMR, ESI-MS) data confirm complexes structures. Ligand, complexes and standard drug were screened for their antibacterial activity against: *Escherichia coli*, *Staphylococcus aureus*, *Pseudomonas aeruginosa*, *Enterococcus fecalis* and *Candida albicans*, to assess their potential as antimicrobial agents ¹⁻⁷.

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SIMULANTS OF THE HUMAN BODY FOR BALLISTIC PURPOSES

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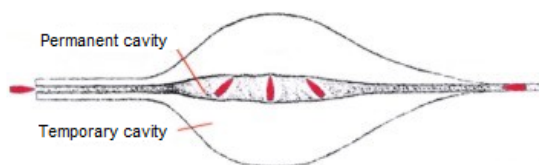
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Abstract

An important direction of governmental institutions created in the view of counteracting the terrorist action is to identify accurately the real conditions of the dynamic impact of munitions with the human body. Although computer simulation and modeling is a great help for learning on the dynamic interaction with the target, and the extended mathematical possibilities may give faster protection solutions than the pure experimental research, the experience shows that the simulations results must be validated through extended testing & evaluation programs.¹

Taking into account the human body simulant concept, this one cannot be replaced with a computer simulation, due to the fact that the behavior evidence requires targets submitted to real environment conditions, with high impact risk. In general, a higher velocity of the bullet implies a higher wounding impact. Theoretically, the bullet wounding effect would depend on the impact energy (kinetic energy). But here, the theory and the practice cannot work together any more. Other factors have a deeper impact on the bullet behavior in animal tissues or other simulants, including the bullet shape, transversal density, weight, velocity and construction.

In this context arises the term of “wound ballistics”, a field that studies the phenomena occurring when the projectile hits a living target: kinetic impact at high pressures and high deformation velocities. In this sense, the effects towards the human body must be assessed, inclusively from medical point of view: tissue tearing, damages, tightening, and bruises, on its way and also around it.²



Therefore, materials' choice and testing is crucial, implying both aspects of the chemistry of solids and interface processes, between skin and organs. The mechanical resistance, the chemical stability, and also the density, become mandatory to explore and correlate.

Munitions behavior through the human tissue

Some of the most reliable materials able to shape the human body and the human tissues are: polydimethyl siloxane, polypropylene, polytetrafluoroethylene, polyvinyl alcohol, polyacrylates, polymethacrylates, polyurethanes, epoxy resins, polyalkyl cyanoacrylates, etc.

Acknowledgements

This paper has been supported by a grant of MEN – UEFISCDI under PARTENERIATE program, project no. 307/2014.

¹ S. Pollak, Gunshot Wounds, Wiley Encyclopedia of Forensic Science, 2009

² M. Manolescu, Teză de doctorat, Academia Tehnică Militară din București, 2011.

TRENDS AND RESEARCHES ON POLYMER-BASED EXPLOSIVES**Teodora ZECHERU^{1,2}, Traian ROTARIU²**¹*Scientific Research Center for CBRN Defense and Ecology, 225 Olteniței Sos., 041309 Bucharest, Romania*²*Military Technical Academy, 31-41 George Coșbuc Bvd., 050141 Bucharest, Romania***Abstract**

PBXs are energetic materials in which an explosive powder is bound together in a matrix using 5–10% by weight of a synthetic polymer. The state-of-the-art explosive fillers and polymer bases are employed as main ingredients, such as: RDX, HMX, TATB (which have been widely investigated), next to innovative fillers, such as CL-20, TNAZ and NTO, which are at the design stage.^{1,2}

PBXs are widely used in military and civil applications due to their high safety, processing ease and superior strength. These materials have several major advantages versus the explosive materials themselves: if the polymer matrix is an elastomer (rubbery material), it tends to absorb shocks, making the PBX very insensitive to accidental detonation and giving a certain immunity against impact, and thus ideal for insensitive munitions.³

The PBX developed in our group (PENTO) consists in an NTO-based explosive filler and a nitrile-butadiene rubber (NBR) polymer matrix. PENTO shows improved properties, in terms of insensitivity and performances, versus RDX-based PBXs, such as stability to friction, to electrostatic discharges, thermal stability, similar velocity of detonation, next to enhanced mechanical integrity.

**Acknowledgements**

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¹ R. Pengelley, N. Gibson, Jane's Int. Def. Rev. 38 (2005) 29–40.

² Q.-L. Yan, S. Zeman, A. Elbeih, Thermochemica Acta 537 (2012) 1–12.

³ M. Jaidann, H. Abou-Rachid, X. Lafleur-Lambert, J. Brisson, Procedia Computer Science 4 (2011) 1177–1185.

**COLLAGEN – PLANT EXTRACT MEMBRANES USED AS SCAFFOLDS FOR SKIN
TISSUE ENGINEERING**

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Herbal compounds and collagen are assuming an important role in tissue repair and have been used as wound healing agents. The aim of this study was to design new composites membranes for wound treatments and to evaluate their *in vitro* biocompatibility in cell culture systems. The membranes were made of natural ingredients: collagen type I mixed in 10:1 ratio with plant extracts obtained from three species traditionally used for treatment of skin wounds, *Arnica montana* L., *Urtica dioica* L. and *Artemisia absinthium* L [1, 2]. The *in vitro* effects of membranes were studied on fibroblasts (NCTC clone 929 cell line) regarding cell cytotoxicity (MTT method) [3], cell morphology (Haematoxylin - Eosin staining) and cell adhesion (Scanning Electron Microscopy - SEM). Cells were seeded in direct contact with the membranes and incubated 24 or 48 h. Controls were cells in culture medium without membranes. First, no significant differences were found among membranes regarding cell viability and all membranes were non-cytotoxic. The highest biocompatibility was observed for collagen - *Arnica montana* L. extract membranes. Secondly, no morphological alteration was observed at the fibroblast cells in direct contact with all membranes at 48h. Finally, the fibroblasts seeded on the tested membranes observed by SEM analysis showed cell adhesion and normal morphology after 24h of incubation.

In conclusion, the data from this study indicate that the tested collagen-plant extract membranes have non cytotoxic effect, provide a good scaffold for cell attachment and have a potential for their future application in wound care treatment. Further studies *in vitro* are necessary to investigate their role in skin tissue engineering.

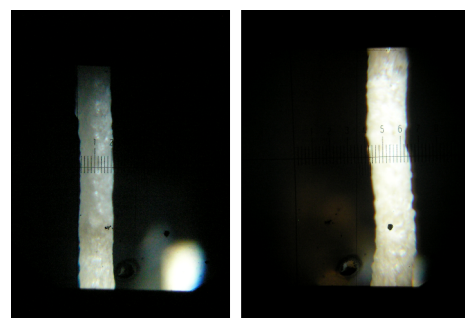
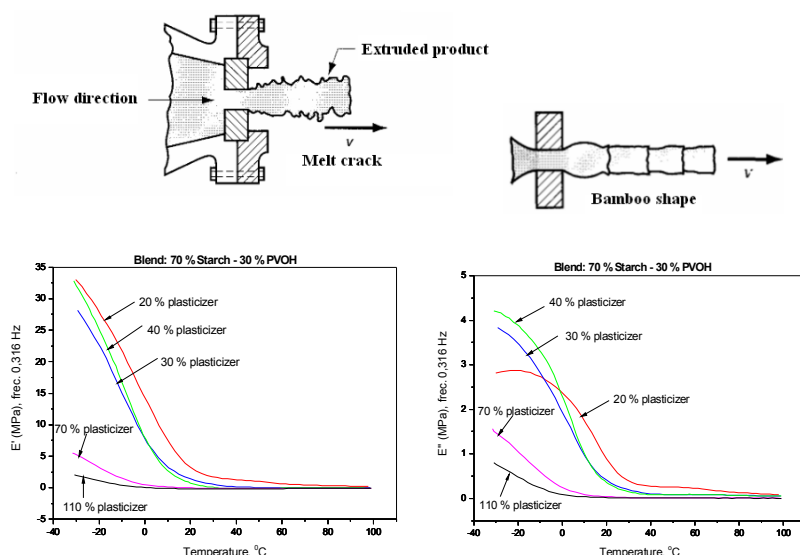
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MELT ELASTICITY CONTROL OF SOME NEW RENEWABLE MULTIPHASE MATERIALS AS POSSIBILITIES TO AVOID THE INSTABILITIES AT EXTRUSION

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Extrusion of polymer melts can be accompanied by rheological abnormalities that compromise the quality of the extrudate products and the final properties of finished products. This behaviour is the starting point of the following undesirable phenomena: extrudate swelling, melt fracture (shark skin), wall slipping etc.¹. These phenomena can be improved or even avoided through several technological measures: changing the working conditions, nozzle remodelling and also improving the formulations². This paper demonstrates the importance of formulations in controlling the melt elasticity and thus in elimination of extrusion instabilities of new renewable multiphase materials. Considering the values of elasticity modulus and melt resistance to flow and their dependence on formulation, compositions which do not present rheological abnormalities at extrusion in selected conditions were selected.



¹ H. F. Giles, Jr., J. R. Wagner, Jr., E. M. Mount III, (2005). Extrusion: The Definitive Processing Guide and Handbook, Plastics Design Library.

² F. M. Duarte, V. C. Barroso, J. M. Maia and J. A. Covas, (2005). J. Polym. Eng., 25: 2, pp. 115-148

APPARENT AND REAL SHEAR VISCOSITY AS METHOD TO CONTROL THE APPLICATIONS PROPERTIES OF NEW MULTIPHASE RENEWABLE MATERIALS

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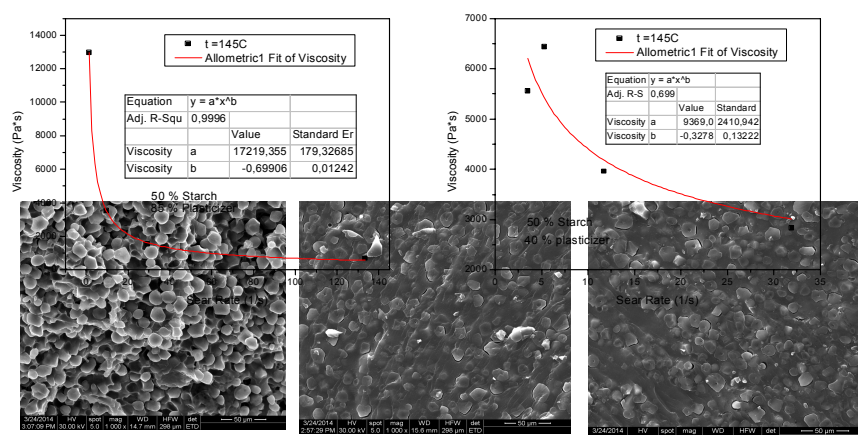
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The paper demonstrates that a good method to select the compositions of new renewable multiphase materials is to calculate both the constants from flow equations¹ established considering the experimental data and the standard deviation of these measurements. The obtained values must be than comparatively analyzed as a function of the formulation and obtaining conditions. The registered rheograms witch render the apparent shear stress and apparent shear viscosity must be corrected (Rabinowitsch and Bagley corrections) to found the real shear stress and real shear viscosity. It was found that the new materials have excellent melt flow without instability or other uncontrolled effects due to their elastic behavior if the theoretical rheological curves are in good agreement with experimental results and the standard deviation are small. The adhesion at interphases between the dispersed phases and continuous matrix is very good if all these conditions are fulfilled.



¹ Heinz Heineman, Polymer Processing Instabilities – Control and Understanding, Marcel Dekker, ISBN 0-8247-5386-0, 2005

NEW MULTIPHAASE RENEWABLE MATERIALS WITH HIGH CONTENT OF NATURAL FIBERS AND MINERAL FILLERS

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PhD. Phys. Eugeniu VASILE³, Eng. Roxana TRUSCA³, PhD. Eng. Celina DAMIAN², Prof. PhD. Eng. Mihai DIMONIE¹, PhD. Eng. Maria RAPA⁴

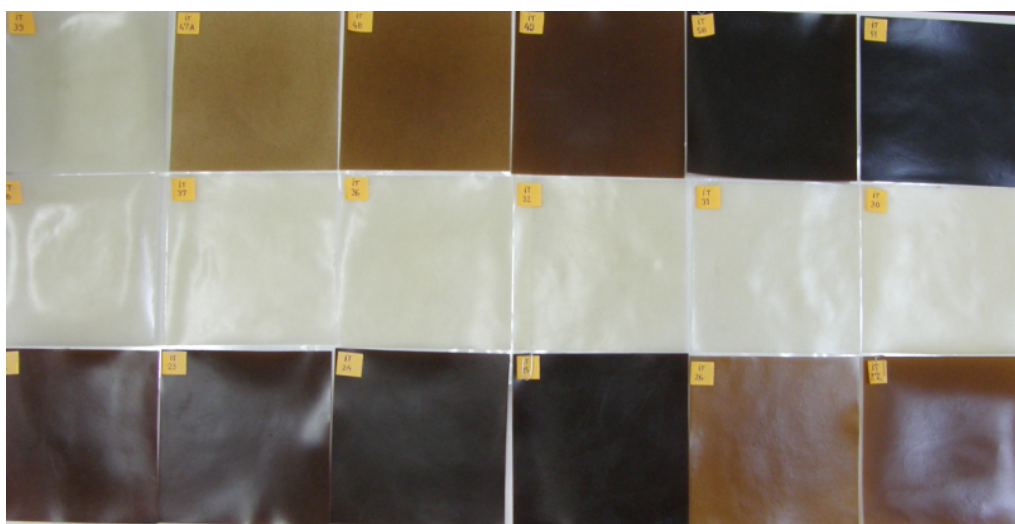
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Starch represents the main biobased and biodegradable polymers with low price and high potential industrial availability in the next decades¹. The use of starch as raw material is limited due to its poor mechanical properties, high hidrophilicity and high density². Starch has been modified with natural fibers as barley straw or grape waste. The paper presents new renewable materials achieved by starch modification at melt processing with cellulose fibers, wood fibers and wood flour. SEM micrographs of the new materials showed good dispersion and adhesion between renewable polymer and natural fibers. The fibers presence diminishes the materials morphological defects and improves the flow in the melded state. The physical and mechanical properties of the new materials were realized through a good correlation of the formulation with the requirements of the desired applications. These new materials were designed for goods with short life.



¹ Harriëtte Bos, Wolter Elbersen, Karin Molenveld, Carlos Cadórniga Market demand for non-food crops - Inventarisation of the present situation

² A. Lopez-Gil, M.A. Rodriguez-Perez, J.A. De Saja, Polímeros vol.24 no.spe São Carlos 2014 Epub May 20, 2014

RHEOLOGICAL PROPERTIES IN THE MELTED STATE AS EXPRESSION OF MISCIBILITY OF NEW PROCESS SENSITIVE RENEWABLE MULTIPHASE MATERIALS

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PhD. Eng. Celina DAMIAN², Prof. PhD. Eng. Mihai DIMONIE¹, PhD. Eng. Maria RAPA⁴**

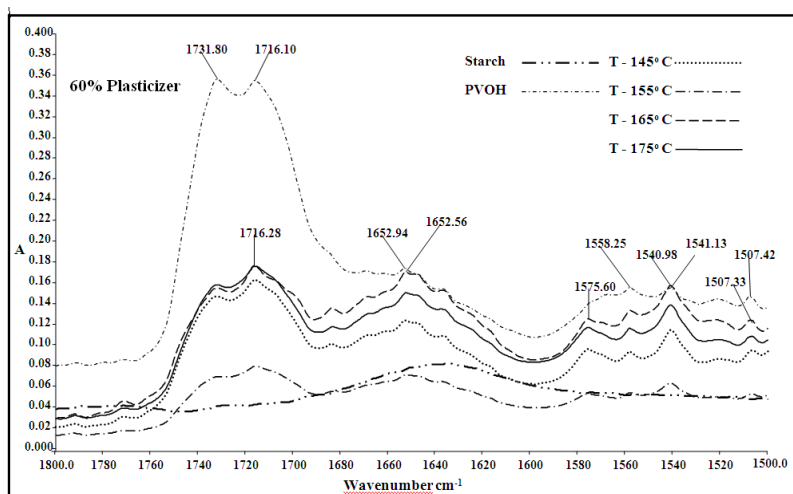
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In the researchers developed to achieve new multiphase renewable materials it was observed that, the quality and properties of the obtained materials depend on the formulation quality and the expertise in controlling the melt rheological properties. The paper presents a study on the influence of the plasticizing level on the main rheological properties of the melt and the possibility to control the component miscibility. Generally speaking the plasticizer are use to improve the material flexibility and to reduce the melt viscosity as possibility to improve the melt processability^{1,2}. It was observed that at low plasticizer content the developed shear rate and flow ration are very small and the flow must faced high internal friction. Therefore, even at high temperature, the melt viscosity does not allow the component proper mixing and obtaining of products with suitable appearance and desired properties. It



was also proved that at low plasticizing level the component miscibility has different values which depend on the melt processing conditions. At high plasticizer content the miscibility degree do not depend by the obtaining conditions.

¹ Richard P. Wool, Polymer entanglements, Macromolecules, 1993, 26 (7), pp 1564–1569

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REDUCTION OF Cr^{6+} TO Cr^{3+} FROM WASTEWATERS USING ZEOLITE – TYPE CATALYTIC MATERIALS

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Because the human society has grown in complexity and in numbers, wastewaters coming from various industrial activities and from agriculture are polluted and have a bad impact over the environment. The most efficient way to deal with this problem is to destroy these pollutants directly at their source before they are released into the environment. There are many solutions that can be used to solve these problems, among them zeolites and all kind of zeolitic materials proving to be one of the best solutions. These zeolitic materials can be formed by entrapping or by direct synthesis of various catalytic active species. Their ability to entrap and, depending on the conditions, destroy in a way or another, various kinds of substances, makes them a very suitable solution for wastewater treatments.^{1,2}

In this study we tried to reduce Cr^{6+} to Cr^{3+} from aqueous solutions in the presence of porphyrinic organic materials deposited on clinoptilolite. The synthesis of these organic nanomaterials was made by direct adsorption in the zeolitic matrix. The synthesized nanomaterials used were TTP/clinoptilolite, FeCl-TTP/clinoptilolite, TPP/clinoptilolite and SnCl_2 TPP/clinoptilolite. After the experiments for hexavalent chromium reduction, the results were improved than in the case where just clinoptilolite was used.

The best results were obtained in the case of FeClTPP/clinoptilolite, when the concentration of Cr^{6+} dropped from 5 mg/l under 2 mg/l.

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CONTACT ANGLES OF THE WOOL FABRICS FUNCTIONALIZED WITH TITANIUM DIOXIDE

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Wool has known applications in the textile industry mostly due to its excellent isolating properties. The surface of wool might be functionalized using semiconducting oxides by techniques with dry particles, by wet covering methods, by physical deposition methods etc. Titanium dioxide (TiO_2) attracted much interest due to its electro-optical and especially photocatalytic properties. The materials containing TiO_2 present a bactericide activity as well.

We have investigated the properties of some wool commercial samples modified by TiO_2 deposition by sol-gel. Several methods were used to routinely characterize the structure and morphology of these samples in original and modified form: thermogravimetric analysis (TG-DTA), optical microscopy, electron microscopy (SEM), elemental analysis by EDX, XPS, X-ray diffraction, FTIR and UV-vis spectroscopy, etc.

Wetting properties are very important ones for further applications; in the aim to evaluate wetting, we have used measurements of contact angle, with a Drop Shape Analyzer DSA 100 (Krüss) equipment and with water as liquid test. The working mode was described previously for different surfaces or for other textiles^{1,2,3}.

Structural and wetting properties were correlated with properties which put in evidence the cleaning effect of the deposited layer.

The TiO_2 layer deposited at low temperature (room temperature) was mostly amorphous.

The results have also shown the influence of the wool pretreatment in plasma for a better deposition.

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THERMO-MECHANICAL BEHAVIOR OF POLYSTYRENE AND POLYPROPYLENE – TiO₂ COMPOSITE FILMS UPON AGEING

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The photochemical degradation of polymers has been widely investigated and largely described in the literature^{1,2}. Initially, the reason was mainly due to the extensive efforts that have been made in order to stabilize polymers to light and weathering and to control photodestruction in industrial and domestic applications.

Nowadays plastic waste disposal has been recognized as a major worldwide environmental issue and different types of methods have been proposed for polymer recycling. Thermal and catalytically degradation of polymer wastes was proposed and represents appropriate methods to transform them into fuel oils³. However, the main problem which remains unsolved is to harvest polymer wastes from the environment.

The method proposed takes into account this issue, chemical stability and unbiodegradability of such wastes together with the necessity to maintain properties of this type of materials during a reasonable period of time. Thus, when such materials will become wastes some degradation processes which started from the beginning will continue in the environmental conditions and to some extent lead to the polymer degradation.

Polystyrene and polypropylene-TiO₂ nanocomposite films were exposed to light irradiation under simulated conditions of solar light in a Xenotest apparatus and the effect of ageing was evaluated by UV-Vis-NIR and FT-IR spectroscopy. Influence of ageing on thermo-mechanical properties of nanocomposite materials were investigated together with structural modifications in relationship with mechanisms of photodegradation.

Anatase has been proved to be efficient photocatalyst for the photodegradation of polystyrene and polypropylene films. In both cases titanium dioxide produce species that lead to some types of radicals which initiate the degradation of the polymer chain as was proved by the detection of functional groups generated due to photodegradation.

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MODELING THE CHARGE TRANSFER AT THE IONIC LIQUID-ELECTRODE INTERFACE IN DIELECTRIC SPECTROSCOPY MEASUREMENT- A MORE COMPREHENSIVE APPROACH

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The dielectric spectroscopy measurements can provide information on the electrokinetic properties of conductive materials such as, the diffusion coefficients and relaxation times for adsorption-desorption at electrodes surface.

The electrode polarization consists of accumulation of the ions at the metal electrodes surface of the measurement system. This effect highlights the nature of the charge transfer processes at the sample-electrode contact area. The main parameters that characterize the interfacial phenomena are the surface structure of the electrodes, the adsorption-desorption phenomena, the difference in ionic mobility of charge carriers.

The nature of the phenomena that occur at the contact area between the electrode and the sample is different and appears differently in the dielectric permittivity spectrum. For this reason it is necessary to elaborate a theoretical model of electrode polarization allowing to study the realistic cases in which the electrodes are ohmic, on their surface occur the adsorption-desorption of charge carriers; in the bulk the ions move by diffusion and drift, and between them there are the generation-recombination processes.

The assumption, explicitly formulated for the model presented here, is that the electric current densities are proportional to the concentrations of carriers adsorbed on the electrodes surface and the electric field (general boundary conditions):

$$J_p(\pm L/2) = \pm K_p^*(p(\pm L/2) - p_{ech}) + S_p E_1(\pm L/2), \quad J_n(\pm L/2) = \pm K_n^*(n(\pm L/2) - n_{ech}) - S_p E_1(\pm L/2)$$

where, K_p^* and K_n^* depend directly on the physical quantities of adsorption-desorption. The plane parallel electrodes are placed in points $x = \pm L/2$.

With this new proposed mathematical model the analytic equivalent of the dielectric permittivity is obtained in a form that allows to determinate the physical quantities from the experimental data.

ANTIBACTERIAL NANOSTRUCTURED MEDICAL DEVICES

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Catheters are tubular medical devices, which are introduced into body in order to eliminate biological fluids or administer a drug. After implantation, the protein or salts from biological environment are adsorbed on the surface of the catheter, and forms a layer planktonic on that adheres bacteria being in free circulation, leading to biofilm formation. Microbial infection developed on surfaces of medical devices is carried out in a progressive manner, specific to plastics used and represent a major problem leading to high medical costs [1]. One way to prevent infection is the surface modification of devices so as to prevent the emergence of bacterial biofilm. Silver is released slowly from the surface of the catheter, thus destroying the bacteria present in the vicinity [2]. Lately, it were used coating methods with silver nanoparticles on the surface of medical devices to prevent bacterial adherence and subsequent biofilm formation. Silver is released slowly from the surface of the catheter, thus destroying the bacteria present in the vicinity [3-5].

This paper presents the development of medical devices based on plasticized PVC, that were coated with an adherent hydrophilic polymer, within it were incorporated silver nanoparticles. We present the comparison of mechanical and biocompatibility properties of PVC samples with antimicrobial activity, those different content of silver nanoparticles varies in the range of 7% to 16% by dry mass.

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COPOLYMERS OF N-VINYLPYRROLIDONE GRAFTED WITH STEROIDAL GLYCOSIDES

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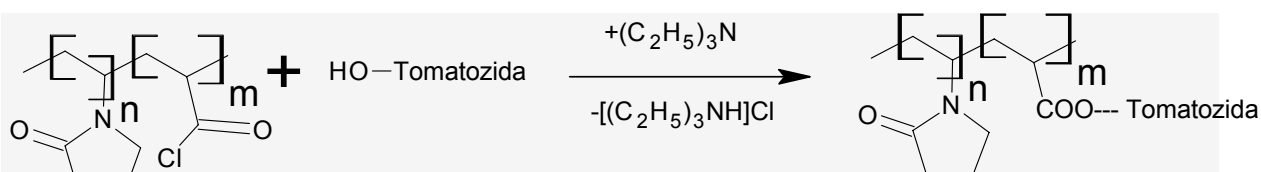
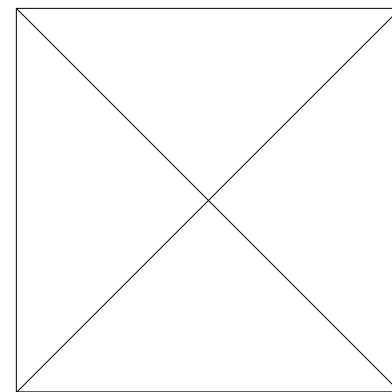
Steroidal glycosides are biologically active natural substances, which accumulate in the roots, bulbs and seeds of the plants acting as secondary metabolites. These compounds exhibit a wide range of physiological activity and are always in the focus of researchers in the field of bioorganic chemistry.

In order to discover new plant sources of steroidal glycosides have been studied a number of plants Solonaceae family, including tomatoes (*Lycopersicon esculentum* L.). Out of Tomato seeds boiling 50% aqueous ethanol summary steroidal glycosides were obtained, which were separated by silica gel column chromatography method and thin-layer chromatography. As a result, there was obtained steroidal furostanol glycoside, referred tomatoside in the form of an amorphous substance of a beige, soluble in water and lower alcohols, with mp. 216-219 °C, IR: $\nu_{\text{max}}^{\text{KBr}}$ 3600 -3200 (OH). Tomatoside empirical formula: $\text{C}_{51}\text{H}_{86}\text{O}_{24}$, molecular weight 1082, $[\alpha]_{\text{D}}^{24}$ (C 1.0, $\text{CH}_3\text{OH}-\text{CHCl}_3$), the structural formula was confirmed with the help of spectroscopy ^{13}C RMN and ^1H RMN, and it represents: 3-O- β -D-Glcp(1 \rightarrow 2)-O- β -D-Glcp(1 \rightarrow 4)-O- β -D-Galp-(25S)-5 α -furostan-3 β ,22 α ,26-triol [1].

The study shows that tomatoside stimulates biological activity of plant physiological development, is an action fitoregulator auxin and cytokines. Increases metabolism, increases plant resistance to adverse weather conditions and illnesses, enhances growth and fruit development also was elucidated fungicidal and antiviral activity tomatoside [2].

In the present time are very promising polymer conjugates obtained by methods of immobilization of biologically active compounds on polymer support, widely used to treat seeds by encrusting. In order to increase the chemical stability, to reduce toxicity and transmit prolong and controlled release properties were achieved by grafting research tomatoside with copolymers of N-vinylpyrrolidone and methacryloyl chloride.

Grafting was done according to the scheme:



Bioconjugate structure of the polymer obtained was demonstrated by means of IR spectroscopy and elemental analysis.

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NEW MATERIALS FOR OBTAINED ENZYME BIOSENSORS**Florentina HUTANU**

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Several procedure for PB deposition on the SPCE electrodes were tested: electrochemical deposition (galvanostatic, cyclic voltammetry) and chemical deposition by the reaction of $K_3[Fe(CN)_6]$ with $FeCl_3$. Also, the influence of the pretreatment of SPE (+1.7V for 3 min in PBS, pH 7.4) and of the stabilization of PB deposited on SPCE (by heating at 100°C) were evaluated. It was optimized the electro-deposition method in the presence of an anionic surfactant. The first sensors for hydrogen peroxide based on PB modified glassy carbon electrode were reported by Karyakin et al ¹. A glucose biosensor, was developed, which was based on Prussian Blue modified electrode with glucose oxidase (GOD) were immobilized on new films based on 2,6 dihydroxynaphtalene (2,6-DHN) copolymerised with 2-(4-aminophenyl)-ethylamine (AP-EA) and onto the screen-printed carbon electrodes.

Cronoamperometry technique is very advantageous due to the fact that the screen printed electrodes allow working with a very low volume of sample, the determination is fast and reproducible, and does not require a time for working electrode polarization. Also this electrochemical technique may be applied for on-field measurements using a portable detector. These biosensors were tested for by glucose chronoamperometry, amperometry and flow injection analysis (FIA) system.

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PREPARATION AND CHARACTERISATION OF POLYMER-CLAY COMPOSITE MEMBRANES

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The use of clay in the polymer–clay composite technology is considered to be a significant technique to produce polymer inorganic composite materials. Small amounts of clay added to the polymers improve the mechanical, thermal, electric, chemical properties of final materials¹.

Solution dispersion and wet-phase inversion methods were used to obtain composite membranes containing polysulfone, N,N-dimethyl acetamide, PEG 350 and small amounts of clay (Cloisite30B).

The final samples were characterized by using various analytical techniques such as Fourier transforms infrared (FTIR-ATR), Environmental scanning electron microscopy (ESEM) and Thermogravimetric analysis (TGA).

FT–IR spectra for the obtained membranes showed the presence of the specific peak of clay (Si-O-Si (asymmetric stretching vibration)) at 1045 cm⁻¹. TGA results indicated that the composite membranes exhibited improved thermal stability compared with the neat sample. The ESEM image of the prepared membranes with and without clay showed cracks, macro and micro pores. The addition of clay (Cloisite 30B) to the casting solution influenced the phase-separation process in the coagulation bath and also improved the wettability and the mechanical properties of dense films.

Acknowledgement: This work was supported by Programme PN.09.09.01.06

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**SYNTHESIS AND MODIFICATION OF STYRENE-ISOPRENE ELASTOMERS BY
GRAFTING OF NORBORNENE VIA RING-OPENING METATHESIS POLYMERIZATION
(ROMP)**

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Anionic sequential polymerization has been used to synthesize styrene-isoprene block-copolymers (SIS) with different polystyrene content. The reactions were carried out in cyclohexane solution through a three-stage process and were initiated with n-butyl lithium.

The grafting of norbornene was conducted by ring-opening metathesis polymerization (ROMP) and the reaction takes place to the double bonds. The ROMP grafting reactions were carried out in toluene with Grubbs II catalyst (1,3-Bis-(2,4,6-trimethylphenyl)-2 (imidazolidinylidene) (dichlorophenylmethylene) (cyclododecene tricyclohexylphosphine) ruthenium), as shown in Figure 1:

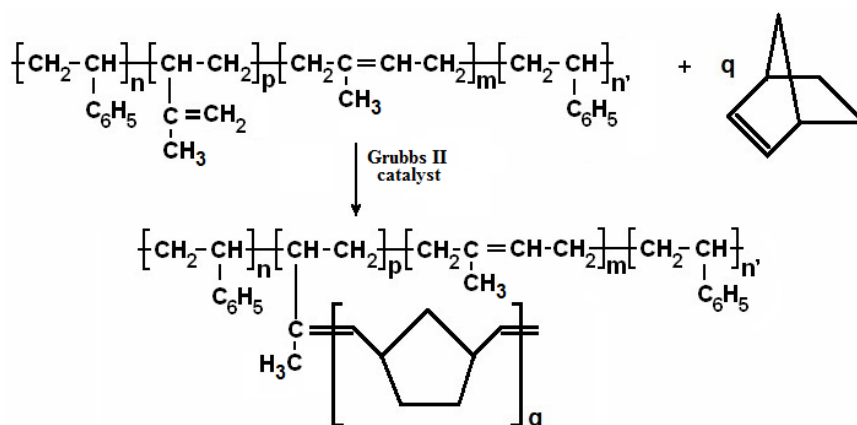


Figure 1. The schematic representation of a ROMP grafting reaction.

The characterization of the grafted styrene-isoprene block-copolymers were performed by Fourier Transform Infrared Spectroscopy (FT-IR), Differential Scanning Calorimetry (DSC) and Thermo-gravimetric Analysis (TGA).

The most application of this polymers is as compatibilizers from polyolefins elastomers blends.

EFFECT OF TITANIUM MICROSTRUCTURED BIOMATERIAL ON THP-1 CELLS **Madalina ICRIVERZI¹, Janina BANITA², Livia SIMA¹, Paula FLORIAN¹, Anca ROSEANU¹**

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Titanium is considered a suitable material for implant applications, an ideal support for tissue-engineering approaches. Surface biomaterial design may provide a microenvironment that support a better host-medical device interaction and integration. We aimed to determine in this *in vitro* study, the effect of gradiently placed interbedded elongated shape structures of 10-45 µm width and 20 µm height covered with titanium on THP-1 cell viability, proliferation, morphology and inflammatory response. Glass coverslip, planar and micrometer scale structured - titanium covered surfaces were cultured with THP-1 cells PMA-differentiated to macrophages. Colorimetric non-radioactive cell proliferation assay performed for 24 and 48 hours showed no relevant cytotoxicity effect irrespective of surface patterning. Using confocal imaging systems, macrophages immunostained for actin and vinculin were analyzed for adherence properties. A preferred clustering arrangement of the cells around the laser engineered microstructure due to enlargement of the contact surface area was observed. The potential inflammatory response of macrophages to microfeatured surfaces was evaluated using an immunoassay-type method (ELISA). THP-1 cells untreated or treated with bacterial endotoxin - LPS (used as control) were investigated for tumor necrosis factor alpha TNF-α release, results indicating no detectable proinflammatory cytokine production for all types of biomaterials tested.

The *in vitro* analysis revealed that the titanium microstructured material exhibits good biocompatibility and might provide an effective support for medical devices that conduct to normal cell function response after implantation.

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Hypericin imprinted poly (methacrylic acid -co - ethylene glycol dimethacrylate) beads using a suspension approach

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Hypericin is a powerful natural naphthodianthrone pigment found in *Hypericum Perforatum*, which has been extensively studied for its antidepressant, antitumor and anti-inflammatory properties¹. The commercial version is however at high reach and cost due to current methods of extractions and purification. Hence, we propose a non-conventional route to separate hypericin from *Hypericum Perforatum* extracts. The study debated in this paper introduces an innovative idea for designing the hypericin-selective adsorbent beads relying on the advantages of molecularly imprinting techniques. However, instead of using the pure template (hypericin- found to be commercially expensive) or a derivate for imprinting, the imprinted cavities were generated using a highly concentrated and purified hypericin extract obtained directly from *Hypericum Perforatum*. Therefore, for the general purpose of the study, a suspension copolymerisation of methacrylic acid (monomer) and ethylene glycol dimethacrylate (crosslinker) was approached to obtain bead-shaped adsorbents (referred as MIPs hereafter) which were further used in specific adsorption processes to underline their selective properties (**Figure 1**).

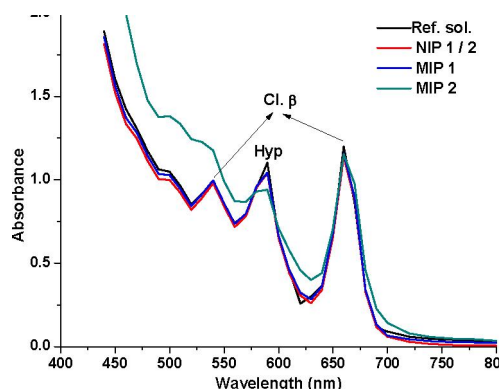


Figure 1 Selective Adsorption of Hypericin

It is noteworthy the fact that the molecularly imprinting technique as synthesis method also brings some economical contributions to the separation process². To fully assess the structure-properties relationship of MIPs, physical and chemical investigations were performed accordingly.

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**COMPARATIVE STUDY OF THE CHARACTERISTICS OF STANDARD RESIN /
MODIFIED RESIN COMPOUNDS BY MOLAR RATIO OF REACTANTS USED FOR
MODIFICATION**

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Multiple possibilities for epoxy resins flexibility modification significantly expand their range of uses not only for traditional composite materials and superior properties surface coatings but also for nanocomposites.

This paper focuses on obtaining of new standard epoxy resin / glycols modified epoxy resins at different molar ratios and on characterization of reinforced product to highlight how different additions of modified resin compound influences flexibility compared to standard epoxy resin.

It is possible to increase flexibility through chemical modification of standard epoxy resins, done by inserting polyglycol chains in their structure.

Polyglycol chains containing ether groups (-C-O-C-) lead to a flexibility increase. The flexibility induced by these groups can be controlled by an appropriate choice of concentration and chain length of the glycol [1-3].

Modifying epoxy resins with glycols induces a wide range of specific properties, demonstrated by the characterization of the products obtained by conventional physical-mechanical and dynamical mechanical analyses (DMA) depending on the nature and the mass ratio of glycol use standard resin / resin modified.

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3 Multiphase and nanocomposites materials - P
**POLYURETHANE NANOCOMPOSITE OBTAINED USING MONTMORILLONITE
MODIFIED POLYETHERPOLYOLS**

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A nanocomposite is a solid and multiphase material, containing a dispersed phase with one or all three dimensions of its particles shorter or equal with 10^{-9} m. The polymeric nanocomposite is definable as a material with polymeric matrix in which is dispersed a nanofiller with the max. 100×10^{-9} m particle dimension. Mechanic, electric, thermal nanocomposites properties are fundamentally different than their components. The reinforcing materials can be strips – ex. aluminosilicates phyllosilicates order¹² appertain or fibres – ex carbon nanotubes fibers³⁴. Polyurethanes are included in reaction polymers products and they are obtained by a polyaddition reaction between a polyol – hydroxyl (-OH) containing groups component – and a diisocyanate – isocyanate ($-N=C=O$) containing groups component in the presence of a catalyst and other components. The nanocomponent is the element of the recipe who allow the polyatomic chains of the macromolecule building between their layers as the result of the polyaddition. The nanocomponent is represented by a layer aluminosilicate appertaining order – phyllosilicates⁵ - and with the typonym montmorillonite. Montmorillonite material has a stratified molecular structure who allow the selfsynthesis of the polyurethane macrochains between their atomic layers as the result of the polyaddition reaction, and at the end of the macromolecular synthesis is completely included in the internal structure of the polyurethane matrix. Existence of the -OH groups in the molecular structure of the montmorillonit lead to chemical links achievement between the polyurethane matrix ant the nanofiller. The polyurethane nanocomposite matrix is obtained as the result of a polyaddition reaction between a polyetherpolyol 3 PETOL 36 3 BO type (glicerine starting) modified with montmorillonite 6 % - gravimetric parts⁶ and 4,4' diisocyanatediphenilmethane MDI with equivalent isocyanate reactance groups. Further tryings that the nanocomposite polyurethane matrix was supposed approve an semnificative improving especially of the thermal properties of it.

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GRAPHENE MATERIALS FOR FUEL CELL APPLICATIONS

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Abstract

Graphene has received significant attention in recent years due to their unique electronic, physical, mechanical, thermal and chemical properties, such as high surface area, excellent conductivity, easy to functionalize and potentially low manufacturing cost. Graphene provides an ideal base for electronics, energy storage devices, sensors, transparent electrodes, supercapacitor, fuel cell. Usually, carbon black is most widely used for support material, although it shows serious intrinsic corrosion under abnormal operating conditions. In consideration of their high surface area, high conductivity, unique graphitized basal plane structure and potential low manufacturing cost, graphene nanosheets have been investigated as a support for low-temperature fuel cell catalysts. Graphene nanocomposites were synthesized as a simple chemical route by chemical oxidation and graphene oxide exfoliation and confirmed by characteristic analysis. The structure, morphology and properties were characterized using X-ray diffraction (XRD) during different preparation steps, Scanning Electron Microscopy (SEM), XPS.

In this work, we prepared graphene-based materials to study the possibility of their using as catalyst support in PEMFC due to the unique structural and electrical properties and due to the prominent characteristics, such as high surface area, relatively uniform pore size and ordered pore structure.

Design and testing of liquid membrane systems for the synthesis of micro and nano particles for use in the controlled release of active substances

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Microstructured and nanostructured materials used in numerous technological and medical applications e.g. as ceramics, polymer composites, filler materials, pigments, electronics, catalysts, and many others. In recent years, micro and nano particles of hydroxyapatite and calcium carbonate have attracted significant interest due to their potential applications in high-capacity drug loading, targeted drug delivery and other biomedical uses. Hydroxyapatite is a highly biocompatible and biodegradable ceramic material. Applications of hydroxyapatite as drug delivery systems for antibiotics, growth factors, anticancer drugs and arthopedic applications are obvious, due to its similarity to the mineral constituent of hard tissues. Calcium carbonate (CaCO_3) nanoparticles are highly porous, biocompatible, biodegradable, and have pH-sensitive properties, which makes them good candidates for biological drug delivery systems.

The aim of this work is to synthesis of micro and nano particles of hydroxyapatite and calcium carbonate and applications of this particle as the vehicles for the sustained release of doxycycline. Calcium carbonate nano and micro particles were synthesized by a micro-emulsion method with Span 80 as surfactant. Bis(2-ethylhexyl) hydrogen phosphate (D2EHPA) was used as the carrier and toluene and kerosene was used as a organic solvent. Nano and microparticle of hydroxyapatite was synthesized by wet-chemical precipitation route. The results obtained indicated that the absorption of doxycycline on hydroxyapatite and calcium carbonate was realized with 64.1% and respectively 97.9% after 30 h under magnetic stirring at room temperature. Studies of desorbtion or release of doxycycline was efectuated into simulated body fluid (pH 7.4) under agitation at 250 r/min.

DETECTION OF THE NITRO-OXIDATIVE SPECIES BY MICROBIOSENSOR-BASED SCANNING ELECTROCHEMICAL MICROSCOPY (SECM)

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The detection of chemicals released by living systems, including the nitro-oxidative species (NOS) is crucial to clarify signal transduction pathways *in vivo* and to advance drug testing by cell-based assays. However, these opportunities come with real challenges for Chemists and Engineers alike. Lately, the SECM based detection methods have drawn intensive attraction lately, due to the simplicity and sensitivity.

Our goal will be described: an advanced system for NOS mapping by μ BS-SECM

The work consists of the following steps:

- Optimize micro(bio)sensors in multi-barrel format to detect several nitro-oxidative species (NOS).
- Recently developed SECM equipment for the new multi-barrel sensor, with optimized methods for sensitive measuring performance.
- Investigate NOS in model matrices by μ BS-SECM enhanced by optical-electrochemical imaging.

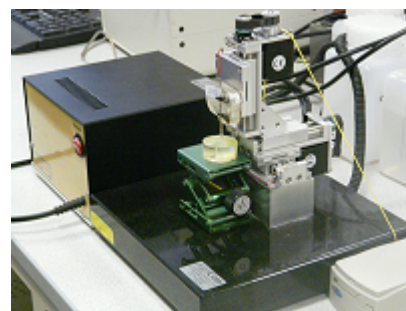


Figure: Picture of the SECM system

Detailed description will be given in the presentation of the recently developed SECM equipment, and the sensor fabrication.

ACKNOWLEDGEMENT

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HYDROPHOBIC AND TRANSPARENT SILICA HYBRID COATINGS FOR POLYCARBONATE SUBSTRATE

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Hydrophobic and transparent silica hybrid films, deposited on polycarbonate (PC) substrate, were prepared by sol-gel process at room temperature, using two coating routes. The **first route** consists in covering the PC substrate by dipping it into acidic solutions, containing tetraethylorthosilicate (TEOS) and different surface modifying co-precursors: octyltriethoxysilane (OTES), phenyltriethoxysilane (PhTES), and diethoxydimethylsilane (DEDMS), when *monolayer-coatings* (samples 1-3) were obtained. The molar ratio between TEOS and co-precursors was 1:1. By the **second route**, the wettability properties of polycarbonate were modified by preparing *bilayer-coatings*. Thus, the PC substrates were firstly dipped in acidic solutions, resulting the first layer (in a similar manner with the first route of coating), which was let to dry at room temperature for 5 days before being covered with perfluoroalchyltriethoxysilane (perfluorooctyltriethoxysilane: samples 4-6, or perfluorodecyltriethoxysilane: samples 7-9). The water contact angle values of the PC surface samples covered with *bilayer-coatings* are higher compared with both, the references and the *monolayer-coatings* (Figure 1). It was possible to observe the chemical surface modifications through FT-IR spectroscopy. The surface morphologies of the coatings were studied using Environmental Scanning Electron Microscopy (ESEM).

Acknowledgement: This work was supported by the POS CCE Programme, contract number 511/31.07.2013, ID/Cod SMIS: 1717/47512 (beneficiary RENAULT TECHNOLOGIE ROUMANIE).

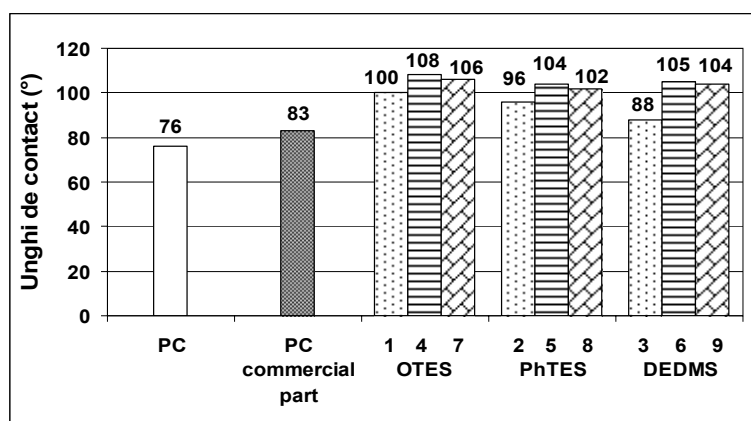


Fig. 1. Static contact angle of water on coated

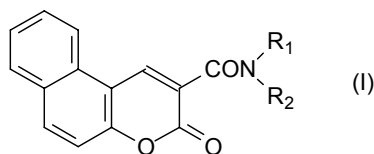
BENZOSUBSTITUTED COUMARINE FLUOROPHORS AS OPTICAL WHITENING AGENTS AND UV ABSORBERS FOR SYNTHETIC FIBERS

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Being an important class of organic heterocycles, coumarin derivatives have been widely reported to exhibit various biological activities, especially with regard to antioxidant and anti-inflammatory activity. Also, coumarin derivatives show outstanding optical properties, which render them useful across a wide variety of applications such as optical brighteners, laser dyes, nonlinear optical chromophores, electroluminescent materials, solar energy collectors, two photon absorption materials, as well as fluorescent labels and probes in biology and medicine¹. Their benzo counterparts, namely benzocoumarins, have been less studied. Akira Takadate and co-workers², studied fluorescence properties of coumarins and benzocoumarins and observed that benzocoumarins and their derivatives with different heterocycles at 3-position are strongly fluorescent.

The paper presents the original results of the coloristical tests effectuated on nine structures of fluorophors derivatives of 5,6-benzocoumarin-3-substituted with the general formula (I).



where: R₁ and R₂ are the same or different and are hydrogen, an alkyl or aryl, a heterocyclic amine rest or R₁ and R₂ form a morpholine ring.

The UV-VIS and fluorescence spectra together with the coloristic characteristics (optimal application concentration and maximum whitening degree on synthetic fibers, light, wetting and thermal fastness) show that besides the requirements imposed to optical brighteners (e.g. rise the whitening degree of the textile support, absorb the UV radiation in the region 330-370 nm and emit fluorescence predominantly in the blue region of the visible spectrum, 440-460 nm), the synthesized structures, without any exception, are efficient UV absorbers for polyester, cellulose acetate and triacetate fibers.

¹ Yi-Feng Sun, He-Ping Wang, Zhi-Yong Chen, Wen-Zeng Duan – J. Fluoresc, 2013, 23, p.123-130.

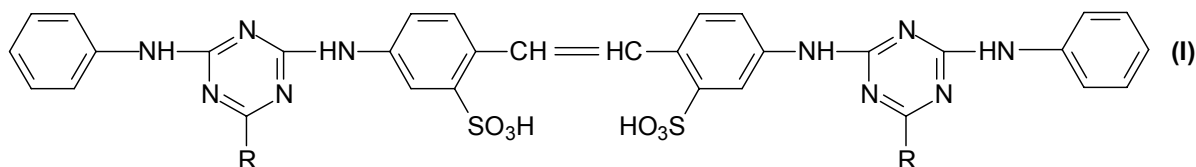
² Rajesha si H.S.Bhojya Naik, H.N.Harish Kumar, K.M.Hosamani si K.M.Mahadevan – ARKIVOC, 2009, p.11-19.

DERIVATIVES OF 4,4'-BIS[(4''-R-PHENYLAMINO-S-TRIAZIN-2''-YL)AMINO]STILBENE-2,2'-DISULFONIC ACID AS ADDITIVES IN WASHING COMPOSITIONS FOR CELLULOSIC FIBERS

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Derivatives of 4,4'-bis[(4''-R-phenylamino-s-triazin-2''-yl)amino]stilbene-2,2'-disulfonic acid (I) are characterized by reduced water solubility, under 10g/l, property useful for detergents compositions.



where R = phenil or morpholinyl

Synthesis of these compounds at temperature under 100 °C goes to amorphous yellow powders, known in literature as α crystalline form^{1, 2, 3}. At temperatures exceeding 100 °C, in water or solvents, with alkali or organic bases and at normal or high pressure are obtained white powders known as β crystalline form^{4, 5, 6}.

Our research has intended to put into evidence the differences in physical-chemical and coloristical behaviour of the two crystalline forms of the compounds described by general formula (I). In this respect were recorded and analyzed IR, UV-VIS fluorescence and XRD spectra, DSC and were made irradiations experiments by exposure one hour to UV light to identify the powders stability. Also, cotton fabrics were dyed and analyzed in order to determine the maximum whitening degree, optimal application concentration and accumulation onto fibres after repeated washings. Finally, the dyed samples were subject to light and wetting fastness evaluation. The results demonstrate the tinctorial superiority of the white β crystalline form.

¹ H. C. James si colab. - *U.S.* 3,951,960 (Cl. C07D 251/54), 20 apr. 1976.

² Ciba-Geigy A.-G., *Brevet Brit.* 1,355,219 (Cl. C07D 55/50), 5 iun. 1974.

³ H. C. James si colab. - *U.S.* 4,005,026 (Cl. C11D 3/28), 25 ian. 1977

⁴ Ciba-Geigy A.-G. - *Brit.* 1,353,690 (Cl. C07D), 22 mai 1974.

⁵ B. Noll si colab. - *Ger.(East)* 145,017 (Cl. C07D 251/68), 19 nov. 1980

⁶ P. Knopp si colab. - *Ger.(East)* 220,326 (Cl. C11D 3/42), 27 mar. 1985

TUNGSTEN OXIDE GAS SENSORS FABRICATED BY PULSED LASER DEPOSITION
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The possibility of using metal-oxide semiconductor gas sensors for realistic monitoring of air quality in an urban environment requires the capability of such sensors to detect low-ppm concentrations of polluting gases.

In this work, gas sensors based on tungsten trioxide (WO_3) which display an enhanced sensitivity to ammonia are presented. Tungsten trioxide is an n-type semiconductor with a wide bandgap, and is very promising sensor material with high sensitivity and fast response time.

Thin films of tungsten trioxide are deposited at 600 °C onto interdigitated sensor substrates by pulsed laser deposition (PLD). The sensing mechanism of such sensors is based on redox reactions between the volatile organic compounds (VOC) and the oxide surface. Therefore highly crystalline nanostructured WO_3 thin films are obtained as revealed by scanning electron microscopy, X-ray diffraction, and Raman microscopy studies. Furthermore, the as-deposited films are demonstrated for ammonia NH_3 detection.

The PLD fabricated sensors operated at 100 °C and 200 °C show an abnormal response which can be attributed to the oxidation of ammonia to NO. At 300 °C, the sensors are highly sensitive in the low ppm range, and their recovery time is in the range of few seconds.

The results shown here evidence that WO_3 gas sensors fabricated by pulsed laser deposition represent a promising platform to detect trace levels of ammonia.

Alexandra Palla Papavlu was supported by the strategic grant POSDRU/159/1.5/S/137750, "Project Doctoral and Postdoctoral programs support for increased competitiveness in Exact Sciences research" cofinanced by the European Social Found within the Sectorial Operational Program Human Resources Development 2007 – 2013.

THE APPLICATION OF POLYMER COMPOSITE MATERIALS ON PROTECTION EQUIPMENTS

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Abstract

The mechanical and physical properties of Polymer Composite Materials (PCMs) are clearly determined by their constituent properties and by the micro-structural configuration. While the fibres are mainly responsible for strength and stiffness properties, the polymeric matrix contributes to stress transfer and provides microclimate protection. The reinforcement of a polymeric matrix with high strength and modulus fibres utilizes the viscoelastic displacement of the matrix under stress to transfer the load to the fibre; this results in a high strength and a high modulus composite material. The aim of this combination is to produce a two phase material in which the primary phase, stiffness determinative, is in the form of fibres and is well dispersed, bonded and protected by a secondary phase, the polymeric matrix.

The PCMs of interest are constituted of different formulation of polyurea and the considered fibres were selected in order to assure superior mechanical properties, respectively they have elevated value for fibre tensile strength: aramid (3.1 – 3.6 GPa) and carbon (2.1 – 5.5 GPa).

PCMs dramatically improve the protection characteristics of chemical protection equipments and foster the development of new ones with better characteristics (reduced mass, advance protection capabilities). PCMs have excellent characteristics, appropriate for protection against chemicals and, in addition, present durability and resistance to the external factors.

Acknowledgments

This work was performed through the Partnerships in priority areas - PN II, developed with the support of UEFISCDI - Ministry of National Education, project no. PN-II-PT-PCCA-2013-4-0707.

CATALYST DEVELOPMENT FOR CARBON MONOXIDE REMOVAL FROM HYDROGEN FUEL CELL

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Proton exchange membrane fuel cells (PEMFC) are being developed for transport applications as well as for [stationary](#) and [portable fuel cell applications](#). Their distinguishing features include lower temperature/pressure ranges (50 to 100 °C) and a special polymer electrolyte membrane.

Although the PEM cell is completely CO₂ tolerant, the anode is highly susceptible to CO poisoning with consequent voltage losses. Low temperature fuel cell systems tolerate only small amounts of carbon monoxide (CO). Thus, the total concentration of CO in the gas stream should be reduced below 10 ppm in order to obtain optimum performance.

In this work we propose to use the catalysts for CO removal from hydrogen used as reactant in the PEMFC. Thus, mixed copper manganese oxide catalysts have been extensively used to remove CO from air due to their low cost. The effect of the preparation conditions of hopcalite (copper manganese oxide) catalyst is investigated for the retention of carbon monoxide at ambient temperature. In the present study the hopcalite is prepared by a novel redox and precipitation method. The catalysts were characterized by means of BET, SEM, EDX, and X-ray powder diffraction. The experiments found the value of the catalytic activity comparable with that of commercial Hopcalite catalyst. The results making them potentially useful in the removal of CO in low and medium temperature PEM fuel cells.

EFFECT OF SEBS AND SBS BLOCK COPOLYMERS ON PROPERTIES OF RANDOM PP

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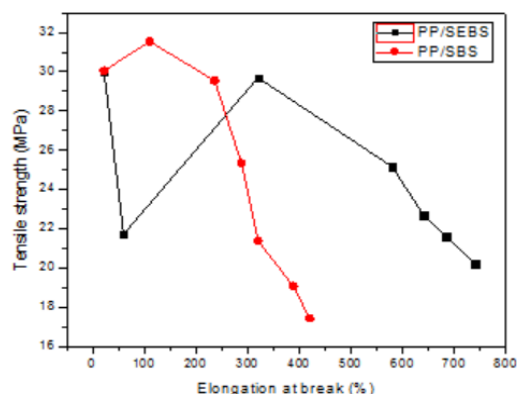
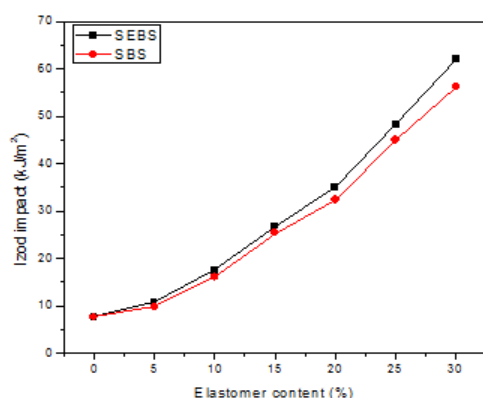
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Polypropylene (PP) is one of the most widely used thermoplastics because of its attractive combination of good process ability and mechanical properties¹. However, its inadequate brittleness limits its versatile application in engineering areas. Therefore, toughening modification has become an important topic for PP.

Blends of random polypropylene β PPR RA 7050 provided by BOREALIS and SEBS (styrene-ethylene/butadiene-styrene) and SBS (styrene-butadiene-styrene) block-copolymers up to 30 wt.% were prepared via melt processing. It was investigated the effectiveness of elastomers on modification on the polymer properties, as tensile properties, impact and thermal properties.

Results showed that elastomers can be used as impact modifiers for PP, with SEBS being more effective toughening agent than SBS. Tensile strength decreased and elongation at break increased, as the elastomer content increased in the PP matrix.



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PELLETIZING ROLE IN MELT PROCESSING OF SOME NEW RENEWABLE MULTIPHASE MATERIALS

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Plastic pellets are typically shaped and produced on a die-face cutter, or right-angle cylinders manufactured on a strand line. The material shaped as pellets is preferred for injection mouldings, profile extruders, and compounders that reintroduce reclaimed scrap into virgin processes^{1, 2, 3}. The paper presents a study on the pelletizing role in melt processing of new



renewable polymeric materials characterized by high melt strength and good resistance to breakage and large range of variation of their composition. The pelletizing of materials was done on a conventional strand pelletizer and the melt being granulated on a Gottferd extruder. The physical and mechanical properties of materials were measured. Depending on material formulation, the obtained pellets were cylindrically shaped, with right - angle edges and good degree of

uniformity. The obtained results have also showed that the pellets quality is mainly controlled by the mixing of liquid with solid components. The formulation controlled too the type of pelletizing, wet or dry in accordance with the presence of soluble components into the material composition.

¹ Michael Berins, *Plastics & Engineering Handbook*, Kluwer Academic Publishers, The Netherlands, 1991, ISBN 0-412-99181-0.

² John Bell, *Plastics Technology*, September 2012.

³ Charles A. Harper, *Modern Plastics Handbook*, ISBN 0-07-026714-6, 1999.

COLL/TiO₂-Ag composite nanomaterials for antimicrobial application
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It is well known that TiO₂ nanoparticles kills cells, bacteria and many varieties of viruses under mild UV illumination, which can presume to have different types of applications in different fields of industries. One of TiO₂ uses is as pigment because of its brightness, high refractive index and resistance to discoloration. Nearly 70% of TiO₂ is used as pigment in paints but also used in glasses, plastic, paper, fibers, food packaging, pharmaceutical, cosmetics and toothpastes. Pure TiO₂ nanoparticles or TiO₂ nanoparticles doped with other materials such silver, for instance, exhibit improved antimicrobial properties.

In this paper, the technology for obtaining nanobiocomposite materials based on COLL/TiO₂-Ag is described. In the first step, TiO₂ nanoparticles were obtained through a sol-gel method followed by the precipitation of the silver over TiO₂ nanoparticles. In the second step, the TiO₂/Ag nanoparticles were added into bovine collagen gel (type I). After a proper homogenization followed by the lyophilization process, the nanobiocomposite materials based on COLL/TiO₂-Ag were morphologically and structurally characterized by X ray diffraction (XRD), infrared spectroscopy (FT-IR), and scanning electron microscopy (SEM) as well by determining the antibacterial activity against *S. aureus*.

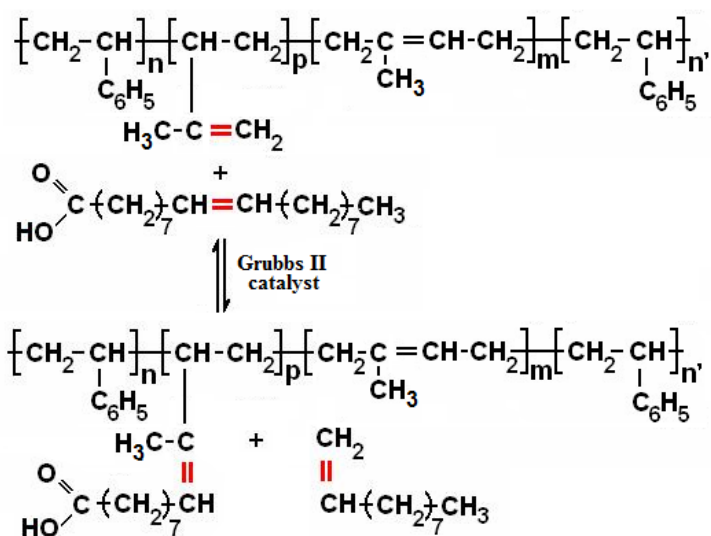
Based on the obtained results it can conclude that silver nanoparticles were homogeneously distributed and assure improved antibacterial activity of the final products/nanobiocomposite. For antibacterial tests, we choose *S. aureus* (gram positive bacterium) because is capable to cause different infection of the skin.

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The resulted styrene-isoprene block-copolymers were modified by cross metathesis with oleic acid, following the reaction:



The modified styrene-isoprene block-copolymers were characterized by Fourier Transform Infrared Spectroscopy (FT-IR), Differential Scanning Calorimetry (DSC) and Thermo-gravimetric Analysis (TGA).

The most application of this polymers is as compatibilizers from polyolefins elastomers blends.

PREPARATION AND CHARACTERISATION OF POLY(LACTIC ACID)/POLY (ε- CAPROLACTONE)/ SYLVER NANOPARTICLES BIONANOCOMPOSITES

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Key words: bionanocomposites, antimicrobial activity, implantable medical devices, biofilm

Currently, the risk of implantable medical devices biofilm associated infections in all fields of medicine occurring especially in immunocompromised patients has increased. One of the most investigated approaches to combat or prevent these infections is represented by the development of novel bioactive materials with antimicrobial properties and increased resistance to microbial colonization and biofilm development.

The objective of this study is to obtain new bionanocomposites of poly(lactic acid) (PLA) and poly(ε-caprolactone) (PCL) loaded with a content of silver nanoparticles (AgNPs) of 0.5 wt.%, 1 wt.% and 2 wt.% respectively, by melt blending and to characterize them in terms of structural, thermal and biological properties.

Antimicrobial activity of AgNPs was tested towards Gram positive (*Staphylococcus aureus* ATCC 29213, *Enterococcus faecalis* ATCC 29212), Gram negative (*Pseudomonas aeruginosa* ATCC 27853, *Escherichia coli* ATCC 8730, *Klebsiella pneumoniae* (IC) 134202) bacterial strains and fungi (*Candida albicans* ATCC 10231) by the broth microdilutions method. Also, the colonization rate and biofilm formation of *Candida albicans* ATCC 10231 on bionanocomposites substrate were studied. *In vitro* cytotoxicity of bionanocomposites was evaluated on the fibroblast cell line (NCTC clone L929) by assessing the cell morphology and cellular viability. Also, the obtained bionanocomposites were analyzed by DSC, FT-IR and SEM.

The results suggest that the bionanocomposites containing AgNPs show high biocompatibility, but only a slightly improved inhibitory activity of fungal colonization as compared with the control without AgNPs.

**NOVEL SODIUM ALGinate - POLY(N-ISOPROPYLACRYLAMIDE)
THERMOREVERSIBLE INJECTABLE HYDROGELS WITH SEMIINTERPENETRATING
NETWORK STRUCTURE**

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Poly(N-isopropylacrylamide) (PNIPAM), one of the most well-known LCST-displaying thermosensitive polymers, has been very much studied, especially for biomedical purposes, due to the LCST close to body temperature (about 32°C), abrupt thermal response and low sensitivity to slight modifications of pH, concentration or chemical environment. However, PNIPAM aqueous gels undergo demixing/syneresis on or soon after gelation, which is an important drawback when applications as injectable hydrogels are targeted.

To improve the stability of the gels, NIPAM was either statistically copolymerized with hydrophilic monomers or the PNIPAM chain was attached to a polymer block with permanent water solubility on the temperature interval investigated. Another approach to reduce or possibly avoid demixing of PNIPAM aqueous gels may be the blending with other hydrophilic polymers, able to keep the water inside the gel. However, to the best of our knowledge, such an attempt to improve the stability of injectable thermosensitive reversible hydrogels has not been reported yet, although blending as a method to tailor some properties of these hydrogels was already described in literature.

The present work deals with the preparation and thermogelation properties of novel injectable thermoreversible hydrogel compositions with semi-interpenetrating network structure based on sodium alginate (SA) – PNIPAM physical mixtures. We showed for the first time that the addition of the hydrophilic SA polymer to the PNIPAM aqueous solution strongly improved the stability against syneresis of the hydrogel formed at 37°C, which may represent in some cases a method to reduce demixing of injectable hydrogels. Furthermore, the thermogelation properties of the SA-PNIPAM aqueous solutions were studied by dynamic rheometry and differential scanning calorimetry as a function of mixture composition and PNIPAM molecular weight and polydispersity.

THERMAL DEGRADATION OF POLY(N-ISOPROPYLACRYLAMIDE-co-5,6-BENZO-2-METHYLENE-1,3-DIOXEPANE) STATISTICAL COPOLYMERS: A KINETIC ANALYSIS

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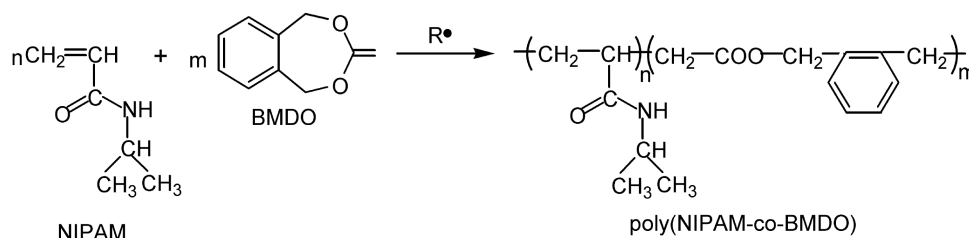
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Poly(N-isopropylacrylamide) (PNIPAM), one of the most well-known LCST-displaying thermosensitive polymers, has been very much studied, especially for biomedical purposes, due to the LCST close to body temperature (about 32°C). However, an important drawback of PNIPAM in such applications consists in its lack of biodegradability due to the backbone being made up only of C-C bonds. Recently, degradable PNIPAM polymers containing hydrolyzable ester groups within the backbone have been prepared by free-radically copolymerizing NIPAM with cyclic ketene acetals, like for example 5,6-benzo-2-methylene-1,3-dioxepane (BMDO, Scheme 1).^{1,2}



The present work investigates by thermogravimetric analysis (TGA) the thermal degradation process of some poly(NIPAM-co-BMDO) statistical copolymers of various compositions, prepared by radical addition-fragmentation radical polymerization (RAFT), in the presence of S-1-dodecyl-S'-(α,α' -dimethyl- α'' -acetic acid) trithiocarbonate as the RAFT agent. The variation of activation energies as a function of global degradation process conversion was calculated using Kissinger-Akahira-Sunose isoconversional method and multiple experimental data sets with different heating rates.³

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INTERACTION BETWEEN MAGNETITE NANOPARTICLES AND CR(VI) FROM INDUSTRIAL WATER

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The nanomaterials have received considerable attention due to their small particle size, large surface area, low cost and ease of preparation¹. By using magnetite nanomaterials is possible to contribute to removal of Cr (VI) from waste water. Hexavalent chromium Cr(VI), is carcinogenic and highly toxic to living organisms because it occurs in soluble chromates that readily cross cell membranes^{2, 3}. Magnetite prepared in the lab has been characterized by specific analytical techniques, as follows:

- By using **atomic force microscopy** (AFM), it could be observed the average of magnetite particles size which is about 10 nm, and the height of the magnetite-chromium compound particles, which is between 25-45 nm. The 3D topographical image for the magnetite-chromium compound shows value of about 43.4 nm for an area of 5 μm .

- **FTIR** was used to understand structure, bonding and reactivity of magnetite and chromium sorbed on its surface. The Cr (VI) uptake increases with temperature thus indicating chemical interaction between adsorbate and adsorbent molecules. Moreover endothermic behaviour also support pore diffusion.

- **Thermal analysis** DSC/TGA results showed that on addition of chromium the exothermic transformation peaks of magnetite to maghemite shifted to higher temperatures. This suggests retard of magnetite to maghemite transformation in presence of chromium by substitution of chromium in the magnetite structure.

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MORPHOLOGICAL AND THERMO MECHANICAL PROPERTIES OF HALLOYSITE/POLYPROPYLENE NANOCOMPOSITES

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Polymer nanocomposites are a very attractive class of materials for both industry and fundamental research. Usually with 1–5 wt-% filler loadings (such as layered silicates or carbon nanotubes), polymer nanocomposites exhibit new and sometimes improved properties compared to conventional polymer composites and can be synthesized employing simple and inexpensive techniques.¹²

Polypropylene (PP) is highly used in various industrial sectors, due to mechanical performance and ease with which they can be improved by the addition of various nanofillers.

Halloysite nanotubes (HNTs) have attracted in the last 5 years the research attention as a new type of additive for enhancing the physical, mechanical and thermal properties of polymers.³ HNT is a natural aluminosilicate clay with a hollow tubular morphology. Halloysite tubes typically have diameters smaller than 100 nanometers with lengths ranging from about 200 nanometers to 2 microns.⁴ Due to naturally exfoliated morphology, Halloysite can easily be dispersed in a polymer matrix without needing to chemically separate particles.⁵

In the present work, morphological, thermal and mechanical properties of nanocomposites based on PP filled by halloysite nanotubes were studied. As compatibilizing agent, maleinized PP (MAPP) was used. No significant change in the crystalline structure of PP nanocomposites was detected. The highest elasticity modulus was achieved for the nanocomposite with 5% HNT. Very good balance of properties was obtained at 2.5:1 MAPP:HNT constant ratio. Storage modulus increased and $\tan \delta$ decreased with increasing of HNT content.

Acknowledgements

Financial support by the EU Commission through Project Evolution-314744 is gratefully acknowledged.

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**RESEARCHING THE UNDERGROUND ATMOSPHERE OF THE CLOSED
MINING WORKS FOR ENSURING THE ADEQUATE SECURITY LEVEL**
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At the exploitation of natural underground deposits in order to ensure the smooth running of the production process, one of the basic conditions is to provide a permanent working atmosphere as close as possible to the surface atmosphere. Permanent informative control together with laboratory control of the underground state mine air shall be done considering the thorough need to determine the mine air composition in the specific activity. Knowing the exact chemical composition and monitoring the underground and behind dams mine air is particularly important for workers safety and security deposits of coal. In order to monitor the chemical composition of the mine air both from mine workings and the back of the dams have been used instrumental analysis methods (direct measurement-gas sensors and gas analyzers chromatography) and the results were interpreted on the basis of the index fire.

Keywords: gas-cromatography, firedamp mines, monitoring, mine air

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QUINOLONE ANTIBACTERIAL AGENTS; SYNTHESIS, CHARACTERIZATION AND QSAR PROPERTIES

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This paper presents experimental data regarding the synthesis of several quinolones (Fig.1). The novel quinolones have been evaluated for „in vitro” activity by determining minimum inhibitory concentration against a variety of bacteria.

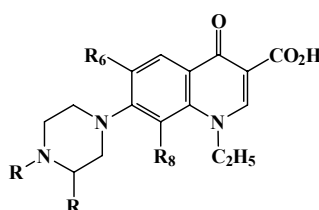
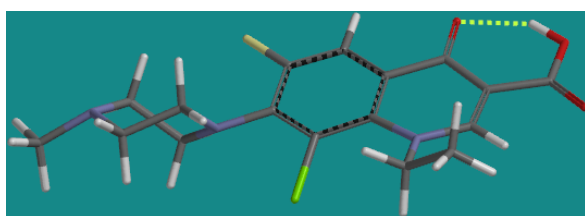


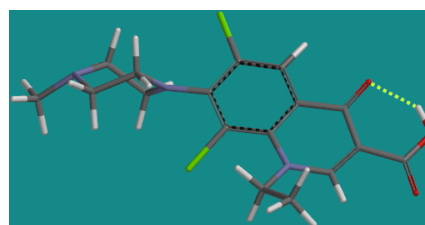
Fig.1 General structure of the new compounds synthesized

where: R = H, methyl, R₆ = F, Cl, R₈ = Cl, H

In addition, a study of their molecular and structural characteristics and properties has been achieved using Spartan 14 software. A computational study to compare molecular properties, QSAR properties and mechanics calculations for a series a novel synthesized quinolones, has been conducted using Spartan 14 Software. For each structure of the analyzed class, the structure 3D used for calculations was generated and its geometry has been optimized by energy minimization, in order to obtain the most stable conformer. (for example, compounds shown in Fig. 1 and 2). For these conformers, the most important topological, conformational characteristics and QSAR properties has been calculated (e.g. angles and distances, dihedral angles, weight, no. of conformers and tautomers, area, volume, ovality, polarizability, log P, energy of solvation, dipole moment, energy of the HOMO and LUMO orbitals).



**Fig. 2 Optimized molecular structure
of a fluoroquinolone**



**Fig. 3 Optimized molecular structure
of a chloroquinolone**

ABOUT THE MATHEMATICAL MODELING OF THE CONTROLLED RELEASE OF DRUGS FROM ORAL DOSAGE FORMS

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In order to decrease the dosing frequency in a treatment, controlled release preparations of drugs are very important in the pharmaceuticals.

Polymers have been used as a main tool to control the drug release rate from formulations, because they offer unique properties which so far have not been attained by other materials. In the last years, polymer chemists, chemical engineers and pharmaceutical scientists are engaged in bringing out design predictable, controlled delivery of bioactive agents¹. Solid dosage forms as tablets are among the most common methods to administer drugs.

Because the microbial infections are the vast growing disorders in the world, a large number of mathematical models were developed to describe the release of antibiotics from oral dosage forms²⁻³. The choice of a valid model depends on the mechanism of drug release, type of drug, type of excipients and composition of the dosage form.

This paper presents the results of a simulation study regarding the release kinetics of two antibiotics, by using different mathematical models. The validity of the selected models is proved by comparing the predictions of the models with the experimental profiles obtained in simulated intestinal fluid (pH 7.4) and reported in the recent literature. The predictions obtained from this study are useful to improve the oral administration of the considered antibiotics and guide further investigations.

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EVALUATION OF FOUR ROMANIAN LINSEED VARIETIES AS RAW MATERIALS FOR INDUSTRIAL APPLICATIONS: PRODUCTION PERFORMANCES AND QUALITATIVE CHARACTERIZATION

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The aim of the research is to evaluate the production capacity of four authentic Romanian linseed (*Linum usitatissimum*) varieties – Alexin, Cristina, Florinda and Junia – developed at the National Agricultural Research and Development Institute of Fundulea (NARDI Fundulea), Romania.

The linseed varieties have high levels of oil, the average seed oil content being 45.4%. According to seed production, three varieties (Alexin, Cristina, and Florinda) showed good productivity, ranging from 1662 to 1820 kg/ha (average values). The seed production correlated with the seed oil content gives the oil production, which is a useful tool for the comparison of linseed varieties in terms of oil productivity. Thus, Cristina variety showed the best average seed production value (1820 kg/ha) and the best oil productivity (817 kg/ha).

For industrial applications linseed oil quality (which is best reflected by the iodine index) is discussed based on fatty acids composition.

The mean fatty acid profile and iodine index for each of the linseed oil samples is shown in Table 1.

Table 1: Fatty acids profile of Romanian linseed oils (molar %, determined by CG)

Variety	Linseed oil composition (mean molar %)									Iodine value (mg I ₂ /100 g oil)
	C16:0	C18:0	C18:1n9c	C18:2n6c	C18:3n3	C18:3n6	C22:0	C20:0	C18:1n9t	
Alexin	4.76	3.56	19.65	15.14	56.75	0.07	0.02	0.05	0.00	191.22
Cristina	4.94	3.36	18.42	17.26	55.80	0.05	0.02	0.05	0.11	191.41
Florinda	4.53	3.82	15.85	15.30	60.34	0.09	0.03	0.05	0.00	197.64
Junia	4.41	3.31	23.95	15.10	53.06	0.02	0.02	0.04	0.09	185.07

The work has been funded by the Sectorial Operational Programme Human Resources Development 2007-2013 of the Ministry of European Funds through the Financial Agreement POSDRU/159/1.5/S/132397.

RELEASE PROFILES OF NOVEL FLUOROQUINOLONE FROM MCM-41 AND MCM-41-NH₂ MATERIALS

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MCM-41 was first introduced as a drug delivery system in 2001¹ and since then this material has been used for the release of numerous active substances. The present paper focuses on the synthesis of MCM-41 and amino-functionalized MCM-41 materials and the release profiles from these materials of a novel fluoroquinolone synthesized by our group².

MCM-41 nanoparticles were successfully prepared using cetyltrimethylammonium bromide (CTAB) as a structure directing agent and tetraethyl ortosilicate (TEOS) as a silica source in aqueous ammonia medium at ambient temperature. MCM-41-NH₂ materials were obtained by post-synthesis method, MCM-41 was grafted with (3-aminopropyl)trimethoxysilane (APTMS) and (3-aminopropyl)triethoxysilane (APTES). The materials were characterized by HR-TEM and FT-IR. Quinolones have a rapid bactericidal activity, with a broad antibacterial spectrum with high *in vitro* activity against Gram-positive and Gram-negative bacteria. The fluoroquinolone used in this study, 1-ethyl-6-fluoro-7-(3-methyl-piperidin-1-yl)-8-chloro-1,4-dihydro-4-oxo-quinoline-3-carboxylic acid (FPQ30), presents good activity against Methicillin-resistant *Staphylococcus aureus*.

The release of FPQ30 from the mesoporous materials was determined in simulated body fluid (SBF) prepared according to literature³. The release profiles of the antibiotic were recorded for 6 hours using the modified HPLC technique⁴. The inlet and the outlet of the HPLC system were placed inside the beaker containing the SBF solution and the sample, while the beaker was kept under continuous stirring.

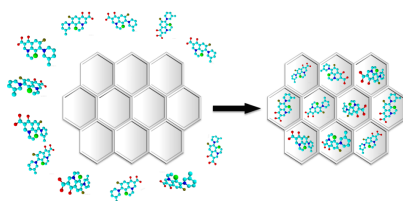


Fig. 1. Schematic loading of MCM-41 with FPQ30

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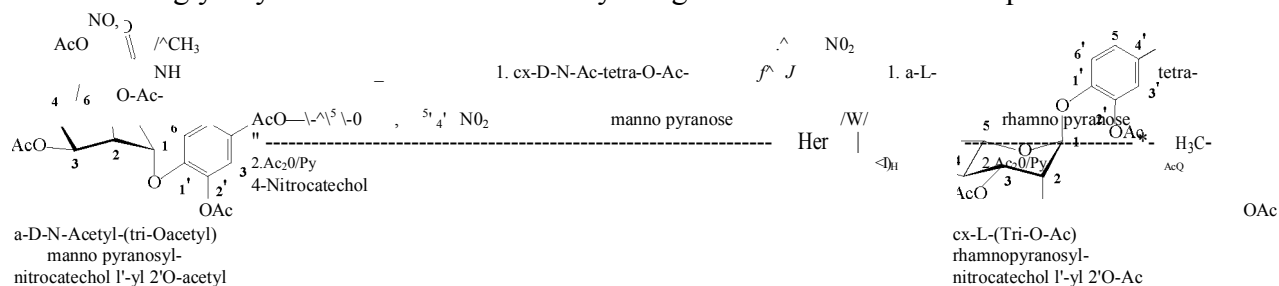
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**PRELIMINARY DATA CONCERNING THE SYNTHESIS OF TWO
CHROMOGENIC GLYCOSIDES OF
4-NITROCATÉCHOL - α -D-N-ACETYLMANNOPYRANOSAMINIDE AND
 α -L-RHAMNOPYRANOSIDE AS SUBSTRATES FOR EXOGLYCOSIDASES
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Monosaccharides, N-acetylmannose and L-rhamnose were peracetylated in the cold so as to avoid formation of furanose rings. The obtained peracetates were crystallized and then used in a Helferich glycosylation of 4-nitrocatechol by using $\text{BF}_3 \cdot \text{OBU}_2$ as chemical promoter¹:



The synthesized glycosides were purified by column chromatography on silica gel and then

characterized chemically, chromatographically and by H and C NMR spectroscopy. Zemplén hydrolysis led to removal of protecting acetate groups and acidic hydrolysis cleaved the glycosidic bonds. Sugars and 4-nitrocatechol were determined colorimetrically. A molar ratio of 1:1 between monosaccharide and 4-nitrocatechol was found in both glycosides. *H

and ¹³C NMR Spectroscopy was accomplished on peracetylated glycosides. NMR Characteristics of 4-nitrocatechol were compared with our preceding data¹ and similarly the spectra of ManNAc^{2,3} and Rhap.^{4,5} There was an excellent agreement between our results and the data from chemical literature. References

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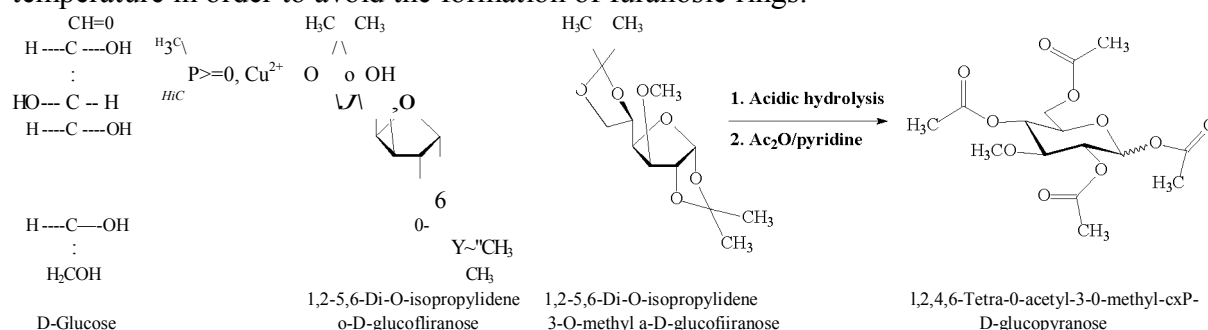
PARTIAL METHYLATION OF MONOSACCHARIDES FOR THE ELABORATION OF A CHROMATOGRAPHIC MODEL USED IN THE SYSTEMATICS OF PLANTS AND MICROORGANISMS AS WELL AS FOR GLYCOSYLATION REACTIONS

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Partially methylated sugars have been found in a remarkable diversity of natural compounds: glycoesters, polysaccharides, phenol-lipids, gangliosides, glycosphingolipids, etc.¹ On the other hand, the fact that partial methylation alters biological status of carbohydrates seems to be really significant.

1,2-5,6-Di-O-isopropylidene α -D-glucopyranose was prepared by acetonation of D-glucose in the presence of anhydrous copper sulfate and sulfuric acid. The structure of 1,2-5,6-Di-O-isopropylidene α -D-glucopyranose was confirmed by H and C NMR analysis, *per se* or preceded by acetylation. Methylation of di-isopropylidene derivative, with methyl iodide/silver oxide in dimethylformamide, led to 1,2-5,6-Di-O-isopropylidene 3-O-methyl α -D-glucopyranose. Isopropylidene protecting groups were removed by acidic hydrolysis and the methylated sugar was alternatively peracetylated or perbenzoylated, both at relative low temperature in order to avoid the formation of furanose rings:



3-O-Methyl D-glucose was also chromatographically compared with D-glucose and a higher mobility was found. Peracetylated derivatives were analyzed by H and C NMR spectra, in comparison with the corresponding peracetylated D-glucose. Good agreement was found between our results and the results from chemical literature.² Since good NMR spectroscopic results were obtained in the case of peracetylated 3-O-methyl D-glucose, the corresponding perbenzoylated derivative was analyzed only chromatographically and by IR spectroscopy.

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COBALT(II) PHTHALOCYANINE SCREEN PRINTED CARBON ELECTRODE FOR STUDYING THE INTREACTION BETWEEN MYOGLOBIN AND PEROXYNITRITE

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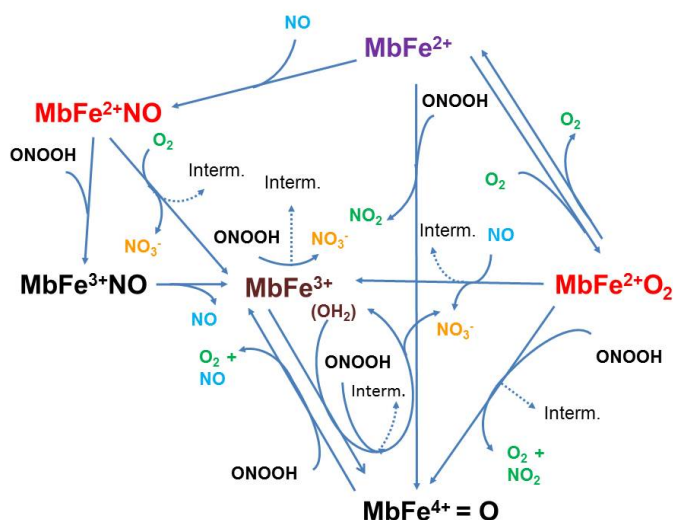
Discoloration, rancidity and alteration of flavor of the muscle foods (fresh or even nitrite-cured ones) are some consequences of redox-activities that occur due to the oxidative species that are scavenged by different forms of myoglobin (the main hemeprotein in the skeletal and cardiac muscles)¹.

Peroxynitrite, formed in biological tissues by the fast reaction of superoxide (O_2^-) and nitric oxide (NO), is a powerful oxidant that promotes lipid peroxidation, DNA and cellular damage in biological tissues. Some decomposition reactions of nitric oxide (NO) and peroxynitrite

(ONOOH) promoted especially by deoxymyoglobin ($MbFe^{2+}$) and oxymyoglobin ($MbFe^{2+}O_2$), with the formation of other myoglobin species (eg. $MbFe^{3+}OH_2$), are presented in the scheme adapted from Møller and Skibsted work².

Herein, a cobalt(II) phthalocyanine modified screen printed carbon electrode (CoPc/SPCE) is used to assess the

antioxidant (scavenging) capacity of myoglobin towards peroxynitrite using electrochemical methods (CV, DPV). Also, UV-Vis technique is simultaneously used to monitor the same reactions and to determine the formed species.



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CONVERSION OF HYDROSOLUBLE P-D-GALACTOFURANOSIDES TO α-L-ARABINOFURANOSIDES AND THEIR CLEAVAGE BY α-L-ARABINOFURANOSIDASE - A

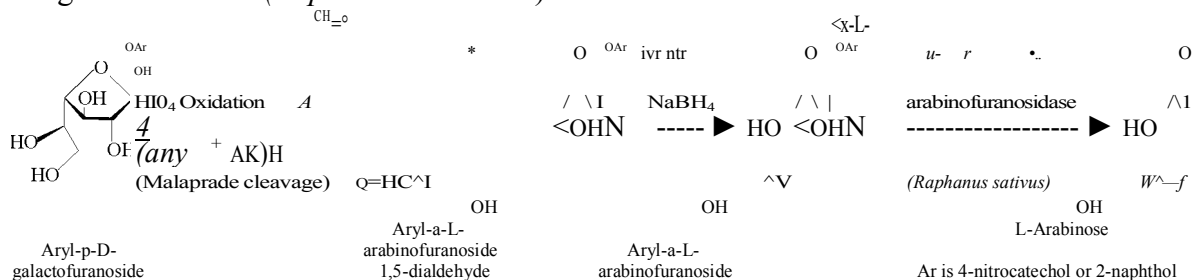
STRUCTURAL PROOF FOR FURANOSIC RING

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D-Galactose, a relatively widespread monosaccharide has a unique property: removing of the C-6, so as to obtain an aldopentose, produces a sugar of an opposite steric series, L-arabinose. In fact, this transformation constitutes inclusively a biochemical pathway. We have used this transformation as an indirect proof for furanositic ring.

1,2,3,5,6-Penta-O-benzoyl α-D-galactofuranose was synthesized by benzylation of monosaccharide at relatively high temperature, a physical factor that facilitates the furanositic ring. The reaction product was purified by crystallization from ethanol and then converted to 1-bromo-1-deoxy-2,3,5,6-tetra-O-benzoyl α-D-galactofuranose, by reaction with hydrobromic acid in 1,2-dichloroethane. Tetra-O-benzoyl α-D-galactofuranosyl bromide served as a donor in a Koenigs-Knorr glycosylation reaction of 4-nitrocatechol or 2-naphthol, in the presence of Ag₂O as promotor. Reaction products, 2,3,5,6-tetra-O-benzoyl α-D-galactofuranosyl-4-nitrocatechol 1-yl (-2-naphthol, respectively) were submitted to Zemplen hydrolysis and then separated by column chromatography on silica gel in a gradient of ethanol in 1,2-dichloroethane. The enzymatic assay of these substrates became a problem since P-galactofuranosidases were found especially in pathogenic organisms. On the other hand, α-L-arabinofuranosidases are widespread in plant tissues.⁴ Our preferred source of enzyme were the germs of radish (*Raphanus sativus* L.) and the reactions are described below:



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A NEW TEACHING STRATEGY FOR ALDOHEXOSES STRUCTURE ELUCIDATION. AN *ENBLOCK* APPROACH OF THE 16 LINEAR ISOMERS

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This new strategy of teaching constitutes an original teaching strategy and it has been found in a teaching process spread out on more than three decades of teaching organic chemistry to the future biologists and biochemists. This new teaching strategy could be also entitled "From The Paradigm of Fischer to the Paradigm Bijvoet-Fischer".

The fundamental problem is a problem of representation; let's imagine that we have to answer to the following question: how could we attribute the correct structural model (and implicitly the corresponding written formula) to an optically active compound, be it (+)-tartaric acid. The answer to this question was given only in 1951 by a paper of J. M. Bijvoet et al. E. Fisher gave a probabilistic answer with a certitude of 50 %. In this way the scientists lived under the paradigm of E. Fischer between 1895 and 1951. By using an artifice invented by them, Bijvoet et al., gave a unequivocal solution. They simply "saw" the atoms of (+)-tartaric acid and consecrated the X rays as being the microscope of chemists. In this way the structure of (+)-tartaric acid and implicitly of (-)-tartaric acid became known. Moreover, the structure of (-)-glyceraldehyde and (+)-glyceraldehyde, as respective precursors of the two chiral isomers of tartaric acid became known. Of the 16 linear isomers of aldohexoses, 8 would give (+)-glyceraldehyde and 8, (-)-glyceraldehyde, by three chain shortening; the first 8 belong to D-series and the other 8 to L-series. The reasoning applied further is for a group of D-isomers. Two chain shortening would led to *mezo* tartaric acid (as in D-glucose) or to (-)-tartaric (as in D-galactose). In this way, the configuration of C-4 of all 8 D-aldohexoses has been elucidated. By similar reasoning, the configuration of C-3 and C-2 of all 8 D-aldohexoses has been elucidated.

DETERMINATION OF THE FATTY ACIDS PROFILE OF SEED OILS FROM ROMANIAN MEDICINAL PLANTS THROUGH SPECTROSCOPIC AND CHROMATOGRAPHIC TECHNIQUES

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The aim of the research is to determine the oil content and fatty acids profile of seed oils from nine Romanian medicinal plant species grown at the National Agricultural Research and Development Institute (NARDI) of Fundulea, Romania. The medicinal plant species taken into analysis are: *Oenothera biennis*, *Camelina sativa*, *Nigella damascena*, *Crambe abyssinica*, *Carthamus tinctorius*, *Salvia sclarea*, *Trigonella foenum-graecum*, *Cnicus benedictus* and *Asclepias syriaca*.

The oil was obtained from seeds by continuous solvent extraction (Soxhlet) in two solvent systems: petroleum ether and chloroform-methanol (1: 1) mixture.

The investigated medicinal plant species have different levels of oil content, ranging from 2.98 (*Trigonella foenum-graecum*) to 30.48 (*Nigella damascena*) g oil /100 g seeds.

The fatty acids composition of oils was determined by gas-chromatography (GC)¹ and ¹H-NMR spectroscopy. In order to evaluate the unsaturation degree of oils, the iodine index was computed from the GC data².

The fatty acid profiles of the investigated seed oils are very different, globally 21 fatty acid methyl esters being identified in chromatograms. Among them, the main fatty acids are: linolenic (C18:3), linoleic (C18:2), oleic (C18:1), stearic (C18:0) and palmitic (C16:0) acid. Other fatty acids such as erucic (C22:1) or *cis*-11-eicosenoic acid (C20:1) were found in high levels in *Crambe abyssinica* and *Camelina sativa* seed oils, respectively.

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SYNTHESIS OF EPOXYSILANE FUNCTIONALIZED SILICA SUPPORTS FOR HUMIC ACIDS IMMOBILIZATION

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Present study reports a new methodology for preparation of epoxy-functionalized silica particles able to immobilize humic acids. Hydroxyl groups are very abundant functional groups in humic substances, and they can react with epoxy groups in the presence of catalysts in alkaline media.¹ Therefore, we studied the possibility of synthesizing silica supports containing glycidyloxy groups. In order to facilitate the connection between functionalized silica particles and humic acids, (3-glycidyloxypropyl)trimethoxysilane (GPTMS) was grafted during the sol-gel reaction to the silica surface, alone or in combination with methylsilane having mono- or tri-methoxy groups.² The newly prepared particles were characterized by Solid State ²⁹Si and ¹³C CPMAS Nuclear Magnetic Resonance (CPMAS-NMR), Fourier Transform Infrared Spectroscopy (FTIR), Dynamic Light Scattering (DLS), Thermogravimetric Analysis (TGA), and Elemental Analysis (CHN). By these techniques was revealed the efficient functionalization of silica nanoparticles with epoxy groups.

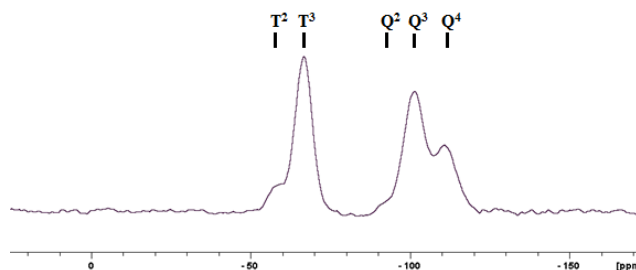


Fig. 1. ²⁹Si CP-MAS NMR spectra of TEOS/GPTMS/MeTMS 20/1/1 sample

Acknowledgement: This material is based upon work supported by the Ministry of National Education – Research Activity, CNDI– UEFISCDI, in the frame of the project number PN-II-PT-PCCA-2013-4-0995/160/2014 (MAIA), Programme PN2 P4 Partnership PCCA 2013”

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**ANALYSIS OF RADIOPROTECTION EFFECT OF AN ALGAE
EXTRACT OBTAINED FROM RED ALGAE ENRICHED
WITH BIOLOGIC ACTIVE COMPOUNDS**

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STOIAN¹**

¹. *University of Bucharest, Faculty of Biology,*

². *Institute of Physical Medicine, Rehabilitation and Medical Balneoclimatology*

Electromagnetic radiation is an important factor that has a powerful influence on the organisms. Different types of radiation have different effects, while some are harmless, the ones that have high energy can determine major changes at a molecular level.

In order to protect themselves, many classes of algae developed different defense mechanisms, through biosynthesis of a family of compounds named mycosporine like amino acids (MAA). This MAA are capable of absorbing UV type radiation, protecting the more sensitive molecule of the cells and literature data show that these compounds have the capacity to protect human skin cells against UV rays of solar radiation.

The objective of this study was to determine if the MAA were capable of protecting cells against X-rays, an electromagnetic radiation with higher energy than UV. The radioprotection was tested using Wistar mouse fibroblast cells cultures by placing between them and the source of the radiation (Siemens opti 150/30/50-100 X-ray machine) an agarose gel who contains different concentrations of an alcoholic extract (235 µg/ml gallic acid equivalent) obtained from *Ceramium* genus of red algae (10%, 1% and 0,1%). Fibroblast culture have been exposed using 3 different intensities of X-rays (between 80 and 170 Sv/h).

Our results (viability tests and metalloproteinase profile) indicate that X-ray protection of the fibroblast culture depends on the intensity of the x-ray and the concentration of red algae extract from agarose gel.

**ANALYSIS OF REMEDIATION EFFICIENCY OF SOME SOILS POLLUTED BY
CRUDE OIL FROM SUPLACU DE BARCAU, ROMANIA**

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Doru GABOR ¹, Nicolae CRACIUN ¹, Ioan ARDELEANU ³, Gheorghe STOIAN ¹**

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Bioremediation is one of the recent popular low cost technologies that can be effectively applied to remediate the soil and groundwater contaminated with petroleum products. Total petroleum hydrocarbons (TPH) represent the measurable amount of petroleum-based hydrocarbons in environmental matrix.

In nature there are several microbes which are capable of detoxifying and degrading the toxic chemicals. Usually, microbes use these contaminants to obtain energy, nutrients or for respiration. During these processes the contaminants are degraded to less toxic or nontoxic end products.

The crude oil from Suplacu de Barcau, N-W of Romania, is characterized by the predominance of the heavy fractions in comparison with the other crude oil from Romania and the world, difficult to be effectively bioremediated. In consequences, chemical methods can be useful to make petroleum-based hydrocarbons more accessible to microbial biodegradation.

The objective of this study was to apply and to evaluate a new chemical method based on ammonium persulfate (APS) oxidation in the aim to make Suplacu de Barcau's hydrocarbons more accessible to microbial degradation. Chemical process has been realized by 1% ammonium persulfate treatment on three different samples with different degree of contamination (Bioremediere 1-TPH=24.5mg%, Bioremediere 2-TPH=42mg% and Platforma- TPH=39mg%) and the process has been monitored on 3 weeks period using different soil enzymatic markers who characterized microbial activity (phosphatases, catalase and total dehydrogenases).

Our results show that 1% APS treatment is very effective in Suplacu de Barcau petroleum degradation on the basis of reduction of TPH (between 25 and 30%) and an increase of enzyme activities (between 17 and 25%).

NITRATE REMOVAL BY CATALYTIC REDUCTION WITH HYDROGEN

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Nitrate concentrations in surface waters and especially in ground waters have increased in many locations in the world and are the main sources of such contamination from the intense use of fertilizers in agriculture, human sewage, and livestock manure.

The European Community has set the maximum permitted level of nitrate in drinking water to 50mg/l, the U.S. Environmental Protection Agency has lowered that level to 10 mg/L. Therefore, reducing the nitrate concentration in drinking water is imperative nowadays in many places, in order to protect the environment and human health.

To comply with the legislation, the removal of nitrate from drinking and waste water using heterogeneous catalysis constitutes promising approach for the destruction of pollutants in water. Hence, heterogeneous catalytic reduction of nitrate to nitrogen that has been suggested by Vorlop et al., [1] appears to be a promising process for nitrate removal from natural waters. More recently, catalytic denitrification has been developed to obtain the selective reduction of nitrate into nitrogen. [2-3]

In this work, a series of reducible catalyst supports such as ceris-zirconia based catalysts ($\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$) have been prepared by a sol-gel technique combined with evaporation-induced self-assembly in organic phase. Optimisation of the temperature and humidity conditions was made correlated with desired properties. Physical properties of the materials were assessed by low – angle and wide angle XRD, N_2 porosimetry, TGA-DTA, Raman spectroscopy and electronic microscopy. From collected results, we demonstrated that our procedure leads to an ordered mesoporous crystalline phase after calcination.[4] The catalytic supports were subsequently impregnated with 1% Pt or 1% Pd using incipient wetness impregnation method. The characterisation results have been correlated with the catalytic behavior of the materials.

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GENERAL INFORMATION ABOUT SHALE GAS RESERVOIRS

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ABSTRACT

In the modern strategy for conventional hydrocarbon exploration (oil and gas), “a petroliferous system” may be defined in a considered area, namely:

- source rocks, which generates oil and gas;
- reservoir rocks (porous and permeable) for fluid accumulation;
- sealed rocks (impermeable formations) and
- Migration path, from source rocks to reservoirs.

This approach was successfully applied during the long history of hydrocarbon (oil and gas) industry in different countries in the world, including Romania.

The discovered and exploited deposits in different geological structures (provinces) were considered as “conventional hydrocarbon deposits”.

Predictable decline of oil and gas production from conventional deposits arise the problem of finding an alternative source of energy. These are represented now by “unconventional oil and gas deposits” extracted from shale gas and tight gas and oil deposits. In addition, coal bed methane (CBM) and gas–hydrates deposits (from deep marine and oceanic areas) are considered.

A significant interest is represented by shale gas deposits. Gasiferous shales are sedimentary rocks with very fine grain size. These shales must be defined as hydrocarbon source rock with TOC (Total Organic Carbon) higher than 1% wt. The shale gas formation satisfies two criteria: source rock and reservoir rock.

The source rocks are compacted formations with very low permeability (0.01 – 0.00001 md) so, the gas may be extracted from the rock by hydraulic fracturing, a technique used for a long time in the oil industry.

Hydraulic fracturing consists in injection of water at high pressure, commonly fresh water, about 98 to 99 % of total volume, and proppant (fracturing material) (about 1% to 1.9% of total volume), usually sand and ceramic particles carried by frack fluid into fractures to keep the fracture open when the hydraulic pressure is released.

For increasing efficiency of the process, hydraulic fracturing is combined with horizontal drilling, opening a long path into formation.

The technology of shale gas was developed in many aspects in the USA, applied in an extensive manner in different fields, with many wells drilled. The gas production increased substantially. Internal production of shale gas covers about 84% from energy needs of USA for 2013.

Shale gas technology extended also, in other countries from Europe and other continents, as an alternative (additional) source of energy.

STEPS TO SUCCESS IN HORIZON 2020 – SOCIETAL CHALLENGES 2

Ioana ISPAS

*International Cooperation Department
Ministry of National Education*

The presentation aim to analyse the most frequent errors made by the applicants on the first call on Horizon 2020 – Societal challenges.

LAW ON EMPLOYEES’ INVENTIONS – A LAW NECESSARY FOR ROMANIA?

Bucura IONESCU

Direcția Brevete de Invenție și Suport al Inovării; Oficiul de Stat pentru Invenții și Mărci

The Special Law regarding Employees’ Inventions (Law 83/2014) was intended to be a single regulation for the inventions created by all kind of employees: of large companies, SMEs, research institutes, universities.

The Law achieves a balance between the following fundamental principles:

1. The inventor’s right - originally an invention belongs to the inventor, as set forth by Paris Convention to which Romania is part from 1920;
2. The employer’s Right on the invention that was performed by inventive mission contract or by acquisition from the inventor, on the inventions made up by using the technical means and the information of the employer in its field of activity;
3. The right of the inventor to be rewarded for his creation.

EXAMINATION OF NOVELTY AND INVENTIVE STEP OF A PATENT APPLICATION

Elisabeta CLEPS

Direcția Brevete de Invenție și Suport al Inovării; Oficiul de Stat pentru Invenții și Mărci

The lecture provides a description of the Rules for substantive examination of novelty and inventive step of a Patent Application, the notifications issued by the Examination Division and the arguments that might be filed by the applicant.

A brief presentation of time limits and loss of rights resulting from failure to respond within a time limit as set forth by the Rules (European Patent Convention and National Law) and possibilities of re-establishment of rights will be provided.

TECHNOLOGICAL TRANSFER IN A GLOBAL COMPETITIVE WORLD

Alexandru Ioan CABUZ

Founder and CEO at Peergate SRL

*Program director - researchforindustry.ro at Romanian Institute of Science and Technology
alexcabuz2@gmail.com*

International patents are expensive but the costs can be covered by industrial partners, if they are identified and attracted in a collaboration, in the first 12 months after the first international filing. Therefore, the main obstacle of Romanian institutions are not the costs, but their lack of connections, visibility and credibility in the relevant industries, in the international markets.

For an efficient exploitation of results, the first step is, therefore, a sustained effort of networking and communication of the institutions in the relevant industries. *Research for Industry* can offer support for institutions that wish to start on this path.

BUILDING AN INNOVATIVE CLUSTER – CUI PRODEST?

Dragos SEULEANU

Magurele High-tech Cluster; Fundatia pentru Democratie, Cultura si Libertate

A short presentation of European and Romanian regulations which support associative forms such as clusters is done. Clusters are groups of independent entities (SMEs, including start-ups and spin-offs, large enterprises, research organizations, catalysts organization like NGOs and Technological Transfer Centers), acting in a specific area, intended to promote innovative activity through mutual interactions, the use of common facilities, exchanges of knowledge and know-how, networking and information dissemination. The leverage role of this type of association for an a higher accession of EU cohesion funds targeted to increased competitiveness and for an enhanced dynamics and flexibility of the business environment, is underlined.

PLANT BIOSIMULANTS INTEGRATION INTO PLANT-BASED BIO-ECONOMY VALUE CHAIN

F. OANCEA¹, T. E. SESAN^{1,2}, S. VELEA¹, P.C. CORNEA^{3,4}, S. DINU⁵, F. CONSTANTINESCU⁵, M. POPESCU¹, C. MINCEA⁵, I. RĂUT¹

1- National R&D Institute for Chemistry and Petrochemistry – ICECHIM, Bucharest; 2 – University of Bucharest, Faculty of Biology, Bucharest; 3 – University of Agronomical Sciences and Veterinary Medicine, Faculty of Biotechnologies, Bucharest; 4- Center for Applied Biochemistry and Biotechnologies Biotechnol, Bucharest; 5 – Research-Development Institute for Plant Protection, Bucharest

Plant biostimulants represent an emerging category of agricultural inputs. These bioproducts foster plant growth and development throughout the crop life cycle, increase nutrient uptake and nutrient efficiency, enhance plant tolerance to biotic and abiotic stresses.

Bio-economy is a trans-sectorial domain encompassing the sustainable production of renewable resources from terrestrial and aquatic ecosystems and their conversion into food, feed, biobased chemicals / bioproducts (including biopharmaceuticals, bioplastics and biomaterials, alternative inputs for agricultural technologies) and bio-energy. Sustainable intensification of plant production is necessary in order to face the challenge for an increased demand for renewable resources for biobased chemicals and bio-energy, without affecting food / feed production.

Use of plant biostimulants produced by conversion of various by-products / wastes represents a practical solution for sustainable intensification of plant production. Such an approach close in a biomimetic manner the plant-based production chain. By-products / waste conversion into plant biostimulants create industrial symbiosis into one of the main bio-economy value chains and increased overall productivity and profitability of lower added value sectors of bio-economy.

We present in this work our contributions to the development of new, innovative, plant biostimulants based on bio-industries by-products. We systematize these contributions in relation to the main categories of plant biostimulants defined by European Union experts. Related to *microbial inoculants* category of plant biostimulants we briefly discuss our contributions regarding the use of bio-fuel byproducts for mass multiplication of plant beneficial microorganisms and their formulation. We used raw glycerol from biodiesel production, as only carbon and energy source in microorganisms growing media, and distiller grains with solubles as nitrogen sources. Sweet sorghum bagasse was used as substrate for edible mushroom production (e.g. by *Pleurotus* cultivation) and the resulted spent material was converted into a chitinolic promoting formulation of beneficial microorganisms from *Trichoderma* and *Bacillus* genera. We recovered fatty acids salts produced during bio-diesel production and we used these as ingredients to enhance the activity of *foliar applied plant biostimulants*. We converted toxic melanoidins from vinasse into beneficial *humic substances* complexes and we obtained a plant biostimulant wherein physiological activities of humic acids and betaines are synergizing. We created an improved *soil biofumigant* by pelletizing the glucosinolate reach co-products from bio-fuels industries. We proposed micro-algae extracts as alternative for *plant biostimulants based on seaweed extracts*. We proved the plant biostimulant effects of *protein hydrolysates / aminoacids mixtures* from micro-algae proteins and mycotoxins contaminated distiller grains with solubles.

Our further intention into this field are considering the plant biostimulants based on active ingredients recovered during the pre-treatment of lignocellulosic material (the key step of bio-refineries processes). *Beneficial elements* for plant cultivation, like silicon, and new categories of *plant growth and development regulators* (e.g. polyamines, oligosacharines, karrikins) are the main targets of our researches for new type of plant biostimulants, which production is integrated into plant-based bio-economy value chain. Infrastructure created by POS.CCE project 645/2014 ID1938 Agri-flux will support these researches.

**INOVATIVE TECHNIQUES FOR REVOLUTIONARY CHEMISTRY
DEVELOPMENT**

Miruna PETRIA

Analitic Laboratory

Flow chemistry (sometimes referred to as plugflow, microchemistry, or continuous flow chemistry) offers exciting opportunities to integrate traditionally separate processes and increase the pace of discovery and development. Flow chemistry has emerged as a new and productive technology for research and development chemists.

Asia 330 is a revolutionary range of advanced flow chemistry products from Syrris. It has been designed by chemists for chemists to enable the widest variety of chemical reactions and ultimate ease of use. The proprietary technology allows automated experiments with or without a PC, and offers maximum chemical resistance with an extensive range of temperatures, pressures, and reaction times on scales from mg to kg. It offers entirely automated reagent injection, synthesis, work-up, product collection and analysis. It features multiple step and multiple reagent reaction capabilities with its 4 pump channels, 4 reagent injection valves, Chip Climate Controller, Heater (and adaptors), glass microreactors, fluoropolymer tube reactors, stainless steel tube reactors, Pressure Controller, FLLEX, Sampler and Dilutor, Automated Collector, Automator, PC and PC Software. All the modules are extremely chemically resistant and can either be fully automated by the Asia Manager PC Software or controlled individually. The Asia FLLEX (Flow Liquid Liquid Extraction) module performs continuous flow aqueous work-up. A FLLEX mixes the organic and the aqueous streams, allows rapid diffusion to occur then splits the flow back to its constituent parts.

The Asia Sampler and Dilutor automatically takes a sample from the reaction and dilutes it by a user defined ratio. It then injects the diluted sample into an LCMS and automatically starts the acquisition of the LCMS system. The Asia Sampler and Dilutor can be used in conjunction with all 3rd party chromatography systems (LCMS, GCMS, HPLC, UPLC, etc.). All experiments are designed and run using the Asia Manager PC Software.

Workshop “AGRO-BIO-ECONOMY – A ROMANIAN APPROACH” – 3
**FLOW (BIO)CHEMISTRY – A POWERFUL TOOL FOR BIO-ECONOMY AND
AGRICULTURE**

Mihaela DONI, Florin OANCEA

National R&D Institute for Chemistry and Petrochemistry – ICECHIM

It is well known that the miniaturization of the fluidic handling devices led quickly to the Lab-on-a Chip technology. Even if originally, microfluidics and milifluidics technologies were dedicated to analytical devices, the discovery of efficiency enhancement of chemical reactions performed in micro/mili fluidic channels induced a revolution in (bio)chemical synthesis. The developed chips and flow chemistry systems translate the working principles of many standard laboratory synthesis techniques onto a chip card or into a micro-flow plant by fitting reagent reservoirs, test tubes, flasks, stirrers, microreactors, separation devices, pumps, valves, etc¹. In this way, the technology enabling synthetic chemistry within micro/mili-fluidics has been advanced through ingenious synthetic designs using multistep sequences to conduct complex synthetic schemes. Continuous flow reactors provide a synthetic platform for the combination of several chemical transformations as a single process. The advantages of the flow chemistry are numerous: reduced reaction times; the ability to conduct superheated / pressurized reactions and to involve hazardous, noxious or unstable intermediates; reduced solvent and expensive reagents / catalysts usage; lower waste generation; full automation, etc. Furthermore, there is the possibility to run reactions over 24 h/7 days in a reproducible and fully automated fashion. This approach accelerates the optimization of the synthesis processes by considerably reducing time delays². Some recent applications include the generation of small compound libraries of thioethers or *N*-alkylated sulfonamides using polymer- supported TBD acting as both a base and an alkylating agent. Some of the most impressive applications of flow chemistry reported more recently have employed multi-step preparation of biologically active substances: di- and tri-peptides, Grossamide, Oxomaritidine, substituted pyrrolidines, trifluoromethyl alcohols, et

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FIELD EMISSION GUN TECHNOLOGY IN *FEI TEM & STEM*: PRINCIPLE AND APPLICATIONS

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PRACTICAL UTILIZATIONS OF TRANSMISSION ELECTRON MICROSCOPY WITH TOMOGRAPHY

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A mandatory requirement for the development and the study of new bioproducts and materials developed under INCDCP-ICECHIM is the need of modern devices for synthesis and characterization. One of the indispensable equipment for imaging with much higher resolution than optical microscopes is the transmission electron microscope (TEM). In INCDCP-ICECHIM was initiated the acquisition and installation procedures of a TEM system composed of several integrated modules to satisfy the institute needs in the study of the properties and structures of different types of materials, in the characterization of bio-products, in the supra-molecular assemblies morphology analysis and their three-dimensional spatial distribution. Additional chosen modules, such as the module for cooling the samples, the module for scanning transmission electron microscopy (STEM), energy-dispersive X-ray spectroscopy module (EDS), the tomography module for selected area electron diffraction (SAED) and low-dose function allong with the sample preparation equipment (robot for vitrification in liquid ethane and the soft line sample preparation with/without cryo-preservation) will contribute to the characterization of such complex materials and structures.

Each module has a specific application of the microscope according to the nature of the samples (biological, organic-inorganic composite conductive, semiconducting, insulating, magnetic or non-magnetic) and their structure (bio-products, hybrid crystalline materials, amorphous and nanocrystalline). Sample preparation equipment will allow viewing of materials in various forms of presentation: compact material (bulk), thin films, wires or powders.

**MODERN TRAINING FOR BIO-ENTREPRENEURS IN SUSTAINABLE
DEVELOPMENT APPLICATIONS**

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The project will develop learning curricula and contents to be delivered to target-group by blended learning in order to provide training in business enhancement in life sciences for sustainable development applications¹⁻³. The products (two training content and two curricula) will be ready to be implemented in the partnerships countries, but also in other European areas due to the increased European dimension. The consortium consists of 4 partners, 2 from Romania (ICECHIM and USAMV Bucharest), 1 from France (Etcharry Formation Development) and 1 from Lithuania (Kaunas Regional Innovation Center), with complementary expertise and competences especially chosen to fulfill the project work program, meaning the two Romanian partners participate with specialists in life sciences research, high education and training, the French partner has experience in delivering training for organizing partnerships and networks for rural sustainable development, and the Lithuanian partner developed training to promote the growth of entrepreneurial spirit. Two products from these foreign partners will be transferred, by integrating them, but also by adapting to an economic sector of interest and by introducing modern blended learning systems, and by increasing the value with a new specific content dedicated to sustainable life sciences applications.

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**BASIC TEMPLATE REGARDING THE ENTREPRENEURSHIP KEY COMPETENCES
NEEDED TO START AND TO DEVELOP INNOVATIVE SME’S IN THE BIO ECONOMIC
SECTOR TARGETED TO SUSTAINABLE DEVELOPMENT APPLICATIONS**

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The result of the project entitled "IMPROVED CURRICULA AND MODERN LEARNING SYSTEM TO PROMOTE THE NEW DIRECTIONS OF BUSINESS ENHANCEMENT IN LIFE SCIENCES APPLICATIONS" (project funded by the Lifelong Learning Program Leonardo da Vinci - Transfer of Innovation) was a “Basic template regarding the entrepreneurship key competences needed to start and to develop innovative SMEs in the bio economic sector targeted to sustainable development applications”. According to this study, the main issues of the matrix of competencies for the entrepreneur which activate in the field of life sciences ¹⁻² are the following:

- 1) Personality characteristics: Self-confidence; Strong sense of independence; Self-efficacy; Self-made/self-belief; Inventive orientation;
- 2) Competencies characterization -Technical Skills respectively knowledge and understanding multi disciplinary and cross disciplinary characteristics of life sciences; Innovation development based on R&D in life sciences field;
- 3) Management and Business knowledge and skills, respectively: Business intelligence; Methods to access to financing, long-term and venture capital financing; Assessment of the market of a product and payment mechanisms within the field of life sciences sustainable applications industry. *Skills and abilities*, meaning: Recognizing opportunities based on innovation; Initiative orientation; Decision making; Creative thinking; Determination; Quick and forward judgment; Persuasion spirit.

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ECOLOGICAL PRODUCTS BASED ON DIATOMACEOUS EARTH AND ESSENTIAL OILS FOR THE RESIDUES AND CONTAMINANTS REDUCTION FROM THE FOOD CHAIN

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One of the most dangerous risk factors for the food chain is represented by the agricultural insect pests and fungal diseases which destroy the crop plants in the field and post harvested yield in storage. Mycotoxins produced by pathogenic fungi in cereal crops are transferred from field to storage, in feed, animal bodies and finally in food products, producing human health disorders. Technical solution proposed by the project is an innovative approach of treatment in the sequence of food chain from storage to animal body grown in farm, with ecological products obtained from bioactive diatomaceous earth and essential oils from renewable vegetal sources with insecto-fungicidal properties. Experienced research specialists of the implementation team of the project will select the best bioactive diatomaceous earth from Romanian local deposits, the most efficacy natural principles from essential oils and the best recipes to obtain modern formulations of ecological products (encapsulated slow release granules and tablets). To attain such ambitious objectives, the mineralogists from GIR will collect, identify, characterize and select the most appropriate mineral constituent for the ecological formulations and the NRDICP Partner will develop laboratory technologies for obtaining vegetal bioactive principles and formulation of original ecological products for grain storage treatment and veterinary feed supplement to be patented and transferred for a larger scale micropilot production. Raw materials, intermediates and final products will be subject to biological screening for selection of the most effective against insects and mycotoxigenic fungi infesting stored grains, in controlled conditions by RDIPP and in production conditions of storage by the farm Agrotehnic. The mycotoxin contamination and the diminution degree of the mycotoxin concentration on stored grains as an effect of the treatment with the ecological product will be quantified by chromatographic, biochemical or electrochemical methods. Agrotehnic farm has a great potential for cereal production and proper grain storage, a good perspective for agro-technological development, with chances to gain a better position on the national and international market with new agro-veterinary products, cheaper, easy available for farmers, rapidly biodegradable, non-toxic for mammals, eco-friendly alternatives to synthetic insecticides and fungicides.

**BIODEGRADABLE THERMAL INSULATING COMPOSITE MATERIALS FOR
BUILDINGS AND INDUSTRIAL EQUIPMENT**

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The project's overall goal is to obtain new biodegradable thermal insulating composite materials and their innovative use in order to increase the thermal efficiency of industrial buildings and equipment.

The project develops existing solutions for obtaining thermal insulating materials from spongy structures formed by fungi grown on lignocellulose waste, via contributions that reduce the disadvantages of the known solutions.

The goal of introducing thermal resistant recycled plastic materials (ex. polypropylene) is to reduce the bio-deterioration potential (by limiting the biocomposite's bio-degradation speed) and to increase the mechanical strength by creating a framework of improved resistance.

Co-cultivating fungi with bacteria that stimulates their growth and forms biofilms on the plastic materials in the mixture aims to reduce the material fabrication time (and to increase the direct economic efficiency) and to achieve compatibility between the hydrophobic (recycled plastic materials) and hydrophilic (lignocellulose material) components.

The absorbing mineral materials (for ex. kieselgur or zeolites) reduce water activity in the substrate (drying in the final fabrication stage), limiting the bio-deterioration potential, providing the required micro-elements to accelerate the growth of microorganisms in the cultivation stage and reducing the risk of fire.

Using the granular bio-preparation with fungus and bacteria spores allows the material to be fabricated in various shapes, by growing it into moulds specially formed for the desired applications, by controlled development on the surfaces it was sprayed along with the growth substrate mixture, by directed *in situ* cultivation to fill cavities. Directed *in situ* cultivation provides the ability to repair the thermal insulating materials created using this process, increases its useful life and eco-efficiency.

The final drying of the resulting process down to less than 10% material humidity is meant to deactivate the microorganisms and to provide the thermal and physical characteristics needed for the intended uses.

By varying the lignocellulose and plastic material mixture composition, as well as using different microorganism groupings (fungi forming the spongy mycelium and bacteria that stimulate fungal growth and make the substrate compatible), materials with different properties, for various uses, may be obtained.

Acknowledgements

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**MULTIFUNCTIONAL AND INNOVATIVE PRODUCTS FOR SAFE AND
BIOENHANCED FUNCTIONAL FOOD FROM NEWLY CULTIVATED PLANTS IN
ROMANIA (MAIA) PN-II-PT-PCCA-2013-4-0995/160/2014 (MAIA)**

Programme PN2 P4 Partnership PCCA 2013

There is at present a growing trend in the consumption of functional foods / food supplements from plants (nutraceuticals), mainly due to: the increased interest in disease prevention; the increasing cost of medical care; significant success in validating the safety and efficacy of functional foods / nutritional supplements; improving the legislative framework for functional foods / nutritional supplements from plants. This tendency causes some negative effects, affecting biodiversity and traditional food crops in their origin areas of maximum interest as nutraceuticals. The content of beneficial phytonutrients in plants significantly depends on the growing conditions.

The main agricultural systems are characterized by advantages and disadvantages. A sustainable agricultural system have a lower impact on the environment and human health, but does not result in formation and accumulation of satisfactory beneficial phytonutrients, existing a higher risk of contamination with nitrates, pesticides. Holistic organic/ecological farming systems lead to the plant productions with a higher content of beneficial phytonutrients, with higher costs, and contamination with mycotoxins and bacteria. One of the proposed solutions to the problem resulting from the compromises existing in the two major systems of agriculture, sustainable/intensive and ecological/organic, is that of "ecological intensification". "Ecological Intensification" is an umbrella term that refers to the various methods/practices of cultivation and technological inputs for enhancing biomimetic biological mechanisms of (self) regulation in agro(eco)systems.

The general project objective is to develop multifunctional and innovative products for protection of nutraceutical plants newly introduced in Romania (*Momordica charantia* and *Passiflora incarnata*) and to stimulate concomitantly formation of biologically-active compounds in these plants, at stable levels and with reproducible biological effects.

This project proposes for the first time to study interaction of silicon, *Trichoderma* and essential oils treatments, protection agents with multiple roles, which activates simultaneously plant defence response. It is the first proposal aiming the development of some products with applicability directly into practice, in which silicon is controlled released from supports, having concomitantly the functional role as a matrix, from which nutrients and volatile oils are smart-delivered, in this way pointing out the possibility of practical use of silicon in order to balance the main signalling pathways in plant defence response, integrated with elicitors for obtaining high productions with raised phytonutrients level.

The expected result through the implementation in practice of these multifunctional products is a save, efficient and affordable way to ensure high yields of nutraceutical crops with a raised content of active beneficial phytonutrients that maintain human health. The functionality of this expected result will be demonstrated for the model studied plants, but the model will be able to be extrapolated to other cropped plants to which the content of beneficial phytonutrients is important

Consortiu structure

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Partner P1 - INCDSB Bucharest - Project responsible: dr. Anca Oancea

Partner P2 - SC Hofigal Export-Import SA - Project responsible: dr. Georgeta Negru

Partner P3 - SC Chemi Ceramic F SRL - Project responsible: Prof. dr. Jozsef Fazakas

**COBALT IONS AND SURFACTANT IONS SEPARATION FROM AQUEOUS SOLUTIONS
USING PUROLITE ION EXCHANGE RESINS**

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In this paper are presented the results of experimental works for the removal of both Co^{2+} ions and of anionic surfactant sodium linear alkylbenzene sulfonate (LABSNa) from aqueous solutions by applying the ion exchange resins- column technique.

With respect to economy and efficiency ion exchange stands between the other two main liquid waste treatments processes of evaporation and chemical precipitation. While evaporation process may yield higher decontamination factors, it is also more costly than ion exchange process. The development of new ion exchangers is narrowing the gap on decontamination factors values between evaporation and ion exchange processes. Chemical precipitation, however, is often less expensive but is not always effective in removing radionuclides from solution^{1,2,3,4}.

The experiments were conducted in two stages: single-component systems (CoCl_2 solutions for Co^{2+} retention, respectively LABSNa solution for anion retention); bicomponent-system (mixtures of CoCl_2 solution and LABSNa solution). The LABSNa anionic surfactant was selected in the experiments because it's the main component of cleaning products and the waste waters might contain such contaminated ions after the equipments from the plants are washed.

Since the aqueous solution contains a mixture of anionic surfactant (LABSNa) and cations, both anionic and cationic resins are required for decontamination. Experimental results obtained in simulated systems using ion exchange resins have shown their effectiveness in retention of cobalt and anionic surfactant, as follows: Purolite NRW 5050 for LABSNa; Purolite NRW 160 for Co^{2+} retention, followed by Purolite NRW 1600 and Purolite NRW 3550; Couple Purolite NRW 160 and Purolite NRW 5050 and mixed resin Purolite NRW 3550 both for anionic surfactant and Co^{2+} retention.

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RADIOCHEMICAL STUDY OF Cs-137 AND Co-60 SORPTION BEHAVIOR ON STRONGLY ACIDIC CATION EXCHANGERS

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Among the objectives of "Danube WATER Integrated Management" Project is the identification of specific methods for treatment of liquid radioactive waste and the definition of their applicability and potential efficiency for particular waste stream processing.

The first goal of this work was to determine Cs-137 and Co-60 sorption behavior on strongly acidic cation exchange resins to optimize the clean-up process of radioactive wastewater. The experimental programme was oriented not only on lab research, but also on the application of tested ion exchangers and combined methods for treatment of liquid radioactive waste aimed at improving the treatment efficiency. The programme was planned to prove, possibly up to a pilot plant scale, the effectiveness of the developed processes for treatment of real radioactive waste.

To optimize the Cs-137 and Co-60 recovery method, dynamic studies have been performed to characterize the sorption behavior of these radionuclides on macroporous strongly acidic cation exchange resins. The following ion exchange resins from Purolite Comp were used in the experiments: NRW1600, NRW160 and C100H.

The following areas have been identified and were recommended for co-operation and joint efforts, in the framework of WATER Project.

- (a) Use of ion exchange resins in combination with other treatment processes;
- (b) Combined processes for treatment of solutions containing surfactants;
- (c) Dynamic column experiments and construction of the breakthrough curves for radionuclides sorption behavior study;
- (d) Determination of the decontamination factor variation with treated waste volume.

The experimental study described in this paper was carried on with the real spent decontamination solution. Therefore, the positive results obtained during this step represent, at the same time, verification of the developed process.

The sorption data acquired in this study are also valuable for the development and optimization of Liquid Radioactive Waste Management System from a nuclear power plant.

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MANAGEMENT OF SPENT ION EXCHANGE MATERIALS

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Spent ion exchange materials from nuclear power plants represent a special type of radioactive waste and pose unique problems in the selection of their treatment options. With the evolution of performance it is now required that spent ion exchange materials meet specific quality requirements prior to disposal. In our work we present the regeneration option of cationic/anionic organic ion exchanger in non radioactive systems. It should be noted that the medium is typically not completely regenerated, up to 90% restoration rate. The fact that regeneration is not complete is an important factor for nuclear grade ion exchangers, because nuclear grade quality is maintained only until the first regeneration. However, in situations in which replacing the spent media is more expensive than the treatment and disposal costs, regenerating spent media remains a desirable practice^{1,3}. In the experimental tests carried out by staff from 7 equip for the regeneration of spent ion exchange cationic resin, were used five types of H⁺ resin form, depending on the porosity and retaining ability: 50 W XI DOWEX (cationic), C100H, NRW 160, NRW 1600 (cationic) and NRW 3550 (mixed) PUROLITE type resins. Spent cationic ion exchange resins retained Co²⁺ or Mn²⁺ non radioactive ion. As regeneration agent was used sulfuric acid solution² in various concentrations: 2, 4, 6 and 8%. In a column filled with spent cationic resin has leaked a certain volume of 2% H₂SO₄ solution, from a dropping funnel with a constant flow, and then was analyzed the content of desorbed Co²⁺ ion from the column in each sample of acidic solution, resulted from the end of the column. It was found that after several successive regenerations appeared a significant decrease in the content of desorbed Co²⁺ ion. Next we started to introduce H₂SO₄ solution of higher concentration such as: 4%, 6%, 8% and continued experimentation, gradually increasing the concentration of the acid. The varied parameters were the liquid flow, concentration and acidity of the regeneration agent. The obtained results showed that our team has obtained very high values of the recovery yield of desorbed Co²⁺ ion, especially in NRW 160 (cationic) and NRW 3550 (mixed) PUROLITE resins, between 99-100%.

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ISOTOPIC INVESTIGATION APPLICABILITY FOR RESEARCH AND MONITORING WATER SOURCES

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Since in many areas of the world relevant long-term data on water resources are missing, the traditional and isotopic methods in combination with mathematical modeling often answer pressing questions about groundwater origin, chemical reactions, fluxes, ages and mixing processes occurring in reservoirs, naturally and caused by man. Only on this basis can relevant strategies for exploration, exploitation and protection of subsurface waters be developed.

So, the isotopic methods are an integral part of modern hydrology. Isotopic investigations contributes to the possibility of getting a detailed insight into the water cycle. Therefore, they are also a means of optimising the treatment of groundwater reservoirs or wells.

Measurements of the environmental isotopes enable observations of hydrological systems in extensive geographical scales and time scales. In the case of difficult groundwater flow-conditions, they are of particular use, for they permit the identification and quantification of involved groundwater or surface components and their elements, which, in most cases, cannot be achieved by classical methods.

This paper aims to present the results obtained in the study called "Research and detailed analysis of groundwater located along the border RO / BG using environmental isotopes“, as part of the project „*Danube WATER integrated management*”.

Keywords: water resources, isotopic methods, research and monitoring water

[Romanian Association of Hydrogeologists - Final Report on the study "Research and analysis using environmental isotopes to groundwater located along the border Romania / Bulgaria "]

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