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**SUSTAINABILITY AND RESILIENCE OF BIOECONOMY – AN ANALYSIS OF EU COUNTRIES  
OFFICIAL STRATEGIES**

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The EU bioeconomy is defined as a trans-sectoral domain, encompassing all economy branches related to bioresources production and processing (bio-based economy). The aim of this study is to analyze selected national strategies and policies which will generate the development of a sustainable and robust, resilient, bioeconomy. Considering most of published official strategies on bioeconomy at EU level, one can find that the main driving force is related to a growing economy and the desire to reach or retain for Europe/EU, a world leading position into this emerging domain.

The published strategies and policies are focusing on the creation of a framework which should promote renewable resource utilization, as medium – long term solution for fossil resources.

Only a few of the disseminated strategies (Germany, Sweden, Finland) acknowledge the global responsibility to contribute to climate change mitigation, by using technologies and processes suitable to a bio-based economy.

The consequences that this extensive utilization of renewable resources will have, or the dependency and utilization of other resources, are often not discussed.

The biofuels case study showing the opportunity of renewable fuels to replace fossil resources is linked to changes in water use, new patterns in land use (indirect land use), and also linked to the intensive use of chemical fertilizers and pesticides. A broader bioeconomy concept and action plan shall capture all innovative potential from bioeconomy sectors (agriculture, forestry, aquaculture, industrial biotechnology, “green” chemistry / biorefinery), maintaining and further developing EU quality of food products and “producing more with less”.

In short, a bioeconomy strategy addresses the production of renewable biological resources and their conversion into vital products and bio-energy. Such Strategy shall be translated in action plans, then into specific and dedicated programs following sectorial needs and cross-cutting topics, leading further to specific projects. Sustainability aspects will generate specific indicators which will give information on existing balance between the economic pillar on one side, and the social and environmental pillars on the other side. Political involvement will have its own input in the development and implementation of such Strategy.

**MICROALGAE- THE GREEN GOLD FOR BIOECONOMY**

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The European Union has adopted recently an ambitious strategy for developing the Bioeconomy in Europe. The decision to include algae biomass in the first place of the list of substances which will count four times their energy content towards the overall 10% EU target for renewable fuels in transport, under Directive 2009/28, represent a strong message about the fact that the development of algae based biofuels will be strongly incentivised vis-à-vis conventional biofuels in the years to come.

On the other hand, algae represents an emerging biological resource of great importance for its potential applications in different fields, including food and feed.

This is a big opportunity of growth for our algae biomass research sector, which can become a provider of revolutionary new generation protein, feed, nutraceuticals and innovative biomaterials.

The Research and development has been done in this area, in the last 10 years, and continues in order to analyze the potential of microalgae for the use in biobased energy, in the food and feed sector.

## WHY MODELLING IN CHEMICAL ENGINEERING?

DobreTanase

Politehnica University of Bucharest

A summary or a complex analysis regarding the cognition methods used by the mans from the old to present times reveal that only two general methods are created for this purpose: 1) the life phenomena research made of modelling and simulation; 2) the life phenomena research by experimentation using physical models. Due theirs independency concerning place and birth date and also due theirs use for all branches of human activities, these methods belong of universal patrimony of the human cognition. With reference to the relation existing between these life investigation methods is not difficult to observe that before to produce a change of one physical model we create a modelling investigation, related to the phenomenon unfolded in the physical model, and consequently we propose more strategies and decide for only one; in the same time the physical model existence create the conditions to measure the effect of adopted strategy and give new impulses for research deepening. So these methods present a dialectics state that show coexistence and coactions. For chemical engineering domain as also for others scientific and technique domains where the one or more materials are physically or chemically transformed a process is abstractly represented as a system characterized by his inputs and exits. The below formal expression where  $y_i$  is the value of one system exit,  $x_j$  and  $z_k$  are the controlled respectively the random system inputs and  $p_l$  introduce the process parameters of the phenomena from the system introduces the mathematical model of process/processes from the considered system.

$$y_i = F(x_1, x_2, \dots, x_N, z_1, z_2, \dots, z_S, p_1, p_2, \dots, p_r) \quad i = 1, \dots, P$$

The paper is oriented to shows the importance of mathematical modelling in the life cycle of a chemical or biochemical product manufacturing. An example of building of a phenomenological models is given in order to show the research capacity of the mathematical modelling and in the order to give an orientation for an answer to the questions *Why modelling* ?. Regarding the question *Why modelling* ?, that also give the title of this paper, we reply that the models use is important because these have the capacity to assist the solving of more important problems. We especially mention [1] that the model use :

- reduce manufacturing costs,
- reduce time and costs in all stages of process life-cycle ,
- increase process efficiency,

- permit a greater understanding of the process and of his operation,
- make the support for all solutions adopted in process elevation and exploitation ,

- insure very easy the technological transfer of the process,
- increase quality of process management ,
- reveal abilities to handle complex problems,
- contribute to pollution diminishing,
- improve the safety of the plants,
- bring new product to market faster,
- reduce wastes emissions in process development,
- improve product quality,
- insure an advanced operators training.

In the sense of this paper process simulation, process design, process parameters identification, process optimization are modes of models use for all life-cycle process stages.

[1] Dobre T., Sanchez J.M., Chemical Engineering Modelling, Simulation and Similitude, Wiley VCh, 2007

# LEWIS ACID-BASE CATALYSTS FOR THE SYNTHESIS OF FINE CHEMICALS

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Particle size is one of the key parameters determining the electronic properties, and as a direct consequence, the catalytic behavior of the supported metals. Sub-nanometric particles were already reported to exhibit beneficial Lewis acid properties for the control of both the activity and selectivity in reactions of importance [1]. However, specific Lewis properties can also be induced in nano-supported metal catalysts.

Based on this importance, the synthesis of metal and alloy nanoparticles of controlled size and shape become a hot topic. Unique properties at the interface between molecular structures and bulk materials can be thus induced following a rational design [2]. Typically, this occurs under strong reduction conditions and requires the presence of a stabilizer able to preserve the above properties.

The aim of this lecture is to present the synthesis of different metal- (Pd, Ru, Au, Pt, Ir) and alloy- (Pd-Au) nanoparticles and their catalytic behavior, focusing on the selectivity effects induced after their immobilization onto inorganic carriers. The preparation of these catalysts was carried out using several routes: i) the reduction of inorganic metal salts with Na[AlEt<sub>3</sub>H] or Na[BH<sub>4</sub>] [3-8] followed by the embedding of the resulted colloids in inorganic matrix supports using the sol-gel techniques (SiO<sub>2</sub>, ZrO<sub>2</sub>, SiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>); ii) reduction of the organometallic complexes under supercritical CO<sub>2</sub> conditions followed by the ionic liquid stabilization of the resulted nano-particles [9]; iii) ionic exchange and deposition/precipitation of the noble metals onto zeolites and metal oxides [10-11]; and iv) impregnation of noble metals onto oxifluoride supports [12].

The characterization of these catalysts evidenced in all the cases the presence of the Lewis acid centers. The concentration of these centers was correlated with other properties as particle size and shape, dispersion, etc. that were determined using an ensemble of techniques: adsorption-desorption of N<sub>2</sub> at 77K, FTIR, DRUV-Vis, SAXS, XRD, XPS, SEM, TEM, Mossbauer spectroscopy, etc. [2-6].

The talk will try to associate all these characteristics with the selectivity effects. All these were checked in various reactions like hydrogenation of C=C bonds in simple molecules like styrene or different cycloalkenes, hydrogenolysis of complex molecules like 1,1a,6,10b-



tetrahydro-1,6-methanodibenzo[a,e]cyclopropa[c] cycloheptenes, diastereoselective hydrogenation of C=O versus C=C in un-saturated aldehydes and ketones like cinnamaldehyde or prostaglandin derivatives, or reduction of nitric oxides with hydrocarbons. The modification of the supported metal nano-particles by asymmetric ligands like Synphos and cinchonidine will be also discussed comparatively with the homogeneous systems in the selective hydrogenolysis of bicyclo[2.2.2]oct-7-enes and hydrogenation of ethyl pyruvate.

Finally, the behavior of the Lewis-type metal catalysts will be compared with that of the free-metal aromatic systems. In this scope it will be presented the synthesis and catalytic behavior of a graphene's family. Comparisons with metal catalysts will be discussed on the basis on advanced characterization of these materials [13].

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**PUBLISHING VS. PATENTING –NEW APPROACH FOR THE SCIENTISTS DILEMA****F. Oancea<sup>1</sup>, S. Velea<sup>1</sup>***1-National Institute for Research&Development in Chemistry and Petrochemistry*

Publishing vs. patenting dilemma is approached on several levels. For scientists essential is to protect their scientific results by publications. Their academic career is nowadays based on the visibility and recognition of their publishing activity. Scientometric aggregated indicators (like Hirsch index, total number of citations, impact factor, score of influence) are essential for career development. Evaluation of scientific research proposals are based on such aggregated indicators, thus the major interest of scientists is to publish – sometime even without considering the possibility to protect intellectual property by patenting.

On Research Organisations (ROs) level, patenting is an essential step for knowledge and technological transfer. But the benefits / incomes generated from patent exploitation should not be overestimated. Value of a patent is not linked to its ownership, but essentially to: (i) technology readiness level (TRL) and (ii) market demand maturity. Therefore, before filing any patent, it is advisable to ascertain the maturity of a new technology / feasibility of its scale-up and how such new technology fits into the market. Big companies, interested on a monopoly on a new technology, are very careful on dissemination of any information about the invention before filing a patent - or even before a patent is granted. Because of this issue, consortia on EU founded consortia (especially those on industry driven Programme, like JU BBI) have as a main pillar Intellectual Protection Rights agreement.

On Founding Authorities patenting and technology transfer is important for the calculation of the societal benefits of the public investment on Research, Development and Innovation. Several Research and Innovation Programme were already established, driven by market and/or industry requirements.

Open Innovation model offers a new approach for this scientists dilemma. Scientists can file a patent application and delay publishing until after the patent filing. Once a patent is filed, applicants receive a filing date to be claimed as priority date, which means that novelty will no longer be destroyed by publishing the technology features. Accelerated publication of patent application, substantiated by a report of the novelty and inventive steps on it, offer a time frame for patent licencing. Dissemination of the results by publication enhances the interest of the economic media for patent licencing. This practice, of combining patenting and publishing, in an open innovation context, is a solution which permits researchers to benefit from both activities.

**METHODOLOGY OF TESTING MYCOTOXINS FROM STORED GRAIN USING MODERN ANALYTICAL TECHNIQUES****Carmen Lupu<sup>1</sup>, Roxana Dudoiu<sup>1</sup>, Elena Radu<sup>2</sup>, Mariana Popescu<sup>2</sup>, Florin Oancea<sup>2</sup>**<sup>1</sup>*Research Development Institute for Plant Protection, Bucharest*<sup>2</sup>*Research and Development National Institute for Chemistry and Petrochemistry – ICECHIM Bucharest*

Continuous monitoring of cereal grains is required to avoid adverse impacts on health and productivity of animals, due to different levels of contamination with mycotoxins that may arise, either after a growing season characterized by favorable weather conditions for infection and fungal development, or after storage under degraded conditions. The new green products that will be developed under the project PEDIOL for the decontamination sequence in the food chain, from storage level to farmed animals, present a significant potential to improve the quality of stored products and functional properties of nutritional feed by reducing mycotoxin level. Monitoring mycotoxin contamination of grain within vegetation and/or storage stage can be performed using several methods. Elaboration of working methodology for mycotoxins involves the development of at least two types of methods: (i ) the sampling methods and (ii ) methods for trace analysis (usually chromatographic or enzyme immunoassay) to quantify mycotoxin. The most modern methods - immunoaffinity columns include: mycotoxin analyzed using specific antibodies; contamination removal for a more accurate analysis; preparation of samples for different analyzes; use in combination with different test methods (HPLC, TLC, fluorescence); washing the sample. Using immunoaffinity column presents the advantages of cleaning and concentrating the sample allowing complex and challenging samples to be analyzed. For simultaneous determination of mycotoxins in grains associated with minimizing the consumption of expensive solvents and shortening analysis, HPLC with fluorescence detection method was recommended (due to the sensitivity and high specificity) coupled with the LC-MS/MS.

**ACKNOWLEDGEMENTS**

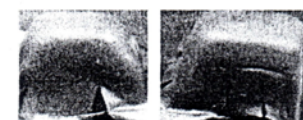
This research work has been performed within PNII Programme Partnerships in Priority Areas, Project PNII-PT-PCCA-2013-4-0425, Contract 156/2014 financially supported by UEFISCDI, Romanian Ministry of Education and Scientific Research

**PROMOVAREA BIOECONOMIEI CIRCULARE ROMANESTEI PRIN FABRICATIA  
PRODUSELOR BIODEGRADABILE CU VIATA SCURTA, REALIZABILE PRIN APLICAREA  
TEHNOLOGIILOR ICECHIM**

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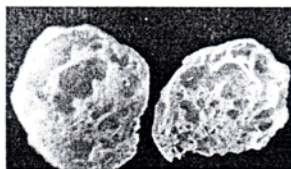
Discutiile vor fi canalizate pe urmatoarele subiecte principale: elemente de noutate stiintifica



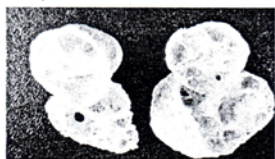
din domeniu specific lucrarilor de cercetare la contractile la care ICECHIM a fost coordinator de proiect, prezentarea produselor noi realizate, la scara de laborator, din noile materiale, dificultatile intalnite la



incercarile de aplicare a acestor cercetari. Dintre elementele de noutate stiintifica se vor accentua aspectele legate de controlul rezistentei la curgere a topiturilor ca metoda de imbunatatire a miscibilitatii



componentilor, imbunatatirea stabilitatii chimice, eliminarea migrarii plastifiantilor, a fenomenului de retrogradare, a instabilitatii topiturilor si imbunatatirea aspectului noilor produse prin imbunatatirea miscibilitatii la nivel molecular, controlul comportarii la biodegradare



prin manipulare morfologica a si prin tratarea componentilor nepolimerici conform unor procedee originale, controlul vascozitatii elongationale ca metoda de selectie a variantelor compositionale prelucrabile prin termoformare, expandare etc. Ce propune discutarea unor probleme legate de pret, capacitatea pietei romanesti de a absorbi produse biodegradabile, cadru legislativ etc. Aceste lucrari au fost efectuate in cadrul



ontractelor ECO-BIO-FOAM, si BIO-MULTI-PACK.



**SECTION 1**

**BIORESOURCES AND  
BIOMATERIALS**

**VEDISAN –a new natural product for eye health and vision improve**

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This paper presents the conducted research to obtain a new natural product for eye health and vision improve, bringing together in a well-balanced association a complex of numerous natural biocompatible and bioavailable byproducts responding through their synergism to the high requirement needs for a proper functioning of eyes.

From the wealth of information that currently exists on the need and possibilities to improve vision and eye health, results that the eye – the vision organ- is extremely pretentious and needs a very wide variety of compounds into bioavailable and biocompatible forms to act simultaneously and synergistically.

Such complexity of beneficial compounds to the demands of the proper eye function can be found only in natural products which by their specific chemical composition and adequate associations between them can achieve the required phytochemical complex.

Thus, the authors studied and realized pharmaceutical formulations, conditioned as oral capsules and/or tablets, based on selected plant material and/or plant extracts from: black mulberry, blueberry, seabuckthorn fruits, barley, carrot, tomatoes peels, selenium yeast and certain essential oils.

Bioactive compounds highlighted in this phytochemical complex made under the name of VEDISAN include vitamins (A, E, K, B complex, especially B2, C), essential fatty acids (omega 3), carotenoids (lutein, zeaxanthin, lycopene,  $\beta$ -carotene), minerals (Zn, Se, Cu, Mn, Cr, P), anthocyanins and proantocyanins, amino acids and amino acids important for the construction and regeneration of eye collagen (proline, hydroxyproline), polysaccharides, flavones, SOD enzyme, amyris acids and phytosterols.

*In vitro* and *in vivo* tests have shown no toxicity, good tolerance to high concentrations, increased antioxidant properties and ability to stimulate cell regeneration and good stability in time of VEDISAN product in capsule form.

# VARIATION OF POLYPHENOL CONTENTS IN VEGETATIVE ORGANS OF TAGETES ERECTA L.

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*Tagetes erecta* L. (marigold), Asteraceae is a medicinal plant whose flowers and leaves have been used traditionally in the treatment of a variety of conditions. Polyphenolic compounds such as flavonoids<sup>1</sup> and tannins<sup>2</sup> have been reported in stem and leaves. We investigated the variation of polyphenol contents in roots, stems and leaves depending on the soil and stage of development.

Sample plants were derived from ecological cultures off two different soils in the South of Romania (a brown-reddish forrest soil with clay loam, sandy texture and glomerular structure and a cernisol and chernozem soil of argic and cambic type, rich in humus) and have been collected at three different stages of development: early bloom (flower buds emergence), full bloom (anthesis) and mature (seeds and fruits formed). Polyphenols were assayed with the Folin-Ciocalteu method. The concentration was modelled with multiple linear regression using the organ, stage and soil as independent predictors. Leaves had the highest polyphenol contents, significantly higher than roots and stems ( $p < 0,001$ ; e.g. in stage II, in plants from brown-reddish forrest soil, mean concentration in leaf was 3.13%, s.d. 0,22 versus mean concentration in roots 0.56%, s.d. 0.09 versus mean concentration in stems 0.65%, s.d. 0.03). Polyphenol concentrations in plants collected from the brown-reddish forrest soil tended to be slightly lower than those from the cernisol-chernozem soil, but the differences were not statistically significant ( $p = 0.2736$ ). Globally there were no significant differences in polyphenol contents between stages II and III, but in stage IV there was a significant decline as compared with stage II ( $p = 0.0147$ ). However, exceptions from these general trends were recorded, e.g. in stems collected from the forrest soil there was a slight increase in the polyphenol levels in stage IV as compared with stages I and II.

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**ANTIBACTERIAL EFFECT OF ESSENTIAL OILS AGAINST MICROORGANISMS ISOLATED FROM MASTITIS OF PRODUCTIVE RUMINANTS**

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Mastitis is a pathological disorder impairing a large number of lactating ruminants around the world. The involved pathogens can be bacterial, viral or fungal. In the case of bacterial mammitis, the antibiotic use is not the best solution because milk can be contaminated with chemical residues and antibiotic-resistance can occur. It is necessary to find solutions to support organic agriculture. New solutions are investigated to research certain technologies and products based on the sustainable chemistry of composites for the treatment and prevention of mastitis in ruminants. This study presents some preliminar results involving: determination of bacteriological profile of mastitis, antibiotic susceptibility testing of isolated microorganisms and the assessment of the antibacterial effect of some natural treatment solutions.

Samples were taken from ruminants (cattle, sheep and goats) both from farms and from households. The morphology of bacterial strains has been described: by macroscopic and microscopic and also biochemical assays, resulting in bacterial identification. The antibiotic susceptibility testing was carried out by disk-diffusimetric method. The microbiota of the 32 assayed samples was diverse, including 8 genera and 18 species, both Gram-positive and Gram-negative.

The obtained treatment solutions (essential oils and mixtures of essential oils and clay mineral) were tested by quantitative and qualitative methods, to reveal their antibacterial effect against bacterial strains isolated from milk samples.

This study presents the research results regarding the effects of certain oils (oregano, thyme, linseed, marigold, myrtle, rosemary) as such or in mixture with green clay, yellow clay, montmorillonite or halloysite.

The final results revealed the antibacterial effects of thyme and oregano oils and the mixtures of these.

**Acknowledgement:**

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**FUNCTIONALISED MESOPOROUS SBA-15 SILICA AS SUPPORT FOR IMMOBILISATION OF BIOLOGIC COMPOUNDS**

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Mesoporous silica materials with ordered porous structure were used as carriers for bioactive compounds because of their biocompatibility, and stable structure with large surface area, high porosity, adjustable pore diameter, and modifiable surface properties. SBA-15 mesoporous silica was obtained, by typically method, as architectonic material of nanoscale precision with well-controlled porous structure by nonionic surfactants (P123) and was functionalized by post-grafting procedure with aminopropyl-triethoxysilane-APTES. Biocompatibility of the inorganic matrices and the possibility of SBA-15 functionalization justified their interaction with bioactive compounds.

The obtained SBA-15 mesoporous silicas were characterized, before and after functionalization, by SEM and TEM electronic microscopy, X-ray diffraction, N<sub>2</sub> adsorption-desorption and IR spectroscopy methods. The effects of the support synthesis conditions on the immobilization of the main active compounds of comfrey phytocomplexe as allantoin and tannins were evidenced. Results shown the variation of allantoin loading efficiency between 11.34 and 53.25%, while for phenolic compounds the variation was lower (10.17-13.79%). The significant effect of on polyphenols release rate was evidenced for comfrey extract in water.

In conclusion, the active hybrid materials were obtained by immobilization of comfrey phytocomplexe SBA-15 mesoporous silicas.

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

**PHYTHOTHERAPY AND GEMMOTHERAPY USED IN DIFFERENT TYPE  
OF AGES (FEEDING DISORDERS)**

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**Natural Detox Complex** is a food supplement with phytocomplex composition which provides a general detoxifying action by neutralizing toxins and eliminate them from the body, has hepatoprotective action, reconstruction of liver cell, stimulates the activity of the gallbladder and stop the apparition of gallstones. The most active part of milk thistle is a group of substances called flavonoids collectively named "silymarin", which has proved its hepatoprotective properties compound of silybin, isosilybin, silidianin, silicristin, taxifolin and quercetin. Of these, silybin is present in the largest quantity, the other components is present in smaller quantities, the plant has maximum action only in combination with other ingredients. Gemmotherapy has an action on organic dysfunctions, each glycerino-alcoholic extract, having a well defined organotropism. Meristems by high content of polyphenols, stimulating the activity of catalase, an enzyme key anti-stress defense system but also by many other compounds with antioxidant activity: malic and gallic acid, catechin, quercetin, epicatechin, procyanidins, chlorogenic acid.

Chlorogenic acid has been shown to inhibit eight-deoxigenaza deshydroxy at the DNA level, where treatments produced significant oxidative potential. Epicatechin and catechin prevent LDL oxidation processes. Quercetin reduces lipid oxidation and stimulates the activity of enzymes glutathione family of enzymes involved in the processes of stress defense and immune processes.

The composition and the special qualities of gemmoderivates, act primarily by stimulating cellular function and tissue homeostasis rebalancing.

**MATERIAL AND METHOD**

The author present the results of a case study, observational, made up of 3 groups: group A of 10 dyslipidemic patients and hepatic steatosis; Lot B consists of 10 patients who presented at the time of enrollment in serum glucose in the range 100-120 mg / dL above the maximum permissible laboratory; Lot C of 10 patients with elevated serum urea.

During the study, patients received:

- Lot A: **Natural Detox Complex** 2 tablets 3 times a day 15 minutes before meals and in the morning - a single dose of *Rosmarinus officinalis* branches gemoderivat; in the evening - a single dose of *Betula pubescens* budsgemoderivat;

- LOT B: morning - a single dose of *Morus nigra* buds gemoderivat; in the evening - a single dose of *Vaccinium myrtillus* branches gemoderivat;

- LOT C: morning - a single dose of *Vaccinium myrtillus* branches gemoderivat and in the evening - a single dose of *Betula pubescens* buds gemoderivat.

The patients were monitored clinically and laboratory (determination of blood liver transaminases: glutamic oxaloacetic-TGO, glutamic pyruvic-TGP, the blood glucose, glycosylated hemoglobin, lipidogram: total cholesterol, HDL-cholesterol, LDL-cholesterol, triglyceride, urea serum) at the beginning of the study (time T0) and at the end (time T1).

Statistical evaluation was performed by test results 't' student and ANOVA.

## **RESULTS**

Among the beneficial effects reported at end of study were:

- balancing main metabolic functions:
  - regulates bowel movements,
  - relieve flatulence,
  - adjuvant in the digestion of fat (resulting in lowering elevated serum thereof: total serum cholesterol by 13.48% and triglycerides by 14.26%)
- hepato-protective properties materialized by lowering elevated serum transaminases: 12.78% for the TGO and for the TGP 11, 46%.

## **CONCLUSIONS AND DISCUSSION**

The action of milk thistle as a remedy for liver diseases is undeniable, considered the plant with the greatest effect on these diseases. The flax seeds contain flavonoids, which favorised regeneration of liver cells and liver ownership increases to resist the action of toxins, stimulates detoxifying hepatic function.

Protective mechanisms of plant meristems are thoroughly researched and demonstrated. Thus, by lowering serum cholesterol and triglycerides prevents the development and progression of vascular atherosclerosis process and progression of steatosis, lipomatosis, plurivisceral fatty degeneration.

Decreased blood glucose prolongs the onset of diabetes, which, once diagnosed, can engage a number of major and minor complications in the body. The decrease in serum urea values means the improvement of the glomerular filtration rate in terms of a normal protein intake (100 g / d) and an infusion of normal kidney.

All beneficial effects of gemmotherapy can be attributed to human telomerase activity, which is in full hypothesis research and debate.

**Keywords:** Natural Detox Complex, gemmotherapy, *Rosmarinus officinalis*, *Betula pubescens*, *Morus nigra*, *Vaccinium myrtillus*

# EFFICIENT CONVERSION OF LIGNOCELLULOSIC BIOMASS IN FURFURAL AND ITS DERIVATIVES

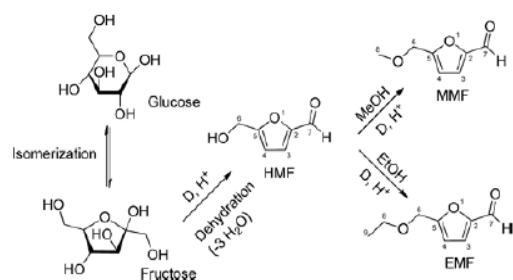
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Lignocellulosic biomass including agricultural and forestry residues is uniquely suited for large-scale production of renewable fuels and chemicals with the potential for minimal environmental impact when properly managed. Lignocellulosic biomass is composed primarily of cellulose, hemicellulose, lignin and water-soluble extractives, in order of typical relative proportions.[1]

Furfural is a natural precursor to furan-based chemicals and has the potential to become a major renewable chemical platform for the production of biochemicals and biofuels. However, current industrial furfural production yields have strongly diminished its competitiveness with petroleum-based alternatives in the global market.[2]



In addition to attractive thermosetting properties and physical strength furfural is a natural precursor to a range of furan-based chemicals and solvents. Figure 1 outline some of these potential chemical products from furfural which have high

value applications as a fuel or fuel additive.[3]

In the present work we were focused on the conversion of pentose and hexose fractions from different lignocellulosic biomass in furfural and respectively 5-(hydroxymethyl)furan-2-carbaldehyde (HMF) and its derivatives: 5-(methoxymethyl)furan-2-carbaldehyde (MMF) and 5-(ethoxymethyl)furan-2-carbaldehyde (EMF) by hydrothermal treatment using water or alcoholic solutions (methanol or ethanol) with different concentrations of mineral acids. The yield of furfural, HMF, MMF or EMF was determined using GC-MS analysis.

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**EXPERIMENTAL RESEARCHES REGARDING THE SYNTHESIS OF POLYFURANS STARTING FROM 2,5-FURANDICARBOXYLIC ACID OBTAINED FROM BIOMASS**

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The polyfurans (PEF) obtained from biomass are non-toxic and biodegradable compounds which have an increasingly higher significance, both in terms of environmental protection and in terms of industrial applications, being able to successfully replace polyethylene terephthalates obtained from oil products (PET). Biodegradable polymeric materials appear to be the most efficient way to eliminate wastes from plastic materials that pollute the environment.

The aim of this research was to obtain the technology for needed to synthesize polyfurans starting from 2,5-furandicarboxylic acid (FDCA) derived from biomass, in a „green way”, in the presence of some catalysts based on non-noble metals<sup>1,2,3</sup>. FDCA is a very stable compound, insoluble in most solvents (only soluble in DMSO) and with a very high boiling point (342 °C)<sup>4,5</sup>.

The reaction was carried out in two stages: i) the obtaining of the 2,5 dimethylfurandicarboxylate monomer (FDE) by the esterification of FDCA with methanol in excess (reaction yield is about 98.8%); ii) the obtaining of PEF by the polytransesterification of FDE with ethylene glycol, under nitrogen (reaction yield 32%). The product was fully characterized by IR and high resolution NMR.

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

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**PROCESS FOR OBTAINING FATTY ACID METHYL ESTERS FROM MICROALGAE OIL**

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Biofuels are an attractive alternative to current petroleum based fuels as they can be used as transportation fuels with little change to current technologies and have significant potential to improve sustainability and reduce GHG emissions. Among the various biomass candidates for biofuel production, microalgae are being considered as a more viable feedstock, because they have faster growth rate and high productivity than plants, requires very little nutrients supply for growth, have high level of oil accumulation and can grow in fresh water or marine environments. Fatty acid methyl ester (FAME) can be produced from algae oil, and can be used as biodiesel, eco-friendly solvent and intermediate for aviation turbine biofuel.

The main objective of this work was to develop a process for the production of FAME from algae oil. Since microalgae oil have a high free fatty acids (FFA) content, when a base homogeneous catalyst is used in the transesterification process, the catalytic activity is decreased by the saponification process. To avoid this inconvenience, a two-step process was necessary. In the first step, FFA were esterified with methanol over an heterogeneous superacid catalyst. The second step, *i. e.* methanolysis of pre-treated oil, was performed over an heterogeneous base catalyst, first in batch and the results were upgraded in a continuous process. The influences of catalyst loading and stability, methanol-to-oil molar ratio and the reaction time on the FAME yield were carefully studied.

In conclusion, the innovative process presented in this work is a promising FAME production process, the total costs will be reduced because the both reaction will be made at atmospheric pressure and mild conditions, and the technology will become eco-friendly, by recycling two heterogeneous catalysts and methanol. FAME producing technologies, investigated first in batch and then upgraded in a continuous flow process, has a great potential for industrial application.

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**THE BIOGAS – A RENAWARE SOURCE OF ENERGY – CHALLENGES AND PERSPECTIVES IN ROMANIA**

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The work underlines the importance of biogas producing in the current context of economical and environmental protection, conducting to replacing of fossil fuels energy sources by various form of renewable. The biogas is one of the main biofuels, able to be produced in countries dealing with huge quantities of various forms of bio based wastes. In this context Romania has an appreciable waste biomass potential, coming from agriculture, forestry, breeding, catering, domestic sources, etc. but not sufficiently valorized.

The biogas can really contribute to growing up of the renewable in the energetic balance of 20% from total energy demand till 2020.

The paper takes in account the state of the art regarding applied technologies in the main develop countries, compared with the Romanian technologies, developed in the period of 1950-1990. The paper stresses on the advantages of the Romanian technologies, one based on perfect mixing (continuous flux) and second on plug principle as regard the main process occurring in the digester.

Depending on capacity of digester, local conditions and energy consumption clients, the produced biogas can be directed to a cogeneration plant, supplied to customers or purified to obtain biomethane. The most applied principle for biogas plant at EU level is cogeneration where electric energy is supplied to the existing grids and the thermal is used both for internal needs (digester) and external consumers (for heating) [1].

The Romanian technologies, which will be more detailed presented, can compete with the available technologies on the market. Their advantages comprise reduced investment costs, simplicity of operation, easy maintenance and versatility of the materials to be processed into digester [2]. The work presents the current and the prospective possible situation in Romania having in mind improving the current situation.

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# A NORBORNANE FRAGMENT AS SUGAR MOIETY FOR OBTAINING NEW CARBOCYCLIC NUCLEOSIDE ANALOGUES

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Synthesis of carbocyclic nucleoside analogues with a constrained skeleton in the sugar moiety is studied extensively to gain knowledge about the interaction between the nucleoside molecule and the pocket of the target protein. A differently functionalized norbornane fragment was used as sugar moiety to obtain molecules with antiviral activity. Though some results were very interesting, the antiviral activity of the compounds was not that expected.

We introduced a different functionalized norbornane skeleton as sugar moiety starting from an optically active intermediate which resulted as by-product in the synthesis of natural prostaglandins and their analogues.

The synthesis followed a sequence of reaction to obtain an amine intermediate which was reacted with specific reagents to build a 6-chloropurine or a pyrimidine ring (uracil, thymine). The key 6-chloropurine intermediate was reacted with selected amines to obtain adenine analogue and 6-substituted adenine analogues.

The structure of the intermediates and of the constrained carbocyclic nucleoside analogues was fully characterized by IR, MS, <sup>1</sup>H-, <sup>13</sup>C- and 2D-NMR spectra. The key 6-chloropurine intermediate and the thymine intermediate was also analysed by X-ray crystallography which confirmed unambiguously the structure of the molecules.

Twenty one of the compounds synthesized were tested for their antiviral activity<sup>3</sup> and 11 for their antitumor activity<sup>4</sup>.

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**NOVEL NOOS SCHIFF-BASE TYPE COMPLEXES OF COBALT, NICKEL AND COPPER IONS.  
SYNTHESIS AND CHARACTERISATION.**

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Novel complexes of the ligand  $H_3L$  2,3-dihydroxybenzilidene-2-mercaptoaniline of type  $[M(H_2L)_3]2H_2O$  where  $M=Co(III)$  (1),  $[M(H_2L)_2]2H_2O$  where  $M=Ni(II)$  (2),  $[M(HL)]_2 2H_2O$  where  $M=Cu(II)$  (3) and  $[M(H_3L)_2](ClO_4)_2 2H_2O$  where  $M=Cu(II)$  (4) were synthesized by template methods and characterized. The complexes features have been assigned from: elemental analysis, electric conductivity, magnetic susceptibility, absorption atomic spectroscopy,  $^1H$ ,  $^{13}C$ -NMR, IR, UV-Vis spectroscopy, electrospray ionisation-mass spectrometry, cyclic voltametry. Analysis suggest octahedral geometry of complexes 1 and 4, square-planar geometry of complex 2 and a dimmer copper complex 3 in a distorted tetrahedral environment. The results indicate that the ligand behaves as bidentate monoanionic NO type versus cobalt and nickel ions and as bidentate NS type and as tridentate dianionic NOS type versus copper ions respectively. Redox behavior of the complexes have been investigated by cyclic voltametry.

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**NON-CLINICAL ANALGESIC EFFECT EVALUATION OF SOME PHARMACEUTICAL DOSAGE FORMS BASED ON EFFECTS POTENTIATION OF ACETAMINOPHEN, ASPIRIN AND CAFFEINE ASSOCIATION WITH CHLORPHENIRAMINE**

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The aim of this study was to investigate the influence of the clorpheniramine dose variation in a fix combination containing acetaminophen, aspirin and caffeine on the mice response when applying an algic stimulus. The envisaged composition act on multiple mediators of the pain and inflammatory process, including prostaglandins, histamine and therefore on the vascular permeability and cell membranes. Due to their action by different mechanisms - local analgesia (the inhibition of prostaglandin synthesis by ASA); central analgesia (para-acetylaminophenol); local antihistaminic effects, decongestant (antihistaminic component); decreased vascular permeability and increased peripheral vascular tone (caffeine) - compositions act at different functional levels and through different mechanisms. This complex action represents the complex pharmacodynamic background of the four associated components potentiation synergism. Following the action of each ingredient through different action mechanisms and different targets, the combination allows 3 to 4 times smaller dosages to have comparable efficiency to other commercial combinations, but reduced side effects and higher patient tolerance. The analgesic effect of the combination was evaluated in 2 experimental pain models using NMRI albino mice. The result show a maximum analgesic effect after 5 days of administration for the combination containing la lowest dose of clorpheniramine.

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

## **ENZYMES - FOOD TECHNICALLY BREWING PROCESS**

**Florin Dumitrescu**

In the brewing process enzymes have an important role especially starch from leaven that promotes some transformations during the saccharification process. This work analyses the main processes during brewing and the enzymes that have an important role for these transformations into foods and chemical technology.

Key words: brewing, enzymes, amylase, maltose, leaven, grist

**CONVERSION OF PHYTOGENIC SILICA REACH FOOD INDUSTRY BY-PRODUCTS  
INTO VALUE-ADDED PRODUCTS**

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We present here a new ERA-IB project, Convert-Si, which aims to develop optimized processes for a value-added conversion of phytogetic silicon reach food industry by-products - cereal husks, cereal bran, brewer / distiller spent grain. One of the main innovative contribution is related to the introduction of a lignocellulose (pre)treatment step, based on new microbial products: hyperactive lignocellulose destructuration enzymes, non-catalytic small proteins from cerato-platanin family (CP), which weaken (ligno)cellulose structure, and metabolites from silicon solubilizing microorganisms (SiM).

The objectives of this project will be achieved through the use of high-throughput experimentation techniques. Miniaturisation of the screening procedures for microbial strains selection, combined with parallelisation will allow an increase of the productivity on ICECHIM and USAMV (partners involved into strain selections) without additional personnel costs. Same approach of miniaturisation, combined with design of experiment (DoE) for optimization by exploring multifactor opportunity spaces, will be used also for development and optimisation of the processes required for nanocellulose production (Medica), mesoporous silica formation (ICECHIM), and/or for production of reinforced bio-based foamed packaging material (WURT). For testing the safety of biobased nano-silica and nano-composites a state-of-the-art high throughput comet assay will be used by Norway SME partner (NGT).

Convert-Si project integrated approach is intended to close a biomimetic industrial symbiosis. The by-products of one conversion process represent raw material for other conversion steps. On the end there are no by-products, the proposed integrated processes being without wastes. We intent to apply this concept of cascade process, for total conversion of industrial plant lignocellulose by-products into value added bioproducts.

**SEPARATION OF OMEGA-3 FATTY ACID ESTERS BY MOLECULAR DISTILLATION  
USE OF ARTIFICIAL NEURAL NETWORK AS MODELING TOOL**

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Fish oils are rich sources of 5,8,11,14,17-eicosapentaenoic acid (EPA, C20:5) and 4,7,10,13,16,19-docosahexaenoic acid (DHA, C22:6). They are the main omega-3 fatty acids and are important functional constituents of the human body.

Since these omega-3 fatty acids have high molecular weights and are thermo-sensitive, the method of choice for their separation and purification is molecular distillation.

In this context the purpose of this study is to optimize the separation process of omega-3 fatty acid esters by molecular distillation. Their separation was performed in two stages of molecular distillation: in the first stage high volatile compounds were removed, so that in the second stage the compounds of interest could be separated.

The molecular distillation process depends mainly upon temperature, feed rate, rotation speed of the rollers and pressure, their optimal values ensuring rich fractions in omega-3 fatty acid esters.

The Artificial Neural Network was used as modeling tool, in order to grasp the link between the aforementioned operating parameters and the performance of the molecular distillation. Several architectures were tested till a good match between the ANN's predictions and the experimental data was found.

Then, using ANN as model, the search for the optimal values of the operating parameters was done.

**OPTIMIZATION OF AN ANALYTICAL PROCEDURE FOR QUANTIFICATION  
OF FATTY ACIDS ESTERS FROM MICROALGAL OIL**

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A precise characterization of algal biomass constituents is an important aspect of research in the cultivation of microalgae in order to obtain biodiesel and high value products. This study was focused on characterization of algal oil after extraction from wet microalgal biomass using KOH-catalized saponification and 20 % boron trifluoride (BF<sub>3</sub>) solution in methanol for a total transesterification.

The lipidic fraction obtained after the oil extraction procedure of microalgal biomass generally contains triacylglycerols (TAG), phospholipids (PL), glycolipids (GL), free fatty acid (FFA)<sup>5</sup> and a high quantity of pigments. Due to this complex composition, the standard method for characterization of animal and vegetable oils cannot be applied<sup>6</sup>.

The aim of this study is to optimize an adequate analytical method for quantification of fatty acids methyl esters (FAMES) from the total lipids extracted from the algal biomass. In the first stage of this research, the standard procedure for obtaining methyl esters of fatty acids was used, but the results were inconclusive. The fatty acids profile in algal oil depends on growing conditions, extraction procedures and preparation methods. Using the microalgal biomass grown in controlled conditions, choosing the optimum extraction method and testing the same lipidic fraction, we have performed a series of experiments with different concentrations of KOH solution in methanol, different reflux times and different sample / KOH solution ratio, for obtaining FAMES. An excessive volume of 20 % BF<sub>3</sub> solution in methanol was added for a total conversion. The fatty acid methyl esters obtained were separated and identified by gas chromatography with mass spectrometer detection, and based on the highest concentration of esters, the best conditions for preparation of FAMES from algal oil were chosen.

**Acknowledgments:** *The work has been funded by the Sectoral Operational Programme Human Resources Development 2007-2013 of the Ministry of European Funds through the Financial Agreement POSDRU/159/1.5/S/137390*

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### ECOLOGICAL LUBRICATING FLUID

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Synthesis of ecological lubricating fluids is an important objective for companies who products lubricants. Depending on the specific machining operations and materials processed can be used three types of cooling and lubricating fluids: mineral oils, synthetic fluids and fluid ECs. Mineral oils are generally mixtures of mineral oil and specific additives. Synthetic fluids are solutions based on non-oil products, additives and water. The semi-synthetic fluids having a low content (10-15%) oil. Fluids lubrication and cooling ECs used in metallurgy and machine building serve as lubrication by reducing friction between tooling and surface to be treated, cooling surfaces in contact, wash by taking swarf from processing area Metal, and its suspension and preventing its re-settling on surfaces in contact. Good corrosion protection is needed piece being processed and tooling, as well as hindering the growth of microorganisms in aerobic and anaerobic prolonged use colloidal system.

Natural oils and fats from various raw materials are eligible for use in formulation of lubricants, where favorable lubricity characteristics and good biodegradability of these bioproducts over the petroleum-based lubricants properties are major advantages for industrial usages of biolubricants<sup>1</sup>.

In this context, our study presents synthesis of an ecological lubricating fluid based on fatty acid methyl esters which will fit in the category of organic products with minimal negative impact on the environment and will replace similar petrochemical products.

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## RELATIONSHIP BETWEEN STRUCTURE AND SURFACE PROPERTIES OF PROTEIN-BASED SURFACTANTS

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An increased interest from research and industry is manifested for protein-based surfactants, due to their lack of toxicity, gentle action on the skin, good surface activity and high degree of biodegradability, determined by amino acid moiety in the molecule<sup>7,8,9</sup>. The paper presents the results on the evaluation of surface properties of protein-based surfactants, synthesized from proteic raw materials: aminoacids, peptides and collagen hydrolysates of variable molecular weight (3000-10000 Da) and fatty acid chlorides, through Schotten-Baumann method. We analyzed the relationship between structure and surface properties (critical micelle concentration –CMC, foaming power, wetting power, hydrophilic-lipophilic balance-HLB). If compared with sodium dodecyl sulfate (CMC<sub>SDS</sub> 2,3 g/L and surface tension at CMC 34 mN/m), it was found that sodium lauroylglycinate and sodium lauroylglycylglycinate have grater efficiency in lowering surface tension at CMC (20,96 mN/m, respectively 28,26 mN/m) . CMC decreases with increasing hydrocarbon chain. Surfactants based on collagen hydrolysates shows lower CMC values than other anionic surfactants, and are effective at lower concentrations in various practical applications. Regarding the foaming capacity of surfactants, it is high in distilled water; in hard water only surfactants based on collagen hydrolysates are effective. The foam capacity and foam stability are positively influenced by increasing the hydrocarbon chain. HLB values determined experimentally by emulsifying tests for the protein-based surfactants are significantly higher than those of anionic surfactants, indicating their good solubility in water and polar solvents. With increasing the length of hydrocarbon chain the HLB value decreases. Due to the high HLB values, the surfactants can be used as emulsifiers in formation of oil / water emulsions, as detergents and solubilizers.

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**ECOLOGICAL COMPONENT FOR MOTOR FUELS BASED ON FURFURAL DERIVATES  
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Concerns about the total or partial replacement of fossil fuels has been directed in recent years on the conversion of biomass in such fuels. Biodiesel is the most known green fuel. Biodiesel content in diesel is limited due to the high value of the freezing point and its density. In this context, the valorization of furfural, the major product obtained by treating of natural polymeric carbohydrates, into value-added products, could correct these drawbacks of biodiesel.

The objective of this research is to obtain furan derivatives by hydrogenation of furfural. The hydrogenation reaction was performed over a heterogeneous catalyst in a continuous system and fixed bed reactor.

The reaction was studied in the following parameter values: 0.2-0.7 MPa, 150-250 °C and furfural mass hourly space velocity of 0.1-0.25 h<sup>-1</sup>.

The synthesized compounds were then studied as blending agents with diesel with the aim of improving diesel properties.

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**CONTINUOUS FLOW MICROWAVE – ASSISTED EXTRACTION OF POLYPHENOLS FROM  
GRAPE MARC**

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Continuous flow microwave assisted extraction (MAE) method for the aqueous extraction of polyphenols from red grape marc of *Vitis vinifera* cultivars Feteasca Neagra, Merlot, Burgund has been studied. Extraction parameters as solid:liquid ratio, temperature, time, microwave incident power, flow rate and size of grape marc grains were optimized. Total polyphenols were determined by Folin–Ciocalteu method. The optimized extraction conditions and evaluation of the extraction yield obtained in this study resulted in extracts with high concentrations of polyphenols and high DPPH (2,2-diphenyl-1-picrylhydrazyl) radical-scavenging activity. In addition, these value-added extracts are promising compounds with applications in functional food ingredients and dietary supplements for animals.

**ANTIOXIDANT CAPACITY DETERMINATION OF PLANT EXTRACTS BY A  
CHEMILUMINOMETRIC METHOD**

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The developed method for antioxidant capacity determination uses oxidation and chemiluminescence of luminol under the influence of reactive oxygen species produced in a Fenton type reaction of hydrogen peroxide with Co(II). The antioxidants from a sample react with the reactive oxygen species and decrease the chemiluminescence signal. The method is based on Co(II)EDTA/luminol/H<sub>2</sub>O<sub>2</sub> system<sup>10,11,12</sup>. Two versions of the method were studied: flow injection and conventional. In the case of flow injection method were studied and optimized the following experimental variables: the flow rates of the reagents, the ratio of Co(II)/EDTA, the injected sample volume, the concentrations of some organic solvents in the analyzed samples. A calibration graph in different experimental conditions was traced by using caffeic acid as a standard. The linear range was from 2.5 to 75 µmol/L. In the case of “batch” method it was drawn a calibration graph by plotting the ratio of chemiluminescence intensities in the absence and in the presence of a standard antioxidant. The calibration graphs were linear in the domain 10<sup>-6</sup> – 10<sup>-4</sup> M gallic acid. The optimized versions of the method were applied for total antioxidant capacity determination of several ethanolic extracts of plant extracts. The accuracy of the method was verified by using standard addition method. A comparison of flow injection and conventional methods was done.

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# PHYTOCHEMICAL ANALYSIS OF ZIZIPHUS JUJUBA MILL. LEAVES

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*Ziziphus jujuba* Mill. (jujube), a member of the *Rhamnaceae* family, has a long history of usage as an edible fruit and traditional remedy in India, China and Japan. The fruits are used as anticancer and hepatoprotective agents. The leaves have hypoglycemic, diuretic, emollient, anti-inflammatory, expectorant and sedative effects, and are used as a blood purifier and in the treatment of diarrhoea<sup>13, 14, 15</sup>. In this study we chemically analysed the jujube leaves as a source of active principles. Three solvents (ethanol 70% v/v, ethanol 50% v/v and purified water) and two extraction methods (refluxation and sonication at room temperature) were investigated. Flavones and polyphenolcarboxylic acids (PCA) were spectrophotometrically assayed by known methods.

To select the best solvent and extraction method for flavones, initially we applied a multiple linear regression model with the method and solvents as dummy variables, which indicated the largest positive influence on extraction for ethanol 70% and the largest negative effect for sonication at room temperature. Therefore, we developed a simple linear regression model, with the solvent as an independent variable. The same approach was used for PCA. For both classes of phytochemicals the models favoured ethanol 70% as the best option for extraction, although the differences against ethanol 50% were not statistically significant and those against water were significant only in the case of PCA ( $p=0.002$ ). With refluxation, average flavone contents (expressed as rutin) in the extracts prepared with the three solvents were:  $0.51 \pm 0.09$  g% (ethanol 70%),  $0.45 \pm 0.07$  g% (ethanol 50%) and  $0.42 \pm 0.05$  g% (water). With the same extraction method, average PCA contents (expressed as caffeic acid) were:  $2.80 \pm 0.21$  g% (ethanol 70%),  $2.60 \pm 0.44$  g% (ethanol 50%) and  $1.70 \pm 0.52$  g% (water).

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**CHEMICAL ANALYSIS OF SOME NEW EXTRACTS OBTAINED FROM *CYMBALARIA MURALIS*  
(PLANTAGINACEAE)**

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*Cymbalaria muralis* is an herbaceous species is belonging to Plantaginaceae family. The plant is native to South and South-East Europe, in present being widespread. Currently, more than 60% of all areas originally where the plant has been reported have disappeared because of using modern materials with an alkaline pH for the renovation of old walls<sup>16</sup>. The species contain several secondary metabolites such as flavonoids and iridoids with potential benefits for human health<sup>17, 18, 19</sup>. In the present paper, we obtained several extracts from *Cymbalaria muralis* aerial parts. The extracts were obtained by solvent extraction, concentration under low pressure, followed by freeze-drying. The total phenolic content (TPC) and total flavonoid content (TFC) were determined by UV/VIS spectrophotometry. TPC was evaluated by Folin-Ciocalteu method and TFC by the reaction with aluminium chloride. The results showed that *Cymbalaria muralis* is a reliable source for further extraction and purification of the phenolic compounds.

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**EVALUATION OF ANTIOXIDANT ACTIVITY OF ROSES ESSENTIAL OIL OBTAINED BY MICROWAVE – ASSISTED EXTRACTION THROUGH INTLI TECHNOLOGY**

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The aim of this study was to investigate the antioxidant activity of rose essential oil obtained by the microwave (MW)–assisted extraction using the Labotron X 6000 equipped with INTLI technology for electromagnetic energy transmission. The essential rose oil was extracted from fresh Rosa Damascena Mill. petals by four methods, namely: hydrodistillation, steam distillation, in organic solvent – hexan and advanced maceration assisted by ultrasounds (US) followed by microwave hydrodistillation. The chemical composition of these extracts was analysed by GC–MS, and the antioxidant capacity by Folin – Ciocalteu method. It was found that the total polyphenolic content and the chemical composition of the extracts depend on the extraction method. Rose essential oil extracted by US/MW method has a high level of polyphenols and demonstrated strong antioxidant activity.

**IMPROVED EXTRACTION PROCESSES OF NATURAL COMPOUNDS USED TO GENERATE  
NEW PHYTOTHERAPEUTICAL PRODUCTS AND COSMETICS**

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The paper presents the conducted studies and developed technologies for increasing the extraction efficiency of natural active compounds from thorn (*Xanthium spinosum*), willowherb (*Epilobium parviflorum*), white nettle (*Lamium album*), thyme (*Thymus vulgaris*) and propolis.

We developed new technologies for obtaining concentrated extract of propolis, which allowed beeswax separation prior to extraction, which usually create big problems. It was also developed a method of direct extraction, without removing wax before extraction and simple procedures of propolis crushing.

On this basis we have developed new technologies for obtaining standardized extracts from willowherb and thorn using as solvent ethanol 70%. Also, were determined new technologies to obtain concentrated extracts of thyme and aerial parts of nettle, using the same solvent.

For the mentioned vegetal extracts were performed detailed analyzes, whose results have proven the efficiency of developed extraction processes, data presented in extenso.

**ANALYSIS OF THE STORAGE STABILITY OF THE WHEATGRASS (*TRITICUM AESTIVUM L.*) JUICE IN TERMS OF ANTIOXIDANT ACTIVITY AND THEIR POLYPHENOLS CONTENT**

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A broad spectrum of health benefits have been attributed to wheatgrass. The fresh juice has high chlorophyll content, essential vitamins (A, B, C, E and K), minerals (iron, calcium, and magnesium), enzymes, amino acids, phenolics (ferulic acid and vanillic acid), dietary fibers. It is considered to be a complete food because it contains every amino acid, vitamin, and mineral necessary for human nutrition<sup>20</sup>.

The objective of this work was to evaluate the stability of the wheatgrass juice through the total polyphenol content (mg, gallic acid equivalents, GAE/g, determined according to the Folin-Ciocalteu method) and the antioxidant activity (mg, Trolox equivalent antioxidant capacity, TEAC/g determined by the 1,1-diphenyl-2-picrylhydrazyl free-radical scavenging assay). The sample was divided into four subsamples of which one (E1) was analyzed immediately and the others were kept at -20°C until analysis 11, 21 and 32 days, respectively. The stability assessment was carried out by the difference between the subsample averages, analyzed at the set time, and the E1 subsample average. Through statistical method for analysis of variance ANOVA<sup>21</sup>, the standard deviation between subsamples and the repeatability standard deviation were determined on the basis of which was established the detection limit of the stability test.

The instability limit of detection of total phenolic content (TPC) was 0.08 mg GAE/g and of antioxidant activity (AA) was 0.11 mg TEAC/g.

Initial properties of the sample are: TPC = 2.15 mg GAE /g and AA = 1.17 mg TEAC /g.

The samples stored at -20 °C for 32 days shows instability towards initial properties.

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## PHYTOPATHOGEN CONTROL OF HORTICULTURAL SHRUBS WITH PLANT EXTRACTS.

### III. *FUSARIUM OXYSPORUM*

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Black currant (*Ribes nigrum* L.) is highly appreciated for its alimentary and therapeutic value of its fruits, young leaves and buds. Since the quality of these products may be impaired by various pathogens, especially fungi, the establishment of biological control measures to protect such a medicinal crop is necessary. Plant extracts can be recommended as a non-polluting and environmental-friendly alternative (organic/green horticulture) in the protection of such medicinal crop [1], [2].

The antifungal activity of nine plant extracts manufactured by Hofigal S.A. against a strain of *Fusarium oxysporum* (Fo 18) responsible for Fusarium wilt of black currant was assessed *in vitro* for the first time in Romania. Among them, the highest inhibitory activity on mycelial growth was found in 20% concentration of *Satureja hortensis*, *Valeriana officinalis* and *Allium sativum* extracts (efficacy between 70% and 80%). At the same concentration, a moderate inhibitory activity (efficacy between 50% and 60%) has been noticed for *Mentha* sp., *Hysopus officinalis* and *Rosmarinus officinalis* extracts. The mycelial growth was less inhibited by *Tagetes patula* extract (42.8%, applied at 20%). No efficacy was noticed using *Achillea millefolium* extract even applied at 20%.

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**DAPHNIA MAGNA AS TOXICITY SCREENING TOOL IN PLANTS CONTAINING NOR-TRITERPENE LACTONES**

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*Caltha palustris* (marsh-marigold) is a perennial herbaceous plant from Ranunculaceae family. Several studies revealed a promising therapeutic profile of this species. Among the therapeutic activities we mention the regulation of the cellular immune response in collagen-induced arthritis in mice and anti-lipase activity<sup>22,23</sup>. These effects could be explained by the antioxidant properties that has been already quantified<sup>24</sup>. Like other species from this family, *Caltha palustris* also contains ranunculoides such as protoanemonin and anemonin. Followed by ingestion, these compounds are responsible for stomach irritation, stomach colic and extreme gastro-enteritis<sup>25</sup>. The nor-triterpene lactones identified in this species, caltholide and epicaltholide<sup>26</sup>, can also be responsible for various toxic effects<sup>27</sup>. In the present work we assessed the toxicity of three extracts obtained from *Caltha palustris* leaves using *Daphnia magna* method, an alternative toxicity bioassay. The lethal concentrations which causes the death of 50% of organisms (LC50) were determined by interpolating on lethality - logarithm of concentration curves. Statistical analysis was performed using GraphPad Prism version 5.0 software (USA). Using this method, the extracts could be further fractionated in order to obtain purified extracts with therapeutic properties.

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**THE EVALUATION OF THE METABOLIC PROFILE FOLLOWING THE ADMINISTRATION OF MELATONIN IN ASSOCIATION WITH IRBESARTAN, ON A HAMSTER EXPERIMENTAL MODEL**

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The pathogenesis of metabolic syndrome is extremely complex, its emergence and chronic evolution, being an incompletely understood field. The complications occurring at the cardiovascular level represent a major concern. With the discovery of the renin-angiotensin system in the central nervous system, it was hypothesized that angiotensin II could be a neuromediator of the regulating nerve network of the cardiovascular system. In these circumstances, the therapeutic use of a blocker of AT1 receptor is extremely important due to the presence of these receptors both centrally and in the periphery. Currently, in therapy there are used several AT1 receptors blocker medicines. Of these medicinal substances, the specialty researches are directed to irbesartan, a selective blocker of the AT1 receptors, administered in arterial hypertension, a coronary heart disease and diabetic nephropathy.

In this context, we decided to investigate, in a hamster experimental model, the antiatherogenic and antioxidant potential, essential factors for the chronical evolution of metabolic syndrome and cardiovascular complications, of irbesartan association with melatonin, one of the most important endogenous free radicals *scavenger*, at the level of different tissular levels. Thus, we evaluated the influence of irbesartan and melatonin, co-administered in a novel pharmaceutical multiparticulate form on the biochemical glucidic and lipidic markers.

Our results showed blood glucose, serum cholesterol and triglycerides lowering effects, this effect being maximum for Irbesartan+Melatonin, highlighting a potentiating effect of the two drugs. The great novelty and the unique scientific profile of the present paper is represented by the use a completely new pharmaceutical form, able to release in the blood stream the two medicines, in order to obtain a sinergic enhanced effect.

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**BIOLOGICAL RELEVANCE OF REVERSE MICELLES STRUCTURE FOR MIMING THE CELL CYTOPLASM**

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Studies of protein crowding and confinement, in conditions similar to cytoplasmic environment, are often hindered by the inadequate experimental methods available to demonstrate their effects outside of cells, especially in relation to one another. Towards addressing this major limitation of the studies, "synthetic cells" were proposed within the past few decades for intracellular biochemistry, one of the proposed example for a simplified mimic of the cell cytoplasm being represented by reverse micelles (RM), nanometer-scale assemblies of surfactants in apolar solvents. By changing the ratio between the surfactant concentration and the water content from inside pools of the reverse micelles (known as the hydration degree,  $w_0$ ), it may be modulated the volume and the characteristics of the water pool. The result is a controlled increasing/ decreasing of protein crowding/ confinement, by default redistribution and modified local concentration of the entrapped proteins.

A simple synthetic model system represented by sodium bis(2-ethylhexyl) sulfosuccinate - isooctane reverse micelles is use for a protocol of manipulating protein crowding and confinement, focused on two enzymes with very different structure, namely peroxidase (I) (a single chain polypeptides, M.W. ~44 kDa) and alcohol oxidase (II) (oligomeric structure with eight identical subunits, each one containing a FAD, M.W. 675 kDa). The study of the relation between these two enzymes in a artificial cytoplasmatic-like environment is supported by the fact that they compose an enzymatic system, the product of the reaction catalyzed by (II), respectively  $H_2O_2$ , being substrate for the other enzyme (I). The experimental runs were conducted in a  $w_0$ -range of 10-30, for each  $w_0$  value, being performed variants of increasing concentration of either (I) or (II), as well as simultaneous increase of both enzymes concentrations.

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**ULTRASOUND ASSISTED - SYNTHESIS OF SILVER NANOPARTICLES**

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Silver nanoparticles by sonochemical route were prepared by changing the molar ratio between metal precursor AgNO<sub>3</sub> and reducing agent tannic acid in presence of poly(vinylpyrrolidone) as stabilising agent. Working solutions were exposed to ultrasonic irradiation at same frequency and power (horn system, 20 kHz, 60% of full power). The samples were characterised by UV – VIS spectroscopy, DLS, TEM, SEM for identification of dimension, shape and distribution uniformity of silver nanoparticles.

## IMPACT OF WATER DYNAMICS ON BIOCATALYSIS PERFORMANCE IN NANOMETER SYSTEMS

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A wide variety of biochemical events occur in very crowded aqueous surroundings, where water is found in nanoscopic environments, where it does not behave in the same manner as it does in the pure bulk liquid. In this context, the impact of the dynamics of water's hydrogen bonding network is fundamental to the performance of these processes.

The highly structured, but heterogeneous, water molecules in reverse micelles (RMs) are representing models for water present in biological systems, such as membranes. A wide range of physicochemical properties of the micellar water, including the hydrogen-bonding potential of the aqueous inner core, can be experimentally varied with  $w_0$ , the hydration degree of RMs ( $[\text{H}_2\text{O}]/[\text{surfactant}]$  molar ratio), therefore providing a controllable reaction medium, extensively used for chemical and biochemical reactions, inclusive for biocatalysis experiments. The number of water molecules per surfactant molecule is conveniently described using  $w_0$ : the smallest RMs ( $w_0 \leq 5$ ) have radii of  $<1$  nm (50–100), whereas the largest ( $w_0 \geq 16.5$ ) have radii of up to 14 nm (~400,000). In this range, it is possible to change the relative amount of the water interacting directly with the interface from a large fraction to a small fraction of the total by increasing the RMs size.

Beside the opportunity to vary dynamics and structure of water molecule, we are using in our biocatalytic experiments the possibility to solubilize substrates with different partition between the apolar and polar phases of RMs. Reaction of alcohol oxidase solubilized in AOT-isooctane RMs is used as a small scale model both for experimental study and theoretical discussions in order to evaluate the correlations between the water dynamics in various  $w_0$ -RMs and enzyme substrates with different coefficient of partition between the polar/apolar phases of respectively RMs.

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

**SCREENING OF MICROBIAL STRAINS WITH LIGNOCELLULOSE DEGRADATION ACTIVITY  
FOR FURTHER PRACTICAL APPLICATIONS**

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Microbial strains with a high lignocellulose degradation activity are useful for several practical applications: (i) lignocellulose biomass biorefinery; (ii) treatment of plant residues on high farming systems; (iii) inoculation of hay baled at high moisture.

We developed a flexible screening procedure, which aim to further identify the suitability for one of above mention application of the strains initially selected for the lignocellulose degradation activity. For lignocellulose biomass biorefinery is important the ability to bio-produce platform chemicals of interest (propanediols, butandiole, glycerol, succinic acid) and thus we screen the lignocellulose degraders strain for such characteristics.

High residues farming systems use permanent soil plant residues coverage and less tillage for a more sustainable crop production. Despite many advantages, there are also negative impacts associated with high residue systems. Plant residues promote the development of soil-borne pathogens, reduce nitrogen availability and could have a delay effect on early stages of cultivated plants. Microbial strains, with concomitant plant pathogen biocontrol and plant growth promoting activities, could compensate drawbacks of high residues farming systems. Lignocellulose material degradation ability represent an additional advantage, increasing the chances for strain establishment on treated fields. We tested the ability of lignocellulose degraders to: be antagonistic toward plant pathogens (on dual confrontation assay); produce siderophores; mobilize phosphorus from calcium phosphate; secrete plant growth stimulating compounds (including volatiles ones). We focused also on strains able to produce 2, 3-butanediol and 1, 2 propanediol. Such strains could be interested for both biorefinery (propane- and butanediol being platform chemicals) and plant growth promotion (such diols being plant growth signals).

For the selection from lignocellulose degraders of strains useful for hay inoculation we screened for the ability to produce short chain fatty acids and vitamins.

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**ASSESSMENT OF SOME ABIOTIC FACTORS ON MICROBIAL BIOPRODUCTS USEFUL IN  
BIOCONTROL OF PHYTOPATHOGENS**

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The environmental conditions may influence the growth of microorganisms, by favoring their growth or slowing their multiplication rate and the synthesis of different metabolites. Parameters such as temperature, aeration, nutrients, pH or tolerance to NaCl can become limiting factors for microorganisms survival. *Bacillus subtilis* and related species can grow in variable pH conditions, maintaining the cytoplasmically pH in a relatively close range, stable to the synthesis of proteins and nucleic acids.

The aim of this work was to assess the influence of the abiotic factors on the biocontrol activity of the microbial bioproducts, based on beneficial strains from *Bacillus* sp..

The bioproducts were tested *in vitro* against soil borne fungi at different temperatures and pH conditions. The results showed that the antagonistic activity of the biopreparates, tested at 27° C and 25° C, against phytopathogenic fungi released antifungal metabolites which inhibited the fungal growth. Also, when different pH values were analyzed, the results reflected that at pH 5.5 and pH 8.5 the biopreparates maintained the same antagonistic effect as in the control variant (pH 7,0).

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# SIGNIFICANCE OF HYDROLYTIC ENZYMES AND **PLANT** GROWTH STIMULATION FACTORS

## OF *TRICHODERMA* IN BIOLOGICAL PLANT PROTECTION

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*Trichoderma* produces a wide range of secondary metabolites that are essential in the signaling, the development and the interaction with other organisms [1, 2, 3]. Out of them, the hydrolytic enzymes play an important role in the enzymatic degradation of cell walls of phytopathogenic fungi during interaction. Siderophores are low-molecular-weight metabolites produced for scavenging iron from the environment and have a high affinity for iron (III). Also, the fungi are involved in the solubilization of bound phosphates making them available to plants. Therefore, the main objective of this paper was to test, under laboratory conditions, four isolates of *Trichoderma* spp., in the ability to produce hydrolytic enzymes (chitinases and cellulases) and plant growth stimulation factors. The experiments were performed with *T. asperellum* T36; *T. asperellum* T50 ; *Trichoderma* sp. T57 and *Trichoderma* sp. T83 from Microbial Collection of ICECHIM. The isolates were evaluated against soil borne phytopathogenic fungi, like, *Fusarium graminearum*, *Rhizoctonia solani*, *Botrytis cinerea*, *Pythium ultimum*, *Sclerotinia sclerotiorum*, *Botrytis allii*, *Verticillium dahliae*, and *Macrophomina phaseolina*. The production of hydrolytic enzymes was higher at *T. asperellum* T36. The strains T36 and T50 have potential in the solubilization of fixed phosphates present in the soil, thereby enhancing soil fertility and plant growth. All the tested strains produce microbial siderophores that can regulate the availability of iron in the plant rhizosphere.

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# INHIBITION OF THE PATHOGENIC STRAIN *PYTHIUM ULTIMUM* UNDER LABORATORY AND GREENHOUSE CONDITIONS

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*Trichoderma spp.* are effective biocontrol agents for several soil-borne fungal plant pathogens including *Sclerotinia sclerotiorum* [1], *Fusarium* and *Rhizoctonia* [2], *Alternaria alternata* [3] and *Pythium ultimum* [4, 5]. In the present study, four *Trichoderma* isolates with antagonistic activity were tested for their ability to reduce or inhibit the root rot produced by the pathogenic strain *Pythium ultimum* in some vegetables, under laboratory and greenhouse conditions. The results of *in vitro* antagonism indicated that the maximum pathogen growth inhibition occurred with *T. aspellerum* T36, for which, after 4 days of incubation in dual cultures, the colony growth of *P. ultimum* reached only 3 cm as compared to 9 cm, in control plates. The pathogenicity test of *P. ultimum* with planting material (pepper) under greenhouse conditions showed that after 10 days inoculation, *P. ultimum* caused a different disease incidence. Hence, the pathogen was not able to infect tomato seedlings, meanwhile the incidence of disease was almost 100% for pea and lettuce seeds. *In vivo* biological control of *P. ultimum* was done with pea seeds and the effect of each treatment was measured by the percentage of the plants survival. The results confirm the capacity of *T. aspellerum* T36 to protect the plant against pathogen, reaching 64.71% percentage of plant survival, as compared with 76.19 % of *T. harzianum* T87 (control). This study led to the selection of potential biocontrol agent against *Phytium*, one of the common pathogen damping-off many vegetables over a variety of terrestrial and aquatic ecological habitats.

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## **DISRUPTION METHODS OF *SACCHAROMYCES SP.* YEAST CELL WALL –COMPARATIVE STUDY**

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Yeast cell disruption is the first step of recovery the intracellular carbohydrates from rigid and very resistant yeast cell walls, used for food, pharmaceutical and agriculture industry. To make the processing more economically viable, efficient cell disruption method should be developed to ensure a low operating cost and high product recovery. In the present study, applicability of different yeast cell disruption techniques was compared.

The raw material was baker's yeast *Saccharomyces cerevisiae* with a dry matter content of 97%. A yeast cell suspension with a concentration of 5% dry matter was prepared in distilled water.

The experimental series included disruption of yeast cells using mechanical and non-mechanical disruption methods such as: homogenization in a bead mill with glass beads 0.5-1.5 mm diameter, for 5x3 min/3min at 580 rpm/min and rated power 100W; ultra-sonication in an ice bath at 20 kHz frequency and 300W acoustic power, operated in pulse mode, four cycles consisting of 5 min pulse on and a 2 min pulse off time; autoclaving at 115<sup>0</sup>C for 15 minutes; autolysis at 50<sup>0</sup>C and 60<sup>0</sup>C, respectively, 200 rpm, for 24 h; enzymatic digestion for hydrolyzing cell walls with specific lysing enzymes.

After cell disruption, sediments of damaged cells isolated by all the methods were collected by centrifugation of the suspensions and the effectiveness of yeast cell disintegration was evaluated, immediately, both by optic microscopy to estimate the number of lysed cell or disintegrated and yeast cell viability determination by use of classical Gram stain.

Among the analyzed disruption methods, the highest degree of breaking the cell walls was observed using autolysis coupled with bead mill homogenization (lake of viable cells). Autolysis as an individual process was less effective (10-15% viability).

The mechanical methods of disintegration are most efficient for yeast rigid cell disruption constituted by polysaccharides, both at small and large scale.

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**MONITORING PLANT PHENOLOGY AND PHOTOSYNTHETICAL PARAMETERS ON  
NUTRACEUTICAL PLANTS TREATED WITH SYSTEMIC DEFENCES ELICITORS**  
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It is known that the products based on consortia of *Trichoderma* strains and essential oils have multiple actions as plant protection agents towards phytopathogens, and growth promotor of plant nutrition, mainly with nitrogen. The aim of our research 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. Therefore, the following treatments in field experimental tests were performed: foliar treatment with 2 levels of the *Trichoderma* propagules concentrations,  $10^7$  and  $10^8$  cfu/m<sup>2</sup>; foliar treatment with essential oils from (included in mesoporous silica (0.6% v/v); soil treatment with porous ceramics; soil treatment with compost - *Trichoderma*. Each variant was done in 4 replicates, in a randomized manner. Plants from the experimental plot were monitored to determine the morphological parameters related to the stomatal water resistance of plant leaves and the quantum efficiency of photosystem II (PSII). The diseases evolutions were also determined. The applied treatments had major influence on *Passiflora incarnata* cultures. It highlights the increasing of effective photochemical quantum yield of PS II of treated young plants and an evident decrease in stomatal resistivity. For *Momordica charantia*, it is not noticed major differences between the treated versus untreated groups in terms of photochemical activity and stomatal resistivity.

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**INFLUENCE OF CONSERVATION MANAGEMENT ON GLOMALIN-RELATED SOIL PROTEIN  
IN A CAMBIC CHERNOZEM SOIL**

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Glomalin-related soil protein (GRSP), a secondary constituent of soil organic fraction, is a hydrophobic glycoprotein rich in iron, with adhesive properties and high resistance to biodegradation, which was suggested to be produced in soil by mycorrhizal fungi associated with plant roots (Rilling, 2005).

Glomalin and associated proteins are essential to ensure the optimal C: N in soil and the natural resistance of granules of soil erosion. Its adhesion fixes soil granules, and its hydrophobicity and ability to reduce surface tension favor the flow of excess soil water in the aquifer (groundwater) or through the ground. Conservation management practices were shown to increase diversity of mycorrhizal fungi (Săle et al. 2015).

We determined the content of GRSP on cambic chernozem soil samples from different horizons (0-15 cm and 15-30 cm), from two lots of experimental field NARDI Fundulea, managed in conservation and in intensive manner. We assessed GRSP using Bradford method for protein, after extraction by autoclaving in alkaline citrate. We found an increase by 23% of Glomalin-related soil protein on conservation system (no tillage, high residues). Glomalin increase in soil is important not only for soil stability, but also for soil fertility and as bio-fixation of carbon dioxide, which contribute to the reduction of greenhouse effect.

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**ANTIOXIDANT ACTIVITY AND *IN VITRO* BIOCOMPATIBILITY OF *PASSIFLORA INCARNATA* L. PLANTS TREATED WITH MULTIFUNCTIONAL PRODUCTS**

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*Passiflora incarnata* L. contains three main groups of biologic active substances: alkaloids, glycosides and flavonoids and many studies showed its therapeutic properties (sedative, analgesic, antispasmodic, anxiolytic)<sup>28</sup>. The aim of this paper was to investigate the antioxidant activity and the *in vitro* biocompatibility of the extracts of *P. incarnata* L. plants treated with multifunctional products: *Trichoderma* consortia, essential oils with nutrients and porous ceramics.

Field experiments on *P. incarnata* L. culture were organized in two randomized blocks where five different treatments with multifunctional products were applied. The plant extracts were analyzed for antioxidant activity using DPPH and ABTS spectrophotometric methods<sup>2</sup> and their *in vitro* cytotoxicity was tested in NCTC fibroblast cell line, according to the international standard SR EN ISO 10993-5 using the Neutral Red assay<sup>3</sup>.

The results showed that the antioxidant activity of plants with *Trichoderma* foliar treatment in concentration of 10<sup>7</sup> CFU/mL was higher than that of plants treated with 10<sup>8</sup> CFU/mL *Trichoderma*. The foliar treatment containing *Trichoderma* induced a higher antioxidant activity than the same treatment applied at soil level. The treatment with thyme oil and nutrients did not influence the antioxidant activity of plant extracts.

The *in vitro* tests on cell cultures showed that the extracts of *P. incarnata* L. were not cytotoxic in the concentration range 50-150 µg/mL, after 48 h of incubation, for all five treatment variants from both blocks I and II. These results were supported by morphological observations presenting the normal appearance of fibroblast cells (spindle-like with round nucleus).

In conclusion, both DPPH and ABTS methods demonstrated that the highest antioxidant activity was presented by the extract of *P. incarnata* treated at soil level. Also, all *P. incarnata* extracts didn't present cytotoxic effect in NCTC cell line in 50-150 µg/mL range.

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**PLANT BENEFICIAL PSEUDOMONAS SPP. STRAINS ISOLATED FROM RHIZOSPHERE**

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Suppressive soils provide a diversity of microbial species, known for their plant beneficial traits. Pseudomonads are major constituents of the rhizobacteria with plant protection and growth promotion abilities. In our study, 18 strains of *Pseudomonas* spp. were isolated from the rhizosphere soils of South and South-East of Romania. These strains were screened for their antifungal activity against five plant pathogens and different mechanisms involved in plant growth stimulation and phytopathogen suppression. *In vitro* antagonistic activity against *Alternaria* spp., *Botrytis cinerea*, *Fusarium graminearum*, *Fusarium oxysporum* f.sp. *radicis-lycopersici* and *Sclerotium bataticola* was revealed by sixteen of the analysed strains. Fourteen of the isolated strains presented good antifungal activity against *Fusarium oxysporum* f.sp. *radicis-lycopersici* pathogen involved in tomato root and crown rot. The enzymatic activity of cellulase, amylase and lactonase, was also studied and the strains with antifungal activity revealed also hydrolytic ability. Plant growth promotion effect on wheat and tomato seedlings was tested on three of the selected strains, showing plant growth promotig ability.

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**BIOLOGICAL ACTION OF PLANT EXTRACTS ON A FUNGAL PLANT BIOSTIMULANT STRAIN OF *TRICHODERMA VIRIDE* PERS.**

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The antifungal activity of nine plant extracts manufactured by Hofigal S.A. against a plant biostimulant strain of *Trichoderma viride* Pers. (isolate Tv 82, Collection of RDIPP Bucharest) was assessed *in vitro*, based on the literature considerations [1], [2], [3], [4]. In general, the development (mycelial growth and sporulation) was not inhibited by the six plant extracts (*Satureja hortensis*, *Achillea millefolium*, *Allium sativum*, *Mentha* sp., *Hyssopus officinalis*, *Artemisia dracunculus* 'sativa'), with the exception of three ones (*Rosmarinus officinalis*, *Valeriana officinalis*, *Tagetes patula*), applied as the 20% conc. Among these, the extract of *Tagetes patula* has inhibited the Tv 82 development, applied as lower concentrations (10% and 5%), inhibition being 54.3% and 50%, respectively. In addition, some of the tested plant extracts (*Satureja hortensis*, *Achillea millefolium*, *Mentha* sp.) proved a stimulative effect on Tv 82 development.

Our present approach add to the early studies on the selectivity of *Trichoderma* spp. to chemicals used in crop treatments [5], [6], new data referring to the use of plant biostimulant fungi, like *Trichoderma* spp., as a new mean for crop treatments. Also, these data sustain the possibility of applying plant extracts as an alternative for crops treatments, especially on organically managed vegetables or medicinal / nutraceutical plants.

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# APPLYING FLOW CHEMISTRY ON TERPENIC ACIDS FOR MULTIFUNCTIONAL BIOPRODUCTS OBTAINING

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Gibberellins (GAs), a class of terpenic acids known for their role as plant growth regulators (PGRs) <sup>29</sup>, are presently studied due to their potential for multipurpose molecular design, including as germination stimulants for cytotoxic plants like Cynaropicrin or Parthenin, or as suicidal germination inducers on parasitic weeds <sup>30</sup>.

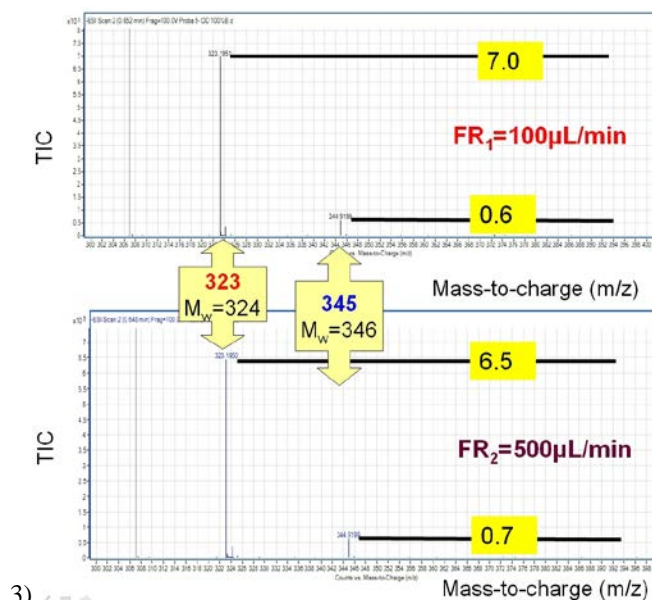
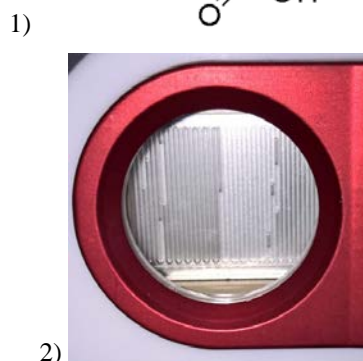
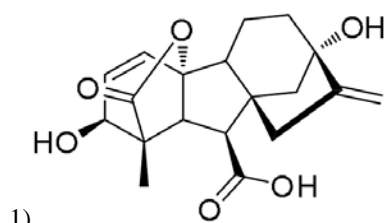


Fig. 1. Gibberellic acid (GA<sub>3</sub>). Fig. 2. 1 mL flow chemistry reactor. Fig. 3. Compounds of GA<sub>3</sub> oxidation.

Using an ASIA 330 (Syrris) equipment, the flow chemistry technique was applied for the incipient studies on the chemical properties of GA<sub>3</sub> (Fig. 1), a bio-compound with great potential for multipurpose molecular design, but for which the experimental data are scarce. As a first investigation it was studied the GA<sub>3</sub> oxidation and its possible reaction mechanisms in various experimental conditions (Fig. 2). An HPLC/Q-TOF-MS (Agilent 1260), working in negative ionization mode ( $M_w-H^+$ ) was used to evaluate the oxidation compounds.

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**NEW WATER-DISPERSIBLE MESOPOROUS SILICA PARTICLES OBTAINED FROM  
NATURAL RAW RESOURCES**

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Mesoporous materials have received a great interest in the last two decades. This interest was motivated by their use in catalysis, followed by finding new areas of application, such as: chromatography, membranes, sensors, biotechnology, nanomedicine, etc.

Present work deals with the possibility to obtain mesoporous silica starting from natural raw resources: sodium silicate and oleic acid (OLA). The interactions between OLA and sodium silicate were firstly studied. It was observed that an optimal OLA/OLANa molar ratio is required to generate vesicles able to stabilize silica particles obtained by the sol-gel process of sodium silicate. The titration of sodium silicate with OLA revealed the dependence between their average size and reagent's molar ratio. DLS and ESEM measurements evidenced the successful synthesis of silica nanoparticles starting from renewable materials.

Next, the influence of these ratios over more complex systems, in which silica was hydrophobically modified by grafting octadecyl chains, was evaluated. These modifications were carried out by using various silica/octadecyltrimethoxysilane (ODTMOS) ratios. The interaction between the oleyl and octadecyl chains resulted in the formation of stable gel-like aqueous systems. The stability in time of the resulted systems and their homogeneity were observed using olive oil as a model-oleophil, red-colored with a commercially available dye (Solvent Red). Mesoporous silica was finally obtained after the removal of water and of the organic chains by thermal treatment. This great dispersing capacity of oleosoluble compounds opens new perspectives for future biomaterials applications.

**Acknowledgement**

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**THE INDUSTRIAL SALT, PRELIMINARY STUDIES ON ITS IMPORTANCE  
AND A NEW WAY TO REDUCE ITS PRICE FOR MANUFACTURING  
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Salt is crucial for many industries. Its compounds make it one of the most important materials in the chemical industry. It is also used in the manufacturing of thousands of other commodities including glass, paper, rubber, and textiles as well as in water softening systems for industry and domestic use. Furthermore, it is used as a de-icing agent and as most commonly known food ingredient. The industrial salt may be useful for its Chemical Applications (Pulp and paper industry, Textiles, Waste and water treatment, Petroleum additives, Dyes and intermediates, Pharmaceuticals) and also as a de-icing agent or for Food Grade Salt and Animal Feed. There are three types of salt extraction: solar evaporation, rock salt mining and solution mining. Each one involves specific technology and manufacturers select the most appropriate technique depending upon the particular topographic and socio-economic conditions in their area of operation. This paper presents our first results obtained for price reduction for Romanian industrial salt preparation, by using two modified manufacturing techniques. The recrystallized salt samples results:

<b>Identification</b>	<b>P 1</b>	<b>P 2</b>
Chlorides	Positive	Positive
Sodium	Positive	Positive
Acidity	Properly	Properly
Alkalinity	Properly	Properly
Ammonium	Properly	Properly
Barium	Properly	Properly
Iron	Properly	NOT Properly
Iodide	Properly	Properly
Nitrites	Properly	NOT Properly
Heavy metals	Properly	Properly
Loss on drying	0,1% (Properly)	0,76 % (NOT Properly)
Na Cl dosage	99, 25 % (Properly)	99, 28 % (Properly)

References:

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**STUDIES ON RHEOLOGICAL BEHAVIOR OF POLY(3-HYDROXYBUTYRATE) USING A  
BRABENDER PLASTOGRAPH**  
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STANCIU Daniela<sup>1</sup>**

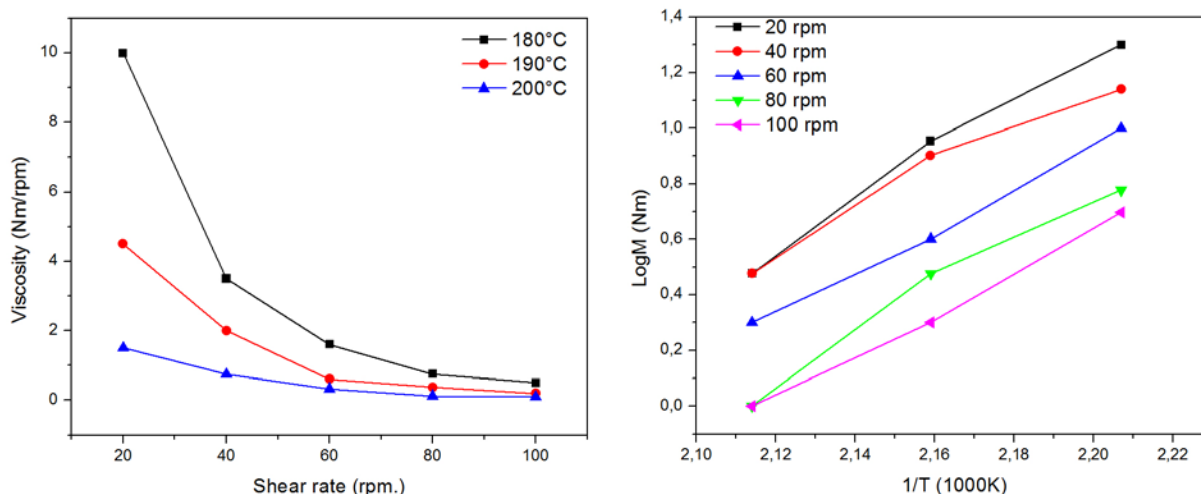
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Rheological behavior of poly(3-hydroxybutyrate) (PHB) was evaluated by analysis of torque-time curves registered during melting in the Brabender Plastograph. Different processing conditions were used: mixed temperatures of 180°C, 190°C and 200°C and rotor speeds of 20 rpm, 40 rpm, 60 rpm, 80 rpm and 100 rpm.

Based on the equations of the non-Newtonian flow behavior assuming that the torque obtained is an indirect indication of the shear stress, while the rotor speed is an indirect indication of shear rate<sup>31, 32</sup>, it was estimated following rheological parameters: melt viscosity, non-Newtonian flow index, flow activation energy and power consumption at melting.

The obtained results are very useful for estimation of PHB processability at industrial scale up.



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# EFFECT OF RENAWARE BIOPLASTICIZER ON SOME BIOPOLYMERS PROPERTIES FOR FOOD PACKAGING APPLICATION

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Most food packaging materials based on conventional polymers, like polyethylene, polyethylene terephthalate and polypropylene are ideal candidates for safe food packaging. Despite of good properties, conventional packaging materials are a huge problem because of their long persistence in environment and nonbiodegradability.

Third generation of materials consisting of fully biobased biodegradable materials represents a potentially sustainable replacement to fossil fuel-based thermoplastics. Among all biobased materials, poly(lactic acid) (PLA), poly( $\beta$ -hydroxybutyrate) (PHB) and poly(hydroxybutyrate-valerate) (PHBV) are considered suitable for promising thermoplastic polymer applications. Because PLA, PHB and PHBV are stiffer and more brittle, their blends with flexible polymers and plasticizer can overcome these undesirable properties<sup>33, 34</sup>.

Some results regarding melt plasticization of PLA, PHB and PHBV with Lapol 108 Masterbach are presented. The amounts of bioplasticizer varied from 0 wt.% to 100 wt.% relative to each polymeric matrix. The effect of plasticizer content on the melt viscosity, thermal properties (DSC), spectral characteristics (ATR-FTIR), tensile properties and oxygen permeability was evaluated in order to improve the properties of investigated biopolymers for food packaging application.

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**THE RESISTANCE OF WOOD - POLY(VINYL CHLORIDE) COMPOSITES  
TO MICROBIAL DEGRADATION**

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The wood-plastic composites have many applications for which the biological durability is an important feature. Different formulations containing wood or other natural fibers were designed [1, 2, 3]. In the present study, several poly(vinyl chloride)-wood flour composites were exposed to microbial degradation during 12 months. The polymeric materials were incubated with fungal strains, like, *Aspergillus niger*, *Candida* sp. and *Penicillium* sp. The biodegradation process was negligible and no significant modifications were observed by the Scanning Electron Microscopy (SEM) and Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR) spectroscopy. Despite the fact that the biodegradation was carried out in the presence of water and the prerequisite for biological degradation of a material was met, the tested samples were very resistant to microbial attack. The formulations contain a nutrient source – wood flour, but the percentage was too low to allow the access of microorganisms. The designed composites prove high fungal durability and the material composition of the formulation could be used for proper applications.

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**BACTERIAL CELLULOSE - POLY(ACRYLIC ACID) INTERPENETRATING POLYMER NETWORKS (IPN) COMPOSITE HYDROGELS CONTAINING NATURAL BIOACTIVE SUBSTANCES**

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Hydrogels are cross-linked hydrophilic polymer materials with water-retaining capacity of tens to thousands of times their dry weight, without dissolving or losing their structural integrity [1]. In the last few decades these materials have found innovative applications in many areas, especially in medicine and agriculture [2].

The present paper deals with the synthesis and characterization of novel Interpenetrated Polymer Networks - (IPN) as bio-friendly hydrogels based on bacterial cellulose and crosslinked poly(acrylic acid) (PAA), in order to provide improved water retention in soils and the water supply for plants, and also the controlled release of natural bioactive substances. Bio-friendly Interpenetrating Polymer Networks (IPN) composite hydrogels based on bacterial cellulose (BC) and crosslinked poly(acrylic acid) composite hydrogels were prepared by grafting crosslinked PAA chains within BC structure. The hybrid hydrogels contained also a bioactive substance. The resulting IPN composite hydrogels were characterized by Fourier Transform Infrared spectroscopy (FTIR), Thermal Gravimetric Analysis (TGA) and in terms of their water absorption. The results showed that the Swelling Degree (SD) values of the synthesized composite hydrogels depended on the polymerization media, on the BC concentration.

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**FACILE SYNTHESIS OF NON-TOXIC SILICA PARTICLES STABILIZED WITH OLEIC ACID**  
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Pollution reduction targets have favored the emergence of studies on aqueous dispersions of vesicular systems from renewable plant resources. Such vesicular systems are formed from pairs of unionized fatty acids (RCOOH) and their alkaline salts (RCOO<sup>-</sup>). Present work is focussed on preparation of biocompatible silica particles, from sodium silicate, stabilised by a vesicular system containing oleic acid (OLA) and its alkaline salt (OLANa).

Silica nanoparticles were generated by partial neutralization of oleic acid (OLA) with the sodium cation present in the aqueous solutions of sodium silicate. At the molar ratio OLA/Na<sup>+</sup> = 2/1, it was achieved the molar ratio (OLA/OLANa = 1/1) required to form vesicles, in which the carboxyl and carboxylate groups have equal concentrations.

In order to obtain hydrophobically modified silica particles, octadecyl triethoxysilane (ODTES) was added to the sol-gel mixture, at different molar ratios. Following interactions between the octadecyl groups from the modified silica and the oleyl chains from the stabilising system, the reaction mixtures converted in stable semi-opaque gels, able to entrap olive oil, used here as a model-hydrophobic bioactive substance. Simultaneous TGA-DSC analysis allowed calculating the water's enthalpy of vaporization for the resulted silica latexes. It was noted a significant decrease of the vaporization enthalpy with the increase of ODTES molar ratio. Particles size and zeta potential were also evaluated. Thus, the highest hydrodynamic average diameter and the most negative zeta potential were recorded for the hybrid in which the molar ratio ODTES/SiO<sub>2</sub> = 1/5.

Being biocompatible, the obtained silica latexes, stabilised by the OLA/OLANa vesicular system, can be used as carriers for hydrophobic bioactive molecules.

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**THE STUDY OF SURFACE AREA AND POROSITY OF MULTIPARTICULATE SYSTEMS LOADED WITH A NON-STEROIDAL ANTIINFLAMATORY DRUG**

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Pellets are small (0,2 – 2 mm), dense, spherical granules, coated or not with polymeric films and intended for oral administration<sup>35</sup>. Usually, pellets are filled into hard gellatin capsules. The formulation of a multiparticulate system designed as pellets containing a non-steroidal antiinflammatory drug (NSAID) such as piroxicam presents several advantages: a fast passage through the pyloric sphincter, independent of gastric emptying and a decreased contact of the NSAID with the gastric mucosa, a reduce gastric irritation, an even distribution of the pellets across the gastrointestinat tract. Furthermore, the drug is released from each pellet in small amounts, leading to a faster dissolution and absorbtion<sup>36</sup>.

A relevant characteristic of pellets is their surface area, much higher than in the case of conventional oral solid dosage forms, such as tablets. Another characteristic is pellet porosity, with a significant influence on the drug release.

The aim of this study was to determine by gas absorbtion the surface area and porosity of inert pellets and of pellets loaded with piroxicam, prepared by extrusion-spheronization<sup>37</sup>, respectively by drug-layering on inert pellets, as well as to estimate the influence of these parameters on the potential mechanisms of drug-release from the pellets.

The surface area of the pellets has increased by loading the pllets with piroxicam, especially in the case of pellets obtained by drug layering (by spraying a piroxicam suspension on inert pellet cores). This can be atributed to a looser structure of the surface of pellets obtained by drug-layering, unlike the pellets obtained by extrusion-spheronization, in which case the preparation technique has determined a less porous, denser pellets. For the drug-loaded pellets, differences in the the average diameter of the pores was observed, depending on the preparation method which was applied.

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**THE 5-AMINOPYRAZOLE. A POWERFUL TOOL IN DESIGNING JANUS KINASES INHIBITORS**

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Kinases are enzymes with an essential role in cancer progression. Several kinase inhibitors are already used for cancer treatment and extensive efforts are made to develop selective inhibitors for other kinases. Therefore, the assessment of the affinity of some structures for specific molecular targets is mandatory. Our study was focused on 5-aminopyrazoles, as drug-like scaffolds and privileged structures for protein kinases. Using data mining techniques, we demonstrated that the aminopyrazole derivatives represent privileged structures for protein kinases, despite their apparent promiscuity. The analysis of the interaction profiles between protein kinases and specific inhibitors, demonstrated their class-selectivity towards protein kinases, suggesting potential antitumor activity. We also showed the importance of the amino group position on the pyrazole ring, indicating a clear difference between the aminopyrazoles isomers in the drug design process. 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.

# MECHANICAL CALCULATIONS AND MOLECULAR PROPERTIES PREDICTION FOR AMINO ACIDS WITH NON POLAR, ALIPHATIC SIDE CHAINS

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In order to predict molecular properties of large molecular systems such as enzyme or receptor proteins and to accurately assess the ligand protein interactions, novel methodologies as approximate methods including semiempirical approaches, reduced-scaling methods, and fragmentation methods are in development, representing new challenges for researchers<sup>38</sup>. The linear scaling approach, by dividing a large system into small subsystems and evaluate the global properties by performing calculations for each subsystem individually, is a method proposed for quantum mechanical calculation of protein - small molecules interactions energy<sup>39</sup>. In this work, a fragmentation approach is proposed by studying separately some amino acids, as model units of proteins, in terms of molecular properties and mechanical calculations, computer aided, using *Spartan 14* software. A series of amino acids having non polar, aliphatic R groups: Glycine (R = H), Alanine (R = CH<sub>3</sub>), Proline (R = -(CH<sub>2</sub>)<sub>3</sub> in cyclic, pyrrolidine structure), Valine (R = (CH<sub>3</sub>)<sub>2</sub>CH), Leucine (R = (CH<sub>3</sub>)<sub>2</sub>CH-CH<sub>2</sub>), Isoleucine (R = (CH<sub>3</sub>-CH<sub>2</sub>-CH(CH<sub>3</sub>))), and Methionine (R = (CH<sub>3</sub>-S-CH<sub>2</sub>)<sub>2</sub>), were compared by examining the calculated values of their properties and mechanical calculations: weight, area, volume, ovality, log P, polarizability, solvation, dipole moment, difference in energy between frontier orbitals, HOMO and LUMO, counts of hydrogen bond donors and acceptors (HBD, HBA), polar surface area (PSA) etc. These calculations were performed on the amino acids generated and optimized 3D structure. The ability of molecules to serve as proton donor or acceptor has been evaluated. Also, the comparison was made in terms of electronic effects of side chain groups, molecular deformability and steric factors. Proline exhibits a rigid conformation due to their cyclic structure, a fact that affects the rate of peptide bond formation between proline and other amino acids. This approach can be extended to other amino acids and be proved to be useful for predicting protein-ligand interactions, important tools in drug design studies and protein engineering.

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**STUDY OF THE ORGAN DISTRIBUTION OF TWO NOVEL RUTHENIUM(III) COMPLEXES WITH ANTICANCER PROPERTIES**

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Ruthenium(III) complexes of general formula  $[\text{RuCl}_3(\text{HQuin})_2(\text{DMSO})]^{401}$  with quinolone ligands norfloxacin and ofloxacin exerted cytotoxic properties in vitro studies on different cell lines. The in vivo studies performed on Walker 256 carcinoma-bearing Wistar rats proved their antitumor activity<sup>2</sup>. In order to establish the complexes effect in cancer with different localization in the organism, a pharmacokinetic study was performed for the evaluation the distribution profile of the complexes in the organs. For this study an ICP/MS method for the quantification of ruthenium from biological samples was developed and validated. Biological samples (liver, kidney, lungs, brain, tumoral and peritumoral tissues) were obtained from Walker 256 carcinoma-bearing Wistar rats, after 5, 10 and 15 days of treatment with the ruthenium(III) complexes. The results point out that the complexes achieve high concentration in the tumoral and peritumoral tissues, with a preferential distribution in liver and kidney.

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

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**STUDIES FOR OBTAINING mcl-PHA (CO) POLYESTERS WITH DIFFERENT COMPOSITIONS**  
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The aim of this work was to obtain medium chain length (co)polyhydroxyalkanoates (mcl-PHA) with controlled composition (containing monomers with 5 - 14 carbon atoms)<sup>41</sup>, through microbial biosynthesis, using *Pseudomonas* spp. strains (from ICCF culture collection of micro-organisms), by varying the carbon sources and the precursors. Glucose and sodium citrate were used as carbon sources. The precursors, sodium octanoate and sodium decanoate were added separately or both (in volume ratio 1:1) in the fermentation media, at regular time intervals (0, 6, 12, 24 hours), in order to assure a constant precursor concentration (0.16% g/v).

Continuing our previous studies on PHAs production<sup>42</sup>, in this work, assays were performed at laboratory level with fermentation media seeded with inoculum cultures of two strains (*Ps. putida* and *Ps. fluorescens*) in a proportion of 10%. The influence on mcl-PHA production of glucose and citrate as carbon sources for strains development, as well as of octanoic (C8) and decanoic (C10) acids, as polymers precursors, were analysed.

The results showed the optimum conditions for metabolizing the fatty acids and the ability of the microorganisms to easierly and more productively metabolize the octanoic acid than decanoic acid. This behaviour was proved in the experimental model of biosynthesis and down-stream processing, to obtain PHA containing predominantly C8 monomers or C10 monomers in different ratios. Furthermore, the data obtained from several experiments in shake flasks, showed the following: in case that octanoate is used as the sole C source and it is totally consumed during the fermentation (16.70-20.04 g/2L fermentation medium), the conversion degree of total C in polymer is of 30.9%, respectively 34%, which corresponds to 3.30-3.32 g/L dry bacterial biomass and to 1.327-1.49 g/L PHA, represented predominantly by PHO (>85%).

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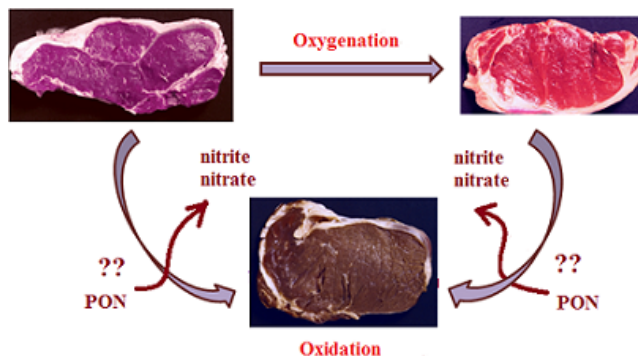
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## FLOW INJECTION SYSTEM FOR THE ELECTROCHEMICAL MONITORING OF PEROXYNITRITE AND ITS REACTION WITH MYOGLOBIN

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For the food industry and for the consumers, as well, it is very important to monitor quality and freshness of raw meat. Different factors are a sign of meat alteration (e.g. discoloration, rancidity, alteration of flavor). One pathway of alteration is the scavenging activity of myoglobin towards nitro-oxidative species (such as peroxynitrite, PON). The lack of MetMb ( $\text{MbFe}^{3+}\text{OH}_2$ ) reducing enzymes systems in meat after slaughter, determines the irreversibility of the oxidation processes of myoglobin. [1]



The color changes are also a sign of this processes. UV-Vis was used to determine the absorption changes during the reaction of PON with myoglobin.

Using a single-line flow injection analysis (FIA) system, we have the possibility to speed up and automatize the detection of peroxynitrite. The electrochemical reduction of PON occurs at cca. 0,1 V on a screen printed carbon electrode modified with the mediator cobalt (II) phthalocyanine (SPCE/CoPc). After the incubation of PON with myoglobin, the PON consumption was monitored by chronoamperometry using the developed FIA system.

Interfering species were also studied, and using the FIA system a remarkable improvement has been observed, making this method selective and sensitive to PON, even if the matrix became more complicated. The system has also a good reproducibility and repeatability. Some preliminary results obtained for meat extracts in PBS pH 9 are also presented. The proposed FIA method showed promising features for studying the relevance of peroxynitrite in meat.

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# MULTI-ANALYTE DETECTION OF DOPAMINE AND CATECHOL AT ELECTROCHEMICAL MICROBIOSENSORS BASED ON MICROELECTRODE ARRAYS

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Dopamine (DA) is a neurotransmitter playing an important role in the functioning of the nervous central system and its quantification in brain has been addressed in the late 80s <sup>43</sup>. Since then, several biosensors for DA have been proposed. This work is focused on the simultaneous determination of DA and catechol (CT) at gold microelectrode arrays modified by biocomposite materials consisting of poly(3,4-ethylenedioxythiophene) conducting polymer incorporating tyrosinase. The microbiosensors are prepared by using a sinusoidal voltages (SV) preparation procedure consisting in the application of a sinusoidal voltage over a properly chosen d.c. potential <sup>44, 45</sup>. The improvement with respect to our previous works lies in the use of SV of fixed frequency value and amplitude. Several electrochemical parameters such as the fixed frequency value and amplitude of SV, the d.c. potential, were optimized. Gold disk microelectrode and gold interdigitated microbands arrays were used as electrode substrates in microbiosensors preparation. The use of low frequency SV resulted in an increased porosity of the biocomposite materials, which determined an increase of the biosensor's sensitivity. A multi-analyte detection protocol for DA and CT determination from a mixture by using voltammetric methods has been developed. The analytical performance of the proposed electrochemical microbiosensors has been assessed. The electrochemical biosensors prepared at low frequency displayed the best analytical performance for two-analyte detection.

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**STUDY OF THE ELECTROCHEMICAL BEHAVIOUR OF SOME LAMIACEAE EXTRACTS**  
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Cyclic voltammetry and differential pulse voltammetry techniques<sup>46,47,48</sup> were used to study the electrochemical behavior of ethanol extracts of some *Lamiaceae* species (rosemary, sage and oregano) obtained by Soxhlet and ultrasounds methods.

A three electrode system consisting of glassy carbon electrode (working electrode), Ag/AgCl (satd. KCl) as the reference electrode and platinum wire as the counter electrode was used for measurements. Experiments were realized for the extracts added in acetate or phosphate buffer solutions at various pH values ranged between 4.5 and 7.4. Cyclic voltammograms were recorded in the 0-800 mV range with a scan rate of 100 mV/s. For differential pulse voltammetry, pulses of the amplitude between 10 and 100 mV were employed.

The two techniques were applied to investigate the antioxidant properties of the extracts. Also mixtures between extracts have been studied in order to check the possibility of synergism occurring regarding the antioxidant activities.

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**NEW STOCHASTIC SENSORS FOR ASSESSING THE EFFECT OF OLEAMIDES ON THE OBESITY**

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Oleamides are materials presenting in 3D a “V” conformation, miming the pores needed for the design of the stochastic sensors due to their ability of providing the necessary channels/pores for sensing<sup>49</sup>. Stochastic sensing is a new approach in electroanalysis, that allow both qualitative and quantitative analysis<sup>50</sup>.

N-adamantyleamide and N, N-dimethyl-N-(2-oleylamidoethyl)amine were synthesized and used as modifiers for the design of new stochastic microsensor based on graphite paste. The sensors were able to determine simultaneously from the whole blood of Wistar rats the three biomarkers: leptin, interleukin-6 (IL-6) and plasminogen activator inhibitor 1 (PAI-1). The sensors were characterized and applied for whole blood measurements. They were very sensitive and reliable for the assay of obesity biomarkers in whole blood. The concentrations of the three biomarkers found using the proposed stochastic sensors correlated well with the decreasing of obesity of Wistar rats.

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**FAST EVALUATION OF POLYETHYLENE BIODEGRADABILITY BY MICROCALORIMETRY  
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Plastic packaging materials represent a large percentage of the materials used for food packaging. Because most of them are not biodegradable, a constant challenge for packaging material technologists is to design environmentally friendly systems containing biodegradable materials.<sup>51</sup> One of the major environmental threat is the slow rate of degradation or non-biodegradability of the organic materials under natural conditions.<sup>52</sup> Polyethylene finds a wide range of applications in daily use because of its easy processing and its low cost. It is used for carrying food articles, for packaging textiles, for manufacturing laboratory instruments and automotive components.<sup>53</sup> During the last years, scientific research groups have studied the biodegradation of polyethylene.<sup>54,55,56</sup> Thermal analysis techniques are useful to measure the thermal properties and the effect of degradation on the structure of biodegradable biopolymers. The aim of this work is to study the thermal behavior of low density polyethylene films with 1% rosemary content using microcalorimetry technique. The biodegradability studies were carried out by incubating the unmodified and modified low density polyethylene films with *Aspergillus Niger*, *Penicillium sp.*, *Bacillus licheniformis* and *Candida lipolytica*. The incubation period was of 50 days, in highly nutritive liquid medium, under stirring, at 37°C. The kinetic analysis started with the isoconversional differential Friedman and integral Flynn-Wall-Ozawa methods. The activation energy was also determined using the differential Kissinger method. Investigation of the kinetics and mechanism of thermal degradation of polyethylene can provide valuable information on its biodegradation.

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**SECTION 2**

**ENVIRONMENT  
ENGINEERING AND  
PROTECTION OF CULTURAL  
HERITAGE**

**ERORI IN TRANSPUNEREA INDUSTRIALA A TEHNOLOGIILOR CHIMICE SI PETROCHIMICE**  
**OPRESCU Ion**  
*HAROM*

Industria chimica si petrochimica din Romania a cunoscut inainte de 1989 o dezvoltare impresionanta. Au aparut marile combinate si s-au dezvoltat vechile intreprinderi din acest domeniu.

Au existat insa si unele erori in ridicarea la scara industriala a unor tehnologii elaborate de diverse firme. Lucrarea prezinta cateva dintre aceste erori, de pe urmatoarele platforme industriale:

<b>Combinatul</b>	<b>Tehnologia</b>
Chimcomplex Borzesti	Obtinerea clorurii de vinil din acetilena - HCl
CFS Savinesti	Oxidarea ciclohexan la ciclohexanol, ciclohexanona
CFS Savinesti	Tetreclorura de etan $\rightarrow$ Cl <sub>2</sub> si C <sub>2</sub> H <sub>2</sub>
Chimcomplex Borzesti	Alcoolii grasi (gaz-lichid-solid suspensie)
Oltchim Rm. Vilcea	Dehidroclorurarea izomerilor inactivi (HCH)
Doljchim Craiova	Catalizator cromit de cupru tablete CrO <sub>3</sub> pentru NMP
Chimcomplex Borzesti	Hidrogenarea anhidrida maleica la gama butirolactona
Elcond Zalau	Conductori electrici emailati

**VITREOUSE COATINGS FOR PRESERVATION OF HERITAGE OBJECTS**

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In last years the interest to maintain historical objects in good conditions has increased. The ancient and middle age historical glasses can be classified as lead containing glasses or soda lime silicate glasses. In their composition transitional elements in quantities below 5%wt are present that have negative influence on the chemical stability of glasses under the attack of atmosphere conditions. With the aim to preserve historical glasses against future weathering, several reference glasses that reproduce the composition of the ancient or middle age ones were designed and prepared by traditional route. The glasses were coated with sol-gel hybrid films by deep coating and their influence on the resistance at aqueous media attack was established.

**DETERMINATION OF A PERFUMING LIQUID IN ALKOXY PROPANOLS AS SOLVENT BY GC-MS AND GC-TCD. THE ELUTION ORDER AND THE McREYNOLD'S CONSTANTS**

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Analytical Laboratory developed a method of analysis and an exact mixing procedure of a Bubble Gum multicomponent perfuming liquid in alkoxy propanols as solvent.

The qualitative analysis was performed by gas chromatography coupled with mass spectrometry (GC-MS) on a Perkin-Elmer Clarus 500 tandem. The components of a Bubble Gum perfuming liquid were separated by gas chromatography on a fused silica capillary column of 60 m with an Elite-5-methyl phenyl silicone MS stationary phase and were identified by comparison to the mass spectra from the NIST and NBS libraries. In total were identified 12 components. The major components identified in the perfuming liquid are: limonene, 3-methylbutyl acetate (isoamyl acetate) and ethyl butyrate. The solvent components were separated by gas chromatography on the same capillary column and four components were identified. The major components identified in the solvent mixture are: 2-propanol, 1-(2-methoxy-1-methylethoxy) and 2-propanol,1-(2-methoxypropoxy).

The quantitative analysis was performed by gas chromatography with thermal conductivity detector (GC-TCD) on a Carlo Erba Model B instrument. It was used a 2 m packed column with Carbowax 20 M stationary phase on a AW, DMCS 80-100 mesh Chomosorb W support.

The Carbowax 20M stationary phase has the most favorable McReynolds constants for alcohols relative to esters ( $\Delta I$  butanol = 536, relative to  $\Delta I$  2-pentanone = 368), being able to increase retention times of the alkoxy propanols with hydroxyl groups from the solvent mixture and to separate these components by the major components without –OH groups in the Bubble Gum perfuming liquid.

After optimizing the operating parameters of the GC-TCD method, the found concentration of the Bubble Gum perfuming liquid in a sample by external standard method was:  $C = 12.9 \pm 0.3\%$  (v/v).

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**INNOVATIVE TRAINING SOLUTIONS OF ENTREPRENEURS  
FROM THE LIFE SCIENCE FIELDS**

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The project developed in the framework of the Lifelong Learning Programme Leonardo da Vinci - Transfer of Innovation, project no: 2013-1-RO1- LEO05-28758 (Acronym BELA) was addressed to a comprehensive target group of people in need of developing competences in Entrepreneurship for a specific, complex, and involving high scientific and technical knowledge economic sector: sustainable development applications bio economy. Main objectives were: (a) To realize a blended learning system comprising face to face learning, but also e-learning, which will offer improved and multiplied ways to assure the ex-post valorisation of the realized vocational training. (b) To finally prepare a vocation training package with dedicated teaching methodology ready to be implemented in the partnerships countries, but also in a large European geographical area and to export to other economic sectors as methods and procedures due to the increased European dimension [1-2]. The technical and scientific quality of the e-learning system and the face to face contents, but also the additional bibliography was positively considered by most trainees. Overall, more than 90% of the trainees appreciated the blended learning system and consider that it is useful for carrying out activities in the bio-entrepreneurship.

**Acknowledgements**

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**KEY COMPETENCES NEEDED TO START AND DEVELOP THE INNOVATIVE SME'S IN THE FIELD OF LIFE SCIENCES**

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One of the result of the project entitled "IMPROVED CURRICULA AND MODERN LEARNING SYSTEM TO PROMOTE THE NEW DIRECTIONS OF BUSINESS ENHANCEMENT IN LIFE SCIENCES APPLICATIONS" was the elaboration of a "Basic template regarding the entrepreneurship key competences needed to start and to develop innovative SMEs". According to this study, the main issues of the matrix of competencies for the entrepreneur from the life sciences are [1-2]: 1) Personality characteristics: Risk seeking; Self-confidence; Strong sense of independence; Self-efficacy; Self-made/self-belief; Inventive orientation; Optimistic orientation; Competitive spirit; Courageous and well organized; Communication capacity; Networking ability; Management capacity; Leadership characteristics; Capacity to work in multi-and cross-disciplinary teams; Adaptation to changing conditions. Only personality tests information will be presented at the beginning of the training products. 2) Bio entrepreneur competencies characterization -Technical Skills respectively Knowledge and understanding technological knowledge about manufacture of bio products and specific services; Intellectual Property Rights specific to bio economic sector; Innovation development based on R&D in life sciences sector. 3) Management and Business knowledge and skills, respectively: Judgment and approach, meaning: Project financial set up and evaluation; Elaboration of a business plan, capacity of building organizations and developing them by inter-company and companies and academia cooperation; Methods to access to financing, long-term and venture capital financing; Economic and social models or regulatory issues from a national and international perspective.

**Acknowledgements**

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### NON –HAZARDOUS PRODUCTS FROM RED MUD WASTE

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Red mud (RM), waste product from the aluminium industry, represents a great environmental issue. The high pH value and Na<sup>+</sup> concentration and its fine granulation are important factors that reduce the possibility of using this waste in various fields. However, by applying treatments which are reducing its alkalinity, the red mud waste can be transformed into a valuable resource for special construction materials and for synthesizing geopolymers, inorganic-organic hybrid compounds or absorbent materials, designed for environmental applications, etc [1,2].

The present work contains the results of the monitoring of the chemical and structural properties of the red mud samples coming from a neutralization process carried out with CO<sub>2</sub> industrial gas flows (5-20% vol) in a continuous system, in the lab (25<sup>0</sup>C, atm. press.). The composition of used raw red mud materials are fluctuating, depending on the source of the mineral: bauxites with 11%- 31% gibbsite containing Al =8.2/10.5%, Fe=27/31% and  $\Sigma Me^{+}/\Sigma Me^{++}=1.059-1.537$

The XRD mineralogical characterization revealed a decrease of some of the initial oxide phases along with an increase in the content of other existent phases or with the formation of new phases (hematite transforms to titanohematite (ilmenite), calcite and cancrinite lower their intensity generating cancrisilite, etc.). The gaseous CO<sub>2</sub> treatment induces the increase of the specific surface of the neutralized materials (from 20 m<sup>2</sup>/g to 35 m<sup>2</sup>/g) and a decrease of about 40% of the  $\Sigma Me^{+}/\Sigma Me^{++}$  ratio. The characterization of the aqueous leaching from the raw RM, as well as from the solids obtained in various neutralization conditions (EN 12457-2 ) [3], emphasized the drop of the pH values from pH 10.9-12.8 to pH 8.5-8.3 and the reduction of electrical conductivity with 80%. The IR spectra of both the initial (NR) and the treated red mud (RMneut) samples showed modifications in several bands.

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**THE INTERACTION OF IMPURITIES CONTAINED IN NATURAL PHOSPHATES ON THE NITRIC ACID DECOMPOSITION**

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The processes that occur during the decomposition of the phosphatic raw materials with nitric acid can be reviewed with the help of the phase equilibrium diagrams in the CaO-P<sub>2</sub>O<sub>5</sub>-N<sub>2</sub>O<sub>5</sub>-H<sub>2</sub>O system. The solubility of these system was presented in the scientific literature by several authors<sup>1,2</sup>.

The majority of the impurities contained in phosphatic raw materials, as well as in other phosphorus containing minerals, reacts with nitric acid and passes in solution with a lower or higher degree. In this way the variation and the quantity of impurities in the phosphatic raw materials influence not only the solution composition with phosphorus content, but also leads to the increase of the nitric acid consumption in the decomposition process, over the stoichiometric ratio needed to bind Ca<sup>2+</sup> under the form of calcium nitrate.

The product obtained from the nitric decomposition of phosphatic rocks is a suspension made from the phosphonitric solution and the insoluble residue. The yields and compositions of the solutions, as well as the insoluble residue content, depend, firstly, on the nitric acid concentration and norm used in the decomposition process, but also on the used type of phosphatic rock.

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<sup>1</sup> "Complex Fertilizers Based on the Nitric Acid Decomposition of Phosphates", [Russian Chemical Reviews, Volume 43, Number 3, 1974.](#)

<sup>2</sup> "Use of phosphate rocks for sustainable agriculture", Fertilizer and Nutrition Plant Bulletin, no.13, Chapter 4, ISBN 92-5-105030-9, 2004.

**BREAKTHROUGH CURVE STUDIES FOR THE REMOVAL OF COBALT FROM AQUEOUS SOLUTIONS ON PUROLITE ION EXCHANGE RESINS**

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The application of ion exchange technique for the removal of cobalt from aqueous solutions was studied. The suitability of Purolite NRW 1600 and Purolite NRW 160 to achieve the desired separation was evaluated. The experiments aimed to provide a basis for comparing results obtained in simulated system and real radioactive wastes. The studies include dynamic experiments and construction of the breakthrough curves.

Ion exchange technique is one of the most common and effective treatment methods for liquid waste. In spite of advanced development, various aspects of ion exchange technique are being studied to improve the efficiency and economy in its applications on liquid wastes<sup>2,3,4,5</sup>. Nuclear grade resins possess high loading capacity and high selectivity and are designed for purification of water in nuclear power operations.

The effects of flow rate (5-15 BV/h), pH (2 and 5), and initial metal concentrations on metal breakthrough profiles were studied. The effects of flow rate and the initial concentration of cobalt in the solution were found to be the most significant. The experiments revealed that the pH value does not affect breakthrough curve crossing the resins.

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**ADSORPTION DECOLORIZATION TECHNIQUE OF  
TEXTILE/ LEATHER – DYECONTAINING EFFLUENTS**

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**Introduction.** Water-pollution control is presently one of the major areas of scientific activity. Effluent discharge from leather, textile and dyestuff industries causing significant health concerns to environmental regulatory agencies. Color is the first contaminant to be recognized in wastewater and has to be removed before discharging into waterbodies or on land. The economic removal of polluting dyes is gaining great importance, particularly as new EC regulations on industrial effluent discharge are at present being enforced. The textile and leather industry is a large consumer of water and therefore produce large quantities of coloured wastewater and the used dyestuffs are released in the effluent, being a major source for polluting the water resources. Adsorption is a method that is preferred over other options because it is rapid, convenient and unaffected to the toxic contaminants. The research proposed a method for decolorization of the industrial wastewater from ICPI microproduction leather dyeing and FROTTIEREX textile factory, using adsorbents macroporous ion exchange resin –IER by passing the coloured wastewater through the column of beds of IER .

**Materials and methods.** In the research we used the following IER-PUROLITE type: strongly basic anion exchanger resins Purolite A500, A500Plus and PFA500MB. The studied industrial wastewaters contains: Acid black 210, Direct black 234, Pigment black 7, Pigment red 122 and Pigment blue 15:3 from ICPI and Violet vinyl sulphone reactive dyes from FROTTIEREX.

Experimental study also involves the identification and characterization of analytical methods for establish the various quality parameters of wastewater and discoloured wastewater.

**Results and discussion** This study shows that the *strongly basic anion exchanger with macroporous structure containing tertiary amine functionalized on the polystyrene crosslinked with divinylbenzene matrix* can be practically used for color removal from the wastewaters containing anionic azo acid and reactive dyes. The decolorization performance of IER is due by the yield of quality parameters of treated wastewater: remove of 95 % for

sulphates, 38-64 % for total nitrogen, 50-85 % for DOC-Cr, 80-90 % for turbidity and ~ 95 % for colour, depending on the type of wastewater: leather or textile dyeing.

**Reference** Dawood,S.,Sen,T.K.: “*Review on Dye Removal from Its Aqueous into Alternative Cost Effective and Non-Conventional Adsorbents*”, Journal of Chemical and Process Engineering 10/2014.

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**FTIR SPECTRAL ANALYSIS OF COLOURED PRINTING INKS FROM A MAP  
OF A LATE XIX-th CENTURY ROMANIAN BOOK**

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The natural organic and inorganic inks, prepared worldwide along the time, derived from plants, animals, and minerals, are rarely pure materials. Mostly, they are mixtures of many components (major, minor and impurities), because of the number of reactions that occur simultaneously in these systems. For this reason, the identification of these components of inks is rather difficult.

The iron gall ink was the most common writing and then printing ink, in Europe, between the XI-th and early XX-th centuries. Gall ink or iron-gall ink was prepared from a mixture of vitriol, which is ferrous sulfate heptahydrate, gallic acid (extracted from galls tree), gum Arabic and water. From the middle of the XIX-th century other dyes were usually added to the ink so that it was more visible while being applied.

The other traditionally ink in Europe was carbon ink or lamp black ink, being favorites because it does not fade, but it was very unstable to moisture. Carbon ink was prepared from soot, in an aqueous medium of animal or vegetable glue. Until the seventh century, both types of inks were used simultaneous, after which prevailed iron-gall ink.

A spectral analysis for colored printing inks, including pigments, used in the late XIX-th and early XX-th century, is shown in this paper. The main spectral technique is Infrared Spectroscopy with Fourier-transformed (FTIR), by using different both transmission spectroscopy in KBr and attenuated total reflection (ATR). The analyses have been achieved to unprinted and inked printed historical papers, from private collection, without patrimony value.

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**STUDY ON THE EFFECT OF USING ORGANOCATALYSTS IN THE SYNTHESIS OF  
POLYESTER-POLYOLS FOR THERMAL INSULATING POLYURETHANE RIGID FOAMS, FROM  
PET WASTES AND RENEWABLE RESOURCES**

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The importance of PET recycling still stands, the huge volumes of wastes resulted continuing to cause serious environmental problems<sup>6</sup>. A main challenge now is to deliver efficient, sustainable, environment friendly and less energy demanding processes to chemically recycle PET. A possible alternative for improving the process conditions, while avoiding the barriers that occur with metal-based catalysts, is given by organocatalysis<sup>7</sup>. On the other hand, the last few decades have witnessed a spiralling growth of interest in using renewable resources. Producing bio-based polymers is one way to ease the environmental impact and our dependence on oil<sup>8</sup>.

This study presents the results concerning the synthesis of tailored polyester-polyols for thermal insulating polyurethane rigid (PUR) foams from PET chemical recycling, using as cleavage and modification reagents renewable, or potentially renewable, monomers such as: linear, branched or cyclic diols, polyols, alkanolamines, vegetable oils, aliphatic dicarboxylic acids or anhydrides, in the presence of some commercial organocatalysts. The polyols were analyzed by physical-chemical methods (hydroxyl index, acidity index, viscosity), FTIR, <sup>1</sup>H-NMR, were tested in PUR foams formation which were further characterized by TGA and DMA, as well as in terms of physical-mechanical properties and thermal conductivity.

The results revealed the correlations between the composition of the reaction mixture, other synthesis parameters and properties of the polyols and PUR foams prepared therefrom.

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**PHYSICAL AND CHEMICAL CHARACTERIZATION OF WASTE ON THE TARNAVENI  
PLATFORM IN ORDER TO RECOVER VARIOUS ELEMENTS**  
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After the industrial activities for obtaining the chromate salts carried out on Tarnaveni Bicapa former platform, around 2.5 million tons waste resulting (green sludge). These were stored as sludge and constitute a source of environmental pollution, especially with chromium.

For this reason, it is appropriate either their storage according to the current rules and legislation concerning hazardous waste storage, either their valorification by separating useful elements.

The company SC Wastes Ecotech SRL in collaboration with specialists from the Faculty of Petrosani has developed a technology to capitalize the useful elements from these wastes. Technology includes the following operations:

- 1) grinding and dehydrating of the green sludge;
- 2) solubilizing of magnesium from the green sludge by CO<sub>2</sub> carbonation;
- 3) precipitating of magnesium carbonate (MgCO<sub>3</sub>) from carbonation solution;
- 4) calcining of magnesium carbonate precipitate (MgCO<sub>3</sub>) in order to obtain magnesium oxide (MgO);
- 5) solubilizing of calcium in cake resulting at the carbonation of the ammonium chloride solution (NH<sub>4</sub>Cl).

After testing the technology at pilot scale, were take samples that were analysed in the Laboratory of physical and chemical analysis from INCDMNR-IMNR, determining the chemical and mineralogical composition by XRD.

Useful elements such as Ca, Mg, Fe, Cr were analysed by different analytical techniques: ICP-OES, FAAS, volumetric chemical methods, from the products obtained in each stage of the technological process.

The results obtained for tests through techniques presented were comparable and were the basis of the balance sheet on technological phases.

Acknowledgment: S.C. Wastes Ecotech S.R.L Comapny–Mr. Turea Victor.



## **FLOURINE VALORIFICATION OBTAINED IN THE FABRICATION PROCESS OF COMPLEX FERTILIZERS**

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The industrial importance of fluorine chemistry has grown in the last decades. Along with the increase of fluorine compounds consumption, the worldwide calcium fluoride ( $\text{CaF}_2$ ) consumption has grown too.

The main mineral from which fluorine compounds are obtained is  $\text{CaF}_2$ , the biggest consumer being the metallurgic industry (75 – 90%  $\text{CaF}_2$ ). For the production of fluorhydric acid and of high purity fluorine salts, „acid grade”  $\text{CaF}_2$  (min. 95%  $\text{CaF}_2$ ) is used. The inferior types (max. 85%  $\text{CaF}_2$ ) are used to produce  $\text{CaF}_2$  concentrates, cements, frosted glass, enamels etc.

Taking into account the technology and raw materials used to obtain complex fertilizers by the nitric acid attack on phosphatic rocks, fluorine is distributed differently in the solid phase, in the phosphonitric extract and in the gaseous phase.<sup>91</sup>

Thus, worldwide, attention is set on phosphatic rocks that are basic raw materials for the production of phosphatic and complex fertilizers. Apatites and phosphorites have a 3-4% fluorine content. For a 50% extraction degree, the fluorine quantity calculated as fluorite (97%  $\text{CaF}_2$ ) is bigger than 1 billion tons. Considering an average fluorine content in phosphates of cca. 3%, the worldwide reserves of fluorine from phosphorites are around 789 million tons.

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<sup>1</sup> “Use of phosphate rocks for sustainable agriculture”, Fertilizer and Nutrition Plant Bulletin, no.13, Chapter 4, ISBN 92-5-105030-9, 2004.

**“SIMULATED ARTEFACTS” IN BIODETERIORATION STUDIES: COMPARISON BETWEEN THE USE OF NATURAL EXTRACTS AND SYNTHESIZED MATERIALS AS ANTIFUNGAL AGENTS**

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The biodeterioration represents a major problem for scientist and museum curators. Some species (*Aspergillus*, *Penicillium*) are found on all objects and in the air worldwide. This supports the theory of a common origin of the fungi contaminating heritage objects: airborne conidia either during their fabrication or during their use. From all the artefacts, paper artefacts are more exposed to fungal attack, because their content in starch, glue, vegetable proteins, dyestuffs, pigments, and other additives that could provide nutrients. The continuous need for new treatments for biodeterioration leads to extensive use of real artifacts, in order to prove the efficiency of the proposed treatments. This is the reason we propose a method to avoid the over use of the real artefacts, by using “simulated artefacts”. The simulated artefacts represent pieces of cardboard kept for six months in dark and humid environment, exposed to environmental fungi. As comparison, we used several fungi-infested books (some more than one hundred years old). The fungi grown on the “simulated artefacts” were compared to the samples collected from the previously mentioned paper artefacts (books) and proved to be involved the same fungal species (*Aspergillus*, *Penicillium* and *Mucor*).

From the proposed recipes (natural extracts and synthesized materials) we selected the most promising ones for comparison of their antifungal effect, on the separate use and on their combined use. Those are lavender and ramsons extracts obtained in 1:1 ethanol: water solution, respectively hydroxyapatite (HAP) and strontium totally substituted hydroxyapatite (SrHAP). These materials presented over 70% antifungal efficiency. The antifungal efficiency was evaluated using the technique of the diluted inoculum on the surface of culture media. The best results were obtained for the combined use of strontium substituted hydroxyapatite/lavender hydro-alcoholic extract.

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**PHOTO-DEGRADATION STUDY OF POLYBROMINATED ORGANIC COMPOUNDS**  
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Brominated flame retardants (BFR) represent chemical substances used within the framework of fire protection, to reduce the risks of ignition and fire propagation.

The aim of this paper is to implement a radiative methodology for decomposition of the BFR which comprise several families, whose principal one gathers Polybromodiphenylethers (PBDE), which are known under three major molecules: penta-BDE, octa-BDE and deca-BDE. These BFR have found widespread applications particularly as additives to polymeric resins and plastics.

In particular, the photochemical degradation reaction pathways of different selected congeners substituted with one or more bromines, are examined.

The selected methodology to generate less brominated congeners was the UV irradiation because photochemical reaction is a non-invasive method with a high degradation potential.

This study was conducted to optimize the parameters which influence the UV irradiation but also to choose the suitable solvent required to have a high efficiency rate of brominated derivatives degradation. Also provides details about the structures of the TBBPA and PBDE congeners before and after the treatment.

The original experimental results confirm the significantly faster and deeper degradation rate of polybrominated molecules compared to the published results obtained by different methods.

**Keywords:** Persistent organic pollutants, UV/Vis irradiation , polybrominated flame retardants, degradation

**STUDY OF WATER QUALITY PHYSICO-CHEMICAL PARAMETERS.**

**CASE ON DANUBE IN BRAILA CALARASI AREA**

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The work presents the results obtained in the preconstruction part of a hydro technical construction which aims to stop the atrophy process of the Dunarea-Veche arm, and to insure the low water flows required in shallow water navigation on the Dunarea Veche channel between Bala and Cernavodă-Hârșova.<sup>10</sup> The evaluated chemical and ecological states were used as reference status for the impact assessment in construction and postconstruction phases. For comparison, historical data from the Transnational Monitoring Network (TNMN)<sup>11</sup>, as a support for the program implemented by The International Commission for Danube Protection (ICPDR) were used.

This work presents the results of the water quality associated with the sediment pollution. The concentration of dissolved fraction for the priority dangerous substances (Cd, Hg) and also dangerous substances (Pb, Ni), and total concentration for the organic micro pollutants were analyzed.

The indicators recommended by the order of the Environmental Ministry and Water Administration No. 161/2006<sup>12</sup> were evaluated and monitored by the hydrochemical point of view. On a four months period, samplings were conducted from seven critical points (april – august 2011) at different depths (0.5 m, 1.5 m, 3 m) in concordance with the standard procedures.<sup>13</sup>

The study showed that the ecological Status in terms of physico-chemical elements supporting the biological elements is between Class II to III, namely *good to moderate*. Water chemical status determined based on concentrations dissolved of priority substances / priority hazardous substances is *bad*. Based on the sediment monitoring in

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<sup>10</sup>Monitoring environmental impact of works to improve navigation conditions on the Danube between Calarasi and Braila, km 375 - km 175 -Raport Final Faza Premonitorizare, INCDPM -2012

<sup>11</sup>TransNational Monitoring Network (TNMN), <http://www.icpdr.org/main/activities-projects/tnmn-transnational-monitoring-network>

<sup>12</sup>Order 161 / 16.02.2006 of the Ministry of Environment , Norms concerning the classification of water quality to establish establishing ecological of water bodies

<sup>13</sup>V. M. Radu, P. Ionescu, G. Y. Deak, . A. Ivanov, E. Diacu, Multivariate Statistical Analysis For Quality Assesment Of Aquatic Ecosystem On The Lower Danube, *Journal of Environmental Protection and Ecology* 15, 2014, No 2, 412–424

accordance with the provisions of the Water Framework Directive<sup>14</sup>, Cu, Hg and partly Ni, chemical status is *bad*; to point out that for the assessment was not considered natural background, no data on the Danube River. For PAHs (polycyclic aromatic hydrocarbons), the chemical quality is *good*, whereas for PCBs (polychlorinated biphenyls) and organochlorinated pesticides is *bad*. The chemical parameters are more relevant in the water quality determinations. Mean values of organic pollutants concentrations in water in all the Critical Points (PC) compared with historical data (2001-2009 years).

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<sup>14</sup>Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy, *Official Journal of the European Union*, 22.12.2000, L 327, 1-73

**CONSERVATION AND RESTORATION OF THE CHURCH ASCENSION ICONOSTASIS FROM GRINDU COMMUNE – PRELIMINARY DATES**

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Present study refers to diagnose, conservation and restoration of an historic monument, the Church Ascension iconostasis from the Grindu commune, belonging to the class A, which means object of national and universal value. The iconostasis, suffered profound alterations that compromise the overview, but also the beauty of this church. In this study, the wood paintings from the iconostasis were investigated. Mechanical degradations (cracks, separation gaps, exfoliations), organic and inorganic deposits, degradations caused by human factor (bumps, scratches, wears) and degradation of varnish layer because of thinning the paint layer on the icons were found. The painting technique used is tempera, in accordance with historical dates and the FTIR analysis results. The composition of the red, blue, green, gilded and white pigments was determined from the XRF<sup>15</sup> data. Of all the interventions that works of art may undergo, the cleaning of paintings is the most contentious<sup>16</sup>. Grouting paint layer gaps, filling holes and protection with Japanese paper were performed first. Dedusting was done mechanically by gently brushing. A series of solvent mixtures in different proportions were trying for cleaning paint layers. The cleaning was done in few steps and monitored by optical microscopy<sup>17</sup>. Good results were obtained with isooctane-isopropanol mixtures, Contrad solution and Damar gloss. Finally, a protective varnish layer was apply, or varnishing of icons.

<sup>15</sup> Emandi, A., Secu, M., Marinescu, M., Cons. Rest. Patr. Cult., 2013, II, 280.

<sup>16</sup> Modestini, D. D., Metrop. Museum J., 2005, 40, 27

<sup>17</sup> Marinescu, M, Emandi, A., Dului, O. G., Stanculescu, I., Bercu, V., Emandi, I., Vib. Spectrosc., 2014, 73, 37

**COMPARISON BETWEEN DIFFERENT ADSORBENT MATERIALS USED FOR COPPER (II) REMOVAL /FROM AQUEOUS SOLUTIONS**

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Since in the last decade wastewater are being generated in increasing amounts many researchers are looking for innovative waterwaters treatment solutions. The purpose of this paper it was the developing of innovative adsorbents for removing emerging contaminants from wastewaters that is more effective, reusable and environmentally friendly.

The sorption of copper from wastewater using iron oxides (obtained from metallurgical wastes) and biochar, pyrolytically derived, produced from various raw materials (from nuts shell, corn cob, strings grape and waste from the beer manufacturing) was studied.

The influence of pH, adsorbent type, initial  $\text{Cu}^{2+}$  concentration and contact time of the removal process were investigated for both cases to see the differences between them and to determine the absorbant which has the best absorption capacity<sup>1</sup>. In order to compare the results obtained after the adsorption process solutions have been chemically analyzed (ICP-OES, FAAS) and absorbent materials have been morphological and structural (XRD, TEM, SEM-EDAX, HRTEM) both before and after using them (its use).

The data obtained from the parameters optimization process were used for determining the adsorption mechanism which led to achieve the equilibrium state. The equilibrium isotherms, for the sorption of copper, were analysed using 2 widely used isotherm models for the sorption of this metal in single system solution. Langmuir and Frenlich isotherms established for various initial copper concentration, for different doses of adsorbent material and for a range of values, were used to fit the equilibrium date<sup>2</sup>. Adsorption process was found to be highly pH and initial concentration of pollutant dependent. Following conducted experiments it found that nano iron oxides have better absorption capacity than all other kinds of used biochars.

<sup>1</sup> E. Bernard, A. Jimoh, Adsorption of Pb, Fe, Cu, and Zn from industrial electroplating wastewater by orange peel activated carbon, International Journal of Engineering and Applied Sciences, Vol. 4, No. 2, August 2013, Pages: 95-103, ISSN2305-8269

<sup>2</sup> S.Bee Abdul Hamid, Z. Zaman Chowdhury, S. Mohammad Zain, Base Catalytic Approach: A Promising Technique for the Activation of Biochar for Equilibrium Sorption Studies of Copper, Cu (II) Ions in Single Solute System, Materials, 7, 2014, Pages: 2815-2832; Doi:10.3390/ma7042815

**THE IMPACT OF HYDROPHOBIZATION AND CONSOLIDATION TREATMENTS ON SOME  
INDIGENOUS LITHIC CALCAREOUS MATERIALS USED IN THE RESTORATION  
INTERVENTIONS OF SOME HISTORICAL MONUMENTS**

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This paper presents experimental data regarding the study of polychromy and aesthetics evolution/behaviour of some indigenous lithic calcareous materials that underwent hydrophobization and consolidation treatments by coating with silicone products, after repeated exposures to UV radiations, artificial (accelerated) aging, respectively, in laboratory conditions. The studied samples were hydrophobized and consolidated with siloxan and silicone mixture solutions, from the range of commercial products destined for stone impregnation and stabilization. The purpose of this research is the identification of materials and procedures for the impregnation of porous limestone used in constructions, especially the one used in face-work masonry, that would be technologically and economically efficient and would allow the respecting of present principles in the scientific conservation. By monitoring the chromatic variations under the action of UV radiations we evaluated the rate of accelerated aging for the natural limestone studied, taken from the Repedea Hill area, Iași county. The experiments follow the chromatic deviation ( $\Delta E^*$ ) but also the microscopic evaluation of coating and the identification of possible elemental composition modifications at the interface between stone and silicone product. For this study were used CIEL\*a\*b\* colorimetry, optical microscopy (OM) and scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX).

**Keywords:** natural limestone, monuments, hydrophobization coating for climatic and mechanic protection, artificial aging, UV radiations, CIEL\*a\*b\* colorimetry, OM, SEM-EDX,



**POLYCHLORINATED BIPHENYL COMPOUNDS (PCBs) DETERMINATION  
FROM WATER BY GAS CHROMATOGRAPHY COUPLED  
WITH MASS SPECTROMETRY (GC – MS)**

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Because they are not biodegradable, PCBs contribute to irreversible environmental pollution, and by ingestion, accumulate in adipose tissue, contributing to endocrine disrupters. By reason of these problems, it is necessary to improve the sensitivity and speed of PCB monitoring technology. In general, PCB is analyzed by gas chromatography with electron capture detector (GC-ECD) using classical columns with packed or capillary columns. These conventional analytical techniques, however, have accuracy problems in PCB detection that can occur due to interference owing to the matrix. The detection method by mass spectrometry, in the variant “Selected Ion Monitoring” contributes to the elimination of some interference between PCBs and some chemical compounds from the matrix.

It chased the development of an analytical method for PCBs determination in water matrix by gas chromatography on fused capillary column coupled with quadrupole mass spectrometry. As the method has been developed in laboratory, the method validation has been necessary studying the following performance parameters: specificity, selectivity, repeatability, intermediary precision, recovery, detection limit and robustness. The development of GC-MS method for PCBs determination in water consisted in establishing of the separation conditions of the analyzed components from water matrix (at an adequate recovery), by liquid-liquid extraction, the establishing of the optimal GC-MS parameters and the validation of this method. In the step of the analytes-matrix separation, PCBs from water samples prepared for analysis was extracted with hexane, carbon disulfide and chloroform through stirring at an appropriate speed followed by separating funnel separation. Were established the optimal GC-MS separation parameters. The detection and quantitative determination by mass spectrometry, in the variant “Selected Ion Monitoring” (MS-SIR) was used. The GC-MS-SIR method performs an adequate separation of PCBs from the water matrix and eliminates some extractible interfering elements with a recovery of 50-120 % and determines the PCBs in the concentration range of 1-100 pg/ml PCB in water (1-100 ng/ml in the solution to be analyzed).

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**TOTAL POLYPHENOLS AND FLAVONOIDS CONTENT AND ANTIOXIDANT ACTIVITY OF  
ROBINIA PSEUDOACACIA AND CRATAEGUS MONOGYNA EXTRACTS**

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*Robinia pseudoacacia* and *Crataegus monogyna* flowers are two beneficial plants due to their medicinal properties.

*Robinia pseudoacacia* (locust) it is found in Romania, especially in the plains and hills. Pharmacology dates related the fact that only flowers are used due to their therapeutic purposes (antispasmodic, antitussive or sedative effects). Other parts of the plant especially bark and seeds are toxic [1].

*Crataegus specie*, known as “Hawthorn”, it is a medicinal plant which is used for the treatment of mild heart diseases. Due to their positive inotropic effect it increases the activation of the heart muscle cells, provides them a well feeding, regulate the blood flow and are coronary dilators [2].

Total polyphenols and flavonoids content, related a major value at locust than hawthorn. Also, the content of polyphenols is higher than flavonoid. For calculation of total content of flavonoids and polyphenols, were used the curves calibration results of catechin, respectively, gallic acid. Results of antioxidant activity are very good, for hawthorn AA% = 79.35 and for locust AA% = 76.43.

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**THE LIQUID MEMBRANE PROCESS OPTIMIZATION FOR SEPARATION OF CADMIUM CATIONS, USING D2EHPA AS CARRIER**

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Liquid membrane processes have been used for many uses in the chemical industry due to its advantages as simultaneous removal and recovery of solutes in a single unit, more effective separation of elements with similar properties and small amounts of extractants [1].

In the literature liquid membranes are classified into three types: bulk, emulsion and supported liquid membranes (SLM). Compared with other liquid membrane systems, bulk liquid membrane (BLM) presents the simplest types for the selective separation, easy to manipulate, while offering good membrane stability [2]. It has been used in various applications such as precious metal recovery [3], toxic metal [5], non-metal [5] and organic pollutant [6] removal from wastewater.

In this paper the transport of cadmium cations through a bulk liquid membrane with D2EHPA as carrier in the organic phase was studied. To optimize the separation process, the influence of the type of solvent used in the organic phase and the effect of receiving phase acidity on the process of transport through liquid membranes was investigated.

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**INVESTIGATION OF RARE EARTH METALS LEACHING PROCESS FOR NEODYMIUM  
RECOVERY FROM SCRAP Nd-Fe-B MAGNETS**  
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Daniel<sup>1</sup>, CAPOTA Petre<sup>1</sup>, PURCARU Victoria<sup>1</sup>**

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The spectacular development of the high-tech technology, the industry for electric and electronic equipment and the emergent technologies has lead to an increase in the amounts of waste containing elements and chemical compounds harmful for the environment and human health. In addition to the disposal problems, the widespread use has also caused a depletion of valuable natural resources such as rare earth metals, particularly neodymium (Nd). This is the result of an increased request for neodymium, used for manufacturing hard magnetic materials (typically used in electronic equipment including hard disk drives for computers), laser systems, eyeglasses, military applications and various other industrial and home applications. The rare earth metals group (Y, Sc, La, Ce, **Nd**, Pr, Sm, Dy, Eu, etc.) was included at the bottom of the priority list of the critical metals for the economy of the European Union<sup>18</sup>. Thus separate waste collection and processing of recycled WEEE is highly necessary. Starting with year 2008, Romania has imposed a minimum collection level of WEEE at 4.0 kg/inh. (while the level is 9.0 kg/inh. in some EU countries)<sup>19</sup>. This research work examined the leaching of rare earth metals from scrap Nd-Fe-B magnet powder, using various extracting solutions. The investigated parameters that influence the leaching process were contact time, type and concentration of leaching agents, and temperature. Ultrasound field irradiation was applied. The results of the investigation show that the amounts of rare earth metals (Nd, Pr, Dy, Sm) released from scrap Nd-Fe-B magnet powder using various leaching agents varied from 78.80% to 99.99% of their total contents. The temperature, concentrations of leaching agents and contact time have a significant influence on the amount of metals leached.<sup>20</sup>

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<sup>18</sup> Critical raw materials for EU, "Report of the ad-hoc working group on defining critical raw materials", (2010);

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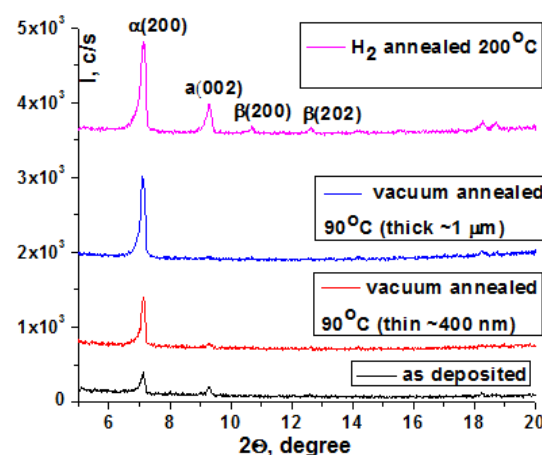
<sup>20</sup> This work received financial support from National Authority ANCS through the project PN09240114/2015.

**SECTION 3**

**MULTIFUNCTIONAL  
MATERIALS AND  
NANOCOMPOSITES**

**STRUCTURAL ANALYSIS OF CuPc THIN FILMS ANNEALED IN DIFFERENT ENVIRONMENTS****Stefan Robu<sup>2</sup>, Dumitru Duca<sup>1</sup>, Galina Dragalina<sup>2</sup>, Tamara Potlog<sup>1</sup>, Valentin Nica<sup>3</sup>***1. Department of Physics and Engineering, Moldova State University, MD 2009, Chisinau Moldova**2. Department of Chemistry, Moldova State University, MD 2009, Chisinau Moldova**3. Faculty of Physics, Alexandru Ioan Cuza University, Iasi 700506, Romania*

Metal phthalocyanine (MPc), with their promise of low-cost manufacturing simple process and possibility of roll-to-roll mass production, have received much attention in the last years [1, 2]. Due to the thermal and chemical stability of MPc materials and their rather small solubility in organic solvents, vacuum sublimation is the most common method used to fabricate the copper phthalocyanine films. CuPc thin films were prepared by thermal evaporation at high vacuum ( $5 \times 10^{-6}$  Torr) on ITO/glass substrates at room temperature. After the deposition films were subjected for annealing in different environments: vacuum and hydrogen, for the same period of time, 30 min. The crystal structure was studied by X-ray diffraction (XRD) using a Bruker-AXS, D8 Advance diffractometer ( $\text{CuK}\alpha$  radiation, 40 mA, 40 kV). The diffraction pattern for the all CuPc films is shown in the figure. The XRD pattern of the as deposited film shows two diffraction peaks at  $2\theta=7.12^\circ$  and  $2\theta=9.28^\circ$  which are corresponding to the (200) and (002) planes of the orthorhombic metastable  $\alpha$ -phase [3]. When the film was annealed in vacuum the diffraction peak situated at  $2\theta=9.28^\circ$  disappeared and the peak at  $2\theta=7.12^\circ$  shifted slightly to smaller angles. For the hydrogen annealed film this peak is shifted more. Various diffraction peaks for the hydrogen annealed CuPc film could be assigned to reflections corresponding to the monoclinic  $\beta$ -phase [3]. This confirms the beginning of the phase transformation by annealing from  $\alpha$ -phase to more stable  $\beta$ -phase.

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**THE STYRENE-BUTADIENE BLOCK-COPOLYMER GRAFTING WITH TETRACYCLINE**  
**Stefan Robu<sup>1\*</sup>, Gheorghe Duca<sup>1</sup>, Viorel Prisacari<sup>2</sup>, Maria Gonta<sup>1</sup>, Vitalie Filip<sup>1</sup>, Paul Ghioca<sup>3</sup>, Lorena Iancu<sup>3</sup>**

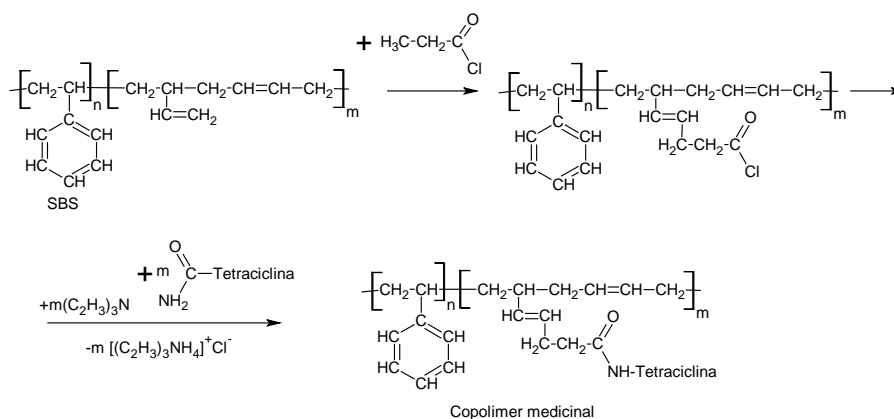
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The synthesis of polymeric materials with antibacterial lengthy properties has been a permanence concern of researchers in recent decades<sup>1</sup>. In previous work the authors have made grafting the ampicillin on styrene-butadiene block-copolymers<sup>2</sup>. The polymeric material with antibacterial properties may be used for making furniture hospital or film coating thereof.

The paper presents tetracycline grafting on styrene-butadiene block-copolymer with high content of vinyl groups (50%). In the first stage it was performed grafting on vinyl groups the methacryloyl chloride and finally tetracycline according to the scheme:



The chemical structure of tetracycline graft polymers and precursors was investigated by IR and <sup>13</sup>C-NMR. Block copolymers with bactericide properties crosslinking by irradiation with UV led to significant improvement in physical and mechanical properties. The tests carried out proved that block copolymers grafted with tetracycline shows no toxicity.

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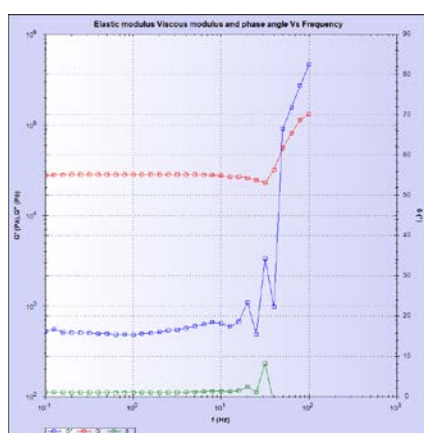
# RHEOLOGICAL PROPERTIES OF HUMAN BODY SIMULANTS FOR MILITARY USE

**Teodora Zecheru<sup>1</sup>, Ciprian Său<sup>1</sup>, Cătălin Zaharia<sup>2</sup>, Claudiu Lăzăroaie<sup>1</sup>**

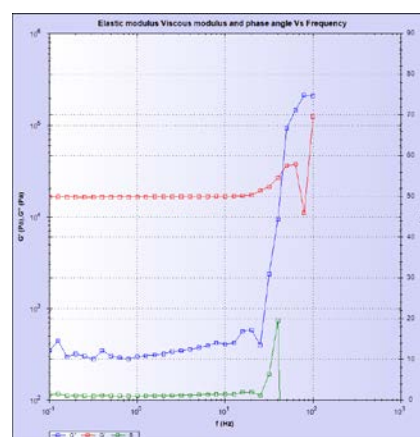
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<sup>2</sup>Polytechnic University of Bucharest, Faculty of Applied Chemistry and Materials Science, Advanced Polymer Materials Group, 1-7 Gh. Polizu Str., 011061 Bucharest, Romania

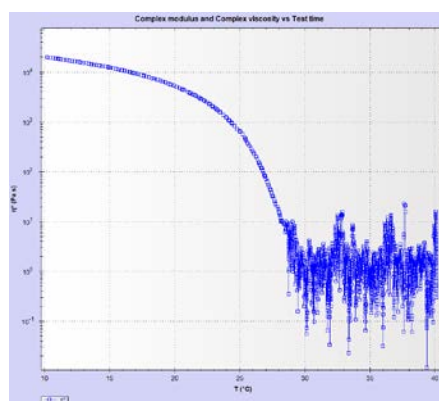
In order to be able to create a feasible synthesis pattern for the human body simulants, before the verification of the ballistic parameters through shooting, in agreement with military standards<sup>3</sup>, one of the best and cheapest solutions of verifying the properties of gelatin-based materials is to perform a thorough check of their rheological properties, in standard conditions.



a)



b)



c)

Rheological determinations: a) Freq. sweep – 5 deg.; b) Freq. sweep – 15 deg.; c) Temperature variation.

## Acknowledgements

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<sup>3</sup> NATO STANDARD AEP-94, Skin Penetration Assessment of Non-Lethal Projectiles, Ed. A, Version 1.



# CATALYTIC AND PHOTOCATALYTIC SYSTEMS FOR DECOMPOSITION OF THE CWAs

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Chemical Warfare Agents (CWAs) are very toxic compounds which might cause severe injuries, death or incapacity in a military conflict. The most common compounds from the military chemical arsenals are the nerve and the vesicant agents.

The production, storage and use of any CWAs are strictly controlled by the Chemical Weapons Convention (CWC), which entered into force in 1997 and requires all State Parties to destroy all stockpiles of CWAs in 10 years [1]. CWC is now extended to 2017, when it is expected that 99% of the original stockpiles which included significant quantities of the most toxic and lethal compounds ever invented, will be destroyed. Although all stocks will be destroyed, the danger of using its in terrorist attacks will be persisting yet.

Herein, we present a very active and efficient decontamination system, environmentally benign, which is able to decompose, rapidly and efficiently, the highly toxic compounds and their degradation products.

This technology uses a suspension of catalysts and photocatalysts in organic solution, able to initiate the decontamination/detoxification reactions of CWAs under visible light.

For this purpose we used freshly prepared metal (La, Cu, or Zn) complex catalysts [2,3] coupled with gold doped TiO<sub>2</sub> photocatalysts (0.5, 1 and 1.5 wt. % Au/TiO<sub>2</sub> samples), under daylight irradiation.

In order to perform the total degradation processes, but also to accelerate the decomposition rate of all chosen toxic compounds from this study, heterogeneous photocatalysis was taken as a proper alternative since this method could be easily applied under benign reaction conditions. The combination of the methanolysis and heterogeneous photocatalysis could be the “golden key” for the development of an efficient and environmental benign system for the decomposition of CWAs.

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**DIFFERENT TECHNIQUES FOR THE PREPARATION OF 1%, 2%, 3% NICKEL/ACTIVATED CARBON ELECTROCATALYSTS FOR PEMFCs**

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The depletion of fossil fuel deposits is one of the major problems of mankind at the moment, which is why efforts are being made worldwide to deliver sustainable and renewable energy resources and to develop new and efficient energy producing technologies. Fuel cells working with bioalcohol have been recognized as a promising alternative for electricity generating devices to suit the current context and demand of mankind, the main challenge consisting in developing an adequate electrocatalyst to get high activity, good stability and high selectivity for the anodic oxidation of the fuel<sup>1</sup>. Carbon based materials are widely used as electrocatalyst because of the high surface area and good electronic conductivity, they are apt to undergo electrochemical oxidation under the practical operation of PEMFCs (Proton Exchange / Polymer Electrolyte Membrane Fuel Cells)

The experimental research has been focused on the preparation of new advanced catalysts for PEMFC anodes, for the synthesis of which we used non-noble metals, thus making the assembly of these fuel cells possible at competitive costs<sup>2</sup>.

This paper presents two methods of preparing the samples of activated carbon doped with different amounts of nickel (1%, 2%, 3%): i) impregnating the dried activated carbon with aqueous solutions of nickel acetate; ii) in situ reducing with hydrazine. We have used activated carbon from coconut shell with the following characteristics: density 560 kg/m<sup>3</sup>; active surface: min. 1000 m<sup>2</sup>/g; iodine: min. 1000 mg I<sub>2</sub>/g; residue on ignition (850°C): maximum 2%.

The samples obtained were characterized by SEM-EDX, using a VEGA II LMU Tescan microscope.

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# ANALYSIS METHOD BY ICP-OES FOR THE DETERMINATION OF PRECIOUS, PLATINUM GROUP AND RELATED ELEMENTS FROM ORES AND TECHNOLOGICAL SOLUTIONS

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The proposed method determines 15 elements (Au, Ag, Pt, Pd, Ir, Os, Re, Rh, Ru, Ge, In, Tl, Hg, Se, Te) from various ores after leaching or from technological solutions by inductive coupled plasma optical emission spectrometry (ICP-OES). The leaching is carried out taking into account the matrix, but generally with aqua regia. The spectrometer used is a 725 Radial Simultan model from Agilent Technologies and it has CCD detectors which allow for each element the selection of several spectral lines (we preferred three) and allows visualization of the adjacent spectral area which enables the detection of interferences even in the case of samples with unknown matrix. Since the spectral interferences are additive, after visualization of the spectra, the correct value remaining is usually the lowest one. Because the content of these elements in the ore is generally low and the samples are presumably homogeneous, in order to lower the limit of detection, a quantity of 2 g is taken of the sample into work and is leached in a 100 ml volumetric flask. Usually, depending on the element and the sample, the limit is 4g/t. The residue remaining after the acid leaching can be dissolved by alkaline melting, in a Pt capsule or crucible. From the obtained melt, removed with HCl and brought in solution in a separate flask, Pt and Rh can no longer be determined because they come from the used capsule. The study carried out using a microwave digester at high pressure and temperature did not bring significant improvements to the dissolution process.

The proposed analysis method for the 15 elements contains 45 spectral lines selected, for which the mutual interferences between these 15 elements and the interferences for another 30 of the most frequently encountered elements (Al, As, B, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Si, Sn, Sr, Ti, V, Zn, Zr) were studied.

A study was also performed in order to optimize the working conditions, identifying the optimum values as: plasma power of 1150 W, observation height of 8 mm; nebulizer argon flow of 0.65 l/min. CRMs and the standard addition method were used for calibration because in plasma depressions and amplifications of the analytical signal can take place, depending on the matrix, the acids used and on the viscosity (chemical and physical interferences). For the ICP-OES technique the linearity of the calibration lines allows the addition of a single standard, after a preliminary determination.

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**THE DIRECT ANALYSIS OF SOLID SAMPLES WITHOUT DISSOLUTION, BY ICP-OES**

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Two techniques were used for the direct analysis of solid samples by ICP-OES.

1. **Laser ablation** (LA-ICP-OES) using the LSX-266 laser system from CETAC.

The solid samples are placed in a cylindrical chamber ( $\Phi=50$  mm;  $h=50$  mm) on a PC controlled platform with a  $0.25\text{ }\mu\text{m/step}$  on x-y-z axis. The laser beam can scan the sample or it can carve into it. The sample can be electrically conductive or not. With the help of a microscope the route and the point of the laser beam can be determined. The laser beam has the following characteristics:  $\lambda=266\text{nm}$ ;  $100\text{-}200\mu\text{m}$  laser spot size; scan speed  $20\text{-}50\text{ }\mu\text{m/sec}$ , power  $0\text{--}9\text{ mJ/pulse}$ ; pulse frequency of  $20\text{ Hz}$ . The zone of the sample and the laser bombardment operation can be photographed or filmed. The sample particles ablated by the laser are carried by a flow of argon ( $0.5\text{-}07\text{ l/min}$ ) to the torch of the ICP-OES spectrometer.

2. **Spark ablation** using the LISA spark system from SPECTRO Analytical Instruments. In this case the samples must be metallic, electrically conductive in order to generate a spark. The samples can be large but with a plane zone of  $\Phi \geq 20\text{mm}$ , or smaller than  $10\text{ mm}$  to be fastened in a device. The spark is generated between the sample and a tungsten counter electrode. The power of the spark and the time of pre-spark or spark can be adjusted depending on the sample type and shape. The sample particles ablated by the spark are carried by a flow of argon to the torch of the ICP-OES spectrometer. The analysis of aluminum alloys with LISA was successful.

These two techniques for the direct analysis of solid samples, without dissolution, are usually used for identification, semi-quantitative analysis. Standards with a composition and structure similar to the sample are required for quantitative analysis. The issue of the contamination of the sample chamber and route should be considered, because the fine ablated particles can be deposited on route. A purging with a high flow of the route between the analysis of standard or samples is not always sufficient to eliminate the “memory” effects.

The ICP-OES spectrometers used are from SPECTRO or Agilent Technologies (Model 725 Radial Simultan). The major advantage of the ICP-OES method is the extended linearity, which reduces the number of standards required for calibration. The calibration can also be done using solutions, but in this case only the ratios of concentrations between elements can be taken in consideration.

Acknowledgements: The study was performed using the infrastructure acquired in the Structural Funds - High PT Met Ctr. 253/2010 project and the Ctr. PN 09.24.44.06/2015 Core Funding Programme funded by ANCS.

# **DESORPTION PROPERTIES OF MCM-41 USING CEFEPIME**

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MCM-41 is a highly versatile material<sup>4</sup>, having large possibilities of tailoring through a carefully chosen synthesis method or through an post-synthesis treatment, either through functionalization with organic groups or through pore-enlargement methods. We chose this material specifically due to its interesting properties and tried to elucidate as best as possible some of the mechanism that involve the process of controlled release kinetics<sup>5,6</sup>. We tried a rather unique approach, trying to add interesting results coming from the field of NMR (nuclear magnetic resonance) spectroscopy to solve and complete the puzzle which arises from the release kinetics of MCM-41 material<sup>7</sup>. The loading of the MCM-41 material was assessed through FT-IR (Fourier Transformed InfraRed)spectroscopy, and the porosity of the MCM-41 material and the characteristics of the surface through TEM (transmission electron microscopy) imaging and BET (Brunauer–Emmett–Teller) technique. The <sup>29</sup>Si NMR spectroscopy comes with some interesting results concerning the type of interaction between the mesoporous MCM-41 silica and the loaded drug, the interaction of the drug with the silica surface changing the intensity distribution in the peaks corresponding to MCM-41. The release kinetic was assessed using a modified HPLC method and confirms a slow release<sup>1,8</sup>.

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**DYNAMIC STRESS MITIGATION OF POLYMER COMPOSITE MATERIALS**

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The remarkable properties of polymer composite material (PCM) led to their use, in the last years, at experiments regarding blast resistant properties. The PCM have been proven to have efficacy on blunt trauma and dynamic stress mitigation.

The key constituents that have been taken into account for obtaining PCMs were: polyurea and functionalized multi-wall carbon nanotubes as reinforcing fibres. The fibres are essentially responsible for the performance improving (strength and stiffness properties), while the polymeric matrix contributes to stress transfer and provides microclimate protection. The reinforcement of a polymeric matrix with functionalized multi-wall carbon nanotubes utilizes the viscoelastic displacement of the polyurea matrix under stress to transfer the load to the fibre; this results in a high strength and a high modulus composite material.

Different percentage of reinforcement fibres and different thickness were expressly used for customizable applications of PCMs, for the following purposes: improving ballistic protection of existing equipments; reducing blunt trauma for protection equipments; additional shield for armoured transport vehicles.

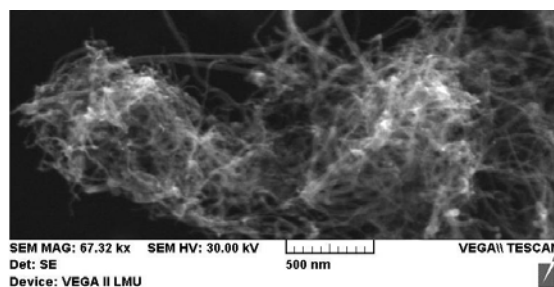


Figure 1. SEM image of multi-wall carbon nanotubes

PCMs have exceptional mechanical characteristics, appropriate for dynamic stress mitigation and, in addition, present durability and resistance to the external factors.

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**STYRENE-DIENE BLOCK COPOLYMERS REINFORCED WITH BENTONITE**  
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The linear styrene-isoprene block-copolymers were synthesized via anionic three stages sequential polymerization of monomers in cyclohexane solution initiated with n-butyllithium, by adding the next monomer only after the total consumption of the previous one. The star styrene-butadiene block-copolymers were synthesized via anionic polymerization of monomers in cyclohexane solution initiated with n-butyllithium, by coupling the diblock polystyrene-polybutadienyl lithium with silicium tetrachloride. At the end of each reaction step, samples were removed from the polymerization reactor in order to determine the monomer conversion and the molecular mass of the constituent blocks.

The block copolymers molecular weight was determined by gel permeation chromatography (GPC) and was characterized by Fourier Transform Infrared Spectroscopy (FT-IR). Physical and mechanical properties were determined on films with a thickness of about 1 mm obtained by centrifugal casting at temperatures not exceeding 60<sup>0</sup> C in toluene solution.

The reinforcement of block copolymers was performed with bentonite Chioar Valley with a content of over 60% montmorillonite with interlamellar space of 15.1 Å.

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

The wide range of physical and mechanical properties of the bentonite SBS and SIS block copolymers composites, allows the easy choosing of the reinforcement degree for blends with properties most appropriate to different applications.

**COLOURED POLYMERIC MICROCOMPOSITES WITH MINIMAL ENVIRONMENTAL IMPACT**  
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The paper presents the research carried out by our team on achieving amphiphilic polymeric microcomposites, colored in ruby and violet shades for natural fibers dyeing (cotton, wool). It was developed the laboratory microencapsulation technology for reactive and metal-complex dyes in a biodegradable natural polymer matrix (calcium alginate).

As coloring materials were used reactive and metal-complex dyes, synthesized at ICECHIM, previously analysed in terms of physicochemical (purity, concentration, FT-IR and UV-Vis spectral parameters) and coloristical performances (hue, intensity, dyeing concentration, resistance to light, water, wet and dry friction, acid and alkaline perspiration, solubility and degree of fleet exhaustion). Their performances are comparable to known foreign brands (BASF, ICI, Ciba). The colored polymeric microcomposites were characterized in terms of morphology (optical microscopy, SEM analysis) and physicochemical (FT-IR and UV-Vis spectroscopy, colorimetric analysis). The colored microcapsules were tested by studying the controlled release of the encapsulated dyes in water, to pH variation. This study is still necessary to the coloristic characterization of colored polymeric microcomposites, to determine the optimal dye concentration in the microcapsules for natural fibers dyeing.

The technologies used in obtaining and applying of colored microcomposites are green and are made with minimal specific consumption and according to environmental information currently existing, both raw materials (reactive and metal-complex dyes, anionic polymer, precipitating agent) and end products show reduced eco-toxicological risk.

**“Bibliography”<sup>9</sup> / “Authors thank to the *Institute of Physical Chemistry ”I. Murgulescu” – ICF (Academy)* for the analyzes carried out in the project”.**

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# VANCOMYCIN SORPTION ON PRISTINE AND OXIDIZED EXFOLIATED GRAPHITE NANOPLATELETS

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Vancomycin (VCM) is an important antibiotic, very efficient in the treatment of severe infections caused by methicillin-resistant staphylococcus. *High concentrations could cause severe side effects*, being very important to determine the adequate VCM concentration levels in human biological fluids. This paper presents the experimental results regarding the adsorption capacity of new type of sorbents based on carbon nano-materials such as exfoliated graphite nanoplatelets (xGnP) and oxidized exfoliated graphite nanoplatelets (ox-xGnP) in aqueous solutions. *The process can be used as a promising alternative for preconcentration before determination of the amount of VCM in biological fluids. The effect of different conditions such as: contact time, initial VCM concentration, temperature and ionic strengths were tested, kinetics and sorption isotherms being established. A spectrophotometric method with UV detection at 220 nm was used to monitor the VCM concentration. The characterization of the nanomaterials, by FTIR spectroscopy, thermogravimetry and scanning electron microscopy, is shown in relevant comparative diagrams and images, before and after the adsorption experiments, in order to prove the good capacity of xGnP/ox-xGnP nanosheets to retain the molecules of VCM.*

**Keywords:** Vancomycin, methicillin-resistant staphylococcus, biological fluids, adsorption capacity, exfoliated graphite nanoplatelets.

# SELF- DISPERSIBLE CARBON BLACK PIGMENT ( C I PBlk 7), PREPARATION METHODS AND CLASSIC AND NEWER AREAS OF USE

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The paper presents the research activities performed to achieve a new process for dyeing natural leather using non-specific coloring materials namely anorganic and organic pigments, e.g. Pigment Black 7 (Carbon Black). Unlike dyes, pigments are totally insoluble substances in water and organic solvents and so they can not be used to dye leather in aqueous media. Unfortunately, it has been found that the distribution of pigments is poor on the surface as well as over the cross-section of leather. In this project, the our team aims to research a process for synthesis and conditioning of pigments to be brought into a form of coloidall solution which can be used to dye leather in aqueous medium. In a first stage we took in research the inorganic pigment carbon black knowing that black is the basis of leather industry.

**Materials and methods** The study was focused on the inorganic black pigment (PBlk 7). The main methods for obtaining self-dispersible pigments with surface-modified was:

- 1) Synthesis: the functionalization of pigment particles by attaching to its surface of functional groups, by means: a) diazotation reaction ( diazonium coupling reaction of pigment with aromatic diazonium salts having a substituent group of sulfonic acid ( $\text{SO}_3^-$ ) and a counter metal cation of  $\text{Na}^+$ , or b) sulfonation (with oleum; or mixture of oleum and sulfuric acid) or sulfonation and oxidation with sodium hypochlorite (  $\text{NaOCl}$ )
- 2) Encapsulation in forms of liposomes with lecithine
- 3) Conditioning: micro/nanodispersion (UltraTurrax T18- 6000 t/min and Ultrasonic Procesor)
- 4) Preliminary experiments dyeing on natural leather with coloidall solutions (nanodispersions) containing carbon black self-dispersible. (Leather dyeings carried out to ICECHIM are promising). The experimental study followed the identification and characterization for phisico-chemical properties and morpho-structural characteristics

**Results** The results obtained until now in the self-dispersible pigments preparation are good but the assessments on their particle size and their distribution are still made at one of the project partners.

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# STUDIES FOR SOLID-PHASE EXTRACTION USING MOLECULAR IMPRINTED POLYMERS FOR NITROFURANTOINE

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Molecular imprinted polymers (MIPs) are a modern class of highly cross-linked polymers that can bind certain target compounds (analytes) with high specificity. The polymers are prepared in the presence of the target molecule itself as the template. The present study is focused on the experimental conditions for obtaining MIPs designated to isolate nitrofurantoin from complex samples in the view of HPLC analysis. Generally, the nitrofurans are used as feed additives for growth promotion in animal husbandry, aquaculture and bee colonies or for the prophylactic and therapeutic treatment of bacterial and protozoan infections. The MIPs prepared by our team were optimized in order to improve their analytical performances, the imprinting factor and the efficiency of binding. These improvements are obtained by a stronger interaction between the monomer units and the template or the use of monomer mixture for copolymerization reaction. In the case of copolymerization reaction, the monomer units will form non-covalent bonds with different functional groups of the same template. The cartridges based on the prepared MIPs are characterized by the breakthrough curves for nitrofurantoin, which were fitted by means of Boltzmann's function. Cartridge capacity, concentration ratio, and analytical recovery were estimated in order to develop an analytical procedure for determination of this compound from different samples. The analytical determinations of this compound from eluate samples were performed by means of UV absorption spectrometry.

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**POLYMER MEMBRANES WITH PLANT EXTRACTS FOR REMOVAL OF  
DYES FROM WASTEWATERS**

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Dyes are used in various industrial processes, such as paper and pulp manufacturing, plastics, dyeing of cloth, leather treatment and printing. The release of dyes into the rivers, ponds or lagoons may cause damage to the quality of the water, the aquatic eco-system and the biodiversity of environment<sup>10,11</sup>. Dyes removal from wastewaters using membrane separation processes provides an alternative treatment.

The main objective of this study is to prepare polymer membranes with/without various amounts of commercial plant extracts. The membranes were obtained by phase inversion technique.

The resulted membranes were characterized by Fourier Transforms Infrared (FTIR-ATR) and Scanning Electron Microscopy (SEM) techniques. From FTIR-ATR spectra for the membrane obtained in the presence of commercial plant extracts a characteristic peak at 2331 cm<sup>-1</sup> was observed. This indicated that the plant extracts were successfully introduced into the membrane structure. SEM images of the prepared materials showed that the introduction of commercial plant extracts into the mesoporous channels reduces the pore size of the membrane.

**Acknowledgement**

The work has been funded by the Sectoral Operational Programme Human Resources Development 2007-2013 of the Ministry of European Funds through the Financial Agreement POSDRU/159/1.5/S/134398 and also it was supported by the grant funded by the Romanian National Authority for Scientific Research, CNDI-UEFISCDI, project number 3.2-1391.

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**THERMAL, MECHANICAL AND MORPHOLOGICAL CHARACTERIZATION OF  
PHA/BACTERIAL CELLULOSE COMPOSITES**

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NICOLAE Cristian Andi<sup>1</sup>, SPĂTARU Cătălin Ilie<sup>1</sup>, LUPESCU Irina<sup>2</sup>, CĂȘĂRICĂ Angela<sup>2</sup>**  
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Polyhydroxyalkanoates (PHA) are polyesters synthesized by a wide range of microbial species, who recently gained considerable interest as bioplastics, for developing new eco-friendly materials. PHAs group consist of polymers with several monomer units and with different molecular weights, which influence their mechanical and thermal properties<sup>12</sup>. Polyhydroxybutyrate (PHB) is the most common member of this biopolyesters group, intensively studied in diverse applications such as food packaging or medical devices (sutures, bioprotheses, drug delivery systems, vascular graft)<sup>13</sup>. PHB utilization in industrial applications is limited by its brittleness and stiffness, a very narrow window in extrusion or injection processing and poor mechanical properties<sup>14</sup>. Different fillers were used to obtain PHB based biocomposites: ethyl-cellulose, bamboo fibers, recycled cellulose fibers, lignocellulosic flour.

Bacterial cellulose (BC) is chemically identical to plant cellulose, but shows higher crystallinity, purity, water retention capacity and superior strength, thus being a very promising filler for PHB. The aim of our work was to fabricate biocomposites based on PHB and BC and to study the influence of BC on the thermal, mechanical and morphological properties of the composites using DSC, TGA, AFM, contact angle, tensile tests. A comparison between two different preparation methods, solvent casting and melting processing, related to the performances of the obtained nanocomposites was discussed in this paper.

**Acknowledgement**

This work has received financial support from UEFISDI by the Program “Parteneriate”, grant 158/2012.

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**MELT RHEOLOGY IN CONECTION WITH TENSILE EXTENSION AND TENSILE STRESS AS METHOD TO SELECT OPTIMUM STARCH FORMULATION FOR THERMOFORMING**

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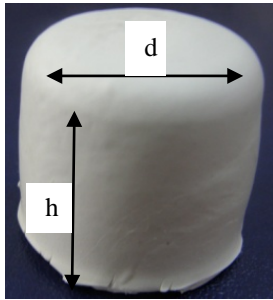
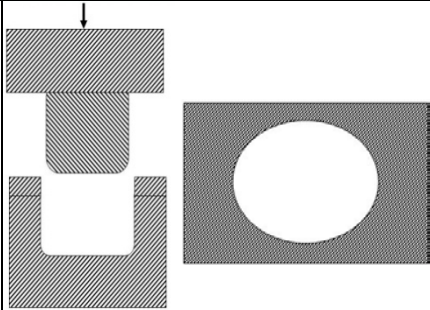
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Renewable materials can be processed in different parts through thermoformation, when several conditions are met. For example suitable elongation viscosity is required, sag resistance (high melt strength at low shear rates), strain hardening (high melt strength at high elongational stress) and specific extensibility properties are also essential. This work presents the results obtained from thermoformed new materials based on starch by correlation with the tensile extension – tensile stress tests. It was observed that the melt rheology is controlling the extesibility properties in solid state and by default the succesfull processing of the new starch based materisls through thermoformation.

SAMPLE SHAPE	MATRIX	SAMPLE DIMENSIONS, CM D X H
		2.5 x 3.7
		2.7 x 2.9
		2.6 x 2.4
		2.6 x 2.8

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**ACKNOWLEDGEMENT** - These researches were supported by UEFISCDI Romania from the grant no. Number 59/2012.

**RELEASE PROFILES OF PEFLOXACIN FROM MESOPOROUS MATERIALS**  
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Since the discovery of ordered mesoporous silica nanoparticles in 1992 (also known as M41S at that time) by the researchers of Mobil Oil Company<sup>15</sup>, these materials have been intensely studied. After 2001<sup>16</sup>, when MCM-41 was first introduced as a drug delivery system, mesoporous silica materials have witnessed an exponential increase in research on biomedical applications due to their properties, such as: high specific surface area, large pore volume and possibility of surface modification. The present paper is focused on the synthesis of MCM-41 and the release profiles of pefloxacin from this material.

MCM-41 was synthesized at room temperature in aqueous medium using tetraethyl ortosilicate as a source of silica and cetyltrimethylammonium bromide. The mesoporous material was characterized by HR-TEM and FT-IR. Pefloxacin (1-ethyl-6-fluoro-7-(4-methylpiperazin-1-yl)-4-oxo-quinoline-3-carboxylic acid) is an antibacterial drug which belongs to the fluoroquinolone class, drugs with a broad antibacterial spectrum.

The release profiles of pefloxacin from mesoporous material were recorded for 6 hours in simulated body fluid<sup>17</sup> at room temperature using the modified HPLC technique<sup>18</sup>.

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# CONTROLLING THE MACROMOLECULAR MISCIBILITY AS METHOD TO ENHANCE THE BIODEGRADABILITY OF STARCH BASED RENEWABLE MATERIALS

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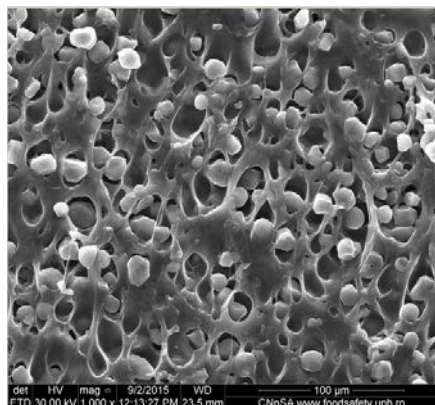
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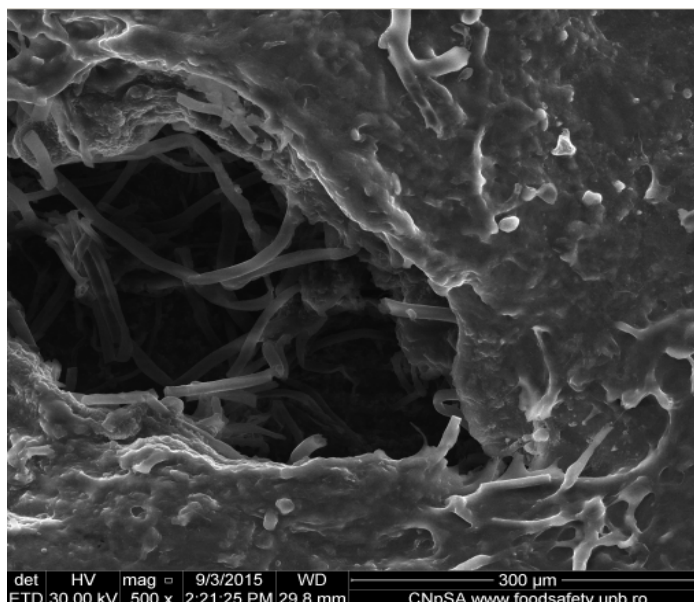
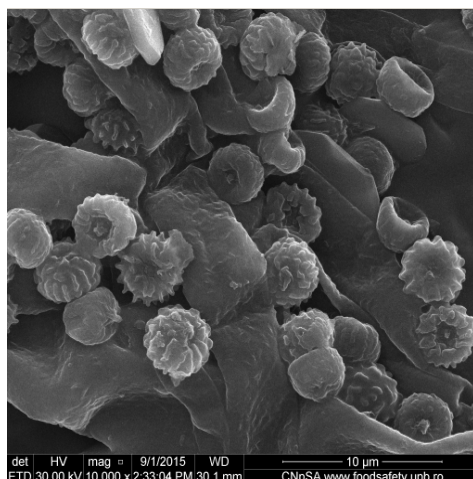
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The paper proves that the biodegradability of renewable materials with total environmental destruction is controlled by the miscibility degree at the molecular level of renewable polymer with the other components, the morphological structuration level and the number and type of



morphological defects. It was found that, depending on these parameters, even at short biodegradation times (168 hours) the process is in various stages of surface biodestruction. The conducted studies involve melt rheological measurements, SEM, AFM, DTA analysis and others emphasizing the biodestruction in the solid state (weight, density, hardness, etc.)



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## CHARACTERIZATION OF INSULATING MATERIALS USED IN ROTATING ELECTRICAL MACHINES

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The insulation of the electric machines represents a main component which can influence the functional parameters. In the past few decades, it has been recognized that the safety margins in the design were excessive and can greatly increase the cost of the rotor and stator. The aim of this study is to characterize the materials in order to innovate a new material with better properties and longer life time.

Two different materials (aromatic polyamide and polyester film saturated with epoxy resin) were used as insulators in rotating electrical machines. After three operational weeks, the electrical machines were disassembled and the insulators were collected in order to be investigated. The results have been compared with the ones obtained on unused materials. Investigations have been performed using different techniques: Fourier Transform Infrared (FT-IR) and Raman spectroscopy and Scanning Electron Microscopy (SEM) coupled with Energy Dispersive X-ray Spectrometry (EDS).

**Acknowledgement:** The research leading to these results has received funding from PN II 2013 (Partnership Programme) under the project PN-II-PT-PCCA-2013-4-0792 “High performance polymeric insulations for electrical rotation machines. Technology and modeling approaches” (IsMach).

**TEXTURAL PROPERTIES OF MESOPOROUS SILICA SUPPORTED KEGGIN-TYPE  
HETEROPOLYACID**

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Three series of phosphotungstic acid (PW) modified mesoporous silica samples have been prepared by a post-synthesis method in an attempt to obtain supported acid catalysts for different catalytic applications: phenols alkylation, hydrocracking of fatty esters, lignin depolymerization, etc. Different ordered mesoporous silica structures, namely MCM-41, SBA-15 and HMS, respectively have been used as support materials.

The influence of heteropolyacid concentration (10-40 wt. % PW) on textural properties of PW modified mesoporous silica samples has been studied.

In order to estimate the parameters characterizing the mesoporous structure of synthesized materials, the nitrogen adsorption/desorption isotherms at 77K have been measured using NOVA 2200e-Quantachrome analyzer.

Some correlations between PW concentration and porous texture features of PW impregnated mesoporous materials in connection with the particular structure of mesoporous silica support have been established.

**SEBS-GRAPHITE COMPOSITES: OBTAINING AND MORPHOLOGICAL CHARACTERIZATION****R. M. Grigorescu<sup>1</sup>, D.M. Panaitescu<sup>1</sup>, C. Damian<sup>2</sup>, P. Ghioca<sup>1</sup>, L. Iancu<sup>1</sup>, B. Spurcaci<sup>1</sup>**<sup>1</sup> *National Institute for Research and Development in Chemistry and Petrochemistry – ICECHIM Bucharest*<sup>2</sup> *University “POLITEHNICA” Bucharest, Faculty of Applied Chemistry and Materials Science, Department Bioresources and Polymer Science*

Polystyrene-*b*-(ethylene-*b*-butylene)-*b*-polystyrene (SEBS) known great interest both in academic and industrial area due to its advantages regarding the easy melt processing, high elasticity and strength, and heat resistance. Graphene is a modern material that can give electro-conductive properties to the host polymers besides important improvement of mechanical, barrier and thermal properties. Bottom-up graphene and top-down graphene can be obtained through selected techniques. The first one can be developed by chemical vapor deposition, arc discharge, epitaxial growth on SiC, chemical conversion, reduction of CO, unzipping carbon nanotubes or self-assembly of surfactants. Top-down graphene is obtained through separation/exfoliation of graphite by mechanical cleavage, direct sonication, electro-chemical methods and superacid dissolution or starting from graphite oxide by colloidal suspension, thermal treatment or chemical reduction, methods that are more economic and suitable for large scale production<sup>19, 20, 21</sup>.

The experiments were directed toward obtaining SEBS-graphene composites by two different methods and analysing the morphology of the new materials. Elastomer composites were obtained by melt compounding the polymer with graphite. During this process, due to the shear forces, the filler could be disintegrated to submicron particles. The improvement of tensile properties was observed. Also, films of SEBS-graphene were obtained by solution casting. First, graphene oxide (GO, obtained by Hummers method) was reduced with hydrazine and then rGO was dispersed in a SEBS solution. The presence of graphene sheets was evidenced by Atomic Force Microscopy (AFM).

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# IMPROVING BIOCOMPATIBILITY PROPERTIES OF MEDICAL POLYMERIC MATERIALS BY USING SILVER NANOPARTICLES

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Polymeric biomaterials for medical applications must to meet European Pharmacopoeia [1] requirements regarding to biocompatibility properties. In this purpose it were performed some plasticized PVC recipes loaded with silver nanoparticles by immersion method [2], to impart antimicrobial properties. In the paper are presented mechanical and thermal properties of the experimental polymeric recipes. Also, it were tested biological properties of recipes by exposing the samples to different strains such as *Bacillus subtilis*, *S. Aureus* and *Candida albicans* [3, 4]. Due to silver nanoparticles content all materials prevents microbial colonisation and biofilm formation by bacterial strains. The results obtained shows that the experimental PVC recipes meets the requirements of the European Pharmacopoeia, and can be used in the manufacture of flexible medical devices, and they are able to prevent biofilm formation on the surface due to content of silver nanoparticles.

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**Acknowledgments.** The researches were financially supported by projects **PN-II-PT-PCCA-94 / 2012 (AntiBioTube)**.

**PREPARATION, CHARACTERIZATION AND APPLICATION OF MODIFIED COMMERCIAL ORGANOCLAY POLYMER MEMBRANES FOR REMOVAL OF INDIGO CARMINE**

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Indigo Carmine or 5,5'-indigodisulfonic acid sodium salt is a dark blue powder used in various industry sectors such as: food industry, textile industry for the dyeing of denim and polyester fibbers, cosmetics industries, pharmaceuticals industries, is usually used as a marker dye to locate the ureteral orifice, severed ureters, or fistulas<sup>22,23</sup>.

The main objective of this study is to test the efficiency of polymer membranes doped without and with commercial organoclay (Cl30B) or modified with vinyltriethoxysilane (Cl30BVy). The obtained membranes were involved in removal of Indigo Carmine dye from simulated aqueous solutions using a laboratory electrodialysis system. Electrodialysis was carried out at a current intensity of 0.05 A. The operation time was of 1 h for each experiment. Concentrations of the aqueous solutions of dye were monitored on UV/Visible spectrophotometer, over a wavelength range of 610 nm. The results indicated that the colour removal efficiency was more than 90 % for hybrid membranes (with Cl30B or Cl30BVy) in comparison with the membrane without inorganic filler whose efficiency was only of 70%.

Membranes were characterized by FTIR-ATR and SEM techniques. FTIR-ATR spectra for the obtained polymer membranes showed the Si-O-Si specific peak that appears at  $\sim 1016\text{ cm}^{-1}$  proving the insertion of various inorganic clays within their highly porous structures. SEM images of the prepared materials showed that the introduction of commercial organoclay modified with organosilyl group into the mesoporous channels reduces the pore size.

#### Acknowledgement

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**SMART HYBRID BIOMIMETIC COATED TITANIUM BIOALLOY  
IN VITRO CELLULAR RESPOSE**

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The need of orthopedic implant with enhanced characteristics to provide bio-functional performances gave rise to new approach strategies<sup>24</sup> that take into account shaping and improving surface of traditional titanium based materials<sup>25</sup>. Using Matrix Assisted Pulsed Laser Evaporation (MAPLE) method, thin complex hybrid coatings having multiple functionalities such as lactoferrin (Lf) and hydroxyapatite (HA) were deposited on Ti alloy.

Data obtained from morphological analysis, SEM, Atomic Force Microscopy (AFM), and qualitative method FTIR used for films characterization, demonstrated that the functional groups in the MAPLE-deposited coatings remain intact while the homogeneity and the roughness of the coatings are related to target composition and laser parameters.

Potential inflammatory response of biomimetic coated bioalloy was explored using an *in vitro* inflammation model, THP-1 cells stimulated with bacterial endotoxins. THP-1 cells treated or untreated with LPS for 18 hours revealed no cytotoxic effect as demonstrated by non-radioactive cell proliferation assay. Lactoferrin and hydroxyapatite coated surfaces conducted to attachment to a higher number of THP-1 cells compared to films embedded with HA or Lf alone, suggesting a better modulation of the cell attachment. LPS addition led to a decrease in the total number of cells irrespective of surface covering. Release of proinflammatory cytokine TNF- $\alpha$  from macrophages was observed only in the case of endotoxin treatment, as determined by enzyme-linked immunosorbent assay (ELISA). The lowest amount of cytokine was detected in the case of Lf-HA functionalized materials.

Smart biomimetic Lf-HA functionalized materials proved to be active in modulation of immune response, thus being a good candidate to improve the performance of bone implants.

**Acknowledgments:** The research leading to these results has received funding from the Romanian Ministry of National Education, CNCS – UEFISCDI, under the project PN-II-PT-PCCA 239/2014

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**NEW SYSTEMS OF CARRIERS LOADED WITH CARROT EXTRACT IN VEGETABLE OILS**  
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Lipidic carriers are transport systems with significant uses in the cosmetic and food industries. The paper presents the synthesis and characterization of lipid nanotransporters loaded with carrot extract in Safflower, Milk Thistle and Sea Buckthorn oils.

The nanotransporters developed were characterized by particle size, the polydispersity index, zeta potential and antioxidant activity. The research results have established the suitability of Safflower, Milk Thistle and Sea Buckthorn oils for encapsulating the carrot extract. The studied nanotransporters showed good stability with zeta potential values between 107-139 nm for free nanotrasporters and 111-144.3 nm for the loaded once with carrot extract.

The determination of the antioxidant activity by the chemiluminescence method showed a better antioxidant activity of loaded nanotransporters with carrot extract than the free once.

The research conducted will be used to develop new products based on natural active ingredients with applications in cosmetics.

**Keywords:** lipidic nanotrasporter, vegetable oils, antioxidant activity

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### Acknowledgement

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# MOLECULARLY IMPRINTED POLYMERS OBTAINED BY WET PHASE INVERSION FOR SEPARATION AND SENSING

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*Scope:* This paper describes the methodology for obtaining molecularly imprinted polymers (MIPs), using the so called wet phase inversion (WPI) method, into two important formats i.e. membranes (MIP membrane as sensitive layer for trinitrotoluene-TNT detection) and pearls (MIP pearls as specific adsorbents for the selective separation of hypericin-Hyp from *Hypericum Perforatum* primary extracts). *State-of-the-art:* Molecularly imprinted polymers (MIPs) are artificially designed sorbents with specific enhanced selectivity towards template structures. Particularly, the WPI is a two-pot synthesis technique, which uses precursor polymer solutions instead of functional monomers to generate non-covalent interactions with the template molecules. Further on, the polymer-template solutions are physically crosslinked (via multiple hydrogen bonds) and turned into membranes or robust MIP pearls by wet phase inversion of the polymer in a proper non-solvent bath; hence, imprinting takes place post-polymerisation, during the phase inversion. The use of molecular imprinting technique also brings with it significant advantages i.e. low-medium complexity of synthesis and reduced preparation costs<sup>26</sup>. It is noteworthy the fact that the two templates (TNT and Hyp) are structurally different, and hence, the functional monomers were also of different nature (i.e. itaconic acid and methacrylic acid, respectively). *Importance and Impact:* TNT (2,4,6-trinitrotoluene) is a widely and inexpensive nitroaromatic explosive compound, commonly used in military and terrorist activities. Its specific detection is important worldwide for environmental protection and national security issues<sup>2</sup>. Hyp is a natural naphthodianthrone pigment with antidepressant, antitumor and anti-inflammatory properties<sup>3</sup> extracted from plants like St. John's Wort (*Hypericum Perforatum*). Unfortunately, the current separation methods make the commercial version of Hyp quite expensive.

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**EFFECT OF CARBON NANOTUBES ON THEIR PROPERTIES EPOXY MATRIX**  
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Nowadays, particular attention has been paid to the manufacture of reinforced composite materials, for which the size of the reinforcement is reduced to the nanometric range. These materials will exhibit enhanced physical and mechanical features as compared to conventional polymeric composites, for which micronic size particles are incorporated.

Among the various reinforcing agents, carbon nanotubes (CNT) are considered as potential fillers for epoxy composite in order to improve their mechanical, electrical and thermal properties as a result of the remarkable properties of their structure[1-3]

However, properties improvement is limited by interfacial interactions occurring between CNT and polymer matrix. Furthermore, the uniform distribution of CNT in the epoxy matrix could reduce the properties improvement. Functionalization of multi-walled CNT can improve mechanical properties and thermal stability of epoxy composites in which they are incorporated as reinforced agents[4-7]. Multi-walled carbon nanotubes functionalized with reactive COOH were chosen for the reinforcement the epoxy network to ensure a good dispersion with the epoxy matrix chemically modified by Polyethylene glycol chains. Further reinforcement of the polymer network has been achieved by curing with an aminic type cross-linking agent, i.e. 4, 4' diamino dimethyl methane (DADM).

The obtained composites were characterized by conventional physico-mechanical methods and by DMA to investigate the effects induced by using CNT. It was observed that a content in reinforcing agent (carbon nanotubes) of 0.5 % results in a properties enhancement, as follows: tensile strenght increases with about 10%, hardness with 15% and the impact strength with 43%.

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**GRAPHENE AS CATALYST SUPPORT FOR FUEL CELL APPLICATIONS**

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PEM fuel cells exhibit good energy efficiency and high power density per volume, but the high costs due to the noble metal catalysts, electrolyte membranes, and bipolar plates coerce the large scale marketing. In view of the potential of using graphene materials as low catalyst support in fuel cell applications, graphene nanocomposites were synthesized as a simple chemical route by chemical oxidation and graphene oxide exfoliation and confirmed by characteristic analysis. Starting from graphite, the preparations of graphite oxide (GO), graphene oxide (GrO) reduced GrO and graphene-based nanocomposites, as well as the functionalization with biocompatible polymers such as poly(diallyldimethylammonium chloride) (PDDA), are described. The structure, morphology and properties were characterized during different preparation steps, using BET method, Scanning Electron Microscopy (SEM), Raman Spectroscopy, TGA analysis.

## NICKEL BASE CATALYSTS AS DUAL FUNCTION MATERIALS FOR CO<sub>2</sub> CONVERSION TO METHANE

**Adriana Marinoiu<sup>1</sup>, Tudor Popescu<sup>2</sup>, Ioan Iordache<sup>1</sup>, Claudia Cobzaru<sup>3</sup>, Corina Cernatescu<sup>3</sup>**

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This article aims to demonstrate the usefulness and applicability of the use of dual function materials (DFMs), based on Ni catalysts, in the methanation reaction. DFMs contain two components: *an absorbing material* and *a catalyst*, encouraging both the capture of CO<sub>2</sub> and it's transformation into fuel. This makes the process of capturing and using CO<sub>2</sub> almost carbon neutral, without the need of any additional heat input. Nickel, although a proper methanation catalyst, requires reduction at a temperature above 400°C in order to become active. Hence, it is less suitable compared to noble catalysts for cyclic oxidation. This issue can be addressed by introducing copper as co-catalyst, since the Ni-Cu-based catalyst is known for it's synergistic hydrogenation effect, i.e. lowering of the activation temperature value. The morphological and structural characterization of DFM materials will be provided through electron-scanning microscopy combined with energy-dispersive X-Ray spectroscopy (SEM-EDX), X-Ray diffraction (XRD), H<sub>2</sub>- and CO-controlled chemisorption, atomic absorption spectrometry (AAS) and specific surface area estimation (BET). Testing of the different DFMs with various catalyst compositions will be performed using the Quantachrome Autosorb-IQ-C chemisorption unit as micro-reactor.

**OBTAINING AND CHARACTERIZATION OF NEW CARBAZOLE-CONTAINING AZOPOLYMER****Alexei MESHALKIN***Institute of Applied Physics of Academy of Sciences of Moldova*

Recently polymer materials with azo dyes become attractive materials for holographic recording due to possibility of surface relief grating fabrication with high diffraction efficiency and resolution. It has been reported that large surface modulations can be obtained on azo polymer films upon exposure to an interference pattern of laser beams.

In this study, novel type of carbazole-based azo polymer have been synthesized through a polymerization azo-coupling scheme. As carbazole-based polymer the epoxypropylcarbazole (EPC) 90% and as azo dye the Disperse Orange 3 (DO) 10% were selected respectively. DO was purchased as a commercial product with dye content 90% from Sigma-Aldrich Company. FTIR characterization of synthesized copolymer EPC:DO has proved the introduction of azo group in polymer matrix confirmed by the peak at  $1580\text{ cm}^{-1}$  in the IR spectrum corresponding to the N = N stretching frequency. Copolymer film was prepared as thin film spin-coated at glass substrate. The film thickness was measured with microinterferometer MII-4 and was 270 nm. The transmittance spectra for obtained films coated on glass substrates were measured over the range 200 – 900 nm. The broad absorption band in the range 420-580 nm with  $\lambda_{\text{max}}=460\text{ nm}$  is assigned to strongly absorbing azobenzene groups. The surface-relief-grating formation process was studied for obtained thin films. An interferometric holographic recording was used to expose linear grating. The interference pattern of DPSS laser beams was produced by two spatially symmetrical polarized beams ( $\lambda=532\text{ nm}$ ). Different gratings were experimentally realized and polarization dependence in the formation of gratings was investigated. We report observation of holographic surface relief gratings with relatively large amplitude on EPC:DO copolymer without any subsequent processing steps. It was shown that s:s-polarization condition is not efficient for SRG formation process. While using two circularly polarized interfering beams (left-circularly polarized: right-circularly polarized LCP:RCP) good quality SRG were direct produced without any chemical treatment and with diffraction efficiency more than 20%.

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**ASSESSMENT OF THE CONCENTRATION OF Ag, Au AND Cu FROM COLLOIDAL SUSPENSIONS AND POWDERS FOR STERILE BANDAGES BY THE FAAS METHOD**

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Colloidal particles of silver, gold and copper have sizes between 1 and 500 nm and are obtained using metals of spectral purity, positively charged electrically in suspension in ultrapure water. The usual concentrations of these elements have values between 5 –150 mg/l. Nanometric colloidal solutions are used in medicine due to their antiseptic and antitumor properties, they are easily absorbed by the human body, they don't have toxic effects and, unlike antibiotics, they do not destroy the intestinal flora.

Nanoparticles of zinc and titanium oxide doped with a contents of 1- 5% Ag, produced in our institute by the Laboratory of Nanomaterials, are used in sterile bandages.

The determination of the metals content by the flame atomic absorption spectrometry method was performed with a ZEEnit 700 spectrometer from Analytic Jena, using the following wavelengths : Au 242.8nm; Ag 328.1 nm; Cu 324.8 nm, in an oxidizing air/acetylene flame.

The colloidal solutions are processed with nitric acid. The determination of Ag is carried out in an ammoniacal medium.

ZnO and TiO<sub>2</sub> nanopowders doped with silver were dissolved with HNO<sub>3</sub> and solubilized in an ammoniacal medium for the determination of silver.

**COMPOSITE PROTON EXCHANGE MEMBRANE FROM SULFONATED POLY(PHENYLENE OXIDE) AND SILICA NANOPARTICLES FORMED IN SITU - PREPARATION AND CHARACTERIZATION**

**Irina Petreanu<sup>1</sup>, Adriana Marinoiu<sup>1</sup>, Claudia Sisu<sup>1</sup>, Mihai Varlam<sup>1</sup>, Radu Claudiu Fierascu<sup>2</sup>, Paul Stanescu<sup>3</sup>, Mircea Teodorescu<sup>3</sup>**

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Poly (2,6-dimethyl-1,4-phenylene oxide) (PPO) from commercial sources was modified by sulfonation to the aromatic rings in order to obtain a material with proton exchange capacity. Further, the sulfonated polymer was used as matrix for preparing a hybrid organic-inorganic composite membrane with silica particles formed in situ, through the sol-gel method, without an organic linker between polymer chain and silica network, as most methods described in the literature for this kind of materials. The membrane samples were characterised through infrared spectroscopy, X-Ray fluorescence and thermal gravimetrically analyzes. Also, the ion exchange capacity (IEC) and the sulfonation degree (SD) were determined by titration and correlated with the water sorption properties (water uptake, area expansion and hydration number). Tensile stress analyzes were performed for the membrane samples, both plain and composite. These properties are useful for polymer electrolyte membrane (PEM) on PEM Fuel Cell.

The results show an improvement of some behaviour such as: area expansion for the hydrated sample, water retention capacity and tensile strength of the composite membranes depending on the amount of silica.

**Keywords:** Proton Exchange Membrane, Fuel Cells, Sulfonated Poly(phenylene oxide), composite polymer-silica, tensile strength, swelling.

**STUDIES ON COMPOSITE BIOMATERIALS OBTAINED BY POWDER METALLURGY**

**Aurora Anca POINESCU<sup>(1)</sup>, Rodica Mariana ION<sup>(1,2)</sup>**

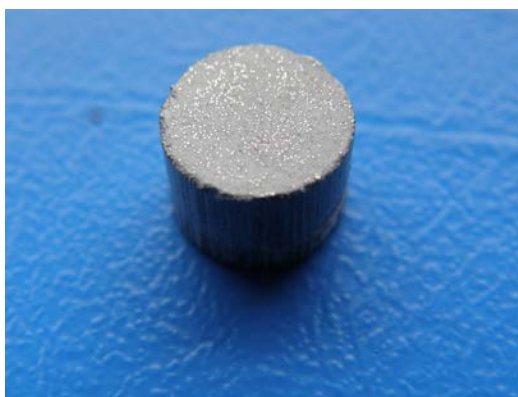
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This paper presents a series of studies and researches on composite materials obtained with powder metallurgy by blending different proportions of powder. Materials used for obtaining metalo -ceramic composite was: hydroxyapatite as ceramic materials and stainless steel 316L - this type of steel used in medical implants like hip implant, joints, etc.[1,2]



*80% HAp and 20%316L*



*70% 316L and 30% HAp*

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# CHARACTERIZATION OF RECYCLED POLYPROPYLENE BLENDS OBTAINED BY MELT ALLOYING WITH STYRENE BLOCK COPOLYMERS

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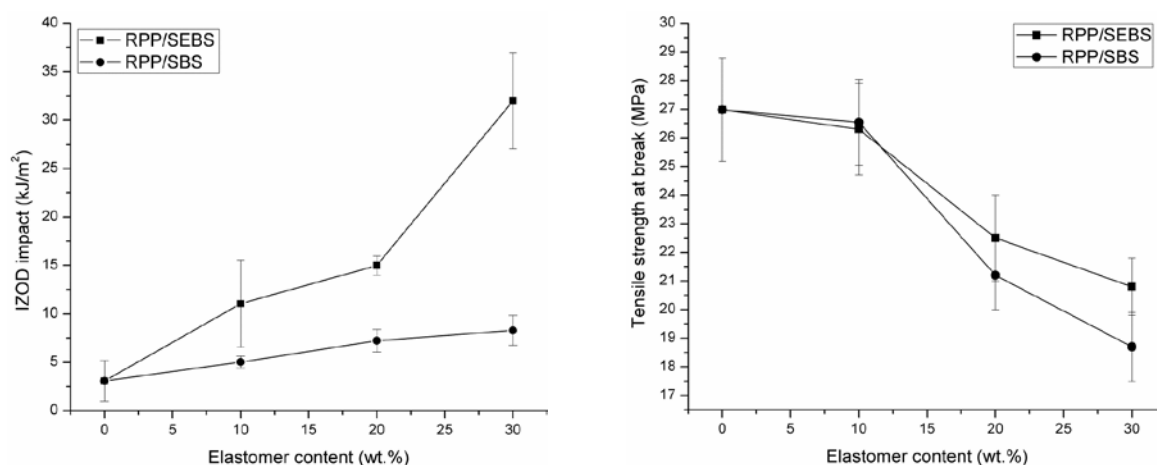
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Polypropylene (PP) is widely used because it presents easy processing, excellent properties and relatively low price. Although its recycling is well established, the mechanical and thermal properties of the recycled products are normally lower than those of the virgin material.

In this work, two commercial block copolymers namely, styrene-ethylene/butylene-styrene (SEBS) and styrene-butadiene-styrene (SBS) were used to enhance the properties of recycled polypropylene (RPP) from post-consumer boxes. The amount of elastomer varied from 10 wt.% to 30 wt.% relative to RPP. The elastomer content influence on thermal properties (MFI, DSC, VICAT, HDT), spectral and structural characteristics (ATR-FTIR, XRD) and mechanical properties (tensile properties, IZOD impact, hardness) of RPP/SEBS and RPP/SBS blends was investigated.



**Fig. 1.** Effect of TPE's content on IZOD impact and tensile strength at break of RPP/SEBS and RPP/SBS blends

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# ESTIMATION OF THE SENSITIVITY AT CHANGING OF WORKING PARAMETERS AS METHOD TO FIND THE WINDOW OF MELT PROCESSING CONDITIONS FOR SOME NEW BIODEGRADABLE MATERIALS

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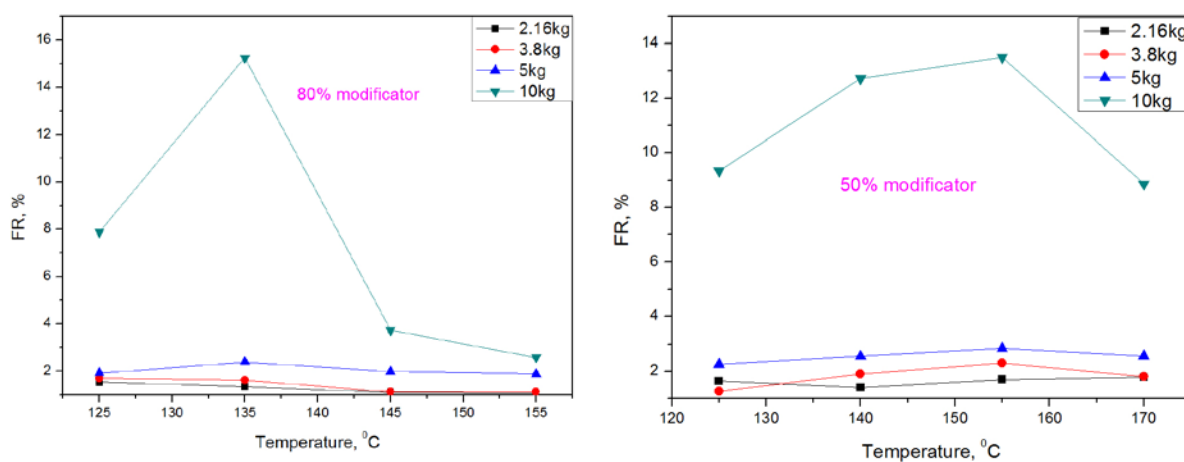
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The obtained results demonstrate that new materials based on starch, seem to be, at low shear rate, no temperature sensitive. At increased shear rate the material sensitivity at changing of melt processing conditions rises as more as the renewable polymer is used in higher quantity. The obtained results reveal also possible destructive processes<sup>27</sup> occurring during transformation of new materials into finished products. The performed studies were considered in selection of optimal working conditions for transformation of new biodegradable materials into finished products. In this way, it was possible, to be avoided phenomena as antiplasticization, retrogradation and exudation of plasticizers which affect the quality and performances of new products.



**ACKNOWLEDGEMENT:** These researches were supported by Executive Agency for Higher Education, Research, Development and Innovation – UEFISCDI Romania by the grant no. 59 / 2012.

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**INVESTIGATION OF POLYMER NANOCOMPOSITES WITH RED MUD CONTENT  
PRODUCTION PROCESS**

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Current situation of water pollution involves advanced purification to meet quality standards for surface water.

Red mud (RM), a solid waste product of the Bayer process of bauxite refining, contains oxides of iron, aluminium, silicon and titanium. Furthermore, its surface bears lots of hydroxyl groups<sup>[1,2]</sup>. Because of these large amounts of oxides, RM could be used in catalytic oxidation processes which are expected to remove pollutants from water.

The present work was aimed at investigating the process of development of nanocomposites with content in RM, using acrylic acid-based crosslinked hydrogels. Moreover, it was also investigated the use of other inorganic compound (kaolin- K or sodium silicate-S) together with RM. To this end, several stages were accomplished. First of all, RM (either itself or with other inorganic) was mixed with acrylic acid and a dispersant. Then, the crosslinking agent was added and polymerization was promoted by adding the redox initiation system. The obtained composites were characterized in terms of their chemical composition by UV spectrometry. Moreover, water uptake tests were carried out, too. UV spectra displayed the characteristic peaks of the raw materials. Differences occurring between samples may be assigned to changes in synthesis conditions. Water uptake behaviour was strongly influenced by the presence of RM as well as by samples preparation conditions.

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**MULTIFUNCTIONAL HYBRID MATERIAL FOR WASTEWATER TREATMENT**

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<sup>2</sup>*University Politehnica Timisoara*

Climatic changes and pollution imposed the necessity to implement international reglementation to ensure a sustainable water management. Also the higher costs to increase water quality have led to further efforts to identify new strategies with high efficiency allowing the water remediation and recycling. For this reason, many researches are focused on development of new performing advanced materials with application in water treatment.

This paper aims to obtain an new hybrid material able to act in an multifunctional way providing an alternative to conventional technologies for waste water treatment. Hybrid material efficiency assessment was carried out using modern analytical techniques: SEM/EDAX, XRD and Ft-IR spectroscopy.

**SPECTROPHOTOMETRIC METHODS FOR ESTIMATION OF MELATONIN AND VITAMIN C  
FROM THE COMBINED CAPSULE DOSAGE FORM**

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The present work aimed to develop a spectrophotometric method for estimation of melatonin and Vitamin C in capsule dosage form.

Melatonin (MEL) chemically is an N – [2-(5-methoxy-1H-indol-3-yl) ethyl] acetamide (figure 1), with application in the treatment of cancer, immune disorder, cardiovascular diseases, depression and sexual dysfunction. Vitamin C or L-ascorbic acid (VIT C), is an essential nutrient for humans and certain other animal species (figure 1).

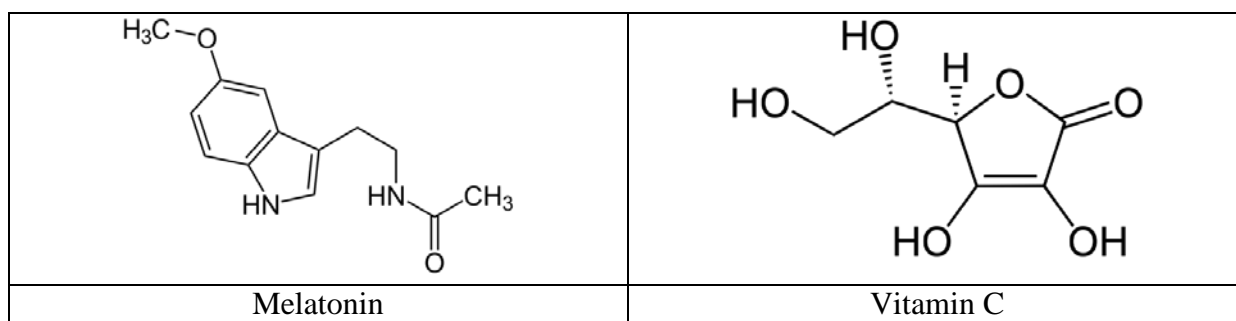


Figure 1. The chemical structure of MEL and VIT C

In order to evaluate the melatonin and VIT C concentration in combined dosage form, firstly, the stock solutions of both the drugs were further diluted separately with methanol to get a series standard solution of 10 µg/ml. The absorbance's were measured at the selected wavelength and absorptivities (A 1%, 1 cm) for both the drugs at their corresponding wavelengths: 277 and 248 nm. The coefficient of correlation for melatonin at 277 nm and Vitamin C at 248 nm is 0.9997 and 0.9989, respectively.

Secondly, twenty capsules were weighed and powdered. The powder equivalent to 10mg of MEL and VIT C was transferred into a 100 ml volumetric flask in methanol. The solution was sonicated for 20 min, and after that was filtered through Whatman filter paper, and the volume was adjusted up to the mark. The stock concentration was 10 µg/ml for MEL and VIT C.

No interference of the excipients from the capsules appeared, so the proposed method is applicable for the estimation of MEL and VIT C in pharmaceutical capsule dosage forms, figure 2.

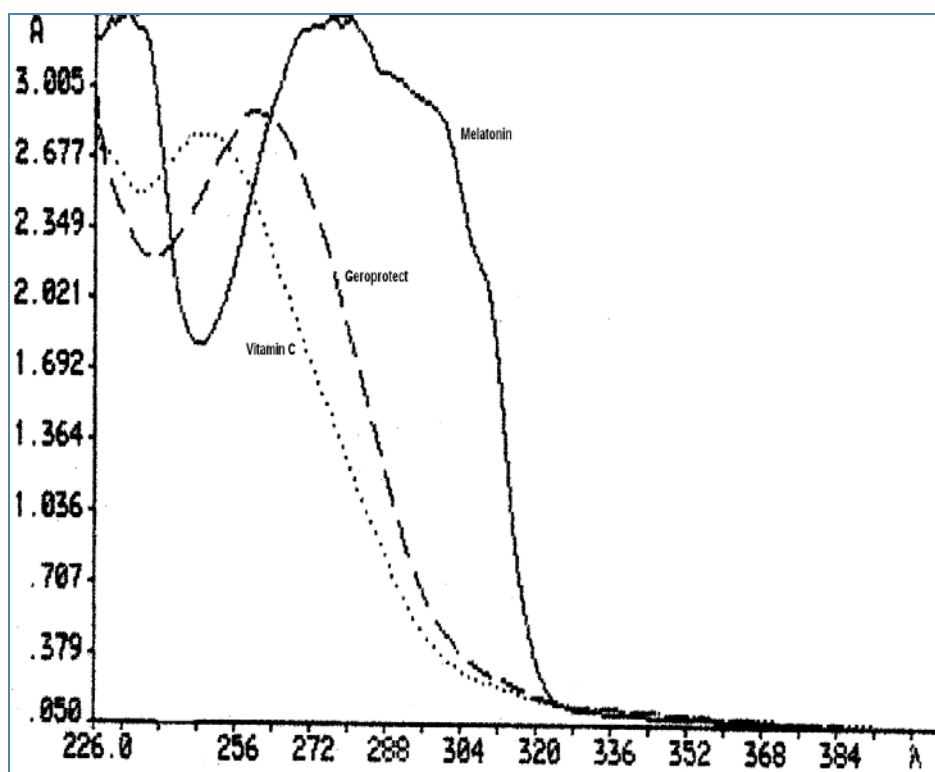


Figure 2. The UV-Vis spectra of Melatonin, Vitamin C and the capsule dosage form

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# NEW MATERIALS BASED ON STYRENE-ISOPRENE ELASTOMERS, MODIFIED WITH CYCLOOCTENE BY GRAFTING VIA RING-OPENING METATHESIS POLYMERIZATION (ROMP)

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Grigorescu Ramona, Nicolae Cristian-Andi, Gabor Raluca, Raditoiu Valentin.**  
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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 cyclooctene 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:

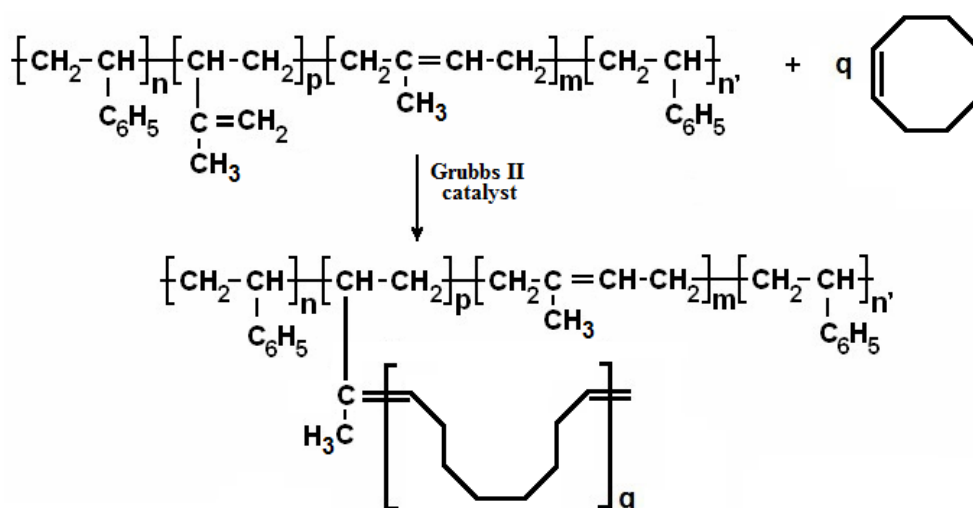


Figure 1. The shematic representation of a ROMP grafting reaction.

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).



# INTERACTION BETWEEN VARIOUS NANOPARTICLES AND Cr(VI) FROM WASTEWATER

**Sofia TEODORESCU<sup>1</sup>, Rodica-Mariana ION<sup>1,2</sup>, Ioana-Daniela DULAMĂ<sup>1</sup>,**

**Raluca-Maria ȘTIRBESCU<sup>1</sup>, Alin-Ioan BUCURICĂ<sup>1</sup>**

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Nanomaterials are increasingly being used in processes for the recovery of heavy metals from aqueous solutions. This application is due to the specific properties of nanomaterials (their small particle dimension).

Being known the second most common inorganic contaminant in waters after lead, chromium is the most toxic especially in the form Cr (VI) because this form is most mobile and toxic as inhalant in carcinogenic and as environmental contaminant [1,2]. Cr(VI) is 500 times more toxic, mutagenic and carcinogenic than Cr(III) [3]. In the retention of Cr (VI) were used several types of nanoparticles, as follows: chitosan, two ion exchangers (CS 34 and AS 14), perlite, zeolite.

The efficiency of different types of nanomaterials has been proved with the following types of analysis: Raman, SEM, UV-Vis.

- By using **Scanning Electron Microscop (SEM)**, it could be analyzed the morphology of nanoparticles such as: shape, size or size distribution of materials at the micro and nanoscale.

- **RAMAN** was used to understand structure, bonding and reactivity of the nanoparticles and chromium sorbed on its surface.

- **Ultraviolet-visible spectroscopy (UV-VIS)** results showed that the most efficient nanomaterial is chitosan. The positive group of chitosan is in a stronger attraction for a negatively charged chromium ion in the solution, resulting electrostatic interactions. In this way, chitosan can be effectively applied for the removal of Cr(VI) from wastewater.

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# PARAMETERS INFLUENCING THE STRUCTURATION LEVEL OF SOME NEW RENEWABLE MATERIALS

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Celina Damian<sup>3</sup>, Rapa Maria<sup>4</sup>

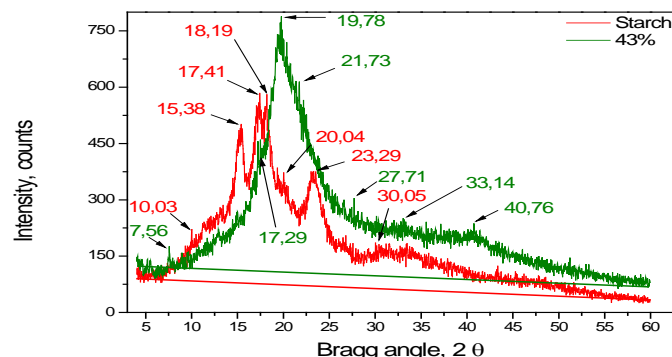
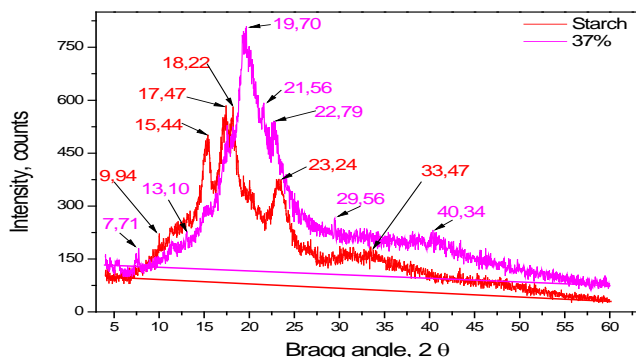
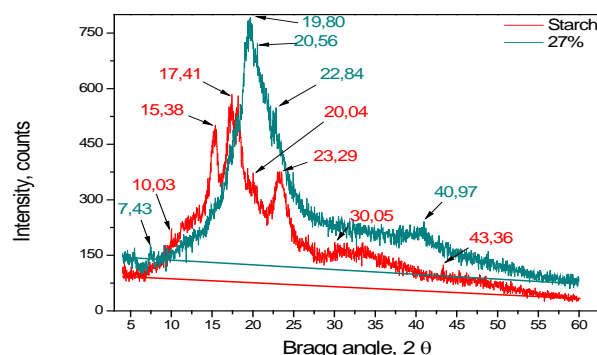
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The paper proves that due to the uncontrolled cluster structure of amylopectin, the tight arrangement of starch chains between those of modification polymers is not possible and so the miscibility of the blend components can not be complet. As consequence the starch with high amylopectin content leads mainly to multiphase, microstructurate materials. This structuration type and level controls thermal, mechanical and dynamomechanical properties of resulted materials. Dependending on the amylopectine molecular characteristics and its percentage in starch, the microstructured character of resulted materials can be more or less pronounced.



**ACKNOWLEDGEMENT** - These researches were supported by UEFISCDI Romania from the grant number 59/2012.

**POLYPROPYLENE/ ALUMINOSILICATE COMPOSITES PROPERTIES**

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The aim of this study is to obtain new material composites based on Polypropylene (PP) and two types of aluminosilicate materials, from indigenous resources. The effect of clay (from Dobrogea-Cuza Voda, Constanta county, Romania) and of volcanic tuff (from Slanic-Piatra Verde, Prahova county, Romania) on the mechanical properties of polypropylene (modulus of elasticity, tensile stress at yield, axial stress at yield and Izod impact strength) was studied. Composites with different percentages of aluminosilicate materials were prepared by dynamical melt processing. The results of this study revealed that the properties of PP are dependent on the chemical structure and proportion of aluminosilicates used. The modulus of elasticity, tensile and impact strength increase by addition of aluminosilicate, while the elongation decreases proving the interaction between polymer and filler. The best properties are obtained with volcanic tuff.

The new material composites can find application in construction and building material industry.

**Acknowledgements**

This material is based upon work supported by the Ministry of National Education – Research Activity, CNDI–UEFISCDI, in the frame of the project number PN-II-PT-PCCA-2013-4-1709 (BIO-THERM), Programme PN2 P4 Partnership PCCA 2013”

**INFLUENCE OF THE ELECTROMAGNETIC IRRADIATION PRETREATMENT ON THE SEPARATION PROCESS IN WET MEDIUM OF THE MESOPOROUS SILICA WITH LOW IRON CONTENT FROM SERPENTINITE MINERALS**

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This research work investigated the effect of using electromagnetic irradiation in a pretreatment stage before the grinding and leaching stage for the selective separation of mesoporous silica with low iron content from serpentinite minerals. The effect of microwave irradiation over the serpentinite rock was evaluated. The rock was then applied an advanced grinding treatment to a particle size under 90 microns, and afterwards was subjected to leaching in concentrated nitric acid solution (50%). The microwave pretreatment has shown a significantly useful effect, permitting a better elimination of magnetic and weakly magnetic minerals with high iron content. After the leaching stage, the mesoporous silica was separated more efficiently and had an iron content of only 0.2 % to 0.3% in the dry silica product, much lower than the range of 3.0 – 3.5% which we have obtained in a previous work<sup>28</sup> without the microwave pretreatment. Therefore, we found that the microwave irradiation pretreatment combined with advanced grinding and a leaching stage is an effective technique for extracting pure compounds from serpentinite minerals.<sup>29</sup>

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<sup>28</sup> RO123556 B1;

<sup>29</sup> This work received financial support from National Authority UEFISCDI through the project ERA-NET MANUNET No. 7074/2013.

**SECTION 4**

**PETROCHEMISTRY AND  
CHEMICAL ENGINEERING**

**FUEL HYDRODESULFURIZATION IN HETEROGENEOUS CATALYSIS**  
**DOUKEH Rami<sup>1</sup>, BOLOCAN Ion<sup>1</sup>, VELEA Sanda<sup>2</sup>, BOMBOS Mihaela<sup>2</sup>, VASILIEVICI Gabriel<sup>2</sup>,**  
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The hydrodesulfurization was studied on a synthetic mixture containing an aromatic compound containing sulfur, i.e. thiophene. The catalysts are of type granulate and have been prepared by impregnation by the pore filling method of an alumina support. Conversion of thiophene was studied on mono metal catalysts (8% Mo /  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and 4% Co /  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) and bi-metallic (8% Mo-4% Co /  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>).

The distribution of the acid strength of the catalyst was determined by thermal desorption of diethyl-amine in the temperature range of 150-600 ° C. Catalyst activation was carried out by sulfur saturating with dimethyl disulfide.

Experiments were carried out on a laboratory plant with a fixed bed catalytic and downflow of the reactants, at a pressure of 30-60 atm, the volume flow of the raw material at a rate of 1-4 h<sup>-1</sup> and a volume ratio of hydrogen / raw materials of 25 \* 10<sup>3</sup> NL / L. The temperature was varied between 175 - 300 °C.

Identification of the resulting thiophene intermediate compounds in the process of hydrodesulfurization was carried out using GC-MS.

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**TECHNODESIGN-ul – REZISTENȚA EDUCAȚIEI INGINEREȘTI**  
**DUMITRESCU Florin**

Industrial design is a complex activity, which involves many steps and levels to deal with, between the environment protection is not only a wish, but a very important component. In the historical stage must be fully aware of our actions effects, heritage for the future of the planet civilizations. The material resources used during a product life cycle, have a very important impact on the environment. This impact could be reduced considering both the quality and the quantity of these material resources.

**Key words:** design, technical areas, ecology, resources

**MODIFIED ROAD BITUMEN WITH POLYBUTENE**  
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Bitumen is modified with different polymers in order to reduces events like rutting, cracking of roads and lowering maintenance costs. For this purpose there are used polymers with plastic and/or elastic properties.

In the experimental program was used a D50/70 road bitumen-type modified with three different types of commercial polybutene in the presence of a dispersant - alkyl polyamine imidazolines of fatty acids. Selected polybutenes have molecular weight (Mn) between 2500 ... 6000 g / mol and a polydispersity index (Mw/Mn) 1.7 ... 1.85 determined by gel permeation chromatography. Modification of bitumen was done in a thermostatted autoclave equipped with vigorous stirring, at 140°C for 4 hours, at a concentration of 3% plastomer and 0.5% dispersant.

Homogeneity of the modified bitumen was evaluated by fluorescence microscopy and were determined the main characteristics of the samples - penetration, ductility, softening point, Fraass breaking point, adhesion to mineral aggregates and thermogravimetric analysis.

Significant improvement of adhesion to mineral aggregates was observed for sample containing polybutene with molecular weight of 6000 g/mol.

**STUDY OF PHYSICO-CHEMICAL PROPERTIES OF  
GASOLINE+BIOALCOHOLS MIXTURES**

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Development of human society requires increased energy consumption. Transportation is one of the main energy consuming fields. Emissions of fuels are toxic and polluting. Environment protection represents a major issue of the XXI<sup>st</sup> Century. Replacement in a certain extent of fossil fuels by biofuels is a way to reduce environment pollution taking into account that biofuels are obtained from renewable energy sources, are non-toxic, biodegradable and lower gaseous emissions. From these reasons, there is an increasing interest in the use of bioalcohols in transportation as additives or fossil fuels replacements<sup>1 2 3</sup>.

To be used as fuels for spark ignition engines, gasoline blends with bioalcohols must be characterized. The main objective of this research was the determination of density, vapour pressure, and octane number of gasoline mixtures with ethanol, i-propanol and n-butanol, fuel properties that affect engine behavior as well as gaseous emissions.

Pseudo-binary mixtures of gasoline with ethanol, i-propanol and n-butanol, respectively, were prepared by weighting, covering the full composition range. Density of the pseudo-binary mixtures varied monotonically without extreme points with values in the range limited by the densities of the pure constituents. A method proposed in literature<sup>4</sup> for vapour pressure prediction of gasoline with alcohol blends was tested. The deviation from the ideal behaviour of gasoline-alcohols mixtures depends on intermolecular interactions between mixture components and on the possibility of azeotropic mixtures formations.

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**PRESSURE AND TEMPERATURE INFLUENCE ON COMBUSTION PROPAGATION IN  
n-BUTANE-AIR GASEOUS MIXTURES**

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*n*-Butane, either pure or as component of Liquefied Petroleum Gas, is extensively used as fuel in automotive engines and domestic heaters. Prevention of fires and accidental explosions of *n*-butane-air gaseous mixtures encountered under various conditions requires knowledge of several combustion indices: the peak explosion pressure, the maximum rate of pressure rise and the normal burning velocity. These indices are also requested for the design of venting devices and for optimization of IC (Internal Combustion) engines.

In the present contribution the combustion of *n*-butane-air mixture was studied in a closed spherical vessel ( $V = 0.52$  L) with central ignition by means of transient pressure-time records. The propagation indices of the confined combustions are reported, for quiescent stoichiometric mixtures at initial pressures within 0.3 - 1.3 bar and initial temperatures within 298 - 430 K. At constant initial temperature, both the peak explosion pressures and the maximum rates of pressure rise follow linear correlations against the initial pressure. At constant initial pressure, the peak explosion pressures decrease with the initial temperature whereas the maximum rates of pressure rise seem to be independent of the temperature variation, within the studied pressure range. Using the temperature variation of explosion pressures, the combustion heat of *n*-butane with air at constant volume and initial temperature, corrected for the endothermic processes in the burned gas, was determined according to a previously described model [1].

The pressure variation in the early stage of closed vessel explosions was used to determine the normal burning velocity of the studied mixture, influenced by its initial pressure and temperature. The experimental burning velocities are examined against computed burning velocities, obtained from the detailed modeling of free laminar premixed flames [2]. For both experimental and computed burning velocities, the thermal and baric coefficients were determined and compared with coefficients characteristic for other fuel-air mixtures.

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**NITROGEN INFLUENCE ON FLAME PROPAGATION IN C<sub>2</sub>H<sub>4</sub>-N<sub>2</sub>O MIXTURES****MOVILEANU Codina<sup>1</sup>, RAZUS Domnina<sup>1</sup>, MITU Maria<sup>1</sup>, GIURCAN Venera<sup>1</sup> and OANCEA Dumitru<sup>2</sup>**<sup>1</sup>*"Ilie Murgulescu" Institute of Physical Chemistry, Romanian Academy, Bucharest, Romania*<sup>2</sup>*Department of Physical Chemistry, University of Bucharest, Bucharest, Romania*

Nitrous oxide, N<sub>2</sub>O, is used frequently in rocketry and in motor racing to increase the power output of engines, since combustion of any fuel with N<sub>2</sub>O develops much higher temperatures and higher explosion pressures in comparison with fuel-air flames. An efficient use of nitrous oxide as oxidizer requires knowledge of maximum explosion pressures, explosion times, and maximum rates of pressure rise, characteristic for the combustion as laminar deflagration of fuel-N<sub>2</sub>O mixtures in confined conditions, under various conditions of pressure, temperature and additives. Dilution with inert gases is the most efficient method for mitigation and even for suppression of explosion in these mixtures.

In the present contribution the propagation properties of C<sub>2</sub>H<sub>4</sub>-N<sub>2</sub>O diluted by various amounts of nitrogen (between 40 – 60 vol%) are reported. Measurements of pressure evolution during the combustion of lean and stoichiometric C<sub>2</sub>H<sub>4</sub>-N<sub>2</sub>O-N<sub>2</sub> mixtures in a spherical vessel (diameter = 5 cm) with central ignition were made at initial pressures within 0.5 – 1.5 bar and ambient initial temperature. For each C<sub>2</sub>H<sub>4</sub> : N<sub>2</sub>O ratio and nitrogen concentration, linear correlations of  $p_{max}$  (maximum explosion pressures) and  $(dp/dt)_{max}$  (maximum rates of pressure rise) versus the initial pressure,  $p_0$ , were found. The amount of heat transferred by the burned gas to the vessel, before the end of combustion, was determined for each flammable composition from the intercepts of  $p_{max}$  vs  $p_0$  correlations. The heat losses appearing during explosion propagation depend on the initial diluent concentration. The data are examined in comparison with similar values referring to ethylene-air mixtures measured in the same initial conditions [1,2], since only scarce published data refer to flammable mixtures of N<sub>2</sub>O [3]. At identical C/O ratios, ethylene-N<sub>2</sub>O mixtures develop higher explosion pressures, shorter explosion times and higher rates of pressure rise as ethylene-air mixtures, as a consequence of the exothermic dissociation of N<sub>2</sub>O under flame conditions.

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# SULFONAMIDE DERIVATIVES OF PHENOXYACETIC ACID; SYNTHESIS AND STRUCTURAL CHARACTERIZATION

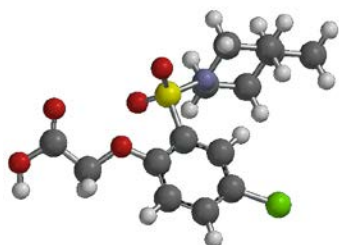
**Pintilie Lucia<sup>1</sup>, Stefaniu Amalia<sup>1</sup>, Caproiu Miron Teodor<sup>2</sup>, Maganu Maria<sup>2</sup>, Oniscu Corneliu<sup>3</sup>**

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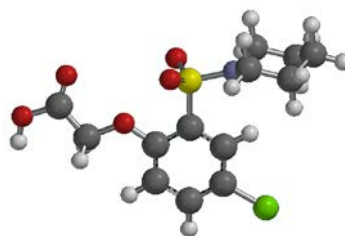
<sup>2</sup>Organic Chemistry Center "C.D.Nenitescu", 202 B Splaiul Independentei, Bucharest 6, Romania.

<sup>3</sup>Technical University"Gh. Asachi"of Iasi, Faculty of Industrial Chemistry, 71, D. Mangeron Av.6600, Iasi, Romania

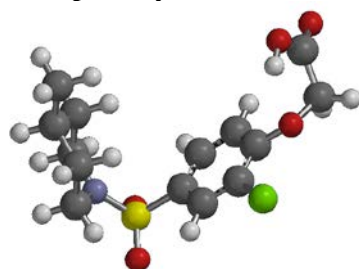
Sulfonamides are today an important class of chemical products characterized by herbicide or growth regulating auxinic effects, by the lack of toxicity towards human beings, animals, bees, and fish and by the fact that they are biodegradable. This paper presents experimental data regarding the synthesis and structural characterization of some sulfonamide derivatives of phenoxyacetic acid. Molecular, topological and conformational characteristics on 3D sulfonamide derivatives optimized structure have been calculated using Spartan 14 Software. For each structure of the analyzed class, the 3D structure used for calculations was generated and its geometry has been optimized by energy minimization, in order to obtain the most stable conformer. NMR and IR spectra of the quinoline compounds have been calculated with Spartan 14 software. After analyzing the experimental and calculated spectra, the correlation between experimental and calculated data has been observed.



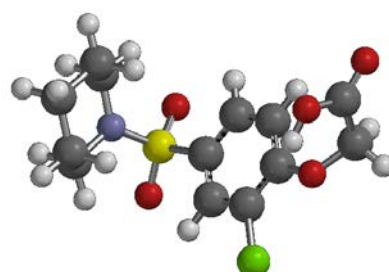
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2-[(piperidino)-sulphonyl]-4-chloro-phenoxy acetic acid



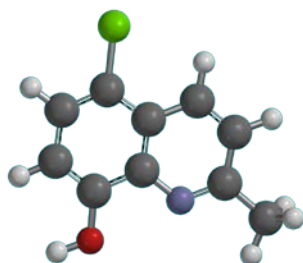
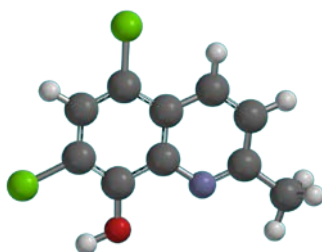
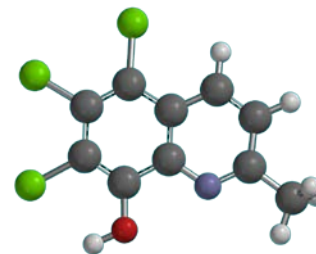
2-chloro-4-[(4'-methyl-piperidino)-sulphonyl]-phenoxy acetic acid



2-chloro-4-[(piperidino)-sulphonyl]-phenoxy acetic acid

**SYNTHESIS AND SPECTROSCOPY STUDIES OF BY-PRODUCTS OF CHLOROQUINALDOL****Pintilie Lucia<sup>1</sup>, Deaconu Mihaela<sup>1</sup>, Stefaniu Amalia<sup>1</sup>, Tanase Constantin<sup>1</sup>, Caproiu Miron Teodor<sup>2</sup>**<sup>1</sup>*National Institute for Chemical-Pharmaceutical Research and Development, 112 Vitan Av., 74373**Bucharest 3, Romania, email: [lucia.pintilie@gmail.com](mailto:lucia.pintilie@gmail.com)*<sup>2</sup>*Organic Chemistry Center "C.D.Nenitescu", 202 B Splaiul Independentei, Bucharest 6, Romania.*

Chlorquinaldol (5,7-dichloro-2-methyl-quinolin-8-ol) presents a significant attention due to its antibacterial activity, antifungal activity, trichomonal and keratoplastic effect and due to the fact it is an important intermediate for the preparation of some biologically active compounds. In the process of the preparation of the chlorquinaldol, by chlorination of 8-hydroxyquinaldine using as chlorinating agent, chlorine gas, have been obtained 5-chloro-8-hydroxyquinaldine and 5,6,7-trichloro-8-hydroxyquinaldine, by-products which contaminate the final compound. This paper presents experimental data regarding the synthesis of by-products of chlorquinaldol. The quinoline compounds have been analyzed through physico-chemical techniques (<sup>1</sup>H-NMR, <sup>13</sup>C-NMR, FT IR, UV-VIS). Molecular, topological, conformational characteristics and quantitative structure-activity/property relationships on 3D quinolones optimized structure have been calculated using Spartan 14 Software. For each structure of the analyzed class, the 3D structure used for calculations was generated and its geometry has been optimized by energy minimization, in order to obtain the most stable conformer. NMR and IR spectra of the quinoline compounds have been calculated with Spartan 14 software. After analyzing the experimental and calculated spectra (<sup>1</sup>H-NMR, <sup>13</sup>C-NMR, IR) the correlation between experimental and calculated data has been observed.

**3D structure of the conformer having minimum energy geometry****5-Chloro-8-hydroxyquinaldine****5,7-Dichloro-8-hydroxyquinaldine****5,6,7-Trichloro-8-hydroxyquinaldine**

**BIOFUELS IN THE FUTURE****IULIAN Olga<sup>1</sup>, Nita Irina<sup>2</sup>, STOICA Georgiana-Raluca<sup>1</sup>, POPESCU Alexandra-Ramona<sup>1</sup>**<sup>1</sup> *Politehnica University of Bucharest, 132 Calea Grivitei, Bucharest 010737, Romania*<sup>2</sup> *“Ovidius” University of Constanta, bd. Mamaia 124, Constanta 900521, Romania*

Biofuels, as possible substitutes for fossil fuels like gasoline and diesel fuel, have acquired a greater importance both in the scientific and the political environments. The benefits of biofuels over traditional fuels include greater energy security, reduced environmental impact as a result of lowered greenhouse gas emissions, increased energy independence for countries that does not hold its own fossil energy resources, and positive socioeconomic impact to the rural sector<sup>567</sup>. Disadvantages: biofuels are more expensive than traditional fuels, and more than that, they compete for agricultural resources with food industry, and may contribute to indirect land use change<sup>8910</sup>. Biofuels market expanding can be achieved as a result of feedstocks diversification, by-products valorization and technologies optimization. Biofuels can be produced from various feedstocks but for now, at industrial level biofuels are obtained mainly from agricultural products. It was demonstrated that biofuels can be also obtained from industrial plants, weeds and algae<sup>11</sup>. For the future, the most promising feedstock for biofuels are microalgae. A way to reduce the production cost of biofuels is by-products valorization. For example, as a result of biodiesel increasing demand on the market, there were developed multiple ways for glycerin conversion to different commercially viable products<sup>12</sup>. From an economic point of view and also, from the environmental and social ones, biofuels seem to be a viable and promising alternative to supply the demand for energy in the years to come.

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# VAPOR-LIQUID EQUILIBRIA AND THERMOPHYSICAL PROPERTIES FOR PROTOTYPE IONIC LIQUID WITH 1-BUTANOL BINARY SYSTEMS

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1-Butyl-3-methylimidazolium halides [bmim]Hal (Hal = Br, Cl, I) are often used as precursors for synthesis of imidazolium ionic liquids with various anions.<sup>13</sup> Containing the simplest possible anions as halides, they can serve as model compounds for various theoretical calculations and molecular simulation.<sup>2</sup> The iodide IL is also considered as electrolyte for solar cells.<sup>3</sup> Thermodynamic properties of the solutions of these ILs in various solvents such as vapour pressures of the solutions and activity coefficients of the components have been rarely studied.<sup>4</sup> These data are essential for the green separation design purpose and for the development of thermodynamic models. Additionally, excess thermodynamic and thermophysical properties are essential for application to the green processes and structural effects explanation. In this work, prototype ionic liquids, 1-butyl-3-methylimidazolium chloride [bmim]Cl, bromide [bmim]Br, and iodide [bmim]I + 1-butanol binary systems are investigated at isothermal vapor-liquid equilibria (VLE) at 363.15 K and low pressures. Activity coefficients and excess Gibbs energies are obtained by correlation of VLE data with thermodynamic models. Refractive indexes for the same systems are measured at 308.15 K and correlated with 4<sup>th</sup> order Redlich-Kister equation. From refractive index vs. composition data and densities of the pure compounds data, the densities, excess molar volumes, surface tensions, dielectric permittivities and their deviations from ideality are predicted using available  $n_D$ - $\rho$  mixing rules and known equations.<sup>5-7</sup> The variation of the excess thermodynamic properties with composition and nature of the anion from the ionic liquid are established and presented. Structural effects reflected in these data are also explained.

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**SECTION 5**  
**PHD SECTION**

**CONTENT ANALYSIS OF METALS AND PERSISTENT ORGANIC POLLUTANTS IN SEDIMENTS  
FROM THE DANUBE BETWEEN CALARASI AND BRAILA SECTION****CODESCU Maria Cristina***Polytechnic University, Faculty of Applied Chemistry and Materials Science*

An important part of aquatic ecosystems assessment is represented by the sediment quality assessment. The sediment represents the trace left after anthropogenic impact that occurs at the level of a river basin due to the fact that the sediment stores much of the compounds which enter the water mass. [1]

Regarding the sediments, good ecological status of the ecosystem shows the state of the system in which the concentrations of persistent organic pollutants remain within the limits set by the quality standards specified in Order 161/2006 of the Ministry of Environment, Table B (Elements and chemical quality standards for sediments - fraction <63 µm). [2] The Order specifies the maximum allowed concentrations (MAC's) for hazardous chemical elements.

Samples were taken from seven critical points during a 4-month monitoring period (April-August 2011), from the Danube between Calarasi and Braila. For each sampling campaign for each critical point, primary statistical parameters (minimum value, maximum and average values) were calculated, from which the average values on monitoring period (April-August 2011) were then established.

By analyzing the samples, the ecological status of ecosystem was evaluated and the chemical status and chemical content of sediments were characterized.

The analysis of the chemical status of sediments took into account the chemical and hydrological conditions of the period previous to the monitoring period, from April to August 2011. [3]

For monitoring of sediment remaining quantities of POPs were determined through the chromatographic method.

Analysis of the metals content of sediments has shown that the chemical status of sediment is bad, the exceedances most frequent of chemical status being recorded at Cu and Hg, while for Pb, As, Cd all values were lower than the limit values set by the quality standards (Order 161/2006).

From the correlation with historical data, it is observed that only for Pb and Ni the concentrations are decreasing: of historical data, Pb concentration of 125 mg / kg and 175 mg Ni / kg) are higher than those measured in the analysed period.

In conclusion, at all Critical Points the sediments are characterized in terms of evaluation criteria - under the Water Framework Directive - by a bad chemical status, mainly due to PCBs and organo-chlorinated pesticides.<sup>1</sup>

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**SYNTHESIS AND FLUORESCENCE OF NEW 3-BIPHENYLPYRROLO[1,2-C]PYRIMIDINES**  
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New pyrrolo[1,2-*c*]pyrimidines having a biphenyl moiety at position 3 have been synthesized by 1,3-dipolar cycloaddition of their corresponding *N*-ylides with activated alkynes. The advantage of performing the reaction in a one-pot three-component approach is the direct formation of the final aromatic compounds, avoiding the formation dipyrimidino-pyrazinic inactivated products.<sup>1-3</sup> The fluorescent properties of the new compounds have been studied. The absorption and fluorescence spectra of the new compounds were recorded and molar absorption coefficients, Stokes shifts, quantum yields and fluorescence quenching in presence of benzoquinone have been calculated. The substituent effects on the fluorescence parameters of the pyrrolo[1,2-*c*]pyrimidine derivatives have been discussed. Correlations between the degree of fluorescence of the pyrrolo[1,2-*c*]pyrimidines and the substituents of the benzoyl moiety attached to the C-3 atom from the pyrrole moiety have been initiated.

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**EXTRACTION AND FRACTIONATION OF PROTEINS FROM „PHORPHYRIDIIUM CRUENTUM”  
BY ULTRAFILTRATION**

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In the current work the extraction and fractionation of phycobiliproteins from the Porphyridium Cruentum (P.C.) microalgae by ultrafiltration (UF) is investigated. Phycobiliproteins are naturally occurring pigments which have been shown to have various uses in several industries, especially in the food industry. The highest interest is in the phycoerythrins mainly due to their high absorption coefficient. Each of these classes holds several types of compounds, each of them having slightly different absorption peaks. The main advantage of choosing P.C. as a raw material for extracting phycoerythrins is that it contains only one type of phycoerythrin and only one type of phycocyanin, thus making the fractionation process easier. In order to reach the soluble components found in P.C., cell lysis at high pressure was performed, followed by centrifugation. In this way the soluble components were separated in the supernatant stream. Concentrating followed by diafiltration, performed with a 300 kDa MWCO membrane, allowed the separation of phycobiliproteins (size<300 kDa) and of all the other components smaller than 300 kDa. The filtrate then went through another concentrating and diafiltration process, this time using a membrane with a MWCO of 10 kDa. Thus, the soluble components with sizes smaller than the 10 kDa were removed. The concentrate contained the desired purified stream of phycobiliproteins, especially of B-PE. The purity of the streams in terms of B-PE concentration was evaluated by the simultaneous evaluation of the concentrations of the different types of phycobiliproteins by a spectroscopic method which implied measuring the absorbance at 565 nm, 620 nm and 650 nm. The quality of the streams was assessed by calculating a purity index based on the concentrations of the phycobiliproteins.

The method was proven to be a straightforward process of obtaining a good quality phycobiliprotein stream from a Porphyridium Cruentum microalgae natural source.

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## SYNTHESIS AND APPLICATION OF SOME AZOIC DYES

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Dyes have a long history and constitute an important component in our daily lives. The dye industry began by using natural plant and insect sources, and then rapidly turned to synthetic manufacturing processes. Unfortunately, several of the synthetic dyes, especially azo dyes, have been found to be toxic and mutagenic, and are banned throughout the world. However, because of their low cost and other desirable properties, the use and manufacture of azo dyes continues even today. Azo dyes are among the largest and most versatile class with the greatest variety of colors, having wide applications in textile, food, plastics, pharmaceuticals, cosmetics, paper printing, leather, and other industries. Approximately half a million tons of them are produced every year all over the world and account for two-thirds of the total dyestuff market<sup>2, 3, 4, 5, 6, 7, 8</sup>.

The paper present the results of laboratory experiments for obtaining some dyes based on 4,4-diamonostilbene-2,2'-disulfonic acid in replace of benzidine, a well known carcinogen diamine long time used in azoic dyes synthesis. The obtained dyes were preliminary tested on textile support and was concluded that the fastness to light and wet treatments are at the level of direct dyes class.

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**THE INTERPHASE TRANSFER BALANCES OF INDOLE-3-ACETIC ACID**

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The indole-3-acetic acid is a growth phytohormone from the auxins class. Plant hormones are biologically active substances, natural or synthetic. They influence development and plant growth.

In this work there were studied a few repartition systems, aqueous phase-organic solvent, for the indole-3-acetic acid. The purpose of the research was carried out to simulate and optimize the processes taking place in a membrane system at the interface feed phase | organic membrane. The organic phases tested were: chlorinated solvents ( $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ ), aromatic hydrocarbons (benzene, toluene) and n-octane in the absence or presence of an extractant such as tributyl phosphate.

The repartition process was assessed by calculating the specific parameters such as: extraction efficiency, distribution coefficient, partition coefficient, dimerization coefficient for indole-3- acetic acid, extraction constant.

The obtained results were interpreted as a function of certain physical properties of the used organic solvents (polarity, dielectric constant).

The best solvent for the extraction of indole-3 acetic acid is n-octane.

The variation of the extraction efficiency depend on the nature of the solvent in order:

n-octane > methylene chloride > chloroform > toluene > benzene;

Distribution coefficient (KD) has the highest values when using n-octane. Partition coefficients (P) and dimerization (D) depends on the chemical nature of the solvent and the higher dielectric constant ( $\epsilon$ ) decreases the degree of dimerization (D) increases.

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**THE EFFECT OF DEXTRAN ADDITION UPON THE THERMOGELATION AND  
DRUG RELEASE PROPERTIES OF POLY(N-ISOPROPYLACRYLAMIDE)  
INJECTABLE HYDROGELS**

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Poly(N-isopropylacrylamide) (PNIPAM), one of the most well-known LCST-displaying thermosensitive polymers, has been very much studied for biomedical purposes due to its LCST (about 32°C) slightly below the human body temperature, rapid thermal response and reduced sensitivity to small pH and concentration changes. However, PNIPAM aqueous gels undergo demixing/syneresis on or soon after gelation, separating into a shrunken gel and a low viscosity aqueous phase, which is an important drawback when applications as injectable hydrogels for either controlled drug delivery or tissue engineering are targeted.

Several methods have been reported to increase the stability of PNIPAM injectable hydrogels. Among them, the one reported by us recently and consisting in mixing sodium alginate, a hydrophilic biopolymer, into the PNIPAM aqueous solution, strongly improved the stability against syneresis of the hydrogel formed at 37°C, as well as its mechanical properties<sup>9</sup>.

The present work deals with the preparation, thermogelation properties and controlled drug release ability of novel injectable thermosensitive hydrogel formulations based on physical mixtures of PNIPAM and dextran (DXT), which is another naturally occurring biocompatible and biodegradable polysaccharide, largely researched for pharmaceutical and biomedical applications, including hydrogel formulations. To the best of our knowledge, no such DXT-PNIPAM hydrogels, having as precursor the aqueous mixture of the two polymers, have been reported in literature to date. We will show within this work that the addition of the hydrophilic DXT polymer to the PNIPAM aqueous solution improves the water retention of the hydrogel formed at 37°C, as well as its controlled drug release properties by strongly reducing the “burst effect”. Furthermore, the thermogelation properties of the DXT-PNIPAM aqueous solutions were studied by dynamic rheometry and differential scanning calorimetry as a function of DXT concentration.

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**SYNTHESIS AND CHARACTERIZATION OF NEW MIXED-LIGAND COMPLEXES OF 5-HYDROXYFLAVONE AND 1,10-PHENANTROLINE WITH SOME LANTHANIDE IONS**  
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Due to their multiple health benefits and chemopreventive properties, flavonoids have received considerable attention from numerous researcher groups around the world. 5-hydroxyflavone (5-hydroxy-2-phenyl-4H-1-benzopyran-4-one, primuletin) is a natural flavonoid with including anti-inflammatory, antiatherogenic, vasorelaxing effects, and antitumoral effects<sup>1</sup>.

The purpose of this study was to obtain and characterize in solid state new mixed-ligand complexes of 5-hydroxyflavone and 1,10-phenantroline with some lanthanide ions, namely: samarium (III), europium (III), and gadolinium (III). The development of new 5-hydroxyflavone- 1,10-phenantroline-lanthanide complexes intends to enhance the antitumor activity of the free ligand and broaden its spectrum of pharmacological activities.

Three novel metal complexes with the composition  $M(C_{15}H_9O_3)(C_{12}H_8N_2) \cdot nH_2O$ , where  $M = Sm, Eu, Gd$ ;  $C_{15}H_9O_3$ =deprotonated 5-hydroxyflavone and  $C_{12}H_8N_2$ =1,10-phenantroline, were obtained. The complexes were characterized by different physicochemical methods: elemental analysis, thermal analysis, conductometric measurements, spectroscopic determinations (UV-VIS, FT-IR, fluorescence). The resulted spectra were interpreted on the basis of the comparison with those of the free ligand.

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**BENEFITS AND OUTCOME OF CHEMOTHERAPY IN MEDULLOBLASTOMA AT  
BORDERLINE AGE IN PROTOCOLS OF ONCOLOGIC TREATMENT. CASE REPORT AND  
LITERATURE REVIEW**

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Background and purpose: Medulloblastoma is a highly aggressive embryonal neuroepithelial tumor that arises in the cerebellum and has a tendency to disseminate throughout the CNS early in its course. Treatment in such tumors is surgery followed by radio and chemotherapy. In patients older than 3 years, the protocol consists of external beam radiotherapy applied to the entire craniospinal axis (23.4Gy)[1<sup>10</sup>]. In younger patients, because of the significant late effects (such as endocrine abnormalities, impaired axial growth, hearing impairment, neuropsychological dysfunction and secondary tumors) [2] of the radiotherapy, the oncologic protocol provides just chemotherapy (alkilating agents, cyclophosphamide, methotrexate)[3]. In this paper we report a case of a 2.8 years old age patient with medulloblastoma and supratentorial metastasis after 2 years the surgical and oncological treatment.

Case presentation: In May 2013 a two and a half year old girl was presented to the E.R. with seizures and vomiting. A MRI was performed and showed a 44/32/30 mm mass located in the vermis of cerebellum. A histopathologic exam confirmed the diagnostic of medulloblastoma. After the surgery the patient was transferred to an oncologic hospital where chemotherapy with cyclophosphamide, vincristine and methotrexate was performed. Because of the age, she did not receive radiotherapy.

Two years later the patient returns for intense headaches. The MRI showed an infiltrative process measuring 25/30/33 mm localized into the white matter of cerebellum and cerebral trunk. Other three tumoral masses were revealed in the right frontal lobe (50/46/45 mm), occipital lobe (26/19/22mm) and pineal lobe (10/9/8mm). In July 2015 a new surgical

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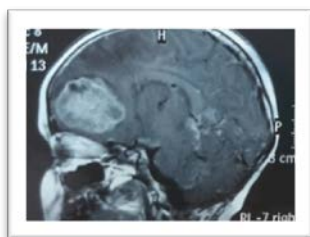
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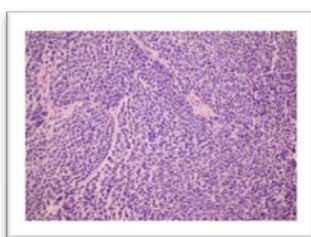
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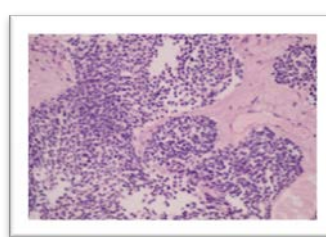
procedure of excision was performed. The histological aspect was the same as the primary tumor.



MRI after 2 years from surgery



HE, 10 X



HE, 20X

**Materials and methods:** For this case report we used as a main selection criteria the histopathologic diagnostic made in embalmed in paraffin tissue, fixed in formalin and colored in Hematoxilin Eosine and Reticulin stain in Pathology Department of Emergency Clinical Hospital Bagdasar-Arseni Bucharest. We also obtained clinical and imagistic data in collaboration with Neurosurgery Department of the same hospital.

**Results:** It has become increasingly clear, especially for medulloblastomas, that outcome is also related to the molecular characteristics of the tumor [4], but this has not been definitively shown for other embryonal tumors. In this paper we present a case of multiple supratentorial metastasis after 2 years of treatment. Because of the age at first diagnostic, the patient did not receive a high radiation therapy, the evolution was apparently favorable but the relapse was aggressive.

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**AZO-DYES FOR COLOURING FOODSTUFFS OF ANIMAL AND PLANT SOURCES****NUTA Alexandrina<sup>2</sup>, SORESCU Ana-Alexandra<sup>1,2</sup>, RADITOIU Valentin<sup>2</sup>**<sup>1</sup>*Valahia University, Materials Dept., 13th Sinaia Alley, Targoviste, 130004, Romania*<sup>2</sup>*National Research and Development Institute for Chemistry and Petrochemistry – ICECHIM, 202 Splaiul  
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The final colour of food and drinks greatly affects consumer choice. Many colorants are therefore added to commercial products to avoid colour losses caused by exposure to light, temperature and/or moisture, to correct natural colour variation and to enhance weak colours<sup>11, 12, 13</sup>. Synthetic organic dyes are widely used in the food industry for colouring products such as drinks, sweets, deserts, and confectionary products. Natural dyes are unstable under processing conditions such as light, oxygen, and pH and are easily degraded, so the use of synthetic organic dyes is considered to be the most reliable and cost-efficient method of colour restoration during food-product processing<sup>14, 15, 16, 17</sup>. Use of synthetic food dyes is strictly controlled by legislation and harmonized across the European Union by Directive 94/36/EC<sup>18, 19</sup> which lists the colours that can be added to food, also defines food stuff to which only certain colorants may be added and their permitted maximum level. The color production industry aims to meet food and drink manufactures needs by providing a full range of colors to suit all applications. In this respect there are presented the experimental data (purity, UV-VIS and IR absorption) for the most widely used monoazodyes, in yellow and red colours, obtained in laboratory.

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**SUBSTITUTED PHTHALOCYANINE DERIVATIVES – MATERIALS WITH POTENTIAL  
PHOTOSENSITIZERS PROPERTIES**  
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Phthalocyanines, aromatic macrocyclic molecules with 18  $\pi$  electron system, have an extended conjugation due to the benzenic rings and, consequently, have a superior chemical and thermal stability which allows them to be used in medicine as substances for diagnosis and treatment<sup>20</sup>. Recent studies led to the identification of new functionalized supramolecular ensembles, linked to nanostructures or mimetic chains antenna type, that exhibit reproductive capacity of the chromophore systems PSI and PSII in photosynthesis<sup>21, 22</sup>.

This paper presents the experimental results for synthesis and physical-chemical characterization of 4 tetra- and octa-substituted phthalocyanine derivatives, zinc and cobalt metal complexes<sup>23</sup>. The compounds were synthesized under microwave irradiation<sup>24</sup>, and characterized by FTIR and UV-VIS spectroscopy and singlet oxygen generation capacity. The conclusion was that zinc complexes are potential photosensitizers in PDT.

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**IDENTIFICATION, STRUCTURAL AND ARCHAEOMETRIC CHARACTERIZATION OF A VIOLIN FROM THE NINETEENTH CENTURY, COPY MODEL ANTONIUS STRADIVARIUS 1713 Marius PADURARU<sup>1</sup>, Ovidiu TANASA<sup>2</sup>, Daniel POTOLINCA<sup>1</sup>, Viorica VASILACHE<sup>3</sup>, Ion SANDU<sup>3</sup>**

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This paper presents the state of conservation, structural and archaeometric characterization of a 3/4 size violin from the XIXth century, a copy after Antonius Stradivarius 1713 model, for the authentication and evaluation of the price catalogue. For this purpose, it shows fixing dimensional data model, dating dendrochronology analysis, the nature of component materials and their conservation status by highlighting the effects of damage and evolutive degradation.

The aim of this study is to gather useful information about the violin to make a suitable conservation and restauration of the artifact<sup>25</sup>.

In order to analyse the degradation and deterioration of wood, modern investigation techniques were involved, like Optical Microscopy (OM), Scanning Electron Microscope (SEM) and Micro-Fourier Transform Infrared Spectroscopy (Micro-FTIR)<sup>26</sup>.

It also offers information about the period in which the violin was manufactured, the provenience of the violin and the factors (environmental and anthropogenic) that influenced the actual state of conservation.

The most important consequences are produced by the environmental factors, especially by the relative humidity (RH). When the RH increases, the wood locks the water molecules to the cellulosic fibrils level with the help of hydrogen connections. The fibrils are changing their volume but longitudinally less so, leading to dimensional changes perpendicular to the fibril<sup>27</sup>.

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# IDENTIFICATION AND CHARACTERIZATION OF THE ILLICIT ARHEOMETRIC GOODS AT THE CROSSING BORDER

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Degradation of cultural heritage artifacts means the disappearance of memory and cultural identity of a state, therefore, future generation will not be able to know the background of the cultural state. For this reason there is a need to improve the security of documents related to the patrimonial goods at border crossing [28]. The paper presents the investigation of a series of heritage artifacts obtained from rooms real evidence and taking into custody for archaeometric and chemometric characterization. The features of the arheometric elements used for identification and patrimonial evaluation were characterized through modern methods such as SEM-EDX, micro-FTIR, thermogravimetry TG-DTG-DTA-DSC, colorimetry through CIE L\*a\*b\* reflection, IR thermography [29]. Using these methods of characterization, the patrimonial goods can be dated, authenticated and preserved and reintroduced into the museum circuit. Also the paper reveals the security features of the patrimonial goods documents at crossing border. The last part of the paper focuses on the measures that should be implemented at border crossing to decrease the illicit trafficking of patrimonial goods.

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**DEVELOPMENT OF  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$  (BST) BASED THIN FILMS BY HYDROTHERMAL – ELECTROCHEMICAL PROCESSES**

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Hydrothermal-electrochemical technique combines hydrothermal process with electrochemical method and consists in electrodeposition of highly crystalline thin films on metallic substrate (working electrode), directly from nanostructured products of hydrothermal reaction. It is particularly important in the case of crystalline oxide products which cannot precipitate out of solution in the absence of an applied electric potential. This method refers to the reaction between species included in the electrolytic solution and the substrate being used as an electrode of the electrolytic cell under hydrothermal conditions<sup>30</sup>.

The advantages of the hydrothermal-electrochemical processes can be summarized as follows:

- a wide range of films on different substrates, multi-layered compounds, functionally graded materials can be prepared;
- high versatility: a variety of compounds can be obtained using this technique, such as perovskites, tungstenates, molybdates, solid solutions of alkaline earth titanates, etc.
- short reaction time of electrochemical process;
- working electrode can be a 2D or 3D metallic substrate.

In this paper, an hydrothermal – electrochemical system comprising an autoclave endowed is used with three electrodes to deposit  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$  (BST) nanostructured materials in aqueous media on Si/SiO<sub>2</sub>/Ti/Au substrates for gas sensors applications. Si/SiO<sub>2</sub>/Ti/Au substrates were suspended in the autoclave as working electrodes (cathode) and the counter electrode was platinate Niobium (anode) in an electrolytic cell (autoclave) of 2 L. The applied pressure was in the range between 40-100 bars higher than the saturation vapour pressure. The influence of pressure, temperature and time on the film thickness and morphology was studied. The porosity of the deposited film depends on the deposition, number of cycles and rate.

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**THERMOGRAVIMETRIC ANALYSIS AND ELECTRON MICROSCOPY SEM FOR GRAPHITE FILMS DEPOSITED BY THE ELECTRICAL DISCHARGES IN PULSE METHOD WITH GRAPHITE CATHODE METHOD**

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Metal surface treatment, is performed by chemical procedures e.g. treatment with oxidizing substances - potassium permanganate, potassium chloride mixed with oxidizing acids HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, or by physical procedures e.g. such as irradiation or corona treatment. The surface treatment is made to modify the chemical composition of the metal surface in a small depth on the order of a few microns, thus obtaining the oxides, nitrides or metal salts. A special surface treatment consists of applying a film of graphite by electrical discharges in pulse, using a graphite electrode connected to the negative pole - the cathode. This treatment is designed to reduce the metallic surface polarity to not develop subsequently affinities with metal or non-metallic materials with which it can come into contact. This paper presents the results of thermo-gravimetric analysis and electron microscopy SEM conducted to graphite pellicle deposited by electric discharge in pulse process. The samples submitted to analysis thermogravimetric were small portions of graphite powder, collected from the surface of the metal. The samples submitted to SEM were small metal plates on whose surface it was deposited a film of graphite. Following the thermo-gravimetric analysis were found the addition of mass in significant values, 1,365-2.769 %. although thermogravimetric analysis was conducted under nitrogen atmosphere. As compared, the study of the graphite samples collected from the electrode does not present this phenomenon. The additions of mass takes place at elevated temperatures and have the following values 222, 99 C° (1,99 %), 476,12 C° (1,365 %), 614,73 C° (2,769 %). The metal plates on whose surface a graphite pellicle was deposited. submitted to an electron microscopic analysis SEM, revealed a number of regular globular formations which are not part of graphite film. This observation corroborated with thermo-gravimetric analysis results, leads to the conclusion that the procedure for obtaining the graphite film also conduct to the obtaining of spatial formation composed of carbon atoms type fullerenes, able to incorporate in a reversible process small molecules (N<sub>2</sub>, HOH) <sup>31</sup>

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**HYBRID NANOSTRUCTURED THIN FILM DEPOSITION BY VACUUM THERMAL  
EVAPORATION AS POTENTIAL METHOD IN SENSORS FABRICATION**  
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This paper describes some results on the deposition of transitional metals with high conductivity acting as sensorial electrodes followed by functionalisation with organic-inorganic hybrid nanostructured thin films via vacuum thermal evaporation. As substrates, commercial Si/SiO<sub>2</sub> wafers have been used. The adherence of the conductive Au film was improved by deposition of a Ti interlayer. The adherence was tested according to the MIL-M-13508C standard. Different hybrid inorganic-organic materials were further tested for compatibility with thermal evaporation deposition technique: tris (8 – hydroxyquinolino) aluminium (Alq<sub>3</sub>); Zinc acetate, Chytosan, Zinc acrylate. Preliminary results show that some results were obtained for deposition of Alq<sub>3</sub> films with a thickness <100 nm. These behavior may be correlated with the higher decomposition temperature observed by DSC measurements.

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## **COLD PROCESS FOR OIL SAPONIFICATION**

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Soap manufacture has a long history since Romans and Celtic people used animal fats and plant ashes for bathing and washing. Superior soaps were made in Europe since 13<sup>th</sup> century when olive oil became more available for the most countries. Laundry and cleaning soaps were gradually replaced with detergents after the First World War, nowadays even body or hand cleansing products being formulated as liquids and gels. Traditional solid soaps are little represented in the way of quantities sold on the market.

Modern trends in the consumer acceptance promote the soft aromatized soap with emollient, hydrating and relaxing properties. Essential oils extracted from aromatic and medicinal plants are included in soft soaps recipes because they demonstrated excellent antimicrobial effects maintaining the health of skin and teguments. Another reason sustaining this trend is the sensitivity of many persons to detergents and commercially made cleaning and body products. Conventional technology of making soaps obtained glycerol as by-product and separately sold as cough medicines and home remedies or used as conditioning agent of various products. Cold process retained this exceptional natural ingredient in soap texture conferring it a soft and gentle aspect.

Present work is the result of the experimental research representing an adaptation of the cold process of making soaps to obtain agricultural soaps for plant protection against pests and diseases from field culture to stored grains. Several kinds of bioproducts were obtained as paste, gel and solid started from cold saponification of sunflower, rape and soy seeds oils. One of the most important advantages of using cold process for oil saponification are the retaining of glycerin in the soap texture and the possibility of avoiding losses of essential oils by vaporization.

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**VALIDATION OF AN ANALYTICAL METHOD FOR THE DETERMINATION OF ANTIMONY IN DRINKING WATER BY INDUCTIVELY COUPLED PLASMA OPTICAL EMISSION SPECTROMETRY, ICP-OES**

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Antimony is an element belonging to the fifth chemical group, which is found in nature mainly as a sulfide mineral (stibnite), widespread in natural environment. It comes from both natural processes and human activity. Its content in rivers is typically lower than  $1 \mu\text{g L}^{-1}$  and even bigger, it does not usually exceed  $0.5 \mu\text{g L}^{-1}$  in drinking water. Over the last decades, the concentration of antimony has considerably increased in water systems, especially in drinking water becoming an important health issue<sup>32</sup>, as a result of human activity.<sup>33</sup> The toxicity of antimony and its compounds is of increased concern worldwide. Long exposures at concentrations higher than  $9 \text{ mg/m}^3$  cause irritation of eyes, skin, and lungs. Exposure at less higher concentrations of  $2 \text{ mg/m}^3$  can cause problems with lungs (pneumoconiosis) and heart (altered electrocardiograms), stomach pain, diarrhea, vomiting and stomach ulcers.<sup>34</sup>

In the present work, an inductively coupled plasma optical emission spectrometry (ICP-OES) method for the quantification of Sb in drinking water, according to the requirements of Law 311/2004<sup>35</sup> and SR EN ISO 11885/2009<sup>36</sup>, was developed. The method has provided good validation parameters for linearity, the correlation coefficient being  $r \geq 0.9985$ , the limit of detection was  $0.58 \mu\text{g L}^{-1}$  and the limit of quantification was  $1.74 \mu\text{g L}^{-1}$ . Repeatability value obtained by analyzing of 10 samples of drinking water closed to the maximum admissible concentration was  $0.55 \mu\text{g L}^{-1}$ . The accuracy value calculated by analyzing eight standard solutions with concentration of  $10 \mu\text{g L}^{-1}$ , closed to the maximum admissible concentration, was of  $+0.31 \mu\text{g L}^{-1}$ . The recovery value obtained was 103%. The extended uncertainty value was  $1.6 \mu\text{g L}^{-1}$  with a confidence level of 95% ( $k=2$ ).

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**KERATINOPHYLIC FUNGI ISOLATED FROM ANIMALS**

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Keratinophilic fungi represent a group of fungi that possess the ability to use keratinized tissues (skin, hair and nails)<sup>1</sup>. Representatives for this group are dermatophyte fungi (*Trichophyton*, *Microsporum* and *Epidermophyton* genera)<sup>2</sup> that can cause infections both in humans and animals. Keratinophilic fungi can be isolated from the soil (geophilic), animals (zoophilic) and humans (anthropophilic). Are known that zoophilic strains producing more severe infections compared to those anthropophilic. The objective of this study was the isolation and identification of keratinophilic fungi from animals, in particular dermatophytes fungi. For this purpose the samples of hair strands and skin scales were collected from rabbits, Guinea pigs and cats infections. Collected samples were incubated at 25°C on specific culture media during four weeks. For the identifications of isolated fungal strains macroscopic and microscopic observations were made. Also were performed the *in vitro* hair strand perforation test and urea hydrolysis test for isolated keratinophilic fungal strains identification. Our results are consistent with those obtained by other authors<sup>3,4</sup>. The isolated keratinophilic fungal strains have been identified as belonging to the *Microsporum* and *Trichophyton* genera. From Guinea pigs and rabbits was isolated *Trichophyton mentagrophytes* var. *mentagrophytes* species and from cats *Microsporum canis* var. *distortum*. These strains are involved in superficial mycoses both in man and animals.

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**TECHNOLOGICAL PROCESS OF PRODUCING SOIL INOCULANTS USING  
ENTOMOPATHOGENIC FUNGI AS ACTIVE INGREDIENTS**

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A novel *Beauveria brongniartii* diphasic spore production technology was developed. The biological material source for bioinsecticide production were "wild" *Beauveria brongniartii* strains isolated from natural epizootic outbreaks in Romanian forests infested with *Melolontha melolontha* larvae; the biological and biotechnological potential of each fungal strain were evaluated for fungal strains selection. Production and formulation technology for obtaining biological insecticide included the following steps: (i) "stock culture" production, (ii) inoculum units production (laboratory inoculum and batch inoculum), (iii) biologically active fungal biomass production. At the end of incubation period, when the nutrient substrate fermentation was complete, the quality control of bioinsecticides was performed by measuring virulence on test insects. The biological characterization of *B. brongniartii* bioformulation revealed the following parameters: conidia yield  $1.55 \times 10^{10}$  / g of final product; conidia viability ranged between 88-99%; *Tenebrio molitor* mortality 98.5%, in laboratory conditions. Field tests were conducted in Moldavian forest nurseries infested with *M. melolontha* larvae. The biological treatment efficacy, quantified as the mortality induced on white grubs, appeared 20-60 days after soil inoculants application. There was a positive correlation between application dose and effect: doses ranging from 100-200 kg fungal inoculant / ha led to 80-100% effectiveness on third instar *M. melolontha* larvae. The results indicated that the experimental spore production technology can be used for large scale production of entomopathogenic fungal inoculants of agricultural and silvicultural interest.

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## TIMELINE EVOLUTION OF MAIZE AND WHEAT PATHOGENIC FUNGI DURING THE STORAGE PERIOD

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Agricultural crops are vulnerable to infections by a wide spectrum of plant pathogens. The increased fungal infection and cross-contamination hazards are associated with the globalization of cereal trade (Waage et al., 2006). Placing on the market safe food and feed products is first and foremost a question of good management practices at each stage of the feed and food chain from primary production to final processing (European Guide to Good Hygiene Practices, 2015). For the stored grain, the bulk grain is considered as an ecosystem in which living organisms (grains, insects, mites and moulds) and their nonliving environment (temperature, moisture and oxygen) interact with one another (Adler Cornel, 2005). The grain losses recorded during storage period on worldwide scale according to FAO estimations are 5-10% of total production. In developing countries, due to reduced possibilities of implementing appropriate technologies, the reported damages during storage period may increase up to 30%.

The paper work presents a study regarding the occurrence and development of specific warehouse micromycetes during the first months of grains storage. In 2014, the cereals which are to be stored on an indefinite period of time is affected by the presence of various pests specific to warehouse ecosystem. Immediately after being deposited, it has been identified the specific microflora for this period, respectively species of *Alternaria*, *Trichoderma*, *Cladosporium*, *Aurobasidium*, *Cephalosporium*, *Sclerotinia*, *Phytophthora* and a reduced percent of fungi belonging to *Aspergillus* and *Fusarium* genera. During 120 days storage period the conducted researches revealed a decrease of vegetation fungi and the predominant development of specific storage mycotoxigenic fungi such as *Aspergillus spp.*, *Penicillium spp.* and *Fusarium spp.*

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**SYNTHESIS OF BIODEGRADABLE GELATIN FILMS PLASTICIZED BY GLICEROL,  
APPLICABLE IN CONTROLLED RELEASE.**

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Hydrophilic polymeric three-dimensional networks with special properties are a subject of great interest in recent research in materials engineering and pharmaceutical industry, due to their applicability as carriers in drug delivery systems.

For biomedical applications were investigated many polysaccharides: pectin, chitosan, alginate, collagen, gelatin, keratin, poly - caprolactone, carrageenan, dextran, guar gum, xanthan gum, hyaluronic acid, of which gelatin is considered to be the ideal matrix due to the natural abundance, biocompatibility and biodegradability, non - immunogenicity respectively<sup>37</sup>.

In this study, microwave irradiation technique is used to synthesize biodegradable gelatin<sup>38</sup> (23% aqueous solution) base films, in admixture with glycerine as plasticizer and PEG, in order to improve the bioadhesive properties.

Gelation occurred by cooling at room temperature, in Petri dishes. Biodegradable films were dried at 24°C for 24 hours.

The effect of some monosaccharides: glucose and fructose (10% aqueous solution), having role in crosslinking, on the structure of hydrogel was investigated by ATR-FTIR, in order to establish the optimal crosslinker.

Was investigated the effect of PEG on the swelling properties of new synthesized gelatin films.

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**OBTINEREA 5-HIDROXIMETIL- FURFURALULUI DIN D-FRUCTOZA PRIN CATALIZA  
HETEROGENA SI HOMOGENA**

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In literatura se gasesc multe tehnologii de obtinere a 5-hidroximetil-furfuralului din D-fructoza, pornind de la deshidratarea diferitelor poli-, oligo-, monozaharide in conditii acidice. In aceste metode sunt reprezentate a gama larga de metode catalitice tip homogena, cataliza heterogena. Randamentele difera de la 20-90% dependente de conditii de reactie ca temperatura, pH, catalizatori, solventi si inhibitori folosite.<sup>39</sup> Catalizatorii homogeni testate fiind reprezentati de acizi mineral ca acid sulfuric si acid fosforic, catalizatori heterogeni acizi Lewis, polimeri rasinice acidice, acizi depuse pe suporti si in lichide ionice<sup>40</sup>

In lucrare se prezinta studiul despre obtinerea 5-hidroximetil-furfuralului, prin deshidratarea D-fructozei prin cataliza acidica. S-a testat si comparat efectele catalizei homogene si heterogene. Catalizatori homogene folosite sunt acidul sulfuric si acidul fosforic. Catalizatori heterogene folosite sunt acidul fosfo-wolframic depuse pe diferite tipuri de suporti silice mezoporoase. S-a urmarit conversia fructozei si selectivitatea raportat la materie prima folosita cat si influenta temperaturii. Analizele a fost efectuate pe aparat de HPLC Jasco, echipat cu o coloana Nucleosil C18.

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Prin Programul PN II – Parteneriate in domenii prioritare, Proiectul: „Sistem tehnologic ecologic integrat pentru obtinerea bioombustibililor avansati”

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