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Carbon nanotube polyaniline composites
Francois - Xavier Perrin, Cyntia Oueiny, Sofie. Berlioz

Since their discovery in 1991, carbon nanotubes (CNTs) attracted the attention of researchers due to their remarkable properties and their interesting electrical, mechanical, physical and thermal conductivity behavior. In particular, this interest is also because of the manufacturing process that becomes more basic and less expensive. But, the low solubility of CNTs in almost all organic solvents allowed the use of polymers to fully disperse nanotubes in solution. On the other hand, polyaniline (PANI) is a conducting polymer studied for many years due to the low cost of its monomer, ease of synthesis, the wide range of conductivity accessible and an exceptional case of doping by oxidation/protonation with insertion of anions by treating the emeraldine base or leucoemeraldine base with an acid solution.

The ability to combine CNT with conducting matrices especially PANI has stimulated much research interest and this presentation will give a focus on this topic.

Toward nontoxic antibiofilm solutions: from marine natural products to original synthetic leads**Yves Blache******Abstract***

Bacterial biofilms cause problems in medical health care since they colonize implants such as artificial joints or catheters while in marine environment, formation of biofilms on immersed substrata, leads to major economic problems which conducted to the use of toxic biocides to eradicate these communities. Although eradication of planktonic bacteria communities has been largely controlled, it has been estimated that bacteria within a biofilm can display up to 1000-fold increased resistance to antibiotic or biocide treatment. In this context, design of original compounds which can limit formation of bacterial biofilms is of great need in view of rational use of biocides (and/or antibiotics) as environmentally friendly solutions. Some of the anti-biofilm techniques that are tested today are aimed to the discovery of new potential anti-biofilm compounds from marine organisms such as sponges, soft corals or algae. In this field, our group purified series of marine natural products as potential antibiofilm leads and initiated a program aimed to establish structure-activity relationships of such natural products as potential antifouling compounds. For this purpose “click chemistry” methodologies were retained as interesting high through processes. Results showed that some compounds exhibited non-toxic specific anti-biofilm activities against marine bacterial biofilms.

Structuration of functional materials for energy production or storage through hard- and/or soft-templating routes

Rudi CLOOTS; Pierre COLSON

In the last 15 years, the "GREENMAT" (Group of Research in Energy and Environment from Materials) mainly developed a research based on functional materials related to energy technologies and environmental themes, providing higher added value.

Our lab specializes in the development and characterization of polycrystalline metal oxides in the form of bulk materials, thick or thin films. In order to meet these objectives, we have progressively purchased or developed a wide panel of synthesis and characterization systems, allowing us to move forward effectively in the research projects currently underway in various areas, including among other, structured materials for dye solar cells and electrode materials for lithium batteries. Beyond the objective of optimizing the performance of a material, a crosscutting to all our research is the desire to study the influence of microstructure on the properties of the material.

Regarding the micro/nanostructuration of thin films, our lab developed a skilled knowledge in the synthesis of micro/nano/mesoporous materials. The use of templates is one of the main strategies for the fabrication of advanced materials with new structures at the nano and micro scales that have attracted considerable research effort over the past decades.

Templates can be classified as 'hard' and 'soft'. Hard templates are usually solid-state materials with particular structure and morphology, whereas soft templates are generally in a fluid-like state. Hard-templating is a conceptually straightforward and highly effective method to prepare hollow structures that mimic and/or complement the original shape of the templates which usually consists of the following steps: 1. Preparation of hard templates 2. Coating the templates with the target shell material; and 3. Selective removal of the templates to obtain hollow structures. Silica particles and polymer latex colloids belong to the group of materials commonly employed as hard templates. On the other hand, soft templates such as supramolecular self-assemblies are a powerful tool for the bottom-up synthesis of nanomaterials particularly mesoporous inorganic solids. In this approach, there is a cooperative interaction between self-assemblies and inorganic species that lead to structuration.

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RESEARCH ON THE USE OF FERTIGATION IN THE CONTEXT OF SUSTAINABLE AGRICULTURE

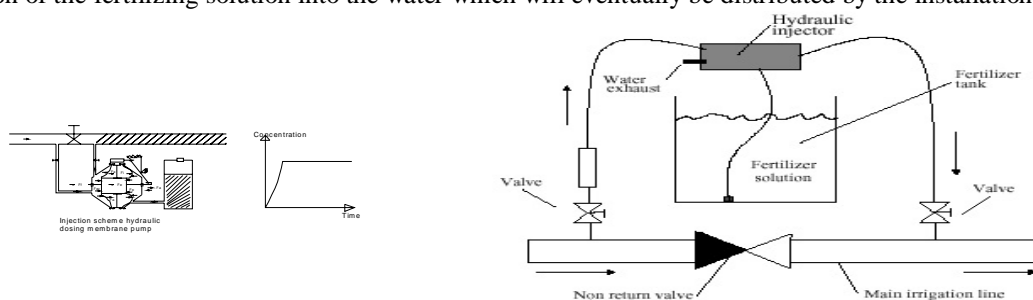
By **BIOLAN ILIE**, NASTASE CRISTINA, VULPE GABRIEL

NATIONAL RESEARCH AND DEVELOPMENT INSTITUTE FOR LAND RECLAMATION,

BUCHAREST, 35-37 OLTENITEI STREET, SECTOR 4, ROMANIA

The method of fertigation consists of applying fertilisers and other chemicals needed for the crop plants and as soil treatment used in agricultural techniques, simultaneously with irrigation water application. One such fertigation installation which is able to apply chemical or organic fertilisers consists of: a tank for storing the chemicals, equipment (pumps, injectors etc.) for the introduction (injection) of these substances into the irrigation water, a control device and the water application equipment. These pumps use the hydraulic energy of the pressurized water which supplies the irrigation installation (machine). In the process of fertigation, fertilisers are thus applied directly with the irrigation water. When the water will be absorbed by the plant roots, fertilisers in the water will also be assimilated.

The equipment used for fertigation comprises the irrigation installation and one pump or a similar device for the injection of the fertilizing solution into the water which will eventually be distributed by the installation.



Fertigation is applied with very good results for high value crops (vegetables, fruit trees, grapevine) with equipment consisting of hydraulic injection devices which work together with drip irrigation installations or micro-irrigation installations.

When applying fertilizing substances using the method of fertigation, it is very important that users understand the main issues regarding the compatibility and solubility of the compounds of these chemicals, being able to acknowledge that certain substances should not be mixed within the tank, while others should not be injected into the system simultaneously.

Tests under experimental conditions with fertigation equipment have been performed within the laboratory of the Bucharest-Berceni Horticulture Research Institute, involving the operation of a drip irrigation installation. The concentration of the fertilizing solution should not exceed values from which there is a high risk of corrosion to either installation components or to the injection pump. The results obtained so far demonstrate that by employing fertigation techniques, one is able to reduce by up to 50% the amount of fertilisers applied per hectare, thus contributing to practicing a sustainable agriculture.

The fertigation installation as a technical solution represents the subject of the Patents – RO no.102887/1993 and RO no. 121612/2007.

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MOLECULAR MODELING FOR SEPARATION OF FATTY ACIDS ESTERS

Cristina ENĂSCUTĂ^a, Emil STEPAN^a, Valentin PLEȘU^b, George Iuliu MARTON^b

*^aThe National Institute for Research & Development in Chemistry and Petrochemistry,
Department of Bioresources, 202 Splaiul Independentei, sector 6, Bucharest Romania,*

*^bCentre for Technology Transfer for the Process Industries, Department of Chemical
Engineering, University POLITEHNICA of Bucharest, 1 Gh. POLIZU Street, Building A,
Room A056, Bucharest Romania*

Ocean fish oils are rich sources of polyunsaturated fatty acids (PUFA), as omega-3 and omega-6 fatty acids, which play an essential role in human diet, due of their capacity to prevent cardiovascular diseases. Especially, two omega-3 fatty acids, ie 5,8,11,14,17-eicosapentaenoic acid (EPA, 20:5) and 4,7,10,13,16,19-docosahexaenoic acid (DHA, 22:6), are important functional constituents of the human body.

The objective of this study was to develop a model to estimate the physical data by Quantitative Structure-Property Relationship (QSPR) methods, focusing on for some ethyl esters of the most common fatty acids. If these methods are formulated for an individual component of FAME, then it is possible to extend them for the components present in mixture. Presently, the QSPR methods are based on simple descriptors like molecular mass, number of double bonds and number of carbon atoms in the fatty acid moiety. The fatty acid ethyl esters were prepared by transesterification of triglycerides from fish oils with ethanol in basic catalysis, followed by purification by distillation. In previous work TurboMoles was used to estimate boiling temperature of pure esters at different pressures, and compared with published data. Same calculations were made now using GAMES, comparing the results for C14:0, C16:0, C18:0, and C20:0 esters. To improve the quality of prediction by molecular calculations, a modification is proposed to molecule total energy in gas phase, to cope the experimental data. Both TurboMole and GAMES are used for those calculations. Antoine model coefficients for considered esters were calculated with both computing instruments. Comparing the modified boiling temperatures, better agreement between experimental data and calculations is obtained. Since the present results revealed a promising perspective, future research will be targeted to calculations of liquid-vapor equilibria. Advanced separation can be obtained by high vacuum distillation laboratory units in 2 stages: a combination of thin film evaporator DSL 5, and short path distillator KDL 5, from UIC GmbH.

DEVELOPMENT OF A PROCESS FOR ENZYMATIC PROTEIN HYDROLYSATES FROM GREEN ALGA *DESMODESMUS COMMUNIS*

Sanda VELEA, Lucia ILIE, Simona GHIMIS, Silvia TUDORACHE, Elena RADU

*The National Institute for Research & Development in Chemistry and Petrochemistry, 202
Splaiul Independentei, 060021 Bucharest, Romania*

Proteins are the most abundant component in the algal biomass, representing more than 40% of the total dry weight, whereas lipids can be found as 20 to 30% of the biomass depending on which strain is used. Therefore the production of large amounts of lipids from microalgae involves the production of a large deal of protein, which can in fact be expected to double the amount of lipids produced. So, it is clear that the protein production must be valorised to make the process economically positive.

Extraction of added-value protein fractions from algal biomass for techno-functional applications in feeds, soil enhancers or as a source of nutrients for the cultivation of microalgae in mixotrophic culture, can considerably increase the commercial value of microalgal biomass.

This paper focuses on the development of a process for enzymatic hydrolysis of cell proteins in green microalga *Desmodesmus communis*. Enzymatic hydrolysis is selected instead chemical hydrolysis to produce a high quality product, rich in essential amino acids, free of toxic degradation products because the process is carried out under mild conditions

The influence of reaction parameters on hydrolysis of extracted biomass with different proteases such as Alcalase 2.5L, Flavorzyme 1000L and Savinase 8.0T was considered, both alone or as a cocktail of enzymes. Significant changes in the degree of hydrolysis (from 30% until more than 70%), were observed which varied by using up to 4% (w/w) units of enzyme on suspension of the treated algae (20%).

The process enlarges the portfolio of products that can be obtained from microalgal biomass and it is a new possibility to enhance the economic viability of microalgae-based biofuels production processes.

SYNTHESIS OF DIESEL ADDITIVE/COMPONENT FROM GLYCEROL CONDENSATION WITH METHYL ETHYL KETONE

**Oprescu Elena-Emilia¹, Emil Stepan², Adrian Radu²; Elena Radu², Enascuta
Cristina Emanuela², Paul Rosca¹**

¹*Petroleum-Gas University of Ploiesti, 39 Bucharest Blv., 100520, Ploiesti, Romania.*

²*National Research & Development Institute for Chemistry and Petrochemistry
ICECHIM, 202 Splaiul Independentei, Bucharest, Romania.*

An important direction for recovery of crude glycerol, obtained as biodiesel by-product, is transformation in additives and components for classic fuels and biodiesel. Due to the high content of oxygen in the structure, glycerin derivatives improves viscosity, lubrication and reduce particulate emissions¹. Such recovery cause biodiesel cost optimization become profitable.

This paper discusses the acetalization of glycerol with methyl ethyl ketone catalyzed by solid superacid $\text{SO}_4^{2-}/\text{SnO}_2$. The synthesized catalyst was characterized by X-ray diffraction, thermogravimetric analysis and FT-IR spectroscopy. The best conditions to maximize glycerol conversion and yield towards glycerol acetal are : molar ratio ketone to glycerol 1.1:1, mass ratio of the catalyst 3 wt % with respect to glycerol, reaction time 4 h. Under these parameters, 98,95% glycerol conversion and 93,86 % yield to glycerol ketal have been achieved .

The obtained glycerol compound was tested as diesel fuel component. The quality parameters of diesel fuel studied were pour point properties, viscosity and flash point.

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Studies on Peptides and Free Amino Acids from *Eupatoria cannabinum*

Adina-Elena Segneanu, Ioan Grozescu, Paula Sfirloaga, Raluca Pop,

Paulina Vlazan, Ion Neda*

National Institute for Research and Development in Electrochemistry and Condensed Matter, Romania, 300569 Timisoara, 1 Plautius Andronescu, Phone 0256-494413, Fax 0256-204698,

Eupatoria cannabinum (Fam. Asteraceae) a herb from Romanian spontaneous flora is well known in traditional medicine for their therapeutical properties^{1,2}.

The major compounds are: resins, flavanone glycosides triterpenes, saponins, sterols, and minerals³⁻⁵.

In recent years there have been numerous researches on biological, immunomodulating and antioxidant activities of *Eupatoria cannabinum* extracts but there are still contradictions relative to this issue.

The paper investigates bioactive compounds, especially free amino acids and peptides from plant extract. The chromatographic (HPLC, GC-MS) studies correlated with spectroscopy methods (UV-Vis, FT-IR and MS) was conducted to identify the amino acids composition.

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AVIATION BIOFUEL FROM MICROALGAL BIOMASS

**Stepan Emil, Velea Sanda, Ilie Lucia, Oprescu Elena-Emilia, Radu Adrian, Enascuta
Cristina-Emanuela**

*Institutul National de Cercetare-Dezvoltare pentru Chimie si Petrochimie ICECHIM, Bucuresti, Splaiul
Independentei 202, sector 6*

Concerns about the depletion of fossil fuel reserves, the impact of anthropogenic CO₂ emissions, and increasing energy demands have encouraged the exploration of new catalytic processes for converting non food biomass into valuable biofuels. Directive 2009/28/EC of the European Parliament and of the Council of 23 April 2009, on the promotion of the use of energy from renewable sources, aims at achieving by 2020 a 20% share of energy from renewable sources in the EU's final consumption of energy and a 10% share of energy from renewable source in each member state's transport energy consumption.

In this favorable context, our research was focused on a new process for obtaining of aviation biofuel, in stringent requirements to the specification of ASTM 1655, such as freezing point, combustion properties, thermal oxidation stability, viscosity, etc. The technological concept is based on complete valorisation of algal biomass, using an integrated system wherein bio-feedstock is subjected first of all to a step of oil extraction to produce algal oil and then the second step dehydrating of de-oiled algal biomass comprising carbohydrates, in the presence of catalysts to yield furan derivatives. Algal oil and furan derivatives will be transformed by hydrogenation in hydroxyl compounds. Finally, by catalytic dehydration, hydrocracking and isomerization processes will result a mixture comprising iso/n alkanes. These are suitable for, or as a blending component for, uses such as an aviation fuel. The reaction intermediates and final product will be characterized analytically by FT-IR and GC-MS methods.

BIOETHANOL PRODUCTION FROM MOLASSES BY IMMOBILIZED SACCHAROMYCES CEREVISIAE

**Călinescu Ioan¹, Trifan Adrian¹, Dima Romulus¹, Teiu Corina¹, Chipurici Petre¹,
Alexandrescu Elvira²**

¹*Politehnica University of Bucharest, Faculty of Applied Chemistry and Material Science,
149 Calea Victoriei, Bucharest, 010072, Romania*

²*Romanian Research and Development Institute for Gas Turbines, COMOTI, 220D Iuliu
Maniu, Bucharest, 061126, Romania*

First generation bioethanol is the leader biofuel produced in the world. It is produced by fermentation of sugars derived from starch or other sugar feedstocks. The development of continuous fermentation process enables automation of the production installation with significant operation cost reduction. The yeast should be immobilized on a support if the continuous fermentation process is carried out in a plug-flow reactor. This study investigates the performance of *Saccharomyces cerevisiae* yeast immobilized on two types of polymeric supports (polyacrylamide and calcium alginate) for the production of bioethanol from beet molasses. The activity of the immobilized yeast is analyzed also in comparison to the free yeast in suspension. The influences of the type of support and of fermentation conditions over the parameters for obtaining ethanol are underlined in this work.

The immobilized yeast was tested in a batch reactor for the fermentation of some molasses solutions. The fermentation rates and the yield of the process were examined to describe the consumption of sugars and the production of ethanol. Bioethanol concentration in the fermentation mixture was determined by gas chromatographic analyses. The sugars type and concentration were determined by HPLC analyses. The effect of different concentrations of molasses on the production of ethanol was evaluated. The inner and the outer surfaces of the fresh and immobilized beads of yeast cells were scrutinized by means of scanning electronic microscopy. The immobilization of yeast on polyacrylamide gel or calcium alginate proceeds with high ethanol production. The advantage of using immobilized yeast on polyacrylamide gel is that the granules are more resistant, and they keep their shape during the fermentation process.

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INVESTIGATION OF ALCOHOL OXIDASE AFFINITY IN REVERSE MICELLES VS. SUBSTRATE NATURE AND HYDRATION DEGREE

**ARSENE Melania-Liliana, DONI Mihaela, JECU Luiza, OCNARU Emilia,
VASILESCU Gelu**

*National Institute for Research & Development in Chemistry and Petrochemistry –
ICECHIM, 202 Spl. Independentei 060021, Bucharest, Romania*

Certain enzymes, especially oxidoreductases, have the potential for biotransformation of hydrophobic compounds. However, the poor solubility of such compounds in water is a critical problem for industrial applications. To overcome this problem, enzymatic reactions of alcohol oxidase in a non-conventional medium, as a special type of water-in-oil micro emulsion (reverse micelles) have been performed.

The tested substrates were alcohols with 1 to 4 atoms of carbon, linear or branched, saturated or unsaturated, aliphatic or aromatic. Substrates susceptible to the conversion catalyzed by alcohol oxidase are differentiated by their degree of polarity which is materialized in the case of AOT-isooctane reverse micelles through different miscibility of the substrates between the two major phases of the reaction environment polar aqueous microenvironment and apolar organic phase.

The catalytic activity of the studied enzyme for various substrates was performed in a large range of hydration degree (w_0), taking into the account that hydration degree is considering to define the characteristics of the reverse micellar environment.

Based on alcohol oxidase affinity values for each substrate, at 5 different hydration degree ($w_0=11, 15, 20, 25, 30$), it has been demonstrated that AOT-isooctane reverse micelles is a suitable media for enzymatic conversion of alcohols with various apolar solvent solubility (from 0% to moderate). However, the enlargement availability of substrates with higher hydrofobicity did not modified the substrate specificity of alcohol oxidase in aqueous medium.

The most important advantage of this new medium is the increased either of the range of substrates which are compatible with the enzymatic reaction and the performance of the reaction in a pseudo-homogeneous water-apolar solvent medium.

NEW TYPE OF MICRO AND NANOPARTICLES BASED ON CHITOSAN AND GELATIN FOR APPLICATIONS IN OPHTHALMOLOGY

LUPESCU (ANDREI) Gabriela¹, Simona BĂCĂIȚĂ¹, Dănuș Costin², Marcel POPA¹,
Cătălina Anișoara PEPTU¹

¹ "Gheorghe Asachi" Technical University of Iasi, Faculty of Chemical Engineering and Environmental Protection, Prof. dr. doc. Dimitrie Mangeron 73, Iasi, 700050, Romania,

² "Gr. T. Popa" University of Medicine and Pharmacy Iasi, Faculty of Medicine, Department of Ophthalmology, Universitatii Street 16, 700115 Iasi, Romania

The advantages of using nanoparticles for targeting different eye tissues include: a) - improved topical passage of large, poorly water-soluble molecules, b) – nanoparticle - mediated drug delivery increases the contact time of the administered drug with its target tissue and c) - nanoparticles allow the possibility of targeted delivery to reach specific types of cancer, such as melanoma, leaving normal cells untouched. One of the most promising natural polymers for being used as drug carrier is chitosan due to its well known properties (biocompatibility, biodegradability, nontoxicity and mocoadhesivity). The work presents original results concerning the preparation and the characterization of chitosan nanoparticles as well as their distribution at ophthalmic level after intraocular administration and in vitro/in vivo cefuroxime release tests. The nanoparticles have been prepared by ionic gelation and double crosslinking (covalent and ionic) in w/o emulsion¹. The characterization of nanoparticles implied FTIR analysis of nanoparticles for evidentiating of the chitosan chemical crosslinking, the morphology of microspheres was evaluated by scanning electron microscopy; the particles size distribution of the products, were measured by laser diffractometry using a Shimadzu laser diffractometer. Particles swelling in different pH environment was studied; cefuroxim loading and release properties has been analysed in vitro and in vivo by UV-VIS, respectively by HPLC-MS.

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¹ Peptu, C.A et al., J. Bioact. Comp. Polym. , Volume 25 (1): 98, Jan 1, 2010

SCREEN PRINTED IMPEDIMETRIC IMMUNOSENSOR FOR SENSITIVE DETERMINATION OF AFLATOXIN B1

**Emilia OCNARU¹, Mihaela BADEA-DONI¹, Melania-Liliana ARSENE¹,
Fabiana ARDUINI², Andrei-Florin DANET³**

¹*National Research & Development Institute for Chemistry & Petrochemistry - ICECHIM,
Spl. Independentei 202, Bucharest, ROMANIA*

²*Universita degli Studi "Tor Vergata", Dipartimento di Scienze e Technologie Chimiche, Via
della Ricerca Scientifica – 00133 Roma, ITALIA*

³*University of Bucharest, Faculty of Chemistry, Sos. Panduri 90-92, Bucharest, ROMANIA*

The aim of this work was the development of a disposable impedimetric immunosensor for the detection of Aflatoxin B1. The proposed immunosensor is based on indirect competitive ELISA procedure performed on screen-printed gold electrodes (Au-SPEs) in the presence of anti-AFB1 antibodies. The immunosensor strips were assembled by covalent immobilizing of the biological component (the AFB1 conjugated to bovine serum albumin) to a self-assembled thiol monolayer on gold. Then, the immunosensors were incubated with samples (or standards) and the antibody anti-AFB1 in order to have a competition between the free AFB1 and the AFB1 bound to the Au-SPE surface for the antibody Anti-AFB1. The EIS signals obtained were dependent on the free AFB1 concentration present in sample.

The method proposed here avoids the use of an immunoaffinity column, which is an expensive and time-consuming step in sample preparation for AFB1 determination by the standard HPLC method. Preliminary data indicate that the developed electrochemical immunosensor is acceptable for analyses of AFB1 at the level required by the official EU regulations.

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IMMOBILIZATION OF ALKALINE PHOSPHATASE ON BIOPOLYMERIC SUPPORT

**Luminita Tcacenco*, Iordachel Catalin*, Elena Berteanu*, Ioana Demetrescu **,
Daniela Ionita**, Mihaela Ionica Enache*, Adina LIDIA Zuav*,**

**National Institute of Research and Development for Biological Sciences, Bucharest,
Romania phone/Fax+4021.220.79.09; lili_berteanu@yahoo.com*

***Politehnica Bucharest University, Faculty of Applied Chemistry and Material Science
Department of General Chemistry, Polizu Street, Bucharest, 011061*

Abstracts: The enzyme immobilization in general, and immobilisation of the alkaline phosphatase on a biopolymeric support especially, constitutes, at present, a much studied technique which has a great importance from the point of view of its practical and scientific applications.

The objective of this study was to obtain new nanostructured composite materials, composed primarily of products based on alkaline phosphatase-ALP (EC3.1.3.1.) and natural polymers, collagen and chitosan.

Thus we have developed a laboratory scale experimental method for alkaline phosphatase immobilization by physical adsorption on biopolymer support method. Various types of scaffolds were prepared by varying compositions of alkaline phosphatase, collagen and chitosan. The scaffolds were fully characterized by Fourier transform infrared (FT-IR) spectroscopy.

The results obtained are promising regarding the use of these supports to ALP immobilization, the enzyme having a large practical use, opening a new perspective for its use in different skin tissue engineering.(1,2)

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CHEMICAL PROCESSES OF INTENSIFICATION AND STREAMLINE OF BIOGAS PRODUCTION BY FERMENTATION OF AGRO-INDUSTRIAL WASTES

Victor COVALIOV, Valentin BOBEICĂ, Olga COVALIOVA

*State University of Moldova, 60, Mateevici str., MD 2009, Chisinau, Republic of
Moldova Tel Fax: +37322.577556; E-mail: victor136cov@yahoo.com*

Production of biogas and other energy resources (oil, alcohol) from vegetal raw material has become an important problem in the development of renewable energy as a fundamental component of the sustainable development concept in the worldwide socioeconomic system. In this work the methane produced from wastewater polluted with organic compounds, distillation residue of winery alcohol, processed fruit and other agricultural products are examined as renewable energy sources. It is known that wastewaters from agricultural processing industries contain about 4-8% of organic matter and are potential pollution sources of surface waters. Using the anaerobic fermentation process, the double effect can be reached – water treatment and biogas production containing 60-70% of methane. The biogas production from these waters for energy purposes requires the enhancing of biomethane contents in biogas, removal of H₂S and other harmful compounds from it. There are possible approaches that can allow to achieve this goal. In this paper we propose several chemical processes, experimentally tested, that made it possible to achieve the desired scope:

- intensification of methanogenesis process using phytochemical catalysts that increase the process rate, respectively decrease the fermentation time up to 2-2.5 times and increase the biomethane contents in biogas from 60-70% to 70-80%. A number of isoprenoid vegetal compounds were identified as such biostimulants;
- reducing the amount of CO₂ and remove H₂S from biogas by absorption with ethanolamine.

The passage of biogas through absorber with ethanolamine leads to CO₂ and H₂S binding according to the reactions: $2\text{RNH}_2 + \text{H}_2\text{O} + \text{CO}_2 = (\text{RHNH}_2)\text{CO}_3$; $2\text{R}_2\text{NH}_2 + \text{H}_2\text{O} + \text{CO}_2 = (\text{R}_2\text{HNNH}_2)\text{CO}_3$; $(\text{RHNH}_2)\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2 = 2\text{RHNH}_2\text{HCO}_3$; $(\text{R}_2\text{HNNH}_2)\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2 = 2\text{RHNH}_2\text{HCO}_3$; $\text{R} = -\text{CH}_2\text{CH}_2(\text{OH})$, and $2\text{RNH}_2 + \text{H}_2\text{S} = (\text{RHNH}_3)_2\text{S}$; $2\text{R}_2\text{NH}_2 + \text{H}_2\text{S} = (\text{RHNH}_2)_2\text{S}$.

When the formed salts are heated up to 100-105°C, they are decomposed, regenerating ethanolamine and eliminating CO₂ and H₂S. Thus, the methane contents in biogas increases from 70-80% to more then 90%, raising its calorific value from 5500-6000 Kkal/m³ up to 7000-8000 Kkal/m³ and reducing its harm to the environment.

TRANSESTERIFICATION OF VEGETABLE OILS WITH DIFFERENT ALCOHOLS

Petre CHIPURICI, Adina IONUTA GAVRILA

*Politehnica University of Bucharest, Faculty of Applied Chemistry and Materials Science,
Department Bioresources and Polymer Science, 149 Calea Victoriei*

Transesterification of vegetable oils to obtain alkyl esters of fatty acids is a process known and extensively studied in recent years¹⁻³.

Using mixtures of alkyl esters of fatty acids can lead to lower diesel oil addiction and reduce greenhouse emissions^{4,5}.

This paper presents transesterification of vegetable oils (rapeseed oil, sunflower oil and cooking oil) with methanol or ethanol in the presence of alkaline catalyst. Esters obtained were used to obtain blends with diesel in different proportions. Properties of mixtures were determined according to SR EN 590.

Table 1. The characteristics determined for diesel mixtures – ethyl esters of fatty acids obtained from rapeseed oil.

Characteristics							SR EN 590	
	Diesel	B5	B7	B15	B25	B100	min	max
Density at 15 ⁰ C, (kg/m ³)	836	838.3	839.2	840.5	847.3	881	820	845
Viscosity at 40 ⁰ C, (mm ² /s)	3	3.1	3.3	3.5	4.2	4.46	2	4.5
Cloud point, (°C)	-7	-7	-6	-6	-5	-4		-10
Flash point, (°C)	54	55	56	58	72	129	45	

Most mixtures are within accepted quality requirements of SR EN 590.

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BIODEGRADABLE POLYMER COMPOSITES BASED ON PLA, STARCH AND LAYERED SILICATE

**FLOREA Dorel, VULUGA Zina, IORGA Michaela, RADOVICI Constantin,
NICOLAE Cristian**

*National Research and Development Institute for Chemistry and Petrochemistry-ICECHIM,
202 Spl. Independenței, 060021, Bucharest, Romania*

Poly(lactic acid) (PLA) is a promising substitute of some petroleum-based polymers due to its mechanical and biodegradable properties. However, PLA is usually more expensive than petroleum - based polymers and also has slow degradability. There has been an increased interest in enhancing the biodegradability of synthetic plastics by blending them with low cost natural biopolymers, like starch.¹ To overcome some problems caused by high intermolecular hydrogen bonds, the addition of plasticizers such as water, glycerol, sorbitol, to pure starch is necessary. The addition of starch as filler to PLA decreases mechanical performance of the composite. The layered silicates (montmorillonite) can be used to improve mechanical, thermal and barrier properties of pristine polymers.²

In this work, the hydrophilic, morphological and thermal properties of the polymer composites based on PLA, starch and layered silicate are presented. Behavior to soil action was evaluated by determining changes in mass. Polymer composites were obtained in dynamical conditions, in a Brabender Plastograph, by directly incorporating 7%, 21% and 35% of natural fillers. The layered silicate was prior modified with starch or starch treated with glycerol. The addition of only a few percent of layered silicates results in reduced water absorption and water vapour permeability. The crystallinity index of polymer composites decreases with increasing starch content. The polymer composites based on layered silicate modified with glycerol treated starch show an intercalated lamellar structure proving the intercalation of glycerol in between the layer of the silicate. The thermal stability of polymer composites is better than PLA and not vary with starch content if untreated starch is used. In the composites containing treated starch, T_g of PLA decreases, as well as thermal stability due to plasticizing effect of glycerol. The biodegradability of polymer composites increases with increasing natural filler content.

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BIOSENSORS BASED ON SCREEN-PRINTED ELECTRODES

Florentina Hutanu, Gheorghe Gutt

'Stefan cel Mare' University of Suceava - Universitatii 13, 720229 Suceava, Romania, tel. 0230 216147, fax 0230 520267. e-mail: florentinah@fia.usv.ro; g.gutt@fia.usv.ro

Screen printing seems to be one of the most promising technologies which allow biosensors to become largely commercialized on the market. Enzymes may be immobilized by a variety of the classical methods. These methods are however complex and meticulous and thus their transfer to an industrial scale production is difficult and expensive. A solution to this problem represents the most innovative technique in the field of biosensors is represented by the deposition of the enzyme by printing it in the same time with the fabrication of the SPE [1]. Unfortunately, electrochemical sensors produced with this method not always have identical analytical parameters. In the case of amperometric sensors the main sources of irreproducibility, with unfavorable consequences for amperometric sensors, are: heterogeneity of the ink used for printing of the chemically sensitive element of electrode resulting though an irreproducible surface of the printed electrode and also the instability in time of the electric contacts and the reference electrode. In addition to the unquestionable advantages, there exist also a number of practical problems in the use of enzymes. To these belong: the high cost of isolation and purification of enzymes, the instability of their structures once they are isolated from their natural environments, and their sensitivity both to process conditions other than the optimal ones, normally narrow-ranged, and to trace levels of substances that can act as inhibitors. However, the significative improvements of these kind of biosensors are mainly expected from two different ways: new printable materials and new support surfaces. With this aim, new attempts for the modification of the working electrode are also in continuous growth, focusing on new ligands, polymers and nanostructured materials [2]. A comparative study regarding the design of the SPE based biosensors will be presented.

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CALCIUM PHOSPHATE COMPOSITES AND THEIR *IN VIVO* BEHAVIOUR

**Radost ILIEVA¹, Stefka TEPAVITCHAROVA¹, Kostadinka SEZANOVA¹, Diana RABADJIEVA¹, Rumiana GERGULOVA¹, Margarita GABRASHANSKA²,
Marin ALEXANDROV²**

¹*Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Acad. G. Bonchev Str., Bl. 11, 1113 Sofia, Bulgaria, radipl@mail.bg*

²*Institute of Experimental Morphology, Pathology and Anthropology with Museum, BAS, Acad. G. Bonchev Str., Bl. 25, Sofia, Bulgaria*

Calcium phosphate ceramics, cements and injectable pastes are suitable bone materials in orthopedic, reconstructive and maxillofacial surgery both because of their composition, close to the mineral part of hard tissues, and of their good biocompatibility and extensive bone conductivity. Also, organic-inorganic (calcium phosphate) composite materials have attracted the researchers' interest due to their likeness to the hierarchical mineral-organic bone structures as regards strength and elasticity.

In this study the ability of two natural bioresorbable polysaccharides - xanthan gum and caragenan, as well as of saccharose and gelatine to provide elasticity and long-term formation of micro and macro porosity in the Ca-P composite implant material was studied with a view to provide cell permeation, attachment and proliferation. Zn-modified-tricalcium phosphate (Zn-TCP) was used as a base for the composite scaffolds. Zn-TCP powders were prepared by the method of precursors precipitation followed by their high-temperature (1000°C) treatment. The Zn-TCP powders were homogenized with the preliminary prepared hydrogels and saccharose and dense pastes were molded as cylinders (2 mm diameters) and lyophilized. The samples were hardened using glutaraldehyde.

The prepared samples were tested in a biomimetic model system (simulated body fluid, pH 7.4 and 37°C) as independent units or in model femurs with simulated bone defects. The best porosity was achieved in the composite material formed by Zn-TCP powder, xanthan gum, caragenan, saccharose and gelatine in a ratio of 465:1:1:10:20.

The in vivo behaviour of the composites thus prepared was tested in experimental rat models. Bone defects were created in rat tibia and were filled with the autologous implants. Histological and biochemical studies were done on the rats with the implants. The obtained results showed good biocompatibility and tissue tolerance to the new implants.

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SURFACTANTS FROM RENEWABLE SOURCES

Adina Ionuta Gavrilă, Petre Chipurici

*Politehnica University of Bucharest, Faculty of Applied Chemistry and Materials Science,
Department Bioresources and Polymer Science, 149 Calea Victoriei*

Biosurfactants are very important because they can replace chemically synthesized surfactants in many industrial applications¹. These biosurfactants can be obtained from renewable substrates, that are readily available and inexpensive². Surfactants based on carbohydrates are biocompatible, completely biodegradable, non-toxic, without odour and taste and non-irritant for skin. For this reason they are used in pharmaceutical, medicine, bioremediation and food areas³.

The purpose of this paper is to develop an efficient enzymatic method for the synthesis of carbohydrate esters of fatty acids. Development of synthetic methods involve improving the outcome of the reaction rate, conversion, regioselectivity, productivity, safety and catalytic stability. The main objective is the development of enzymatic methods for obtaining glucose esters with fatty acids, using solvents as adjuvants in the esterification process. The experimental program followed the influence of various parameters on the conversion of fatty acids (temperature reaction; enzyme concentration; type of fatty acid; solvent type).

The results of experiments show the possibility of obtaining glucose fatty acid esters by enzymatic esterification. Increasing temperature lead to a high acid conversion, but a temperature above 60 °C produces denaturation of the enzyme. Increasing the enzyme concentration leads to an increase in fatty acid conversion. A significant increase occurs up to 12% enzyme concentration, higher concentrations lead to small increase of acid conversion and does not justify the use of large amounts of enzyme.

The advantages of enzymatic synthesis are higher yields and milder reaction conditions, resulting in high quality products with low energy consumption.

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THE USE OF AMMONIUM PERSULFATE AS A NOVEL OXIDANT IN DELIGNIFICATION TREATMENT OF DIFFERENT RAW MATERIALS

Manea Vasilica^{1*}, Lăpugean Alexandru², Necula Mădălina², Câmpeanu Gheorghe³, Israel-Roming Florentina³, Nicu Ioana², Stoian Gheorghe²

¹ National Institute for Chemical - Pharmaceutical Research and Development - ICCF Bucharest, Microbial Biotechnology Department, *corresponding author: z18silvia@yahoo.com

² Department of Biochemistry and Molecular Biology, Faculty of Biology, University of Bucharest

³ Applied Biochemistry and Biotechnology Center BIOTECHNOL Bd. Mărăști, no. 59

Wastes and by-products from agro-industrial processes (non-grain and non-food sources) are abundantly produced in the world every day, and have modest, if any, applications. In this circumstance, the second generation of biofuels production is thought to use lignocellulose feedstock such as raw material ^[1]. These wastes, sources of lignocellulose constitute important substrates in fermentative processes directed to biofuel production. The structural carbohydrates in the plant cell wall are wrapped up in lignin. Therefore, a very effective way, but not the only option to significantly increase biomass digestibility is lignin degradation or separation (delignification). The operation is aimed to increase the digestibility of constituent sugars through increment in gross material pore size ^[2, 3]. Many of delignification methods employ mineral acid, alkaline or/and oxidative reaction conditions that lead to reduction of molecular weight of lignin and consequently to pass it into a solution ^[1-5]. The aim of this study was to evaluate the feasibility of delignification of different lignocellulose feedstock (grape stalk, depleted stalk sweet sorghum, and wheat straw) using ammonium persulfate as oxidative agent. Treating finely divided lignocellulose material for 2 h at 121°C with diluted solution of ammonium persulfate (1% and 3% respectively) and extracting it with diluted alkali (1%) readily delignifies all studied materials.

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ADDED VALUE PROTEIN BEVERAGE FROM WHEY VALORIZATION FOR SUPPORT OF SPORTIVE EFFORT

**Diana PASARIN, Florin OANCEA, Camelia ROVINARU,
Gheorghe RACEANU, Liliana ANTON, Lidia PREDA, Malina AVRAM
*Institutul National de Cercetare-Dezvoltare pentru Chimie si Petrochimie –
ICECHIM, Spl. Independentei nr. 202***

The purpose of this study relates to valorize of whey (resulted in large quantities from milk processing in cheese and casein) as a 100% natural protein drinks, fortified, rehydrated and rebalanced to support sportive effort.

Whey represents 85-90% of the volume of processed milk. From a production of 10 million tons worldwide cheese whey results 85-90 million tones of whey with high nutritional properties due to its content in lactose, water, proteins, minerals, fats and vitamins. It is estimated that the food value of 3 kg whey is equivalent to that of one kg of milk, the amount of energy being 795-1046 kJ/kg, depending on the content of lactose.

Whey protein has a high biological value comparative with proteins from egg, soy and casein from milk containing branched amino acids (leucine, isoleucine, valine), which stimulates specific intracellular pathways associated with muscle protein biosynthesis.

Valorization of this product is required not only for its valuable composition, but also because the discharge of whey pollutes the natural environment, biological oxygen consumption being 50 g / l whey compared to about 0.3 g / l of waste water discharged from urban centers. Irrigation with whey lead in time to an excessive mineralization and like animal feed is not economically efficient, 1kg of protein being obtained from 1.7 t whey.

For valorization of whey are searched various alternatives, this by-product can be 100% used, by recovery of all useful substances in its composition.

Objectives proposed are: characterization of physical, chemical and microbiological properties of raw materials (sweet whey, acid whey); establishing and fortifying drink recipes based on whey, selection and implementation of advantageous variant from point of view organoleptic, economically and nutritionally; selection of the conservation and packaging method.

MEDICINAL WATER PRODUCT FORTIFIED WITH AGLUTENIC FIBERS

Camelia Rovinaru, Diana Pasarin, Sanda Velea, Gheorghe Raceanu, Liliana Anton, Mariana Popescu, Lidia Preda, Malina Avram

*Institutul National de Cercetare-Dezvoltare pentru Chimie si Petrochimie –
ICECHIM, Spl. Independentei nr. 202*

The study aims achievement of a functional product based on medicinal mineral water, enriched with dietary fiber gluten-free, competitive on intern market, as niche product for people with celiac disease, and consumers interested in providing an optimal diet. Dietary fiber added and existing physiologically active compounds in the medicinal water will be a health source by consuming.

Nutritional studies support the idea that a diet rich in dietary fiber, which are non-starch polysaccharides (arabinoxylans, cellulose, dextrans, inulin, lignin, waxes, chitin, pectin, beta-glucans) and oligosaccharides, non-digested or absorbed by the body, is associated with risk factor decreasing, correlated with cardiovascular disease, diabetes, cancer and obesity. Since the recommended daily fiber intake by the U.S. National Academy of Sciences for adults is theoretically 20-35 g / day average, proposed product will increase the amount of dietary fiber daily, un-ingested only by eating fruits and vegetables.

The raw material, medicinal mineral water, is one of the few authentic medicinal, ferruginous, carbohydrates, calcium, magnesium, carbogaseous waters. The composition, rich in minerals, is recommended to treat digestive and liver disorders, diuresis cure, arthritic manifestations and anemia. By enriching this mineral water, in optimal proportions, with allergen-free fibers (gluten), natural flavors and sweeteners will get a drink with a consistent texture and special taste, as an alternative to human nutrition in terms of daily intake of minerals and fiber.

Objectives proposed are: achieving physical, chemical and microbiological analyzes of raw materials, establishing several types of functional drinks, selection and realization of advantageous variant from point of view organoleptic, nutritional and economic, establishing conservation method and the method of packing / marketing.

ENZYMATIC COMPOSITES SYNTHESIZED BY COVALENT IMMOBILIZATION ON POLYMER MEMBRANES

T. Sandu^{1,2}, A. Sârbu², C. M. Damian¹, H. Iovu¹

^[1] *Universitatea Politehnica – Strada Polizu 1-7, Bucuresti*

^[2] *INCDCP-ICECHIM, Splaiul Independentei 202, Bucuresti*

The aim of the present study was to prepare enzymatic composites by covalent immobilization on polymer membranes and to determine the optimal conditions for the enzyme immobilization. The enzyme was immobilized in order to enhance its pH and thermal stability.

In order to meet these purposes two polymer membranes were prepared using an acrylonitrile-vinyl acetate copolymer (AN-AV, with a ratio of AN/ AV in the monomer mixture of 2.35) and polyvinyl alcohol (APV). According to literature information polyacrylonitrile-based membranes are often used as supports for enzyme immobilization ^[1]. Both membranes, M1 and M2, were prepared from mixtures of the copolymer with different contents of APV, by the coagulation of the polymer solutions in a bath composed of a water-isopropanol mixture.

Because membranes themselves are not able to covalently immobilize enzymes, these membranes were functionalized with glutardialdehyde. The functionalization leads to –CHO groups insertion on membrane surface. These groups are further used for enzyme covalent immobilization. Tyrosinase from mushrooms is the enzyme which was immobilized. This enzyme is also known as phenolase, phenol oxidase, polyphenol oxidase or o-diphenol oxidase, depending on its substrate specificity ^[2].

The functionalization and enzyme immobilization effect on the membranes composition (FTIR) and thermal behavior (TGA and DSC) was extensively studied.

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CALCIUM PHOSPHATE POWDERS IN DEPENDENCE OF SYNTHESIS MEDIUM

Kostadinka Sezanova¹, Diana Rabadjieva¹, Stefka Tepavitcharova¹, Rosica Petrova², Elena Vassileva³

¹*Bulgarian Academy of Sciences, Institute of General and Inorganic Chemistry, Acad. G. Bonchev Str., Bl. 11, 1113 Sofia, Bulgaria, ksezanova@abv.bg*

²*Institute of Mineralogy and Crystallography, BAS, Acad. G. Bonchev Str., Bl. 107, 1113 Sofia, Bulgaria*

³*University of Sofia "St. Kliment Ohridsky", 1, James Bourchier Blvd., 1164 Sofia, Bulgaria*

In this study the effect of the method of biomimetic synthesis, the reaction medium and the further precursor treatments on the chemical and phase composition, crystal size and morphology of calcium phosphates was examined. Nanosized calcium phosphate precursors were biomimetically precipitated by the method of continuous precipitation in four types of reaction media at pH 8. The initial substances (CaCl_2 and K_2HPO_4) were dissolved in phosphorus- or calcium-free simulated body fluid (SBF) (Ca/P mol ratio = 1.67). The examined reaction media were as follows : (i) SBF as an inorganic electrolyte system; (ii) organic (glycerine) modified SBF (volume ratio of 1:1); (iii) polymer (10 g/l xanthan gum or 10 g/l guar gum) modified SBF (volume ratio of 1:1) and (iv) polymer-organic modified SBF (SBF:glycerine:hydrogel volume ratio of 1:0.5:0.5). Lyophilization, calcination at 300°C, washing, followed by new gelation, lyophilization and step-wise sintering were performed.

It was found that the reaction medium has an influence on the chemical composition and size but not on the morphology of the calcium phosphate powders. In all studied cases bi-phase calcium phosphate fine powders with well-shaped spherical grains, consisting of tricalcium phosphate (β -TCP) and hydroxyapatite (HA) with Ca/P ratio of 1.3-1.6 were obtained. The presence of glycerine increased the content of hydroxyapatite.

Modification of the SBF medium with xanthan gum, guar gum or glycerine (used single, but not in combination) decreased the particle size of the product. Thus, about 65% of the particles precipitated in pure SBF medium and in a mixture of glycerine, xanthan gum and guar gum were sized from 0.5 to 0.8 μm , whereas the particles precipitated in polymer (xanthan gum or guar gum) modified SBF were about two times smaller – 0.3-0.5 μm . Two maxima in the particle size distribution curve were observed in the glycerine-containing precipitation media: 30% of the particles were sized about 0.1 μm and 26% – 0.5-0.7 μm , which points to the easier nucleation than crystal growth in this case.

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BIO-BASED POLYMERIS FOR NON-TOXIC BIODEGRADABLE PACKAGING MATERIALS

Madalina ZANOAGA, Fulga TANASA

“Petru Poni” Institute of Macromolecular Chemistry, Iasi, Romania

41 A Grigore Ghica Voda Alley, Iasi, Romania

The need for packaging can be linked to the progress of civilization and need to preserve perishables for longer period of time. Conventional plastics are produced starting from oil, are not recyclable and, usually, end up in landfill sites or uncontrolled into the environment, where they remain up to 1000 years to degrade, generating toxic waste. Therefore, there is a great need to develop environment friendly biodegradable packaging materials which do not cause environmental pollution. Biodegradable packaging materials neither promote any waste disposal problems, nor affect the trade and safety of products.

Bio-based packaging materials are obtained from renewable agricultural resources. Biodegradable polymers made from cellulose and starches (i.e., amylose, hydroxylpropylated starch and dextrin) have been used for decades. As well as polylactide, polyhydroxyalkanoate (PHA), polyhydroxybuterate (PHB), and a copolymer of PHB and valeric acid (PHB/V). Films derived from plant and animal sources such as zein (corn protein), whey (milk protein), collagen (constituent of skin, tendon, and connective tissue), and gelatin (product of partial hydrolysis of collagen) are also of high interest. Synthetic polymers can also be made partially degradable by blending them with biopolymers, incorporating biodegradable components (such as starches), or adding bioactive compounds.

This paper analyses some aspects concerning the bio-based packaging materials, such as variation of properties during storage, degradation rate under specific conditions, release of toxic by-products, etc. Taking into consideration these criteria, the suitability of bio-based polymers from agricultural resources to be used as packaging materials will be assessed.

SURFACE HETEROGENEITY BY INVERSE GAS CHROMATOGRAPHY

Bucur Ilie

Applied Systems SRL, Str. Mitropolit Nifon Criveanu nr.27, Craiova, bucur_il@yahoo.com

A chromatographic technique and a procedure for the characterization of surface properties of solids with developed surface properties are presented.

The theoretical development is based on Brunauer-Emmett-Teller (BET) adsorption model and the experimental arrangement is a gas chromatograph, modified and completed.

Compared to other methods, the technique and a procedure may be applied even in the catalytic process operating conditions and the adsorption experiments can be conducted without release out, during experiments, of activated or stabilized catalyst. So, we can study the catalyst, beginning with an initial activation phase, up to blocking of active surfaces by different components during complex and long-time research ^{1, 2}. The IGC methods obtain data in dynamic conditions, giving valuable complementary data over static methods.

The IGC methods were successfully applied to adsorption characterization of fibers, polymers, thin-films, powders, drugs, etc. and to some surface properties, such as contact angle measurements, which can hardly be studied by other methods ³.

The studied catalyst, a Fe-Cr oxide industrial catalyst for high temperature CO conversion (COIT), used in ammonia fabrication, is placed in the chromatographic bulk column as adsorbent stationary phase. After appropriate reduction of catalyst, we used nitrogen as carrier gas and n-heptane as adsorbate.

. By processing of adsorption isotherms, using BET model, we obtain informations on the adsorption enthalpy⁴. We described the surface heterogeneity of the catalyst in terms of the variation of calculated BET adsorption enthalpy vs. coverage degrees.

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HYBRID MATERIALS BASED ON ZSM-5/DOXORUBICIN/CHITOSAN AS DRUG CARRIERS FOR CANCER THERAPY

Cristina Ileana COVALIU¹, Eugeniu VASILE², Daniela CULITA³,
Ioana JITARU¹, Horia IOVU¹

¹Univeristy Politehica of Bucharest

²Metav Research & Development

³“Ilie Murgulescu” Institute of Physical Chemistry

Abstract

The need of cancer treatments increases while the number of people which die due to this ill increases, this is the reason why seek an alternative treatment whit less site effects and high efficiency is inevitable. ZSM-5 zeolite with high specific areas containing drugs and biocompatible polymers may represent an useful alternative (Fig.1). The objectives of this research were the preparation and characterization of two types of hybrids based on Na-ZSM-5 and NH₄-ZSM-5 containing doxorubicin and chitosan and used them as cytotoxic drug carriers systems in cancer therapy. The Na and NH₄-ZSM-5 were synthesized by sol-gel method combined with hydrothermal method starting from aluminum nitrate and sodium silicate using tetrapropylammonium hydroxide as template agent. The products formed were washed, dried and calcined at 580⁰C respectively. The final hybrids containing zeolite-doxorubicin-chitosan and the intermediar materials obtained were characterized by XRD, FTIR, TEM and thermal analysis. Also, nitrogen adsorption-desorption isotherms were determined revealing the specific surface area values and the pore size distribution. Furthermore, the pattern of doxorubicin release from the chitosan–ZSM-5 hybrids carriers was affected by pH.

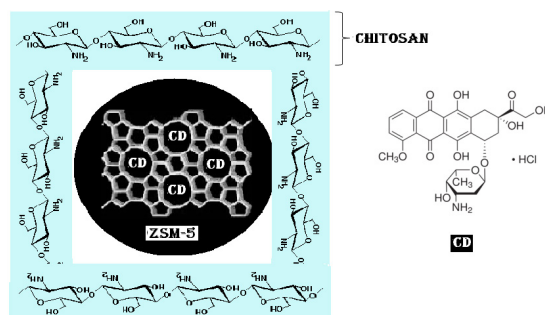


Fig. 1 Scheme of the hybrid materials consisting of ZSM5 zeolite, doxorubicin (CD-cytotoxic drug) and chitosan

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THE COMPOSITES OF WASTE POLYPROPYLENE MODIFIED WITH STYRENE-ISOPRENE BLOCK-COPOLYMERS. THE MOLECULAR MASS EFFECT OF STYRENE-ISOPRENE BLOCK-COPOLYMERS

Ghioca Paul*, Spurcaci Bogdan*, Iancu Lorena*, Coserea Ramona *, Cincu Cornel, Degeratu Cristinel**, Gardu Radita*****

** Institutul National de Cercetare- Dezvoltare pentru Chimie si Petrochimie –ICECHIM- Bucuresti, Splaiul Independentei, Nr. 202 060021, Bucuresti, Romania*

*** Universitatea Politehnica Bucuresti, Splaiul Independentei, Nr. 313, Sector 6, 060021, Bucuresti, Romania*

****Institutul de Cercetari pentru Acoperiri Avansate-ICAAB-dul Theodor Pallady 49 A , Bucuresti, Romania*

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

The block copolymers molecular weight were determined by gel permeation chromatography (GPC) and were characterized by Fourier Transform Infrared Spectroscopy (FT-IR), mechanical properties, differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), thermo-gravimetric analysis (TGA).

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

The present research focuses especially on establishing the molecular mass of linear styrene-isoprene block-copolymers which ensure the highest modified in melt state of waste polypropylene.

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

REGISTRATION FORM Priochem 8:

Name: **MIR Mohammad Alavi Nigjeh**

Scientific title / position: Associate Prof./ Academic staff

Institution: IMAM KHOMEINI INTERNATIONAL UNIVERSITY

Institution Address: DANESHGHAH STREET, IMAM KHOMEINI INTERNATIONAL UNIVERSITY, FACULTY OF SCIENCE, DEPARTMENT OF CHEMISTRY

Phone: +989121935414

Email: drmm.alavi@gmail.com

Fax: +982813780040

Wish to participate: with paper

Paper Type: oral communication

Section: Multifunctional materials and nanocomposites

Paper Title: polyurethane rigid foam nano-composites by incorporation of fictionalized nano particles

Authors: Mir Mohammad Alavi Nikje, Zahra Gholinataj

THERMO-ANALYTICAL INVESTIGATION OF STRUCTURE AND BIODEGRADABILITY OF LOW DENSITY POLYETHYLENE

**Adina Magdalena MUSUC^a, Mihaela BADEA DONI^b, Luiza JECU^b, Adriana RUSU^a,
Vlad Tudor POPA^a**

*^aRomanian Academy "Ilie Murgulescu" Institute of Physical Chemistry, 202 Spl.
Independentei, 060021 Bucharest, ROMANIA.*

*^bNational Research & Development Institute for Chemistry & Petrochemistry – ICECHIM,
202 Spl. Independentei, 060021 Bucharest, ROMANIA*

The increasing use of synthetic films leads to a series of ecological problems due to their non-biodegradability [1-4]. Current food packaging must be resistant to immediate microbial attack in order to prevent food contamination due to damaged packaging before expiration the product warranty, and on the other hand must be biodegradable in order to meet the environmental protection [5-7]. Polyethylene is one of the synthetic polymers widely used as packaging material. In natural form, it is not biodegradable. To make polyethylene biodegradable requires modifying its crystalline degree, molecular weight and mechanical properties that are responsible for its resistance towards degradation [8]. The biodegradability studies were carried out by incubating the low density polyethylene films (LDPE) modified with natural antioxidants with *Aspergillus sp.* in liquid media for 50 days. The structure of the samples before and after microbial attack was investigated using the following methods: optical microscopy, X-ray diffractions (XRD), Fourier Transform Infrared Spectroscopy (FT-IR) and microcalorimetry (microDSC).

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Talon Participare Priochem 7:

Nume: **APOSTOL** Petru

Funcția: cercetator stiintific

Institutia: Institutul de Fizica Aplicata

Adresa: Chisinau, str.Academiei 5, R. Moldova

Telefon: +373(22) 738150

Email: apopetru@gmail.com

Fax: +373(22) 738149

Doresc sa particip: Cu Lucrare

Tipul lucrării: Poster

Sectiunea: Materiale multifunctionale si nanocompozite

Titlul lucrării: '\\Synthesis and optical properties of PbSe nanoparticles in aqueous solutions\\'

Autori: Apostol Petru, Mihail Revenco.

**NOVEL NANOCOMPOSITES BASED ON SILICA/ ACRYLONITRILE-VINYL
ACETATE COPOLYMER: SYNTHESIS AND CHARACTERIZATION**

Anita-Laura Ciripoiu¹, Andrei Sarbu¹, Francois-Xavier Perrin², Anamaria Lungu¹

¹*National Research-Development Institute for Chemistry and Petrochemistry-ICECHIM
Bucharest, Splaiul Independentei 202, district 6, Bucharest, Romania*

²*University of South Toulon-Var, Laboratoire Matériaux Polymères Interfaces et
Environnement Marin, BP 132, 83957 La Garde Cedex, France*

Research on inorganic-organic hybrid materials has become one of the fastest developing areas of materials chemistry¹. Hybrid materials can be used for interesting applications in many fields: electronics, coatings, sensors, optics and ceramics². Synthesis of host-guest systems by radical polymerization is a typical example of using porous materials as reaction vessels for chemical reaction in confined pores. Several vinyl monomers inside silica pores have been utilised until present to obtain the organic/inorganic hybrid materials by guest polymerizations.

The main goal consists in the exploitation of silica properties for functional materials obtaining. The porous channel system of inorganic host offers unique opportunities for the synthesis of new nanostructured materials and our objective is to study the copolymer networks formation in internal structure of pores. The novelty is represented by the used guest copolymer.

The present work refers to the possibility of inorganic-organic nanohybrids obtaining, starting from mesoporous silica, in which the radical polymerization of acrylonitrile-vinyl acetate copolymer proceeds. In order to synthesise the composites were used different ratios between silica and copolymers and also different ratios between acrylonitrile and vinyl acetate in copolymer. In order to realize the main objective consisting in the effect of the host structured particles on the final properties of composite materials thermal and physical analysis of new materials were investigated using FTIR, SEM, TGA and DSC.

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INVESTIGATION OF POLYMER NANOCOMPOSITE BASED ON HYDROFOIL ORGANIC POLYMER, CdS AND ISOTHIOCYANATO-CHALCONE

S. Robu¹, I. Culeac², M. Iovu², G. Dragalina¹, A. Popusoi¹, M. Enachi³, P. Petrenko²

¹Moldova State University, Mateevici Str. 60, Chisinau, MD-2009, Republic of Moldova

²Institute of Applied Physics, Academiei Str. 5, Chisinau, MD-2028, Republic of Moldova

³Technical University of Moldova, Stefan cel Mare Str. 168, Chisinau, MD2012, Republic of Moldova

Nanocomposite materials have attracted much attention for application in photonics and non-linear optics due to their interesting properties and for the possibility of tuning of their physical and chemical parameters through varying the size of nanoparticles. We present here experimental results on polymer-based nanocomposite material made of styrene with butyl methacrylate (SBMA) (1:1), *isothiocyanato-chalcone* (ITCC) and inorganic semiconductor CdS. The photoluminescent nanocomposites based on SBMA, isothiocyanato-chalcone and CdS were prepared by simple chemical method using organic solvents instead of water.

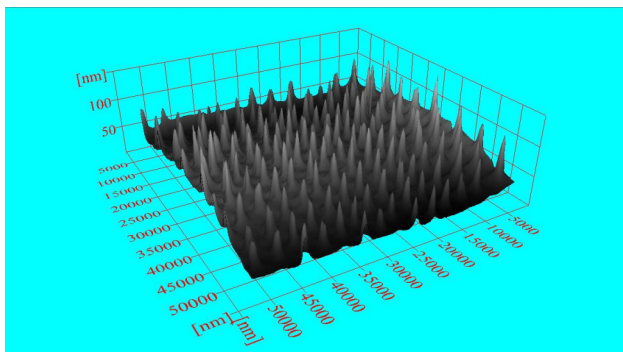


Fig. 1. AFM image of the nanostructured surface of the thin film SBMA+10%ITCC+10%CdS deposited on a glass substrate covered with SnO₂.

The concentration of CdS semiconductor particles was varied in the range 0-20 %. Thin film composite samples have been characterized by UV-VIS absorption and photoluminescent (PL) spectroscopy, X-ray diffraction, as well as by atomic-force microscopy (AFM). Examination of the thin film surface by AFM shows that the surface of the composite can be described as quasi-ordered structure with conic-shaped elements, 25-50 nm high, almost regularly distributed on the surface of the films. The X-ray diffraction pattern correlates with the corresponding value obtained from the UV-VIS absorption spectrum, and was found to vary in the range 9-17 nm. The PL emission spectra have been registered at room temperature under the excitation of UV nitrogen laser beam at $\lambda=337$ nm. The nanocomposite samples exhibit a strong luminescent band in the range 400-650 nm, with the photoluminescent maximum varying slightly in dependence of the CdS concentration. It is supposed that PL is associated to surface-state emission.

MULTI-COLOURED AQUEOUS PIGMENTS INK FOR DIGITAL TEXTILE PRINTING

*ATHANASIU Angela Anca, DEACONU Marian, IONITA Elena, OPROIU Loti Cornelia,

ALIFANTI Constantin, FILIPESCU Căţalin, POPESCU Alina***,
CHIRIAC Laura **, CRACIUN Constantin**

*INC-D pentru Chimie si Petrochimie-ICECHIM Bucuresti (DT C P)

*** INC-D Textile –Pielarie Bucuresti;

** Universitatea Babes Bolyai-Centrul de Microscopie Electronica- Cluj Napoca,

Digital textile printing is based on four components: ink, the printer, the print head and software. For a proper color resistant and print performance is essential is ink that causes the fabric characteristics: color, strength, cough and toxicological impact.

The objective was to obtain a range of inks for inkjet printing and their application to textile materials. To achieve this goal, coloring matters must be micro / nanodispersion and the optimum particle size to be between 20 nm and 200 nm.

Ink jet printing is a process without impact, where ink droplets are produced and deposited on a substrate such as paper, transparent film or fabric, in response to an electronic pulse. Typical systems inkjet printing are either continuous wave ink or like "drop on demand".

In the inkjet inks, pigments have been used recently or as substitutes dyes, either alone or in combination with them. Pigments shows superior properties compared to dyes, in areas such as water resistance and light image density, thermal stability, chemical and oxidation dyes and compatibility with other media compatible with both treated and untreated with. In addition, the pigments are generally non-mutagenic

The biggest problem regarding the use of pigments is micro / nanodispersion and stabilization of particles in liquid medium. Powder pigment particles are generally very hard and in a state of congestion. For preparation of inks for inkjet printing, pigment must to be nanodispersed and stabilized in this form, because the level of dispersion characteristics directly affect the final print.

Highlighting and morpho-structural characterization of microencapsulated liposomes with organic pigments was done by 3 methods of highlighting, respectively) transmission electron microscopy (TEM) with digital image pickup device, b) microscopy video camera and direct learning opportunity in phase contrast, darkfield, DIC and fluorescence.

Nanodispersion inks were obtained by two methods: preparative methods for obtaining **liposomal-based inks** by microdispersion and nanodispersion organic pigments and **subsequent functionalization processes** through the synthesis of organic pigments [surface was modified pigments bloom attaching organic groups] followed by pigmental micro / nanodispersion.

COMPETITIVE BATCH REBINDING IN DIOSGENIN MOLECULARLY IMPRINTED POLYMERS (D-MIPS)

Stefan-Ovidiu Dima^{a,b}, Andrei Sarbu^a, Tanase Dobre^b

^aNational Research and Development Institute for Chemistry and Petrochemistry ICECHIM,
Splaiul Independentei 202, Bucharest

^bPolitehnica University of Bucharest, Splaiul Independentei 313, Bucharest

Section 2: Multifunctional materials and nanocomposites

The binding capacity of diosgenin imprinted (D-MIPs) and non-imprinted polymers was evaluated from batch rebinding studies. The conditions were: 0.1 g of pearls type MIP AN:AA 80:20 in 8 mL solution with three concentrations: 0.2%, 0.4% and 0.6% of template and competitors in ethanol. Three competitor molecules were chosen for crossreactivity tests against the template (diosgenin – D): inulin (I), hydrocortisone (HC) and stigmasterol (ST).

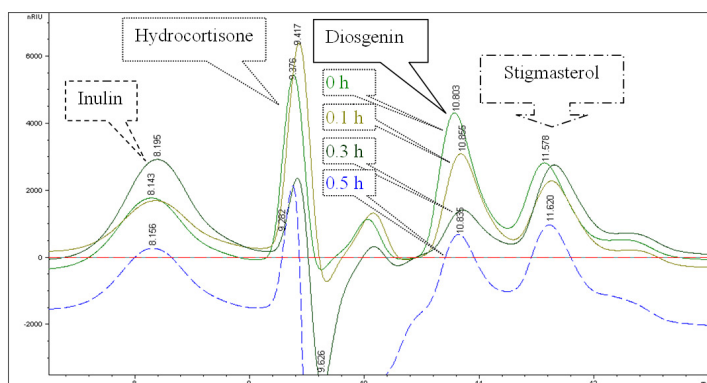


Fig. 1. Overlaid chromatograms of 0.2% solutions (D+ST+HC+I) at four different adsorption moments (0, 0.1, 0.3 and 0.5h).

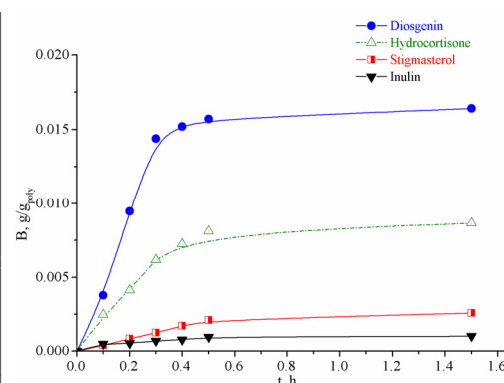


Fig. 2. The selectivity of the binding sites for the template (diosgenin), as determined in the solid phase.

The adsorption capacity B ($\text{g}_i / \text{g}_{\text{polymer}}$) was calculated with eq. (1), in which c_i and c_f (g/L) were the initial and final concentrations of specie “i” in solution (were “i” can be replaced with D, ST, HC and I), V_s (L) was the volume of the initial solution and m_p (g) was the quantity of polymer taken into account. The affinity of specie “i” for the binding sites can be calculated with the eq. (2), where ΣB represent the sum of all adsorbed species in MIP.

$$B = \frac{(c_i - c_f) \cdot V_s}{m_p}, \quad (1)$$

$$A_i = \frac{B_i}{\sum B}, \quad (2)$$

The crossreactivity based on the imprinting effect might be categorized into four classes: (i) high binding for the template (affinity 54% for D), (ii) intermediate crossreactivity for substances with similar structure and similar functional groups (affinity 31% for HC), (iii) low-intermediate crossreactivity for substances with similar structure (affinity 11% for ST) and (iv) low binding for structurally non-related compounds (affinity 4% I).

CHARACTERIZATION OF SOME HYBRIDE MATERIALS TYPE ENOXYL/CLAY

Gonta Alexandru, Lupașcu^{1*} Tudor, Popovici² Eveline, Hristodor Claudia

Institute of Chemistry, Academy of Sciences of Moldova, 3 Academiei str., MD 2028,

*Chisinau, Republic of Moldova *E-mail: lupascut@gmail.com*

Alexandru Ioan Cuza University, Faculty of Chemistry, 11 Carol I Boulevard, 700506, Iasi, Romania

In recent decades there is an increasing trend of using wine products, separated by extraction in order to obtain therapeutically efficient products. Enoxyl is a biocompatible complex, patented by the Academy of Sciences of Moldova, produced by chemical modification of grape seed extracted enotannins.¹ The physico-chemical analysis showed that Enoxyl is very hygroscopic compound,. For this purpose this research is an investigation on improving the physico-chemical properties of drug Enoxyl with the use of new composite clay. The main goal of this research is to obtain and characterize hybrid materials Enoxyl / clay, obtained by encapsulation of Enoxyl in montmorillonite cationic type clay, for pharmaceutical use. The impregnation method at room temperature was used.

Structural and morphological characterization of materials was performed using nitrogen adsorption isotherms, which allowed studying the specific surface area and pore volume.

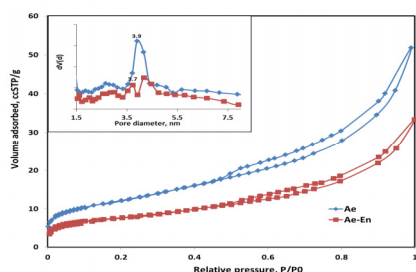


Figure 1. Nitrogen adsorption isotherms at 77K for the studied samples: a-clay (EA), b-Enoxyl (En), c-Enoxyl/clay (Ae-En)

General shape of the isotherm, according to IUPAC type IV² isotherm, is characteristic to porous adsorbents. Emergence of differences in terms of porosity characteristics after encapsulation of Enoxyl between clay layers indicates that the encapsulation process took place. The isotherm specific for the Enoxyl encapsulated in the clay has a deformed hysteresis loop which leads to broad distributions of pore size, with extremely uneven pore sizes.

The material obtained should be regarded as hybrid organic-inorganic nanomaterial with potential applications in cosmetic and pharmaceutical industries due to its antioxidant and antibacterial properties.

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PRUSSIAN BLUE MODIFIED SCREEN-PRINTED ELECTRODES

**Florentina Hutanu^{1,2}, Emilia Ocnaru², Melania-Liliana Arsene², Gelu Vasilescu²,
Mihaela Badea-Doni²**

¹ 'Stefan cel Mare' University of Suceava - Universitatii 13, 720229 Suceava, Romania, tel. 0230 216147, fax 0230 520267. e-mail: florentinah@fia.usv.ro

² National Institute for Research & Development in Chemistry & Petrochemistry, 202 Spl. Independentei 060021, Bucuresti, Romania, tel. 021-315.32.99, fax: 021-312.34.93, e-mail: mihaela.badea@icechim.ro; ocnaru.emilia@icechim.ro

By modifying an electrode surface with Prussian Blue, it is possible to easily detect hydrogen peroxide at an applied potential around 0.0 V versus Ag/AgCl, thus making possible coupling with oxidase enzymes while also avoiding or reducing electrochemical interferences. In addition, the use of Prussian Blue in the development of biosensors for food analysis has captured the interest of many research groups and led to improved methods for the detection of glutamate, galactose, alcohol, fructosyl amine, formate, lysine and oxalate [1].

A comparative study regarding different procedures for modifying the carbon screen-printed electrodes (SPE) with Prussian Blue (PB) was carried out in this work. Several procedure for PB deposition on the SPE electrodes were tested: electrochemical deposition (galvanostatic, cyclic voltammetry) and chemical deposition by the reaction of $K_3[Fe(CN)_6]$ with $FeCl_3$ [2]. Also, the influence of the pretreatment of SPE (+1.7V for 3 min in PBS, pH 7.4) and of the stabilization of PB deposited on SPE (by heating at 100°C) were evaluated.

The developed sensors were optimized with respect to the lowest limit of detection achieved for amperometric detection of H_2O_2 . Analytical parameters, such as detection limit, linearity range and sensitivity have been evaluated, together with operational and storage stability.

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THE STYRENE-BUTADIENE BLOCK-COPOLYMERS WITH THE POLAR GROUPS

**Iancu Lorena, Ghioca Paul, Spurcaci Bogdan, Coserea Ramona, Nicolae Cristian,
Gabor Raluca**

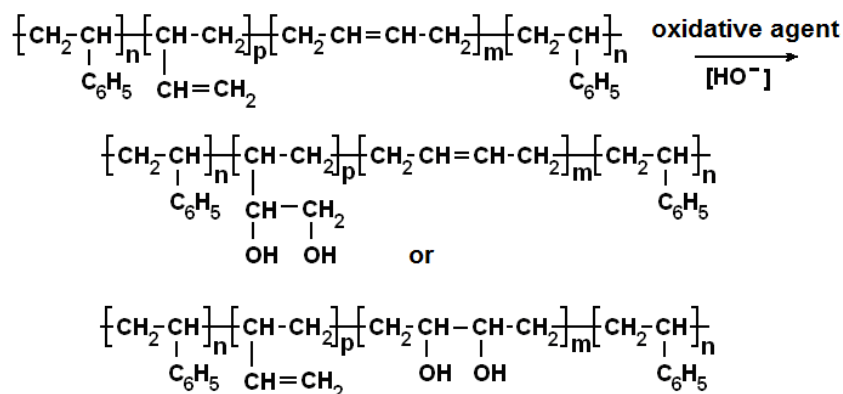
*Institutul National de Cercetare- Dezvoltare pentru Chimie si Petrochimie –ICECHIM-
Bucuresti, Splaiul Independentei, Nr. 202 060021, Bucuresti, Romania*

The styrene-butadiene block copolymers have been functionalized in butyl acetate solution by the reaction of block copolymers with different oxidative agents (potassium permanganate, potassium dichromate and potassium persulphate).

The following styrene-butadiene block-copolymers were modified with different oxidative agents:

- radial styrene-butadiene block-copolymer with 40% polystyrene and 50% vinyl content
- linear styrene-butadiene block-copolymer with 30% polystyrene and 10% vinyl content
- linear styrene-butadiene block-copolymer with 30% polystyrene and 35% vinyl content.

The functionalization reactions of the styrene-butadiene block copolymers were carried out at 25 °C, for 8 hours at the constant polymer concentration using different oxidative agents in mildly basic medium, as following scheme:



The functionalized block-copolymers were investigated by Fourier Transform Infrared Spectroscopy (FT-IR), Differential Scanning Calorimetry (DSC), Dynamic Mechanical Analysis (DMA) and Thermogravimetric Analysis (TGA).

MODIFICATION OF PHYSICAL-MECHANICAL PROPERTIES BY THE PRESENCE OF
FLEXIBLE CHAINS IN EPOXY NETWORKS

*The National Institute for Research & Development in Chemistry and Petrochemistry –ICECHIM 202 Spl.
Independentei, 0060021, Bucharest, Romania*

LADANIUC Magdalena Adriana, DUMITRACHE Liviu, GABOR Raluca,

PAVEN Horia

Due to a large versatility, epoxy resins have many uses in various fields such as paints and varnishes, adhesives, casting and encapsulation resins, engineered materials and stabilizers[1, 2,3]. However, epoxy resins based on bisphenol A (DGEBA) have the disadvantage of a high rigidity. One of the ways to improve this feature is to introduce flexible chains in their molecular structure [4].

In this study as flexible structures were considered small polyether molecular chains. Depending on the molar ratio used resulted in two types of molecular structures including:

- terminal hydroxyl groups produced by the use of excess glycol;
- epoxy terminal groups produced by the use of excess resin.

Accordingly, by product were synthesized and the flexibility effect induced by them on three-dimensional epoxy network. Given the relatively high viscosity, modified epoxy resins were homogenized.

Hot diaminodiphenyl type hardener methane (DDM) and resin-hardener mixture was poured into teflon moulds, the specimen being crosslinked according to the temperature program as: 7h/60⁰C, and 7h/120⁰C. The samples obtained were physico-mechanical characterized (density, tensile strength, elongation, flexural strength, impact strength, hardness Shore) and were assessed against unmodified resin properties. Comparative analysis of physical-mechanical properties and DMA have found that the introduction of flexible chains in epoxy resin structure produces a variation of physical and mechanical characteristics as result of long chains of polyether and mixing ratio of weight concentrations.

It was also found that the physical and mechanical properties of the produced resins synthesized with terminal hydroxyl groups do not produce the same sharp decline as with epoxy resins epoxy terminal groups.²

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INORGANIC/ORGANIC HYBRID BASED ON KAOLIN POWDER WITH ORGANIC DERIVATIVES

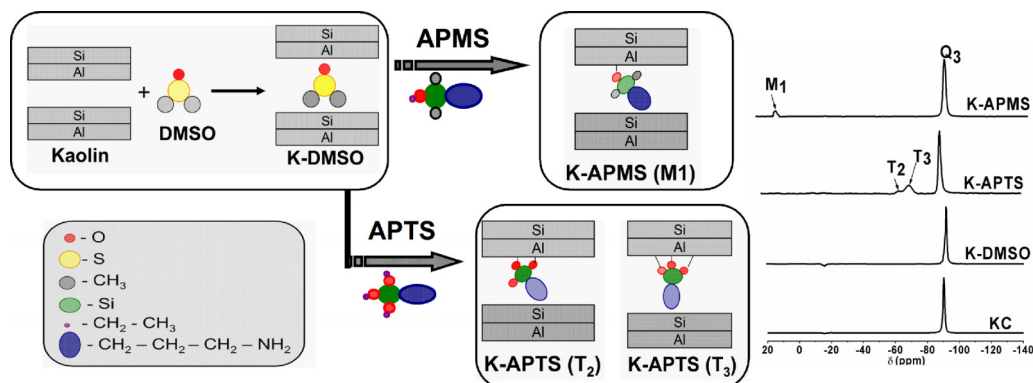
Anamaria Lungu¹, Francois-Xavier Perrin², Andrei Sarbu¹, Dan Donescu¹, Anita-Laura Ciripoiu¹, Mircea Teodorescu³

¹National Research-Development Institute for Chemistry and Petrochemistry-ICECHIM Bucharest, Splaiul Independentei 202, district 6, 060021 Bucharest, Romania

²University of South Toulon-Var, Laboratoire Matériaux Polymères Interfaces et Environnement Marin, BP 132, 83957 La Garde Cedex, France

³Polytechnic University, Department of Bioresources and Polymer Science, Calea Victoriei 149, 010072 Bucharest, Romania

The grafting and intercalation process of two types of aminosilanes: an amino trifunctional ethoxysilane (APTS) and an amino monofunctional ethoxysilane (APMS) on the kaolin (K), was performed using dimethyl sulfoxide (DMSO) as intermediate product intercalated onto kaolin pallets. The organofilization reaction of kaolin with amino monofunctional ethoxysilane (APMS) was investigated for the first time.



The inorganic-organic materials were analyzed by TGA/DTG, FTIR, XRD and NMR in order to verify the presence of both grafting and intercalation process. The results showed that the grafting/intercalation process was influenced by aminosilanes functionality. Different behaviours on organofilization reaction between APMS and APTS with kaolin sample pre-intercalated with DMSO molecules could be explained by the ability of APTS molecules to condense each other.. In case of organofilization reaction with APMS molecules it was not possible to lead to bridges between kaolin layers, therefore the intercalation of APMS molecules was as efficient as in cases of APTS molecules which exhibit a higher reactivity.

Polymer nanocomposites for public buildings floors

MARIN Laurentiu

MARIN Catalina

Institutul National de Cercetare – Dezvoltare pentru Chimie si Petrochimie

ICECHIM

Bucuresti, Splaiul Independentei nr. 202, sector 6, 060021

A public institution is a juridical entity in which the access of the persons is absolute free. Schools, city halls, councils, public order institutions, juridical courts, hospitals and dispensaries may be considered public institutions.

Public institutions have a specific characteristic: High pedestrian traffic values. So, in time, the floor can sustain an abrasive wear. In case of soft materials floors the abrasive phenomenon is more accentuated (ex. floors made of wood have short duty service due the low wood resistance). The concrete mosaic and metallic floors have a very good resistance but they became greasy in case of moisture or snow and can conduct to accidents.

The research proposal of this project is to realize floor coatings with high abrasion resistance, slipproof and fire proof characteristics for public institutions and for other places with high pedestrian traffic values based on polymer nanocomposites. These coatings are made at the working place and in short time can be used. The coatings can be used for repairing the damages of the old floors, to do new floors and to increase the slipproof characteristics of the metal and concrete mosaic floors and fire proof of wood floors.

The polymeric material selected for the coatings was the polyurethane. The polyurethane is a versatile material, which can be easily obtained in situ, and can achieve a large place of physical properties. With an adequate silicate can form interesting nanocomposites with new properties. The research team experience in polyurethanes was another motivation for polyurethanes choosing.

The nanocomposite polyurethane matrix / silicate was obtained starting from a modified phyllosilicate in which a polyurethane macrochain was built as a result of a polyaddition isocyanate / hydroxyl process.

THE INFLUENCE OF THE SILICATE EXFOLIATION DEGREE ON THE BIODEGRADABILITY OF SOME NANOCOMPOSITES BASED ON STARCH

Doina DIMONIE¹, PETRACHE Marius¹, GHIUREA Marius¹,
Celina DAMINA², Radu SOCOTEANU³, Sanda DONCEA¹,
RADOVICI Constantin¹, Luiza JECU¹, Liliana ANTON¹

¹ The National Research and Development Institute for Chemistry and Petrochemistry –
ICECHIM, 202 Spl. Independente, Bucharest, Romania

² Politehnica University Bucharest, 313 Spl. Independentei, Bucharest, Romania

³ "Ilie Murgulescu" Institute of Physical Chemistry, 202 Spl. Independentei,
Bucharest, Romania

The silicate exfoliation is a main topic in polymeric bio-nano-hybrids realising. Even often the silicate delamination at melt processing is realised, the procedure has many limits especially because of the polymers degradability. Therefore a silicate delamination procedure that can be applied before silicate incorporation, at melt processing, into the polymeric matrix was designed.

The paper present the influence of the exfoliation degree of multilayered silicate on the biodegradability of new nanocomposites based on starch. The results showed that the biodegradability (fig.1) is conditioned by the silicate exfoliation degree (fig.2) and after 21 days of biodegradation, the studied nanocomposites loose entirely the polymeric imprint (figs3,4).

Fig. 1

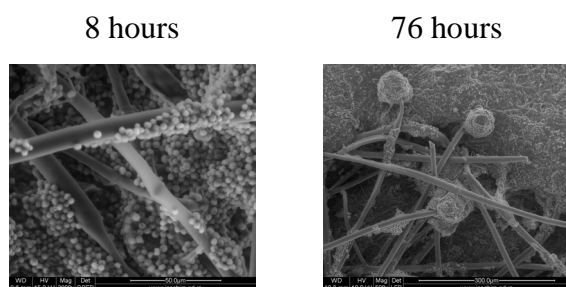


Fig. 3

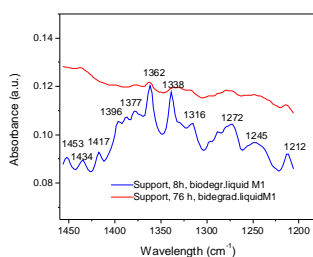


Fig. 2

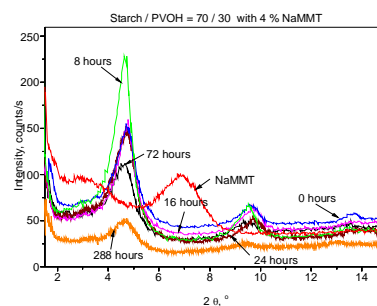
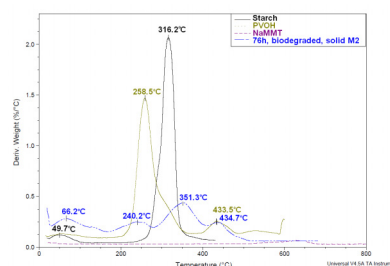


Fig. 4



Thermal stability of metalloporphyrins

Simona-Florentina POP, Rodica-Mariana ION

*Analysis Department, National R&D Institute for Chemistry and Petrochemistry – ICECHIM,
060021, Bucharest*

popsimfc@yahoo.com

Metalloporphyrins have relatively high thermal stability, which makes them attractive candidates for high temperature catalytic process [1]. Thermogravimetry (TGA) have been used to examine the thermochemistry, to study the thermal stability and thermal decomposition of the new complexes of porphyrins. The composition of these compounds were determined from the TGA curves. A systematic study of the stability of tetra-p-phenyl-porphyrin (TPP) and its metallic complexes with [Ni(II), Co(II), Mg(II), Ti(IV), W(VI) and VO(IV)] through thermogravimetry (TGA/DTG) has been carried out. Some informations about thermal stability, thermochemistry, and thermal decomposition of this materials, have been discussed.

Metal complexes derived from porphyrins are fairly stable to thermal and oxidative decomposition, and parameters of that process depend on the number of axial ligands. The central metal ions have some marked influence on the thermal stability of the compounds [2]. All these compounds are stable up to the temperature range 400-600 °C and decompose in an almost single major stage, which is used for kinetic parameters evaluation. In certain cases, a second minor decomposition stage is obtained.

Keywords: metalloporphyrins, thermal stability

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THE GRAFTING OF STYRENE-BUTADIENE ELASTOMERS BY RING-OPENING METATHESIS POLYMERIZATION (ROMP)

**Spurcaci Bogdan*, Ghioca Paul*, Iancu Lorena*, Coserea Ramona*,
Nicolae Cristian*, Gabor Raluca*, Raditoiu Valentin*,
Dragutan Valerian**, Dragutan Ileana****

** Institutul National de Cercetare- Dezvoltare pentru Chimie si Petrochimie – ICECHIM -
Bucuresti, Splaiul Independentei, Nr. 202, Sector 6, 060021, Bucuresti, Romania*

*** Centrul de Chimie Organica "Costin D. Nenitescu" al Academiei Romane, Splaiul
Independentei Nr. 202B, Sector 6, 71141 Bucuresti, Romania*

In the first step, some styrene-butadiene block-copolymers (SBS), with different vinyl content, were synthesized via anionic three stages sequential polymerization of monomers, in cyclohexane solution, initiated with n-butyl lithium.

The elastomer with vinyl groups content was controlled by introducing of different amounts of tetrahydrofurane in the polybutadiene block synthesis.

In the second step, the styrene-butadiene block-copolymers with different vinyl content, were grafted at vinyl groups by ring-opening metathesis polymerization (ROMP), with norbornene.



Grafting reactions by ROMP were performed in toluene, in the presence of Grubbs II catalyst (1,3-Bis-(2,4,6-trimethylphenyl)-2 (imidazolidinylidene) (dichlorophenylmethylene) (cyclododecene.tricyclohexylphosphine) ruthenium.

The grafted SBS block-copolymers were characterized by gel permeation chromatography (GPC), Fourier Transform Infrared Spectroscopy (FT-IR), differential scanning calorimetry (DSC), Nuclear Magnetic Resonance Spectroscopy (C^1 and C^{13} NMR), and thermo-gravimetric analysis (TGA).

STUDY OF THE INFLUENCE OF ETHYL ACRYLATE - BUTYL ACRYLATE COPOLYMER ON THE CHARACTERISTICS OF ROAD BITUMEN

Vasilievici Gabriel¹, Beica Vasilica², Bombos Mihaela³, Bombos Dorin¹

¹*Petroleum - Gas University of Ploiesti, 39 Calea Bucuresti, 100520, Ploiesti, Romania*

²*CESTRIN, 401A Iuliu Maniu, 061101, Bucharest, Romania*

³*National Institute for Research Development for Chemistry and Petrochemistry- ICECHIM-
Bucuresti, 202 Spl. Independetei, 060021, Bucharest, Romania*

The use of polymers for road bitumen modification is made in order to improve the performance and durability of roads, to reduce the frequency of road maintenance and to provide a longer service life³. The polymers used to modify bitumen include thermoplastic elastomers, thermoplastic and thermosetting polymers^{4,5,6,7,8}.

In this paper we studied the modification of a paving grade bitumen D50/70 with ethyl acrylate - butyl acrylate copolymer in order to improve main characteristics of bitumen.

Bitumen omogenization with copolymer was performed at four different concentrations of copolymer in an closed cylindrical vessel equipped with a stirrer for mixing and an electric heating system with automatic temperature range at 135°C for 3 h. Modified bitumens were characterized by determining the main characteristics of road bitumen: adhesiveness, penetration, softening point, ductility, Fraass breaking point and characteristics after aging .

The results indicated that bitumen modified with ethyl acrylate - butyl acrylate copolymer show better adhesion between bitumen and aggregate in the range 2...5% copolymer. The ageing properties of the modified bitumen were more pronounced at higher concentrations of polymer.

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NEW POLYPROPYLENE NANOCOMPOSITES BASED ON NON-COVALENTLY FUNCTIONALIZED CARBON NANOTUBES. STUDY OF PROPERTIES

Fulga TANASA, Madalina ZANOAGA

“Petru Poni” Institute of Macromolecular Chemistry, Iasi, Romania

41 A Grigore Ghica Voda Alley, Iasi, Romania

Non-covalent functionalization of carbon nanotubes (CNTs) is a promising approach in terms of improving CNTs dispersion. However, even if a good dispersion has been achieved in a specific polymer matrix by melt blending, co-precipitation or *in-situ* polymerization using unmodified CNTs, they are generally poorly dispersed within polymeric matrices, resulting in a slight improvement of composites properties.

Non-covalent functionalization of CNTs is, basically, a compatibilization and relies on the use of polymers bearing aromatic molecules able to undergo π - π stacking with the CNTs surface. This technique allows nanotubes to preserve their structure and electronic properties unmodified.

When the matrix is also functionalized, good results are expected. In example, polypropylene-graft-maleic anhydride (PP-g-MA) has been used as a compatibilizer to improve the unmodified CNTs dispersion within polymeric matrix¹⁻², but the conductivity improvement was not satisfactory.

Due to their ability to impart their properties to the corresponding composites, even at a low content, as consequence of their high aspect ratio, CNTs are used in various applications as compound/nanocomposite materials, electronic devices, nano(bio)sensors or gas storage materials, etc., they are all intensively investigated.

In this paper, we are introducing a new series of nanocomposites based on modified PP, namely PP-g-MA, grafted with aromatic moieties, namely aminomethylpyridine (AMP) or amino-pyrene derivative (Py-NH₂), able to interact with the surface of CNTs. In the case of Py-NH₂, the amine group serves to anchor the molecules by reaction with maleic anhydride functions of PP-g-MA. The effect of the dispersion method on the properties of the nanocomposites was studied by rheological and conductivity measurements. Experimental results showed that both compatibilizers were able to increase the conductivity of PP/CNTs nanocomposites.

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**STUDY ON THE INFLUENCE OF A LAYERED SILICATE ON THE THERMAL
AND MECHANICAL PROPERTIES OF NOVEL HYBRID COMPOSITES
BASED ON AN ALIPHATIC COPOLYAMIDE**

Madalina Zanoaga, Raluca Darie, Fulga Tanasa

“Petru Poni” Institute of Macromolecular Chemistry

41 A Grigore Ghica Voda Alley, Iasi, Romania

Aliphatic polyamides (nylons) are an important group of thermoplastics which find many new industrial applications due to their good processability, high mechanical strength and durability and excellent solvent resistance. Use of layered silicates (clays) as reinforcement has recently gained momentum for designing new polyamide composites endowed with a wide array of markedly enhanced properties. The enhanced properties of these hybrid composites include mechanical, thermal, barrier, and flammability and are related to the dispersion and nanostructure of the layered silicate in the polymer matrix.

The novelty of this work is the fact that we use a layered silicate from our region (a Romanian bentonite) and a random copolyamide. The effect of bentonite on composites properties was analyzed comparatively with a commercial layered silicate, namely Montmorillonite K 10.

A small amount of clay (5%) was used. Composites were prepared by melt compounding. The new hybrid composites were characterized by thermal and mechanical analysis. Properties of the polymer-clay composites were compared to those of neat copolyamide.

Thermogravimetry analysis indicated a similar thermal behavior between copolyamide and its hybrid composites. This can be attributed to interactions between polymer chains and the clay components.

The mechanical tests yielded in interesting and promising results. Addition of only 5% clay has led to a tremendous improvement in the stiffness of hybrid composites. Tensile tests indicated that the elastic modulus of hybrid composites increased with 44-48%, while the tensile strength was not significantly affected. The elongation at break of composites registered a spectacular increase: 252% (the samples become very ductile), while the ductility decreased when Montmorillonite K10 was used as additive.

Generally, data suggested that the Romanian clay can be used as a reinforcing additive in copolyamide hybrid composites with better results than Montmorillonite K10.

BIOSENSORS BASED IN TYROSINASE AND ELECTRON MEDIATORS FOR DETERMINATION OF ADRENALINE

D. Tutunaru¹, I.M. Apetrei¹, C.V. Popa (Ungureanu)², C. Apetrei³

¹*Faculty of Medicine and Pharmacy, "Dunarea de Jos" University of Galati*

²*Faculty of Food Science and Engineering, "Dunarea de Jos" University of Galati*

³*Department of Chemistry, Physics and Environment, Faculty of Sciences and Environment,
"Dunarea de Jos" University of Galati, 47 Domneasca Street, 800008 Galati, Romania.*

E-mail: apetreic@ugal.ro

Abstract

Adrenaline or epinephrine, a hormone secreted from the adrenal glands, is an important catecholamine for message transfer in mammalian central nervous systems [1]. It is present in nerve tissue and body fluids in the form of cations. Several studies show that numerous diseases are related to changes in its concentration [2]. The quantitative determination of adrenaline is of high importance in the areas of pharmacology and the life sciences.

This research reports tyrosinase (Ty) based biosensors using screen-printed electrodes modified with cobalt(II) phthalocyanine and Prussian blue, respectively, for the determination of adrenaline. The tyrosinase was immobilized onto the modified screen printed electrode by casting method followed by cross-linking with glutaraldehyde. The Ty catalyzes the oxidation of adrenaline to the corresponding o-quinone, which is electrochemically reduced at a potential of -0.220V vs. Ag/AgCl. The best analytical responses were obtained employing 340U/electrode and 0.1 M phosphate buffer solution (pH 7.0). The analytical curves were linear for adrenaline concentrations of $1.89 \cdot 10^{-6}$ to $1.22 \cdot 10^{-5}$ M. The recovery of adrenaline in pharmaceutical samples ranged from 98.5 to 100.7% and the results obtained using the developed biosensors are in agreement with those using the standard method.

Acknowledgments

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SERINE-PROTEASE INHIBITORS FROM NATURAL SOURCES, TO ACHIEVE ANTIALLERGIC PRODUCTS

**Authors: Andreea COZEA, Viorica CARABELA Georgeta ALEXANDRU,
Gabriel IVOPOL, Mihaela NEAGU, Natalita BORDEI**

S.C. HOFIGAL EXPORT IMPORT S.A. ¹Intrarea Serelor nr.2, sector 4, Bucharest, Romania, Research and
Development Departament

Risk of several types of skin allergies and eczema because of a group of enzymes, serine proteases, introduced in the human body from the outside, we decided to study a „antidote"-serine- protease inhibitors. In this case it was necessary to achieve products with the role of inhibitors of serine-protease from vegetal material for that have been studied a large vegetal material, especially seeds, knowing that it are the richest organs with serine-protease inhibitors.

Finally we chose flaxseed, to determine the content of serine-protease inhibitors, proteins, lipids, other possible enzymes (protease, amylase, lipase). Various methods for extractions have been applied to obtain higher values of serine-protease inhibitors and have been selected the best option. The complex of serine protease inhibitors was assessed by inhibition of an serine- protease, named trypsin, which was chosen as a model for the study. The kinetics of enzymatic reaction was followed by a rapid method using as substrate N-benzoyl-L-arginine-4-nitroaniline (BAPA) and inhibitory activity was determined starting from the diference between a trypsin solution activity and activity of the same trypsin solution at different times after addition of inhibitor. Trypsin acts on the substrate with the formation of 4-nitroaniline that have blue color which absorbs at $\lambda=405$ nm.

Based on the results obtained on the inhibition activity we studied a formula and a finished product dosage form for an external use gel. We selected plant extracts and essential oils with therapeutic properties able to potentiate the synergism antiallergic effect of serine protease inhibitors obtained.

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**BIOTRANSFORMATIONS WAY
TO KINETICS REACTIVITY FROM TIME**

Florin M. Dumitrescu

*Colegiul Tehnic „General David Praporgescu”
str. Taberei nr. 2, 145200, Tr. Măgurele – Teleorman*

Biotransformation is the chemical modification (or modifications) made by an organism on a chemical compound. If this modification ends in mineral compounds like CO_2 , NH_4^+ or H_2O , the biotransformation is called mineralisation. Biotransformation means chemical alteration of chemicals such as not limited to amino-acids, toxins, drugs in the body render nonpolar compounds polar they're not reabsorbed in renal tubules. Drug metabolism is example of a biotransformation typically the body deals with a foreign compound by making it more soluble, to increase the rate of its excretion; there are a number of different process that can occur; the pathways of drug metabolism can be divided into Ist, IInd phases. Phase I reaction includes oxidative, reductive and hydrolytic reactions a polar group is either introduced or unmasked, so the drug molecule becomes more water-soluble and can be excreted. Reactions are non-synthetic in generally produce water soluble, active metabolites of metabolites are generated by hydroxylating Cytochrome P450. Phase II reaction involve covalent attachment of small polar endogenous molecule such as glucuronic acid, sulfate, or glycine to form water-soluble compounds as a conjugation reaction final compounds have a larger molecular weight. Functional genomic and metagenomic approaches are increasing our understanding of the relative importance of different pathways and regulatory carbon flux environments and for particular compounds and they are accelerating the development of bioremediation technologies and biotransformation processes - enzymatic biotransformation.

Key words: *biotransformation, genomic – omic derivatives, pharmacokinetics*

COMPARATIVE DETERMINATIONS FOR CERTAIN PHYTOTHERAPEUTICAL SUBSTANCES FROM INDIGENOUS HERBS

Mihaela NEAGU¹, Luntraru V.¹, N. Bordei¹, A., Cozea¹, G.A. Traistaru¹

¹ *S.C. HOFIGAL EXPORT IMPORT S.A. Serelor no.2, sector 4, Bucharest, Romania,
Research and Development Departament*

This paper presents physical-chemical analysis of extracts from some fruit of indigenous medicinal plants for their added value in phytotherapy for heart disease preparations (food supplements), for improving of blood circulation. Studied fruits were: chokeberry (*Aronia melanocarpa*), rosehip (*Rosa canina*), bilberry (*Vaccinium myrtillus*) and hawthorn (*Crateagus monogyna*), with high content in antioxidant activity compounds. The main compounds studied in these papers are: flavones, phenols and anthocyanins. Fruit extracts studied are important sources of antioxidants.

Oxidative stress is involved in developing of many chronic diseases such as cardiovascular disease, neurodegenerative disorders, inflammatory arthritis, autoimmune diseases, diabetes, ageing and even cancer. In modern society the risk under oxidative stress is high, so we really need powerful protection against it, achieved through an adequate consumption of antioxidants in diet (fruits and vegetables) or dietary supplements.

Following research conducted by authors experimental results showed increased anthocyanin content in all analyzed fruits. Thus: extracts from the fruit of chokeberry, rosehip, hawthorn and bilberry with large amounts of anthocyanins, proanthocyanins and other antioxidant activity compounds with beneficial effects for the heart and arteries contribute effectively for improving health, especially in cardiovascular diseases, improving elasticity of blood vessels. The three extracts can be combined in certain proportions, within certain pharmaceutical formulations with high antioxidant activity, mainly for cardiovascular and eye disease.

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NEW FUNGAL POLYSACCHARIDES WITH ANTITUMOR PROPERTIES

Ioana Nicu, Gheorghe Stoian

Department of Biochemistry and Molecular Biology, Faculty of Biology, University of Bucharest, no. 91-95, Splaiul Independentei, sector 5, postal code 050095, Bucharest, Romania.

Fungal polysaccharides have been studied for many years, especially in countries like Japan or China where mushrooms were used in traditional medicine in the treatment of hepatitis, hypercholesterolemia and cancer¹. Those studies showed also, that many polysaccharides possess antitumor properties and have a low cytotoxic effect on normal tissues². Therefore, we investigated the biological effects of some new compounds isolated from two species of edible mushrooms that are native to our country. Thus, we extracted polysaccharides from *Cantharellus cibarius* and *Craterellus cornucopioides*, the first one came from Covasna County and was harvested in June, 2011 while the latest was purchased from Carnic prod SRL Târgoviște.

Polysaccharides were obtained using the protocol described by Mizuno et al.³; their purity and molecular mass were determined using liquid chromatography and their sugar content was assayed by TLC after trifluoroacetic acid (TFA) hydrolysis. Caco-2 cell line (an epithelium adenocarcinoma cells) was used in order to determine antitumor effects of this new compounds.

Our research concluded that these two polysaccharides have similar molecular weight; they contain glucose and arabinose, are resistant to hydrolysis with sulfuric acid, but are easily hydrolyzed with TFA.

MTT tests showed that both polysaccharides possess maximum of antitumor effects on Caco-2 cell line after 48 h at 1 mg/ml (*Cantharellus cibarius*) and 0.2 mg/ml (*Craterellus cornucopioides*) respectively.

Stable dispersion of MWNTs in water and synthesis of polyaniline/MWNTs composites

QUEINY Cynthia*, BERLIOZ Sophie, PERRIN François-Xavier
Laboratoire MAPIEM, Université du Sud Toulon Var,
France, Avenue Georges Pompidou, 83162 La Valette-Cedex

Substantial van der Waals attraction between carbon nanotubes makes difficult to achieve a good dispersion in water. To obtain dispersions of individual carbon nanotubes, which were initially in bundles, covalent and noncovalent methods were adopted. Covalent methods involve functionalization of the carbon nanotubes with chemical groups (generally COOH) to improve their solubility in different solvents. However, these processes damage and scatter the nanotubes; defects *are* created and consequently the electrical and mechanical properties of *carbon* nanotubes were altered¹⁹. Noncovalent methods imply the use of surfactants that adsorb onto the nanotube surface via π - π stacking or hydrophobic interactions. This method keeps carbon nanotubes intact, thus their mechanical properties should not change and surfactants can be easily removed by washing. That's why; first of all, we report here *a* facile approach to *a* noncovalent dispersion of MWNTs by using amphiphilic phosphonic acids *as* surfactants.

Once the MWNTs *are* dispersed, we envisaged the synthesis of polyaniline and multiwall carbon nanotubes coated polyaniline via an *in situ static* interfacial polymerization technique. The structure and morphology of the binary composites have been investigated by *a* variety of techniques including scanning electron microscopy SEM, transmission electron microscopy TEM, thermogravimetric analysis TGA, fourier transform infrared spectroscopy FTIR, ultraviolet-visible spectroscopy UV-Vis, Raman spectroscopy and X-ray diffraction XRD.

* contact : oueiny@univ-tln.fr

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SYNTHESIS AND ANTIBACTERIAL ACTIVITY OF QUINOLONE DERIVATIVES

PINTILIE Lucia¹, NITA Sultana¹, CAPROIU Miron Teodor²,

DIACONU Alexandra¹, NEGUT Catalina¹, TANASE Constantin¹, COCU Florea¹

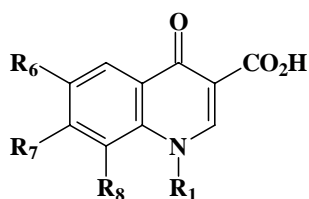
¹ *National Institute for Chemical-Pharmaceutical Research and Development, 112 Vitan Av., 74373 Bucharest 3, Romania*

² *Organic Chemistry Center "C.D.Nenitescu", 202 B Splaiul Independentei, Bucharest 6, Romania.*

The discovery of fluoroquinolones after 1980 represented a decisive step forward for chemical anti-infectious therapy. A large number of fluoroquinolones are used today in medical practices and some of them are deemed by leading pharmacologists to be of vital importance to anti-infectious therapy. The research for an ideal quinolone continues worldwide. Such a quinolone must be biologically active on a large spectrum of gram positive and gram negative bacteria, aerobic and anaerobic germs and mycobacteria, must have as few side effects as possible, excellent solubility in water and to be taken in orally.

The goal of our reserch work was to obtaine by synthesis new quinolone derivatives with the general formula:

Figure 1



R₁ = alkyl, *p*-nitro-phenyl, *p*-amino-phenyl;

R₆ = hydrogen, fluor, chlor, methyl

R₇ = heterocycle;

R₈ = hydrogen, chlor.

The novel quinolones was evaluated for „in vitro” activity by determining minimum inhibitory concentration against a variety of bacteria. In conclusion, the results of the present paper indicate that substituent combinations in the quinolone ring might produce powerful antibacterial agents.

NEW POLYMERIC MATERIALS WITH ANTIMICROBIAL PROPERTIES BASED ON STYRENE-BUTADIENE COPOLYMERS GRAFTED WITH METHACRYLIC ACID AND AMPICILLIN

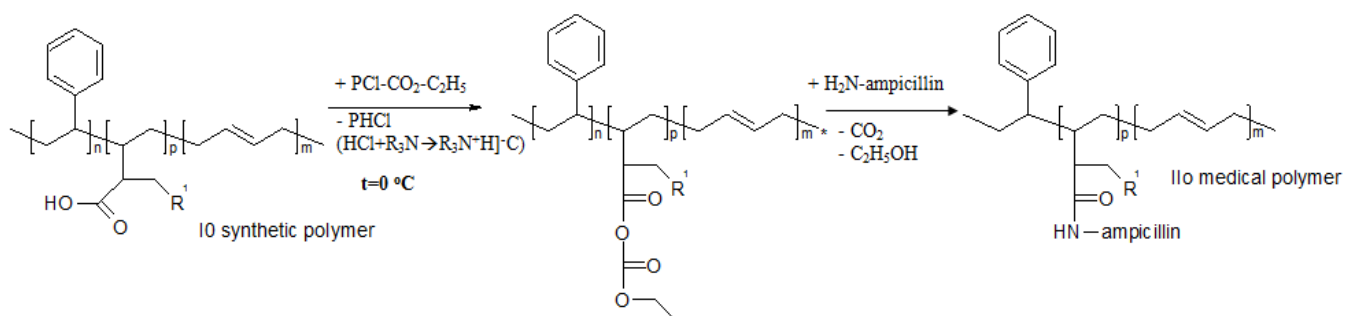
ROBU Stefan¹, FILIP Vitalie¹, GHIOCA Paul², SPURCACIU Bogdan², IANCU Lorena², COSEREA Ramona², PRISACARI Viorel³

¹ *Universitatea de Stat din Moldova, str. A. Mateevici, 60, MD-2012, Chisinau R. Moldova;*

² *Institutul National de Cercetare-Dezvoltare pentru Chimie si Petrochimie ICECHIM, Spl. Independenței, 202, Sector 6, Bucuresti,*

³ *Universitatea de Stat de Medicină “N. Testemiteanu”, Bd. Stefan cel Mare 165, Chisinau, R. Moldova.*

Many papers published in the last years literature were dedicated to the research of medical polymers with prolonged effect and of polymers with antimicrobial, antifungal and other properties^{10, 11}. In order to develop new medical polymers, the butadiene-styrene copolymers (SBS) synthesized in ICECHIM Research Institute were grafted with methacrylic acid and then coupled with antibiotics from ampicillin group as following:



The coupling reaction of SBS copolymer (M=89000) with methacrylic acid was achieved at 80 °C in the presence of azobisisobutyronitrile (AIBN) as initiator. Grafted polymer purification was performed by sedimentation in methanol. The polymer-analogue transformation of SBS-ACM copolymer with ampicillin was realized at 0 °C with ethyl chloroformate. The purification was made in diethyl ether. IR spectroscopy and elemental analysis were used to confirm the structure of the support polymer SBS-ACM (I₀) and of the medical one (II₀). The bacteriological tests demonstrated the high antimicrobial effect towards gram-positive and gram-negative microorganisms and the fact that the new material can be used for shaping objects with clinical uses.

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NEW POLYSACCHARIDES WITH ALKALINE PHOSPHATASE MODULATORS EFFECT

**Mădălina STĂICULESCU, Ioana NICU, Cristina STURZOIU, Gheorghe
STOIAN**

*Department of Biochemistry and Molecular Biology, Faculty of Biology, University of
Bucharest, 91-95, Splaiul Independentei, sect. 5, Bucharest, ROMANIA*

Alkaline phosphatases (EC 3.1.3.1), a group of dimeric enzymes¹, have an important role in intestinal homeostasis and exists in three major forms: intestinal, placental and tissue non-specific. These enzymes are involved in phosphomonoesters hydrolysis, in breakdown of dietary cholesterol and also in calcium absorption². Phosphatase expression and activity can be modulated by some nutrition compounds, such as carbohydrates³. Literature data showed that some polysaccharides have demonstrated prebiotic effect *in vitro* and *in vivo* ⁴. The aim of our researches was to evaluate two new polysaccharides modulating agents for phosphatase activity in Cobb's 500 hybrid broilers and Wistar rats' small intestines. In this context we used a β (2-1) polysaccharide (inulin) and a β (2-6) microbial polysaccharide (levan), the last one produced by a nonpathogenic Gram negative bacterium, *Z. mobilis*. We analyzed this particular enzyme from duodenum, jejunum and ileum after inulin or bacterial levan (2 mg/mL) treatment.

Our results showed a significantly enzymatic activation effect on intestine Wistar rats, especially on ileum segment by both polysaccharides, more than 170% and 70%, respectively comparative with control. On the other hand, alkaline phosphatase from broilers small intestine was activated in duodenum and jejunum segment only by inulin; ileum alkaline phosphates were 50% activated by microbial levan. Such modulation comportment can be explained by the interaction between polysaccharides and enzymes and its effect therefore enhance enzyme activity.

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HIGH PROTEIN SOLUBILISATION IN MICELLAR WATER-PROTIC IONIC LIQUID SYSTEM

Claudia Simona Stefan¹ and Mérièm Anouti²

¹University "Dunarea de Jos", Faculty of Food Science and Engineering, Galati, Romania

²Université François Rabelais, PCM2E Laboratory (EA 6296), 37200 Tours, France

The solubility of proteins plays a key role in industrial processes of the pharmaceutical and food industries. Proteins have low solubility in water and dehydration of aqueous solution containing the protein macromolecules leads to destruction of protein structure. Recently, ionic liquids have become very popular green solvents used in biochemical process such as separation and purification of the protein by crystallisation [1,3,4], in biocatalysis and in the pharmaceutical industry. ILs can be broadly classified into two groups, protic and aprotic ILs. Protic ionic liquids (PILs) are synthesized by proton transfer from a Brønsted acid to a Brønsted base, which creates proton donor and acceptor sites and can lead to the formation of hydrogen bonds. This research is focus on a protic ionic liquid based on pyrrolidinium [Pyr]⁺ cation and carboxylate [C_nH_{2n+1} COO]⁻ anion with length chain which process micellar properties in mixture with water [2]. We have chosen as target protein the well-known hen egg white lysozyme (Ly). Results of this study shown that this media can be solubilised great quantities of protein. Many experimental method as dynamic light scattering, transmission electron microscopy (Figure), differential scanning calorimetry and rheological measurements were used to better understand the higher solubility of lysozyme in pIL than in water.

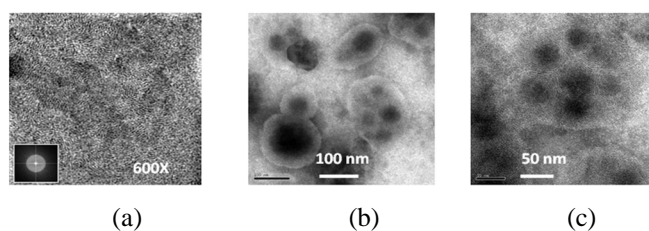


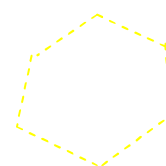
Figure: Transmission electron micrographs of lamellar structure for pure protic ionic liquid in absence of lysozyme (a) and binary [Pyr]⁺[COO]⁻(aq)/Ly mixture (b) and (c).

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**CERCETAREA COMPOZITIEI CHIMICE A FRUCTELOR, FRUNZELOR SI A
RAMURILOR TINERE CU MUGURI SI FLORI DE PADUCEL, DIN ZONA
BALCANICA SI ROMANIA, IN VEDEREA VALORIFICARII LOR
MAI EFICIENTE IN FITOTERAPIE**

**¹MANEA Stefan, Viorica TAMAS, Mihaela NEAGU, Gina TRAISTARU, Andreea
COZEA,**

²Elda MARKU, Lulezim SHUKA

¹S.C. HOFIGAL EXPORT IMPORT S.A. ¹Intrarea Serelor nr.2, sector 4, Bucharest,
Romania, Research and Development Departament

²TIRANA University, Faculty of Natural Science, Boulevardi "Zogu I, Tirana, Albania

In the context of the importance of phytotherapy, but also due to climate changes and increased pollution, the quality of medicinal plants as raw material is essential. The authors of the study chose hawthorn (*Crataegus monogyna*) spontaneous flora from Albania and Romania, as one of the most used herbs for the cardiovascular and nervous system. Considering Albania as having a favourable Balkan climate, we have researched in parallel the same organs of *Crataegus monogyna* from both countries, collected in 2011, dried in controlled conditions (max 40°C) finely ground and analysed in terms of their main phytotherapeutic compounds.

The main phytotherapeutic compounds determined were: total flavones, anthocyanins and proanthocyanins, polyphenolcarboxylic acids, tannins, ascorbic acid, crataegic and ursolic acids, and two groups of enzymes - (oxido-reductases and hydrolases). The antioxidant activity was also determined and as essential nutrients (total proteins, lipids, carbohydrates, minerals).

The methods used are in the current edition of Ph. Eur and Ph. Rom Xth ed. and for the identification of other compounds we used chromatographic methods (TLC) and methods of dosing of chemicals pesticides (HPLC). Much interesting data was obtained from this complex study and is very useful for both countries to use such as plant material, based on good scientific knowledge, to obtain new natural preparations for cardiovascular diseases. The full paper presents in detail, the comparative studies for the plant material described in tables and charts for the results of all mentioned plant material from both countries.

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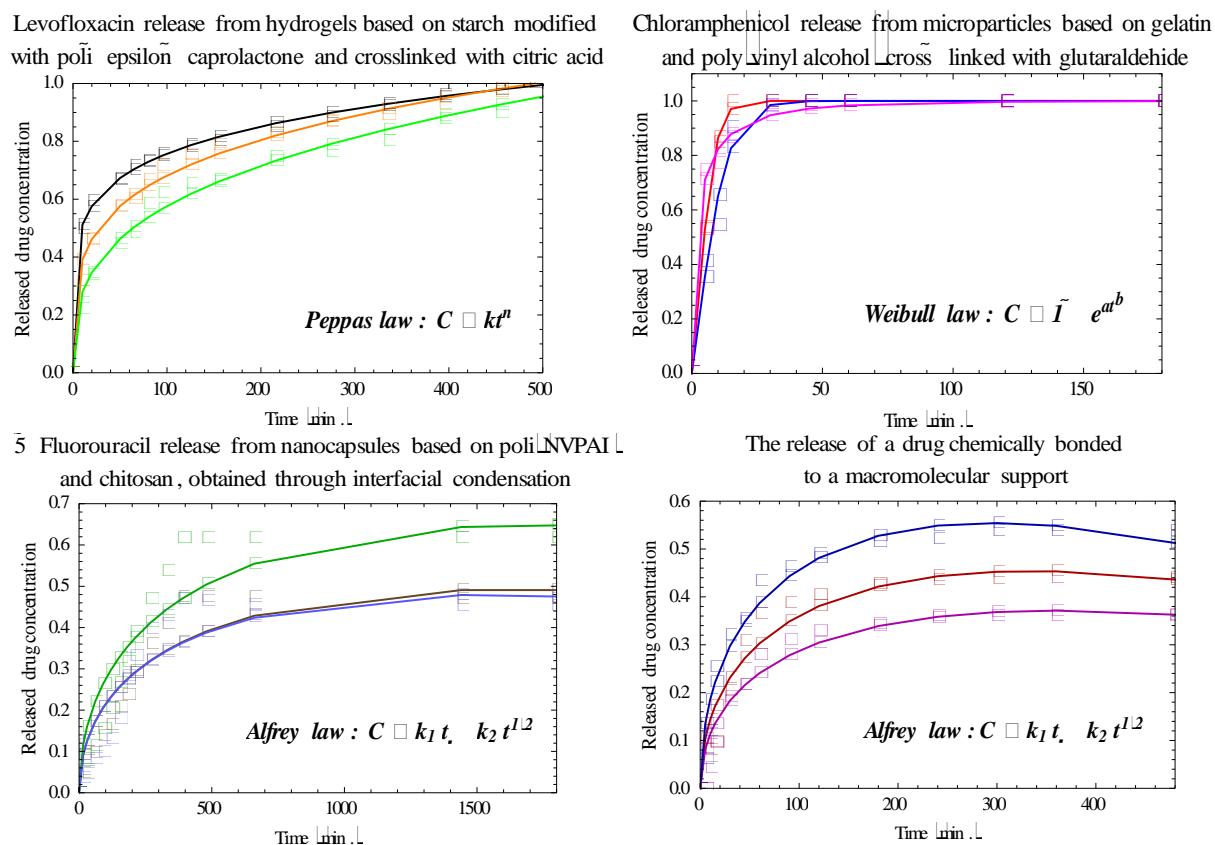
NONLINEAR POWER TYPE LAWS – UNIVERSAL CHARACTERISTIC OF DRUG RELEASE FROM POLYMER MATRICES

Simona Bacaita, Ancuta Uliniuc, Catalina Peptu, Delia Iurea, Radita Aparaschivei, M. Popa

Faculty of Chemical Engineering and Environmental Protection, "Gheorghe Asachi"

Technical University of Iasi, Prof. dr. docent Dimitrie Mangeron Rd., No. 73, Iasi, Romania

The polymer matrices as drug carriers have the property of controlled release. The analyses of the laws that govern the release have shown that these are power type laws or their derivatives. This fact indicates the existence of some self-structuring processes in which the system finds its own evolution path towards a stable equilibrium state, the difference being the system constants. Some examples are presented in Figs.1., where the filled point are the experimental ones and the joined empty point are the theoretical ones.



Figs. 1. Release kinetics for different kind of drug loaded polymer matrices

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NATURAL SANOGENETIC FOOD SUPPLEMENTS - MEDICAL JELLY

Authors: V. Tamas, N. Bordei, A. Cozea.

*¹S.C. HOFIGAL EXPORT IMPORT S.A. ¹Intrarea Serelor No. 2, Sector 4, Bucharest,
Romania, Research and Development Department*

The authors have realized based on honey and plant extracts with sanogenetic properties, new formulas and presentation forms for natural supplements.

The objective is to find an more agreeable alternative for consumption – jelly, compared to traditional formulations (tablets, capsules, etc.) simultaneously having beneficial effects, specific for health. Between several formulas studied was considered to be of general interest two products: jellies for prevention, amelioration and treatment of various forms of cold, cough, laryngitis, pharyngitis, etc.. and jellies with calming effect, sedative, for stress reducing and for improve quality of sleep.

Jellies for the relief of colds, hoarseness etc. contain in their composition some fruit juice concentrates, extracts of Echinacea and vitamin C, with antioxidant effect and to stimulate local immunity, and essential oils of sage and eucalyptus with antiseptic effect, which helps reducing infections and together with other components of the formula increases the capacity of the body's defense against cold weather illnesses. Jellies with calming effect have in their composition concentrated elderflower extracts, St. John,s wort, hawthorn fruit and lavender essential oil. Absorption of all active substances in sanogenetic products are described by synergism between compounds and medicinal plant extracts compounds from honey, and cause specific beneficial effects for humans.

Food supplements made jellies contain no synthetic additives and it are made exclusively with natural flavor extracts.

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NEW RESEARCH IN OBTAINING OF COSMETIC PRODUCTS BASED ON NATURAL INGREDIENTS WITH PROTECTIVE, REGENERATIVE AND BEAUTY CARE EFFECTS ON SKIN AND HAIR

Stefan MANEA¹, Viorica TAMAS¹, Viorica CARABELA¹, Georgeta ALEXANDRU¹

¹ S.C. HOFIGAL EXPORT IMPORT S.A. Serelor no.2, sector 4, Bucharest, Romania,
Research and Development Departament

Scientific research undertaken in skin and hair physiology have brought a substantial scientific information on nutritional and regenerating potential of api and phyto compounds in the development of new natural and organic cosmetics

Thus, results of studies and clinical trials of propolis, one of the most amazing natural products that bees give us, have demonstrated multiple possibilities for use in: food, cosmetics, pharmaceuticals and apitherapy.

The chemical composition of raw propolis have been reported mostly: resins, waxes, essential oils, pollen, carbohydrates, amino acids, vitamins, enzymes, minerals and impurities. The most important pharmacologically active constituents of propolis are: flavonoids in the group which come flavones, flavonols, flavonoids, and various phenolic and aromatic compounds which are antibacterial, antifungal, anti-inflammatory, antitumor, antioxidant and analgesics.

At the same time, the variety and complexity of extracts from medicinal and aromatic fresh plants rich in nutrients with high efficiency for epithelial tissue as in antioxidant and antimicrobial compounds , growing interest for new beauty products.

Beginning from content and bioactive properties of propolis and from the possible synergism with certain herbal extracts, the Hofigal company proposed to develop new effective preparations of skin and hair care .

This products content a complex biologically active based on propolis and a few natural ingredients from herbal extracts such as: natural oils (flax, sea buckthorn, milk thistle, hemp), essential oils (lavender, sage, basil, mint, rosemary, eucalyptus), plant extracts (aloe, marigold, liquorice, dandelion, birch sap), gemmoderivates, concentrate juices.

The new offer of our cosmetics is:

- Skin and eye creams: moisturizes, nourishing, protective and regenerative;
- Lotion against hair loss;
- Solid lip care creams.
- Gels and mouthwash hygiene and dental care for the teeth area;

Extremely rich in trace elements, amino acids, polysaccharides, polyphenols, vitamins, enzymes, carotenoids, grows factors it provides energy, hydration, and protection against cellular aging. The new products that we realized satisfy the entire ecological concept through plant material used: renewable, without toxicity, with protective and regenerative effect of skin tissue exposed to pollutants

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LUMINESCENCE STUDIES ON LUMINOL IN DIFFERENT ENVIRONMENTS

Alexandru Chivulescu, Emilia Ocnaru, Melania Arsene, Mihaela Badea-Doni

*National Research & Development Institute for Chemistry & Petrochemistry - ICECHIM,
Biotechnology Department, Spl. Independentei 202, Bucharest, ROMANIA*

Luminescence techniques, especially chemiluminescence (CL), have evolved in the last few years especially due to their sensitivity and simplicity. However, there are still some problems when applied to real samples, due to their poor selectivity. An interesting alternative may be the reversed micellar (RM) medium [1, 2]. Reverse micelles are self-organized aggregates formed by surfactants in organic solvent, and nanometer sized water pools are formed by the solubilization of water in their polar cores. The observations that denaturation of proteins can be prevented in reverse micelles have spurred even more interest in the application of these self-organized multi-molecular assemblies as either drug delivery carriers or life-mimicking systems. When performed in RM medium, the selectivity and also the sensitivity of CL reactions can be dramatically improved due to the bioseparation capability of the reversed micelles.

Studies regarding the fluorescence and chemiluminescence of luminol in different environments have been conducted. These include aqueous media, at several pH values, as well as RM medium (AOT – iso-octane). Luminol solutions with pH ranging from 7 to 13 were tested in regards to the excitation spectra, and two absorption bands were observed for all the above: one in the 260 nm region and another around 380 nm. Emission FL spectra were also recorded, for each of the two excitation wavelengths, and a correlation was developed between the fluorescence intensity and the pH value. Furthermore, fluorescence emission following the luminol reaction with hydrogen peroxide in presence of potassium ferricyanide was studied. The enhancing effect of reverse micelle environment on the fluorescence intensity of luminol was also tested.

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THE STUDY OF PROLONGATION EFFECT OF SOME ANTITUBERCULOUS POLIMERIC DRUGS BASED ON N-VINYLPYRROLIDONE AND OTHER

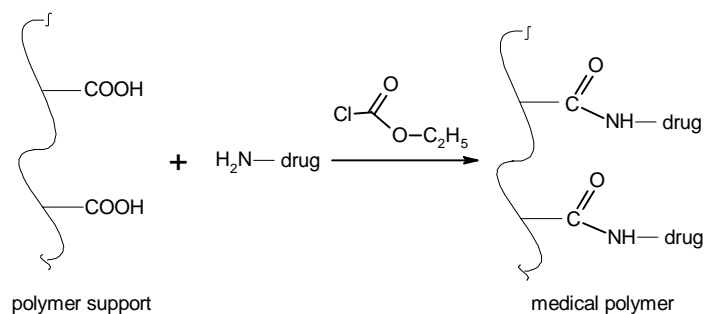
Ivancic Albert, Duca Gheorghe, Brînză Diana, Robu Ștefan

State University of Moldova, 60, Mateevici str., MD 2009,

Chisinau, Republic of Moldova

Analysis of the scientific data has shown that the number of articles dedicated to obtaining of polymeric antituberculous drugs with prolonged effect has increased lately. Commonly, these medicinal products are less toxic and manifest biological activity for a longer time compared with the micromolecular drugs. Therefore, in order to obtain new polymeric antituberculous drugs, the copolymers of N-vinylpyrrolidone with methacrylic acid or dextran were coupled with the antituberculous substances such as isoniazid, streptomycin, and other.

The synthesis and purification of medicinal polymeric substances were accomplished with ethyl chloro formate according to the scheme:



Chemical structure of conjugated polymers with isoniazid and streptomycin was confirmed by IR-spectroscopy, which demonstrated the appearance of new vibrations: $\nu=3200$ cm⁻¹ and other, due to formation of peptidic group $\text{—}\overset{\text{O}}{\parallel}{\text{C}}\text{—NH—}$.

The study of prolongation effect has been performed using the method of dialysis of aqueous solutions through a semipermeable cellophane membrane. According to this method, the drug released by polymer in aqueous medium pass through membrane into a aqueous medium. The transition of drug to the water has been detected using UV-spectra in the wavelength range 200-300nm.

It has been found that unlinked isoniazid passes through the semipermeable film for 20-30 min, while the diluted copolymer solutions - up to several hours. Slow detachment of the antituberculous drug from the polymer support can be the cause of the phenomenon .

ELECTROCHEMISTRY AND DETECTION OF LIPOIC ACID

Mariana Marin¹, Cecilia Lete¹, Bogdan Manolescu² and Mihaela Badea Doni³

¹*Romanian Academy, Institute of Physical Chemistry, Bucharest,
Romania, mariana_marin12@yahoo.com*

²*University Politehnica of Bucharest, Faculty of Applied Chemistry and Materials Sciences,
Department of Organic Chemistry, Bucharest, Romania*

³*National Research –Development Institute for Chemistry and Petrochemistry, ICECHIM,
Department of Biotechnology, Splaiul Independentei, 202, 061821 Bucharest, Romania*

α -Lipoic acid ((*R*)-5-(1,2-dithiolan-3-yl)pentanoic acid) is a disulphide derivative of octanoic acid with strong antioxidant properties. In the human body the lipoic acid **LA** is reduced to dihydrolipoic acid (**DHLA**). Both oxidized and reduced forms of LA diminish the oxidative stress by scavenging of reactive oxygen species (**ROS**), nitric oxygen species (**RNOS**) or by metal chelating. Moreover, the LA can regenerate other endogenous antioxidants, such as glutathione, vitamin C and vitamin E. The influence of pH on electrochemical oxidation of LA at platinum electrodes using cyclic voltammetry and differential pulse voltammetry was studied. The response of the platinum electrode towards LA was founded to be linear within concentration range 50 and 800 μ M. The obtained sensitivity of platinum electrode for LA was $4.17 \times 10^{-7} \text{ A}/\mu\text{M}$.

DETERMINATION OF HEAVY METALS IN TEA INFUSIONS BY ION CHROMATOGRAPHY

Iulian MINCA^{1,2}, Ana Maria JOSCEANU², Cornelia GURAN², Mariana MATEESCU¹,
BACALUM FANICA¹, SARBU LILIANA¹

¹National Research & Development Institute for Chemistry and Petrochemistry ICECHIM, Bucharest, Romania.

²University Politehnica of Bucharest, Department of Inorganic Chemistry, Physical Chemistry and
Electrochemistry, 1-5 Gheorghe Polizu Street, Sector 1, Bucharest, Romania.

Tea is one of the most popular beverages in the world [1]. Tea plays a major role in terms of the intake of a number of nutritional trace elements in humans and can be beneficial to health or may have an adverse effect if present in large amounts [2]. The presence of trace elements in tea plant depends mainly on soil composition in which are grown, atmospheric agents and the degree of pollution is pollution.

A ion chromatograph Dionex ICS 3000 system with UV detection by vis detection at 530 nm and means of post column derivatisation with 2-(4-pyridylazo resorcinol), was employed for quantification of heavy metals content in black, white and green tea infusions, such as Cd^{2+} , Ni^{2+} , Zn^{2+} , Cu^{2+} and Co^{2+} with minimum sample pre-treatment [3].

Items that are in the ppm level in commercial tea bags: Cd is found in high concentrations (2.36 and 8.16 ppm in black, white and green tea).

On the other hand, the amounts of Zn, Cu, Co and Ni are much lower, as expected. Elements have a concentration range of ppb. The sum of these elements should be monitored for possible adverse effects on the body. The values for cations of Zn^{2+} , Cu^{2+} and Co^{2+} in samples green, white and black tea are: 12.60 to 154.79 ppb, 34.50 to 104.12 ppb and respectively 0 to 254.81 ppb. Also from experimental data resulted that values for cations of Ni^{2+} are lower: 0 and 24.69 ppb. Elements such as Co are considered powerful and toxic pollutants, and are found in low concentrations. The reported heavy metals content is comparable to previously reported results in literature [4].

The proposed method has several advantages over other quality recommended monitoring methods: analysis is achieved in a shorter time, with good resolution, displaying higher sensitivity, and lower detection limits.

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REGISTRATION FORM Priochem 8:

Name: MUSARAJ Adanela

Scientific title / position: Dr.

Institution: University of Durres

Institution Address: CURRILA

Phone:

Email: adanela.musaraj@yahoo.fr

Fax:

Wish to participate: - Please choose -

Paper Type: poster

Section: Chemistry in medical and pharmaceutical applications

Paper Title: A combined NMR and molecular dynamics stimulation study to determine properties of antagonists against experimental autoimmune lupus erythematoses

Authors: Adanela Musaraj, Suela Kelliçi, Vahe Mokin, Tahsin Kelliçi

THE DEPENDENCE OF THE CROSSLINKING TIME IN THE IONOTROPIC ALGINATE HYDROGELS OBTAINING BY THE CONTROL METHOD OF CALCIUM IONS LOCAL CONCENTRATION

Doina DIMONIE¹, Inna TRANDAFIR¹, Marius PETRACHE¹, Raluca GABOR¹, Cristian NICOLAE¹, Radu FIERASCU¹, Anisoara CIMPEAN², Roxana TRUSCA³, Simona POP¹, Liliana ANTON¹

¹ *The National Research and Development Institute for Chemistry and Petrochemistry – ICECHIM, Spl. Independentei, 202, Bucharest, Romania*

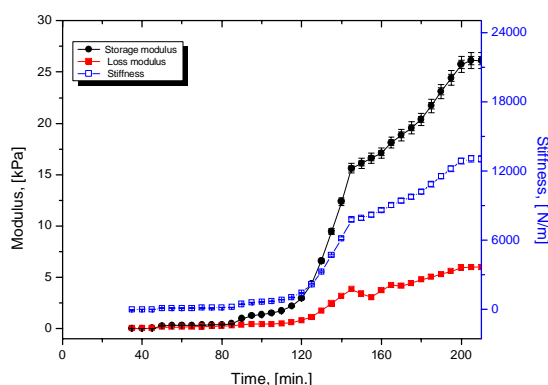
² *Bucharest University, 36-46 Mihail Kogalniceanu Blvd., Bucharest, Romania*

³ *Metav Research and Development, C.A. Rosseti Str., Bucharest, Romania*

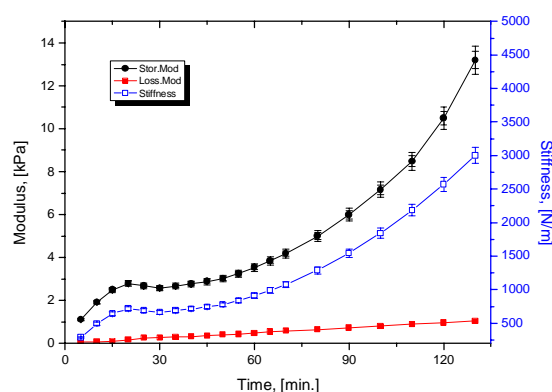
Sodium alginate based hydrogels, mainly obtained by ionic crosslinking, have been widely used in a variety of biomedical applications. Ionic crosslinking is most often realized with calcium cations (Ca^{2+}) which react with the alginate guluronate blocks. Since this reaction takes place with high-rate, in uncontrollable manner, the resulted hydrogel are irregular rigid, pearls that cannot be modeled for different applications. The study compared the obtaining of thin layer shaped sodium alginate hydrogels through the following two different methods: a) "in situ" chemical generation of calcium ions, and b) diffusion – controlled migration of calcium ions into the reaction medium.

The obtained results show that the two procedures present the following characteristics:

1. The values of all dynamic - mechanical properties are significantly higher if the hydrogels is obtained by diffusion controlled method;
2. The gelling process according to diffusion controlled method, systematically runs with induction period (Fig.1.a). The induction period is absent in case of the in situ generation of crosslinker, regardless the way of crosslinker formation (Fig.1.b).



a)



b)

Fig. 1

THE MECHANISM OF THE CALCIUM IONS MIGRATION IN THE IONOTROPIC ALGINATE HYDROGELS OBTAINED ACCORDING TO THE CONTROLLED FICKIAN DIFFUSION METHOD

Doina DIMONIE¹, Inna TRANDAFIR¹, Marius PETRACHE¹, Anisoara CIMPEAN², Eugeniu VASILE³, Roxana TRUSCA³, Radu FIERASCU¹, Liliana ANTON¹

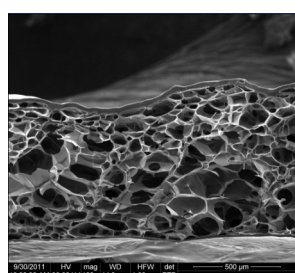
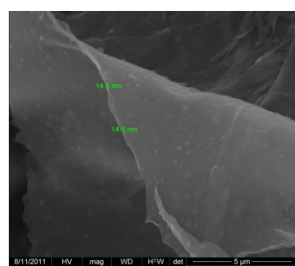
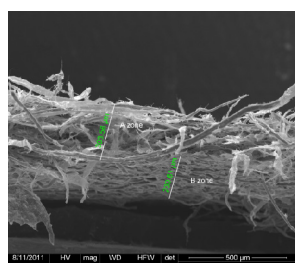
¹ *The National Research and Development Institute for Chemistry and Petrochemistry – ICECHIM, Spl. Independentei, 202, Bucharest, Romania*

² *Bucharest University, 36-46 Mihail Kogalniceanu Blvd., Bucharest, Romania*

³ *Metav Research and Development, C.A. Rosseti Str., Bucharest, Romania*

The diffusion controlled migration of calcium ions inside the reaction medium through a filter paper, with selected porosity is a good method to get ionotropic layered shaped alginate hydrogels for adipose tissue regeneration¹².

Because of the higher calcium ions concentration in the upper side of the culture



plateau wells, under the filter paper and new appeared hydrogel, is formed a continuous, perforated, 12 -14 nm-thick alginate membrane placed on the hydrogel surface, under the filter paper. This continuous perforated membrane is formed because in this area, the concentration of the calcium ions is high. On the membrane surface, very small pores (20-30 nm), uniformly distributed and CaCl_2 particles were observed¹³. The small pores membrane are probably the main channels which allow the calcium ions to diffuse to the lower areas of the culture plate wells. Consequently, the calcium ions movement occurs through all these mentioned barriers, from higher concentration to lower those (Fick's first law). The concentration gradient decreases over time (Flick's second law). Because of the higher Ca^{2+} ions in the upper part of the wells and low at the bottom, the hydrogels pores sizes are narrow at the top larger at the wells bottom. Under well selected crosslinking conditions, thin layer shaped alginate hydrogel with appropriate mechanical, morphological, transport and biological properties for soft tissue regeneration was achieved.

¹² Patent application no.A / 01263/29.11.2011

¹³ Doina Dimonie, Inna Trandafir, Anisoara Cimpean, E.Vasile, Bianca Galateanu, Radu Fierascu, Marius Petrache, "Morphological structure of some hydrogels designed for adipose tissue regeneration obtained based on controlled migration", 5TH International Conference "Biomaterials, Tissue Engineering&Mediacal Devices", Constanta, Romania, 29th August – 1st September 2012

DISPOSABLE BIOSENSORS FOR DETERMINATION OF DOPAMINE

C.V. Popa (Ungureanu)¹, I.M. Apetrei², D. Tutunaru², C. Apetrei³

¹*Faculty of Food Science and Engineering, “Dunarea de Jos” University of Galati*

²*Faculty of Medicine and Pharmacy, “Dunarea de Jos” University of Galati*

³*Department of Chemistry, Physics and Environment, Faculty of Sciences and Environment, “Dunarea de Jos” University of Galati, 47 Domneasca Street, 800008 Galati, Romania.*

E-mail: apetreic@ugal.ro

Abstract

Dopamine (DA) is one of more important catecholamine neurotransmitters in the central nervous system of mammals [1], and dopamine biochemistry is assumed to be associated to several diseases, such as schizophrenia and Parkinsonism [2]. For that reason, quantifying its presence in drugs and human body fluids is very important.

This work reports tyrosinase (Ty) based biosensors using screen-printed carbonaceous (carbon nanotubes - CNT, carbon nanofibers - CNF, and graphene - GPH) electrodes for the determination of DA in pharmaceutical formula. The enzyme was immobilized onto the carbon working electrode by drop and dry method followed by cross-linking with glutaraldehyde. The detection was performed by measuring the cathodic current due to the reduction of enzymatically formed dopaquinone at a low potential, -0.250V vs Ag/AgCl reference electrode. The experimental conditions for the tyrosinase immobilization, as well as for the main variables that can influence the amperometric current were optimized. Under these optimum conditions, the disposable biosensors were characterized. The capability of detection was ranged between 0.24 μ M and 4.3 μ M for novel developed biosensors. Finally, the biosensors were applied to the determination of the dopamine in pharmaceutical formula.

Acknowledgments

This work was supported by a grant of the Romanian National Authority for Scientific Research, CNCS – UEFISCDI, project number PN-II-ID-PCE-2011-3-0255.

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HPLC AND UV-VIS COMPARATIVE DETERMINATIONS OF CERTAIN ANTIOXIDANTS IN *SALIX SPECIES*, *ROSMARINUS OFFICINALIS* AND *ORIGANUM VULGARE*, NATURAL SUBSTITUTES OF ASPIRIN
POPESCU Mariana, RIZEA Gabriela Denisa, IONESCU Daniela, IVOPOL Gabriel,

IVOPOL Maria

S.C.Hofigal Export Import S.A. Str. Intrarea Serelor Nr. 2, Sector 4, Bucuresti

Well known for their rich content of antioxidants, willow bark (*Salix species*), rosemary leaves (*Rosmarinus officianlis*) and origani (*Origanum vulgare*) can be used as natural substitutes of aspirine [1-3].

HPLC and UV-VIS comparative determinations of polyphenols, flavone and antocianidine derivatives were performed in plant powders and in their extracts. By HPLC methods were identified various polyphenolcarboxylic acids (chlorogenic, rosemarinic, caffeic, ferulic, p-coumaric), polyphenol - β -glicozide (salicina) besides flavone derivatives (rutin, kaempherol, apigenin, quercitin).

UV-VIS spectrophotometric comparative determinations emphasized rich contents of polyphenolicarboxilic acids and flavone derivatives in all studied plants. The performed determinations were used in the obtaining of natural food supplements aspirine substitutes.

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SYNTHESIS, STRUCTURE, AND ANTILEUKAEMIA (HL-60) ACTIVITY OF N-(2,4-DIMETHYLPHENYL)HYDRAZINECARBOTHIOAMIDE AND ITS AZOMETHINE DERIVATIVES

**Artur Sargun¹, Aurelian Gulea¹, Alic Barba², Angela Jalba¹, Donald Poirier³,
Pyotr Petrenko⁴, Yuri Chumakov⁴**

¹Department of Chemistry and Chemical Engineering, Moldova State University, 60 Mateevici street, Chisinau, Moldova

²Institute of Chemistry, Academy of Sciences of Moldova, 3 Academiei street, Chisinau, Moldova

³Oncology and Molecular Endocrinology Research Centre, CHUL Research Centre and Université Laval, 2705 Laurier boulevard, Québec City, Canada

⁴Institute of Applied Physics, Academy of Sciences of Moldova, 5 Academiei street, Chisinau, Moldova

N-(2,4-dimethylphenyl)hydrazinecarbothioamide **1**, as well as its five azomethine derivatives have been obtained by condensation of **1** with: 3-formylpyridine **2**, 4-formylpyridine **3**, 3-formylthiophene **4**, 2-formylquinoline **5**, and salicylaldehyde **6**. All substances have been tested as inhibitors of human leukaemia (HL-60) cells growth. Antileukaemia bioassays have

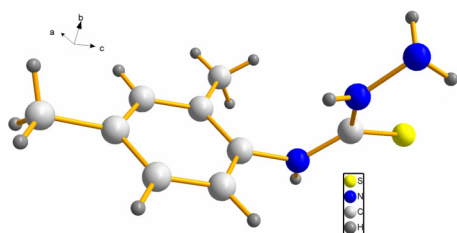
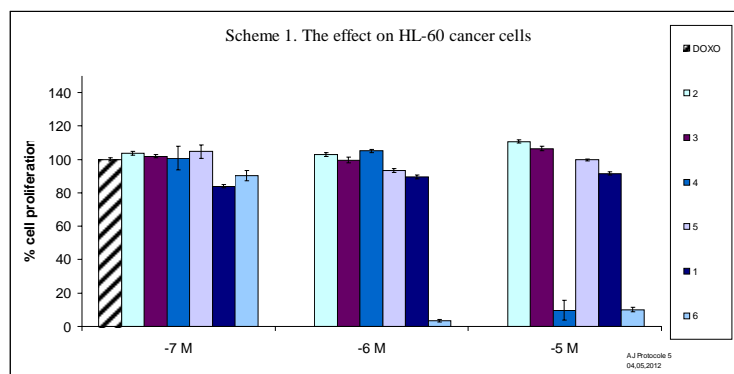


Fig. 1. Crystal structure of **1**



shown that the antiproliferative activity is manifested mainly within the concentrations 10 μ M and 1 μ M, and increases in the following series: **2** \leq **3** < **5** < **1** < **4** < **6** (Scheme 1). Therefore, the most active compounds **4** and **6** should be further studied as potential alternatives to traditional antileukaemia drugs. Moreover, from this study we have inferred that in order to synthesise highly antiproliferative active azomethines from **1**, it should be condensed with aromatic carbocyclic or heterocyclic aldehydes or ketones, which contain donor atoms (such as O or N) in the *orto* position to the carbonyl group (e.g. salicylaldehyde, etc.).

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“IN VIVO” PREBIOTIC EFFECT OF *ZYMOMONAS MOBILIS*’ LEVAN

Cristina Sturzoiu¹, Anca Dinischiotu¹, Ionelia Taranu², Gheorghe Stoian¹

¹ *Department of Biochemistry and Molecular Biology, Faculty of Biology, University of Bucharest, 91-95, Splaiul Independentei, sect. 5, Bucharest, ROMANIA*

² *National Research Development Institute for Animal Biology and Nutrition (IBNA), 1, Calea Bucuresti., Balotesti, Ilfov, ROMANIA*

A prebiotic is a non-digestible food¹ ingredient that selectively and beneficially affects host, by stimulating the activity of colon's bacteria², supports or favors the development of prebiotic microorganisms. Prebiotics are energy source as substrates for *Bifidus* bacteria² who are involved in inhibition of many pathogenic bacteria. Also they improve the health by reducing the number of gastrointestinal tract pathogenic germs (*Salmonella* sp., *E. coli* or *Clostridium* sp.)^{3,4,5}. Literature data show that inulin and oligofructans are excellent prebiotics when they are administered *in vivo*⁶. In this context, the aim of this study was to assess the prebiotic effect of levan produced by Gram negative bacterium, *Z. mobilis*. Bacterial levan was administered to Cobb 500 hybrid broilers, in 1% and 3% concentrations during two weeks, consecutive with the administration of pathogenic bacteria in the food. Our results show that the levan supplementation has a positive influence on growth performance of experimental models. The weight gain remains increased up to 28 days after the special treatment was stopped. Microbiological analysis revealed a significant reduction of pathogenic bacterial contamination, a small number of aerobic mesophilic bacteria and a little fungal infection into gastrointestinal tract.

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NON-INCINERATIVE ECOLOGICAL NEUTRALIZATION OF WASTES

**Ilie Bucur¹, Emilia Ghiță¹, Georgiana Vasile¹, Anca Georgiana Inel¹,
Lucica Roșu², Ovidiu Zlatian²**

Applied Systems SRL, Mitropolit Nifon Criveanu street, no. 27, 200467, Craiova,

Dolj, e-mail: bucur_il@yahoo.com

*¹University of Medicine and Pharmacy, Craiova, Department of Microbiology, Craiova,
Str. Petru Rareș nr. 2*

We present a new ecological and economical alternative to landfill or incineration of wastes, issued in the last years named mechano-thermal treatment. The procedure consists in mill mechanical processing, completed with sterilization due to high temperature produced by friction heat released.

So, many shortcomings, as infectious potential generated by the landfill storage or global warming and atmospheric pollution associated with incineration can be avoided. By applying this procedure the waste become environmentally safe product, compatible with natural biotic cycle, unrecognizable (as odor and aspect) and can be used as fertilizers or combustibles¹⁻³.

The application of the method means, essentially, in water evaporation, contracting volume, lowering weight and thermal sterilization of the infected waste materials, due to high temperature achieved by friction heat generated by mechanical crushing.

In this paper, to prove the application and effectiveness of the procedure, we use different raw materials (fish, meat, plant debris) and different work conditions, in a special elaborated laboratory installation. We analyze the evolution of some significant parameters of the final processed products vs. raw waste: weight, density, caloric power and the microbial content.

Experimental results show a very low humidity, doubling density, 40-50% weight loss, mean caloric power close to coal caloric power and complete sterilization. The characteristics of the final products demonstrate the possibility of successful application of this cheap and non-pollutant technique.

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MICROENCAPSULATION OF KMnO_4 IN MODIFIED WAXES FOR USE IN SOIL DECONTAMINATION

**Doina DIMONIE¹, PETRACHE Marius¹, Cristina COSMA², Inna TRANDAFIR¹,
Liliana ANTON¹, Simona Florentina POP¹,**

¹ *The National Research and Development Institute for Chemistry and Petrochemistry – ICECHIM, Spl.
Independentei, 202, Bucharest, Romania*

² *The National Research-Development Institute for Industrial Ecology– ECOIND, 71-73 Drumul Podu
Dambovitei Street, sector 6, Bucharest, Romania*

The microencapsulation of KMnO_4 in order to obtain matricial system microspheres, with diameter smaller than 100 μm , for using in decontamination of oil infested soil¹⁴ is not an easy task, especially if methods which can be applied in practical conditions is looking for.

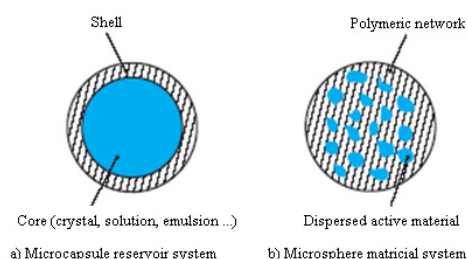
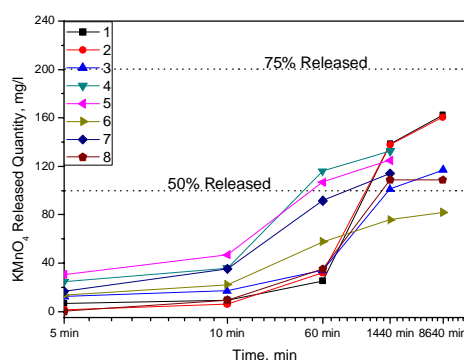


Fig.1

For practical considerations, it has been selected spraying as microspheres obtaining method and various waxes as polymeric network. The influence of the following spraying parameters on the microspheres ability to release the KMnO_4 , has been studied: spray pressure, the quantity of oxidant incorporated into the microencapsulation material, nozzle size, the influence of the reactant particle size. For a better adequacy of microsphere properties with the application requirements, the selected waxes have been physically modified in order to improve their solubility in certain solvents, density and softening/melting temperatures.

By correlating all of the above mentioned parameters microspheres with good solubility, low degree of agglomeration, which released 75% of the reactant in 7 days (Fig.2) have been obtained.

Fig.2



¹⁴ Kang Namgoo et al – Production and Characterization of Encapsulated Potassium Permanganate for Sustained Release as an In Situ Oxidant, Ind. Eng. Chem. Res., 2004, 43, 5187-5193

ASPECTS OF IMPROVING THE BIODIESEL PROCESS EFFICIENCY

Nicolae Sdrula¹, Cristina Șerbănescu¹, Dorin Groapă¹

1 - S.C. IPROCHIM S.A., 19-21 Mihai Eminescu Street, Bucharest, Romania

For near or long term future the demand of clean alternative energies becomes more stringent due to limiting utilization of fossil fuels and restrictions. The European Parliament approved the proposals of European Council for years 2020 as following: 20% reduction of current emissions of CO₂, covering with 20% of the energetic demands by renewable energetic sources and 20% the enhancing of energetic efficiency.

The producing and growing up of biodiesel amount on the market is essential to fulfill the targets of communitarian Directives regarding the contribution of biofuels in the total consumption for transport (10%). In a previous work [1] the effectiveness of membrane biodiesel production and glycerol purification were pointed out.

The actual tendency of growing up of biodiesel production imposes increases of entire process efficiency where glycerol plays an important role.

The paper takes in consideration the preparation of biodiesel in a membrane reactor, having some advantages when compared with classical stirred reactor, i.e. lower cost of operation, long life catalyst and easily operation with less labor and high quality Biodiesel, meeting ASTM- D-6751 and EN-14214.

Glycerol as by-product is provided to be turning in account by two alternatives: First choice is referring to glycerol purification for cosmetic applications where a High Efficiency Electro-Pressure Membrane (HEEPM™) technology is applied.

Second choice provides production of Green hydrogen using crude glycerol. The glycerol can be converted to a hydrogen-rich synthesis gas in a pyrolysis reactor and steam reformer. The hydrogen is processed in further purification steps until it reaches the level of quality needed for fuel cell cars and buses.

The basic characteristics of the processes are presented offering to any investor a first overview upon the possibility to choose the more proper one, showing that the glycerol processing and valorisation is the key factor of the efficiency for a certain biodiesel process.

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IN VITRO BIODEGRADATION OF KERATIN BY DERMATOPHYTES

Mariana CĂLIN CONSTANTIN, Iuliana RĂUT, Gelu VASILESCU,
Melania Liliana ARSENE, Luiza JECU

*National Research and Development Institute for Chemistry and Petrochemistry-ICECHIM,
Spl. Independentei 202, Bucharest, Romania*

Dermatophytosis is a superficial infection of the keratinized tissues including nails/claws, hair and stratum corneum of the skin¹. The fungi that cause these infections are known as dermatophytes, that include the imperfect fungi of the genera *Microsporum*, *Epidermophyton* and *Trichophyton*, classified based on the formation and morphology of their conidia (structures of asexual reproduction)². These microorganisms are divided on the host preference and natural habitat into zoophilic (animals), geophilic (soils) or anthropophilic (humans), respectively. Their activity is based on the ability to obtain nutrients from colonized keratinized materials, usually nonliving ones. The term “keratinophilic fungi” is used for all fungi for which keratinized substrates are the natural habitat³. Keratinophilic fungi are ecologically important group as they play a significant role in the natural degradation of keratin substrate and residues⁴.

Since they have been found to be the agents responsible for human mycoses and since they occur in abundance in sewage sludge and soil, studies on fungal incidence are of hygienic, epidemiological and ecological significance. In present work, the keratinolytic activity of several dermatophytes as *Trichophyton* and *Microsporum* were tested using human hair as the substrate. *In vitro* tests were performed in Petri plates on yeast extract medium. The strains activity was considered by culture morphological study and microscopic analysis of developed colonies. Among the tested strains, *Microsporum canis*, *Microsporum canis* var. *distortum* and *Trichophyton mentagrophytes*, var. *mentagrophytes* presented the ability to stick human hair. Further researches will be continued to evaluate the antifungal activity of vegetal extracts against dermatophytes causing hair deterioration.

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**ELECTROCHEMICAL BEHAVIOUR OF HEAVY METAL COMPLEX
COMPOUNDS AT THE WASTE WATER TREATMENT****Olga COVALIOVA***University of the Academy of Sciences of Moldova, 3/2 Academiei Street, Chisinau, MD 2028,
Republic of Moldova**Tel: +37322577556; E-mail: Covaleva.Olga@yahoo.com*

To prevent the heavy metals and other toxic ions release in natural environment due to the discharges of untreated plating and rinsing solutions is an important problem from both ecological and economical viewpoint. It is crucial to avoid the environmental pollution and uncontrolled losses of resources. Today treatment technologies are not always efficient and cost saving and sometimes they can even provoke the secondary pollution. Electrochemical treatment of industrial waste waters is among the most promising technologies as it implies the same principles as the main technologies and does not require introducing of any additional chemicals into the treated solution. However, till now this method was given insufficient attention.

The electrochemical behaviour of some *d*-metal complexes was studied and discussed from the point of view of waste water treatment requirements. Studies performed in the model plating solutions of Zn, Ni, Cu ammonia and pyrophosphate complexes, polynuclear Cr complexes has shown that use of the conventional reagent treatment will be inefficient to purify these waters. Examination of potentiodynamic polarization curves registered in studied solutions has shown that due to the formation of Zn ammonia complexes, alkaline treatment will not ensure Zn removal from these solutions. It was also found that to ensure the Cr(VI) removal, the electrocoagulation method can be applied which entails the formation of hydroxides. The research has shown that the approach on heavy metal removal from used plating solutions may be different, depending on treated solution composition.

The peculiarities of chrome complexes in acid solutions are described. It is shown that due to these peculiarities, it would be possible to apply the electrochemical oxidation-reduction processes for the treatment of such solutions. These processes are influenced by the passivation of electrode surface, which can be removed either by the abrasive-mechanical cleaning, or application of pulse electrolysis with the periodic short-term alteration of current polarity.

In the process of electrochemical treatment of zinc (II) and chromium(VI)-containing waters with the contents of ammonium ions, chromium (VI) ions will be reduced to chromium (III). It is shown that this reaction occurs not only and not mainly on cathode, but rather due to the interaction of chromate-ions with iron (II) ions or hydroxides, which are formed during the anodic dissolving of iron electrode. Therefore, using of electrochemical treatment with the dissolving iron electrodes, must significantly enhance the treatment degree of zinc-chromium-containing plating waste waters.

Theoretical aspects of pulse electrolysis during the cathode reduction of Zn(II) and Cr(III) complexes are discussed. Electrochemical studies, including chrono-potentiometry and measuring the pH of cathode layer, have revealed the possible aspects of non-stationary electrolysis. There is a possibility to activate the electrode surface and govern the process. The high power consumption for the charge of double electric layer of cathode is marked, which entails the necessity to minimize the non-production costs.

Treatment of textile wastewater containing direct and active dyes in the presence of anionic surfactants and Ethylene glycol

GONTA Maria, Duca Gheorghe, Matveevici Vera, Mocanu Larisa, Iambartev Viorica

Moldova State Universit, Departament of Industrial and Ecological Chemistry

It was studied the textile dyes lower concentrations dye active RA (active red) and PA (orange active) in model solutions with initial concentration 50 mg/l in the presence of surfactant anonymous (sodium lauryl sulfate), concentration of which varies from 20 mg/l to 60 mg/l and their combined treatment with coagulant (aluminum sulfate), followed by their adsorption by active coal.

It was established that RA dye is removed from model solutions up to health standards (by value of chemical oxygen demand COD-Cr = 5,0-8.0mgO/l) in the presence of anionic surfactant with C.init . = 20 mg/l only to their treatment with aluminum coagulant. With increasing surfactant concentration up to 40-60mg/l concentration of organic substances remaining after COD-Cr value is greater than the allowable. The most effective way to remove RA dye and surfactant amestecl by the method, when the concentration ratio RA: surf. = 1:1. With increasing surfactant concentration dye vs. RA (C(RA) = 50mg/l and C.surf . = 60 mg/l), the effect of their adsorption by active carbon decreases, but the concentration of COD-Cr remaining after the adsorption, is within acceptable limits.

To achieve the proposed tasks coagulation process was studied catalytic oxidation followed by ethylene glycol (EGL) or adsorption. Further coagulation and oxidation was studied textile dyes directly lit red (RAD), blue light directly (AAL) in the presence of EGL in model solutions using aluminum sulfate and Fenton reagents depending on the coagulant concentration, hydrogen peroxide, the concentration of iron (II) and during treatment

The coagulation process of textile dyes studied in the presence of EGL. It has been determined that COD-Cr decreases from 65mgO/l up to 10.6mgO/l (50mg/l or AAL-RAD and 30mg/l EGL). With increasing dye concentration and EGL (100 mg/l, 200mg/l for dyes and 30mg/l 60 mg/l for EGL) COD-Cr coagulation after reaching 15.6 mgO/l. It was found that adsorption or oxidation processed after coagulation did not lead to effective treatment of these systems.

By optimizing the process of oxidation in the presence of direct dyes EGL for the same range of concentrations (50mg/l or AAL-RAD and 30 mg /l EGL) the CCO-Cr has decreased up to 10.0 mgO/l, and after adsorption has reached 3 mgO/l, which also corresponds to the CMA for COD.

STUDIES ABOUT THE SINERGISTIC EFFECT OF CELLOBIOHYDROLASE AND β -GLUCOSIDASE IN THE HYDROLYSIS OF CELLULOSE

GURGU Leontina^{1,2}, Julia MARIN-NAVARRO², Julio POLAINA²

¹ Faculty of Food Science and Engineering, "Dunarea de Jos" University of Galati,

Domneasca Street, No. 111, 800 008, Galati, Romania

² Instituto de Agroquímica y Tecnología de Alimentos, CSIC, Paterna, Valencia, Spain

Cellulose degradation requires the combined action of at least three types of enzymes: endo- β -1,4-glucanases (EG, EC 3.2.1.4), cellobiohydrolases (CBHs, EC 3.2.1.91), and β -glucosidase (EC 3.2.1.21). From a structural point of view, there are CBHs with different molecular architecture which are classified as glycoside hydrolases belonging to different families (1). A first objective of this study was to express a cellobiohydrolase encoding gene (*cbhB*) from *A. niger* into *S. cerevisiae* as a preliminary step to obtain yeast strains with improved properties for cellulose fermentation. Another objective was to obtain a yeast strain with cellobiohydrolase and cellobiase activities, by simultaneous expression of *cbhB* and the β -glucosidase gene *bgl1* from *Saccharomycopsis fibuligera* (2, 3). The ORF sequence of *cbhB*, which encodes an enzyme belonging to family GH7 of the glycoside hydrolase classification, was amplified from genomic DNA of *A. niger*, fused to the sequence of the signal peptide of the glucoamilase *Stal* from *S. cerevisiae* var *diastaticus* and expressed in *S. cerevisiae* under the control of a galactose inducible promoter. We have obtained physical evidence of the simultaneous expression of *cbhB* and *bgl1* in *S. cerevisiae* by analysis of the proteins secreted by the double transformant. While the cellobiase activity could be proved by using *p*-nitrophenyl glucoside as the substrate, cellobiohydrolase activity could not be measured effectively due to the absence of an appropriate substrate.

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BULK LIQUID MEMBRANES FOR SEPARATION OF CADMIUM IONS FROM AQUEOUS SOLUTIONS

Mariana Mateescu^{1,2}, Liliana Pacurariu^{1,2}, Irina Fierascu², Fanica Bacalum², Gheorghe Nechifor¹, Minca Iulian²

¹*Faculty of Applied Chemistry and Materials Sciences, University 'Politehnica' of Bucharest, Romania, e-mail:*

marinamateescu@yahoo.com

²*National Research Development Institute for Chemistry and Petrochemistry ICECHIM,
Bucharest, Romania*

Compounds of cadmium in the environment has a negative effect on human health. A lot of technologies can be used to remove this toxic metal from effluents, such as precipitation, solvent extraction, ion exchange, etc. Among these technologies, liquid membrane technique has gained an importance for its use in the separation and concentration of cadmium compounds from wastewater [1]. Although this technology is still in research or development stage, the separation of chemical species using liquid membranes attracted the attention due to its advantages in comparison to conventional separation operations such as using a small amount of solvent, high selectivity, ease of installation and energy utilisation [2,3].

In this study a bulk liquid membrane contained D2EHPA (di-2-ethylhexyl phosphoric acid) as carrier in toluene was used to separate cadmium ions from aqueous solutions. The results of this study showed that the duration of contact and carrier concentration plays a significant role on separation of cadmium with bulk liquid membranes. Experimental data showed that using a carrier concentration of 0.2 M D2EHPA in the organic membrane, the removal efficiency of cadmium ions through liquid membrane after 20 hours was about 70%.

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PREPARATION AND CHARACTERIZATION OF POLYMER INCLUSION MEMBRANE WITH D2EHPA AND TOA AS CARRIERS

Liliana Pacurariu^{1,2}, Mariana Mateescu^{1,2}, Gheorghe Nechifor².

¹ *Faculty of Applied Chemistry and Materials Sciences, University 'Politehnica' of Bucharest, Bucharest, Romania*

² *National Institute for Research & Development in Chemistry and Petrochemistry - ICECHIM Bucharest, Spl. Independentei nr. 202, Bucuresti, Romania*

The stability of polymer inclusion membranes (PIMs) relative to other liquid membranes is amongst the major reasons for the recent rejuvenation of interest in carrier-mediated transport for selective separation and recovery of metal ions as well as numerous organic solutes. This is reflected by an increasing number of PIM investigations reported in the literature over the last two decades [1]. Polymer inclusion membrane (PIM) system with cellulose acetate polymer as support and tri-n-octylamine (TOA) and di(2-ethylhexyl)phosphoric acid (D2EHPA) as carriers has been developed which provides rapid metal ion transport with high selectivity, as well as easy setup and operation.

The PIMs are formed by casting cellulose triacetate (CTA) from solution to form a thin film. The casting solution also contains an ion exchange carrier (TOA and D2EHPA) and a membrane plasticizer (e.g., an o-nitrophenyl alkyl ether 2-NPOE). The membrane is used to separate aqueous source and receiving phases, but does not utilize an organic solvent to maintain this phase separation. Therefore, PIMs are simpler to use than SLM, and do not suffer from loss of the organic solvent. SUGIURA et al. [2] first utilized cellulose triacetate (CTA) membranes for carrier-mediated transport of metal ions from an aqueous source phase into an aqueous receiving phase.

The efficiency of the membrane transport was optimized as a function of pH, stirring speed, aqueous phases and membrane composition [3]. PIM was characterized by using FTIR and Scanning Electron Microscopy (SEM).

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STUDY OF ADSORPTION KINETICS AND ZETA POTENTIAL OF PHOSPHATE AND NITRATE IONS ON A CELULOSIC MEMBRANE

G.H. NECHIFOR¹, PASCU D. E.², PASCU (NEAGU) M.^{2,3}, TRAISTARU G. A.

¹ Department Chemistry Engineering, Politehnica University of Bucharest, Faculty of Applied Chemistry and Material Science; 1-5 Polizu St, 11061 Bucharest

² Department Chemistry Engineering, Politehnica University of Bucharest, Faculty of Applied Chemistry and Material Science; 1-5 Polizu St, 11061 Bucharest

³ SC HOFIGAL S.A. Analytical Research Department, 2 Intr. Serelor, Bucharest-4, 042124, Romania

In the context of process industries, membrane cleaning is one of the most important concerns from both economical and scientific points of view. The characterisation of membrane surface by using zeta potential technique provides a more appropriate tool to study the cleaning performance and membrane integrity. The use of zeta potential technique to characterize the cleaning effect on membrane surfaces has very little precedence in literature. The effects of concentration, temperature and pH on membrane zeta potential were also investigated. The temperature was not found to have any significant effect on membrane zeta potential; however, the effect of pH and concentration of ions had pronounced effects on the surface charge and zeta potential.

Also, we studied the kinetics adsorption of phosphate and nitrate ions on a cellulosic membrane. Adsorption studies were performed according to two parameters: pH and concentration solutions. Since the pseudo first order kinetics satisfactorily described the adsorption process Arrhenius equation was used to calculate apparent activation energy. Langmuir equation characterized very well the experimental data for both nitrate ion and phosphate ion. Maximum adsorption capacity for nitrate ion was higher compared to that of phosphate ion which means that cellulose membrane has a much higher adsorption capacity for nitrate ion than phosphate ion. The result of this study demonstrated that the potential use of cellulosic membranes for nitrate and phosphate ions removal from wastewater.

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**PRODUCT FOR STRENGTHENING AND PROTECTION OF HISTORIC
MONUMENTS AND *IN SITU* IMPLEMENTATION PROCESS**

POPESCU Mariana, VELEA Sanda, OANCEA Florin

National R&D Institute for Chemistry & Petrochemistry – ICECHIM – Bucharest, Romania

A novel biomimetic organic-inorganic bioactive composition from renewable resources and a bio-inspired technique of *in situ* mineralization were proposed for the reinforcement and long-term protection of damaged stone and old brick walls facades of historic monuments and buildings against biodeterioration.

The main goal of the research was to provide an eco-effective alternative to conventional methods and means for the sustainable protection of the architectural heritage. The technical solution was the *in situ* biomineralization of an environmentally friendly bioactive composition containing non-toxic and non-corrosive materials from renewable natural resources, for conservative remedy of biodeteriorated monumental stone-type surfaces. The main raw materials were: gelatin or collagen wastes from industrial processing of animal skin and bone joints, phosphate and calcium sources, volatile oils from aromatic plants and approved European biocides (Directive 98/8/EC). Colloidal products were inserted into the pores of brittle stone by capillary suction, which solidified the components through self-assembly with mineral particles to restore mineral strength, stability and resistance against a broad spectrum of biodeteriogens (algae, fungi, mosses, lichens). The application process mimics the biochemical mechanism of mineralization of animal hard tissues (shells, bones) for protection and mechanical support. Like organic minerals in marine shells, teeth and bones of mammals, original biomimetic system developed special properties: lightweight, mechanically robust, versatile and durable. The active compositions developed high remanence due to their ability of self-assembly by natural contact with atmospheric oxygen and gradually release the active principles from the biodegradable polymer matrix. The innovative technical solution patented (A01078/2011) the double action of original bioactive compositions to strengthen support based on biomimetic approach and long-term protection of architectural facades against biodeterioration using a bioinspired technique of *in situ* implementation. The treatment strengthens facades avoiding the need of repeating treatments as, for example, laser cleaning and the danger of loosing material by the currently used mechanical brushing, thus saving the historic or artistic appearance and structural integrity of the building, with reasonable costs, conventional devices for application and minimal human effort.

PHYSIOLOGICAL AND ENVIRONMENTAL FACTORS AFFECTING THE GROWTH AND SPORULATION OF *TRICODERMA SP.*

Iuliana RAUT¹, Mariana CALIN¹, Luiza JECU¹, Tatiana Eugenia SESAN²

^[1] INCDCP-ICECHIM, Spl. Independentei 202, Bucharest

^[2] University of Bucharest, Faculty of Biology, Spl. Independentei 91-95, Bucharest

Trichoderma is considered to be one of the most versatile and effective biocontrol agents studied¹. The species contains an arsenal of mechanisms and antimicrobial metabolites capable to fight against different pathogens. Optimization of *Trichoderma* culture conditions is the preliminary step towards the selection of most efficient antagonistic strains^{2, 3, 4}.

The objective of this study was to investigate the influence of physiological and environmental factors upon the growth and sporulation of antagonistic *Trichoderma sp. T36*. Some important parameters to be considered are: culture medium composition; influence of carbon and nitrogen source; the effects of temperature and pH. The influence of tested factors was evaluated with the colony diameter of microbial culture grown on solid medium in Petri plates. The growth was favoured by PDA, MEA OM, M1 nutrients media, with best results on M1 medium. This medium was selected for further experiments concerning the study of various carbon and nitrogen source. A wide range of carbohydrates as carbon source has been tested, among them the best results were obtained in media with ribose, D mannose, fructose, dextrose and arabinose, around 6.75 cm diameter of colony zone. Also citric acid was found to be an good and rapid available carbon source. It was investigated the effect of inorganic and organic nitrogen source. The lowest diameter colony was found for KNO₃, KNO₂ and NH₄Cl while the highest were for NaNO₃ and NaNO₂. *Trichoderma sp. T36* presented a good growth and sporulation on media supplemented with valine, alanine, L lisine, isoleucine and L serine. As regarding the environmental factors, *Trichoderma* growth was facilitated in cultures performed at 25-27°C temperature and pH from 4.0 to 5.5.

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**STUDY OF POLLUTION GENERATED BY THE MINING SITES OVER THE
WATER QUALITY FROM THE MURES RIVER BASIN, IN HUNEDOARA
COUNTY**

SZOLLOSI-MOTA Andrei, PRODAN Maria, NĂLBOC Irina, LORAND Toth

INCD –INSEMEX Petroșani, str. G-ral Vasile Milea, nr. 32-34, Petrosani, Hunedoara

The mining industry on the environment exercise great influence manifested in all phases of technological processes of minerals mining and preparation.

Storage ponds tailings resulting from the processing of minerals in preparation plants are relatively large, sometimes altering fundamentally zone morphology and the content of pollutants become factors and sources of air pollution - through dust - and water - through suspension, flotation reagents and metal ions.

The study aimed to determine the concentrations of heavy metals and characterization in terms of pollution, the main water courses feeding the Mures river, in Hunedoara County. For performing the measurements has been used atomic emission spectrometry with inductively coupled plasma. On-site observations, data collected and analysis of ecosystem toxic elements (heavy metals) from flowing streams that drain the mine waters in the area lead us to the consideration that industrial branches and especially the mining industry is a major source of pollution even after decades of closure. Water and sediment samples with the highest concentrations of heavy metals in river Certej were collected from areas heavily affected by acidification activity. At present the concentration of heavy metals in rivers in the area are above the permissible limits for many metals, some of them overcome ten times the maximum permissible concentration. Due to mining activity in the area, some rivers were affected, those waters with a strong acid.

THERMOPLASTIC BLOCK-COPOLYMERS AS COMPONENT FOR BLENDS BASED ON CONTAMINATED POLYETHYLENE AGRICULTURAL WASTE

Fulga TANASA¹, Madalina ZANOAGA¹,

Natalya BUSKO², Antonina BARANTSOVA², Vladimir GRISHCENKO²

¹ "Petru Poni" Institute of Macromolecular Chemistry, Iasi – ROMANIA

41 A Grigore Ghica Voda Alley, Iasi, Romania

² Institute of Macromolecular Chemistry, Kiev 48 Kharkivske shausse, Kiev, – UKRAINE

Today, waste plastics can be an important resource of raw materials for new products. In recent years, polymer blends based on polymer waste have received increasing interest at industrial, ecological and academic level. Compatibility is the fundamental issue deciding on the further use of a blend. Since most polymer pairs are immiscible, due to a poor interfacial adhesion, blends display poor mechanical properties. This problem is the cause of major difficulties faced in recycling of mixed plastic waste.

Both miscible and immiscible polymer blends are of concern to industry. When the end property lies between the properties of the individual polymer components, miscible blends are preferred. The possibility of broadening the applications range for recycled materials through the addition of mineral fillers, elastomers or other additives, should also taken into consideration. Under these circumstances, the study of thermoplastic block copolymers (BCPs) used for waste recycling is of great interest both from a scientific and from a technological point of view.

This paper deals with the use of BCPs as effective modifiers for the polyethylene waste recycling. Two novel thermoplastic BCPs based on an aliphatic copolyamide (A) and an oligodiene with isocyanate end groups (B) were used for obtaining blends with agricultural polyethylene waste (s-PE). The characterization results indicated that s-PE/BCPs blends have improved mechanical properties in terms of elasticity in both cases, and tensile strength in the case of s-PE/ABA blends, which make them fit for various applications (interior design, light furniture, packaging, etc.).

Based on these conclusions, we can state that it is possible to use these novel BCPs in blends with secondary polymeric materials. This is a convenient alternate method for waste recovery and recycling. Also, the possibility of using these block copolymers as compatibilizing agents for polyamide–polyolefin blends will be further studied.

**METHOD OF THE INITIAL VELOCITIES AT THE DEMONSTRATION OF THE
SELF-ACCELERATION AND SELF-INHIBITION PHENOMENA AT THE
PYROLYSIS OF SOME HYDROCARBONS**

Vasile MATEI, Traian JUGANARU, Dorina MATEI

Oil and Gas University of Ploiesti, 39 Bucuresti Bvd., Romania

“The initial velocity” is an important kinetic concept, with important results in the kinetics of the reactions in the contact catalysis. It was applied for the pyrolysis of propane diluted with inert gas, nitrogen, to various proportions, so as to also vary the partial hydrocarbon pressure. Propane pyrolysis was carried out in the laboratory flow reactor, with the inside diameter of 24 mm and the equivalent length of the reaction zone of 10 mm. The reactor is centrally provided with a sheath of quartz, the same material as the reactor, sheath through which a thermocouple can be located for the measurement of the axial temperature in the reactor, in order to assess the axial profile of the temperature. The propane and nitrogen feed, to various proportions, was done by estimating the flow rate with rotameters calibrated for nitrogen, from pressure cylinders. The temperature of the isothermal reaction zone is of 800 °C, nitrogen dilution was 11.30 and 60% vol., while the reaction times vary between about 0.1 and 0.9 seconds.

“The initial velocity” is a function depending on the initial concentration C_o of the reactant the initial velocity, $r_o = f(C_o)$. If the thermal cracking reaction of propane is taken into account, namely, that for the formation of reaction products, it is possible to define an instantaneous reaction velocity, $r = g$ (instantaneous concentration of ~~reagent~~ reactant A). One can define an instantaneous reaction velocity, r^* , depending on the instantaneous individual concentration, C_A .

The values of r and r^* can be compared by the ratio r/r^* depending on the conversion.

If one obtains a straight horizontal line against the intersection of r/r^* axis, the pyrolysis reaction of the propane diluted with inert gas is non-self-inhibited or non-self-accelerated by the reaction products, if the experimental points r/r^* are under or above the horizontal line, the pyrolysis reaction of propane is self-inhibited or self-accelerated by the reaction products.

COMPLEXES OF 5-BROMO-2-HYDROXYBENZILIDENE-2-MERCAPTOANILINE.

Georgeta Zamfir¹, Nicolae Stanica², Constantin Draghici³, Angela Kriza⁴.

1. Technical Collegium Mircea cel Batrin, 52 Feroviarilor Street, 012207, Bucharest, Romania. 2. Institute of Physical Chemistry of Romanian Academy, 202 Splaiul Independentei, 060021, Bucharest, Romania. 3. Institute of Organic Chemistry of Romanian Academy, 202 Splaiul Independentei 060023, Bucharest, Romania. 4. University of Bucharest, Faculty of Chemistry, 23 Dumbrova Rosie Street 020462, Bucharest, Romania.

Transitional metal complexes, by template synthesis with the ligand 5-bromo-2-hydroxybenzilidene-2-mercaptoaniline type: $[M(HL)_2] \cdot nH_2O$, where $M = Ni(II)$, $n=1$ and $M = Cu(II)$, $Zn(II)$, $Cd(II)$, $n=0$, were obtained [1,2]. Complexes were characterized with: elemental analysis, IR, UV-Vis.-NIR, 1H -NMR, ^{13}C -NMR, EPR spectroscopy, electric conductivity and magnetic susceptibility. Elemental analysis suggest M:L of 1:2 stoichiometry for all complexes. Complexes are colored solids and decompose at high temperatures ($300^\circ C$). They are insoluble in common organic solvents, soluble in DMF and DMSO and are nonelectrolytes. Complexes have weak antibacterial activity. Ions of $Cu(II)$ have octahedral geometry, $Ni(II)$ ions have square-planar geometry, and $Zn(II)$ and $Cd(II)$ ions have tetrahedral geometry. Ligand acts as ONS monoanionic ligand for $Cu(II)$ ions and as NS monoanionic ligand for $Ni(II)$, $Zn(II)$ and $Cd(II)$ ions [3-5].

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THE CALORIMETRIC STUDY OF SOME NITRATES WITH AMINO ACIDS CATION**Daniela GHEORGHE^a, Ana NEACSU^a, Iulia CONTINEANU^a, Speranta TANASESCU^a***Institute of Physical Chemistry "Ilie Murgulescu", Splaiul Independentei 202, Bucharest*

A complex calorimetric study by combustion calorimetry and differential scanning calorimetry (DSC) was performed for a series of nitrates synthesized in laboratory having different α -amino acids cations, namely glycine, alanine, glutamic acid and threonine. The thermochemical characterization of studied compounds was obtained by experimental determination of the combustion and formation enthalpies, as well as of the temperatures and enthalpies of solid-liquid and polymorphic transitions. The obtained results highlight the lower values of the enthalpies of formation of the nitrates compared with that for the properly amino acids because of the lowering of the number of possible hydrogen bonds in their crystalline network which favors crystal hardness. The DSC thermograms of the nitrates on heating in the temperature range 30 – 300⁰C noted the existence of a transition solid - liquid for GlyNO₃ and AlaNO₃ followed by a polymorphic transition, and a polymorphic transition for GluNO₃ and ThreNO₃. Different structures of the α -amino acids used in synthesis, namely two with aliphatic chain (alanine and glycine), one containing a second group –COOH (glutamic acid) and one with a –OH group (threonine) is reflected in the values of experimental determined parameters. The obtained results are important considering that in the literature are not mentioned experimental values of the combustion and formation enthalpies and there are no differential scanning calorimetry measurements for the compounds investigated in this study. Must be also mentioned the many applications of this class of compounds – organic crystals called “semi-organic compounds” - in various fields like telecommunication, optical data storage and optical information processing. Last but not least they are used in the synthesis of amino acid based ionic liquids.

Round table: **Inovarea durabilă – motorul dezvoltării bazate pe cunoaștere**

INOVAREA DURABILA- MOTORUL DEZVOLTARII BAZATE PE CUNOASTERE

Ana-Maria Popilian

INCDP-ICECHIM Bucuresti

CUNOASTEREA si **INOVAREA** sunt elemente cheie care stau la baza strategiei Europa 2020. Strategia de Inovare sprijina **DEZVOLTAREA DURABILA** in contextul unei economiei bazate pe cunoastere prin promovarea unui climat favorabil inovarii si a spiritului antreprenorial si prin stimularea cooperarii intre mediul de afaceri si cel al stiintei in vederea valorificarii rezultatelor cercetarii pentru o crestere inteligenta, durabila.

Round Table

SUSTAINABLE INNOVATION:

ENGINE OF KNOWLEDGE BASED DEVELOPMENT

Ana-Maria Popilian

INCDP-ICECHIM Bucuresti

KNOWLEDGE and **INNOVATION** are key elements of Europe 2020 Strategy. Innovation Strategy supports **SUSTAINABLE DEVELOPMENT** in the context of a knowledge based economy by promoting a favorable climate for innovation and the entrepreneurship and stimulating cooperation between business and science in order to capitalize the research results for **SMART AND SUSTAINABLE GROWTH**.

Round table: **Instalație pilot demonstrativ pentru reducerea dioxidului de carbon din emisii industriale – de la conceptualizare la dezvoltare tehnologică**



ORGANIZATORI



PROGRAM

Masă rotundă

“Instalație pilot demonstrativ pentru reducerea dioxidului de carbon din emisii industriale – de la conceptualizare la dezvoltare tehnologică”

26 octombrie 2012, orele 11

Sala de consiliu, et 1, INCDCP-ICECHIM

10:30 – 11:00 Inregistrare participanți

Deschiderea oficială

11:00 – 11:15 Dr. ing. Sanda VELEA – Director General INCDCP - ICECHIM

Prezentări

11:15 – 11:30 Ing. Lucia ILIE, Director proiect LIFE 10/ENV/RO/000734 –
“Instalație pilot demonstrativ pentru reducerea dioxidului de carbon din emisii industriale – de la conceptualizare la dezvoltare tehnologică”

11:30 – 11:45 Ing. Ioan VACARCIUC, proiectant
“Proiect tehnologic pentru sistemul de captare-procesare gaze de emisie cu CO₂ pe platforma industrială CET Vest, □n sistem integrat fotosintetizator”

11:45 – 12:00 Ing. Viorel FĂTU, cercetător ICDPP
“Utilizarea lipidelor extrase din biomasa algală”

12:00 – 12:30 Discuții

12:30 – 13:00 Pauză de cafea

Round table: **Promovarea utilizării zeoliților naturali autohtoni în tehnologii de epurare a apelor**



W O R K S H O P

c u t e m a :

**“ Promovarea utilizării zeolitilor naturali
autohtoni in tehnologii de epurare a apelor”.**

26 octombrie 2012, ora 10⁰⁰

organizatori:

Institutul National de Cercetare-Dezvoltare
pentru Chimie si Petrochimie
ICECHIM

Institutul National de Cercetare -
& Dezvoltare pentru Metale Neferoase si Rare
IMNR

Program de desfasurare a lucrarilor

1. Prezentarea proiectului: “Valorificarea unor produse naturale in domeniul epurarii apelor uzate industriale cu continut de hidrocarburi” (Bacalum Fanica, Liliana Sarbu, INCDCP-ICECHIM);
2. Studiu mineralogic comparativ al tufurilor din Romania, continand zeoliti cu valoare economica (M. Ghita, Stoiciu Florentin, INCDMNR-IMNR);
3. Consideratii privind obtinerea unor coagulanti neconventionali din deseuri provenite din industria aluminei si aluminiului, cu potential in tratarea apelor incarcate cu hidrocarburi (Mara Luminita, Teodorescu Romanita, INCDMNR-IMNR);
4. Aspecte privind utilizarea coagulantilor neconventionali, $[\text{Fe}(\text{Al})]_n$ /tuf zeolitic, in tratarea apelor poluate cu hidrocarburi (Sarbu Liliana, Bacalum Fanica INCDCP-ICECHIM);
5. Compozite de tip clinoptilolit-hidrotalcit si utilizarea acestora in depoluarea apelor reziduale (R. Zavoianu¹, O.D. Pavel Univ. Bucuresti).
5. Pauza de masa.
6. Discutii si concluzii asupra realizarii si oportunitatilor valorificarii rezultatelor proiectului; perspective privind alte directii de utilizare a tufurilor zeolitice.

TRENDS AND CHALLENGES IN PETROLEUM FUELS QUALITY

Bogdan DOICIN, Cristina BARBU, Ion ONUTU, Dorin STANICA-EZEANU,

Oil and Gas University of Ploiesti, 39 Bucuresti Bvd., Romania

Automotive fuels quality evolution is correlated with new engines needs (better performance and smaller consumption), environment concerns (smaller petroleum products consumption and smaller emissions), and refining capacity (adequate prices and fuel availability). On the basis of these factors limit, have been manufactured and will be formulated fuels becoming cleaner. For the most widely used petroleum fuels (gasoline, oil, diesel) standard specifications were developed, both in U.S. and Europe (TIER, EURO etc.), which provide features as well as environmental limitations. A key feature in all these specifications was the sulfur content.

A special attention should be paid to current and especially future reformulation of gasoline, jet and diesel fuel oil by the addition of bio components. Be reconsidered influences these additions and the impact on the quality specifications and test methods.

The main contributor to lower vehicle emissions over the past 30 years has been the introduction of vehicles with exhaust catalysts. Certain fuel properties are important to enable these catalysts to operate effectively over the life of the vehicle. Unlike lead, sulphur is a naturally occurring element in crude oil. Fuel sulphur levels should be set to match the corresponding vehicle emissions control technology in each regional market.

Regarding the specs of gasoline and diesel fuels, Romania is moving fastly, the Euro norms being already applied.

For automotive gasoline the objectives were: to reduce sulfur content, to reduce T_{90%} and FBP, to limit maximum contents of aromatic hydrocarbons and maximum contents of olefins, to increase the oxidation stability and to specify also unwashed gum, to study the bioethanol influence.

Fuel specifications and testing have been an integral part of the development of aviation fuels. The adding of certain of biofuels has an impact on Jet fuels specifications.

Trends in Diesel fuel quality are: to increase the cetane number, flash point, to specify the T_{95%} from distillation curve and to reduce the maximum density, sulfur content and contaminants, impact of biodiesel.

A particular impact will have biofuels which could be added to fuel automotive vehicles, as blending substitutes for diesel and gasoline petroleum products.

TRENDS IN PETROLEUM REFINING

Paul ROSCA, Dorin STANICA EZEANU

Oil and Gas University of Ploiesti, 39 Bucuresti Bvd., Romania

Crude oil is and will remain the main source for fuels production. Besides increasing of oil consumption it is observed a significant change of petroleum product demand. The market reports a severe reduction of heavy fuels consumption and an increasing of Diesel fuels. New restrictions on the emissions demand a very high purity for petroleum products.

The new market forces and environmental constraint regulations for oil products associated with a decrease of crude oil quality have lead to major changes in the refining schemas:

- new processes for upgrading the bottom of the barrel by hydroconversion, de-asphalting, coking or visbreaking of vacuum residue;

- new processes for environmentally friendly fuels production like hydrofining (HDS, HDN, metal removal) of residues, reformulated gasoline processes (alkylation, polymerization, isomerisation, etherification)

- additional hydrogen production from partial oxidation or steam reforming.

Individual technologies and better planning and blending alone will not necessarily lead to success. Today's challenges require a more integrated approach. Technological solutions must be combined with programs to achieve operational excellence and improve enterprise management.

GLOBAL OUTLOOK ON PETROCHEMISTRY

Gheorghe IVĂNUS, Dan MIHĂILESCU

SChR – section Chemical and Petrochemical Technology, no. 1 Polizu Street, Bucharest

The fossil fuels such as oil, natural gases and coals still represent the only energy resources that can continuously assure, in our days, the energy requirement of mankind.

Between 2005 and 2030 the world population will increase by 30%, the world economy will double while the energy requirement will increase by 40% that is to 325 million barrel per day, in oil equivalent. Despite some pessimistic scenarios regarding the depletion of oil reserves, in the period we make reference to, oil and other fossil energy resources will secure 80% of the world energy requirement while the alternative energy resources so much in media attention, wind, sun energy, bio -fuels etc. will not cover more than 2% in 2030. At present they assure only 0.5%. The upstream nonintegrated oil refineries with crude resources and particularly the downstream ones, with petrochemical production, face difficulties in turning fuels to good account.

In the countries with advanced oil industry three systems of refinery – petrochemistry integration are performed, depending on the oil quota, as follows:

- moderate integration, converting between 5 – 10% of crude into petrochemical products;
- high integration, converting between 10 – 25% of the crude processed into petrochemical products;
- petrochemical refineries, converting over 50% of the crude processed into petrochemical products.

The engineers in Romania conceived the integration of the oil refineries with petrochemistry since 1960 and performed it as such until 1989, representing 16% of the used crude.

The orientation to the nonconventional renewable resources is justified only as possibilities of partial replacement of the fossil resources for the petrochemical industry and it does not induce any shade on the use of petrochemical products that will last a long time even after the assimilation of some new raw materials. The necessity of petrochemical products will not disappear at the same time with the oil resources and the change of the raw materials but the processes will adapt to the new sources.

A complex petrochemical plant diagram will be presented.

PRESENT PROBLEMS OF PETROCHEMISTRY

Vasile MATEI

Oil and Gas University of Ploiesti, 39 Bucuresti Bvd., Romania

The present petrochemistry is based on turning to better account some individuals, rarely fractions, of crude-fossil fuels and natural gases. The petrochemical technology, a rich and profitable branch for the development of the petroleum processing industry, is a branch of the organic chemical industry. It tries to solve the challenges of present time that will answer the certitudes of the future. Sooner or later, the fossil fuels will be depleted, accordingly one appeals to present resources, still great, of coal, fossil fuel but particularly to renewable sources in the petrochemistry and to the logistic ones "green chemistry", the petrochemical development of biomass. Therefore the biomass BECOMES MORE AND MORE a petrochemical raw material.

A primary classification of the petrochemical units is based on the reactive primary product type obtained, created by a certain present petrochemical plant. There are three types of "key" plants: steam reforming of hydrocarbons, out of which synthesis gas and hydrogen result, hydrocarbon hydrolysis (steam cracking) resulting particularly ethane and propylene but also butadiene and isoprene, RC plant of non -aromatic naphtha, resulting mononuclear aromatics of petrochemical interest. The tonnage of the petrochemical products varies from the order of millions of tons/month up to several tons/day in the case of special materials.

The petrochemical plants diagrams can vary according on the nature of the raw material, the opportunities of raw material and product sale. Petrochemistry is necessary now and in the near future but it needs to appeal to advanced technical and economical knowledge and important financial resources.

The discussion on a variant of petrochemical diagram is of a complex nature and becomes interesting when there are opportunities on the world market of present petrochemical end products.

A complex petrochemical plant diagram will be presented.