# SICHEM 2018

## BOOK OF ABSTRACTS

**6 – 7 September 2018**

**Romanian Chemical Engineering Society**

**Romanian Chemical Society**

**Academy of Technical Sciences – Chemical Engineering Section**

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

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# BOOK OF ABSTRACTS
# SICHEM – 2018

## PLENARY LECTURES

# *In-silico* design of Genetic Modified Micro-organisms (GMO) of industrial use, by using Systems Biology and (Bio)Chemical Engineering tools

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The work is a systematized and reasonable short review of the main published contributions of Dr. Maria in the field of metabolic processes simulation related to the central carbon metabolism (**CCM**) and, in particular, modelling the dynamics of the gene expression regulation (**GERM**) and of the genetic regulation circuits (**GRC**) in living cells. Application of biochemical engineering, and of nonlinear system control principles and concepts to the modeling of complex cellular processes on deterministic bases are briefly presented with including a rich list of references. These models are essential for understanding and simulating the **CCM**, useful to *in-silico* design of genetically modified micro-organisms (**GMOs**) with applications in industrial biosynthesis, medicine, environmental engineering, vaccine production, biosensors, etc.

A special attention is paid to contributions related to dynamics simulation of the gene expression regulatory modules (**GERM**) and of genetic regulation circuits (**GRC**) in living cells, by promoting novel concepts of a novel cell modelling framework, that is the so-called “variable-volume-whole-cell” (**VVWC**) models. The relatively novel concept of ”whole-cell” simulation of cell metabolic processes has been reviewed to prove its advantages when building-up dynamic models of modular structures that can reproduce complex metabolic syntheses inside living cells. The advantages of the more realistic **VVWC** approach are briefly underlined and exemplified when developing kinetic representations of the gene expression regulatory modules (**GERM**) that control the protein synthesis and homeostasis of metabolic processes. After a brief presentation of the general concepts and particularities of the **VVWC** modelling, both past and current experience with constructing effective **GERM** models is reviewed, together with some rules used when linking **GERM**-s to build-up models for optimized globally efficient genetic regulatory circuits (**GRC**), by using quantified regulatory indices evaluated vs. simulated dynamic and stationary environmental perturbations.

The topics belongs to the emergent field of ***Systems Biology***, defined as “the science of discovering, modelling, understanding and ultimately engineering at the molecular level the dynamic relationships between the biological molecules that define living organisms” (Leroy Hood, Inst. Systems Biology, Seattle). Systems Biology is one of the modern tools, which uses advanced mathematical simulation models for *in-silico* design of **GMOs** that possess specific and desired functions and characteristics. The present work makes a short review of the (bio)chemical engineering principles and deterministic modelling rules used by the Systems Biology for modelling cellular metabolic processes. [1-2]. This involves application of the classical (bio)chemical engineering modelling techniques (mass balance, thermodynamic principles), algorithmic rules, nonlinear system control theory, and bioinformatics rules. The metabolic pathway representation with continuous and/or stochastic variables remains the most adequate and

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preferred representation of the cell processes, the adaptable-size and structure of the lumped model depending on available information and the utilisation scope.

Exemplifications of using such modular **GRC** models for *in-silico* design of **GMO** of industrial use include the own experience on improving several bioprocesses, that is five case studies of high complexity, referring to [3]: 1) *In-silico* design of a genetic switch in E. coli with the role of a biosensor; 2) *In-silico* design of a cloned *E. coli* with a maximized capacity of mercury uptake from wastewaters; 3) *In-silico* design of a genetic modified *E. coli* with a maximized capacity of succinate (SUCC) production; 4) *In-silico* design of a genetic modified *E. coli* with a modified glycolytic oscillator; 5) *In-silico* modulate the bioreactor operating conditions with a modified *E. coli* to maximize the production of tryptophan.

1. Maria, G. (2017) A review of some novel concepts applied to modular modelling of genetic regulatory circuits, Series: Current Trends in Biomedical Engineering & Biosciences, Juniper publishing house, 1890 W Hillcrest Dr, Newbury Park, California 91320, (USA), (50 pag.), ISSN: 2572-1151 (USA), ISBN (USA) 978-1-946628-03-9. https://juniperpublishers.com/ebook-info.php.
2. Maria, G. (2017) Deterministic modelling approach of metabolic processes in living cells - a still powerful tool for representing the metabolic process dynamics, Series: Current Trends in Biomedical Engineering & Biosciences, Juniper publishing house, 1890 W Hillcrest Dr, Newbury Park, California 91320, (USA) (50 pag.), ISBN 978-1-946628-07-7(USA). https://juniperpublishers.com/ebook-info.php.
3. Maria, G. (2018) In-silico design of Genetic Modified Micro-organisms (GMO) of industrial use, by using Systems Biology and (Bio)Chemical Engineering tools, Series: Current Trends in Biomedical Engineering & Biosciences, Juniper publ. Inc., 1280 Vintage Oak St, Simi Valley, California 93063, (USA), in-press (150 pag.), ISBN (USA). https://juniperpublishers.com/ebook-info.php.

**Motto:**

> **“All models are wrong, but some are useful”**
> **Box, George E.P., Draper, Norman, R. (1987). *Empirical model-building and response surfaces*, p. 424, Wiley, ISBN 047 1810339.**

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Technische Chemie, ETH Zurich
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Technische Biochemie, Univ.Saarlandes,
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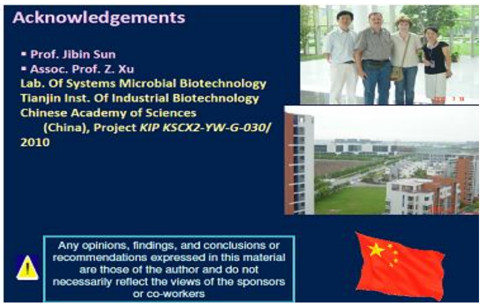
▪Dr. Mara Crisan, Ing. Marina Mihalachi (co-workers for applications)

Prof. Stefan Szedlacsek group of enzymology from Institute of Biochemistry of the Romanian Academy (Bucharest, Romania)

Prof. A. Zeng group from TU Hamburg (DAAD Project A/09/02572 / 2009 Germany)



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▪ Assoc. Prof. Z. Xu
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Tianjin Inst. Of Industrial Biotechnology
Chinese Academy of Sciences
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Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author and do not necessarily reflect the views of the sponsors or co-workers

# Syntheses of Advanced Nanomaterials for Electrochemical Biosensors and Energy Storage Applications

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The existing carbon materials can be classified into activated carbon (0-dimensional), carbon nanotubes (CNT) (1-dimensional), graphene (2-dimensional) and carbon foams (3-dimensional). Among these, graphene is well known to be the top candidate; However, preparation of graphene from graphite is an intricate procedure that can lead to an explosion during the oxidation of graphite. Similarly, the preparation of CNT also has some practical difficulties due to the complicated instrument setup. Fascinatingly, the preparation of ACs is simple, environmentally friendly and cost-effective. For the first time, Pongam seed shells-derived activated carbon and cobalt oxide (~2-6 nm) nanocomposite (PSAC/Co3$O_4$) is prepared for the high performance non-enzymatic glucose sensor and supercapacitors. Remarkably, the fabricated glucose sensor is found to be exhibit an ultra-high sensitivity with a lower detection limit, and long-term durability. Moreover, the PSAC/$Co_3O_4$ electrode possess an appreciable specific capacitance and long-term cycle stability. The high surface area carbon porous materials (CPMs) synthesized by the direct template method *via* self-assembly of polymerized phloroglucinol-formaldehyde resol around a triblock copolymer template were used as supports for nickel nanoparticles (Ni NPs). Further electrochemical measurements by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) also revealed that the Ni/CPM modified electrodes showed excellent sensitivity (59.6 µA $\mu M^{-1}$ $cm^{-2}$) and relatively low detection limit (2.1 nM) toward the detection of Hg(II) ion. The system is also been successfully applied for detection of mercuric ion in real sea fish samples. Furthermore, a facile method has been developed for fabricating selective and sensitive electrochemical sensor for the detection of toxic metal ions, which invokes incorporation of palladium nanoparticles (ca. 3–4 nm) on fruit peels-derived porous activated carbons (PACs). The Pd/PAC-modified GCEs were exploited as electrochemical sensors for the detection of toxic heavy metal ions, viz. $Cd^{2+}$, $Pb^{2+}$, $Cu^{2+}$, and $Hg^{2+}$, which showed superior performances for both individual as well as simultaneous detections. For simultaneous detection of $Cd^{2+}$, $Pb^{2+}$, $Cu^{2+}$, and $Hg^{2+}$, a linear response in ion concentration range of 0.5–5.5, 0.5–8.9, 0.5–5.0, and 0.24–7.5 µM, with sensitivity of 66.7, 53.8, 41.1, and 50.3 µA $\mu M^{-1}$ $cm^{-2}$, and detection limit of 41, 50, 66 and 54 nM, respectively, were observed. Moreover, the Pd/PAC-modified GCEs is also show perspective applications in detection of metal ions in real sample, as illustrated in this study for a milk sample. In addition, the synthesis of highly dispersed and stable ruthenium nanoparticles (RuNPs; *ca*. 2–3 nm) on porous activated carbons derived from

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*Moringa Oleifera* fruit shells (MOC) is reported. The as-prepared MOC carbonized at 900 °C was found to possess a high specific surface area (2522 $m^2 g^{-1}$) and co-existing micro- and mesoporosities. Upon incorporating RuNPs, the Ru/MOC nanocomposites loaded with modest amount of metallic Ru (1.0–1.5 wt%) exhibit remarkable electrochemical and capacitive properties, achiving a maximum capacitance of 291 F $g^{-1}$ at a current density of 1 A $g^{-1}$ in 1.0 M $H_2SO_4$ electrolyte. These highly stable and durable biomass carbons modified electrodes, which can be facily fabricated by the eco-friendly and cost-effective route, should have great potentials for practical applications in energy storage, biosensing, and catalysis.

1. Chen, S.M. et.al (2015) Honeycomb-like Porous Carbon−Cobalt Oxide Nanocomposite for High-Performance Enzymeless Glucose Sensor and Supercapacitor Applications. ACS Appl. Mater. Interfaces., 7, 15812−15820.
2. Chen, S.M. et.al (2015) Nickel Nanoparticle-Decorated Porous Carbons for Highly Active Catalytic Reduction of Organic Dyes and Sensitive Detection of Hg(II) Ions. ACS Appl. Mater. Interfaces., 7 (44), 24810–24821.
3. Chen, S.M. et.al (2016) Palladium Nanoparticles Incorporated Porous Activated Carbon: Electrochemical Detection of Toxic Metal Ions. ACS Appl. Mater. Interfaces., 8 (2), 1319–1326.
4. Chen, S.M. et.al (2016) Ruthenium nanoparticles decorated curl-like porous carbons for high performance supercapacitors. Scientific Reports. 6, 19949.

# Professor Ionel A. Atanasiu – my Professor's Professor

Dănuț-Ionel VĂIREANU*

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Born in 1894, on September 25, in Galaţi, Prof. Dr. Docent Ionel A. Atanasiu, is one of the founders of the electrochemistry discipline in Romania. Graduate of the Vasile Alecsandri High School of Galaţi, he enrolled in 1913 at the University of Bucharest, Faculty of Sciences, Physical Chemistry Section, from where he enlists as a combat officer in the Romanian army. He actively participated in the First World War, is injured and declared invalid of war. He returned to the university, finished it well in 1920, and on the 1st of January 1921 he was appointed assistant at the Institute of Industrial Chemistry of the University of Bucharest. Between 1924 and 1926 he attended the University of Nancy, receiving a scholarship, where he specialized in electrochemistry and defended his doctorate in electrochemistry in 1926. He returned to Romania, and in 1926 he was appointed Head of Section of the Institute of Industrial Chemistry. He introduced electrochemistry as a university study discipline and in 1938, with the establishment of the Faculty of Industrial Chemistry at the Polytechnics of Bucharest, Professor Ionel A. Atanasiu laid the foundation of the electrochemistry discipline as a stand-alone discipline, separating it from the discipline of analytical chemistry. In 1951 he was promoted to Professor, and in 1954 received his Docentiate Doctorate in Technical Sciences and became Head of the Department of Electrochemistry and Physical Chemistry. He is remembered as an exceptional professor with a tremendous academic capacity, who did not raise the tone of his voice ever, and never offended anybody, a true Lord, although he was of a francophone formation, a professor you enjoyed seating the exams you had to be perfectly prepared for it, if you did not want to run the risk to have the subjects explained to you again. He publishes an impressive number of personal contributions (papers, articles, books, laboratory notebooks), some of them are still referenced and quoted today, and raised generations after generations of outstanding electrochemists, being their PhD supervisor, even after 1969, when retired and was appointed as a Professor Emeritus. An immeasurable loss occurred in the world of the academic community in the cold winter fatidic day of 19th of December, 1978, when Professor Ionel A. Atanasiu passed away, his loss being felt deeply by all those who knew him.

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# Design of a master degree in chemical engineering integrated with bachelor degree

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The outcome specifications for graduates and masters of science in Chemical Engineering adopted by the Romanian Agency for Quality Assurance in Higher Education (ARACIS) are well known and the universities struggle to fulfil these requirements.

However, the state of education in Chemical Engineering is not entirely satisfactory for every actor in Romania: students, employers, teachers and society. Students are not happy about the crowded curriculum, dificulties in learning, too much exams. Employers and society would like superior skills, especially in communications but also in some technical points. Teachers complain about low quality of students' knowledge at the entry and their attitude towards study.

The issue may arise from transforming the vetust undergraduate programmes with 5 years duration into 4 year – programmes, in the Bologna process, by compressing all the curricula and also adding new topics, as the society evolved. Also, let's bear in mind that undergratuate studies in Romania offer a complete specialization, unlike studies in other European countries. Then, a 2 year-master degree intended for in-depth study, competences and abilities is difficult to put into effect, in contradistinction to the research master degree which is clearly defined.

The European Network for Engineering Accreditation (ENAEE) also recognizes, in the frame of Bologna process, the Master degree programmes integrated with Bachelor degree (Master awarded). This includes min.270 ECTS credits.

So, we designed such an integrated degree for Chemical Engineering exemplified on the specialization Petroleum Processing and Petrochemistry, by taking into account the National specific of our educational system. We hope that the efficiency will improve this way.

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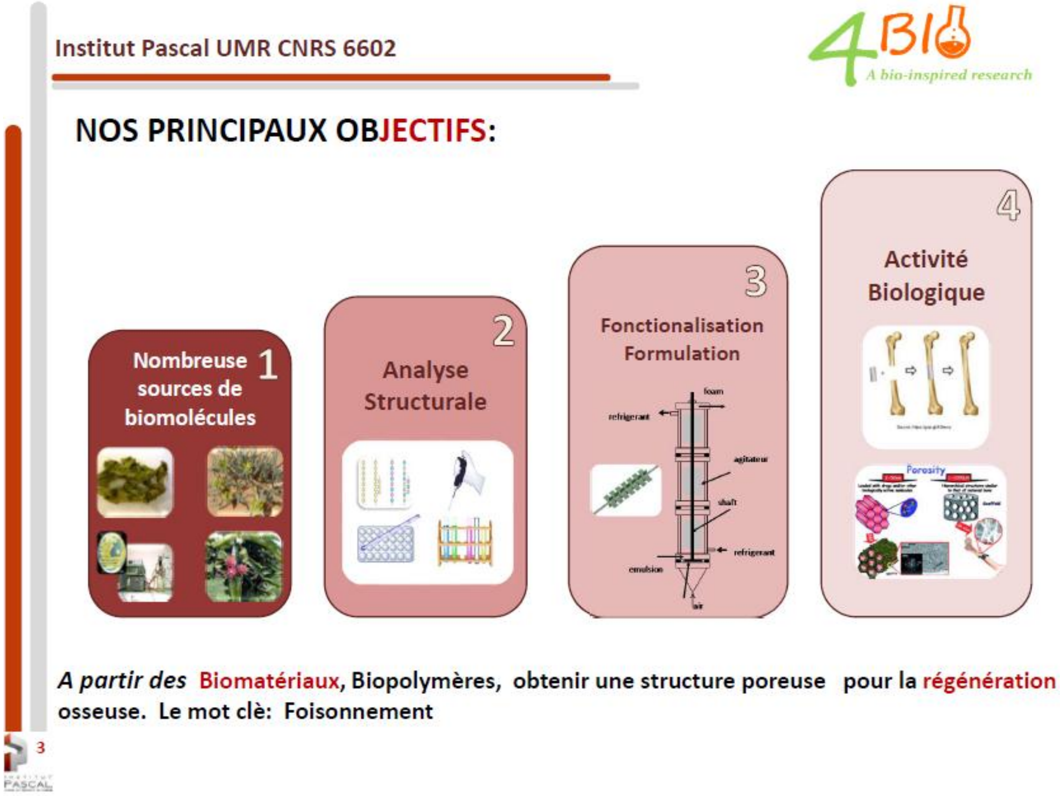
# Production of porous material based on chitosan for bone generation under steady state flow condition

Gholamreza DJELVEH[*]



Institut Pascal UMR CNRS 6602

**NOS PRINCIPAUX OBJECTIFS:**

1 Nombreuse sources de biomolécules

2 Analyse Structurale

3 Fonctionalisation Formulation

4 Activité Biologique

*A partir des* Biomatériaux, Biopolymères, obtenir une structure poreuse pour la régénération osseuse. Le mot clè: Foisonnement

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# Romanian Chemistry Company: Beginning and Expected Future

Board Chairman Virgiliu BĂNCILĂ[*]

*Chimcomplex SA, Borzești, România*

> *"After the IT sector, Romania's chemical industry has the second-largest growth potential, it has the all resources, energy, gas, minerals, industrial platforms, labor force and plenty of market, what more could it need?"*
> *(Reported by Luiza Ilie, February 2018 https://www.reuters.com/article/us-romania-chemicals-chimcomplex/romanias-chimcomplex-plans-expansion-drive-after-acquisition-idUSKCN1G72BZ)*

As an essential part of SCR Group, the strongest industrial group in Romania, Chimcomplex SA Borzesti is one of the most important chemical producers from Romania.

Chimcomplex https://www.chimcomplex.ro

Chimcomplex
Membra a grupului
SCR

Excellence in chemistry

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# BOOK OF ABSTRACTS

# SICHEM – 2018

# KEYNOTE LECTURES

## A – Chemical and biochemical engineering (CBE)

# Supercritical fluid technology: a sustainable and scalable approach for advanced material design and recycling

Cyril AYMONIER[1*], Marie CLAVERIE[1,2], Marta DIEZ-GARCIA[1],
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Supercritical fluid flow synthesis technologies are developed from the beginning of the 90's in the field of advanced materials by design. This technology of material processing is continuous, fast (few tens of seconds), sustainable and scalable and gives access to high quality nanostructured materials with unique physico-chemical properties, meaning which can not be obtained with other synthetic methods.

After a brief introduction on supercritical fluids, this presentation proposes to describe the principle of the preparation of advanced materials using this continuous process. A focus will be proposed on the *in situ* characterizations developed in the last 10 years to be able to understand, model but also to master the formation of nanostructures in supercritical fluids. As an illustration, we will present the first proof of the synthesis in few tens of seconds of geominerals, namely talc, in a continuous millifluidic process. Very interestingly, this synthetic talc exhibits unique properties as its hydrophilicity knowing that naturel talc is hydrophobic. In this new field of geomineral synthesis, we went one-step forward with the demonstration of the possibility to prepare highly crystalline geominerals in just few seconds again but under thermodynamically metastable conditions with the synthesis of the torbermorite mineral which is not abundant in nature but very interesting in the construction industry. The mastering of the chemistry coupled with one pot multi-step processes opens the road towards the continuous design of multifunctional materials as illustrated with functional layer double hydroxide. All these materials can now be produced from laboratory scale for research & development investigations to pilot scale for industrial purposes.

Beyond the design of advanced nanostructured materials, near- and supercritical fluids are also powerful reaction media to offer innovative processes in the field of material recycling. This will be illustrated with the recycling of carbon fibres from carbon fibre reinforced polymers (CFRPs). Compared to pyrolysis, fluidized bed and low temperature processes, which are other studied approaches for CFRPs, solvolysis in near- or supercritical fluids is a great alternative to recover fibres as it provides a high retention of mechanical properties and fibre length and a high potential for material recovery from resin. A second example will concern the recycling of scrap magnets.

The benefits of the sub- and supercritical continuous route include not only better performances for advanced applications but also environmental issues associated with the synthesis process. This will be emphasized with the studies performed using LCA approaches coupled with risk assessment ones.

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# Control Strategies of the Waste Water Treatment Plant

Vasile-Mircea CRISTEA[*], George OSTACE, Melinda VÁRHELYI,
Marius BREHAR

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Restoring the quality of the wastewater has been continuously growing in importance due to the large increase of the water consumption implied by modern life, human activities and to the exponential population growth. The wastewater treatment plant (WWTP) plays the key role in this enterprise and its efficiency is providing guaranties for keeping clean and safe the sources of this crucial molecule for life.

One of the most widespread technologies for the secondary treatment of wastewater is the activated sludge process. Inspired from processes taking place in nature, the activated sludge technology is able to ensure the digestion of the dissolved and suspended organic matter, in association to the removal of the nitrogen and phosphorous nutrients.

Operation of the WWTP has to conform to regulations becoming more and more demanding in order to impose the safe and clean environment requirements. Efficiency of the WWTP operation has to guarantee not only the quality of the effluent water by also to satisfy economic demands, such as minimizing the operating costs and maximizing the production of biogas obtained by anaerobic digestion. Achieving all these objectives is only possible by using monitoring and control systems implemented on computers having also the ability to run dynamic simulation models for the WWTP.

This work proposes and tests by simulation a set of control strategies for the water line of the WWTP, aimed to keep its operation within the allowed limits and to reduce operating costs. The challenging control tasks emerge not only from the complexity of the biochemical processes involved but also from the continuously changing flow and concentration of the WWTP influent, showing also seasonal and weather (dry, rain, storm) dependent characteristics.

The WWTP simulation is performed using the Activated Sludge Models no. 1 (ASM1) and no. 3 (ASM3), with Ludzsak-Ettinger, $A^2O$ and Bardenpho configurations. They have associated the primary and secondary settlers. PI and Model Predictive Control algorithms are used to implement the control strategies. Control of the Dissolved Oxygen, Ammonia, Nitrates and Nitrites in different locations of the WWTP water line are investigated and simulation results are compared to reveal the limitations and incentives of the proposed control approaches.

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# Carbon nanostructures from hydrocarbon pyrolysis: Synthesis and surface evolution

S.V. SAVILOV*, N.I. OSIPOV, A.S. IVANOV, V.V. LUNIN

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Different types of carbon nanomaterials can be represented by 0D (carbon dots, nanoonions), 1D (nanotubes, nanofibers) and 2D (nanflakes, graphene) quasi-molecules as well as 3D structures (foams). All of them demonstrate unique and adjustable electrophysical and surface properties, which make them promising for different applications. Incorporation of nitrogen in sp$^2$-carbon layers during their synthesis accelerates electron transfer, provides protonation of nitrogen and induction of the negative charge on the adjacent carbon atoms that increases electron capacity and makes heterosubstituted materials an excellent media for energy storage and catalysis.

Physical and chemical properties of carbon nanostructures depend on the type and content of heteroatoms incorporated in the carbon frame as well as on surface groups. That is why oxidative and thermal treatment as well as further modification is crucial for tuning their behavior. Particularly, the presence of carboxylic, anhydride, lactone and phenol groups induces the acid behavior of the carbon surface whereas carbonyls lead to the base properties. At the same time acid groups promote fine dispersion of metal particles on nanomaterials surface, that is important for catalytic properties.

Present work gives the general impression on carbon nanomaterials, including heterosubstituted, can be obtained pyrolytically. It is mostly focused on nanotubes and nanofibers, few layers nanoflakes and foams. The results of HRTEM, XPS, and thermal analysis of these materials are described to trace structural and chemical properties evolution of the materials under discussion. The examples of the application of them in catalysis and energy storage systems are given.

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# Control of heterogeneous reactive distillation

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Reactive distillation offers significant advantages such as reduced investment and operating costs. An important class of reaction systems which can be efficiently performed by catalytic distillation comprises two reactants (A, B) and two products (C, D). Often, one product is the high-boiling species and is obtained as bottom stream, while the other is involved in a low-boiling azeotrope and is obtained as distillate. This azeotrope has the beneficial effect of displacing the chemical equilibrium, but also the disadvantage of an impure distillate. However, when heterogeneity of the azeotrope makes possible a liquid – liquid split of the condensed distillate, the reactant-rich phase can be returned to the column as reflux, while the product-rich phase is on the side of the distillation boundary which allows obtaining the top-product with high-purity.

However, the controllability of the process is as important as the economics. Integration of reaction and separation in a single unit makes the control more difficult. Firstly, the reactants must be fed in the stoichiometric ratio, which cannot be achieved by simple ratio control or other feed-forward techniques due to unavoidable measurement and control implementation errors. Secondly, both decanter-outlet flow rates must be used for controlling the level of corresponding phases, removing in this way one degree of freedom (reflux or distillate rate) which in conventional distillation is normally used for direct or inferential control of distillate purity. Last but not least, the use of concentration control loops is often restricted due to significant lags, reduced reliability and high costs of concentration measurements.

In this contribution, we present a novel class of control structures with one-point temperature control applicable to heterogeneous reactive distillation. The flow rate of one fresh reactant sets the production rate. The product purity is achieved by temperature control manipulating the reboiler duty. Monitoring the phase ratio (i.e. L/D) and adjusting the second reactant feed is the key element in ensuring the correct stoichiometric ratio. When L increases, it indicates that the reactant starts to accumulate, and therefore less amount shoylde be added. This control philosophy can be implemented in different ways. Moreover, design modifications (such as feeding one reactant in the decanter) are suggested, in order to reduce interactions, improve the controllability and speed-up the disturbance rejection. The efficiency of these novel control structures is illustrated using several case studies. Overall, the new control structures are resilient to a much wider range of disturbances compared to the different schemes suggested in the literature.

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# BOOK OF ABSTRACTS

# SICHEM – 2018

# KEYNOTE LECTURES

## B – Applied organic, inorganic, and supramolecular chemistry (AOISC)

# Towards future materials based on natural resources

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The most abundant natural polymer on Earth, i.e. cellulose, has been already implemented as a key source for a wide variety of products [1]. Cellulose, due to its biochemical similarity with human extracellular matrix components is readily recognized and accepted by the body. Moreover, cellulose, inherit numerous advantages including natural abundance, relative ease of isolation, and room for chemical modification to meet varying technological needs. Obviously, from extraction to the end-product, cellulose suffers a long chain of processes including delignification, extraction, purification, often derivatization (functionalization). The most common processes involving chemical modification of cellulose includes oxidation reaction [2-5]. *N*-hydroxyphthalimide (NHPI) as one of the best and modern catalysts, having great performances in oxidation reaction, when through a homolytic scission of the >N-O-H bond, the active species, phthalimide-*N*-oxyl radical (PINO) is formed, has been extensively used for the selective oxidation of cellulose, Figure 1 [6-8].

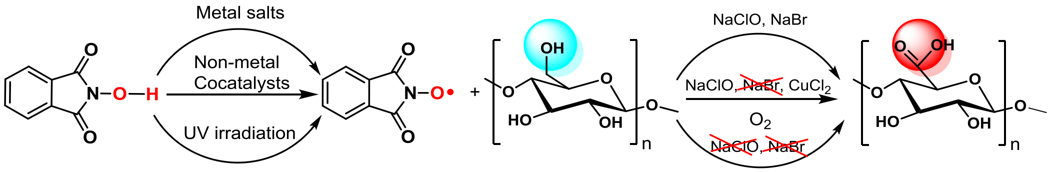

*Fig. 1 Cellulose oxidation performed by N-hydroxyphthalimide under various reaction conditions*

This presentation gives an overview of the most recent achievements made by our group, in the field of cellulose oxidation and the applications of the resulted products.

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# Towards the plasmonic optical nanopore for single molecule analysis

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Recently the USB-size portable solidstate nanopore device called MINion with an electrical detection technique for single molecule analysis was developed by Oxford Nanopore Technology. However, the large error rates were reported by several journals, even though the significant error reduction was developed after the invention of the portable nanopore device. Furthermore, most of biosensor devices are utilizing the optical detection technique. Hence, we introduce the optical nanopore fabrication by using plasmonic optical enhancement effect. First, the Au thin films were vacuum-deposited on the nanometer thin SiN film, followed by removal of SiN film and by drilling Au apertures by using focused ion beam (FIB) technique. Then, electron beam irradiations on the specimens either by using low energy field emission electron beam microscopy (FESEM) or high energy Transmission electron beam microscopy (TEM) have been carried out to form the nanopore as in Fig1. In addition, the periodic grooves, or the periodic Au aperture array were fabricated on the Au sample in order to provide strong plamonic optical enhancements. During electron irradiations on the fabricated Au surface, we observed the diffused binary Au-C membrane due to Ostwald ripening and also the unstable Au-C mixed phase change via spinodal decomposition. We found that the Au cluster diffusion would depend upon the electron beam fluencies. We also observed irregular melting and diffusion of Au particles under electron beam influences. These may be due to the lower melting point of the Au particles and stable high melting temperature from Au clusters with magic numbers. However, the exact understanding and detailed phenomena are further to be investigated.

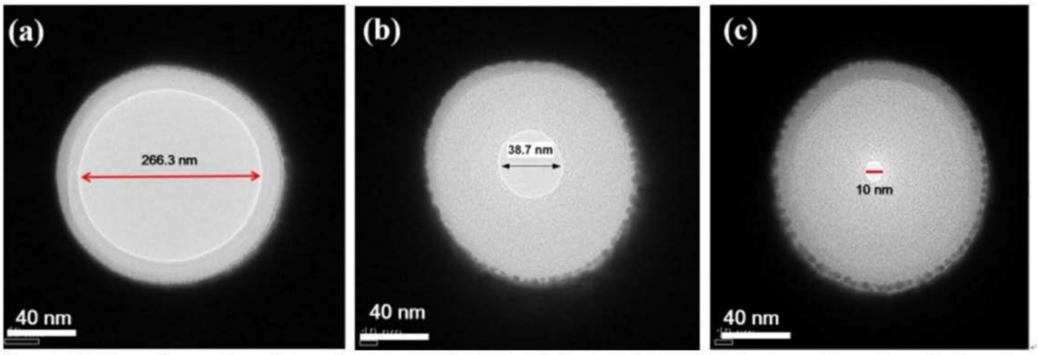

Figure 1. Pore formation dependent upon the 2 keV, 1.4 nA FESEM electron beam irradiation for 1 min (a) , 3 min (b), 5 min (c). The corresponding diameter is measured to be 266.3 nm, 38.7 nm, and 10 nm, respectively.

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# Oxidation resistance of $Fe_3O_4$ thin films doped with metal elements

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Iron oxides exhibit half metallic, ferrimagnetic, and semiconducting properties because of phase transformations from wüstite ($Fe_{1-x}O$) to magnetite ($Fe_3O_4$), to maghemite ($\gamma$-$Fe_2O_3$), and finally hematite ($\alpha$-$Fe_2O_3$) as oxidation proceeds. These properties may be exploited for a range of applications. In particular, $Fe_3O_4$ forms inverse spinel structure with $Fe^{2+}$ in octahedral B site and $Fe^{3+}$ in both tetrahedral A site and octahedral B site, inducing a relatively low electrical resistivity by hopping electrons between $Fe^{2+}$ and $Fe^{3+}$ at temperatures exceeding 120 K (i.e., Verwey transition [1]).

To maintain the performance of devices that contain $Fe_3O_4$ and extend its use in other applications, the transition temperature of $Fe_3O_4$ needs to be elevated. In powder form, iron oxide doped with metal elements exhibited oxidation resistance, elevating the transition temperature from 773 K to 923 K [3]. When cast as a film, it is still unclear how metal-doped $Fe_3O_4$ thin films resist oxidation.

An oxidation resistance of $Fe_3O_4$ thin films doped with Ge, Mo, W, and Mg was investigated following the two steps: i) a metal-doped $Fe_3O_4$ thin film was first deposited using radio-frequency sputtering with metal chips set on a ceramic $Fe_3O_4$ target. ii) the deposited film was subsequently annealed in air at temperatures from 673 K to 973 K.

The magnetization of undoped $Fe_3O_4$ thin film decreased as the annealing time increased until it completely disappeared after 1 day at an annealing temperature of 673 K due to phase transformation to weak ferromagnetic $\alpha$-$Fe_2O_3$. The Mg-doped film exhibited similar behavior, while the W-, Mo-, and Ge-doped films maintained relatively large magnetization values, even after annealing times that exceeded 300 days. The Ge-doped film exhibited the greatest stability with an activation energy of 490 KJ/mol, which was 2.5 times larger than that of undoped film. At 673 K, the structure of the Ge-doped $Fe_3O_4$ thin film transformed to a heterostructure that consisted of $\alpha$-$Fe_2O_3$ and $Fe_3O_4$ that contained Ge, in which the $\alpha$-$Fe_2O_3$ layer (<200 nm) grew on the surface of the film during the heat treatment. Furthermore, magnetization increases from 3.1 kG (as-deposited) to 3.7 kG (after 500 days) despite the heat treatment in air. The inclusion of Ge allows $Fe_3O_4$ to resist oxidation. This result indicates that an inclusion of Ge exhibits an oxidation resistance of $Fe_3O_4$.

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# BOOK OF ABSTRACTS

# SICHEM – 2018

# KEYNOTE LECTURES

## C – Biomaterials and composites in chemical and biochemical applications
## (BCCBA)

# A glimpse on the effect of CNT on titania in terms of catalytic action and environmental aspects

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In recent scenario composites are much focused due to their versatile applications in terms of superior properties. Titania is an important ceramic material available in various polymorph like anatase, rutile and brookite. It is used primarily for pigments in dye, colorants, nucleating agents in glass-ceramics, semiconductors, antibacterial agent and photocatalyst. Nano tubes of titania are of growing interest in environmental, energy applications because of enhancement of structure dependent photoelectronic properties. Carbon nano tube is broadly available as SWCNT (Single Wall CNT), MWCNT (Multiple Wall CNT) depending on the nature of applications and is actually the member from fullerene family. The CNT is primarily focused for superior mechanical, electrical conductivity, thermal conductivity and others. Nanoscale structure of nanotubes along with covalent bonding imparts high resilience, high tensile strength, good thermal and mechanical stability. CNT also contain porous carbon having uniform, regular pore size, structure, interconnection of pores leading to tailoring of surface properties. Above combination of physical properties make CNT one of the candidates for catalyst and adsorbent in future industrial applications. Adsorption of organic sulphur compounds in diesel fuel to surface of composite catalyst material is a vital interest at present scenario for desulphurization process to have clean fuel.  Reduction of recombination rate must be focused and shift of catalytic action in visible region are the two major challenges for photocatalyst. CNT also enhances photocatalytic activity mainly by three ways like 1) acting as a sink for electrons for enhancing lifetime of separated charges 2) surface impurity dopant creating band gap energy states 3) forming Ti-O-C or Ti-C defects sites to enable visible light absorption and photocatalytic actions. Proper attachment of CNT on titania or Titania on CNT is a challenge which guides electron-hole recombination rate thus controlling electron density on the interface. Mechanism of attachment of nano crystal to carbonaceous species like graphene nanoribbons, CNT are of vital interest having anisotropic growth pattern of nanocrystal from carbon based material. Such facts lead to proper surface engineering causing enhancement of specific properties. Photocatalytic degradation of organics and desulphurization to produce clean fuel are vital aspects for environmental protections as well as to reduce green house gas emissions.

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# Elaboration and characterization of biocomposites from epoxidized sunflower oil and alfa fibers

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The aim of the present study is to develop biocomposites based on modified sunflower oil as resin and short natural fibers from Alfa plants (*Stipatenacissima L.*) as reinforcement.

Epoxidized sunflower oil (ESFO) was first chemically modified via acrylation reaction to obtain acrylated epoxidized sunflower oil resin (AESFO). The AESFO resin was then copolymerised with styrene as co-monomer. Operatory conditions of this modification were optimized. The mechanical properties (stress at break and elongation at break) of the prepared samples were characterized. Then, alfa fibers treated with a 5% NaOH solution were used as bio-reinforcement at various levels. The prepared biocomposites were characterized in terms of mechanical properties and scanning electron microscopy (SEM).The best results were obtained with the ratio of 7.5 wt %.

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# PEEK-PVDF blends and their nanocomposites with nano hydroxyapatite and multiwall carbon nanotube biocompatibility, rheology and morphology

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Polyether ether ketone (PEEK) is a semi-crystalline, durable plastic and radiolucent, biocompatible material which can be machined such as bone which is preferred somehow to metallic biomaterials. Polyvinylidene fluoride (PVDF) is used in wide range of applications and also as biocompatible implanting material and its textile is used as scaffold to strengthen and to enhance the regeneration of new tissue. PEEK in the meantime it is a hydrophobic and biologically inert plastic that require to be modified chemically or physically to increase the adhesion strength and the intention of osteoblasts to grow on the surface of PEEK. There have been efforts to incorporate hydroxyapatite (HAp) micron and also nano size particles into PEEK in a proper amount capable to accelerate the metabolic activity and mineralization of osteoblast. The PEEK implants surfaces can be treated and coated with HAp or titanium by deposition photo-chemically or by sputter coating, electron beam deposition and thermal plasma spray. Carbon-fiber and nanotubes has been used to enhance thermal, mechanical, electrical and rheological properties of PEEK polymer use in orthopedic implants and in bone cement. It may be necessary in some application to tailor the bio-mechanic of implants to minimize damage to adjacent bones by using rubbery PVDF in blend with PEEK to enhance the mechanical performance of implant by balancing the stiffness of PEEK by the toughness of PVDF. In this research polyether-ether-ketone (PEEK) is melt blended with polyvinylidene fluoride (PVDF) and reinforced with Nano Hydroxyapatite (HAp) and multiwall carbon nano-tube (MWCNT). The viscoelastic behavior of samples are studied by small amplitude oscillation rheometry and the morphology of systems characterized by using scanning electron microscope SEM. The different biological properties of the samples such as cell attachment, growth, proliferation and cellular morphology are also investigated. In all percentage of PVDF in the blend, the complex viscosity is positively deviated from mixture rule which can be due to the considerable interfacial interaction between PEEK and PVDF. The enhanced compatibility of the blends is approved by semi-circular shape of Cole-Cole plots more pronouncedly at higher PVDF content than 7.5 wt%. The mean particle size of PVDF droplets increase from 0.65 micron for 5 wt% to 0.89 and 1.2 micron respectively for 7.5 and 10 wt% with an elongated none spherical droplets. The optical absorbance of PEEK/PVDF and PEEK/PVDF/HAp decreased as compared to neat PEEK as control after one day of culture time. It is found that the nano-composite containing 0.5% MWCNT shows higher cell viability with decreased optical absorbance. The images of fibroblast cells show that the cells are grew up with a spindle like morphology and the spread of cells in hybrid nano-composites PEEK/PVDF/(HAp+MWCNT) are more pronounced.

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# BOOK OF ABSTRACTS

# SICHEM – 2018

# KEYNOTE LECTURES

## D – Green applied chemistry and agro-resources valorization

## (GACARV)

# Microstructure and properties of activated carbon fibers deriving from liquefied wood

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The microstructure and properties of activated carbon fibers deriving from liquefied wood was discussed in this paper. The results indicate that (1) As the increase of activation temperature or activation time, the BET specific surface area and total pore volume were increased. At 650-800℃, the micropores were formed, and no change when the burn-off being more than 45%; At 850-950℃, the micro/mesopore size was enlarged, when the burn off being more than 75%, the Smi decreased sharply; when the burn-off was more than 90%, the maximum mesopores ratio was about 49.5% and mesopores at 2-5.8 nm were formed. (2) WACF prepared at higher temperatures possessed more carbon and less of elements O or N.

The relative content of the graphitic carbon decreased as the temperature increased. （3）The specific capacitance (Cs) of WACF reached 280 F $g^{-1}$ in 1 M $H_2SO4$ electrolyte; The Cs retention ratio after 2000 charging-discharging cycles at 10 A $g^{-1}$ reached up to 99.3%. The good supercapacitor performance of WACF was due to large Smi (2300 $m^2g^{-1}$) and mesopores at 3-4 nm connected reciprocally.4）Compared with the ACF activated by steam at the same temperature, the samples ACF-KOH-3 have more small micropores (<0.7 nm) in addition to more mesopores in the range of 2-4 nm, and The KOH-activated ACF had more oxygenated functional groups on their surfaces.

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# BOOK OF ABSTRACTS

# SICHEM – 2018

# ORAL PRESENTATIONS

## A – Chemical and biochemical engineering (CBE)

# Extraction optimization of cupric ions by cloud point

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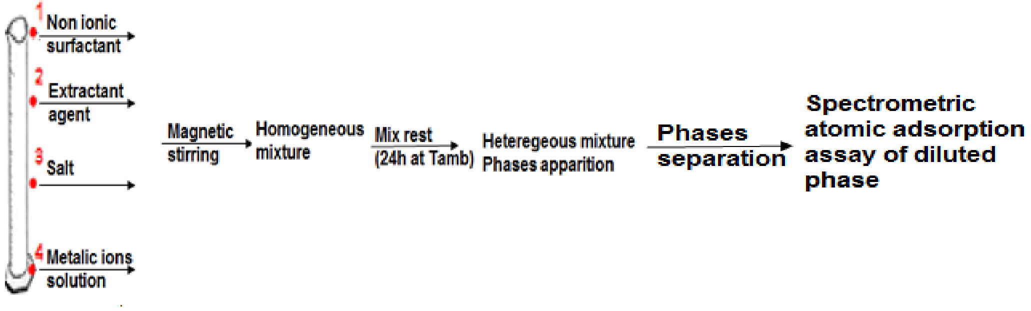
Human activities have considerably increased the release of various pollutants into the environment, some of which are toxic not only to flora and fauna but also to humans. Thus, an environment that is preserved and free from metallic toxic threats, water and healthy food is a growing concern. Better production and less pollution are the challenges facing the industry in any sector. To this end, the chemical industry generally strives to reduce environmental impact by using renewed, environmentally friendly and cost-effective industrial processes.

In addition, several pre-concentration and separation techniques are known, as well as the cloud point extraction (CPE) [1-3]. In order to optimize the operation of a coacervate extraction process, it is extremely important to take into account, on the one hand, the choice of the surfactant, which must be the most efficient and, on the other hand; and to know well the evolution of the factors that governs the effectiveness of this technique. The extraction experiments showed that the cupric ions are extracted with the following optimal parameters: pH 2.0; Concentration of $LI_M$ equal to 0.08M; Triton X-100 mass ratio equal to 0.1%; $KNO_3$ mass ratio equal to 1%; at ambient temperature.

The reaction of extraction of cupric ions by coacervat is instantaneous. From the first minute, a good yield of 93.2% (almost the maximum) is obtained.

Under these optimal conditions, coacervate extraction makes it possible to extract 5000 times the maximum permissible concentration of $Cu^{2+}$ in industrial effluents in a single operation and with no energy input (no heating).



Appropriate procedure for the study of the extraction of metal ions by coacervat

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# Adding value to waste vegetable oils through thermal processing

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Depletion of fossil resources, such as petroleum and gas, leads to necessity of switching to renewable resources for fuels production. Vegetable oils are worthy to be taken into account as long as they don't compete with food industry. For this, non-edible oils and waste cooking oils can be processed. Seldom, they are used as fuel oil but adding-value to them would be more attractive; obtainable valuable products are diesel-like and kerosene-like fuels [1], and also low molecular weight hydrocarbons, especially monomers [2]. A variety of processes can be applied: the thermal cracking in presence or in absence of an inert gas, over an inert solid material, in presence or in absence of steam, or using catalysts.

The team performed original experiments related to the thermal cracking of waste vegetable oils in a batch reactor [3], and in a continuous reactor [4], in different reaction conditions. Despite the fact that temperature was limited to 650 $^{o}$C, good yields of olefins (up to 29% wt) were obtained, especially in steam cracking, comparable with others' data [5] and also comparable with those from liquid hydrocarbon fractions processed in steam cracking. The steam-feed ratio is the same as in the industrial process (0.3:1-1:1), so processing waste oils together with hydrocarbon feed is possible, provided that mixture is or homogenous or in stable emulsion.

Apart of olefins, other interesting products with good yields are: light hydrocarbons in the cracked gas, kerosene-like and Diesel-like fuels. On the other hand, $CO_2$ + CO in high yields (up to 17%) are specific for vegetable oil thermal cracking and disposal or chemical transformation arise a challenging problem.

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# A comparative study on biochemical ethanol production of *Ulva lactuca* macroalgae

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Green algae are plant systems that during their development synthesize a large number of chemical compounds by photosynthesis. From this, heavy polysaccharides such as cellulose reach high concentrations in mature algae (sometimes exceeding 50% by mass of dry matter). Bioethanol can be produced by biochemical methods of *Ulva lactuca* specie by transforming polysaccharides into fermentable sugars and fermentation using appropriate microorganisms.

Algae were harvested from the beaches of the Romanian Black Sea seaside during the summer of 2016. In order to have an efficient process, *Ulva lactuca* sp. has been used in two ways: very fresh or dry, to avoid the gelling process [1].

The process proposed in this work involves several steps of physical pretreatment of algal biomass needed to prepare the hydrolysis medium [2]. In enzymatic hydrolysis, cellulase from Aspergillus niger is the enzyme most commonly used for the degradation of polysaccharides. A commercial yeast of *Saccharomyces cerevisiae* was used to start the alcoholic fermentation.

The concentration of volatile substances and ethanol in the fermentation was determined by the SR 184-2 reference method, using the CHEM Model OH-1 glass apparatus.

Under the same conditions, ethanol yields are higher in case of fermentation with yeast of hydrolyzate from fresh *Ulva lactuca sp.* (max. 0.0234 g alcohol/g d.m.) than fermentation with yeast of dried *Ulva lactuca sp.*(max. 0.0211g alcohol /g d.m.).

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# Parameters Estimation in New Kinetic Model for Mild-Hydrocracking Reactions

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With the decreasing of sulfur limit in commercial fuels, the integration of a mild-hydrocracking unit became the preferred upgrading method for the typical European refinery. Efficient technology and operation of the hydrocracking plant can be achieved by predicting the products yield with a model based on the kinetics of the complex reaction network.

At first, this work aimed to validate the kinetic parameters of a 6-lump model for the mild-hydrocracking process reactions, found in literature [1]. Industrial data were collected and the computer simulation environment Berkeley Madonna was used, but the original parameters of the model needed further adjustment. Then, the model was reduced by eliminating unnecessary reaction paths. So, the simplified model includes 5 products and 6 reaction rate constants. Each constant was expressed by Arrhenius relationship and the values of pre-exponential factor and activation energy were estimated in a non-linear approach with a software compiled in MATLAB, PARES [2]. Then, simulations in Berkley Madonna programme were performed again. The errors decreased considerably and the resulted kinetic parameters had the same order of magnitude as found by other authors [3].

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# Natural gas dehydration using glycol water absorption and membrane techniques

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Dehydration of natural gas provides safety issues during transportation avoiding pipeline corrosion. The water absorption with glycol is the most attractive technology as it requires relative low energy due to the hydrogen bonds between water and glycol (Mono-Ethylene-Glicol, Di-Etylene-Glycol or Tri-Ethylene-Glycol). The classical process diagram [1] comprises two steps: absorption of water and regeneration of glycol. Particular configurations can be conceived aiming to overcome the presence of water vapors in the dry product [2]. A drawback of absorption with glycol is the simultaneous absorption of aromatic compounds that will be emitted from the solvent regenerator overhead, raising environment problems. The present work analyzes several gas dehydration configurations, based on glycol water absorption, from economical and environmental point of view using process simulation tools. Different cooler-absorption configurations, two possible heating sequences for water rich glycol are analyzed in order to put into evidence the advantages and drawbacks of each solution. Some recent studies [2] are dealing with the necessity of the elimination of aromatic hydrocarbons absorbed in the glycol (mainly BTEX). This may be realized using a stripper that is installed between the flash tank and the glycol regenerator. The utility of such a solution is also analyzed, starting from some technologies proposed in literature.

The membrane techniques used for natural gas drying did not prove so far to be economically and technically efficient due to the ratio between partial pressure of the component of either sides of the membrane, which is a draw back regardless the membrane efficiency [2]. In the present work, the use of membranes as adjacent tools, leading to hybrid separation sequences is studied for both water and aromatic hydrocarbons final elimination.

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# On ultrasound for biofouling: prevention of barnacle cyprid settlement

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Marine biofouling which refers to the accumulation of undesired organisms on the man-made structures is a problem for nearly all man-made structures immersed in the sea. It significantly increases global carbon emissions by increasing fuel demand and generating additional maintenance costs, which can run into billions of dollars annually for marine industries. Among the fouling organisms, barnacles are one of the most serious macrofoulers due to their sizes and gregarious colonization of solid surfaces. Biocides and other related chemical means can be highly effective on the barnacle fouling prevention; however, they are generally damaging to the environment and are consequently subjected to regulations limiting their widespread implementation. In this paper, we present results in the application of ultrasound on barnacle cyprid settlement and exploratory behaviour. We found that exposure to 20 kPa ultrasound at the frequency of 23 kHz for 5 mins reduced cyprid settlement significantly. Also, ultrasound exposed cyprids demonstrated an altered exploration behaviour and secreted less temporary adhesives. Furthermore, to reduce the possible consequence that higher ultrasound may impose to other marine organisms, the effectiveness of lower intensity ultrasound was explored. We found that exposure to ultrasound (5 kPa) at frequency of 23 kHz reduced cyprid settlement but generated no increased mortality or observable change in the cyprid's exploratory behavior. Considering energy saving purpose, the efficiency of intermittent ultrasound operation mode was explored and same inhibitory as continuous operation was found. Results indicate that ultrasound may present a promising and energy efficient strategy for antifouling applications with proper design.

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# Influence of feed quality on ultrafiltration membrane productivity and efficiency

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An ultrafiltration membrane, usually, has the pore sizes in the range 0.001 and 0.1 μm. The ultrafiltration process is recommended for separation, mainly from liquids, of small particles (solid, gel and big molecular association) and implies the passing through the membrane of dissolved compounds, while colloid and suspended matters are rejected. In the nuclear industry field, ultrafiltration can be used for removal of substances present in aqueous radioactive waste in colloidal or suspended form. In ultrafiltration application, accumulated particles or macromolecules form a fouling layer on the membrane surface, known as a gel layer and the properties of this gel will affect the performance of the separation in a significant manner [1]. The experimental investigation of an ultrafiltration process was conducted at IFIN-HH, DMDR, in a modular installation for aqueous radioactive waste purification, using a spiral-wound polysulphonamide membrane. A $2^3$ factorial plan was used to establish correlations between dependent and independent variables of ultrafiltration process and statistical models were obtained to describe permeate volumetric flux and permeate total suspended solids. The results were shown elsewhere [2].

A simulated aqueous waste obtained by adding of fresh clay in actual waste was used to estimate the effect of solid concentration of processed ARW on membrane clogging. Other operating factors were as follows: temperature: 25°C, ultrafiltration pressure: 0.25 MPa, pump flow rate: 5 $m^3/h$, ultrafilter area: 5 $m^2$, capacity of feed and colecting reservoirs: 10 $m^3$. A generator function of random variable $n$ (blocked pores number at membrane surface) was built to express the time evolution of the permeate flow rate. The clogging parameters, $\alpha$ and $\beta$, were identified by experimental measurements, minimizing mean quadratic deviation between the experimental and calculated permeate specific flow rate.

A mathematical model of an ultrafiltration device composed by a system with 13 differential equations completed with algebraic equations was established to describe the concrete action of units of ultrafiltration arrangement.

The results obtained in this experimental study are very useful in determining the performance criteria for ARW treatment by ultrafiltration, related to acceptable limits for variability in productivity and efficiency.

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# Mathematical modelling and optimization of pillared clay preparation processes

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Modified clays by pillaring processes are used especially as adsorbents in restraint of gaseous pollutants ($CO_2$, $NO_x$, $NH_3$, $SO_x$, $H_2S$). By pillaring, the clay specific surface area is changing, its porosity becomes permanent, the pores spaces are formed creating a distance in the layer for the retention of the gas molecules and a surface acidity is created for gas molecules attraction.

Clay pillaring process implies several specific steps such as: pillaring agent preparation (NaOH and $AlCl_3$ solutions), clay intercalation, intercalated clay ageing, decantation of the clay to the liquid mother, washing, filtration, drying and calcinations of the clay and it is influenced by different parameters.

In this study, two of these parameters namely the quantity of aluminum cations reported at clay amount ($x_1$) and the calcination temperature ($x_2$) were optimized using a $3^2$ factorial design. Their variation levels are shown in Table 1.

**Table 1. C**onsidered parameters and their levels of variation

| Parameters | Code | Values | | | Step |
|---|---|---|---|---|---|
| | | $x_i^{\min}$ | $x_i^{med}$ | $x_i^{\max}$ | $\Delta x_i$ |
| Quantity of aluminum cations / clay amount (mmol·$g^{-1}$) | $x_1$ | 5 | 12,5 | 20 | 7,5 |
| Calcination temperature (°C) | $x_2$ | 300 | 400 | 500 | 50 |

The other parameters affecting the pillaring process were maintained constant at the following values: concentration of the clay - raw material: 2%, the molar ratio of the pillaring agent $OH^-$ / Al 2:2, *p*H of the intercalated solution: 4, clay drying temperature: 120°C, clay drying duration: 4 hours, calcination duration: 2 hours. Three different response functions were monitored in the experimental design: the basal spacing - determined by X-ray diffraction ($Y_1$), the surface acidity - determined by thermo-desorption ($Y_2$) and the specific surface area - determined by Brunauer Emmett and Teller method ($Y_3$). The mathematical equations describing the evolution of these functions were:

$$Y_1 = 1{,}794 - 0{,}006 \cdot x_1 + 0{,}018 \cdot x_2 - 0{,}014 \cdot x_1^2 - 0{,}127 \cdot x_2^2 + 0{,}003 \cdot x_1 \cdot x_2$$

$$Y_2 = 0{,}431 + 0{,}026 \cdot x_1 - 0{,}060 \cdot x_2 - 0{,}003 \cdot x_1^2 - 0{,}118 \cdot x_2^2 + 0{,}004 \cdot x_1 \cdot x_2$$

$$Y_3 = 142{,}98 + 8.962 \cdot x_1 - 6.423 \cdot x_2 + 2.602 \cdot x_1^2 - 36{,}233 \cdot x_2^2 - 9{,}420 \cdot x_1 \cdot x_2$$

The developed mathematical model established that the use of a quantity of aluminum cations / clay amount ratio of 18,2 mmol·$g^{-1}$ and a calcination temperature of 404 °C lead to a basal spacing of 1,78 nm, a surface acidity of 0,445 mmol·$g^{-1}$ and a specific surface area of 148,67 $m^2 \cdot g^{-1}$.

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# Biogas - a significant vector assuring energy for Romanian villages from renewable sources

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The biogas can really contribute to growing up of renewable till 20% from total energy demand till 2020. The work tries to underline the importance of biogas producing both for renewable energy production and for significant contribution to reducing of the environment pollution. The actual context, characterized by dangerous arising of pollution, determined mostly by burning of fossil fuels, became most important the reduction of dependency of these fuels. The green energy may be produced by many methods comprising wind turbines, solar panels, thermal pumps, biomass burning plants, geo-thermal stations, etc. The current Romanian “green” map provides the following potential of bio-resources: 65% biomass, 17 wind turbines, 12% solar energy, 4% micro-turbines, 1% photo-voltaic and 1% geo-thermal.

Based on a very actual study, 95% of the rural dwellings are not connected to the Romanian national grids, the people of this area being dependent on traditional warming systems. These sources comprise mostly fire woods, and a small part of natural gas.

Since the rural people represents about 50% of Romanian citizens, the improving of current situation, may reduce the impact upon environment, parallel with obtaining of renewable feasible energy. Out of these, by National Electrification 2012-2016, was identified the current situation of non-electrified villages in Romania, indicating a number of around 100.000 households. Based on these information, the revitalization of renewable, including biogas, may substantially improve the situation, since the bio resources, manure matters, residual sludge from treatment of used waters or other organic wastes, generally are available on the rural area

The paper may sustain the advantages of the Romanian technologies, based on perfect mixing (continues flux [1]) or on plug principle (horizontal flux [2]), both with high yield. Depending on capacity (power plant), local conditions and energy consumption demands, the produced biogas may be directed to a cogeneration plant, supplied to customers or purified to obtain bio-methane.

The most applied principle for biogas plant at EU level is cogeneration, producing electric and thermal energies, where electric energy may be supplied into existing grids and the thermal may be used partially for internal needs (digester) and external consumers (for heating) [3]. For each case the optimal solution have to be based on a feasibility analysis study. The current work underlines the advantages of own technologies, which are conducting to energy saving and environmental protection as well.

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# Modelling the Allam cycle. A high efficiency supercritical power process

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The purpose of this paper is the modelling of the Allam cycle, a brand new supercritical carbon dioxide power process with virtually no emissions with the aide of Aspentech`s powerful Hysys simulation tool.

The Allam cycle offers an emission free alternative to power generation from carbon-based fuels for lower costs than traditional, emitting technologies by employing high pressure carbon dioxide as the working fluid instead of steam, as seen in traditional processes. [1]. In conventional cycles, the separation and removal of low concentration combustion derived impurities such as CO2 results in a large additional capital cost and increased loss of power. As a result, removal in conventional cycles can increase the cost of electricity. One of the main advantages of the Allam cycle stems from its virtually inexistent carbon emissions as well as the high efficiency and small plant footprint. [2].

The semi-closed-loop Allam cycle scheme was developed and simulated using Hysys V9, following a comprehensive study of Rodney John Allam`s original work for his patent. While the Allam cycle is still in it`s pilot phase, a commercial level cycle was modelled. It`s feedstock felixibility was also studied by variations in the fuel used from commercial natural gas to landfill gas and biogas while observing the impact on power efficiency.

Further opportunities in improving the cycle`s power efficiency were studied by assessing the possibility of thermal integration with a cryogenic oxigen providing air separation unit which it is naturally bordering. The state of the art tehnologies, responsible for the mechanical wellbeing of the core Allam cycle are also mentioned, ranging from the high powered Toshiba turbine to Heatric`s layered plate heat exchangers [3].

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# The study of catalytic cracking performance improvement by the addition of the second stage of regeneration

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Starting from a model adapted to simulate the operation of an industrial catalytic cracking plant, we propose to improve the performance of this system by adding a second stage of regeneration. Advantages of the model with two regenerators instead of one regenerator model can be found in the enlargement of feeds, increasing the quantity and quality of gasoline produced, and a higher production of propylene. Fluidized catalytic cracking is part of the petrochemical industry since the 1940s. Despite the well established technology until now, continued development is essential, especially for refineries that have shifted production to obtain higher value products. Advanced diagnostics and design tools accelerate the development process and results can be found in some innovations. [1]. Since cracking is one of the plants decisive influencing overall economic efficiency of the refineries, is of great interest, through the use of reliable predictive models, to obtain information about the behaviours of plants and to the modification of their operating parameters or geometrical characteristics. Along the time, different parts of catalytic cracking plant (feedstock distribution system, riser, spent catalyst regeneration system) have been enhanced to better respond to new market requirements.

In this paper we intend to highlight the benefits of an improved system of regeneration of the catalyst by the addition of the second regenerator. In a previous contribution, we report results of the test that modelling a catalytic cracking industrial plant in operation in a refinery in Romania. In this study we demonstrated that the performance of the industrial plant on the yields of gasoline, diesel, coke and regenerator temperature can be estimated with an accuracy of less than 4.8 % wt. Based on the tuned model was simulated for functioning of the plant in various operating conditions, but improving economic performance is limited.

In this study we propose to estimate the potential of performance improvement of the catalytic cracking plant previously studied [2] under the conditions of the introduction of the second stage of catalyst regeneration. Among the possibilities for increasing the performance of fluid catalytic cracking units, introducing a supplementary stage of regeneration is one that can enlarge the basis feed, increase the amount and quality of gasoline produced, and the production of propylene. Techniques to improve regeneration studied until now relate to high temperature regeneration, regeneration by cooling, using specific catalysts, the addition of a additional stage of regeneration.

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# BOOK OF ABSTRACTS

# SICHEM – 2018

# ORAL PRESENTATIONS

## B – Applied organic, inorganic, and supramolecular chemistry (AOISC)

# Pharmaceutical application of recombinant Human Serum Albumin dimer

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Human serum albumin (HSA) is the most abundant protein in the blood. It is clinically used in the treatment of severe hypoalbuminemia and as a plasma expander. Recently, investigations on numerous modified HSAs with new functions have been attempted. Among these modifications, HSA-dimer has great potential for clinical applications as a plasma expander and a drug carrier. The pharmacokinetic properties of the HSA-dimer and its potential medical applications as a drug carrier will be discussed in comparison with HSA-monomer.

Recombinant HSA-dimer was produced using the yeast Pichia pastoris expression system. The pharmacokinetics of the $^{125}$I-labeled HSA-monomer and dimer were evaluated in rats. The $t_{1/2}$ for HSA-dimer was 1.5 times longer than that of HSA-monomer, indicating that HSA-dimer has a better blood retention property. Moreover, the vascular permeability of HSA-dimer was lower than that of HSA-monomer, suggesting that the escape of HSA to the extravascular space during inflammation can be reduced by dimerization. Interestingly, the accumulation of HSA-dimer in C26 solid tumor tissues has been found to be 1.8 times higher than the HSA-monomer. These results indicated that HSA-dimer could be a good candidate as a cancer drug carrier. On the other hand, nitric oxide (NO) has been shown to have potential use in cancer therapy. In fact, a number of attempts have been made to develop new antitumor drugs using NO donors. We developed S-nitrosated HSA-dimer (SNO-dimer), and examined its anticancer property. SNO-dimer was found to specifically deliver large amount of cytotoxic NO into tumor. Furthermore, using C26 tumor bearing mice to evaluate the EPR effect of NO delivery, the extravasation of Evans blue in the tumor tissue after treatment with SNO-dimer was compared with the SNO-monomer treatment. As a result, SNO-dimer enhanced the EPR effect significantly. It was also noteworthy that SNO-dimer in combination with Doxil inhibited tumor growth compared with Doxil alone.

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# The influence of hydrocarbon chain length on the surface properties of gluconolactone-based surfactants

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The class of carbohydrate-based surfactants had been developed by major manufacturers of active substances and detergents after the increase of legislative restrictions on environmental protection. Carbohydrates, as natural raw materials, derived from renewable vegetal resources are used mainly in fabrication of alkyl polyglycosides. Sorbitan and sucrose fatty acid esters or ethoxylated sorbitane and sucrose fatty acid esters are also used on an industrial scale as emulsifiers and solubilizers in food, cosmetics, and pharmaceuticals [1, 2, 3].

In this paper we present the synthesis of bolaform gluconolactone-based surfactants with $C_8$ and $C_{12}$ hydrocarbonate chains, in mild reaction conditions and the influence of hydrocarbon chain length on the surface properties of synthesized surfactants. The structural characterization of 1,12-digluconamidododecane and 1,8-digluconamidooctane was made by Fourier transform infrared spectroscopy. The visualization of aggregates was performed by optic microscopy in the case of 1,12-digluconamidododecane and transmission electron microscopy for 1,8-digluconamidooctane. By heating a 0.2% suspension in water: ethanol 1: 1 to 70 ° C, followed by cooling, it was found that 1,8-digluconamidooctane undergoes a crystallization process, hexagonal crystals being visualized by optic microscopy. We note the vesicular aggregates formed in the 1,8 - digluconamidooctane solution with dimensions between 200-300 nm, visualized by transmission electron microscopy. The surface activity of surfactants was evaluated with a KSV Sigma 700 automated tensiometer, using DuNouy Ring technique. 1,12-digluconamidododecane solutions present a moderate efficiency in reducing the surface tension of water, while 1,8-digluconamidooctane is more efficient in reducing the surface tension of water at low concentrations.

In conclusion, the length of hydrocarbon chain influences the solubility, surface properties and the self-assembling properties of synthesized surfactants.

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# The effect of oxidative processes on the migration of elements in historical tailings pond

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The problem of sulphide oxidation and the associated generation of acid rock drainage (ARD), as well as the dissolution and precipitation processes of metals and minerals, are the most important environmental concern in mining today. The objective of the present study was to characterize and evaluate the Romanian historical tailing of Sasar-Red Valley, near Baia Mare. Tailings samples collected from different depths were characterized in term of mineralogical and chemical composition of the materials, weathering profile characteristics, its acid generating potential (ARD) and elements distribution in depth. Acid base accounting (ABA) tests in conjunction with net acid generation (NAG) tests classified the samples into the category of 'potentially acid generating'. The chemical and mineralogical analyses reveal the presence of a strong oxidation process at the tailings pond surface due to the weathering of sulphide minerals, in particular pyrite which is responsible for production of acidic water. Three zones were identified on the tailing surface: an upper oxidation zone (reddish-brown-yellow coloured, acid generation and metal release), a hardpan layer (acid neutralization and metal accumulation) and a reduction zone (grey coloured, limited water movement, low oxygen diffusivity). As a result of acid generation process the pH of the water decreases once sulphide oxidation starts. Under low pH conditions, ferric sulphate may be oxidized to ferric iron, which is capable of oxidizing other minerals such as copper, zinc or cadmium sulphides. With gradual increasing of the pH level, the dissolved metal load generally decreasing. This paper presents a synthesis of works performed in the Improve Resource Efficiency and Minimize Environmental Footprint (REMinE) project.

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# $Cu_2O$ layers obtained by electrodeposition

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In the present work was studied the deposition of $Cu_2O$ layers by using electrochemical methods [1-4]. Electrochemical growth of cuprous oxide particles was studied by using two different solutions based on copper sulfate and copper acetate. Structural and morphological properties of cuprous oxide layer were investigated using X-Ray diffraction measurements and Scanning Electron Microscopy. Experimental data showed that using electrochemical deposition were produced cuprous oxide particles with cubic structure and dimensions in range of hundreds of nanometers to few micrometers.

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# The four different culture media influences on the polymer biosynthesis

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The culture media composition can dramatically influence the polymer amount obtained by biosynthesis. The type and amount of carbon and nitrogen sources affect the metabolic behaviour of the microorganism and, further, the amount of metabolites secreted in the media. The carbon sources used for the media were sucrose, fructose, glucose, milk and aqueous fruit extract from *Hippophae rhamnoides*. The last two are also rich nitrogen sources due to the protein and polyphenols contained. The *Hippophae rhamnoides* fruits are very rich in active compounds with various effects on the organism. The major components are already identified, including significant amounts of minerals, vitamins, polyphenols, phytoestrogens, phytosterols, lipids, carotenoids, tocopherols and ascorbic acid [1]. In this paper we monitor four different culture media composition in order to obtain a better behaviour of the lactic acid bacteria regarding exopolysaccharide (EPS) biosynthesis. In this order, the polymer biosynthesis was strongly influenced by the presence of milk in media, yielding 6.1 g/L dry-freezing biopolymer. The culture media containing aqueous fruit extract from *Hippophae rhamnoides* determined an improvement of the EPS biosynthesis, yielding 4.8 g/L freeze-dried biopolymer. Comparing with normal culture medium supplemented with different sugars, the amount obtained is remarkable. Taken this into consideration, the aqueous fruit extract from *Hippophae rhamnoides* can be used for EPS biosynthesis, being a low-priced substrate compared with milk substrate. Further, the FTIR spectra of the samples are very similar with Dextran 40000. The presence of protein residues is proved by the presence of the amide I and amide II bands (1672 $cm^{-1}$ and 1544 $cm^{-1}$), which are not registered in the dextran standard spectra. In the $^1H$ NMR spectrum several signals belonging to the glucose units can be observed in the region 3.5-4.1 ppm, while the protons from position 1 of the α-(1→6)-linked glucose units appear as a doublet at 4.99 ppm. In this order, the structural analysis revealed that the resulted EPS have dextran structures, with protein residues covalently attached to the structure, which is the normal situation regarding microbial polymer biosynthesis processes.

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# New hydrogels prepared by using poly (vinyl alcohol) and tempo-oxidized cellulose

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A new approach for the preparation of poly (vinyl alcohol) (PVA) - cellulose based hydrogels by freezing/thawing method was conceived. PVA is a biodegradable polymer, largely used in the last years for the production of biodegradable hybrid materials, as a substitute of traditional polyethylene or polypropylene polymers [1]. These materials have proved beneficial applications in water filtration, paper industry, mats and films production and packaging [2]. Due to its abundance and renewable character, combined with excellent mechanical properties, biodegradability and biocompatibility, cellulose gained in the last decade a lot of interest, being placed as a key component in preparation of wide range of materials, including hydrogels. Hydrogels are generally defined as polymeric structures which are able to retain large amounts of solvent, without their dissolution [3]. In this paper, we propose the use of various amounts of water soluble tricarboxy cellulose, ranging from 0.1% to 25% (wt.) acting as a multifunctional key component, and also as cross-linking agent, with increased strengthening and stiffness properties for the preparation of PVA hydrogels. The as resulted hydrogels were fully characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM). Moreover, the self-healing properties of the prepared hydrogels were highlighted by the rheological measurements.

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# Extraction of valuable products from tomatoes

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Tomatoes are part of the world's most consumed vegetables, consumed both fresh and processed. Worldwide, millions of tons of tomatoes are processed, being used as raw material for the production of juices, sauces, purees, pasta and canned foods. Tomato processing results in 20-40% of tomato waste that does not have commercial value, although it is a rich source of nutrients and biologically active compounds. Tomatoes contain large amounts of carotenoids, the main carotenoid being lycopene, 70-90% is found in the skin, five times larger than in the pulp. Lycopene is a compound of interest because its introduction into the body is associated with the ability to reduce the onset or evolution of many diseases and even cancer. Tomato seeds contain 18-27% of oil consisting of 20% saturated fatty acids and 80% unsaturated fatty acids. Fatty acids are very important in human diet, being essential components of all membranes, gene regulators and compounds that play a key role in the metabolism. The purpose of this paper is to recover valuable compounds from tomatoes, based on extraction from plant matrix, purification of extracts and analysis of products. The researches were oriented on recovery of valuable products from four specific Romanian varieties of tomatoes like Prekos, Rila, Galben and Olandez (purchased from market, peeled and dried at temperatures of 50°C and 70°C): lycopene and fatty acids, using the solvent extraction method. Dichloromethane and acetone-hexane mixture were used for lycopene extraction and hexane for seed oil extraction. Influence of some factors was analysed: variety of tomato, drying temperature, the extraction solvent, etc. Different analysis methods (UV-Vis spectrometry and FT-IR spectroscopy) were used to determine the lycopene content. The fatty acids profile was determined by gas chromatography techniques (GC-MS, GC FID). The maximum amount of lycopene recovered from the analysed tomato varieties is 103.266 g of lycopene / 100 g of dry tomatoes at temperature of 70 ° C of Prekos tomato variety subjected to Soxhlet extraction with acetone-hexane mixture during 6 hours. After extraction and the distribution of methyl esters in tomato seed oil obtained is 55,36-55,39% methyl linoleate, 22,85-23,96% methyl oleate, 15,07-15,08% methyl palmitate and 5,6-6,46% methyl stearate.

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# Structural behaviour of SnSSe layers deposited by thermal co-evaporation

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Currently, novel and new semiconductor materials are being investigated widely to develop economic and environmentally benign solar cell technology. Tin sulfoselenide (SnSSe) is one such semiconductor that possesses the properties similar to both tin sulphide (SnS) and tin selenide (SnSe). By suitably controlling the SSe ratio in the films it is possible to tailor the physical properties of SnSSe that are suitable for any device applications. In the present work, SnSSe layers were deposited using thermal co-evaporation method at different substrate temperatures that vary in the range, 200 - 350°C. A detailed structural investigation of as-deposited SnSSe layers was carried out using grazing incidence X-ray diffraction (GIXRD) and Raman spectroscopy techniques. The GIXRD analysis showed that all the as-grown films were polycrystalline in nature with the (111) plane as preferred orientation, exhibiting orthorhombic crystal structure. The other structural and microstructural parameters such as crystallite size, lattice stress, dislocation density of the films and their dependence on substrate temperature were also evaluated and analysed. The Raman studies revealed the characteristic modes of both SnS and SnSe that were in support of XRD results.

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# The influence of cerium on the textural properties and acidity of catalysts used in the furfural hydrogenation process

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Recently, fossil fuel reserves have begun to diminish considerably, forcing the world to seek alternatives for energy and liquid transport fuels [1,2]. Due to the abundance and the possibility of regeneration, a viable alternative is the conversion of biomass into chemical derivatives that can be used as precursors in obtaining a wide range of chemicals, such as furfural and 5-hydroxymethyl furfural [2].

Furfural is an important chemical solvent, and by its hydrogenation using different metal catalysts, the major product obtained is furfuryl alcohol (FA), an intermediary for the production of cement, adhesives, casting resins and coatings. Other products like tetrahydrofurfuryl alcohol (THFA), 2-methylfuran (MF), tetrahydro-2-methylfuran (THMF) can be obtained from the hydrogenation of furfural [3]. From the literature study, it was observed that a wide range of metals, such as copper, platinum, palladium, molybdenum, nickel, cobalt, is used to obtain catalysts used in the hydrogenation process of furfural [4], [5].

The main objective of this paper is to study the influence on the textural properties and acid strength of metal catalysts when using cerium as a promoter. The metal catalysts selected for testing were characterized by determining the textural properties using the BET equation on the adsorption isotherm; pore size and distribution were determined by applying the BJH method on the branch of isotherm with hysteresis. The acid strength distribution was determined by applying the diethyl-amine thermal desorption method.

Further tests, like XRD, FTIR, SEM for determining the structural properties of the catalysts will be made to better characterize the influence on catalysts properties when using cerium as a promoter for metal catalysts used in the furfural hydrogenation process.

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# Modeling and simulation of a glycerol acetylation process

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One of the technologies used for the valorization of glycerol (a high amount byproduct resulting in the biodiesel synthesis) is its esterification with acetic acid, in order to obtain esters with application in food and cosmetics industry, as fuel additives or raw materials in different chemical processes. The glycerol esterification with organic acids is a reversible chemical transformation carried out in liquid phase using acidic catalysts. The most active catalysts are inorganic acids, but the solid acid catalysts are preferred in order to avoid environmental issues regarding the separation, neutralization and disposal of reaction wastes.

The main aim of this work is to evaluate the adequacy of a reactive distillation process to synthesize glycerol acetates with high yields. In order to achieve this goal, the thermodynamic and vapor-liquid equilibrium models for glycerol acetylation system implemented in Aspen Hysys commercial simulator were evaluated based on own experimental determinations and published data. The predictions of usual thermodynamic relations were compared with experiments conducted in a semi-batch system, using toluene as entrainer, in a modified Dean Stark apparatus.

The simulation of the semi-batch glycerol acetylation system was performed using a previously determined kinetic model developed over an Amberlyst 35 ion-exchange resin (Banu et al, 2018). Th simulation of the process using UNIQUAC (liquid phase) and VIRIAL (vapor phase) thermodynamic models provided close values for theoretical and experimental glycerol conversion and acetates yields.

The main conclusion is that reactive distillation technique is a suitable alternative for synthesizing glycerol triacetate with high yield.

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# BOOK OF ABSTRACTS

# SICHEM – 2018

# ORAL PRESENTATIONS

## C – Biomaterials and composites in chemical and biochemical applications
## (BCCBA)

# Composite materials based on active carbon from biomass residues and zinc oxide nanoparticles for photocatalytic degradation

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The conversion of biomass residues into value-added products is in line with European directives for environmental protection, which are imposing stringent rules on the implementation of non-polluting organic waste recovery processes. Using biomass residues and processes like pyrolysis and thermal activation or calcinations, we were able to develop new materials for photodegradation processes of organic compounds from wastewaters. Recent studies involved the fructification of biomass residues into active carbon (CA) in order to obtain composite materials for photocatalytic degradation reactions of organic compounds from contaminated water. Furthermore, the degradation of organic polluting agents can also be performed successfully in the presence of metal oxides such as ZnO, $TiO_2$, $ZrO_2$, etc. due to their photocatalytic properties, relatively low synthesis costs and non-toxic actions towards environment.

The properties of CA obtained from biomass and used for water purification depend on the nature of biomass, pyrolysis and activation conditions [1].

Thus, in the first step, our study involved three different types of biomass, such as: a) algal residues, b) cherry pits and c) bacterial cellulose which were pyrolyzed and further activated in different conditions in order to obtain CA.

The recovery of ZnO NPs by sedimentation or filtration could be a difficult task due to the decreased size of the inorganic particles [2]. For this reason, the next step consisted in the direct generation of ZnO nanoparticles (ZnO NPs) on the surface of CA. The CA, ZnO and CA-ZnO composite materials were characterized by FT-IR, SEM, and XRD. The photocatalytic process involved the degradation of methyl orange (MO) under UV light conditions.

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# Production of carbon nanocomposite materials from secondary raw materials

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Along with metals and polymers, composites and composite coatings are becoming increasingly common today. Earlier studies were carried out [1] on composite electrochemical coatings of a copper electrode. Coatings containing particles of a carbon nano material were obtained. Interest in such materials is associated with their specific use in various industries, including in the form of solid lubricant in antifriction coatings, which significantly reduce the coefficient of friction and wear. Reducing the coefficient of friction by means of such coatings, it is possible to achieve several very positive results at once: increasing the service life of parts and saving on additional lubricants.

When manufacturing such materials by electrolysis, carbon nanoparticles are incorporated into the matrix of the base metal, which significantly changes the properties of the electroplating coating and this is connected with the structure, surface and composition of the carbon particles.

The Institute of Inorganic Chemistry and Electrochemistry of Javakhishvili Tbilisi State University has experience in obtaining carbon material from secondary raw materials (various polymer waste, nutshells, sawdust of trees, bamboo, etc.). In connection with the possibility of using such carbon materials, it is very important to study the specific surface area and the composition of the obtaining materials.

Carbon materials obtained from secondary raw materials are investigated in this work. The composition of the secondary carbons was studied by use of Hitachi3030Plus scanning electron microscope. The obtained data is given in the Table 1.

Table 1. The composition of carbon materials obtained from secondary raw material.

| Elem. | Raw material – Hazel. shells | | | Raw material – Sawdust | | | Raw material – Polym. waste | | |
|---|---|---|---|---|---|---|---|---|---|
| | AN Series | norm.C [wt.%] | Atom.C [at.%] | AN Series | norm.C [wt.%] | Atom.C [at.%] | AN Series | norm.C [wt.%] | Atom.C [at.%] |
| C | 6 K-series | 83.83 | 90.11 | 6 K-series | 92.38 | 95.39 | 6 K-series | 87.14 | 92.89 |
| O | 8 K-series | 9.79 | 7.90 | 8 K-series | 4.93 | 3.82 | 8 K-series | 5.99 | 4.79 |
| K | 19 K-series | 2.78 | 0.92 | 19 K-series | 1.09 | 0.35 | | | |
| Ca | 20 K-series | 1.56 | 0.50 | 20 K-series | 0.57 | 0.18 | | | |
| S | | | | | | | 16 K-series | 1.74 | 0.69 |
| Zn | | | | | | | 30 K-series | 1.66 | 0.32 |
| Si | | | | | | | 14 K-series | 1.44 | 0.66 |

The obtained results allow selection of particular carbon materials in the production of composite electrochemical coatings with a copper matrix.

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# A new catalytic system for greener oxidation of cellulose

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*N*-hydroxyphthalimide (NHPI) as one of the best and modern catalysts, having great performances in oxidation reaction, when through a hemolytic scission of the >N-O-H bond, the active species, phthalimide-*N*-oxyl radical (PINO) is formed, has been extensively used for the selective oxidation of cellulose. Generation of the PINO radical is possible only if a suitable cocatalyst, able to abstract a proton from the O–H bond in NHPI, is present, like as metal cocatalyst salts (generally transition elements such as cobalt, manganese, lead, copper, iron, nickel, and even their mixtures), non-metal cocatalysts, which mainly imply the presence of peroxides, nitrogen dioxide or nitric acid, aldehydes, anthraquinone, hexafluoroacetone, and even enzymes of the lacasse family.

In this presentation, we propose a new, innovative protocol for the cellulose oxidation using NHPI in a metal-free system, Fig. 1. The generation of the active radical species PINO is possible due to the presence of sodium hypochlorite and sodium bromide, as actual oxidants. The hypohalides present in the system take over the role of the metal cocatalyst, oxidizing in the first stage of the process the NHPI to its free radical counter partner, PINO, able to initiate the catalytic cycle of oxidation.

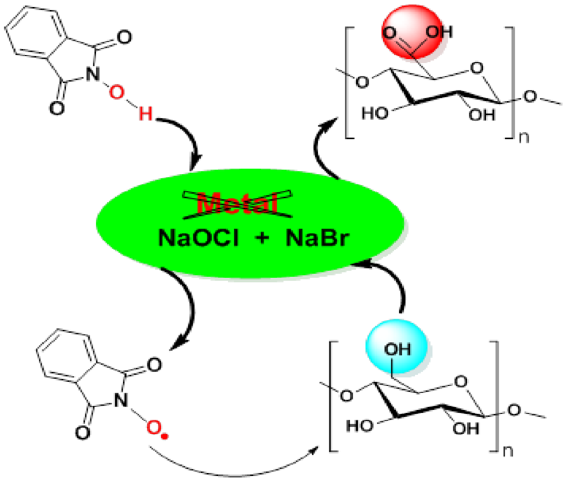

Fig. 1 Cellulose oxidation performed by N-hydroxyphthalimide in the presence of the NaOCl and NaBr.

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# Antioxidant loaded dextran coated magnetic nanoparticles for biomedical applications

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Nanomedicine is a new concept which implies the medical application of nanotechnology. Nanomaterials can be functionalized with different kinds of molecules or biological structures. Magnetic nanoparticles are a promising field of nanotechnology with a wide range of applications, such as medical diagnostics and treatments, magnetic immunoassay, waste water treatment, catalyst support, biomedical imaging, cancer therapy, information storage, genetic engineering (magnetofection). In the biomedical field, they can be used as therapeutic agents in the treatment of many diseases. A local therapy using magnetic nanoparticles claims that by directing the active agent in the damaged body region, many common side effects can be reduced. The efficiency of a drug delivery system is based on the encapsulation of the active agent and the successful transport and delivery of the drug. This study focuses on the synthesis and characterization of an antioxidant loaded magnetic nanoparticulate system with potential use in the therapy of coronary artery disease. The therapeutical approach is based on the use of the magnetic properties of these nanosystems to attach them to a stent placed in an atherosclerotic artery, where they can deliver the scavenger. One of the major causes of the plaque formation is considered the process of lipid oxidation by reactive oxygen species. Magnetic nanoparticles were synthesized by co-precipitation, coated with dextran and functionalized with protocatechuic acid, an antioxidant found in Chinese herbal plants. The complex was studied by dynamic light scattering (DLS), electrophoretic light scattering (ELS), Fourier transform infrared spectra (FT-IR), energy dispersive X-ray analysis (EDX). Also, the potential biological applications indicated new methods of characterization, such as drug release tests and DPPH tests (for antioxidant activity). All the characterization methods show a good potential for the use of nanosystems as therapeutic agents, where the antioxidant has the potential of scavenging dangerous reactive oxygen species and reducing the local oxidative stress.

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# Polymer-supported N-Hydroxyphthalimide as catalyst for naturally occurring biopolymers

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Pullulan, a water-soluble extracellular neutral glucan synthesized by the fungus *Aureobasidium pullulans* were subjected to the *N*-hydroxyphthalimide (NHPI) oxidation. This organocatalyst has attracted considerable interest because it is non-toxic, it can be easily prepared from phthalic anhydride and hydroxylamine, and it demonstrates high activity even under mild conditions. The catalytic activity of NHPI is a result of its ability to be converted to the phthalimide-*N*-oxyl radical, which effectively abstracts the hydrogen atom from the compound to be oxidized, Fig. 1.

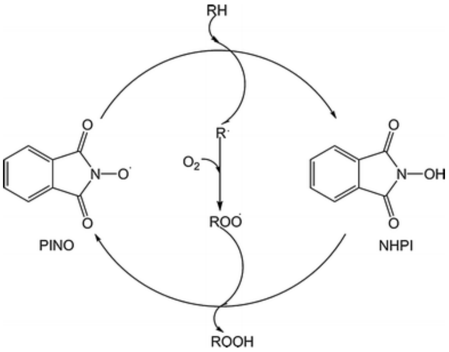

Fig. 1. Mechanism of hydrocarbon oxidation in the presence of NHPI

In this connection, this paper, present a new approach to obtain carboxyl-functionalized pullulan derivatives, in the presence of NHPI immobilized on (aminomethyl) polystyrene and (chloromethyl) polystyrene via amide or ester bonds. This NHPI-polymer support has demonstrated a good catalytic activity for oxidation of pullulan and also the possibility of recovery and recycling. The oxidation were performed in the presence of sodium bromide and sodium hypochlorite, under mild conditions, at room temperatures, atmospheric pressure and pH = 10.5. The carboxylic moiety formation was evidenced by Fourier Transform Infrared Spectroscopy (FTIR) and Nuclear Magnetic Resonance (NMR) analyses.

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# Binary blended small-molecule cathode buffer layer materials for highly efficient organic photovoltaic cells

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In this topic I will present our concept, design rational, and the photovotaic properties from a series binary blended small-molecule cathode buffer layer (CBL) maetrials for fabricating high-efficiency organic photovoltaic cells. As an example, I herein show that the old and famous dye, N719, can be utilized as high-efficiency, alcohol solution-processible cathode buffer layer (CBL) material. N719 and the binary N719:PrC60MAI CBL, respectively, affords 10.50%- and 11.46%-efficiency, single-junction ternary polymer solar cells. The work function of the Al cathode can be modulated between −3.3 eV and −3.9 eV simply by controlling the binary components weight ratios, which is due to the weight-ratio dependent re-arrangment between the four kinds of cations and anions [1]. With this binary blend as the CBL, a PCE of 11.3% was achieved from a new nonfullerene small-moelcule acceptor [2].

The synthesis to this C60 derivative is relatively complicated and this inevitably increases the cost, while the future application for commercialization requires low-cost but high performance CBL materials. We therefore turn a cheap phosphorous derivative, tetraphenylphosphonium bromide (QPhPBr), with which and its binary blend with N719 as the CBL, high-efficiency fullerene and nonfullerene polymer solar cells have been realized [3, 4].

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# Stabilized metal chalcogenides nano-film electrodes with high solar energy conversion

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Attachment of electro-active species to the surface of a given semiconductor (SC) electrode permanently affects its photo-electrochemical (PEC) properties. Depending on the charge of the electro-active species, the flat band potentials may be shifted up (more negative) or down (more positive). The shift value depends on the applied ion charge density at the surface. Up to 300 mV shifting has been achieved here. Moreover, the electro-active species behaves as charge transfer catalyst across the electrode/redox junction. This increases the charge (holes or electrons depending on the type of the SC) transfer rate between the SC electrode and the redox couple. By doing so, the SC electrode can become more stable to photo-corrosion. All such advantages can be gained simply by attaching the proper electro-active materials to the proper SC electrode. The attachment can be performed by either chemical linkage or more recently by embedding the electro-active material inside a polymer matrix. The new technique has been successfully applied to monolithic and to polycrystalline SC electrode systems. Monolithic n-GaAs electrode showed up to eight fold enhancement in conversion efficiency. Polycrystalline film electrodes, involving nano-particles of semiconductors (CuS, CuSe, CdSe, CdTe, and others), are are globally known to be unstable and yield low conversion efficiency (in the order of 1.0% or less) under PEC conditions. Stability and efficiency of such new types of electrodes have been enhanced here by the new technique. Conversion efficiency values of 4.4, 8.0, 15.0% and 18.0% have been observed from CdSe, CdTe, CuS and CuSe film electrodes, respectively. Such values have not been reported for pristine metal chalcogenide film electrodes before. This presentation will critically highlight our results observed throughout the last 15 years, as compared to other literature. The new model proposed for the efficiency and stability enhancement will also be rigorously presented. Future prospects of applying our approach at larger technological scale will also be discussed.

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# BOOK OF ABSTRACTS

# SICHEM – 2018

# ORAL PRESENTATIONS

## D – Green applied chemistry and agro-resources valorization
## (GACARV)

# Preliminary study to assess the potential of sunflower leaves as a low-cost sorbent material for zinc ion removal from synthetic aqueous solutions in batch mode

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The use of zinc is widespread, with major inputs to the aquatic environment being likely from the manufacture of alloys, from galvanising and paper production [1]. Though zinc is potentially less toxic compared to others heavy metals, special care needs to be taken in order to prevent its accumulation in the environment [2]. The conventional methods of zinc (II) ions removal from wastewaters, become inefficient and expensive especially when the heavy metal concentration is less than 100 ppm [3-5]. This situation has in recent years led to the search of alternative low cost adsorbents including biosorbents, wastes from agriculture or industry and natural materials for the removal of pollutants such heavy metal ions from aqueous solutions.

This work presents the first results obtained from a preliminary study to assess the potential of sunflower leaves, as a low cost sorbent, for the removal of zinc ions from aqueous synthetic solutions. This sorbent is abundantly available through our country and the world. Kinetic data and equilibrium sorption isotherm were measured at natural solution pH in batch conditions. Two simplified kinetic models from the literature including a first-order rate equation and a pseudo second-order rate equation were selected to describe the metal sorption kinetics. The experimental metal sorption equilibrium data were analysed using two simplified models from literature: Langmuir and Freundlich models, in their linear forms.

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# A new phytotherapeutic product with health-promoting effects in rheumatic ailments

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This paper presents the studies carried out by the authors for identifying a combination of native plant sources that are rich in certain natural compounds that have anti-inflammatory and analgesic effects, and on this basis developing new products that have an increased efficiency in rheumatic ailments.

The following plants were selected for this purpose: willow bark (*Salix alba* cortex), well-known as containing precursors of aspirin that have inhibitory effects upon the activity of enzymes that generate inflammation and pain; rosemary, aerial parts (*Rosmarinus officinalis* herba) and oregano, aerial parts (*Origanum vulgare* herba), that bring other important anti-rheumatic compounds. We mention tri-terpenic acids (ursolic acid and its isomers) that have an anti-inflammatory effect, significant anti-inflammatory and analgesic flavonoids and tannins, choline, vitamins B3 and C, amino acids and peptides, essential oils, and minerals that have analgesic and soothing effects, and support local blood circulation and repair of the affected area.

The complex of plant compounds obtained as a concentrated extract, by the association of three plant products in certain processing conditions, was used in preparing a new anti-rheumatic product – Salicilol gel. This is presented in the form of a gel for topical use, and was tested with very good results in the "Alexandra" Natural Therapy Centre in Breaza, Prahova County, Romania.

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# Hydrogels based on bacterial nanocellulose for controled drug delivery

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Nanocellulose (NC) is a biopolymer with many appealing properties like high mechanical strength, high surface area, chemical stability, hydrophilicity, crystallinity, transparency, biocompatibility, magnetic and electric susceptibility, proton conductivity, rich surface chemistry, and availability, cellulose being the most abundant renewable organic material produced in the biosphere [1-3]. These properties make NC very interesting for applications in the biomedical and pharmaceutical fields NC for wound dressing, virus-removal filters, drug-delivery systems, scaffolds, tissue regeneration, or bioprinting [2,3].

In the present study the raw cellulosic material was represented by Kombucha membranes, a by-product obtained during the fermentation of tea broth by a symbiotic culture of bacteria and yeast (SCOBY). By acetic fermentation it results a special kind of cellulose, never-dried bacterial cellulose, which can be converted into nanocellulose by different physical-chemical methods [1]. Never-dried bacterial nanocellulose (NDBNC) has specific properties that result from its biosynthesis particularities, especially higher hydrophilicity (up to 99%), surface area, transparency, and flexibility. Based on these properties, we have elaborated a procedure to develop hydrogel formulations using NDBNC, chitosan and Poloxamer 407. The hydrogels were analytically characterized using FTIR, TGA, DSC, XRD, TEM and adsorption-desorption experiments to evaluate the drug delivery properties of these new hydrogels.

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# Evaluation of BTEX in an automobile manufacturing followed by risk assessment associated the exposed workers, Iran

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In recent years, many national and international expert groups have considered specific improvements in risk assessment of chemical pollutants. This study has considered to assess the risk of workers exposed to the air pollutants, benzene, toluene, xylene, and ethylbenzene (BTEX) in an automobile manufacturing in Iran.

A cross-sectional research was done. Methods number 1501 and 7602 of the National Institute of occupational safety and Health (NIOSH) were used for sampling and analysis of BTEX in the air. A total of 40 BTEX samples were taken and analyzed by Gas Chromatography-Flame Ionization Detector (GC-FID). Finally, the relative risk of blood cancer caused by exposure to benzene was estimated.

The result demonstrated that, workers were exposed to BTEX during their work in manufactory. Among the organic pollutants in the breathing zone of workers, benzene was hazardous chemicals at high risk level. Following the estimation of relative risk of blood cancer caused by exposure to benzene, workers cumulative exposure to benzene was obtained to be 23.1 ppm per year and the capture relative risk was 1.1. The significant relationships were also seen between the workers exposed to benzene in both age and work experience, so that, degree of exposure decreased steadily with increasing age and experience ($P<0.001$).

This research demonstrated that from organic pollutants studied in this research, benzene had the highest exposure risk. Also, painting hall workers were directly exposed to benzene possibly increase the blood cancer risk. Therefore, in order to reduce risk assessment associated with the chemicals, an essential occupational protection program is needed to be considered in industries like automobile manufacturing.

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# Estimation of hydrocarbons biodegradaton rate from soils contaminated with oil

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Worldwide, in oilfield areas, there are soils polluted with petroleum hydrocarbons, which need to be remediate by using appropriate treatment technologies. Bioremediation is a cost-effective and environmentally friendly treatment method that uses the ability of microorganisms to degrade organic compounds [1].

The rate of hydrocarbons biodegradability depends on the nature of oil contaminant, soil type and optimal conditions for stimulating of biodegradation activity (presence of appropriate microorganisms in an adequate number, temperature, humidity, nutrients, pH and oxygen availability) [2].

Laboratory bioremediation tests were conducted for two soil types (clay and loam) contaminated with two types of crude oil (light and heavy oil). The efficiency of the bioremediation process was monitored by analysis for total petroleum hydrocarbons (TPH) concentration of all soil samples and by the ratio between C17/pristane and C18/phytane (for soils contaminated with light oil). C17 (N-heptadecane) and C18 (N-octadecane) are more easily biodegradable than pristane (2,6,10,14 tetramethyl pentadecane) and phytane (2,6,10,14 tetramethylhexadecane) that are heavily biodegradable iso-alkanes [3]. These ratios remain constant through evaporation, but decrease very much with oil biodegradation. The lower the C17/pristane and C18/phytane ratios, the more biodegradable the crude oil [4].

The highest rate of biodegradation of crude oil was obtained for loam soil contaminated with light oil, where was registered a decrease in TPH concentration from 5% to 1% after about 5 months of treatment with inoculum, nutrients, loosening agents, surfactants, microelements. The lower hydrocarbon biodegradation rate was recorded for the variant using clay soil contaminated with heavy oil, where the decrease was from 5% to 3% for the same treatment period.

Based on the results of these tests, a program for the remediation of soils polluted with hydrocarbons has been developed.

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# Emphasizing the cellulose containing wastes pretreatment, in order to make them more available to further biosynthesis

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This paper presents the obtained results concerning the optimization of the cellulose containing wastes pretreatment, in order to make them more available for the fungal enzymatic attack.

The cellulase is an enzyme complex which breaks down cellulose to beta-glucose. It is produced mainly by symbiotic bacteria in the ruminating chambers of herbivores. Aside from ruminants, most animals (including humans) do not produce cellulase, and are therefore unable to use most of the energy contained in plant material.

Cellulase refers to a family of enzymes which act in concert to hydrolyze cellulose. Cellulases are widely distributed throughout the biosphere and are most manifest in fungal and microbial organisms (1).

Our studies were carried out by using fungal strains, selected from the natural sources by a specific screening and without any genetic engineering applications, in order to realize a technology friendly with the environment.

The studied parameters were represented by a thermal pretreatment and then the use of different doses of some chemical reagents. The substrates consisted in few mixed wild plants or a mix containing straw and stalks (2).

When the hydrolysis tests were conducted only with a complex based on cellulases, the obtained glucose was further used as a substrate for obtaining yeasts biomass or ethyl alcohol, while an additional step of hydrolysis made by using the laccase may conduct us to obtain biogas from lignocellulosic grain wastes like straw and stalks. Two types of substrates are presented here. That one named “A” consists in a mixture of *Dactylis glomerulata* and *Medicago sativa* (alfalfa) The variant named “B” was brought from a grassland with unfertilized soil.

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# Comparative exposure analysis of hazards related to ammonia road transportation. A case study for Valea Oltului area, Romania

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The economy of developed and developing countries is based, to a certain extent, on chemical industry. This activity is strongly related to the transport of hazardous materials (HAZMAT), as they can be either the raw material or the final product. In the case of developing countries, like Romania, the current road transport infrastructure for dangerous substances might not be well optimized to meet basic safety requirements. Considering a growing traffic volume for both people and goods, the probability for an accident involving hazardous or non-hazardous materials to occur is increasing, leading to possible disruption in the usual traffic activity along with significant material and human losses. A transport accident involving HAZMATS can produce effects on a larger scale than a regular accident, so the necessity to develop studies in this area is self-evident.

This study is focused on highlighting the hazards related to ammonia road transportation as well as modelling the possible effects of a transport accident, in order to conduct an exposure analysis. The detailed study of these elements, considering also the vulnerability, underlies the process of risk assessment on a road or a particular sector. The hazards associated to ammonia transport are toxic dispersion and explosion, several threshold values for pollutant concentration and overpressure being identified in order to determine the maximum distance of the manifestation area. In this study, two road sectors were analyzed: first road sector is part of the European road E81(between Tălmaciu and Râmnicu-Vâlcea) and the second sector is part of the A1 Highway (which is planned to connect Sibiu and Pitești). The previously mentioned highway sector is not yet built, but the related documentation was elaborated and included in the Romanian Transport Master Plan. The relevance of a comparative exposure analysis on the two sectors lies on the fact that it can provide useful information to the decision-makers regarding the optimal routes for HAZMAT transport in the area. It can also contribute to the cost-benefit analysis in the planning phase of the new highway.

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# Break-point chlorination drawbacks for a complex impurified groundwater sources ($NH_4$, Fe, Mn) potabilization treatment

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Chlorine is the only chemical oxidant used in drinking water treatment for the ammonium removal. Break point chlorination takes place at a pH range of 7-8 with significant efficiencies, the chlorine demand for oxidation of $N\text{-}NH_4^+$ being influenced by pH, $N\text{-}NH_4^+$ concentration, $Cl_2$: $N\text{-}NH_4^+$ ratio and temperature.

Taking into consideration chlorine reactivity against most of the inorganically oxidizable compounds ($NH_4^+$, $NO_2^-$, $SO_3^{2-}$, $S^{2-}$, $Fe^{2+}$, $Mn^{2+}$, $Br^-$) and organic compounds (humic acids, organic compounds with nitrogen within the molecule) the chlorine dose for $N\text{-}NH_4^+$ oxidation varies across a large domain $Cl_2$: $N\text{-}NH_4^+ = (7.6 \div 20) : 1$, being experimentally determined for each source that requires treatment.

For a special case of an impurification matrix resulting from the association between $N\text{-}NH_4^+$ concentrations above 1 mg /L, alkalinity < 200 mg $HCO_3^-$ /L and organic nitrogen compounds (organic N > 1 mg/L), the impossibility of a practical treatment was demonstrated do to: (1) the chlorine action on the organic nitrogen structures that leads to their degradation with ammonium release, there for the chlorine demand for initial $NH_4^+$ + the formed $NH_4^+$ oxidation being very high, above 60 mg/L and (2) the water pH becomes acid (pH = 3-5) during the chlorination process due to the low buffering capacity of the water.

In this paper chlorine treatment at different $Cl_2$: $NH_4^+$ ratios under specific work conditions is presented comparatively for a few groundwaters containing a variable amount of $N\text{-}NH_4$ (0.96 ÷ 2.35 mg/L) and organic N (0.04 – 1 mg/L).

The article presents the reagent selection ($Cl_2$, $KMnO_4$, $ClO_2$) and the oxidation parameters (pH, dose, reaction time) of $Mn^{2+}$ found in the groundwater source in concentrations of 83-92 µg/L.

Furthermore, the adapted water treatment flow for groundwater with this type of impurification matrix is also presented.

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# Heavy metals adsorption properties of alginate beads from a brown seaweed in the Black Sea (*Cystoseira barbata*)

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Pollution with heavy metals is an important health risk which also impacts ecological systems. Alginate beads or even algal biomass could prove to be an interesting choice to be run in batch or continuous mode [1].

*Cystoseira barbata* is a brown seaweed found naturally in the Black Sea, on the Romanian coast. Given the current interest for applications involving renewable and biodegradable materials of biological origin, valorization of this seaweed could be possible in the long run. One such application may involve the development of systems for the adsorption of heavy metals from polluted waters.

Dry algal powder and alginate beads from *C. barbata* are tested in order to determine their adsorption properties with respect to lead (II) and copper (II) ions. They are compared to alginate beads obtained from a commercial alginate powder.

*C. barbata* has been recovered from the seashore in Mangalia (Romania), washed and dried at room temperature. The algal powder was obtained by milling and then sieving on a 500 µm mesh. Alginate was extracted from the *C. barbata* powder after a primary depigmentation, followed by acidic and basic treatment. The neutralized extract was partially purified by ultrafiltration and precipitated by precipitation with ethanol. The shape and size of the alginate beads was optimized with respect to some factors (i.e. salt concentration, alginate concentration ……) using a binocular microscope.

Kinetics experiments were evaluated for the 6 substrate/metal pairs. Adsorption isotherms were also determined. The concentrations of lead(II) and copper(II) were determined in solution. From these values, the quantity of adsorbed metal ions was determined by mass balance. The concentration measurements were done using an Agilent 4200 MPAES instrument.

We observe that the algal powder and the alginate beads from C. barbata have a good adsorption capacity with respect to lead(II) (445 mg/g) and copper(II) (84 mg/g), although inferior to that of the commercial product which adsorbed 722 mg/g of lead(II) and 171 mg/g of Cu(II). The C. barbata had a lower affinity, 63 mg/g for copper(II) and 277 mg/g for lead(II).

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# Optimisation of the ultrasonic assisted lipase catalysed reaction of acetic acid with isoamyl alcohol

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Isoamyl acetate is one of the most important esters in food industry. Since 1976, 1174 patents containing isoamyl acetate were published. Most experimental approaches used hexane or heptane as solvent which are toxic and undesirable for cosmetics and food products.[1] The high industrial demand for "green" isoamyl acetate lead to the introducing of lipase catalysed solvent-free system. In the past, isoamyl acetate, the banana flavour, was produced by extraction from natural sources [2] witch was difficult. Other alternative ways include using fermentation method, too expensive for commercial exploitation [3], chemical synthesis using strong acid and alcohol that use polluting liquid acids as catalysts, need a post treatment and are costly for industrial application [4].

A new method of esters production using lipase has been found to be more economic compared to previous methods, with mild operation conditions, high degree of purity of the products and their acceptability as green in the food industry [5]. A good method of enhancing the enzyme-catalyzed process is the use of an ultrasound assisted system. The effects of acoustic waves on enzymes are the thermal effect that can lead to lipase distortion, the effect of free radicals and the effect of shear forces caused by microstreaming [6].

In this study we optimized the continuous process of enzymatic ultrasound assisted esterification, finding the optimal configuration for the synthesis reactor. We determined the efficiency of ultrasounds under various conditions using a method of determining the ultrasound power with para nitro phenol and we have highlighted the effects of acoustic microstreaming using a method of dissolving hardly soluble salts.

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# BOOK OF ABSTRACTS

# SICHEM – 2018

# POSTER PRESENTATIONS

## A – Chemical and biochemical engineering (CBE)

# Drying of medicinal plants – Experimental and modelling

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Medicinal plants contain various compounds which are valuable bioactive ingredients in pharmaceuticals, phytopharmaceuticals, nutraceuticals, cosmetics, and food [1,2]. Drying process can have a significant effect on the quantity and quality of these bioactive ingredients [2]. Experimental determination of drying curves and process modelling are essential to design, control, and optimise the drying process.

Aspects concerning the convective drying of celandine (flowers, stems, and leaves) and the extraction of bioactive compounds from dried material were analysed in this paper. Extracts of celandine (*Chelidonium majus*) have antioxidant, antiinflammatory, and anticancer potential [3].

Celandine drying was performed using a MB23-Ohaus thermobalance (at 80, 100, and 120 °C) and two types of food dehydrators (at 80 °C), *i.e.*, Tribest Sedona Express SDE-P6280 and Magitec MT-7670. Dynamics of $U(\tau)$ and $dU(\tau)/d\tau$, where $U$ is the moisture content given as mass ratio and $\tau$ the time, were experimentally determined for each temperature level in thermobalance and food dehydrators. Dynamics of $U(\tau)$ were predicted using a theoretical model based on Fick's second law. The values of effective diffusivity ($5.5\text{-}17\times10^{-9}$ $m^2/s$), which were adjusted from experimental data obtained for three temperature levels in the thermobalance, were processed applying Arrhenius equation, resulting in an activation energy of 33 kJ/mol. The value of effective diffusivity obtained at 80 °C in thermobalance ($5.5\times10^{-9}$ $m^2/s$) was used to simulate the drying dynamics in both food dehydrators and a good agreement between experimental and predicted data was achieved.

Soxhlet extraction of bioactive compounds from dried plant was conducted at 2.5/1 liquid/solid mass ratio and various ethanol/water mass ratios (25/75, 50/50, 75/25, 100/0). The extraction was most effective using pure ethanol as an extracting agent.

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# Fixed bed adsorption of volatile organic compounds onto activated carbon – Experimental and modelling

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Volatile organic compounds (VOCs) may be odorous species, precursors of photochemical oxidants, and some of them are very detrimental for human and environment, even at a very low concentration level. Consequently, it is imperative to control and diminish their emissions from contaminated air. There are two categories of VOC control techniques, *i.e.*, destructive (thermal and catalytic oxidation, bio-filtration) and recuperative (adsorption, absorption, condensation, membrane separation). Among them, adsorption is a highly efficient and relatively inexpensive technique [1]. Porous materials having large specific surface area and pore volume, including activated carbon (AC) and its derivatives, alumina, natural clay, natural and modified zeolites, are the most frequently applied adsorbents [2]. AC is widely used as an adsorbent due to its low cost and great accessibility. Performances of fixed bed adsorption of VOCs from gas streams are generally influenced by the gas flow rate, operation temperature, characteristics of adsorbate (nature, size, density, molecular weight, boiling point, vapour pressure, polarity index) and adsorbent particle (nature, size, shape, density, specific surface area, porosity, pore size distribution, surface chemistry), as well as by the adsorbent bed height.

Fixed bed adsorption dynamics of 1,2 dichloroethane (DCE) from air stream were measured and predicted in this paper. Adsorption of DCE onto AC was performed by flowing gas method in a laboratory set-up at various levels of process factors, *i.e.*, air superficial velocity (1.8, 3.6 cm/s), operation temperature (25, 45 °C), and fixed bed height (7, 14 cm). Adsorption performance under studied conditions, evaluated as saturation adsorption capacity, ranged from 0.32 to 0.48 g/g. A kinetic model relied on equations of species mass balance in the gas phase, Langmuir equilibrium and overall adsorption rate was used to predict the adsorption dynamics. Adsorption rate constant ($1.8\text{-}15\times10^{-4}$ $s^{-1}$) and desorption rate constant ($0.1\text{-}20\times10^{-5}$ $s^{-1}$) were adjusted based on experimental data. Effects of process factors on its responses, *i.e.*, saturation adsorption capacity, adsorption and desorption rate constants, were quantified by statistical models.

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# Natural wool for removal of crude oil and refined oil/products from water surface. The crude oil retention and the phenomenon of capillary migration

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Insoluble oils, including crude oil and a variety of refined organic liquids, can causes harm to the marine environments. The best way to reduce the potential environmental damage is to swiftly and efficiently remove as much as possible of the spilled oil from the water surface. The ideal sorbent material itself ought to be fully biodegradable, superhydrophobic, hydrorepellent and oleophilic, suitable for the sorption of oil in presence of water. The use of natural sorbents for the removal of oil spills has attracted attention and is considered among some of the most attractive options as a result of their effectiveness, reusability, low cost, environmentally friendly as well high sorption capacity. In the present work, natural wool from sheep breeding was choose as a natural oil sorbent for oil recovery and remediation of marine surface contaminated by oil spills.

The aim of the current study is to highlight the capacity of natural wool to adsorb crude oil, gasoline and diesel fuel and establishing its potential usage for oil spill clean-up. This is timely not just because of the need to remove contaminants from the environment, but because it is environmentally friendly and also encourage the principle of converting waste to wealth.

The obtained results suggest that natural wool fibers can be a suitable sorbent material for spilled oil retention on marine surfaces, with performance that are competitive with the materials of synthetic origin proposed for similar applications. Wool fibers retain the oil because of their structure - they have an oleophilic outer cuticle that is covered by lanolin, which repels water. The phenomenon of sorption by capillary action has been highlighted, a phenomenon that removes petroleum products from the affected environment. Initially, the adsorption rate is high, after which the adsorption rate begins to gradually decrease. Due to capillarity, the wool retains in its structure the analyzed oil products. In 3 min, the wool retaines 1.53% more diesel than Crude Oil and 3.65% more gasoline than Crude Oil. The results obtained indicate that there is a rapid increase in the sorption of the various oils in the first 5 min after which it proceeds at a slower rate until equilibrium after 45 min.

In conclusion, the natural wool is a good candidate for the clean-up process of marine oil spill, competitive with other synthetic sorbents normally used. Initially, the rate of retention is high, and as the oil product is sorbed, the amount of petroleum product decreases. As crude oil is retained by the natural wool sorbent, the oil film shrinks, leaving in some parts water without crude oil. Also in both experiments, the major difference between the samples is the degree of fibres compaction (dependent on the fibre density) in the sample. The second sample has double quantity of wool compared to the first sample, however it did not retain the double quantity of crude oil.

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# Identification of the rheological behavior of magnetic fluids

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Magnetorheological fluids (MRF) are suspensions of micron size ferro- or ferrimagnetic particles dispersed in a carrier fluid. Surfacted magnetic fluids are widely used in technological devices for dynamic sealing, heat dissipation, damping, but also in biomedical applications as magnetic drug targeting, contrast enhancement for Magnetic Resonance Imaging (MRI) or magnetic separation of cells. Due to their various applications, in order to correctly design the appropriate equipment it is very important to have accurate data concerning their phisical properties, inclusive the rheological behaviour. Absolute viscosity is one of the most important parameters in the development and modeling of applications that involve fluid flow. Therefore, proper characterization of viscosity must be carried out at a shear rate that is relevant to the specific process. Therefore, knowledge of the formulas, on which the models are based and the limits of their applicability is strongly necessary.

The purpose of the present study is to identify among various models (Bingham, Ostwald de Waele, modified power law, Cross, Casson, Robertson-Stiff) describing non Newtonian fluids, the ones that fit best the actual flow curve of a magnetic fluid. The fluid used for the experiments was a suspension of 10% in volume carbonyl iron powder having as carrier liquid a mineral oil, AlSt as surfactant and additives. The data achieved in experimental measurements found in recent literature were used for the identification of the model parameters by optimization techniques and then to decide, by comparison, which of the models characterises best the visosity of the fluid. It has been considered that the model which gives the lowest absolute average percent error between the measured and calculated shear stresses is the best one. That model with identified parameters could be used to realize accurate simulations. Another goal is to determine how the intensity of the magnetic field applied on the magnetorheological fluid influences the rheological effect and also if several models must be used for the same fluid as a consequence of varying the magnetic field intensity.

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# Integrated System of Fed Batch ABE Biosynthesis and Solvent Recovery by Pervaporation

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The growth of *Clostridium acetobutylicum* on aqueous media with glucose gives the metabolites acetone, ethanol and butanol with butanol as major compounds. The process characteristic bioreactors operate at a slow acid pH (4.5) with a culture medium temperature in the range of 36-38$^0$C. In the case of batch and fed batch bioreactors the control of butanol concentration in the culture media is recommended in order to reduce it toxic effect on bacterial system. The exiting of metabolites from batch or fed batch bioreactors by using of a membrane ultrafiltration –pervaporation system appears to be an interesting solution, which support an opportunity analysis by use of modelling and simulation. The developed mathematical model of fed batch bioreactor coupled with an ultrafiltration-pervaporation unit has been used for establishing of bio reaction species dynamics and also for process optimization when it imposes the maximization of solvents production. In this working system the substrate concentration in the bioreactor feed, the initial culture volume in bioreactor, the surface and the separating performances of ultrafiltration and of pervaporation units near to switching time and stripping time are the process control variables.

The purpose of this paper is to illustrate how to exploit fed batch reactor coupled with ultrafiltration and pervaporation in order to maintain the cellules inhibition growth at the level which maximize the amount of produced solvents. To do this in the mathematical model of the coupled process the kinetics characterizing the biochemical reactions was adopted after Volesky and Votruba [1]. The ultrafiltration is needed in the system in order to protect the pervaporation device face with membrane clogging phenomena. On the other hand the recycling of ultrafiltration retentate contributes to a good mixing in bioreactor and return here the active Clostridium acetobutilicum cellular mass.

A mathematical modeling was developed for the coupled processes of batch-fed batch solvents biosynthesis in *Clostridium acetobutylicum* culture on glucose substrate with pervaporation of solvents from reaction broth. It was used to develop a reliable comparison between the dynamic profiles of concentration for different products in the fermentation broth and in the solvents separator.

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# Black Sea algae biomass as an alternative resource in biofuels production

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The conversion of Black Sea algae biomass into third-generation biofuels appears in the context of European environmental disposition and imperative need to compensate for the depletion of national oil reserves.

Macroalgae are lower plants that accumulate high lipid and protein content along with low-molecular-weight carbohydrates that are the major source of biofuels.

In the context of literature on topic [1], and according to our own works, the following directions of algae recovery resulted for the production of biofuels:

- Obtaining biogas with attractive yields for industrial production (up to 35 $m^3$ $CH_4$ / t fresh algae) using algae mixed with sludge from municipal wastewater treatment plants and possibly mixed with other biomass;
- The production of gaseous, liquid and solid fractions by algal pyrolysis, fractions which are biofuels themselves or can be constituents of blending with classical fuels; algae decompose at lower temperatures and provide higher gas yields compared to traditional biomass;
- Bioethanol can be produced from any marine algae species that contain an appreciable amount of polysaccharides. Polysaccharides are decomposed by hydrolysis into simple, fermentable sugars. Conversions of reducing sugars to 89% have been achieved, but the greatest limitation of ethanol yield is given by their low content in total sugars from hydrolysates.

Worldwide, processing applications of industrial algae occupy a fairly low share in the energy sector. Therefore, it may be considered that a high level of innovation is needed to make these processes more economically attractive.

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# Two dimension model for nickel tetracarbonyl synthesis

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The chemistry of metal carbonyls has been of considerable interest for several decades mainly due to reactivity of these compounds in respect to several classes of organic ligands, and also by their applications in catalysis and in realization of some electronic devices [1]. The first metal carbonyl, $Ni(CO)_4$, was prepared since 1890 by the reaction of metallic nickel with carbon monoxide. This procedure found application immediately and has been used for industrial preparation of pure nickel [2]. This synthesis method is still present. So $Ni(CO)_4$ can be obtained by passing, at atmospheric pressure, a CO current through a layer of Ni particles. No high temperature is required so that the Ni particles layer is mentained at 90 – 100°C. There are kinetic analyzes on the unfolding of this gas-solid chemical reaction where the considered mechanism comes to show that the process can be controlled by the mass transfer around the particle [3]. In this paper the diffusion of CO toward the reactive Ni surface is considered as basic process, that control the synthesis. On this basis was obtained the expression that shows the value of CO flow rate toward Ni particle of R radius. The particle burning time was computed for cases when the CO concentration around the particle and the global constant of the surface reaction are known. For a layer of Ni balls the mathematical model was established showing:

i) the evolution of molar CO fraction, of molar $Ni(CO)_4$ fraction and of total molar flow rate along of layer (z coordinate) and;
ii) the time dynamics of Ni reactive particle radius ($\tau$ coordinate).

A 2D model integration procedure has been implemented in Matchad 15, so that the process can be simulated for different operating conditions. As example it shows that for a 5 m high reactor, initially fulled with 1 mm Ni particles and fed with pure CO at 1 bar and 0.01 m/s fictive velocity, at 100°C, was obtained:

i) the space and time evolution of CO and $Ni(CO)_4$ molar fractions;
ii) the nickel particle radius distribution along the bed, when steady state is obtained and respectively;
iii) the nickel particle flow rate that must feed the Ni layer at steady state process evolution.

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# Air drying of aromatic plants coupled with recovery of volatile compounds

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Aromatic plants are usually dried up to a final moisture content of 8-15% at which the microbial spoilage is highly minimized. Air convective drying is the most used method, but it can severely affect the composition of vegetal material and its organoleptic properties. The quality of dried plants mainly depends on dryer type and drying conditions in terms of temperature, duration, air relative humidity and flow rate [1]. The content of essential oil components of aromatic plants diminishes at temperatures over 30 °C. Accordingly, in order to minimize the loss of volatile compounds, plant drying is usually performed at temperatures below 50-60 °C [1]. This paper aimed at studying the air convective drying of fixed-bed jasmine flowers coupled with recovery of volatile compounds from the effluent of drying column by fixed-bed adsorption onto activated carbon (AC). Jasmine flowers contain many volatile compounds that have medicinal benefits and are important ingredients in perfumes, cosmetics, flavourings, and food [2].

Coupled processes of air drying (50 °C) and adsorption (30 °C) were studied in a bench scale setup. Moisture mass fraction of fixed-bed vegetal material and mass ratio of volatile compounds adsorbed onto AC were measured at different values of air superficial velocity ($w$=0.12-0.30 m/s). AC adsorption capacity was up to 0.2 $\mathrm{kg/kg_{AC}}$, whereas drying and adsorption rates were up to 0.0065 $\mathrm{kg/(kg_{wm}\cdot min)}$ and 0.0035 $\mathrm{kg/(kg_{AC}\cdot min)}$, respectively. Air drying of thin-layer jasmine flowers was performed in a moisture analyzer. Layer moisture content was measured at various levels of drying temperature (50-120 °C). Drying rates of jasmine flowers were up to 0.055 $\mathrm{kg/(kg_{wm}\cdot min)}$ and increased with an increase in the process temperature. The performances of drying and adsorption processes were predicted under different operating conditions.

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# Extended the service life of a rotary screw compressor by choosing the right oil

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The paper presents the comparative research performed for the selection of a right oil for rotary screw compressor that is part of the natural gas compression equipment. The choice of a compressor lubricant depends on the type and construction of the compressor, the gas composition to be compressed, the degree of compression and the final outlet temperature. Selecting the right lubricant is a key factor in providing a long service life for rotary screw compressors. In conjunction with proper use, and good equipment maintenance and operation, it can help deliver exceptional performance and significant cost savings to compressor manufacturers and users.

In this work, three types of oil have been studied: mineral oil, synthetic hydrocarbon (PAO) and PAG fluid.

An important factor for the lubrication of bearings and rotors is the right viscosity of the lubricating oil, which should under all operating conditions comply with the instructions provided by the compressor manufacturer. In rotary screw compressors, the compressed gas and the lubricant come into contact with each other.

The solubility of natural gas and other hydrocarbons is much higher in petroleum oils and polyalphaolefin (PAO) synthetics compared to other commonly used synthetic base stocks such as polyalkylene glycols (PAG). That is expected because both hydrocarbon gas and petroleum based oils are similar molecules consisting primarily of C-H bonds unlike diesters and PAGs, which are relatively polar.

INCDT COMOTI is currently an important producer of natural gas compression groups, equipped with oil injection screw compressors. These equipment are difficult to implement because of the wide range of natural gas intake parameters, the chemically and abrasively aggressive gases, wet gases, as well as the very rigorous gas parameters at the compressor outlet. Three types of oil from three different screw compressors were analyzed. Functional analysis as flash point and cinematic viscosity have been made but also FTIR analysis was carried out in order to determine the chemical transformations that occured during the compressor's work. A mineral base oil is affected both related to base characteristics and inner structure, faster than a synthetic PAO or PAG oils.

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# The analysis of the ABE synthesis process in the semi-continuous process with gas stripping

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The analysis of the ABE synthesis in the semi-continuous process with gas stripping is a field with greatest interest in the preoccupation of all mankind for finding new renewable energy sources and technologies that require a low energy reduction, but also a long-term sustainability.

Near to bioethanol and biodiesel, which are commonly used, the biobutanol is a promising biofuel in the future. Until the middle of the last century, acetone-butanol-ethanol (ABE) anaerobic fermentation in the presence of *Clostridium* genus bacteria, *e.g. C. acetobutylicum*, *C. beijerinckii*, *C. saccharoper-butylacetonicum*, was applied on industrial scale to synthesize the biobutanol [1].

ABE fermentation can be performed in batch, fed-batch or continuous reactors. Batch fermentation is the simplest biosynthesis way but its productivity is limited by substrate and product inhibition. Fed-batch fermentation is adopted to avoid substrate inhibition and achieve a high cell density.

ABE biosynthesis modelling has been used for quantitative characterization of intricate biochemical process describing the dynamics of glucose transformation in ABE, CO2, and H2; design, simulation and the optimization of ABE synthesis reactor; design, simulation and optimization of ABE synthesis reactor coupled with ABE separation system and the analysis of final reaction mass processing [2].

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# Process design for etherification of FCC gasoline's olefins *in situ*

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Some ethers (MTBE, ETBE, TAME, etc.) are added to the gasoline as octane number boosters. At present, they are produced in well established technologies, from alkenes and alcohols. An unconventional but efficient way for producing these compounds is in situ, the reaction taking place between the alcohol and the alkenes contained by the gasoline [1].

Original experimental data [2] demonstrated that the process is feasible with good results, so the next step was to design the industrial process. The flowsheet of the process includes a reactive distillation column, where the etherification reactions take place and a separation of gasoline in two products is performed: the stabilized gasoline also containing the ethers and the light hydrocarbon fraction also containing the excess alcohol. Since the stabilized gasoline is the main product, from the light fraction, alcohol has to be separated, and recycled to the reactive distillation. This can be achieved by the extraction of the alcohol with water followed by alcohol-water separation. The $C_5$-$C_6$ alkanes fraction separated in this process has a calculated octane number around 70 which can be a component for the commercial gasoline or it can suffer isomerisation to increase this number. Also, if the alcohol excess is small (e.g.1.2:1 molar ratio towards the alkenes contained in gasoline), it is not need to separate it but the light fraction with alcohol can be added to the gasoline pool, reducing the alcohol quantity added to the commercial product.

The process was simulated in CHEMCAD, taking as a model the study in ASPEN of Luyben [3]. The present simulation is more complex, since there raw material was multicomponent and simulations were performed for methanol, ethanol and isopropanol.

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# Organic superbases as heterogeneous catalysts for biodiesel production

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Biodiesel production should evolve from a process using fresh vegetable oil as conflictual feedstock or multiple process stages due to main product separation and purification into a more sustainable process using alternative second generation feedstock and heterogeneous catalysts, supporting a more energetically economic and environmentally friendly process [1,2]. Building a catalyst from such a strong organic base and using it to heterogeneous catalyse biodiesel production will significantly reduce the total amount of process energy, will ensure a higher reaction rate, a shorter residence time, an easier product separation, and will reduce the total process costs by reusing the same catalyst in multiple production cycles.

A heterogeneous catalyst was prepared using activated carbon (AC) as catalytic support which was impregnated with previously synthesised strong organic base and used to catalyse transesterification reaction of vegetable oils to biodiesel. AC was obtained from cherry pits pyrolysed at 750 °C for 1 h using $CO_2$ as sweeping gas, activated at 1100 °C in the presence of $CO_2$ and steam, and then functionalized with $HNO_3$. The organic strong base was then impregnated onto catalytic support by immersing AC in alcoholic solution, distilled at 105 °C, and activated at 1200 °C using $N_2$ flow.

Biodiesel production was performed by continuous transesterification of vegetable oil with methanol (1:6 molar ratio) in two fixed-bed catalyst reactors. An external bifunctional vessel acted as a separation funnel allowing to monitor glycerol formation and to separate the glycerol from the mixture flow.

Influence of catalyst loading, reaction time, and reaction temperature on the biodiesel yield was investigated. The highest biodiesel yield (97%) was obtained at 65 °C reaction temperature, 6:1 methanol to oil ratio, 1% (wt) catalyst to oil and 1 h reaction time, concluding that this strong organic base can successfully substitute NaOH or KOH as catalyst while converting vegetable oils to biodiesel.

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# Using STOAT 5.0 software for SBR processes simulation

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The purpose of this paper is to simulate the SBR (sequencing batch reactors) processes from the Eforie Sud Wastewater Treatment Plant using the STOAT 5.0 simulator.

The technologies used for wastewater treatment have seen significant developments in the last 20-25 years, being established by the requirements imposed by the legislation for environmental protection, as well as by the European Parliament's directive on the promotion of the use of energy from renewable sources. [2,3]. Processes in SBR are identical to those in continuous operation tanks, with the exception that aeration and settling occur in the same tank. Here the processes take place sequentially, compared to the classic version, where the two phases are simultaneous. [1]. The SBR procedure is a discontinuous / time-oriented procedure. The discontinuous / batch operation of SBR comprises the following successive process phases over a cycle: filling, nitrification, denitrification, phosphorus and carbon decomposition reactions, sedimentation / settling phase (clear water discharge and excess sludge discharge) and transition / waiting.

One of the main advantages of using SBR technology would be high effluent quality due to primary pollutants reduction (96% ammonium and 88% phosphates). The system allows automatic control for suspended solids concentration and for the solids retention time. The sewage plant scheme was designed using the STOAT 5.0 simulator. [4]. Eforie Sud Wastewater Treatment Plant was monitored by collecting and analyzing samples from the influent and the values obtained were introduced in STOAT 5.0 simulator. Several simulations were performed based on the inlet flow and the operating time of each SBR. The results were compared with those obtained in the laboratory.

Following the performed simulations, three modelings were carried out, the conversions of ammonium, nitrates and phosphorus being used as dependent variables and total volume flow and the reaction time being used as independent variables. The simulations results are in line with the practical results obtained in the laboratory and their values fall within the limits imposed by the authorities.

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# Drying of aromatised vegetable materials with recovery of volatile organic compounds

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The present paper proposes a drying solution of vegetal materials, applicable to aromatic vegetable materials, which is expressed by a process of drying in a fixed bed coupled with a process of recovery of volatile organic compounds, by adsorption on active carbon [1, 2]. The object of the present procedure is to: i) dry at least one type of vegetative material containing flavoring volatile (sages in present case), in the conditions of a coupled process (drying and volatile recovery), ii) raising experimentally  the curves of drying and adsorption of flavoring volatile, for conditions determined by the combination of process factors and iii) quantitative analysis of the drying and adsorption curves, that respond to the changes of the temperature and flow rate of the drying agent that can be used for development, in the sense of raising an industrial process. The first part of the paper analyzes the drying with the simultaneous release of volatile compounds from leaves of sage stalks using a diffusion model that determines the dependence of temperature by the diffusion coefficient for humidity and volatile [3]. The second part of the paper presents the fixed-bed drying installation with the recovery of the compounds by the adsorption on an active charcoal and shows how to exploit the experimental data showing the dynamics of the fixed layer of dried vegetal material. In the same time it show the experimental information regarding retain the volatile compounds from the residual drying agent into active charcoal.

The recovery of valuable volatile compounds by coupling to the drying process will transforms a conventional drying process into one that can be more competitive, by making it possible to leverage volatile organic compounds in aromatized plants, which for many of them are particularly valuable.

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# The effect of the additives on the rheology of some types of drilling mud systems

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This study is designed to provide information on the properties and performance of drilling mud in view of future prospects. Starting from the idea that refers to the influence of compositional and operating factors on the properties and performance of drilling mud, the subject of this study is, the effect of additives on rheology of some types of drilling mud systems.

Drilling fluids are classified according to their basic material and other primary ingredients. There are the water based mud and oil based mud.

Regarding the drilling fluid technology, there are a number of elementary properties on which an analysis is compulsory so that, after the study, it can be determined which is the most appropriate for the base oil. These include kinematic viscosity, pour point, flash point, temperature stability, hydrolytic stability.

Of the above mentioned properties, only those that have a significant impact on the rheological and hydraulic behaviour of the studied fluid are analyzed. In order to optimise the performance of oil well drilling, it is critical to use drilling mud with better rheological properties.

There are a series of additives which were used together with drilling mud, leading for increase and optimise the performance of oil well drillling.

For water based drilling mud was used a non – ionic and anionic surfactant as an additive to optimise their rheological behaviour.

On the other hand, for the oil based drilling mud, was used a biodegradable ester, as an alternative to synthetic base oil. Many more esters were formulated as drilling fluids, by investigating the combinations of different carboxylic acids and alcohols, in order to improve the properties of esters and ester based drilling fluid. The reaction of saturated carboxlic acids with linear or branched alcohol produce esters, which yield more stable rheological properties.

It was found that, the long chain of non-ionic and ionic surfactant, might result in a more viscous fluid. Moreover, the non-ionic and anionic surfactant in water based drilling fluid, improved and stabilised the rheology behaviour.

Measuring and designing the kinematic viscosity of drilling fluid, leads to produce a good mud for remove the cuttings, hold cuttings in suspension when not circulating, increase the ability of the drilling fluid to tolerate solids and water, whether added as integral components or accumulated during the mechanism of drilling into formations or by formation water intrusion.

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# Dissolution kinetics of suspended particle in liquid agitated systems

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From minerals dissolution to reconstructing food powders, processes in which solids are dispersed and dissolved in liquids under stirring have a large share in industry [1]

Solids dissolution is, in most cases, a complex process composed of at least four steps: wetting, sinking, dispersing and dissolving [2]. Thus, dissolution rate depends on numerous factors, some independent and some intercorrelated: physicochemical properties of solvent (pH, ionic strength, viscosity) and solute (solubility, particle size distribution), processing factors (temperature, pressure), factors relating dissolution apparatus (tank geometry, type of mixing equipment, mixing speed) and not only [2 – 4].

Our research focuses on dissolution of benzoic acid (BA) since it is widely used in food industry (especially beverages and juices preservation). While it does not affect the odor or taste of food, BA has a big disadvantage: it has a very low solubility in aqueous solutions. The main purpose of this study is to identify the influence on dissolution kinetics of three main process factors: agitator speed, solution temperature and sugar content. A $2^3$ factorial design (three factors and each factor has two levels) is employed to achieve process optimization.

Based on the obtained experimental data the mathematical correlation for the dimensionless Sherwood number was developed. Similar with equations reported by others, it can be used to estimate partial mass transfer coefficients [1, 5]. The partial mass transfer coefficients obtained experimentally and the calculated values, using the correlation, are in good agreement.

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# The effect of temperature on water diffusion coefficients when drying a porous material

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Seasoning (drying) is a process required for wood to be used for many reasons: reduces weights, confines shrinking and swelling, increases strength, as well as electrical and thermal insulating properties. Drying process control is, consequently, of great importance in wood technology. Usually wood is dried in some combination of natural air drying, accelerated air drying, pre-drying and kiln drying [1]. Over the years numerous studies were reported, from just empirical to combined experimental and theoretical analysis in steady or unsteady state [2]. The obtained results are widely variable because of the complexity and variability of the wood structure and drying conditions [3].

This research presents a practical approach by means of experimental measurements and mathematical modelling of the wood drying process. Thus, drying curves were obtained experimentally in simplified conditions: flat wooden disks, constant drying air composition. Experiments were conducted by varying disks thickness and air temperature.

Based on the obtained curves, the main characterizing parameters of wood were identified: water (moisture) diffusion coefficient and mass transfer coefficient for wood drying. A numerical integration method was developed to solve the diffusion equations in this purpose. The results indicate that the effective diffusion coefficient increses both with air temperature and with disk thickness. The temperature has the same possitive effect on mass transfer coefficient, while disk thickness increase determines a decrease of its value. As noted by others [4], our results indicate that wood drying is a dynamic and complex process of simultaneous heat and mass transfer influenced by many independent factors, especially microstructural properties of the material.

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# Statistical model to characterize process factors influence on partial mass transfer coefficient in Rotating Biological Contactors

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Rotating Biological Contactor (RBC) represents an attached growth bioreactor widely used to provide secondary or advanced level of wastewater treatment (biodegradable matter and nitrogen removal) from early 1900s [1]. Basically, RBC consists of a series of discs, on which microorganisms becomes attached to forming the biofilm. The disks are mounted on a horizontal shaft, partially submerged in wastewater. By disk rotation, microorganisms are supplied with oxygen from air and substrate from wastewater. The performance of RBC is influenced by many factors related to microorganisms, hydraulic loadings, geometrical and mechanical characteristics of the system [1, 2].

The present study aims to determine partial mass transfer coefficients in a gas-liquid system, operated similar to an enclosed RBC to evaluate the influence of the physical and hydrodynamic parameters. Thus, by varying gas and liquid flow, submergence degree and rotational speed we obtained partial mass transfer coefficients for carbon dioxide in water and oxygen in gaseous phase. The obtained values are consistent with those reported by others [3], but (as expected) are lower than data obtained in "complete" RBC systems, where microorganisms are present [4,5].

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# Economic optimization and dynamic control of propylene production by metathesis of 2-butene

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Propylene is mainly obtained from naphtha steam crackers and catalytic cracking units. Relatively small amounts are obtained from other processes, reason for increased interest in alternative technologies such as propane dehydrogenation, olefin metathesis and methanol-to-propylene. Olefin metathesis has a good potential for producing high value products (such as propylene) from low-value raw materials (such as olefinic LPG fractions).

This contribution continues the previous work (Maxim and Bildea, 2018) concerning the conceptual design of 2-butene metathesis process, with the objective of economic optimization and controllability assessment.

Thus, the economic optimization of the 2-butene olefin metathesis process was investigated, considering: a) the reactor preheating section (the Feed Effluent Heat Exchanger – Furnace – Reactor) and b) the distillation section comprising four typical distillation columns. The optimization was performed using Aspen Plus, with the total annual cost (TAC) as objective function to be minimized. The heat exchanger network (HEN) for the unit was evaluated using Aspen Energy Analyzer, for maximizing the energy recovery. Overpressure protection was implemented by sizing pressure safety valves for critical equipment using Aspen Safety Analysis for different scenarios. The dynamic behavior of the unit was investigated using Aspen Dynamics considering as disturbance the throughput of the unit.

Maxim, A, Bildea, C.S. (2018) Conceptual Design of propylene production by metathesis of 2-butene. Sci. Bull. B Chem. Mater. Sci. UPB, 80(1), 47–62.

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# Dynamics and control of a heat pump assisted azeotropic dividing-wall column for biobutanol purification

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Biobutanol is considered a competitive biofuel over ethanol and fossil fuels, being produced in the ABE fermentation process. Butanol is characterized by low water miscibility, flammability, corrosiveness and can be used without any special engine modification. Recently (Patrascu et al., 2018), the energy requirement for downstream processing of ABE mixture was reduced to 2.7 MJ/kg butanol, which represents just 8% of the energy content of butanol (32 MJ/kg butanol). The novel integrated design „*heat-pump assisted azeotropic dividing-wall column*" combines three distillation columns into a single unit that allows over 58% energy savings compared to a conventional distillation sequence. However, good controllability is necessary to take the full advantage of the energy savings offered by this process.

This work presents the dynamics and control of a highly integrated azeotropic dividing-wall column used for biobutanol purification. A rigorous, pressure-driven dynamic simulation was developed in Aspen Plus Dynamics. After adding basic PID controllers (flow, pressure, liquid level and temperature) to the base-case process, the system could not be stabilized and failed when subjected to small disturbances. For example, when the feed flowrate was increased, the temperature of the feed-side stripping section decreased, less vapors were compressed, and less energy was transferred to the feed-effluent heat exchanger and to the side reboiler. As a result, even less vapors were generated, and the system shut down.

The controllability of the system is improved by adding an additional small heat exchanger to the feed-side stripping section. This increases the energy requirements by less than 10%, but provides a new manipulated variable which can be used to stabilize the system. Moreover, adding concentration controllers ensures that products purity is kept constant when feed flowrate or composition disturbances occur.

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# Design, optimisation and control of TAME process separation section

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The octane rating indicates the performance of the gasoline and aviation fuels, more precisely the maximum compression ratio at which a particular fuel can be utilized in an engine without „knocking" of the fuel / air mixture. Gasoline with high octane numbers are used in high performance engines that require high compression ratios. Tetraethyllead, used in the past as octane enhancer, was forbidden because of its toxicity and it was replaced by other octane boosters, as light ethers. Amongst them, the methyl-tert-butyl ether (MTBE) - employed on large scale in the 1990s – was phased out because polluting the ground water. Currently, MTBE is replaced by the more environmentally-friendly tert-amyl methyl ether (TAME) and ethyl-tert-butyl ether (ETBE). TAME is obtained by the reaction of methanol with amylenes from the Light Cracking Naphtha (LCN) fraction. The reaction takes place in an adiabatic, fixed-bed tubular reactor. The reactor effluent contains, besides the TAME product, the unreacted amylenes, the inert C5 alkanes and the excess of methanol. Separation of methanol from the reactor effluent is difficult due to formation of an azeotrope with C5 components. Traditionally, this separation is performed by extracting methanol using water as solvent, followed by methanol recovery and recycle. The disadvantages of this technique are related to contamination of the raffinate (which is sent to the gasoline pool) with water and to the energy required for methanol recovery.

In this contribution we investigate the applicability of pressure-swing distillation for separating the methanol / C5 mixture of the TAME process. The flowsheet structure and a base-case design were established based on vapour-liquid equilibrium and using Aspen Plus as flowsheeting software. Then, the process was optimized with the goal of minimizing the energy requirements. The decison variables were the operating pressures and reflux ratios, while the optimisation was constrained by the use of cooling water in condensers and low-pressure steam in reboliers. Additional energy saving was achieved by heat integration. The economics of the process was evaluated using Aspen Economic Analyzer. Finally, the controlability of the process was investigated by dynamic simulation performed in Aspen Dynamics. The results demonstrate that, for the TAME processes, the pressure-swing distillation is a viable alternative for separation the methanol / hydrocarbons mixture.

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# Pyrolysis with direct flame in biochar processing

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The new pyrolysis methods bring certain enhancements in obtaining pyrolysis products and enhancing the overall efficiency. These methods are in a continuous development [1]. This paper analyses such a new method – *pyrolysis with direct flame* and the way in which it increases the efficiency of obtaining biochar and other pyrolysis products. This method enhances the global performance of the process, including through a more efficient use of the thermal energy. In order to obtain these benefits, the working parameters of an own design charcoal manufacturing machine were optimized. An advantage of the pyrolysis with direct flame is the efficiency increasing by 10-15% of the heat transfer from the heat source to the pyrolysis raw material, comparing with the best method currently used (auto-thermal heating). In the auto-thermal heating, the necessary heat flow for pyrolysis is generated by the partial burning of the raw materials and, sometimes, by burning a part of the pyrolysis products [2]. In comparison with this, the heating with direct flame has the advantage that it uses waste, which is cheaper than the raw materials. Also, this method can be better controlled and it allows a quicker heating, which means a faster pyrolysis. In this way, the thermal energy consumption is reduced and implicitly the process efficiency increases.

The installation of pyrolysis with direct flame uses a gas to produce a flame without oxygen excess, in order not to oxidize the wood used for pyrolysis or the resulted pyrolysis products (charcoal, non-condensable gases – carbon monoxide, carbon dioxide, methane, ethane, pyroacids – especially acetic acid, methanol, tar and heavy oils). In order to reduce the cost of the fuel used in the process, the used gas is obtained by wood waste gasification. In conclusion, pyrolysis with direct flame is a method which enhances many operational parameters in a pyrolysis plant: increases the thermal transfer, makes the burning and pyrolysis control more efficient, simplifies the plant and makes it more reliable, reduces the pollution, lowers the installation's operational costs and also the fuel costs. Due to our innovations to the pilot plant and by using the results of the test runs, all the initially considered functioning parameters were improved in different proportions.

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# BOOK OF ABSTRACTS

# SICHEM – 2018

# POSTER PRESENTATIONS

## B – Applied organic, inorganic, and supramolecular chemistry (AOISC)

# Electrochemical characterization of graphite/polyester composite

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Constant researches have been made worldwide for finding novel materials for different applications. Advanced composites reinforced with micro and nanoscale materials can be applied almost everywhere due to their very good mechanical, electrical and optical properties. It is know, for example, that the addition of carbon nanotubes to a polymeric solution can improved the mechanical properties of the resulting fibers and/or material [1]. The materials based on graphite/polyester composite were found to be robust, polishable, easy to machine and were studied as biosensors for hydrogen peroxide [2].

The paper presents preliminary results of the characterization of graphite/polyester composite membranes using physical characterization (water uptake, thickness measurement) and electrochemical characterization (electrochemical impedance spectroscopy) [3]. The composite membranes were obtained by the addition of different concentrations of graphite (0, 1, 3, 5, 7 and 10% graphite) in polymer with different concentrations of polyester (3, 5 and 10% polyester). The thickness, water uptake after immersion for 1 hour and 24 hours in distilled water and electrical parameters (ionic conductivity and electrical capacitance) were studied. Water uptake showed the highest value for the composite with 5% graphite and 3% polyester after 1 and 24 hours of immersion in distilled water (36.7 and 49.41% respectively). The electrochemical impedance spectroscopy showed that the membrane with the highest value of ionic conductivity was the membrane with 10% graphite and 10% polyester (0.008038 S $cm^{-1}$ ionic conductivity), the conductivity decreasing with the decrease of the graphite concentration. The results showed that the presence of graphite in the composite influences the physical and electric parameters of the membrane, leading to a higher water uptake and a higher ionic conductivity, the membranes having potential applications in different areas for example energy storage as supercapacitors and photovoltaic.

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# Noble metal nanoparticles from Kohlrabi peel: green synthesis and antioxidant activity

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In recent years there has been a constant progress regarding the methods used for the synthesis of different shaped metallic nanoparticles, focusing especially on noble metal nanoparticles such as silver nanoparticles (AgNPs) and gold nanoparticles (AuNPs) due to the numerous applications in different scientific fields. Different methods are used for the preparation of both AgNPs and AuNPs, involving both chemical and green routes. Among the major advantages of methods involving green chemistry: cost effectiveness, eco-friendliness and they do not require the use of toxic chemicals.

The present paper describes the green synthesis of silver nanoparticles (AgNPs) and gold nanoparticles (AuNPs) using aqueous extracts of pale-green and purple Kohlrabi peel (*Brassica Oleracea* Gongylodes Group), a vegetable with numerous health benefits (e.g.: fights cancer, improves heart health, lowers blood pressure, decreases the risk of diabetes and obesity, reduces C-reactive protein, etc.). The potential capacity of the two species of Kohlrabi to bioreduce $Ag^+$ to $Ag^0$ was investigated by means of different spectral techniques (e.g.: FTIR, UV-Vis, absorption). UV-Vis spectra were recorded for both AgNPs and AuNPs at different times (0, 30, 60, 120 minutes and also 24 h after synthesis) and the results are specific for both metalic nanoparticles. The size of the biosynthesized metalic nanoparticles was determined by means of diffraction light scattering measurements (DLS) and the results are in the nanometer range.

In conclusion, a new way to synthesize AgNPs and AuNPs is reported by using aqueous extracts of Kohlrabi peel. The experimental results prove that both metallic nanoparticles are obtained and all the physical-chemical analysis show that the biocompounds found in Kohlrabi (e.g.: saponins, flavonoids, carbohydrates, etc.) can act both as reducing agent as well as capping agent.

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# Electrochemical studies on reinforced BTSE coatings deposited on anodized aluminium

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This paper discusses the properties of the 5%BTSE films reinforced with cerium sulphate, deposited on a pre-treated aluminium substrate. The pre-treatment applied to the aluminium substrate prior to the silane film deposition consists of an anodisation process performed in acidic media. In order to determine the substrate properties and the anticorrosive properties of the reinforced 5% BTSE films, one has employed several techniques such as scanning electron microscopy, electrochemical impedance spectroscopy and potentiodynamic polarization.

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# Corrosion testing on structural materials of CANDU NPP equipment

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Corrosion is one of the processes related to the degradation of construction materials of equipment from a Nuclear Power Plant (NPP). In a CANDU (CANadian Deuterium Uranium) NPP, there are two key equipment (the reactor and the steam generator) which, due to unavailability caused by corrosion degradation, generates huge economic losses [1]. For this reason, there is a particular interest in the research programs concerning the behavior of the structural materials of the equipment from NPPs primary and secondary circuits [2].

In the Nuclear Materials and Corrosion Department from Institute for Nuclear Research Pitesti, research was carried out which the aim to characterize the structural materials corrosion behavior in order to identify the optimal operating conditions in the purpose to ensuring the structural integrity of the key equipment and to predict the lifetime for the safe long-term operation of CANDU NPP. The knowledge and experience acquired are an integral part of the technical and scientific support activity dedicated to the safe operation of the equipment and the CANDU NPP Lifetime Management Programs (PLIM) [3].

Corrosion tests were carried out in laboratory, pilot and industrial facilities (the autoclave system at Cernavoda NPP Unit 1). The fluid in which the samples taken from the structural materials of the main equipment, the demineralised water, were recirculated in the installations, coming in contact with the exposed samples. Testing conditions (pressure, temperature, physical and chemical properties of water) specific to the CANDU NPP primary circuit were assured in all three types of installation and for the secondary circuit only in the first two types of installations. After different testing periods, the samples were extracted and subjected to various types of analysis: visual, gravimetric, optical microscopy, SEM, X-ray diffraction, electrochemical methods, microhardness determinations [4]. The goal of the paper is to describe the corrosion testing facilities, the types of specimen supports, the materials, the shape and the characteristics of the samples as well as to synthetically present the testing programs and examples of the main experimental results.

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# Epoxy anticorrosive systems based on metal phthalocyanines

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The corrosion affects society because of the cost, the waste of natural resources, at a time when concern for environmental preservation is growing, as well as the inconveniences related to human life and safety. The effects of corrosion result in aesthetic damage, high operating and maintenance costs, plant closures, contamination of products, safety and reliability effects, and legal liability of manufacturers. The most important ways of action of anticorrosive coatings are: creating a barrier between the substrate and the environment, inhibiting the corrosion process and sacrificial coating.

As is known from current practice and from the state of the art, there is a great deal of concern in the use of metal phthalocyanines as anticorrosive agents in various film-forming materials. Besides the fact that these pigments are commonly used in decorative paints for blue and green shades, as such or together with other organic or inorganic pigments, these compounds have the advantage of associating with the formation of layered structures, which leads to both obtaining a barrier-type effect and the hardening epoxy resin.

The paper presents a study on the efficiency of using metal phthalocyanines (Cu, Zn, Fe complexes) as such or substituted for obtaining two-component anticorrosive epoxy paints. The phthalocyanine-type chemical compounds are commercially available or have been synthesized in the laboratory by known methods. The experimental studies on the effectiveness of the epoxy anticorrosive on carbon steel substrates in aggressive environments containing chlorides were performed using electrochemical methods of investigation as a potential variation in open circuit, potentiodynamic polarization and electrochemical impedance spectroscopy. It has also been studied the behavior of anticorrosive coatings in aggressive environmental conditions using methods of accelerating the degradation processes of coatings by chemical or physical actions of higher intensity (eg by changing the temperature, humidity, pH, etc.) aiming both at the efficiency of the anticorrosive action of phthalocyanine pigments and the influence of these parameters on certain properties of the coating materials (color, gloss, adhesion, etc). The experimental data show that the use of phthalocyanine pigments is a viable choice in obtaining of advanced corrosion coatings, being a very good alternative for the total or partial replacement of zinc phosphate, currently predominantly used for the recognized anticorrosive effect.

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# Bimetallic Nanostructured Electrochemical Sensors for Biomedical Applications

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The ability to detect disease-associated biomolecules, such as disease-specific metabolites (glucose, dopamine, insulin, $H_2O_2$) is essential not only for disease diagnosis in the clinical setting but also for biomedical research. Nanotechnology, with its enhanced sensitivity and reduced instrumentation size, has a continuous focus to improve the current bio-diagnostic capacity with respect to specificity, speed and cost.

Electrochemical methods have the advantages of being simple, sensitive, selective and applicable for small amounts of sample. Also electrochemical sensors can be fabricated with small dimensions suitable for placement directly into biological samples. Modification of electrodes with suitable materials facilitates the electrochemistry of the redox or non-redox biological compounds, which generally results in increased selectivity and sensitivity of the determinations.

The integration of nanomaterials into sensing systems is presented in this work, regarding the electrochemical detection of some important biomolecules. Electrochemical sensors based on bimetallic nanoparticles and different forms of carbon have been intensively studied as electroanalytical measurement devices.

Ni-Co nanoparticles with different sizes and distributions have been comparatively electrodeposited on three carbon materials, graphene, carbon nanotubes (CNT) and fullerene and assessed by voltammetry and amperometry towards oxidation of **glucose** [1].

Bimetallic Ag-Au based electrochemical sensors have been constructed for the sensitive and selective detection of **dopamine**, which is a chemical messenger released by neurons in the signaling process in nervous system. Using a double pulsed technique we were able to control the silver and gold content in the electrodeposited nanoparticles and to optimize the response to dopamine [2].

Mixed metal oxide nanoparticles (Ni-Co-oxide) and carbon nanotubes materials (CNT) has been showed to be an active and stable bifunctional catalyst for oxidative detection of **insulin** in aqueous solution at physiological pH, with a very good sensitivity [3].

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# Environmental pollution and additional doses calculation for critic groups, generated by geological exploration areas of uranium ores

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This article presents the research findings establishing the environmental impact and calculation of doses received by population from critical groups was, of complex works geological [1] Leaota Mountains, respectively Stoenesti area. The researches for radioactive ores from Leaota Mountains have been made in 1959 – 1989 period and they have got as result the integration of all mineralization, anomalies and mineralization clues in inside of three major structures.

Following field investigations were identified: 3 dumps in Leota of SV on Izvorul Zanoagei creek, 11 dumps in the Leaota of SE mainly on river Badeanca and 2 dumps in the river Leaota V on Negulet creek.

Natural radionuclides pollution sources ($U_{nat}$, $Th^{232}$, $Ra^{226}$, $K^{40}$) are represented by the three dumps which were recorded gamma dose rate values up to 0.45 μSv/h and concentrations of radionuclides in the material dump of up to 118 ppm $U_{nat}$ and 0.59 Bg/g $Ra^{226}$ (values above the limits of ecological restoration)[2]; mine water from galleries G3 Zanoaga, G7 Danis, G5 Danis and G2 Badeanca and 3 holes $Rn^{222}$ galleries where concentrations are above the allowed (55 Bq/m$^3$) [2], for example, in gallery G3 Zanoaga reach up to 2230 Bq/m$^3$.

Evaluation of radionuclide contamination of the environment was made by measurements, laboratory tests (mainly by gamma spectrometry and inductively coupled plasma spectrometry) [3,4] and interpretation of results by making maps of their distribution and comparison with the legislation.

The calculation of doses received by population from critical groups was made by starting from general data regarding the radioelements distribution in the sources of mining exploration as well as those with genesis complex, taking different scenarios in study, located both in mining perimeters (scenarios 1, 3 and 4) and critical groups (scenarios 2 and 5). All the scenarios, except for the 1st, have negligible values of additional doses or at the background level, not over exceeding the 1 mSv/year value – additional doses value for population.

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# Studies on the use of indigenous natural materials as selective sorbents for Cs in the treatment of aqueous radioactive waste

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Radiocesium is the most environmentally significant radionuclides of liquid radioactive wastes. It is a difficult metal to remove from aqueous radioactive waste through standard precipitation practices since most cesium salts are very soluble.

Volcanic tuff of Slanic and Dobrogea basalt, two natural, indigenous materials, with the potential for adsorption of metallic ions were evaluated regarding their potential for the removal of radiocesium from actual low and intermediate level radioactive waste (LILW) solutions.

Laboratory batch experiments have been carried out at IFIN-HH, DMDR in order to evaluate the action of various influencing factors on the sorption process of cesium ions to these materials

These materials present the following advantages: high mechanical and thermal stability, chemical inertia, good ion exchange and adsorption properties, selectivity for metallic ions, low costs and high availability. High mechanical and thermal stability, as well as chemical inertia, are strong points taking into account that they might require further immobilization for final storage as secondary radioactive waste.

The two materials were structurally and radiologically characterized by X-ray diffraction, X-ray fluorescence and gamma spectrometry, respectively. The chemical and mineralogical compositions were determined, and their radioactivity was found to be similar for tuff and significantly lower for basalt, compared to the natural soil of Romania.

Batch adsorption experiments were conducted to determine the effect of contact time, average particle diameter of the sorbent, sorbent / waste ratio, pH and temperature. Our studies revealed that approximately 90% of 137Cs radioactivity is retained on both materials at a contact time of 6 hours, a mean particle diameter of sorbent in the range of 0.63 mm - 1 mm, a sorbent/solution of 137Cs ratio of 15%, neutral pH for tuff and pH 12 for basalt and a temperature of 45 °C.

Therefore, the satisfying adsorption capacity and selectivity to Cs ions indicated that volcanic tuff of Slanic and Dobrogea basalt may be a viable alternative, for the removal of Cs from LILW solutions.

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# Drinking water quantity risk management. Risk analysis of the incomplete quantity of potable water distributed to consumers using Analytica Software

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Drinking water quality risk management is based on the identification and analysis of hazards, risks, their analysis, the probability of occurrence and potential severity of the consequences, with the aim of obtaining and distributing safe water to consumers. The principles of the Food Safety Management System (which is a preventive risk management system) are based on the application of a method that prioritizes the hazards and risks and the establishment of the necessary security actions to reduce them to an acceptable level [1] [2]. In order to analyse the risks to the water supply system, we must take into account the entire traceability chain from the raw water source to the consumer's tap, including treatment technology. In order to ensure safe drinking water for consumers, it is essential that the combined efforts of the parties involved in the treatment and distribution of water [2]. Water supply systems can be described as a series of successive steps that need to be followed to obtain safe drinking water in line, and each step requires careful management that includes: monitoring control to prevent contamination of water sources, water treatment, and its monitorising prior to distribution, water storage and provision of water for consumers, safe water distribution through proper maintenance of the distribution system, monitorising of the quality of drinking water distributed to consumers [2].

In the Study Case presented it is exposed the risk analysis of the insufficient amount of drinking water distributed to consumers using the Analytica software. Analytica is a software for risk assessment in various applications. Analytica features fully integrated risk and sensitivity analysis for analysing models with uncertain inputs; powerful facilities for time-dependent, dynamic simulations; powerful graphing capabilities; and over 200 financial, statistical, and scientific functions for calculating just about any type of mathematical expression [3] [4].

Analytica software offers an integrated risk and sensitivity analysis for uncertainty-entry models and powerful facilities for time-dependent dynamic simulations. [3] [4]

The Study Case describes the Analytica software's ability to analyse and anticipate the water demand in a seasonal tourist town, where the economical activities and population size vary quite a lot between during the cold season (October - April) and during the warm season (May - September) [4].

The analysis presented may allow water operators to understand the potential impact on water resources. It can be used as input to management analyses, periodic analysis and updating of water shortage emergency procedures, and to initiate a new water supply process and real-time monitorising of water resources [4].

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# Classification and property-modeling of natural products based on spectral data analysis

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The classification of natural products according to geographical and biological sources, as well as the estimation of main properties based on rapid analyses is of great concern for their characterization and selection according to user needs. The present paper investigates the capabilities of various multivariate statistical methods in the analysis of Romanian bee-pollen starting from IR spectra. As most chemical analytical methods are based on solvent extraction followed by liquid chromatography and/or colorimetric and enzymatic analysis, spectral techniques, more rapid and non-destructive, are considered promising alternatives. The present work presents the results obtained in bee-pollen classification according to botanical and geographical origin and main properties (polyphenols, sugar, flavonoids and proteins content) estimation starting from FTIR-ATR data.

47 pollen samples were collected using pollen traps fixed at hive entrance in apiaries from Bucharest, Buzau, Dambovita, Cluj, and Salaj counties, during the 2015 and 2016 floral seasons. Botanical origin was ascertained by palynological analysis, as described previously [1]. All samples were analyzed for proteins, carbohydrates [1], total polyphenols and flavones [2]. IR spectra were recorded in the 4000-400 $cm^{-1}$ range. The mathematical modeling was performed in the frame of Matlab (Mathworks, Massachussetts, USA, version R2015) applying Savitzky-Golany smoothing algorithm and several chemometric tools for classification: principal component analysis (PCA), k-nearest neighborhood (kNN), support vector machine classification and partial least squares (PLS) for property modeling. The results obtained proved that distinct classes of bee-pollen could be visualized. The capability of classification of new pollen samples recommends these methods for practical applications. The PLS property modeling gave good results; the correlation coefficients of the polynomial estimation are 0.9 and higher. These results recommend the FTIR analysis for quick assignment of an unknown sample to a given pollen source, mainly in terms of botanic origin, and an initial estimation of its main properties.

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# Engineering lipid coated polymeric nanoparticles loaded with curcumin for cancer therapy

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Curcumin (diferuloylmethane; 1,7-bis (4-hydroxy-3-methoxyphenyl)-1,6-heptadiene -3,5-dione) is a hydrophobic polyphenol obtained from *Curcuma longa*. Curcumin is worldwide used in various biomedical applications due to anti-inflammatory, anticarcinogenic and antimicrobial properties [1,2]. The main limitations for biomedical application of curcumin are low bioavailability and high metabolism in the gastrointestinal tract. Several strategies have been employed to overcome these limitations, like encapsulation in drug carriers [3]. The objective of this study was the synthesis of lipid coated polymeric nanoparticles, consisting of a polymeric core and a lipid shell, and their evaluation for drug release of curcumin.

Lipid coated polymeric nanoparticles loaded with curcumin were prepared by using nanoprecipitation method and a vigorous mixing with a liposomal suspension. Entrapment efficiency of curcumin and curcumin release from lipid coated and uncoated polymeric nanoparticles were assessed. Also, various models like: Zero-order, First order, Korsmeyer-Peppas, Higuchi and Hixson-Crowell were applied to evaluate the release data.

The formulations showed good entrapment efficiency and the *in vitro* release study showed a slow release of curcumin.

Lipid coated polymeric nanoparticles may represent new promising drug carriers for cancer therapy. However, further studies are necessary to demonstrate the potential antitumor activity.

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# Hydrogenation of furfural in order to obtain components for gasoline

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Concerns about the total or partial replacement of fossil fuels has been directed in recent years on the conversion of biomass in such fuels [1,2].

Hydrogenation of furfural in order to obtain furan derivatives, components for gasoline was studied on two catalysts NiCoMoBa /γ $Al_2O_3$ - $SiO_2$ and NiCoMoBa /γ $Al_2O_3$ - H ZSM5.

The two catalysts with various NiCoMoBa loading was prepared by using the impregnation method. Catalysts characterization where performed by determining the acid strength and textural characteristics. Acid strength distribution of prepared catalysts was performed by thermal desorption of diethyl amine in the temperature range 20-600ºC and thermal analyzes were performed on a DuPont Instruments. Textural characteristics of catalysts – pore size distribution, specific surface area, pore volume were determined using NOVA 2200e Gas Sorption Analyzer Quantachrome. The nitrogen adsorption/desorption isotherms were recorded at 77K in the relative pressure range p/po=0.005-1.0. The specific surface area was determined by the standard Brunauer-Emmett-Teller (BET) equation. The total pore volume was estimated from the volume adsorbed at a relative pressure p/po close to unity. The pore size distribution and mesopores volume were obtained from desorption branch of the isotherm by applying the Barrett-Joyner-Halenda (BJH) model.

The catalytic performances were evaluated using hydrogenation reaction of furfural. The hydrogenation reaction was carried out in a continuous tubular reactor.

For both catalysts the main reaction products identified with a gas chromatography system (GC-MS) are tetrahydrofurfuryl alcohol, methyl tetrahydrofurfuryl ether, furfuryl alcohol and furfuryl methyl ether.

NiCoMoBa /γ $Al_2O_3$ - $SiO_2$ catalyst showed higher activity than catalyst NiCoMoBa /γ $Al_2O_3$ - H ZSM5. The yield in ethers was higher forNiCoMoBa /γ-$Al_2O_3$ - $SiO_2$ catalyst at a pressure of 60 bar and temperatures below 200°C.

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# $ZnIn_2Se_4$ films grown by chemica bath deposition for solar cell application

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$ZnIn_2Se_4$ (ZIS) thin films have been grown using a chemical bath deposition technique. The precursors used were 0.05M equimolar solutions of zinc chloride, sodium selenite and indium trichloride, dissolved in di-ionised water, while the complexing agent used was ammonia. The layers were deposited onto glass substrates using bath temperatures ($T_b$) in the range 60°C to 90°C, keeping the other variables constant. The as-grown layers were characterized to determine the chemical and physical properties. All the grown films were polycrystalline in nature with the (112) peak as the preferred orientation. The evaluated crystallite size varied in the range 50 - 53 nm with the change of bath temperature. The films had an optical transmittance of 70 % and the energy band gap of the films was found to vary in the range, 2.85 - 3.29 eV with the change of $T_b$. Photoluminescence studies revealed the presence of $V_{Zn}$ and/or $V_{In}$ as defects in the films. The electrical measurements showed that the layers were n-conductivity type with a resistivity of 1 MΩ-cm. Thin film photovoltaic solar cells were developed using sprayed $CuIn_{0.8}Ga_{0.2}Se_2$ and ZnO:Ga as the absorber and window layers respectively.

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# BOOK OF ABSTRACTS

# SICHEM – 2018

# POSTER PRESENTATIONS

## C – Biomaterials and composites in chemical and biochemical applications
## (BCCBA)

# Selective transport and removal of Cd(II) from the Ni-Cd batteries leaching with polymer inclusion membranes (PIMs)

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Cadmium is known as an extremely toxic industrial and environmental pollutant and however it is used in different industries and in the fabrication of Ni-Cd batteries. PIMs have been involved as affinity membranes for recovery of cadmium by facilitated transport from the aqueous solutions using selective carriers [1]. In this paper a couple of carrier and plasticizer as tricaprylmethylammonium chloride (Aliquat 336) and 2-nitrophenyl octylether (NPOE) respectively were tested in PIMs with cellulose triacetate (CTA) as base polymer support [2,3] for selective removal of Cd(II) from the Ni-Cd batteries leaching. In this separation system the effect of carrier and plasticizer content and the transported metal flux ($J_i$) through membranes were studied. The influence of chloride concentration, in feed and stripping phases, on metal transport and the influence of Cd(II) concentration on the membrane flux has been also investigated. The Cd(II) recovery efficiency obtained in 7 h were 90,6 % and the transport metal flux were about 1.7 $\mu$mol $m^{-2}$ $s^{-1}$. In presence of Ni(II) from the acid leaching Ni-Cd battery the Alliquat 336-based PIMs showed greater selectivity towards Cd(II). After repeated experiments the PIMs have shown a very good stability and a constancy of the transmembrane transport flux. The goal of this study was to propose an alternative solution to remove and recovery of Cd(II) with PIMs from the recycled Ni-Cd batteries, which is important not only for the environmental reasons but also for the economic ones.

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# Phytosynthesised metallic nanoparticles: synthesis and applications in crop protection

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In the years, a new area of research gained the interest of the scientific community: the phytosynthesis of the metallic nanoparticles. The *green* approach allows synthesis of nanoparticles with specific characteristics (considering the desired applications) [1]. For the characterisation of such nanoparticles, several analytical techniques were successfully applied (such as X-ray diffraction, X-ray fluorescence, electron microscopy) [2], together with methodologies developed for the evaluation of their potential uses (evaluation of the antioxidant potential, antimicrobial properties, cytogenotoxic potential etc.) [3, 4].

Our paper presents to the activities of the project *Increasing the institutional capacity of bioeconomic research for the innovative exploitation of the indigenous vegetal resources in order to obtain value-added horticultural products (BIOHORTINOV)* aimed towards the development of innovative recipes based on phytosynthesised nanoparticles for reducing the biocenotic stress in horticultural crops.

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# Development of new nanomaterials for the restoration/conservation of cultural heritage artifacts

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The deterioration of cultural heritage artifacts represents a main concern for specialists working in several areas: history, conservation science, materials science, biotechnology, etc. In the last decades, with the development of nanotechnology and the restriction of some potential harmful substances that were currently applied for reduction of biodeterioration, new alternatives emerged for the reduction of the biodeterioration of the cultural heritage artifacts [1].

Our group previously proposed the application of synthesised apatitic materials with enhanced antimicrobial properties for this application [2-4]. Our paper presents the activities of the project *Multidisciplinary complex project for the monitoring, conservation, protection and promotion of the Romanian cultural heritage (RO-CHER)* aimed towards the development of innovative recipes based on nanomaterials (adapted for two types of support materials - ceramic and paper), in order to reduce the impact of cultural heritage artifacts biodegradation.

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# Development and evaluation of antimicrobial products with controlled delivery

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The improvement of drug delivery systems is intended to use more efficient chemical or physical barriers to control the rapidity of release and to ensure the preferred dose maintenance.

In this sense, the development of delivery systems is strictly dependent on the choice of a suitable carrier agent capable of controlling drug release [1-2].

The present paper addresses the development of systems aimed at the use in various medical or environmental applications. For the synthesis of the materials two methods were used. *The first method* involved antibiotics absorption (0.1 g of ampicillin, neomycin or erythromycin) from aqueous suspension (1g of MMT or Bentonite dispersed in 20 mL distilled water). The obtained suspensions were allowed to stir for 6 hours. Following stirring, the samples were filtered and dried. Finally, ampicillin, erythromycin or neomycin loaded montmorillonite/ bentonite powders were obtained. *The second method* was performed by vacuum assisted absorption. Therefore, 1g of MMT or bentonite was kept under vacuum for 30 min and after this a solution of 0.1g antibiotic (ampicillin, erythromycin or neomycin) dissolved previously in 3mL solvent was added, quickly followed by turning off the vacuum to reach atmospheric pressure. After drying, the sample was vacuumed again and additional 3mL of pure solvent was added to force the antibiotic molecules to get into the pores, these steps being repeated twice. These samples highlight different release profiles, which mean that both the nature of support and drug as well as the loading procedure influence the delivery profile. The analyzed samples showed antimicrobial and antifungal activity on various strains thus creating the premises of their use in various medical or environmental applications. Moreover, the obtained clays can be considered for obtaining systems that are even more complex.

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# The useful applications of Metal Organic Frameworks (MOFs) in manufacturing detector devices for organic compounds with explosive potential

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Metal-organic frameworks (MOFs) are a subclass of coordinating polymers having metal ions or groups coordinated with organic ligands to form mono-, di- or tridimensional superstructures [1]. A huge variety of inorganic and organic components can be used to construct MOFs, and this versatility has enabled the rational design and assembly of materials having novel topologies and exceptional characteristics. Luminescent MOFs could be a suitable choice for manufacturing detector devices for organic nitro-derivates with explosive potential due to their turn-off fluorescence properties. To design them, the molecular geometry and molecular nature of the ligands is essential, ultimately providing the final structure and topology of the material. Among organic ligands, an important class is represented by the carboxylic acids, which are the most involved in the construction of luminescent MOFs. In this work, 1,4-benzenedicarboxylic acid (BDC) as an organic bidentate linker was used due to its structural rigidity, the diversity of coordination geometries and the possibility of facilitating the formation of large gap structures, while zinc and europium were chosen as the metal clusters (connectors). Zinc benzene-dicarboxylate (Zn-BDC) and Europium benzene-dicarboxylate (Eu-BDC) nanorods were synthesized starting from zinc acetate dihydrate and europium dihydrate acetate via a cetyl trimethylammonium bromide (CTAB) surfactant-assisted technique [2]. Eu-(BDC) was also synthesized by hydrothermal technique, starting from europium nitrate and terephthalic acid [3]. All compounds were characterized by powder X-ray diffraction, FTIR, UV-Vis and fluorescence spectroscopy. XRD assays confirms the crystallinity of the synthesized samples as well as the differences that underlie the europium compounds synthesized on different routes. MOF compounds with europium are structurally different and this is observed in fluorescence behavior. The product of europium acetate and disodium terephthalate exhibits a particularly pronounced fluorescence at 600nm (1000 a.u.), unlike its counterpart, the MOF synthesized from europium nitrate by hydrothermal process. Both compounds show a fluorescence extinction after nitrobenzene treatment, but at different levels respectively in the 570 ÷ 650 nm range for the europium nitrate compound and 670 ÷ 720 for the creatine compound derived from europium acetate.

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# A comparative study of pure Mg/Mg–based alloys for metallic implants application

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Nowadays, intense research is focused on the development of *"smart implants"* based on biodegradable metallic materials. A great advantage of using pure Mg/Mg alloys as biodegradable metallic materials for biomedical implants is mainly due to their degradability, excellent biocompatibility, low density and relatively low cost. Once introduced into the body, Mg is progressively dissolved, so there is no need for the secondary surgery to remove implants after the surgery regions have healed. The major issue and one reason why they are still not popular is their rapidly corrosion rates in physiological environments. This makes their biodegradability to be faster than the time required to heal the bone.

We report a comparative study between pure Mg and extrudable Mg–CaZnZr alloys. Electrochemical measurements, impedance Spectroscopy and *in vitro* immersion tests were conducted to evaluate the corrosion resistance of biodegradable metallic samples into physiological fluids. Before, during and after investigations the samples were physical-chemical analyzed by Infrared Spectroscopy, Scanning Electron Microscopy, X-ray Dispersion Spectroscopy, hydrogen release, Inductively Coupled Plasma-Mass Spectrometry.

The obtained results provide the basis for the design of new alloys with improved corrosion properties to be used as biodegradable metallic implants.

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# Retention of anthracene on functionalized anionic clays - layered double hydroxydes in wastewater treatment processes

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In this work, we studied the retention of anthracene on anionic clays hydrotacites. Anthracene is a pollutant that can result from different industries (for exemple industrial aromatic chemistry, plastics industry, such as: PVC, dyes, adhesives, insecticides and others). For this work we have prepared different anions of anionic clays (Mg-Al in different ratios, Mg-Al-Cyclodextrin) Mg-Al-LDH, hydrotalcite – like anionic clay, denoted as LDH, is obtained by the co-precipitation method at constant pH. Their behavior was studied concerning theyr retention of pollutants. Lamellar double hydroxides (LDH), also called anionic clays, are positively charged layered materials containing divalent and trivalent cations. The electro-neutrality of the material is ensured by the presence of inter-foliar anions, solvated by water molecules. These materials have an exceptionally flexible composition, which gives them exchange, intercalation, conduction and other properties, opening up wide areas of application because of their wonderful characteristics in terms of economy, polyvalence and easy preparation methods, high surfaces, uniform compositions of sharp criticality, lamellar structures, high ion exchange capacities and memory effects. According to a new procedure, several types of Mg-Al-HDL materials were obtained starting from different amounts of aluminum or magnesium nitrates/chlorides/sulphates, by co-precipitation at constant pH with sodium hydroxide. In addition, the cyclodextrin that has functionalized the materials, brings an increase concerning the adsorption capacity of those.

To control the efficiency of antracene retention, we monitored the anthracene concentration by spectrophotometric analysis at a wavelength of 252 nm. Also, we have worked with different quantities of adsorbent material and respect the other working conditions: dynamic regime; constant temperature; constant pH; time interval: by 0 up to 100 minutes. Contact time is an important parameter for the study of anthracene retention in both clay samples. This determination reveals information regarding the optimal contact time to our adsorbent material with the polluted solution.

Also, the hybrid material obtained (LDH with β-CD) develops a higher potential concerns the retention capacity of the pollutant, almost double. We can conclude that the obtaining hybrid organic - inorganic materials increases the properties of the original materials. Using this material, adsorption isotherms were determined as a function of agitation rate and temperature. The conclusion of this work was that we obtained favorable results concerning the retention of this pollutant on this clay-based material, prepared in our laboratories.

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# Uses of composite materials of the smectite type in catalytic ozonation

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Advanced oxidation processes are a set of chemical treatment methods and procedures used to remove pollutants present in wastewater by oxidation through the reaction who involve hydroxyl radicals (OH-) formation. Oxidative processes usually refers to a subset of chemical processes which employ UV light, hydrogen peroxide ($H_2O_2$) and ozone ($O_3$). These processes are sensitive to variations in temperature, pH, pollutant concentration, ozone concentration, the amount of catalyst used and the duration of the oxidation of pollutants is high. In order to remove these shortcomings, in this paper we propose the preparation of heterogeneous cationic catalysts, based on chemically modified composites materials of the smectite type, and testing them to remove different dangerous food dyes. Cationic clays are made up of tetrahedral and octahedral units maintained by interlabel cations. These may be trioctaedric and diocatadic depending on the predominant cations of $Al^{3+}$ and $Mg^{2+}$ respectively in the octahedral unit. Chemicals added to the manufacture of various foods in order to improve their properties and extend their shelf-life are named food additives. Additives that have been used and tested for at least 6 years and certified at European level are symbolized by the letter "E". The aditivives with emphasis on dyes that we want to oxidize are on the list of carcinogens: Blue Patent V (E 131), Acid Red (E 123), Food Green 4 (E 142), Tartrazine (E 102) and Sunset Yellow (E 110). Food dyes as can be seen on food labels are found in considerable amounts that can affect human health causing various untreatable illnesses. Smectite clays used in industry, commercial or chemical products, can be divided into three types: Ca-Mg smectites, Na smectites and Fuller's. For our research we propose to work with natural cationic clay like montmorillonite, because in România, those type appear in nature in large quantities in Countys: Maramureş, Hunedoara, Alba, Timiş, Caraş - Severin. Montmorillonite is a smectite clay extracted from bentonite, which is distinguished by two tetrahedron sheets arranged in the hexagonal rings. The interlaminar spacing of the montmorillonite varies between 1.0 - 1.2 nm and the distance of the T-O-T layer and the sheet is 0.65 nm. By catalytic ozonation processes can be achieved a total mineralization of food dyes into $CO_2$ and water only if are added a optimum amounts of catalyst and oxidizing agent, and find the optimum pH, time and concentration of the organic substrate.

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# BOOK OF ABSTRACTS

# SICHEM – 2018

# POSTER PRESENTATIONS

## D – Green applied chemistry and agro-resources valorization
## (GACARV)

# Obtaining activated charcoal support starting from vegetal wastes

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The purpose of this paper was to use and add value of some vegetal cellulosic wastes, rich in carbon, useful raw material for obtaining the active charcoal by pyrolysis. The modern techniques of investigation, promoted by scientists and supported by studies, sustain the development of new useful products as filler for air filters. This plant material consisted of *Hyppophae rhammnoides***,** *Ribes nigrum* - sprigs and *Aloe arborescens* cakes. Sprigs and cakes, remaining after plant exploit, were pyrolized and turned into charcoal to be used on air filters, as support for fixing noxious compounds, unwanted for the maintaining of health.

To achieve experimental investigation "The pyrolysis in fixed flow" was applied using plant material samples. The experimental pyrolytic system used was a modern one, and mass loss of the layer of pyrolytic oil accumulation and temperature field in different areas of the facility were online monitored.

The plant material and charcoal obtained in that study were analyzed morphologically and structurally, by fast laboratory techniques: **SEM** (with a Vega Tescan LMU II apparatus) and **I**nfrared **S**pectroscopy (FT-IR) (using a prestigious FT-IR spectrometer -Shimadzu, Japan). As a result of the production of activated charcoal from plant material wastes and following its morphological and structural analysis, the following can be concluded: FT-IR spectra obtained from plant wastes material prior to the pyrolysis process, reveal large amounts of cellulose, hemicellulose and lignin, and the presence of specific oils especially at *Hyppophae rhammnoides* wastes compared with the others wastes.

From the SEM images, the porosity of the active carchoal was obtained. The wastes ware carbonized at high temperatures in the presence of vapors, forming internal porous structure with variable particle diameters between 10 and 120 µm. Active charcoal made from *Hyppophae rhammnoides* - sprigs has a small pore size - 10 µm and has a high specific surface area and superior adsorption characteristics compared to other charcoal types that have with a larger pore size (100-120 µm) and nonhomogeneous dispersion in the case of *Aloe arborescens* charcoal.

Active charcoal resulting from *Hyppophae rhammnoides* - sprigs, following the pyrolysis process, following charcoal activation technology that involves the development of pores in terms of weight loss and the advancement of temperature and activation time, starting with ultramicroporosity, which is gradually transformed into micropores and then into mesopores, has good features to be used to make filling for air filters.

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# Assessment of radiological risk for people working in coal mines

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The paper presents the results of some measurements regarding the gamma debit dose, the radon concentration and the uranium concentration in the Jiu Valley coal mines.

Carbon (coal), as any material from the environment contains discrete quantities of naturally occurring primordial radionuclides such as $K^{40}$, $U^{238}$, $Th^{232}$ and their disintegration products. By combustion they pass into slag, light (flying) ash and hot smoke gases. In this way, existing radioactive substances in coal are scattered on large surfaces. Natural radioactivity determinations have determined that by burning, concentration usually occurs about 2-5 times, the upper concentration limit being 10 times. Most natural radionuclides have poor radioactivity and a major role in soil radioactivity is owned by $K^{40}$ with 40%, the $U^{238}$ series with 20% and the $Th^{232}$ series by 28%. In 100 grams of ground crust substance, natural radionuclides create the following activities: $K^{40}$ about 80 Bq; $U^{238}$ about 3.7 Bq (about 52 Bq the entire series); $Th^{232}$ about 4.13 Bq (about 49 Bq the entire series).

The measurements were carried out in order to characterize the possible existing radioactive sources in the Jiu Valley coal mines and to determine the influence of pollutant radionuclides on the health of the professionally exposed personnel. On the basis of these results the additional dose, which the staff from the coal mines in the Jiu Valley is exposed to, was calculated.

The total effective dose has two components: the effective external dose - is due to external gamma irradiation; it is determined experimentally by measuring the debit dose in the place where it is evaluated and the effective internal dose - due to inhalation and ingestion of radionuclides; In case of radionuclide $Rn^{222}$ inhalation, it is determined experimentally by measuring the concentration of radon activity in the place where it is evaluated.

International Radiation Protection Norms and those in Romania admit an additional dose of 1 mSv / year for a person in the population; this value is added to the effective dose due to the external environment in the area investigated.

From the calculations of the additional annual effective doses, it results that a person working underground for 2000 hours / year receives an additional effective dose of 0.281-0,382 mSv / year.

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# Quantification method of ochratoxin A in cereal and cereal products

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Isolated for the first time in 1965, ochratoxin A (OTA) is a secondary metabolite produced by filamentous fungi species, especially *Aspergillus* and *Penicillium* [1,2]. OTA has received increasing attention worldwide because of its wide distribution in cereals and foodstuff, *e.g.*, corn, barley, wheat, soy, rye, rice, sorghum, vegetables, spices, dried fruits, coffee, oilseeds, nuts [1-4].

Recent reports from worldwide organizations stated that food products are frequently contaminated by OTA. The important effect of OTA in human health has impelled the food safety organisations to set a maximum residue level (MRL) in different cereals and foods. Therefore, the Commission of the European Communities has limited the admissible level of OTA taking into consideration the risk related to consumption as follows: 5 µg/kg for unprocessed cereals and 3 µg/kg for all products derived from unprocessed cereals [5].

The main objective of this study is developing a quantifying method for determination of OTA in agricultural products using a quick, simple, and cost effective reverse-phase ultra-high performance liquid chromatography (UHPLC-FLD). It is considered a classical and stable method, available on most analytical laboratories for routine determinations, due to OTA strong natural fluorescence activity [1]. Several matrices have been used: maize, wheat, barley, and two-rowed barley as representative cereals for method validation. Under the optimized conditions, the OTA extraction was carried out using a mixture of methanol and sodium hydrogen carbonate (60:40 v/v) as a solvent and the purification was performed using an immunoaffinity column. The method is suitable for the determination of OTA at a level $\geq 2$ µg/kg. The validation study showed a good recovery ($\geq 70\%$), with an intra-day and inter-day relative standard deviation less than 13% and 15%, respectively. The standard measurement uncertainty was $\leq 20\%$ for all the matrices. The method was successfully developed and validated for cereals and derived products, being in compliance with MRL allowed according to European Commission legislation.

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# Attempts of cadmium (II) ions removal from synthetic aqueous solutions using almond (soft shell) peel as an eco-friendly sorbent material in batch mode

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Cadmium is attracting wide attention of environmentalists as one of the most toxic heavy metals. The major sources of cadmium release into the environment by waste streams are electroplating, smelting, alloy manufacturing, pigments, plastic, battery, mining and refining processes [1,2]. Current technologies for cadmium removal from wastewater such as: precipitation, ion exchange and adsorption lack a sufficiently high affinity and selectivity to reduce residual cadmium to the levels dictated by ever more stringent government regulations [3]. This situation has in recent years led to a growing interest in the application of biomaterials technology for removal of trace amounts of toxic metals from dilute aqueous wastes.

This work studied the possibility of using an agricultural solid waste: almond (soft variety) peel, as an inexpensive sorbent for the removal of cadmium (II) ions from synthetic aqueous solutions. This material is abundantly available in Algeria, hence cost effective sorbent. The metal sorption equilibrium and kinetics tests were performed at natural solution pH in batch conditions. The effect of two parameters such as: contact time and initial metal concentration on metal sorption, has been studied. Two simplified kinetic models including a pseudo first-order and pseudo second-order models were selected to analyse the metal sorption kinetics. In order to describe the metal sorption isotherm mathematically and to obtain information about the maximum metal sorption capacity of this sorbent tested, the equilibrium data were analysed using Langmuir and Freundlich models.

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# A reconditioning procedure of some Li-Pol batteries

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This paper discusses a procedure of reconditioning some lithium-polymer batteries, presenting operating faults, and sent normally for destructive recycling. Before the reconditioning process, one should perform a preliminary evaluation in order to determine the actual characteristics of these types of batteries, such as voltage, charging and discharging capacity, to decide their suitability for the reconditioning procedure. If the electromotive force of the batteries is too low and the apparatus will not accept the charging step, one may add another battery to the circuit in order to increase the voltage enough to accept a charging step. After the evaluation step, a reconditioning procedure is applied, consisting in charging/discharging stages at controlled current values. After the reconditioning stage, these batteries may be used as initially intended, if the final characteristics are similar to the initial ones or may be used in some other less demanding applications.

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# The study of rocks and soils in areas affected by uranium mining exploitations

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mailto:l.harvey@cisa.comUranium exploitation activities have a negative impact on the environment, both through landscape modifications, as well as changes in environmental factors such as water, air, soil, flora, fauna and zonal communities. Overall, the exploitation and exploration activities of the uranium mineralizations and heavy metals have a short and long term impact on the environment by the degradation of the landscape and especially by the deterioration of the environmental factors quality. Inside all types of rocks and soils within the uranium mining perimeters can be found the radionuclides belonging, mainly, to the natural radioactive series of $U^{238}$, $U^{235}$, $Ra^{226}$, $Th^{232}$ and $K^{40}$.The radionuclides distribution is not uniformly, there are some areas on Terra, where the are in great concentrations, as well as some sort of rocks in which uranium and thorium are more abundant. In our country such areas are the perimeters of the mines for exploitation and exploration of uranium ores, and the nearby territories The main purpose of protective measures is to prevent the dispersion of uranium in the environment, thus preventing a further population irradiation In order to assess the impact of uranium mining exploitations it must to analyze the results of the gamma dose rate measurements (for radioactive elements - uranium, radium, thorium, potassium and minerals that accompany the mineralization) for the rocks and soils harvested from the dumps and their surroundings in the selected study area (Zimbru perimeter, county of Arad, Romania). The aim of this study is to identify and characterize the sources of pollution for rocks and soil with natural radionuclides and heavy metals, to assess the impact on these two environmental factors for an abandoned uranium mining perimeter and also to see what the results of the analyzes and interpretations for the rock and soil samples collected from dumps and their surroundings have highlighted.

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# Extraction of bioactive compounds from blackberries pomace

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Blackberries are known from long times as wild fruits, but now they are also cultivated worldwide. They are mainly used in food industry to produce: juices, jams, alcoholic drinks, but could be also fresh consumed. In Europe, Serbia is the leading producer of blackberries. Romania has also very good conditions for blackberries cultivation, but in 2005 only 100 ha were cultivated with these fruits [1]. Blackberry pomace is a valuable by-product from blackberry juice processing which is rich in many bioactive compounds, such as anthocyanins, polyphenolics and oil (especially in seeds) [2,3].

The aim of this work is to propose a valorization scheme of blackberries pomace through extraction using aqueous/organic solvents. Polyphenolics and anthocyanins were extracted using ethanol-water mixtures at different temperatures from dried blackberries skin and were optimized using a $2^3$ factorial design. The statistical analysis has revealed that solid/liquid ratio and temperature are the most important influencing factors of extraction efficiency. The best conditions for anthocyanins extraction were: solid/liquid ratio 1g/50 mL, extraction temperature 60°C and time 1h. For polyphenolics extraction the best conditions are quite similar as for anthocyanins extraction: solid/liquid ratio 1g/50 mL, extraction temperature 60°C. The only difference is that the extraction time must be 2h.

Blackberries seed oil was also extracted using hexane as solvent and the experiment was optimized using a $2^3$ factorial design. In this case the most important parameters were temperature and extraction time.

Moreover, this study suggested that blackberries pomace could serve as a valuable source for bioactive compounds.

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# Electrochemical recovery of metals from WPCBs: Evaluation of direct accessible metals content

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The increased amount of electric and electronic equipments (EEEs) is a major concern for environmental protection and raw materials preservation. Furthermore, due to the more demanding customers and rapid technological development, the global quantity of waste electrical and electronic equipments (WEEEs) was up to 41.8 Mt in 2014 and was forecasted to be 50 Mt in 2018 [1]. Although the waste printed circuit boards (WPCBs) represent only 3-5% from the WEEEs amount, they concentrate 40% from the value of the recoverable metals [2].

Due to the WPCBs relatively high metal content (e.g. Cu, Ni, Fe, Al, Zn, Sn, noble and rare metals, etc.), it is necessary to develop new, economical and eco-friendly recycling technologies. In this context, the WPCBs composition and structure represents a key factor for the selection of the optimal technical solution Moreover, the improvement in EEE's manufacture led to continuously modification of their composition toward reducing metals consumption, especially noble metals.

In order to evaluate the fluctuation of the direct accessible metals content of WPCBs, a number of 10 different generation personal computer motherboards (PCMBs), released between 1998 and 2008, were partially dismantled, chemically dissolved and the resulted solutions were analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES). The obtained results revealed that the costs for metals recovery from PCBMs can be significantly reduced by a minimal mechanical pre-treatment (removal of Li batteries, aluminium heat sinks and cylindrical electrolytic capacitors). From another point of view, for the tested PCMBs, the content of exposed metals is relatively constant, maintaining a revenue of about 2100 USD/t. Moreover, the value of metals still remained in chips, SMD and depopulated PCBs, omitted in this study, can also increase the income. Finally, it is worth to note that, after RoHS directive took effect in 2006, the lead content decreased significantly, simultaneous with the increase of tin content.

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# Study of hydrogen peroxide electrosynthesis using a modified Micro Flow Cell® filter press reactor equipped with different types of carbonaceous materials as cathode

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Hydrogen peroxide (HP) is one of the most important reagents [1] with many applications, like chemical industry and depolution processes. Nowadays, hydrogen peroxide electrosynthesis (HPE) is very studied as key step of the electrochemical advanced oxidation processes proposed for the remediation of a large variety of dangerous pollutants from wastewater [2, 3]. The efficiency of HPE process is strongly influenced by the cathodic materials and operational conditions. In this context, consistent studies were focussed on the HPE via partial oxygen reduction on carbonaceous materials due to their advantages [4] and significant efforts were made to optimize the experimental parameters such as electrolyte composition, pH, etc. [5].

Our work consists in the evaluation of the HPE process efficiency for different carbonaceous materials such as graphite, reticulated vitreous carbon (RVC) and graphite granules used as cathode. The HPE test were completed in modified Micro Flow Cell® filter-press reactors equipped with DSA-$O_2$ electrodes as anodes, Nafion117 membranes as separators and two reference electrodes of Ag/AgCl/$KCl_{SAT}$ type. During the measurements, unbuffered low ionic strength solutions (0.05 M $Na_2SO_4$, pH=4.2) and air were used as electrolyte and oxygen source, respectively. Comparison between the behaviour of these three types of cathodic materials and optimisation studies of HPE process were made. Operational parameters such as electrolyte or air flow rates and cathode applied potentials were optimized for all types of tested cathode materials. The optimal conditions for the HPE process have been established taking into account the best values of the current efficiency, specific electrical energy consumption and final concentration of accumulated HP. The amount of electrogenerated HP was monitored in real time with an original flow-through amperometric detector [6] _ENREF_3and confirmed finally by titration using potassium permanganate.

All optimisation tests were carried out for 1 hour at the room temperature (~ 25°C), using 100 mL of fresh solutions as catholyte and anolyte.

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# Preliminary investigations for the valorization of grape seeds after the oil extraction

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The target of zero waste imposes new approach for all the industrial processes [1]. The wine industry produces a large amount of wastes that has to be valorized as imposed by ecologic as well as economic reasons.

The grape seeds comprise around 17 % from the winery wastes. A main valorization of seeds is the separation of the oil, which makes 11-14 % from their content. The interest for the grape seed oil is due to the fatty acid profile of this oil displaying a high content of polyunsaturated fatty acids [2]. After the oil extraction there still are high quantities of residual materials requiring further valorization.

Possible solutions for such valorization have been investigated. The performed experimental work suggests some issues for obtaining new valuable products.

In case of oil separation by extraction with a non-polar solvent (hexane, petroleum ether, etc.) the majority of polyhydroxyphenols present in the grape seeds remains into the defatted seeds. Thus their extraction with polar solvents like ethanol/water is recommended. Mixture of polyhydroxyphenols have been obtained by such procedure and analyzed by UV-Vis, FT-IR and NMR spectroscopy. Based on literature data some components have been identified. These antioxidant mixtures may be used as food additives or as nutritional supplements.

The crashed grape seeds may be a good adsorbent. Their application to waste waters with textile dyes purification seems to be another solution for valorization. Attempts to purify waters containing an acid dye (Acid Blue 62) have given good results.

Another way of valorization is the pyrolysis of the lingo-cellulosic waste. Depending on the heating temperature, different class of organic compounds may be identified into the IR performed spectra, like: ketones and aldehydes or carboxylic acid at 370-500 oC and, over 800 oC, only carbon black. The last product may be also used as adsorbent for acid dyes, based on to the content in Ca and K ions evidenced by EDAX.

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# Electrochemical dissolution behaviour of several metals from WPCBs in different bromide-based electrolytes

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Waste printed circuit boards (WPCBs) are the most valuable components of the electrical and electronic equipment wastes [1], which contain various metallic materials including precious metals. The concentration of the noble metals, particularly Au, Ag, Pd and Pt is higher than in their primary resources, which makes WPCBs potential sources of recyclable metals.

Moreover, WPCBs contain different hazardous elements, including heavy and toxic metals that may cause significant environmental pollution during the conventional waste treatments by landfilling or incineration. Hence, the WPCBs recycling is necessary for resource recovery, but also for the environmental protection. Apart from the mechanical separation (crushing, electrostatic separation and vibration), which is usually used in the pre-treatment process for increasing the metal content of the WPCBs, the currently used techniques for the metals recovery includes hydrometallurgical and pyrometallurgical techniques. However, these methods may cause secondary pollution, through the high volumes of generated effluents and the release of dioxins and furans in the atmosphere, respectively [2].

In an attempt to develop an innovative and ecofriendly technology for the recovery of the metals from WPCBs, the electrochemical dissolution behaviour of several metals (Ag, Au, Cr, Ti) was investigated in three different bromide-based electrolytes with varying pH-values. The experiments were performed by electrochemical techniques (open-circuit potential, potentiodynamic polarization and electrochemical impedance spectroscopy).

The experimental results showed that the nature of the metal and the pH-value of the electrolyte significantly influence the dissolution behaviour of the metals. The efficiency of the applied dissolution treatments was estimated based on the calculated dissolution rates of the metals. The obtained corrosion potential values were used to describe the dissolution resistivity of the metals in the three bromide based electrolytes.

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# A comparative study of the omega 3, 6, 9 fatty acid composition of certain indigenously-sourced plant oils for cosmetic use

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Plant products represent important sources of natural bioactive raw materials, that are frequently used therapeutically and in cosmetics.

This study has evinced fatty acids of the omega 3, 6, 9 type from certain plant oils that have been obtained by cold-pressing the seeds or fruits of: hemp (Cannabis sativa), milk thistle (Silybum marianum), sea buckthorn (Hippophae rhamnoides), and safflower (Carthamus tinctorius).

The analysis of the selected plant oils, concerning the 'omega-type' fatty acid content was carried out by gas chromatography coupled with mass spectrometry (GC-MS), using an NIST library of reference spectra.

Hempseed oil contains over 90% unsaturated fatty acids, of which 50-60% linoleic acid (omega-6) and 15-20% alpha-linolenic acid (omega-3). Omega-3 fatty acid is utilised for giving the body's cell walls flexibility, sheathing nerves, and as a metabolic precursor for other compounds essential for the body's ongoing health. Milk thistle seed oil (due to its fatty acid content of 44% linoleic acid, 30% oleic acid, 16% palmitic acid, and 4% linolenic acid), is used in cosmetics due to its soothing and nourishing properties, being in and of itself a useful cosmetic product. Sea buckthorn fruit oil contains omega 3, 6, and 9 fatty acids, and is distinguished in that it contains over 30% palmitoleic acid (omega-7), which is especially useful for stimulating cellular functions and likewise the skin's regenerative processes. Safflower seed oil contains remarkably high levels of over 75% linoleic acid (omega-6), which in combination with the stimulating effects of its serotonin derivatives gives safflower seed oil its increased fibroblast production properties, the fibroblast cells thus sustaining the skin's integrity and maintenance.

The plant oils were studied, selected and confirmed as having exceptional compositions due to the presence of essential and non-essential fatty acids, along with liposoluble vitamins, glycol- and lipo-proteins, sterols, and carotenes to mention but a few. These plant oils are used for developing a varied range of high-quality cosmetic products at Hofigal SA.

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# Edible flowers – Composition and antioxidant activity

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Edible flowers improve the aesthetic aspect and taste of food as well as they can have beneficial effects for human health, *e.g.*, a high nutritional value, antioxidant and antimicrobial properties [1-3]. Their chemical composition and nutritional value heavily depend on flower species, geographical region, season, storage and processing conditions. Generally, proximate composition of edible flowers consists of 80-90% water, up to 15% total carbohydrates, 1-3% proteins, 1-2% ash, and up to 1% fat [2]. Determination of content of phenolic compounds, pigments, vitamins, and minerals is essential to evaluate the health effects of these flowers [1-5].

This study aimed at establishing the content of phenolic compounds, sodium, vitamins A and C as well as the antioxidant capacity of several species of edible flowers, *i.e.*, *Ipomoea coccinea*, *Jasminum communis*, *Gladiolus imbricatus*, *Tropaeolum majus*, and *Viola tricolor*. Extraction experiments were performed in various solvents at different levels of temperature and liquid-solid ratio. Statistical models were used to assess the effects of process factors on its responses.

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# Study of simple sugar release using microbial strains from vegetal waste

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Cellulose from agriculture and forestry is a potential as cheap and renewable feed stock and vegetal waste which is abundantly available in nature and is produced annually approximate 1.3 billion tons. Cellulase (E.C. 3.2.1.4) is one of the enzymes responsible to break down the lignocellulosic materials into simple sugars. It has remarkable applications in areas such as alternate energy, textile detergent, cattle feed, pharmaceutical industry, food, nutrition and agriculture industry [1]. Although standard chemical process of breaking down cellulose into simple sugars is easy, the enzymatic process is pollution-free, economical and cost effective [2]. Because of these above mentioned reasons, most of the industries have increased their demand for less expensive cellulase with value added application. This gives a new horizon to find cost effective cellulose producing microorganisms.

The present study follows to identify optimal operating parameters for the cultivation of three native cellulase-producing microorganisms. The goal is to achieve a high conversion rate of the vegetable waste substrate into simple sugars. Three mold strains were used (*Trichoderma viride*, *Aspergillus oryzae* and *Sporotrichum pulverulentum)* and vegetable waste sources (corn cobs and hay) as a cellulosic substrate – carbon source. Two cultivation modalities were studied: in the shake flask (under micro aeration conditions) and in stirred bioreactor (intense aeration conditions). The glucose concentration in the culture medium was determined using the DNS - glucose assay method applied to the samples taken throughout the microbial growth. The experimental results obtained indicated that the high productive celluloses is *S. pulverulentum* strain cultivated on the hay carbon source substrate in continuous stirred and aerated fed-batch bioreactor.

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# Green Corrosion Inhibitor for Mild Steel in Neutral and Acid Solutions

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In order to prevent mild steel corrosion during immersion in different aggressive media, recent research studies now focus on the development of non-toxic, inexpensive and environmentally friendly corrosion inhibitors as alternatives to different synthetic compounds, inhibitors derived from natural extracts, readily available from a wide range of renewable sources.

As the extraction process is a simpler and low-cost procedure, this paper attempts to assess the inhibitive effect of natural plants selective extracts obtained from indigenous flora. Thus, the alcoholic extract from *Juglans Regia* buds (JRB) can be valorized after the expiration date by using it as a green inhibitor.

The inhibitor effects of this vegetal extract tested at different concentrations has been determined by various electrochemical techniques in 1N NaCl, 1N $H_2SO_4$ and 1N HCl solutions using a thermostated three electrode electrochemical cell. The next step was to determine the kinetic parameters and hence the corrosion rate. The inhibition effectiveness was found to increase with increasing extract concentration, up to a limiting value.

The addition of the JRB extract in the corrosive solution decreases the charge capacitance facilitating the formation of an adsorbed layer over the steel surface. By comparison, the inhibition efficiency of JRB in 1N NaCl solution was observed to be twice as high as in different acidic solutions with similar concentrations. The cumulated results suggest that this natural extract may serve as effective inhibitor for the corrosion of mild steel in different aggressive acid and neutral solution

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# Fuel gases by carbon dioxide metanization

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In Romania, a country with a tradition over a century in the natural gas and oil industry, methane was discovered in 1908, in the Sărmăşel area, Mureş County. Romania has the world's pureest methane deposits, up to 99.9%. The usage of methane gas has been steadily increasing due to its energy and technological advantages. Ussually, 1 $Nm^3$ of methane gas is energetically equivalent with 1.313 t of anthracite or about 0.9 t of crude oil. By burning methane, large amounts of $CO_2$ are obtained, and different methods must be identified for its recovery and transformation into valuable products. In the literature study various methods of $CO_2$ capture and its transformation into combustible gases were presented.

The purpose of this work was to design an energetic efficient process to obtain fuel gases from $CO_2$ in two steps: $CO_2$ capture from flue gases in alkaline solutions and its methanisation by hydrogen addition. Based on the chemical reactions, the thermodynamic and kinetic models, this two units were modeled using the Aspen Plus simulator. Material and energy balances were done to obtain specific consumption of raw materials and utilities, and the process heat integration analysis was performed to find oportunities of reducing utilities consumptions. Heat flow of 16.6 MW cand be recovered and was identified the posibility of generating medium pressure steam (22 MW) and low pressure steam (0.92 MW) as a feasible solution. Due to this energy savings, the total cost decreased by 14% compared to the pre-integration value, without taking into account the gain from the sale of heat generated by thermal integration. Also, the environmental impact analysis demonstrates that carbon dioxide emissions are considerably reduced (by over 64%).

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# Coal combustion gases heat recovery

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Coal has been an underrated source of energy for a long time, given the fact that, by simply burning the solid material, the level of harmful emissions would exceed the accepted limits, leading to an unfriendly process to the environment, as well as to an unfeasible one. For that matter, in the last decade, alternative methods of using the coal have been researched. Coal gasification is a well – proven technology that provides an excellent way of using vast resources of coal in an efficient and clean manner. The process is actually decades old, but recent rises in the price of natural gas have made it more economically viable nowadays. The process implies partial oxidation of coal by a mix of oxygen and high pressure steam in order to produce synthesis gas, a mixture composed mainly of carbon monoxide, hydrogen and carbon dioxide. It has various applications, ranging from being used as a feedstock for producing various chemicals (methanol and liquid fuels) to generating an important amount of electricity.

This paper deals with revovery of a syngas heat to produce steam and to generate power. The most profitable path found was the use of synthesis gas obtained in the coal gasification combined cycle, which couples the high efficiency of gas turbine cycles with steam turbine cycles. The gasification of lignite in a fixed – bed Lurgi reactor was simulated usin Aspen Plus simulator, considering solids generated by user based on experimental date. The great amount of heat recovered from the hot gas exiting the reactor was used to produce high pressure steam, which was recycled in the process, thus significantly reducing the operating costs. Very high pressure steam was also generated from the heat given by the combustion zone. This particular type of steam was used in a two-stage steam turbine and produced electricity, which was enough not only to sustain the gasification process, but also to make it more profitable. The design process has significant benefits regarding the environment.

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# Methanol to olefines (MTO) from syngas-design a sustainable process

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The main purpose of this paper is to study the synthesis of methanol and light olefins using syngas as a raw material. Syngas is a cheap source since it can be made from various carbonaceous materials such as: coal, biomass, natural gas, plastic waste, etc.

The process of converting methanol to light olefins (MTO) provides an additional route for the production of ethylene and propylene. Besides these in the MTO process, butenes and pentenes are also produced. Olefin synthesis takes place in two steps. First methanol is obtained from syngas in the presence of $CuO/ZnO/Al_2O_3$ catalyst and then it is converted to olefins. These processes were simulated using Aspen HYSYS. The design of the methanol process requires a compression area, a reaction and a separation area. Reaction zone have been simulated with *Plug Flow Reactor* model from ASPEN HYSYS v9 and the SRK property package was used. A heterogenous kinetic model was used to describe the chemical reactions involved. Methanol separation takes place in a distillation column for which NRTL property package was chosen. The MTO process requires a pumping zone, a reaction and a separation zone. A simple kinetic model was used to describe the reactions involved in the olefin formation.

A sustainable MTO process was design by heat integration analysis in order to maximize the heat recovery and minimum utility usage.

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